



**MINERAL RESOURCES ENGINEERING
SCHOOL**



Applications of petroleum geochemistry in reservoirs

By

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Abstract

This thesis is structured in two main parts-theoretical and practical part. The theoretical part will be mainly focused on the detailed description of the application of geochemistry in oil production and exploration, through explaining the role of geochemistry in the hydrocarbon asset management, in identifying new exploration or missed pay zones, in delineating reservoir compartmentalization by explaining the fingerprinting approach in assessing the reservoir continuity, etc. Additionally, it will be presented how the geochemistry aids in maximizing the waterflood efficiency, as well as its importance in the prediction of the flow assurance problems. In this part, the application of the reservoir geochemistry will be also discussed together with the application of the geochemistry studies in the maturity assessment, oil-oil, oil-source rock correlation. Furthermore, related to the application of the light hydrocarbons, which is the main focus in the practical part, will be discussed the postgenerative alteration processes and its characterization through the application of the light hydrocarbons.

In the practical part, a set of light hydrocarbon ratios will be applied on 146 sample set of oils from Western Canada. Using the compositional data of these oil samples, the compositional changes in the samples caused by the postgenerative processes will be detailly observed.

Introduction

For the past twenty years, the geochemistry has been widely applied in the field of production and reservoir engineering. Through the years, the geochemistry has proven to be an effective and inexpensive tool in solving production problems, such as maturity evaluation, oil-oil, and oil-source rock correlation and source-rock recognition (*Kaufmann et al., 1990*). It has also found an important application in the prediction of the hydrocarbon fluid composition in the potential target, as well as in the identification of producing or non-producing intervals, casing leaking, and production allocation. These approaches are mainly based on interpretation of the compositional differences in terms of reservoir continuity.

The advanced understanding of the physical and chemical laws that have major control over the petroleum composition, such as the sourcing, source-rock maturity, thermochemical sulfate reduction, thermal cracking, and the other postgenerative alteration processes, allows incorporation of the dynamic aspects into the interpretation. This contributes to a more reliable prediction of the fluid heterogeneity composition, which aids in its defining on a field scale (*Smalley et al., 2004*). Additionally, the compositional variations provide better understanding and prediction of the unexpected production behavior. Their identification is also essential in the process of defining the production pattern.

Basically, petroleum geochemistry represents a branch of the geochemistry that studies the principles of the origin, generation, migration, accumulation, and alteration, providing an important knowledge that has a significant application in the field of exploration and production of oil and gas. In general, the geochemical knowledge of the source rock and the knowledge of the processes of generation, migration, and accumulation combined with the geochemical and the geophysical features of the sedimentary basin under evaluation, are the most important factors in the process of determination of the most favorable conditions of the petroleum exploration targets.

As a result of the development of new analytical techniques such as gas chromatography and gas chromatography-mass spectrometry, the application of petroleum geochemistry experienced further developments in many areas of petroleum exploration and production. In recent years, the utilization of such techniques in solving production and reservoir problems has been especially emphasized. For example, the maturity evaluation is generally done by utilizing optical parameters, such as the vitrinite reflectance, whereas most of the organic

compounds present in the petroleum are analyzed using pyrolysis or gas chromatography. Additional, more advanced techniques, such as gas chromatographic-mass spectrometry, inductively coupled plasma, and atomic absorption spectrophotometry, provide detection of inorganic compounds present in trace level concentrations, while the mass spectrometry has been widely used in the isotopic investigations of crude oil and gas, providing a better overview on the geochemistry application.

In the following of this paper will be discussed the application of the geochemistry in production and reservoir engineering, with a special accent on the application of the light hydrocarbon ratios in the characterization of the genetic maturation, affiliation, water-washing, biodegradation, and other alteration processes.

In the first chapters (chapter 2.1. and chapter 2.2.) of this thesis are presented the classification and the composition of crude oil, where the main focus is on the importance of the distribution of the compounds for the classification of oil, as well as the importance of the oil composition in the reservoir characterization and exploitation, as presented in chapter 2.4. The next two chapters (3 and 4) are focused on the application of geochemistry in oil production and exploration, as well as the application of reservoir geochemistry. The third chapter includes the representation of how the geochemistry aids the hydrocarbon's asset management, its contribution to the identification of new exploration opportunities or missed pay zones, the significance of the geochemical analyses in the attempts to delineate the reservoir compartmentalization providing a detailed description on the oil fingerprinting approach in the reservoir's continuity assessment. Furthermore, this chapter contains information on the application of the geochemical techniques in predicting flow assurance problems and thus on its contribution to the optimization of the waterflood efficiency or other recovery processes. The main accent in the fourth chapter is in the application of the reservoir geochemistry, explaining how the reservoir geochemistry finds an application in the development of the field filling and mixing models, as well as the application of the geochemical data in the reservoir and the importance of the application of the geochemical techniques for the development of reservoir engineering investigations, such as for example in locating tar mats. This chapter also provides a better insight into the application of the NSO

geochemistry, describing the influence on the NSO compounds on the reservoir wettability, which is also related to the assessment of the migration volumes.

The biomarkers and their application are presented in the fifth chapter, mainly due to their importance in the determination of the stratigraphic origin and migration pathways, using their traces found in the related sources and crude oil.

In the sixth chapter, the main focus is on the maturation of the organic matter. Consequently, all types of maturity parameters and their application will be reviewed here, whereas in the next chapter (chapter 7) are discussed the oil-oil and oil-source rock correlation, explaining the type of correlation parameters that are used in these correlations. In chapter 8 is reviewed the postgenerative alteration processes that affect the petroleum composition, which is related to the application of the compositional ratios of the light hydrocarbons in the determination of these secondary processes. A detailed discussion of how these ratios are applied in the characterization of the biodegradation, evaporative fractionation, water washing, etc. will be presented in the practical part of the thesis.

1.Theoretical part

1.1. Classification of crude oil

Through the years various classifications of the crude oil have been proposed. Numerous geoscientist and petroleum refiners suggested various physical and chemical parameters used in the classification, depending on the main purpose of classification. For example, petroleum refiners are mostly interested in the quantity of successfully distillate fractions (e.g. gasoline, naphtha, kerosene, gas oil, lubricating distillate), and their physical and chemical properties (density, viscosity, boiling point, cloud test, etc.). On the other hand, geologists and geochemists are more focused on identifying and characterizing the crude oils, as a means to relate them to source rocks and to assess their thermal maturity as well. Accordingly, they rely on the chemical and structural information of crude oil constituents, especially molecules that convey genetical information. This is the reason why molecules present at a very low or trace levels, such as high-molecular-weight *n*-alkanes, steroids, and terpenes, usually are of great interest.

Typically, there is a great variation of the information obtained from the crude oil composition. There is a large number of methods and distillation results-Hempel, Enger and other, often including some additional fraction measurements (refraction index, density, viscosity, etc.). Around thousands of Analysis have been carried out, mostly performed on crude oils originating from Canada and the United States, including several hundreds of oils from other countries.

In the last 15 years have been made numerous analyses based on the content of various structural components in crude oils (alkanes, cycloalkanes, N, S, O compounds, aromatics), and the molecular distribution within each type of oil. Still, the distillation results are more numerous and less frequently published than this type of analysis.

1.1.1. Historical background of the crude oil classification

Since the beginning of the century, Smith (1968) proposed a unique review of the main classification of crude oil. Nowadays, well-known and most frequently used classification of crude oil, which is based on specific gravity and distillation on two main fractions of distillation (Table 1), has been set up at the U.S. Bureau of Mines by Smith (1972), Lane and Garton (1935).

Although this classification was successfully applied to intercompare several crude oils from certain provinces in the United States, thanks to the rapid progress in the organic geochemistry and the higher quality level of derived information, it became clear that this classification was ambivalent. Nevertheless, rather a different chemical composition of oils could result in the same grouping of these oils in the classification and additionally, different geological situations, except changes with depth, cannot be taken into account. Therefore, a new classification based on geochemical parameters is proposed, since the U.S. Bureau of Mines can hardly be hardly developed any further with respect to more compositional information on oils.

Specific gravity		Base	Base
Key fraction I 245-275°C (Atm.pressure)	Key fraction II 275-300°C (40 mmHg)		
≤ 0.8521	≤ 0.8762	paraffinic	paraffinic
≤ 0.8521	0.8767-0.9334	paraffinic	intermediate
≤ 0.8521	≥ 0.9340	paraffinic	naphthenic
0.8256-0.8597	≤ 0.8762	intermediate	paraffinic
0.8256-0.8597	0.8767-0.9334	intermediate	intermediate
0.8256-0.8597	≥ 0.9340	intermediate	naphthenic
≥ 0.8602	≥ 0.9340	naphthenic	naphthenic
≥ 0.8602	0.8767-0.9334	naphthenic	intermediate
≥ 0.8602	≤ 0.8762	naphthenic	paraffinic

Table 1. Classification of crude oils (*According to Lane and Garton, 1935*)

Later, different classifications have been proposed by Schanen (1950), Creanga (1961) and Radchenko (1965). On the contrary, the refinery practice proposes a classification based on the refractive index, density and molecular weight (n. d. M.). All these classifications have not been extensively applied in the past, which is the reason why they are not further discussed.

This newly proposed classification is based mainly on the content of various structural types of hydrocarbons, such as alkanes, cycloalkanes/naphthenes, and aromatics, including

N.S.O compounds (resins and asphaltenes). It also takes into consideration the sulfur content, as well. The content of alkanes, naphthenes and aromatics is considered here as a result of analytical methods:

- all data refers to the portion of petroleum fluid in boiling range above 220°C at atmospheric pressure;
- paraffin content includes *n*- and isoalkanes, except the alkyl chains, substituted on cyclic nuclei;
- naphthenes include all molecules containing one or more saturated cycles, but no aromatic cycle;
- aromatics include all molecules containing at least one aromatic cycle; these molecules may include condensed saturated cycles and chains substituted on the nucleus;

Considering the peculiar distribution of crude oils and geochemical consequences from it, when several oils were plotted in triangular diagrams (showing their relative composition with respect to the whole crude oils and with respect to the hydrocarbons only), which are another way of using correlation matrix, was the essential basis for the proposal of a new classification.

The concentration of saturates in crude oil is taken into consideration as the first parameter in this type of classification. This is negatively correlated to the aromatics, resins, asphaltenes and sulfur content. The distribution of saturated hydrocarbons is explained by two models, which are clearly separated by a minimum at 50%. The cut here is used to separate two different populations of crude oil, one more paraffinic or paraffinic-naphthenic, and the other more aromatic or asphaltic. The 50% minimum corresponds to the 1% minimum if the distribution of sulfur in the crude oil.

Additionally, another important cut, based on the alkane concentration, can be introduced among the crude oils. Separation of another class of crude oils comes from the distribution of *n*+ isoalkanes, that shows a minimum at about 10%. This class generally represent degraded oils; the low content of *n*+ isoalkanes is commonly due to biodegradation.

1.1.2. Classes of crude oil

When considering the previous classification, crude oils can be divided into paraffinic and naphthenic if the total content of saturated hydrocarbons is over 50% in particular crude oil.

Therefore, in order to be more practical and for future use in connection with geological environments, additional boundaries are justified by the minor cuts established at 40% alkanes and cycloalkanes. These two boundaries separate paraffinic oils from intermediate-paraffinic oils and those from naphthenic oils.

When the total content of saturated hydrocarbons is less than 50%, the oil is considered to be more aromatic, which means that the total content of the aromatics, asphaltenes and resins is greater than 50%. According to the previous consideration based on the alkane content, there is an additional boundary that separates aromatic-intermediate oils (containing more than 10% $n+$ isoalkanes), and heavy degraded oils (with less than 10% $n+$ isoalkanes).

The latter class is divided into two subclasses:

- aromatic-asphaltic oils with less than 25% naphthenes
- aromatic-naphthenic oils containing more than 25% naphthenes

Aromatic-naphthenic oils usually contain less than 1% sulfur, whereas aromatic-asphaltic oils are high-sulfur oils. It is important to be noted that the minor cut here corresponds to a difference to the sulfur content.

The low sulfur-crude oils mostly belong to the paraffinic, paraffinic-naphthenic and naphthenic classes. On the other hand, high-sulfur crude oils mostly belong to the aromatic intermediate class. If they are degraded, they would belong to the aromatic-asphaltic class.

1.1.3. Characteristics of the principal classes of crude oil

With the crude oil classification, so far have been identified six principal classes of crude oil. These classes and their characteristics will be further discussed in this text.

The paraffinic class is mainly comprised of light crude oils. Some of them are fluids, and some are high-wax or high-pour-point crude oils. The viscosity of these high-pour-point oils is high at room temperature (due to a high content of n -alkanes $>C_{20}$), whereas at elevated temperatures (30-35°C) it becomes normal. Their specific gravity is below 0.85 and the viscosity is generally low, except when high-molecular weight n -alkanes are abundant. The amount of resin plus asphaltenes in these type of oils is less than 10%, while the aromatic content is subordinate and mostly composed of mono- and diaromatics, usually including

monoaromatic steroids. Sulfur content is low to very low and benzothiophenes are very scarce. This class is comprised of some oils from the Paleozoic from North Africa, the United States and South America, some of the lower Cretaceous oils from the basins bordering the South Atlantic Ocean, and some Tertiary oils from West Africa, Indonesia, Lybia, and the Pannonian basin in Central Europe. Most of the oils associated with the Green River and Flagstaff formations of Unita Basin, Utah, belong to the high-wax type.

The paraffinic-naphthenic class of oils has a moderate resins-plus-asphaltenes content (typically 5 to 15%) and low sulfur content (0 to 1%), while aromatics represent 25 to 40% of the hydrocarbons, and benzo and dibenzothiophenes are moderately abundant. Their density and viscosity attain higher values than in the paraffinic class but remain moderate. This class encompasses numerous crude oils from Devonian and Cretaceous of Alberta, from the Paleozoic of North Africa and the United States (except the Permo-Carboniferous of the Permian basin). Here are also included Cretaceous and Jurassic oils from the Paris, North Aquitaine and North Sea basins, Cretaceous and Tertiary oils of West Africa, some Tertiary oils from Indonesia, and Cretaceous and Lower Tertiary oils from North Africa.

The naphthenic class is constituted of a few crude oils only. Some oils from the Jurassic and Cretaceous of South America can be referred to this class, together with some immature oils. Nevertheless, this class includes mainly degraded oils with less than 20% $n+$ isoalkanes, that originate from the biochemical alteration of paraffinic or paraffinic-naphthenic oils with low sulfur content, even though they had been exposed to degradation. Characteristic specimens were found in USSR, in the North Sea, and in the Gulf Coast area.

The aromatic-intermediate class mainly comprise heavy crude oils. The resins and asphaltenes are present in a concentration of 10-30% or sometimes even more, while the sulfur content is above 1%. Aromatics amount to 40 to 70% of hydrocarbons and the monoaromatics concentration is very low (especially those of steroid type). Generally, thiophene derivatives, such as benzo- and dibenzothiophene are abundant (25-30% of the aromatics or more). The specific gravity of these oils is usually high attaining values more than 0.85. This class includes most crude oils from Jurassic and Cretaceous of the Middle East, Jurassic and Lower Cretaceous of Alberta, from the Permo-Carboniferous of the Permian Basin, some Upper

Cretaceous-Tertiary oils from West Africa and some oils from California, Venezuela and Mediterranean.

The altered crude oils mainly represent the classes of aromatic-naphthenic and aromatic-asphaltic oils. Due to biodegradation, the alkanes are first removed from the crude oil. Later, during the more advanced stages of degradation, most of the monocycloalkanes may be removed. This process is followed by oxidation as well. Therefore, most aromatic-naphthenic and aromatic-asphaltic are heavy, viscous oils originally resulting from degradation of paraffinic, paraffinic-naphthenic, or aromatic-intermediate oils. The content of resin-plus-asphaltene compounds is typically above 25% and sometimes may reach 60%. However, their relative content and the sulfur quantity may vary according to the type of the original crude oil.

The aromatic-naphthenic class is primarily derived from paraffinic or paraffinic-naphthenic oils. The tar-like oil in the Lower Jurassic sands of Malagasy, when altered contain mostly resins and keep a low content of sulfur (below 1%) and have an asphaltene ratio of 2 or more. Also, the heavy oils of the Emeraude field contain ca. 25% resins and the sulfur concentration is 0.4 to 0.8% (*Claret et al., 1977*). The same applies to Lower Cretaceous oils of West Africa.

The aromatic-asphaltic class of oils comprises of a few true, apparently nondegraded oils from Venezuela and West Africa. Nevertheless, it mainly includes oils resulting from alteration of aromatic-intermediate crude oils, which is the main reason why these oils are heavy and viscous. The result of the alteration is usually an asphaltic oil, or tar, in which the sulfur amounts from above 1% and may reach up to 9% in extreme cases. The resin and asphaltene concentration in these oils is very high, ca. 30 to 60% and have a lower resin: asphaltene ratio than in the aromatic-naphthenic oils. Heavy asphaltic oils from Venezuela and South Africa belong to this group together with the most degraded tar sands from Western Canada, Athabasca oils with ca. 5% content of sulfur in the MacMurray area, Peace River, and Wabasca.

All of these six classes of crude oils are unevenly abundant. Most of the nondegraded oils belong to three classes only:

- paraffinic and paraffinic-naphthenic oils, frequently generated in deltaic or coastal sediments of the continental margin, or in nonmarine source beds. They contain low amounts of sulfur, usually less than 1%.
- aromatic-intermediate oils (with more than 1% sulfur content) regularly deposited in a reducing environment and generated in marine sediments.

The previously explained evaluation is based on the frequency of different oils investigated. However, when taking into consideration the production and the total amount of known reserves, the relative importance of the classes has changed.

With respect to quantity, the aromatic-naphthenic, then the aromatic-asphaltic and the aromatic-intermediate class represent the most important classes. The first two comprise the enormous reserves of heavy oils and tar sands from Eastern Venezuela, Athabasca, etc., the third class (aromatic-intermediate) encompasses large accumulations of crude oil in the Middle East.

The class of naphthenic oils is comparatively rare and represents the other extreme. Due to the affection of postgenerative alteration processes and evaluation, its classification may progressively change in the future (*Evans et al., 1971*). The thermal evolution results in an increase of the paraffin content and diminution of aromatic and heavy constituents. In advanced stages, the composition approaches the paraffin pole, due to which a paraffinic-naphthenic oil, at shallow or medium depth, might be transformed into a paraffinic oil at greater depth. The shift away from the paraffinic pole resulted from biochemical degradation of alkanes, usually represents the alteration. After the alteration, an additional increase of resins and asphaltenes may result from oxidation.

Consequently, through alteration normal paraffinic-naphthenic oils may be transformed into aromatic-naphthenic. Additionally, some aromatic-intermediate oils may be changed to the aromatic-naphthenic class or even to the aromatic-asphaltic class of crude oils.

When summarizing the previous discussion, we can come up with the following conclusions:

- the classification of crude oils is done using the $n+$ isoalkanes (paraffin), cycloalkanes (naphthenes), and aromatic compounds content as essential parameters.

- the main three classes of normal crude oils are: paraffinic oils (mostly containing normal and isoalkanes, and less than 1% sulfur), paraffinic-naphthenic oils (containing both linear and cycloalkanes with less than 1% sulfur) and aromatic-intermediate oils (containing less than 50% saturated hydrocarbons and more than 1% sulfur).
- the three additional classes resulted from alteration and evaluation processes (that usually generate heavy oils of aromatic-naphthenic or aromatic-asphaltic classes) and they are the paraffinic and paraffinic-naphthenic oils (usually degraded into aromatic-naphthenic oils with moderate sulfur content) and the aromatic-intermediate oils (degraded into aromatic-asphaltic oils with a high sulfur content).

1.2. The composition of crude oil

Petroleum consists of complex hydrocarbon mixtures, such as paraffins, naphthenes, aromatic hydrocarbons and gaseous hydrocarbons (C₄-C₁₀ range) (*Mukhulynov et al., 1964*). As previously mentioned, depending on the hydrocarbon's predominance the crude oil can be classified as oils with a paraffinic, intermediate or naphthenic base. Despite these types of hydrocarbons, in the crude oil's content are also present nonhydrocarbons such as sulfur, oxygen and nitrogen compounds, and some minerals as well.

The hydrocarbons present in the crude oil usually can be normal, branched (or cyclic saturated hydrocarbons) and aromatic, while the unsaturated hydrocarbons, often referred to as olefins are normally absent.

All the types of compounds usually present in the petroleum will be explained in the next few paragraphs.

1.2.1. *n*-Alkanes

Their content can be very low in heavy degraded oils but generally, they amount to 15-20% or sometimes they are present in concentrations of 35%. Almost all linear *n*-alkanes (C₁-C₄₀ or beyond) have been so far identified in the crude oil. Their abundance decreases regularly with increasing the number of carbon atoms (beyond C₁₀), while the low molecular weight *n*-

alkanes (C₅-C₇) reach the highest values for a single component. For example, the *n*-heptane accounts for 4.4 vol % of Fasken crude oil, Ordovician, Texas, (Smith, 1968).

Certain crude oils have high cloud points, generally due to high molecular weight *n*-alkanes (>C₂₀). The cloud point refers to the temperature at which there is an occurrence of a cloud of wax crystals when the oil is chilled. This types of oils often have high-wax content.

The amount of *n*-alkanes is greatly dependent on the genetic conditions, and especially on the organic facies. Those oils delivered from terrestrial organic matter usually contain large quantities of *n*-alkanes. The same is true for the high-wax oils, while those oils generated from marine organic- matter yield more cyclic compounds.

It is important to mention that during the stage of catagenesis, there is a tendency towards an increase of the *n*-alkanes concentration as the maturity proceeds further, resulting in a series of crude oils of similar origin. On the contrary, the biodegradation results in a decrease of the *n*-alkanes amount.

1.2.2. Isoalkanes

The highest individual concentration of isoalkanes is found in the C₆-C₈ range, specifically 2-methyl or 3-methyl hexane and/or heptane and it represents more than 1% of the total volume percentage. Martin (1963) made a significant contribution to the understanding of normal and isoalkanes distribution. In a detailed analysis performed on light hydrocarbon fractions from various source rock and various ages, it has been noted that the decreasing order of abundance of five hexane isomers was practically the same in all crude oils, which is the same case for the nine heptane isomers. A comparable order of abundance was found by Poulet and Roucache on lower Paleozoic crude oils. The one tertiary carbon atom (2-methyl or 3-methyl) is the most frequent configuration present in the C₅-C₈ range, whereas the configuration with two tertiary carbon atoms is less present. One quaternary carbon atom or more than two tertiary atom configurations are less likely to be identified in this range (Smith, 1968).

The reason for the strong predominance of normal, iso- and anteisoalkanes (2-methyl or 3-methyl) can be explained by the long alkyl chains originated from the alkanes, acids, and alcohols from higher plant's and microorganism's waxes. Furthermore, the cracking of heavier molecules results in *n*-alkanes, isoalkanes, anteisoalkanes, and aromatics.

Some C₁₀ isoalkanes, such as 2,6-dimethyloctane and 2-methyl-3ethylheptane are highly abundant in the crude oils, amounting to 0.55 and 0.64% of Ponca City crude oil, respectively. Their predominance is due to their origin from monoterpenes of higher plants.

The isoprenoids are the most remarkable molecules in the medium-molecular weight range, particularly for their importance with respect to the petroleum genesis. This group is represented by isoalkanes from C₉ to C₂₅ with one methyl branch on every fourth carbon atom. The most abundant among them are pristane (tetramethylpentadecane C₁₉) and phytane (tetramethylhexadecane C₂₀). Usually, together they average up to 55% of all acyclic isoprenoids and pristane is often more abundant than the phytane. In some high-wax paraffinic crude oils of nonmarine origin from the Copper, Gippsland, and Bowen-Surat Basins, pristane may reach 4 to 10 (*Powel and McKirdy, 1975*). Due to the unlikely mode of cleavage of the precursor, the isoprenoids C₁₇ and C₂₂ are generally absent. The squalane and lycopane-C₃₀ and C₄₀, respectively, are irregular isoprenoids present in certain crude oils, while other important isoprenoids often are C₁₆ and C₁₈.

The paraffin wax usually contains high molecular weight isoalkanes and anteisoalkanes (2-methyl and 3-methyl), present especially in certain crude oils, such as in the Unita basin oils (derived from nonmarine source beds) or the Indonesian oils (derived from a paralic environment).

1.2.3. Alkenes

The alkenes as unsaturated chains are very unstable, and therefore their presence in the crude oils is very untypical. Nonetheless, very small quantities of *n*-hexane, *n*-heptane and *n*-octane were identified in the Pennsylvanian crude oil. Also, the presence of some polycyclic cycloalkenes (e.g. steranes and hopanes) have been recently confirmed in ancient sediments and in certain crude oils (*Hollerbach, 1976*). It is important to be mention that these type of compounds have not been actively investigated up to recent years.

1.2.4. Cycloalkanes

One of the most important constituents of petroleum are the low molecular weight derivatives of cyclopentane and cyclohexane (< C₁₀) as well as those cycloalkanes themselves.

Among them, the methylcyclohexane is usually most abundant. The methylcyclopentane is also important, and usually, both of the methyl derivatives are more abundant than their parenting molecules (cyclopentane and cyclohexane). The alkylcycloalkanes with less than 10 carbon atoms represent cyclopentane and cyclohexane derivatives.

Those of high molecular weight mono- and dicyclic usually contain one long, linear or lightly branched chain and several short methyl or ethyl chains (*Hood et al., 1959*). This type of cycloalkanes amounts to 50-55% of the total cycloalkanes $< C_{10}$ and generally the abundance of mono- and dicycloalkanes decreases regularly as a function of the molecular weight, i.e. the number of carbon atoms.

The tricycloalkanes average 20% of the total naphthenes and the presence of some types of tricycloalkanes decreases as a function of the molecular weight, beyond twenty carbon atoms. A very peculiar compound that has been extracted in a very small amount from the Hodonin crude oil (*Landa and Machaek, 1933*) and the Ponca crude oil (*Mair et al., 1951*) is the adamantane or the tricyclodecane.

The structure of tetra- and pentacycloalkanes is directly connected to the tetracyclic steroids and the pentacyclic triterpenes, and they usually amount up to 25% of the total naphthenes $> C_{10}$. The tetracyclic steranes distribution is mainly from 27 to 30 carbon atoms, whereas the triterpene pentacyclic distribution has its maximum from 27 to 32 carbon atoms, and sometimes extends up to 35 atoms. Generally, these types of cycloalkanes are predominantly present in immature and young crude oils, also rich in resins, polyaromatics, and asphaltenes. Due to their high optical rotation, they are the main reason for the optical activity of the fossil hydrocarbons.

Even though the total amount of cycloalkanes of source rocks and petroleum is similar, the mono- and dicycloalkanes are generally more abundant in crude oils compared to their quantity in the petroleum. On the contrary, the quantity of tetra- and pentacycloalkanes is higher in petroleum than in the source rocks.

1.2.5. Aromatics

These types of molecules generally contain only aromatic rings and chains and include one to four condensed aromatic rings and a small number of short chains. The most frequent

compounds belonging to this basic type are benzene, naphthalene, phenanthrene and anthracene, pyrene, benzanthracene, and chrysene. On the other hand, the second fundamental type consists of a five-membered ring in addition to the six-membered rings, such as fluorene, benzofluorene and fluoranthene, and benzofluoranthracene. Among the most abundant are benzene, naphthalene, and phenanthrene. The major components in each type are the alkylated derivatives comprising one to three additional carbon atoms and not their parenting molecules as expected. For instance, the benzene is usually less abundant (up to 1% of the crude oil), whilst the major constituent of the alkyl-benzene type is frequently toluene, reaching up to 18% of crude oil, and in some cases xylene considering that the total o-,m- and para-xylenes may amount up to 1.3% of crude oil. The same applies to the naphthalene type with a distribution that reaches its maximum from C₁₂ to C₁₃ (di- or trimethyl naphthalene) and also the phenanthrene type with a maximum at C₁₆ or C₁₇ (di- or trimethyl phenanthrene). All distributions decrease rapidly beyond this maxima, normally due to the lack of long chains. Usually, the higher-boiling alkylbenzenes, naphthalenes, and others which occur at low concentrations commonly contain two to three methyl groups and one long chain (*Hood et al., 1959*).

Some individual methyl derivatives, such as phenanthrene are not evidently related to biological precursor molecules (*Radke et al., 1982*). Also, the preference of mono-, di- and trimethyl derivatives can be explained if the naphthalene and the phenanthrene series have been mostly generated by fragmentation of steroids and terpenoids.

Generally, the alkylphenanthrenes are largely predominant, whilst the alkylanthracenes presence is less predominant. Also, noncondensed aromatic types such as diphenyl are also known in minor quantities.

1.2.6. Naphthenoaromatics

These compounds generally constitute the largest percentage of the high boiling fraction of hydrocarbons. Typically they include one or several condensed aromatic rings, which are combined with naphthenic rings and chains.

Compared to the polyaromatic hydrocarbons in the paraffinic-naphthenic crude oils (from detrital sedimentary sediments), mono- and di-aromatics are significantly abundant.

Frequently, the aromatic types become predominant after an important thermal evolution and therefore the naphthenoaromatics are much more present in young and shallow immature crude oils than the pure aromatics.

The naphthenoaromatics often show various types of structural arrangements. For example, the bicyclic indane, tetraline, and their methyl derivatives are usually abundant and have been identified in several crude oils. Also commonly present are tricyclic tetrahydrophenanthrene and derivatives, out of which the tetracyclic and the pentacyclic molecules are of particular importance. Their concentration may be important in naphthenic or naphthenic-paraffinic crude oils.

1.2.7. Sulfur compounds

After carbon and hydrogen, sulfur is the most abundant atomic compound in the crude oil, usually present in the medium or heavy fractions of crude oil. However, the presence of sulfur is particularly not related to the heaviest fractions, as is the case with nitrogen. Generally, in the low and medium molecular weight is associated with carbon and hydrogen, whilst in the heavier fractions is part of large polycyclic molecules comprising N, S, O.

The four main classes of sulfur compounds present in the light and the medium fractions of crude oil are thiols (mercaptans), sulfides, disulfides, and thiophene derivatives. The thiophenic sulfur amount increases with maturation, whereas the nonthiophenic compounds are present in immature oils (*Ho et al., 1974*).

Most of the thiols have a lower molecular weight and they can be thought of as derived by hydrogen sulfide when substituting alkyl or cycloalkyl radical with a hydrogen atom. Normal and isoalkanethiols, cyclopentanethiol and cyclohexanethiol have been detected in petroleum (*Smith, 1966*).

The sulfides are usually of very low abundance and are derived from hydrogen sulfide by substitution of the two hydrogen atoms by alkyl groups, whilst the alkylaryl sulfides are substituted by one aromatic ring and one alkyl group. In the disulfides, the sulfur bridge consists of two sulfur atoms instead of one as in the sulfides. Few of them, such as those in the range from dithiabutane to dithiahexane were identified in the low molecular range.

The thiophene can be described as a five-membered unsaturated ring, comprised of one sulfur and four carbon atoms, often behaving as the benzene ring. The crude oils generally lack higher quantities of thiophene, but benzothiophenes, dibenzothiophenes, and benzonaphthothiophenes are significant constituents of crude oils that contain high amounts of sulfur. Consequently, they are less present in the low-sulfur crude oils. The dibenzothiophenes are frequently the most important group of thiophenic compounds in mature or altered crude oils, containing high sulfur content. Considering the molecular weight distribution, the substituted derivatives are generally more abundant than the parenting molecules. The maximum content usually corresponds to molecules consisting of two to three additional carbon atoms-dimethyl-, trimethyl-dibenzothiophene. The same is true for the benzonaphthothiophene. An exception here is the benzothiophene's distribution sometimes covering a broad range of molecular weights.

1.2.8. Nitrogen compounds

The largest quantities of nitrogen compounds have been identified in high molecular weight and high boiling point fractions and also the nitrogen content in crude oils is usually much lower than that of the sulfur. The average value on crude oils is 0.094% by weight and about 90% of the crude oils contain less than 0.2% of nitrogen. We can distinguish three groups of crude oils, according to the nitrogen content: high-nitrogen content oils ($N > 0.25\%$), normal and nitrogen-poor petroleum. Compared with normal crude oils, degraded asphalts are enhanced in nitrogen content, due to the increase of resins and asphaltenes.

The high molecular weight fractions in which most of the nitrogen content is associated with, are in fact polycyclic aromatic compounds containing more or less at random different heteroatoms (N, S, O). A certain number of those medium and low fractions containing nitrogen compounds are known from naphtha and gas oil fractions, where about 25 to 30% of these fractions consist of basic nitrogen compounds, such as pyridine and quinoline, and the rest of these fractions are constituted of nonbasic molecules, such as carbazoles and indoles (*Seifert, 1969*).

The porphyrins generally contain four pyrrole nuclei and metal, mostly vanadium or nickel.

1.2.9. Oxygen compounds

The acids are common constituents of immature, young crude oils and generally, they are the most common groups of compounds containing oxygen. Isoprenoid acids together with some fatty acids, mainly in a range from C₁ to C₂₀ have been detected in several crude oils. Also, the naphthenic acids represent one of the most important constituents in various naphthenic and asphaltic crude oils from Venezuela, California, and USSR, and some of them are might have been generated from degradation (chemical or biochemical oxidation) of the original crude oils. Those who contain hopane skeleton are surely original constituents of the oil.

The amount of carboxylic acids has been investigated in young and immature Californian oils by Seifert and Howels (1969). According to their studies, they amount up to 2.5% by weight of crude oil. Additionally, they separated a large number of carboxylic acids depending on which type of hydrocarbon structural types they belong to. From this study has been concluded that the naphthenic and naphthenoaromatic types are most abundant, followed by polyaromatic and heterocyclic types (*Seifert and Teeter, 1970*). Since some of the carboxylic acids are an indication that the animals contributed to the formation of petroleum, their identification is of great importance (*Seifert, 1973*).

The group of pentacyclic acids with a hopane skeleton is the most frequently present group of oxygen compounds in the crude oil. Ourisson et al., (1977) that they are derived from bacterial lipids, such as the bacteriohopane tetrol and other bacterial membrane constituents.

Generally, the cresols and numerous phenols are highly present in the acidic fractions of crude oil (*Seifert and Howels, 1969*). The rest of the oxygen compounds, such as dibenzofurans, alkylic or cyclic fluorenones, and ketones are identified in trace quantities.

1.2.10. Resins and asphaltenes

This group of compounds is represented by high molecular weight compounds that usually contain N, S, and O and are known as resins and asphaltenes. The asphaltenes and the resins constitute the heavy ends of the crude oil due to their complex structural configuration, which includes polycyclic aromatic or naphthenoaromatic nuclei, chains, and N, S, O heteroatoms.

Therefore, they are mostly considered as the natural high molecular weight end member of the naphthenic-aromatic and aromatic series. When the molecular weight increases (beyond ca. 600), there is a greater possibility that the molecules contain one or more heteroatoms in their configuration, which means that all the constituents contain N, S, O compounds and that there is no pure aromatic and naphthenoaromatic molecule in the heavy end. In the cyclic structures, these N, S, O atoms in the heavy ends sometimes are substituted for carbon atoms. Also, they often contain metals as well.

The precipitation by propane separates resins and asphaltenes from the rest compounds present in the crude oil, whilst when doing precipitation with *n*-pentane and *n*-heptane we separate the soluble resins from the insoluble asphaltenes. According to this, based on the separation procedure we can easily distinguish the resins and asphaltenes. Also, there are several procedures available for resins and asphaltenes preparing, which results in compositions that slightly differ. Usually, the resins are separated from hydrocarbons by gas chromatography and the asphaltenes precipitate from crude oil by *n*-hexane and *n*-heptane. Additionally, it should be taken into consideration that the molecular size and the polarity are parameters that can compensate to each other (*Long, 1979*), which is the reason why the same procedure can be used to precipitate different compounds from the different crude oil, including compounds from synthetic oils, such as shale oil or coal liquids (*Bockrath et al., 1979*).

The quantity of asphaltenes plus resins amounts up to 10 to 40% in aromatic-intermediate oils as it has been already mentioned in the text. In paraffinic oils, they are present with less than 10% and in paraffinic-naphthenic oils usually, amount less than 20%. In normal, or non-degraded oils the asphaltenes only amount from 0 to 20%, whereas in heavy degraded oils, such as the oils in Athabasca and Orinoco basins, they are present in a concentration from 25 to 60%. Generally, they are more abundant in bitumen source rocks than in the corresponding crude oils. Resins and asphaltenes with this type of origin (from bitumen source rock), are not identical with the related petroleum compounds, even though they are closely related.

According to some authors, the asphaltenes in crude oil are most probably dispersed by the action of resins (*Speight et al., 1979; Pfeifer and Saal, 1940; Speight, 1980*).

Often the high viscosity of the oil and the water in oil emulsion are due to the abundance of asphaltenes. Therefore, should be paid special attention to the asphaltene concentration when crude oil is produced.

During pyrolysis at about 300-350°C, some light hydrocarbons are generated, while the oxygen from the carbonyl or the carboxyl group is eliminated. The yield of heavy hydrocarbons, hydrogen sulfide, and methane increases beyond this temperature, reaching its maximum at a temperature of 410-470°C. This type of pyrolysis of asphaltenes can provide significant information on their possible role in the petroleum generation and also provides information about their structure. Certainly, the most important reason for performing this pyrolysis is that the behavior of the asphaltenes during pyrolysis can be easily compared to that of the kerogen (*Moschopedis et al., 1978*).

Chape (1982) provided significant information when submitting asphaltenes and kerogen separated from crude oil to a selective fragmentation of ether bonds. He identified glycerol ethers comprising C₂₀ and C₄₀ isoprenoid chains typical of the membranes of the Archaeobacteria. Furthermore, some other researchers have included asphaltenes behavior during pyrolysis in their studies. For example, Rubinstein et al., (1979) compared the asphaltenes naturally present in the Prudhoe Bay oil with the yield of pyrolysis product from the pyrolysis of asphaltenes present in the related oil. This resulted in identifying a number of constituents, such as *n*-alkanes, *n*-isoalkanes, aromatics and polycyclic naphthenes comparable to those of the Prudhoe Bay crude oil and also olefins generated during the petroleum cracking. Arefjev et al. (1980) showed that the pyrolysis products can be used for reconstruction of the degraded paraffinic fraction. Also, more recently has been found a significant similarity between the distribution of the principal constituents in pyrolysis products and the relative abundance of pyrolyzed asphaltenes in ten different crude oils in the study made by Behar (1983).

In all of the previously mentioned studies has been analyzed comparable structure units comprising kerogen and asphaltenes. Actually, the asphaltene constituents in source rocks should be considered as small fragments of kerogen, which are generally created through the elimination of heteroatomic or another type of bonds. Therefore the overall structure may be preserved from the kerogen to the heavy ends of the crude oil.

1.2.11. Organometallic compounds in crude oil

Crude oils often contain metals, particularly nickel and vanadium. Such examples of crude oils that contain various amounts of metals are the Paleozoic crude oils from the USA and Allegra, containing less than 1 ppm and the Boscan crude oil from Venezuela, which contains up to 150 ppm nickel and 1200 ppm vanadium. The Venezuelan crude oils generally reach the highest values of metal content.

Since the metals are usually present in the resins and asphaltene fractions, there is a good correlation between metals, sulfur, and asphaltenes. Therefore, degraded oils enhanced with asphaltenes, contain more metals than the non-degraded oils, due to the metal-asphaltene correlation.

Despite the nickel and vanadium as the most abundant metals in the crude oils, other metals, such as iron, chromium, iron, arsenic, cobalt etc., are also present in minor quantities, but their presence can not be easily detected as in the case of nickel and vanadium, i.e. it is difficult to evaluate if they commonly occur in the crude oil. Some part of them, particularly the vanadium, are incorporated in the porphyrins. They contain a tetrapyrrolic nucleus inherited from hermin or chlorophyll and vanadium or nickel. Also despite the nitrogen, they contain oxygen and some other metals such as iron and copper that might be identified as well.

The porphyrins are not stable at higher temperatures and they are generally associated with the resins fractions. This could be an explanation of why in crude oils with lower densities and lower resins and asphaltene concentrations, the porphyrins are present at trace levels. For example, the reason for the low concentration of porphyrins in the Cambrian and Ordovician crude oils is the low process of plant evolution during early Paleozoic times (*Louis, 1967*).

Despite the porphyrins, metals can be associated with other complexes. Namely, the vanadium accounts for up to 70% in some crude oils being associated with other complexes. Alternatively, the metal can be incorporated in a porphyrin nucleus, the latter bearing complex substituents (*Tynan and Yen, 1967*).

As the sulfur and vanadium can be eliminated through some steps of hydrotreatment of the heavy fractions of crude oil, there is a good correlation between them, which means that vanadium is mainly incorporated in structures where the sulfur plays an important role.

1.3. Covariance analysis of the main constituents of crude oil

It is known that the gross composition of crude oil, i.e. the sum of the main constituents of the crude oil, i.e. the saturated hydrocarbons, aromatics, resins, and asphaltenes, is equal to one. This is an indication that they are not independent parameters and show a high degree of covariance. Additionally, when dealing with concentrations of specific compounds such as monocycloalkanes, thiophenes, etc. or with other physical and chemical parameters such as the sulfur content, viscosity, etc., we can observe one more dependence between these parameters.

Covariance analyses can be useful in giving an explanation for the relationship between sulfur, the aromatic constituents and the resins and asphaltenes as the heavy end fractions. For that purpose, we should think of the origin of sulfur in the crude oil and the mode of the solubility process of asphaltenes in crude oils.

Generally, the sulfur is not a major constituent of biogenic molecules, so we can assume that this element was introduced in the organic matter, either into the kerogen at the early stages of diagenesis in young sediments or into crude oils.

Taking into account these assumptions, the sulfur-aromatics relationship can be interpreted in two ways. According to the first one, the sulfur is predominantly associated with molecules containing an aromatic cycle, whereas according to the second interpretation the sulfur is incorporated in the organic matter as a promotor of aromatization (when combining with saturated or partly unsaturated cycles) or cyclization (when combined with unsaturated chains).

Irrespective of their original abundance in the bitumen of source rocks, there is a strong correlation between aromatics and resins-plus-asphaltenes. This strong correlation is most probably has to do with the way asphaltenes are solubilized in crude oil by resins and aromatics and thus transported during migration.

The dependence of some physical properties on the content of sulfur is another aspect of the problem. Also, the abundance of the high heavy end members or the resins and the asphaltenes is closely related to the sulfur content. If we take this fact into consideration, we can conclude that the oils with a high concentration of resins and asphaltenes, generally have higher values of viscosity, but the resins and asphaltene content is not the only reason for this. The resins and asphaltenes are predominantly abundant in the high-sulfur content oils and

dominate any other possible cause for the increased viscosity, which makes the correlation between the density, viscosity and the sulfur considerably better.

Speaking of the physical parameters, the pour point is the only parameter that is independent. Therefore, the pour point provides unique information, which cannot be easily provided by other parameters. Namely, the pour point is an indicator for the high-molecular-weight *n*-alkanes presence in the crude oil.

On the other hand, the other crude oil constituents, such as tetra- and pentacyclic naphthenes, correlate with the chemical and physical parameters to a certain degree. Taking into account all these considerations we can come up with the following conclusions:

- highly-aromatic crude oils contain more tetra- and polycyclic naphthenes, thiophene derivatives and polyaromatics compared to the other oils. Additionally, these types of oil contain proportionally fewer monoaromatics;
- immature low-aromatic oils contain a considerable amount of naphthenes, whilst in the advanced stages of evaluation, the paraffin, alkylbenzenes and cyclic naphthenes are predominant;

1.4. The importance of the oil composition in the reservoir characterization and exploitation

During the initial appraisal and development of an oil and gas reservoir, the main aim is conceiving a development strategy that will provide maximum recovery efficiency and optimal exploitation of the reservoir. The main tool behind this development is the reservoir characterization. This tool comprises of details of the reservoir in terms of rock and fluid properties. Nowadays, thanks to the advanced development in oil and gas technology, the reservoir description contains more detailed information. Namely, the data obtained from the drilled wells is no longer limited to pressure only, but it also comprises of data on temperature, in-situ stress, and most importantly petroleum composition data as well. The presence of multicomponent mixtures, structures, heterogeneities, structures, heterogeneities, and thermal gradients are also taken into account in this detailed information required for the characterization of the reservoir.

It is known that in general, in the preproduction stage the reservoir fluids, while the temperature gradient is considered to be negligible. Of course, these assumptions are not valid for all of the reservoirs but are often used in the calculations since they can considerably simplify them. For example, in the case of the deep and tilted reservoirs, the thermal gradients are not considered as negligible.

Speaking of the petroleum composition, as an important factor that is often considered when characterizing a reservoir, the vertical or areal compositional variations are commonly observed. For example, vertical variations have been observed in many reservoirs, such as in an oil-saturated sandstone reservoir in the Campos Basin in Brazil (*Padua, 1997, 1999*), in the Anschutz Ranch East field, and the Brent and Statfjord reservoirs in the North Sea Brent fields respectively (*Schulte, 1980; Metcalfe et al., 1988*). In addition to those of the vertical plane, the occurrence of horizontal compositional variations has been noted in a reservoir in the Middle East (*Hamoodi et al., 1994*) and in the Ghawar Khuff reservoir in Saudi Arabia, where Temeng et al. (1998) documented a decrease in the hydrocarbons and condensate content and the increase of acid gas content with depth and temperature.

Generally, the occurrence of the vertical compositional variations is a result of the capillary forces, gravity and vertical temperature gradients (usually geothermal gradients). Also, the presence of both horizontal and vertical gradients may be attributed to numerous factors, such as for example the presence of additional driving force, such as diffusion, chemical reactions, the presence of horizontal thermal gradients, etc.

The occurrence of these compositional variations majorly affects the compositional distribution in petroleum. These compositional variations are often expressed in terms of reservoir continuity. Such information about the reservoir continuity is of great importance in the decision-making process for reservoir exploitation. Also, the distribution of the petroleum components is often used for the reservoir characterization, such as determining the presence of structures and the extent of the reservoir, which again is valuable information when planning the production.

There are numerous studies that investigate or predict the influence of several factors on the compositional changes in petroleum in reservoirs with existing temperature gradients, such as for example the convection and diffusion, that represent a common reason for the horizontal

and vertical compositional variations. These studies represent valuable lead for the production engineers in terms of the expectations of optimal recovery and exploitation.

2. Applications of geochemistry in oil production and exploration

Nowadays, geochemistry is proven to be a crucial and powerful tool in oil production. The improved and deeper knowledge about the processes of generation, migration, accumulation, and the timing of oil formation relative to the trap formation allows more efficient ways of managing the hydrocarbon asset, enhancing the recovery processes, identifying missed pay zones, etc. In the following will be additionally discussed the other applications of geochemistry despite those that were discussed in the previous sections.

2.1. Geochemistry and hydrocarbon asset life

In general, petroleum geochemistry plays a crucial role in the determination of the variations or the compositional changes that occur during the petroleum generation, migration and accumulation. The recognition of these variations is of great importance for proper and efficient management of the hydrocarbon asset. By measuring the compositional changes and detecting their variations, the geochemistry represents an effective tool for decision making during each stage of the hydrocarbon asset life.

The basin evaluation and prospect evaluation, discovery drilling, developmental drilling, production, enhanced recovery, abandonment, and reclamation are the general stages that each hydrocarbon asset experiences. Each stage of this life cycle requires different information necessary for the proper management and development of the asset. For example, during the earliest stages of the asset's life, it is quite important to determine whether the basin contain economic quantities of oil and gas, to locate the largest accumulations, to evaluate the oil quality, as well as to determine the distribution of oil versus gas. On the other hand, during the late stages, the pay allocation, the reservoir compartmentalization, the locations of missed opportunities, the proper functioning of the production equipment, etc. are the essential information required for the decision-making process. Using all these information, the

petroleum engineers are able to make a decision whether the enhanced recovery techniques work in a proper way or not, and also this information can give an indication whether the reservoirs are fully trapped.

So far, it has been proven that the petroleum geochemistry is a powerful science providing useful techniques that give an important contribution in minimization of the exploration risks by providing means to identify mixed-sourced petroleum, missed pay zones, also to allocate comingled zones, etc. The application of the geochemical techniques when exploring oil and gas allows profound understanding of the petroleum's generation, migration and accumulation processes.

This knowledge is essential for the decision-making processes related to drilling. As more samples become available, the geochemical techniques become more efficient in defining complex basin filling histories, identifying the petroleum source and providing an explanation for the unusual distribution of oil and gas. The forecasting efficiency for locating hydrocarbons during the exploration stage is especially increased when applying the geochemistry techniques together with geophysics. Namely, the conjunction of these two sciences increases the efficiency of about 63% (*Sluik and Parker, 1986*).]

In case of identification of complex basin, filling histories is paid special attention to the analysis and interpretation of the complex composition of petroleum fluids. Since the petroleum composition is mainly dependent of the type of original source rock material and its maturity and is also majorly affected by accumulation or postgenerative alteration processes, such as biodegradation, water-washing evaporative fractionation, and others, the petroleum composition is an important indicator of the type of source rock, as well as of possible alternative processes.

For example, in the study applied on an offshore tertiary rift basin in eastern Asia, performed by Bisada and Elord et al., 1993, the compositional analysis of each of the oils from the three deltaic systems from which the basin is comprised, has shown that 1oil from the northern accumulation was probably sourced from hypersaline lake facies, whilst the oil from the southern accumulation was sourced from freshwater lake facies. On the other hand, the central accumulation was determined to be a mixture of two oils, which was explained by the fact that this accumulation had isotopic and compositional characteristics of both types of

sources. Additionally, the geological findings confirmed the two oil types were generated from separate generative settings. Also, according to the geological findings, it was indicated that the mixed oil was accumulated at a ridge, whose location allowed receiving and accumulating oils from both freshwater and hypersalinity facies.

Furthermore, the importance of geochemistry in accessing significant parameters, such as the distribution of oil versus gas, heavy oil versus light oil, high-sulfur versus low-sulfur oil, etc. is illustrated in the study done by Anka and Callejon et al., 1996, in the Barinas Basin, Venezuela. The integrated geochemical-geological approach together with the use of computer simulations, proved that, opposite of the expectations, the source of the oil was the La Luna formation, located at a larger distance of the basin, and not the nearby La Morita formation. Additionally, it has been indicated that the basin had a complex basin history.

Namely, it has been found that there is an initial impulse of oil that filled the shallow and subsequently degraded reservoirs, whereas the rapid thrusting of source rock sequences and of the buried reservoirs located in the northern part of the basin resulted in cracking of the reservoired oils from the deeply buried sections, which caused the generation of gas condensates from the local source rocks (Anka and Callejon et al., 1996). Additionally, it has been revealed that the mature source rocks located in the central and the southern parts of the investigated basin expelled oil in the upper reservoirs. This filling history provides a proper explanation for the oil distribution in the reservoir. The study confirmed that in the central and the southern parts of the basin there is a prevalence of light oils, whereas in the northern part there is a prevalence of gas condensates. On the other hand, on the southern part of the basin, heavy degraded oils are commonly present (Anka and Callejon et al., 1996).

Knowing that despite the principal processes of petroleum generation, migration and accumulation, the enhanced recovery and production processes are also a major factor that alters the composition of the petroleum, its monitoring becomes a powerful tool for characterization of these processes. Therefore, nowadays there is majorly increased application of the geochemistry in production and enhanced recovery processes, providing an enhancement of the hydrocarbon asset life in the same time.

2.2. Identifying new exploration opportunities or missed pay zones

The geochemistry represents the ultimate tool that is effectively applied for the identification of new or missed opportunities during the stage of exploration and development. For example, in case of reservoir's uplift, there is a sudden change in the pressure-temperature reservoir, which under the right conditions causes a separation of the oil in two phases and migrating of the light phase towards the shallower parts of the sedimentary basin. This phase separation history is easily indicated by the distinctive geochemical composition of the resulting condensate and the residue. If the condensate portion is first encountered during drilling, this means that residual hydrocarbon accumulation is probably somewhere down-dip, whereas in the case where the residue is encountered first, the light phase has probably migrated and accumulated up-dip.

2.3. Delineating reservoir compartmentalization

Nowadays, the high-precision techniques and analysis of the hydrocarbon composition have been successfully employed in the delineation of the reservoir compartmentalization and reservoir communication. The knowledge about the reservoir's geometry and the location of any possible faults or permeability barriers is essential in the stage of oil and gas production. Having in mind that the petroleum composition is sensitive to changes during the processes that take place in the reservoir, it is obvious that petroleum fluids from different reservoir compartments would have a different composition.

An example of the application of geochemistry in the determination of the reservoir compartmentalization is the study performed by Ramos and Callejon et al., 1999, within a gas field in Mexico. Several samples of this gas field had been investigated for their isotopic and component compositions. As a result, it was confirmed that the gases produced from different fault blocks have a different composition, but it was also noted significant compositional differences among gases that were produced in the same fault blocks. Any significant difference was interpreted as the possible existence of a barrier enabling fluid communication, knowing that the rate of gas diffusion is generally relatively rapid. This allowed utilization of the data for the purposes of identification of unknown barriers within the fault blocks,

providing a profound understanding of the fluid's movement within the investigated field. Additionally, the subsequent comparison proved that the geochemical conclusions were consistent with the 3D seismic data.

Thanks to the geochemistry were provided key information crucial for distinguishing between two geological interpretations of the field. The ambivalent geological information in this study lead to two interpretations of the location of the significant faults within the field (*Kaufman, Ahmed, et al., 1989*). In order to find a distinction between the two models, the results of the analyzed oils from the producing wells were presented in star diagrams. It should be noted that the plot of the data on a radial axis enables easy recognition of differences. According to the interpretations of the results, only three groups of similar oils were consistent to one of the provided geological interpretation, clarifying that the geological interpretation was more correct, improving the knowledge about the filed required for future developments.

In general, the reservoir compartmentalization can be done by integration of the geological, geochemical and engineering data. The main aim is a determination of the sealing capacity of the potential no-flow barriers. In such a case, the oil geochemistry provides a very inexpensive key tool for interpretation of the ambiguous geological and engineering information (*Kaufman et al., 1990*).

Since the reservoir compartmentalization generally refers to the presence of fluid flow barriers between two fluid sampling points, petroleum geochemistry is considered to be especially useful in providing information required for the evaluation of the reservoir continuity, which is different from the implications of other data types, such as for example pressure decline-curves, RFT pressures, fault juxtaposition or Allen diagrams, etc (*Hwang et al., 1994*). This means that the petroleum geochemistry represents an effective tool for the identification of vertical and lateral flow barriers within a given reservoir. Usually, in order to access the reservoir continuity, the most commonly used tool in the geochemistry is the oil fingerprinting, which will be additionally discussed below.

2.3.1. Oil fingerprinting approach in assessing the reservoir continuity

In general, the oil fingerprinting technique is based on the integration of the geochemical information with the geological and engineering data. This technique is of great importance in

the process of accessing the reservoir continuity (*Slentz, 1981; Hwang and Baskin, 1994; Sunadararaman et al., 1995*). There are several variations of this technique. One of these variations is the comparison of the relative abundances of the “inter-paraffin” peaks of each oil sample. The main aim, in this case, is the comparison of the compounds that elute from the gas chromatography between the normal paraffin. Initially, have to be identified corresponding inter-paraffin peaks in all of the samples, after which is performed a comparison between several hundred ratios of closely spaced inter-paraffin peaks with the corresponding ratios in other samples, which allows identification of the ratios that differ the most between the investigated samples. In the and, the values for these ratios for each sample are generally plotted on “star” plots, where the composition of each oil is represented by a “star”. Each point on the star corresponds to the value for a given peak ratio. The star plots constructed in this way help in the differentiation of discrete groups of samples. In order to assess the reservoir compartmentalization, these data have to be combined with any other available geological or engineering data.

Often, in case of lack of communication between two samples, a large number of ratios will in one oil sample will probably differ by more than 10% from the corresponding ratios in another oil sample, whereas none of the several hundred inter-paraffin compound ratios of oils which are in fluid communication will differ by more than 10% from the corresponding ratios in oils with which they are in communication (*Kaufmann et al., 1990*). In general, these ratios are commonly distributed throughout the range C₈-C₂₀, indicating that as the number of ratios with significant differences decreases, the chance for lack of communication also decreases, knowing that the analytical reproducibility for the ratios of closely spaced inter-paraffin peaks is typically 1-3% (*Kaufmann et al., 1990*). In the case of gravitationally segregated oil columns, there are some exceptions. Namely, in such oil columns, the reservoir discontinuities are identified from the discontinuities in otherwise gradational changes in composition with depth (*Kaufmann et al., 1990*). As previously mentioned, the C₈-C₂₀ range is the most diagnostic range for the reservoir continuity assessment, taking into account that the lower molecular weight compounds are not subjected to comparison, since they are mostly affected by evaporative losses during the sample handling. It is important to be mentioned that this approach is effective for comparison of gas chromatography data only in case of a small number of available samples. In the case when the number of sample increases, a

summarization of all of the compositional variabilities between the samples is no longer possible using a single star plot, knowing that the number of possible compartments also increases. Therefore, in order to evaluate the compositional variability in large sample sets, several star diagrams should be required. Each of these diagrams is designed so as to give an answer to a specific question about the reservoir architecture. When making a general comparison of gas chromatography data for a large number of samples, the gas chromatography peak that had been used to generate several star diagrams is statistically compared and used in the construction of a single cluster analysis diagram (*Hwang and Baskin, 1994*).

There are several possible reasons for the compositional differences among the samples. For example, the different filling histories represent a significant reason for the compositional differences in the oils from two separate compartments, even in the case when these oils originate from the same source (*Masterson et al., 1997; 2001*). Also, the processes such as biodegradation, water-washing, and evaporative fractionation do not affect the identically sourced oils at the same extent, which leads to the different composition in the petroleum from separate compartments. An additional reason for the compositional differences might also be a fact that the oils are delivered from different source-rocks. Knowing that oils from different source rocks generally have different times of generation, as well as different migration paths, the presence of more than one source rock in the sedimentary basin will certainly cause the occurrence of different reservoir compartments that most probably will be filled with different mixes of oil from the respective sources (*Schoellkopf et al., 1998, 2000*).

The fact that a given star diagram can be constructed only from the data that had been acquired from the same instrument within a several day analytical period is an important aspect of this fingerprinting approach (*Kaufmann et al., 1990*). Generally, the data from a given diagram cannot be compared between instruments mainly due to differences in the analytical conditions that can be a possible reason for the occurrence of subtle differences in the peak resolution. The differences in the peak ratios are a common indication for this. Also, the data that was collected from the same instrument several months apart cannot be compared on a single diagram, taking into consideration that the analytical conditions might possibly change during the analysis of the samples.

In case of assessing the reservoir continuity in a gas accumulation, a greater range of geochemical analyses might be included, such as gas composition, gas chromatography data for the gas condensates, isotopic composition of carbon or hydrogen in specific gas species, as well as isotopic composition of carbon or hydrogen of the paraffins in the gas condensate, etc.

2.4. Maximizing the waterflood efficiency and monitoring of the produced fluids

Often, the results obtained from the geochemical techniques are crucial in the process of planning and optimizing a waterflood program in a given field, as in the case of the study of the Central Lago field, Venezuela, in which were investigated the means of enhancing the recovery efficiency. In this study performed by Elord and Vierma et al., 1997, were analyzed samples from different sand units in order to be identified the fluid flow units within the reservoirs, which is particularly important for optimization of a waterflood project. The data obtained from the geochemical techniques provided significant information about the reservoir connectivity and the fluid flow barriers, that is necessary for monitoring and planning of such enhanced recovery processes.

Knowing that the petroleum fluids are majorly affected by different geological processes, as well as by different types of processes that take place in the reservoir, the petroleum composition is of particular importance for investigating the hydrocarbon generation, migration and entrapment history. The enhanced recovery processes together with the production, usually change the petroleum composition. Taking into account that they change the composition in a predictable way, any compositional change in the produced fluids might be an indication of an occurrence of changes in the reservoir characteristics. These changes might also indicate some complications with the production equipment, or in some cases, changes in the subsurface conditions. Such changes can be easily identified at a low cost by periodical monitoring of the produced fluids. This periodical monitoring and geochemical analysis of the produced petroleum represent useful tools that might be of particular importance when solving numerous production issues. For example, the geochemical methods can be very

effective in predicting flow assurance problems, recognizing production tubing failure, or detecting cementing failure, etc.

2.5. Application of geochemistry techniques in predicting flow-assurance problems

An example of the application of the geochemistry methods when predicting the tubing failure is the case of using gas chromatography analyses of the oils from a deeper, high-pressured zone and a shallower, low-pressured zone, that were produced from separate tubings. The analyses showed that the oils from these two different zones were completely different which is the reason why they could be easily distinguished. But, many years later, the same analyses revealed that oil samples were actually the same and that they matched the high-pressured zone's oil. The main reason behind this was the breaching of the containment of the high-pressured oil and its flowing towards the low-pressured zone, which was probably caused by corrosion. This indicated that the production from the two tubings was mainly from the high-pressured zone.

In another similar case, the oil was mainly produced from the Monterey formation, which represents the high-pressured zoned, whereas the shallower, low-pressured Sisquoc zone was cemented. The analyses made during the production revealed the presence of fluid behind the well casing. According to the results, this fluid did not match the Monterey's oil, but the comparison of this casing fluid to the oil of the low-pressured zone confirmed that the fluid matched the Sisquoc's oil. This was a major indication that the cement job had failed.

The deposition of solid components, such as asphaltenes, resins and gas hydrates, and their precipitation generally cause plugging problems during the production processes. Therefore, the characterization and quantification of the asphaltenes and resins using geochemical analyses is a crucial step during the stage of field appraisal. Recent studies have suggested that the early prediction of the precipitation problems during the exploration stage is of particular importance in the selection of the production areas that do not exhibit tendencies to precipitates solids, avoiding problems during production. Also, this is the proper way to achieve planning and inclusion of the costs of specialized production techniques.

Additionally, the use of geochemical techniques in the identification of the source of environmental contamination is also common. The geochemistry is certainly capable to successfully address the environmental issues related to petroleum exploration and production. For example, in the study performed by Keith Kvenvolden et al., 1993, was investigated the residual tar sand from the Prince William Sound basin, following the Exxon Valdez spill happened in 1989. Numerous samples of tar sands had been collected from the nearby beaches and other areas around the basin. The identification of the source was done by using the carbon isotopic composition.

The results of the analyses performed in 1990, showed matching of the tar sand samples with the Alaska oil that was spilled from the Exxon Valdez. Some years later, the analyses were performed on samples mostly yielded from the California oil. After some investigations, it was confirmed that contamination in the Prince William Sound has mainly resulted from the destruction of the asphalt storage facility, located in Valdez. The destruction of this storage facility caused a spill of large amounts of asphalt into the investigated basin. It was assumed that the Valdez oil had dissipated, whereas most of the asphalt remained in the Alaska oil due to its higher resistance to evaporation and degradation.

3. Applications of reservoir geochemistry

Generally, the organic geochemistry is mainly focused towards exploration. Prediction of the hydrocarbon potential, evaluation of the thermal maturity, as well as quantification of the volumes of generated petroleum reserves are the main objectives of the geochemistry. Through the years, the major priority of the geochemistry application become oil production, as well as finding optimal solutions for reservoir-related problems. On the other hand, the main focused of the inorganic geochemistry is mainly towards defining the reservoir quality and description of the rock properties. Therefore, most of the inorganic geochemistry studies ignore the geological and the geochemical information included in the reservoir and include discussions focused on the rock matrix. Speaking of the reservoir geochemistry, its aim is understanding the vertical and lateral heterogeneities in the reservoir, which is especially important for the exploration, production and the development strategies enhancement. Another important aim

of the reservoir geochemistry is understanding the interaction between the rock, water, and petroleum, which allows understanding the influence of this interaction on the petroleum wettability, viscosity and formation of special features in the reservoirs, such as for example the tar mats.

In the following section will be discussed the ways of applying geochemistry techniques in the reservoir engineering studies.

3.1. Development of field filling and mixing models

According to different studies whose objective is the occurrence of compositional heterogeneities in the reservoir and reconstruction of the reservoir's filling and mixing, the petroleum initially enters the reservoir's pores associated with the coarser lithologies, with the lowest entry pressures. As the migration proceeds further, the increased buoyant pressures lead to the propagation of the petroleum into the small pores and trapping of the residual water formation water. When arriving from one side of the trap, the freshly generated petroleum displaces the previously generated petroleum laterally and vertically. This prevents widespread mixing in the petroleum column (*England and Mackenzie et al., 1989; England 1990*). When a second source becomes mature during the filling process, or when the maturity increases, the physical and chemical nature of the petroleum continuously changes, ensuring vertical and lateral compositional variations in the petroleum column as the process of reservoir filling is completed. These compositional variations might be also introduced by water washing or biodegradation of the petroleum column.

Attempting to establish the physical and chemical equilibrium in the petroleum column, the molecular diffusion, as well as the density-driven mixing eliminates the inherited compositional variations. According to the studies performed by England and Mackenzie et al. (1989), the diffusive mixing is generally rapid vertically within individual oil columns, which leads to the establishment of gravitationally segregated concentration gradients, whereas the diffusive mixing occurs relatively slow across large fields. On the other hand, about the density-driven mixing was concluded that it occurs geologically slow in fields with low permeability, and in the reservoirs characterized by high permeability this type of mixing is generally rapid from a geological point of view.

An especially important implication of England's study is that the elimination of the lateral compositional variations that have been inherited in the process of reservoir filling should be avoided. Since many chemical compositions may produce fluids with identical densities, in some cases, the lateral density gradients may have been eliminated avoiding homogenization of the petroleum's chemical composition. Additionally, the mechanical instability within a given petroleum column would suggest the occurrence of barriers to vertical mixing. The model for the hydrocarbon fraction in clastic reservoirs of high permeability was validated by several case studies, according to which, petroleum columns in giant fields characterized by high-quality reservoir connectivity are in general vertically homogeneous and laterally heterogeneous (*Stoddart et al., 1995; Horstad et al., 1995*).

According to the principles of the scales at which occur the fluid heterogeneities in the reservoir, at the kilometer to tens of kilometers scale, at kilometer scale, the gradients in GOR and maturity parameters may indicate filling, whereas vertically in scales of a few to a hundred meters, the compositional steps may indicate barriers (confirmed by heterogeneities in salinity or $^{87}\text{S}/^{86}\text{S}$ ratios in case of aqueous samples, or by heterogeneities in the biomarkers). At pore scale to molecular scale on reservoir surfaces, or within fluid inclusions, the compositional variations may provide information about the reservoir state, or in some cases about the paleofluid composition.

3.2. Geochemical techniques crucial for the development of reservoir engineering investigations

The development of new techniques developed by the petroleum geochemists, such as modifications of the gas and liquid chromatography, and mass spectrometry, had a major contribution to the development and improved application of the reservoir geochemistry. Since they allow rapid obtaining of the gross, molecular, and isotopic composition of the reservoir fluids and core extract, they are considered to be key analytical techniques in the field of reservoir geochemistry. These three key analytical methods are the thin layer chromatography-flame ionization detection, thermovaporization-gas chromatography-flame ionization detector or -mass spectrometry, and determination of the $^{87}\text{S}/^{86}\text{S}$ isotopic composition of the salts that have precipitated from residual water or formation water that evaporated during the core storage.

In particular, the thin layer chromatography-flame ionization detection permits high-resolution screening of reservoir core solvent extracts, which enables complementation of the Rock-Eval screening and evaluation, whereas the determination of $^{87}\text{S}/^{86}\text{S}$ ratio also known as isotopic composition, provides information about the composition of the water that is originally present in the reservoir. Nowadays, the thermovaporization-gas chromatography-flame ionization detector or -mass spectrometry automatic devices allow obtaining of high-quality gas chromatography and mass spectrometry data in reservoir cores (*Stoddart et al., 1995*).

In general, it is favorable the sampling programs to be comprised of all the available sample types including produced gases, oils, and waters, well-test fluids (DST/RFT), as well as cores and cuttings. The analytical strategy usually starts with a rapid screening of a large number of samples, later followed by a more detailed analysis of the selected samples. All the produced oils and gases should be subjected to liquid chromatography, gas chromatography or mass spectrometry-gas chromatography analyses. The geochemical analytical program usually contains screening of 400 to 450 core extracts that are generally analyzed by thermal desorption-gas chromatography, which is followed by thermal desorption-gas chromatography-mass spectrometry analyses of 150 to 200 selected core samples (*Bjoroy et al., 1991; Stoddart et al., 1995*).

The fluid samples are of special interest since they provide a detailed analysis of fluid that is mobile under well-test or production conditions. They are usually inadequately sampled, which is the reason why they should be carefully archived as fluids that are initially present in the reservoir. They are especially important in the determination of the compositional differences, which is impossible without reference to the initial state of the reservoir fluids. On the other hand, the reservoir core extracts are especially important for obtaining information about the reservoir's residual fluid. In the case of petroleum, they are obtained by extraction with organic solvents, whereas in the case of precipitated salts, the reservoir core extracts are obtained using deionized water. Immobile phases may be also included together with the remains of the fluid that was present in the reservoir porosity during the process of core recovery. It is important to be mentioned that the core extracts are not sufficient for a complete reconstruction of the fluid composition, but allow a better understanding of the compositional variations. On the other hand, the production fluids that are subjected to well test analyses

allow complete compositional characterization. Although they can be produced from a significant depth range covering several productive reservoir zones, they provide limited information about the spatial variations in the petroleum composition.

Numerous studies have confirmed that reservoir core extracts and the DST fluids have similar hydrocarbon fingerprints, whereas the presence of non-hydrocarbons in both of the sample types can be different, depending on the solvent type using in their extraction. Namely, the core extracts contain considerably more non-hydrocarbons compared to the corresponding well-test fluids (*Hillebrand and Leythaeueser 1992; Stoddart et al., 1995*). By analyzing the content of fluid inclusions, the aqueous and petroleum paleofluid can be sampled in core and cutting samples. According to some studies, as the core extracts, the petroleum trapped within the fluid inclusions may also be characterized by the higher presence of non-hydrocarbons compared to the bulk fluid from which they were formed (*Macleod et al., 1993*).

3.3. Application of geochemical data

The plots of petroleum fraction concentrations and molecular parameters on both vertical logs and maps, as well as the separate plots of produced fluids and core extract data, are common conventional approaches to visualization and analysis of the geochemical data. In general, the determination of tar mats, the water-oil contact, or the assessment of the reservoir filling-draining scenarios are obtained by using cross plots of petroleum concentrations obtained from core extracts analysis. Porosity data and conductivity logs may also be useful in this purpose. It should be considered that the visual analysis should be confirmed with statistical analyses.

The geochemical data is highly valuable when solving various problems related to production. For example, the results from the comparison of the data obtained by high-resolution gas chromatography fingerprints of crude oils, displayed by star plots have been successful to a variety of production tubing leakage and reservoir continuity problems. Also, the principal composition analysis represents another useful tool that allows observation of multivariate data which is required for the identification of the compositional similarities between the analyzed samples (that can be represented on score plots), as well as for defining the relationships between the variables (usually presented on loadings plot). The scores plots

have proven to be a successful tool that provides quick and easy separation and recognition of different petroleum populations, whereas the loadings plots have a special role in the identification of the compositional differences between different petroleum populations. Another advantage of the principal component analysis is the production of latent or reduced variables that actually represent the principal components that provide a description of the data variance expressed in terms of the existing variables. Downhole or across a given reservoir, the principal component scores can be plotted as a condensed variable summarizing all of the data set variances.

For example, the different petroleum populations in the Tor formation and the overlying Ekofisk Formation was proved by the vertical distribution of the molecular data in the plots of molecular parameters obtained from a thermal desorption-GC-MS analysis of core samples versus the production well's depth of the Eldfisk Field. This vertical distribution was present as well in the plots of the scores of each sample obtained by principal component analysis of the biomarker dataset. Additionally, the principal component analysis, as well as the visual analysis, confirmed that these two petroleum populations are divided by the Ekofisk/Tor boundary (*Stoddart et al., 1995*). Such an equivalent use of engineering and geochemical data proved that the use of molecular data set has an important role in early identification of the flow barriers within the reservoir.

Furthermore, there are several techniques available searching for new populations elsewhere in the reservoir or in another one, once they have been located (which is commonly done by using t-tests). Such a technique is the artificial neural networks that generally have application as predictive pattern recognition techniques and can be trained for recognition of features such as tar mats when core-extract data is available. Also, they can be usually trained to recognize sediment facies and depositional environment signatures from electric log suites (*Herz et al., 1990; Baldwin 1991; Cardon et al., 1991*).

When used together with geological, well-test and engineering data, the reservoir geochemical studies represent an effective reservoir description tool, taking into account the advantage that the reservoir geochemistry data can be collected and interpreted early in the field appraisal, or directly after the wildcat drilling, as long as core, fluid or cutting samples

have been obtained. As discussed below, each sample type contains a different type of information.

a) Fluid samples

The examples of vertical and lateral compositional variations that indicate variations in both bulk and molecular properties in the reservoir petroleum, are generally used to infer the maturity and source facies of populations within the reservoir, or to identify the maturity gradients across fields, and thus infer the fill points of reservoir segments and locate satellite fields. Furthermore, they can be used to detect leaking production strings, to infer laterally extensive, in-reservoir barriers, or to aid in the siting of the production wells.

In general, the vertical compositional variations in the water leg indicate the presence of barriers to fluid flow. This is particularly important for correct locating of the perforations within the water injection wells. On the other hand, the variations in brine chemistry or CO₂ content across a field could have a major impact on the solution of scaling problems during production, whereas the unrecognized salinity variations would lead to errors in the estimation of reserves.

b) Core extracts

Determination of the extent of drilling mud contamination is the initial step in the study of core extracts. Namely, the oil-based muds are problematical for petroleum analysis, whilst the water-based muds are potentially worse for residual salt analysis (*Smalley et al., 1992*). Usually, the reduced concentrations of the petroleum-derived polyaromatic hydrocarbons are an implication of contamination by diesel-rich oil-based muds. This type of contamination can be also detected from the GC fingerprints (*Larter et al., 1991*). It is important to be mentioned that such contaminations do not represent a major problem for the geochemical analyses since it has been proved that reliable biomarker data can be still obtained even from highly contaminated cores. Speaking of residual salt analysis, the determination of the extent of penetration of drilling mud into the core is particularly important in such type of analysis. This can be achieved by determination of the ⁸⁷S/⁸⁶S ratio of salts leached from samples that were taken from transects across cores with a range of permeabilities (*Smalley et al., 1992*). This provides the establishment of the extent of penetration which gives greater confidence to the

sampling programme, in which are generally included samples taken from the hart of the cores from the lower permeability zones. Additionally, the Rock-Eval technique can be used for reservoir cores screening, which provides information on the bulk petroleum concentrations (S1 yield) or information on the heavy-oil or tar mat zones (*Karlsen and Larter et al., 1989; Ghenima et al., 1991; Wilhelms and Larter et al., 1994; Wilhels et al., 1995*).

c) Fluid samples

In general, the fluid inclusions are small samples of fluids that have been previously present in the reservoir and trapped in diagenetic cement. In the case of precipitation of the host material, the information on the salinity of the present water can be provided from aqueous inclusions. The estimation of the timing of mineral precipitation is done by using a combination of the time-temperature curve for the formation and homogenization temperatures of the fluid. Also, the comparison of the salinity of the water present in the reservoir might be a useful indicator of whether there was a water replacement in the reservoir since the formation of the fluid inclusions.

Generally, in order to produce interpretable data, the inclusions in carbonates are usually analyzed by thermal decrepitation-GC-MS, whereas those within silicates might require careful cleaning and crushing of separated cement phases (*Karlsen et al., 1993*). This implies that the inclusions are analyzed in the same manner as the core samples and the produced fluids. In the case when a sufficient sample can be extracted, valuable information on the source, maturity, and composition can be easily derived. Taking into account that the thermal maturity of the petroleum can be assessed using their fluorescence spectra, which requires calibration against a specific petroleum province using geochemical data (*McLimans 1987*), it is more favorable to assess the source and maturity through direct geochemical measurements. For example, *Nedkvitne et al., 1993*, used biomarker data to show that a carbonate or are-sourced oil was present in the Ula Field when the reservoir was at about 50°C. The complexity of the reservoir filling was revealed by the presence of second minor source rock in the area which was mature long before the marine source. The presence of the second source was suggested by the present oil sourced from a clastic marine source-Mandal Formation. These authors have also shown that the determination of the petroleum distribution, as well as the fluid-inclusion study, have a special contribution to the enhancement of the conventional

reservoir geochemical study. Since most fields are not filled in a simple tank-line manner, the information on how the reservoir has actually filled is a particularly important input into decisions relating to field connectivity and drainage.

As previously mentioned, the time-temperature-pressure histories combined with the homogenization temperatures can be used to determine the timing of the formation of the fluid inclusion, which also provides information on the timing of the fluid displacement within the reservoir block, or the timing of the compositional changes of the fluid. Since the determination of the actual trapping temperature and pressure of the inclusion from the homogenization temperature depends on the PVT properties of petroleum than those of water, it is usually assumed that the composition of the petroleum is identical to the composition of the locally reseroired oil. This approach has not been proved to be realistic since numerous studies implied that the petroleum in the inclusions is generally enriched in NSO compounds (*Macleod et al., 1993*).

3.4. Application of geochemistry in locating tar mats

Generally, the compositional variations in the polar species such as resins and asphaltenes do not equilibrate vertically within connected petroleum columns, as in the case of the hydrocarbon compositional variations (*Stoddart et al., 1995*). The tar mats represent asphaltene-rich petroleum zones, usually occurring in light paraffinic oil reservoirs, that can be up to a few tens of meters thick (*Jones and Speers 1976; Dahl and Speers 1976*). Their occurrence is detrimental to the reservoir quality since it is known that, they contain immovable reserves, as well as low permeability intra-reservoir flow barriers. Also, they have usually formed close to zones of geological discontinuities such as OWCs, or sometimes above permeability contrast. This suggests the possibility of deaspahlatation problems occurrence (*Wilhems and Larter, 1994*).

Numerous studies have proved that the tar mats occurrence is the result of the asphaltene precipitation. These asphaltenes are usually from the oil charges and their precipitation happens due to subtle changes in the physical and chemical solubility factors of the crude oil, which have been induced by the gas solution. Thermal alteration or pressure and temperature changes during the migration can also be a reason for their formation *Wilhems and Larter,*

1995). According to the latroscan analysis of core extracts, the small tar mats that have a thickness up to one meter, are common features in the light-oil reservoirs. The understanding of the subtle changes of the phase behavior of asphaltenes in crude oil is an accurate base for the development of models that can predict the formation of tar mats (*Hirschberg, 1984*).

3.5. Influence on the NSO compounds on the reservoir wettability and application of the NSO geochemistry

Many authors have confirmed that compared to the oil produced from the same reservoir zone, the core extracts are more enhanced in NSO compounds. One of the reasons for this enrichment is the loss of evaporative loss of light material from the cores during the storage. Additionally, certain authors, such as for example Horstadd (1989), concluded that the polar species are naturally retained during the oil production. Also, it was noted an occurrence of a polar-rich rim on some reservoir cores. This suggests that the core recovery may sometimes produce enrichment on the edge of the core. In the study of the Eldfisk Field performed by Stoddart et al. 1995, has been shown that molecular composition of the neutral nitrogen compounds in this field is heterogeneous on a meter scale and that is out of equilibrium with the mobile compositionally homogeneous produced oils. Some nitrogen species that have been extracted from the cores in such case are immobile and thus isolated and out of equilibrium with the bulk oil charge. Understanding the adsorption processes of the NSO compounds on reservoir surfaces is of major importance in the attempt to understand the influence of such processes on the reservoir wettability. Although there is strong debate over the physical meaning of wettability determinations, there is abundant literature evidence to indicate that many reservoirs are of intermediate or, more probably, mixed wettability (*Treiber et al. 1972*), with a significant oil-wet fraction. According to many calculations and observations, the strongly absorbing N and other compounds might have a considerable influence on the reservoir wettability. It is important to be mentioned that many of the key advances in the understanding of the adsorption of the NSO compounds on reservoir surfaces have been made using bulk analyses, which clarifies that the geochemists may have limited scope for the application of the GC-based technology to the higher molecular weight long chain alkylated polar fractions that are most likely the reason for the alteration of the reservoir surfaces.

The application of the NSO geochemistry in petroleum engineering is an area of potential development. As mentioned in the previous sections, the core extracts have higher NSO content than the DST. Also, according to Glaso (1980), the increase of the NSO content in a given oil by 15 % could result in reduction of the API gravity and consequently changing of the bubble point for several hundreds of psi, which would mean that the PVT properties of the core extracts or the reservoired petroleum could be different from those of the well-test oils.

Commonly, when matching the actual production history of a given field with the simulations, several discrepancies can be noted, generally due to some uncertainties about the rock properties (*Stoddart et al., 1995*). The fluid compositional variation is also equally important, especially in the case when the well-test oils have a composition different from the composition of the total petroleum in the reservoir. Usually, when are indicated differences between the nitrogen species distribution and their concentration in the core extracts and the produced oils of a given reservoir, it is clear that the utilized PVT procedures are valid (*Stoddart et al., 1995*). In such case is suggested an enrichment of NSO compounds on reservoir surfaces with implications for reservoir wettability.

3.6. Assessment of the migration volumes

It is known that during the secondary migration significant volumes of petroleum are generally lost in the carrier system, which is commonly caused due to the updip or upsection movements of the petroleum. This loss of petroleum volumes majorly affects the prediction of potential reserves (*Mackenzie and Quigley, 1998; England et al., 1987; Larter and Horstad, 1992*). According to the mass balance calculations, the oil-saturated portion represents 1 to 10 % of the porous carrier volume (*England et al., 1987*). Knowing that a certain percentage of the carrier system might retain some amount of oil, the well-constrained estimates of the total carrier volume are necessary for the accurate assessment of the migration losses.

The main doubt in such cases is to determine how much water and rock the petroleum charge interacts with, during the process of migration from the source to the trap. It is important to mention that the drainage volumes are inferred from the mass balance calculations, as well as from the seismic data since the migration pathways are rarely drilled (*Macgregor and Mackenzie, 1986*). Theoretically, direct determination of the migration volumes can be done

using the chemistry of petroleum, as well as of the associated water. But, the geochemical indicators based on hydrocarbon species, that have resulted from the attempts to use petroleum composition in order to assess the migration distances, are qualitative and have found little application (*Seifert and Moldowan, 1978*). Therefore, a better approach is using a range of compound classes that exhibit the range of chemical properties that are suitable for the task, i.e. range of compounds that partition differently between the oil, water, and rock during the process of migration and are certainly contained in the petroleum.

In general, some phenolic compounds are partitioned between the oil, water, and rock, and other compounds, such as alkyliquinolines and alkylcarbazoles are strongly adsorbed onto the mineral surfaces or solid organic matter, whilst some compounds, such the long *n*-alkane chains are strongly retained in the oil. Only a few compounds, such as for example short-chain carboxylic acids are strongly partitioned into the aqueous phase (*Barth and Riis, 1992; Barth and Bjorlykke, 1992*). Therefore, the composition of petroleum is considered to be a function of the generated petroleum's composition, as well of changes induced by a variety of possible interactions between water and rock along the primary and secondary migration pathways, or in the reservoir itself (*Lafargue and Barker, 1988*). As indicated by the relative abundances of the selected compounds in the reservoired petroleum, the extent of change represents a potential way to measure the migration volumes. Since the relative and absolute concentrations of the petroleum-derived compounds in formation waters are potential indicators of the water/oil ratios (*Macleod et al., 1993*), it is clear that the most effective approach for assessment of the migration volumes will certainly involve a study for both waters and oils.

Additional progress in this area has been made using nonpetroleum species. For example, Ballentine et al., (1991) used noble gas data in order to assess the fluxes of water that is involved in the accumulation of gas in the Pannonian Basin.

Generally, the species whose functional groups are capable of strong hydrogen or acid/base interactions, such as carbazoles, carboxylic acids, phenols, and quinolines are those who are characterized by strong interactions with minerals and water. Also, Sandvik et al., (1992) suggested that most of the aromatic and non-hydrocarbon components present in the petroleum are also significantly partitioning into solid organic matter. According to various observations, there is strong experimental and empirical evidence for the adsorption of the nitrogen species

onto mineral surfaces, as well as for the fractionation of individual nitrogen compounds during the migration (*Charlesworth, 1986; Bonilla and Engel 1988; Brothers et al. 1991; Yamamoto, 1992; Li et al. 1992, 1995*). Furthermore, in many migration pathways were detected enrichments in some NSO compounds (*Miles, 1990*). Numerous experimental studies have suggested that the extent to which individual pyrrolic compounds are adsorbed from a certain organic phase onto a polar surface is strongly determined by the steric effects that are related to the alkylation position relative to the active pyrrole functionality. Also, these studies suggested that the pyridinic nitrogen compounds and the compounds with exposed functionality adsorb more strongly than the pyrrolic compounds and the compounds in which the pyrrole functionality is shielded by adjacent methyl groups, respectively (*Li and Larter, 1993*). Generally, the differences between the nitrogen compounds between the petroleum and the source-rock extracts could result from several processes.

Using several studies of the restoration of cores for laboratory analysis performed by Cuiec (1977) and of the rate of partition of petroleum compounds from oil spills into water, performed by Southworth et al., (1983), has been observed that the equilibration system of the NSO compounds between the oil, porewater, oil-wet organic matter and initially water-wet mineral phases in a given reservoir or carrier system, would be established within a maximum of a few years within a static oil column. On the other hand, the equilibration of the petroleum species that contain water and rock masses, surrounding the migrating oil, will majorly depend on the relative rates of the petroleum migration. The equilibration of these petroleum species will also depend on the diffusion from the stringer into the surrounding water-rock system. When assumed that is established local equilibrium in the oil-saturated fraction, the distribution will be affected by the following factors: the aqueous solubility of the component, from the oil-water partition coefficient, the distribution coefficients that describe the equilibrium between the oil-wet organic matter and the oil, and between the water and the water-wet mineral phases, the relative masses or volumes of the four present phases. In general the properties such as distribution coefficients, aqueous or hydrocarbons solubilities, oil-water partition coefficients etc. are dependent on the extent of alkylation and the position of the alkylation relative to the active functional group, which means that as the alkyl substitution increases, the aqueous solubilities and the distribution coefficients decrease, whereas the partition coefficients and the hydrocarbon solubilities increase (*Lyman et al., 1982*).

Speaking of the nitrogen compound, it is known that the source and maturity effects may influence their abundance in the petroleum, but are less likely to affect their relative abundances. The extent to which the nitrogen compounds are retained within the source rock or the secondary migration pathways can be determined in different ways, depending on the type of the surface. The environmental literature suggests that for example, in the aquifer the adsorption of hydrophobic species happens mainly onto organic matter where the TOC exceeds 0.1 % (*Lee et al., 1988; Perlinger and Eisenreich, 1991*), while the kerogen have high sorption capacity for the petroleum species (*Pepper, 1992; Sandvik et al., 1992*), which implies that the minerals will affect both the hydrophobic and the hydrophilic species, whereas the solid-phase organic matter in deeply buried sediments are important for hydrophobic compounds adsorption (*Sandvik et al., 1992*).

In order to determine the distribution of solutes between the migrating oil, the water, and the rock surfaces, such as kerogens or bitumen, is used a model in which are included complex sets of differential equations, that potentially involve non-equilibrium diffusion descriptions and partitioning processes in addition to advection. This means that this model represents a simplified equilibrium partition model that gives an illustration of the main factors that are involved in an equilibrium three-phase partition process.

The mass balance and the partition of a given component within the system, when assuming a simplified water-wet porous medium, or established equilibrium between oil and water, and the water and rock, has the following form:

$$C_i V_o = C_r V_r + C_o V_o + C_w V_w$$

$$P = \frac{C_o}{C_w}$$

$$K_d = \frac{C_r}{C_w}$$

Where: C_i represents initial component concentration in oil (kg/m^3), V_o is the oil volume (m^3), C_r is the concentration adsorbed on the rock (kg/kg), M_r is the mass rock (kg), C_o is the final concentration in oil (kg/m^3), C_w is the concentration in water (kg/m^3), V_w is the water volume (m^3); P represents a partition coefficient between water and oil, and K_d represents distribution coefficient between rock and water;

Solving for C_o , C_w , and C_r , the following equations are obtained:

$$C_o = \frac{C_i PV_o}{K_d M_r + PV_o + V_w}$$

$$C_w = \frac{C_i V_o}{K_d M_r + PV_o + V_w}$$

$$C_r = \frac{C_i K_d V_o}{K_d M_r + PV_o + V_w}$$

In the case of negligible adsorptive interactions ($K_d \rightarrow 0$) the equation for C_o becomes:

$$C_o = (C_i PV_o)/(PV_o + V_w)$$

In the case when single volumes of water are contacted and equilibrated one at a time, this equation has the following form:

$$C_o = C_i(PV_o)/(PV_o + 1))^{V_w}$$

In more realistic situations, in which the oil, water, the oil-wet rock, and the water-wet rock are simultaneously in equilibrium, are obtained more complex situations.

Similar progress has been made using a model illustrated by the *n*-hexane/benzene ratios. In this case, it should be considered that the benzene partitions more significantly into the water. Also, the changes in the *n*-hexane/benzene ratios along the migration pathway will be controlled by the partitioning between oil and water, when considering the oil-gas phase equilibrium as unimportant. These ratios in the model were used to make preliminary estimates of the maximum water/oil ratios of hundreds for one suite of North Sea petroleum, in which was concluded that the small water/oil ratios and the occurrence of petroleum in water-soluble or adsorptive compounds are most probably an indication that the petroleum sources and traps are connected by relatively few, but efficient rivers of oil.

4. Application of biomarkers

The biomarkers represent preserved lipid components frequently found in the coal's bitumen or in the kerogen. They have significant importance because they can be linked with biological precursor compounds due to the preservation of their basic skeletons in a

recognizable form through the stages of diagenesis and much of the catagenesis. The oxygen-containing functional groups are part of many biomarkers. They generally undergo the same processes of defunctionalization as the bulk organic matter. During the stage of catagenesis, part of the biomarkers may chemically bond with the kerogen structure, as incorporated low-molecular-weight biomarkers. Otherwise, they remain relatively unaltered, mainly due to encapsulation within resistant macromolecular structures, making them an important factor in their preservation.

During the stage of diagenesis, they undergo the same reactions as other biological groups, such as defunctionalization, aromatization, and isomerization. Mainly the processes of isomerization of biomarkers occur during diagenesis and catagenesis. Generally, the major isomerization occurs due to the incorporation of double-bond structures, namely the steranes in unsaturated biomarkers. In this stage is also common the configurational isomerization at stereogenic centers, but the occurrence of this type of configuration is associated with a higher temperature, usually common at the stage of catagenesis and the geochemical stage of coalification as well. In both of these types of isomerization, depending upon whether the hydrogen bonds with one or two electrons with the carbon atom, there is a migration of hydrogen atom, either in the form of hydrogen radical or hydride ion. An important role in these geochemical processes have mineral surfaces, such as clay particles.

Generally speaking, the biomarkers are present in crude oils in minor quantities (less than 1% wt). At late stages of diagenesis, occurs a transformation of the biomarker's functionalized precursor compounds into hopanes, steranes, and aromatic steroids. The pristanes and phytanes are most commonly frequent among the biomarkers and they can be easily linked to precursors, which is not the case with the rest of the hydrocarbons. They are mostly incorporated in the kerogen structure, as discrete molecules, at the late stages of diagenesis, while some portion of biomarkers can become part of the kerogen structure and later released during the stage of catagenesis.

Mostly they are in the form of hydrocarbons and represent the most important molecular source indicator in ancient sediments at late stages of diagenesis. All source-related biomarkers are very useful tools for studies of correlating crude oils.

The fatty acids and the sterols represent the most studied classes of biomarkers. The biomarkers can be analyzed together with the units of which the polysaccharides (monosaccharides) and the lignin (phenolic compounds) are formed. Their distribution provides significant source-related information.

- a) Fatty acids occur in either free or bonded forms and have various important roles in the living organisms, considering that most of them are cellular membrane constituents, such as phospholipids, protective coatings, such as wax, etc.. The palmitic acid is the most abundant among them. Over 500 fatty acids are present in higher plants and microorganisms, but the most abundant are relatively few in number. Multicellular algae's fatty acids are generally similar to those present in the microorganisms. Among the saturated straight-chain fatty acids, the long-chain components, in the range from C₂₄-C₃₆, have an important contribution in the higher-plant detritus to sediment, which why the chain length is an important indicator of the source rock. Additionally, the unsaturated, branched or the hydroxy fatty acids can provide more specific information.
- b) Sterols are present in organisms in free forms, such as the steryl esters or bond form, such as glycosides. Terrestrial and marine invertebrates contribute a range of C₂₇-C₂₉ sterols. Also, these types of sterols are present in fungi, where the ergosterol (C₂₈ compound) is predominant. The C₂₈ sterols are highly abundant in phytoplankton, whilst the C₂₇ sterols, particularly the cholesterol, are usually dominant in zooplankton. This distinction among the sterols contribution of different groups of organisms is done by the distribution of the carbon-number of regular sterols in young sediments.

The triangular plot of C₂₇, C₂₈, and C₂₉ provides significant information for the environment, i.e. aids in distinguishing marine, lacustrine, terrestrial and estuarine environments. This differentiation is based on unique associations of contributing organisms (*Huang and Meischen, 1979*). As a simplistic approach to the sterol distribution, this plot cannot always provide accurate information on the contributing groups of organisms.

For example, the distribution of sterol in phytoplankton obtains considerable variation. Namely, the distribution varies from the dominance of a single component in marine

eustigmatophytes and some diatoms to 10 or more major sterols, as in some dinoflagellates (*Robinson et al., 1987*).

Sterols have been recently identified as dominant in cyanobacteria (*Volkman et al., 1988*), but the synthesis of sterols and cyanobacteria is debatable (*Quirisson et al., 1987*) and according to the recent studies sterols have a low abundance (*Summons et al., 2002*).

5. Maturation of organic matter

Most of the chemical and physical properties of the organic matter change due to the thermal evolution. Therefore, these properties represent the main basis for thermal maturity evaluation. The chemical analysis of extractable bitumen, physicochemical analysis of kerogen and the optical examination of the kerogen are one of the most common methods for thermal maturity assessment. Various techniques for thermal maturity evaluation had been compared by Hood and Castano (1974). According to these comparisons, they proposed a scale known as Level of Organic Metamorphism (*Hood et al., 1975*).

5.1. Molecular maturity parameters

The gasoline-range hydrocarbons, the carbon-preference index, and the biomarkers are one of the most commonly used molecular parameters for thermal maturity assessment. These parameters will be more detailly explained in the next few paragraphs.

1. Light hydrocarbons

The light hydrocarbons of the gasoline range (C₄-C₁₀) usually account for 30% of the bulk oil and generally constitute the greatest volume percentage of the volatile oils and condensates. There are various theories about their origin. According to the theory proposed by Kissin and Thompson, they might have been generated with thermal degradation of hydrocarbons, that have been previously generated from kerogen together with rearrangements catalyzed by acidic clay (*Kissin 1987; Thompson 1979*). These light hydrocarbons are of particular importance

since any information that can be provided by them is majorly representative of the bulk oil. The most important components from this range are the C₇ components due to the isomer ratios provided by their isomers. These ratios are mainly used for correlation (*Phillipi 1981*).

According to some assumptions, the ratio of the acyclic alkanes to cycloalkanes increases together with the thermal maturity. Additionally, it has been proposed that the polycyclic alkanes form cyclopentanes and cyclohexanes when subjected to cracking. Those cyclopentanes and cyclohexanes undergo ring-opening and form acyclic alkanes as the temperature increases (*Phillipi 1975; Thompson 1979, 1983*). Taking into account these assumptions, the two most commonly used parameters in the correlations used for thermal maturity assessment, i.e. the heptane and the isoheptane value increase as the maturity increases.

Mango's model (*Mango 1990*) suggested that steady-state catalytic rearrangements of the *n*-heptane compounds in which are also included some transition metals and cyclopropane intermediate is responsible for the formation of the cyclic C₇ compounds and of various branched compounds. As a result of the opening of different bonds in the cyclopropane intermediate, the 2,4-dimethylpentane and 2,3-dimethylpentane are formed.

However, this model is not universally accepted, although it implicates on the use of the light hydrocarbons as thermal maturity parameters (*ten Haven 1996*). Since the light hydrocarbon distribution affects the maturity parameters and the light hydrocarbon distribution depends on the variations in the original contribution to kerogen, it should be paid special attention to the maturity differences (*Odden et al., 1998; Hayes 1991*).

The basic concept of the light hydrocarbons application as maturity parameters takes into account the fact that the living organisms do not synthesize a spectrum of C₃ to C₈ hydrocarbons, especially not naphthenes or aromatics. Additionally, as compared to the C₁₅₊ hydrocarbon fraction, these light hydrocarbons are generated from kerogen at higher rates as the maturity increases.

Generally, most of the techniques used for isolation of the light hydrocarbons include gas chromatography and according to the molecular range of the analyzed compounds are classified as gas analysis of either cutting gas or headspace gas (in range from C₁ to C₄), and

gasoline-range analysis of cores and cuttings (in range from C₄ to C₈). The main purpose of all these methods is to collect and store the samples immediately after the recovery in gas-tight containers. The analysis of the headspace gas is one of the simplest methods. The headspace gas is accumulated in the sample container at ambient temperature and a known volume of the headspace is taken by a syringe and injected in the gas chromatograph. The yield of the hydrocarbons that accumulate in the headspace can be increased by heating the sample below 100°C and by using high speed grinding on the rock sample (*Hunt, 1975*). Some other extraction techniques use continuous mobilization of the low boiling hydrocarbons from the source rock and their accumulation in a cold trap. This procedure is usually carried out by combining heating and grinding either under reduced pressures or by using auxiliary gas (*Le Tran, 1975; Philipi, 1975*). Since the solvent has to be removed by evaporation, this method can be applied only for higher molecular ranges of hydrocarbons with more than six carbon atoms. Various authors tried different techniques for isolation of the light hydrocarbons. For example, Johnathan et al., (1975) used thermal vaporization on the hydrocarbons C₆-C₁₅ fraction, which was subsequently analyzed by gas chromatography, whereas Le Tran (1971) isolated light hydrocarbons by acid digestion of the mineral matrix.

The variation of the composition obtained by the analysis of the cutting gas (from C₁ to C₄) and the gasoline-range (from C₄ to C₇) made by Bailey et al., (1974), can be summarized in the following way:

- Diagenetic stage in which the main component of the gas is methane and the gasoline fraction is lean;
- Catagenetic stage where the gas contains more C₂ to C₄ hydrocarbons, whilst the gasoline fraction becomes rich due to the presence of more components
- Metagenetic stage where the gas is mainly constituted of methane and the gasoline fraction is again lean;

Different authors proposed the application of the distribution of the main classes of the hydrocarbons of C₆ or C₇ in the maturity studies. For instance, Philipi (1975) used C₇ hydrocarbons and the triangular plots of the distribution of the paraffin, naphthenes, and aromatics. In his studies has been concluded that the paraffin abundance increases as the maturity proceeds, which is marked by a shift towards the paraffin pole. The same applies to

the higher molecular ranges, such as the C₁₅₊ fraction, whose abundance also increases with the maturity. Additionally, he used the concentration ratios of several compounds as maturation indexes (e.g. *n*-hexane and methylcyclopentane).

A similar approach was used by Thompson (1971), who established the “heptane” value” as a paraffanicity index, using large data of light hydrocarbons.

2. Carbon preference index (CPI)

This index allows the numerical representation of the odd-over-even predominance of the *n*-alkanes in a particular range and is often used as a maturity parameter in cases where *n*-alkanes from higher plant waxes are predominant (C₂₅-C₃₃ range) (*Bray & Evans 1961*).

In general, the CPI values reach a value of 1 as maturity increases. Consequently, immature higher plant contributions usually have values greater than 1. One of the reasons for such values might be the loss of the high-OEP component during the expulsion of the hydrocarbons. Also, some alkyl chains in the kerogen matrix, that produce the *n*-alkanes with no odd or even predominance, could possibly dilute the original OEP-higher plant distribution. The values of CPI less than 1 are not common and have been detected in *n*-alkanes with less than 23 carbon atoms, present in sediments of various ages and deposited in different environments. In such a case, the EOP might be a result of direct microbial biosynthesis (*Grimatt and Albeiges 1987*).

This index is based on the progressive change of the long-chain *n*-alkanes during maturation. Since these alkanes are generated as a result of the higher plant waxes contribution, it is assumed that the fingerprint of the long-chain alkanes reflects the contribution of the higher plants in most marine or terrestrial environments. Under these conditions prevail molecules with an odd number of carbon atoms, while with the kerogen degradation during the stage of catagenesis, new alkanes without predominance are formed. Therefore, the molecules with the odd-number predominance gradually disappear. There are several formulations for the CPI value, and consequently, there are various limitations used for their application.

Generally, the CPI value depends on the type of organic matter, as well as from its maturity. According to some studies, the samples from the same age, that have been brought to the same burial temperatures, showed different CPI values. The reason behind this is the fact that the original distribution of the *n*-alkanes and the amount of the newly generated alkanes determine

the alkane distribution. On the contrary, the same values of CPI may correspond to the different quantities of petroleum, depending on the kerogen type, since the *n*-alkane content in the petroleum varies according to the type of kerogen.

High CPI values are an indication of immature samples, but low CPI values do not necessarily indicate high maturity. Low CPI values can alternatively indicate lack of higher *n*-alkanes originated from terrestrial input. CPI values of 0.8 or less, may be observed in evaporative sediments with an even predominance, which could also point to immaturity.

3. Biomarker transformations

The isomerization of pristane at C-6 and C-10, of hopanes at C-22, of steranes at C-20, and the aromatization of the C-ring monoaromatic steroidal hydrocarbons, are important reactions that could be considered as potential maturity parameters. Most of the biomarker indicators, except the ratio of the short-chain to long-chain triaromatic steroids, have reached their endpoints prior to the end of the oil generation window and generally operate at low maturities. This limits their application in determining whether the potential source rocks have reached the onset of the catagenesis. The effective range of the maturity parameters can be extended by using the relative abundance of some families of biomarkers. For instance, the 18 α -neohopanes are less thermodynamically stable than the 17 α -diahopanes but more stable than 17 α -hopanes, which means that the abundance of the diahopanes increases towards the end of the oil window (*Kolips et al., 1994; Moldowan et al., 1991*). Despite the several cases where there is an increase of particular biomarkers at the end of the catagenesis, where higher temperatures prevail, there are some examples where the concentration of particular biomarkers rapidly drops with increasing the maturity during the stage of catagenesis, as in the case of the 28,30-dinorhopanes (*Peters and Moldowan 1993*).

During the stage of catagenesis, the variation in the isoprenoidal distribution is also common, and it can be used as a maturity indication. It has been proved that the pristane:phytane ratio changed with the coal's thermal evolution (*Brooks, 1970*). This observation can be also applied to kerogens of comparable compositions, although no comparable variations have been observed in type I and II kerogens. In all types of organic matter, the ratio of isoprenoids to *n*-alkanes decreases with depth and the rate of this decrease is not related to the amount of the generated alkanes and hydrocarbons, due to the fact that

isoprenoid chains are linked with the kerogen by weak bonds. However, the pristane:*n*-C₁₇ and the phytane:*n*-C₁₈ ratios can provide valuable information on the thermal maturity evaluation.

Naphthenes distribution has been also considered with respect to thermal evaluation. As a result, the naphthene index (NI) has been defined as the percentage of 1-ring naphthenes plus 2-ring naphthenes in the 420-470°C isoparaffin-naphthene fraction (*Phillipi, 1965*). The NI allows quantification of the progressive dilution of the biogenic-4 and 5-ring naphthenes by more simple mono- or dicyclic naphthenes generated from kerogen (*Kolips et al., 1994*). In general, the original content of polycyclic naphthenes may vary and therefore, different source rocks cannot be compared directly to each other. Their content can be usually low in kerogen type III and high in the types I and II of kerogen.

4. Isomerization of methyl groups in aromatic hydrocarbons

The dimethylnaphthalene index (DNI) and the methylphenanthrene index (MPI) are one of the molecular parameters developed from studies of type III kerogen and coals, and by following certain limitations they can be applied on the kerogen II type (*Kvalheim et al., 1987*).

The dimethylnaphthalene index represents the ratio of the decrease of the less thermodynamically stable isotope or the 1,8-dimethylnaphthalene (1,8DMN) and the amount of the total dimethylnaphthalenes with increasing maturity (*Alexander et al., 1984*). Since the dimethylnaphthalenes are volatile, they can be easily lost during isolation. According to some suggestions, the DNI operates across the oil window.

The methyl phenanthrene ratio MPR allows comparison of the α and β methyl substituents and is a ratio of the 2-methyl phenanthrene to 1-methyl phenanthrene. At 1.7% Ro increases linearly from 1 to 5 and below 1.0% Ro is usually variable (*Radke et al., 1984*). The methyl phenanthrene index, on the other hand, is more complex and is based on the relative abundances of phenanthrene and its four major methyl homologs (*Radke and Welte 1983*). The potential for methylation of the phenanthrene at lower maturity, the isomerization of the methylphenanthrenes, and the demethylation of the methylphenanthrenes at higher temperatures are incorporated in this maturity parameter. Consequently, the value of this parameter reaches 1.6 at the end of the oil window, after which it rapidly decreases (*Radke et al., 1986*).

5.2. Optical maturity parameters

In general, the advantage of using the optical parameters for measuring the organic matter thermal maturity is providing means to locate organic matter of different origins and to measure their evolution. For instance, the high level of carbonization reflectance might indicate older kerogen fragments. In the following paragraphs will be presented some of the optical parameters.

1. Carbonization of Palynomorphs

Based on the progressive change in the color or the structure of the spores, pollens or other microfossils, can be distinguished several scales of maturation. The changes of the initial color (yellow) into brown-yellow indicates the stage of diagenesis or if the color changes in brown that could be an indication for catagenesis, whereas the black color implies metagenesis. Usually, spores and poles that have reached the stage of metagenesis are no longer suitable for stratigraphic investigations, which is an indicator that most of the structural alterations occur at the stage of diagenesis and metagenesis. The thermal alteration index and the stages of preservation of the palynomorphs are represented on scales proposed by Staplin (1969) and Correia (1967).

2. Vitrinite reflectance

The vitrinite reflectance is one of the most used optical parameters applicable for defining the coalification stages. Different groups of macerals in the kerogen structure show different reflectance values. The reflectance of both vitrinite and intertinite increase as the thermal maturity increases.

Huminite-vitrinite reflectance is one of the most optical techniques and it probably represents the best optical tool available for determination of the thermal maturity of source rock. There are several limitations that have to be considered when using this technique. For example, we should keep in mind that the vitrinite is almost absent in kerogen type I and moderately abundant in type II kerogen, whereas it is certainly most present in the kerogen type III (*Alpern, 1980*). Also, it should be noted that the oil and gas zones defined by the

reflectance intervals are only approximate. Since the kerogen type III has a composition similar to the vitrinite macerals, it is expected that they will have a similar reaction to the temperature increase, and therefore, there is no reason that the kerogen type I or type II will have same transformation rates as the kerogen type III or the vitrinite. This means that different source rocks that has the same thermal history and have the same values of vitrinite reflectance do not necessarily reach the same stage of evolution, in terms of the oil and gas generation zone. On the other hand, due to the difference between the vitrinite and the kerogen, and differences in the kinetics of the hydrocarbon generating processes, the source rocks that have different thermal histories may reach same values of the vitrinite reflectance.

When correlating the huminite-vitrinite reflectance with other maturation parameters and with the occurrence of the oil and gas fields, three stages can be distinguished:

- $R_o < 0.5$ to 0.7% -indicating immature source rock at the stage of diagenesis
- 0.5 to $0.7\% < R_o < 1.3\%$ -indicates the main zone of oil generation at the stage of catagenesis; oil window
- $1.3\% < R_o < 2\%$ -indicates the stage of catagenesis and the zone of wet gas and condensate generation
- $R_o > 2\%$ -indicates the stage of metagenesis; dry gas zone

3. Fluorescence

The fluorescence of various liptinite constituents is visible when they are subjected to blue or UV light. The light emitted by kerogen as a result of this excitation can be characterized by its color spectrum and intensity (Alpern *et al.*, 1972; Ottenjan *et al.*, 1974). In general, in shallow immature samples, the fluorescence is intense and during the stage of diagenesis and particularly at the catagenesis, it starts to decrease, until it completely disappears at the end of the oil zone. Also, progressive changes in the color spectrum can be also noted, i.e. the fluorescence light changes its color from yellow to red, as catagenesis increases. Since the reflectance and the fluorescence cover different parts of the maturity scale, they can be considered as complementary tools. The abrupt decrease in the fluorescence can be noted at the beginning of the oil generation zone, where the vitrinite reflectance is low.

5.3. Pyrolysis maturity parameters

There are various pyrolysis methods available for obtaining parameters applicable for thermal maturity assessment. Most of the pyrolysis methods yield the following parameters used to characterize the type of organic matter:

- S1-the amount of naturally generated hydrocarbons or free hydrocarbons, volatilized by moderate heating at 200-250°C
- S2-the amount of hydrocarbon generated during pyrolysis
- S3-amount of released carbon dioxide
- Tmax -recorded at the maximum of the hydrocarbon generation during pyrolysis

Different methods provide a measurement of different parameters. For example, some methods only measure the parameters S1 and S2, whereas other methods, such as the method of Espitalie et al. (1977) measures the parameters S1, S2, and S3. According to some authors, the migration ratio $S1/(S1+S2)$ and the temperature Tmax are one of the most important parameters when determining the stage of thermal evolution (*Claypool and Red, 1976; Espitalie et al., 1977*). The ratio $S1/(S1+S2)$ is of particular importance because despite it represents a valuable parameter for determining the maturity, it also allows quantitative evaluation of the generated hydrocarbon. Since this ratio increases with depth, due to the possibility of microreservoirs occurrence in the source rock, it is necessary to plot the variation of the transformation ratio $S1/(S1+S2)$ (in case of migration absence) versus depth. The accumulations in the microreservoirs would be identified by the abnormally higher values than the average curve.

On the other hand, the temperature index Tmax is not affected by the migration phenomenon and it also increases progressively. Since the numerical scale changes with the rate of heating, this parameter should be calibrated. What is important about the Tmax parameter is that it can be correlated with vitrinite reflectance, $S1/(S1+S2)$ or other maturity parameters. For example, in the kerogen type III, there is an excellent correlation between Tmax and vitrinite reflectance. Also, it represents one of the most valuable maturity parameters for type I and types II kerogens.

The Rock-Eval pyrolysis method of Espitalie et al. (1977) provided valuable information on the dependence of these two parameters from the type of organic matter. From these studies, it has been concluded that the Tmax parameter is influenced by the type of organic matter at the beginning of the catagenesis and during the stage of diagenesis, whilst the S1/(S1+S2) is not influenced by the type of organic matter during the stage of catagenesis and metagenesis. In general, Tmax exhibits higher values in the marine or lacustrine kerogen types (type I and type II) and lower values in the gas-prone kerogen (type III), but in the peak zone of the oil generation and in the gas zone, Tmax has almost equivalent values for each type of kerogen.

The total organic carbon and the carbon ratio are also valuable maturity parameters. They are characterized by dependence on the kerogen type, which was proved in studies performed by Gransch and Eisma (1970), who made a comparison between the total organic carbon and the residual carbon after pyrolysis at 900°C and used their ratio as an indicator for the maturity increase. When interpreting this ratio it is important to keep in mind that the increase in the ratio can be due to change of sedimentation from one to another sedimentation bed.

Different authors used different pyrolysis conditions to calculate the ratio of volatile carbon to the total organic carbon, or used gas chromatography to compute the ratio between various hydrocarbons (*Bordenave et al., 1970; Leplat and Noel, 1974*). In general, the main use of pyrolysis is providing a compositional analysis of the bitumen.

5.4. Chemical maturity parameters

These parameters used for thermal maturity assessment are generally based on changes in the kerogen properties during evolution. Different physical or chemical parameters experience changes at different stages of maturity. For example, the hydrogen content mostly changes in the stage of catagenesis and the oxygen content changes at the stage of diagenesis. Most of the techniques used for determination on maturity based on chemical parameters are considered as techniques used for research purposes.

One of the most commonly used tools for maturity evaluation is the elemental analysis of kerogen. This analysis plotted on a van Kleveren diagram allows proper indication on the stage of maturity (*Melver et al., 1967; Laplante, 1974; Tissot et al., 1974*). When combining the

elemental analysis with the huminite-vitrinite reflectance, it can be concluded that it is not sufficient to know only the carbon content or the H/C ratio, but complete, or at least analysis of the C, H and O content is required. The reason for this is that two different types of kerogen that are at different stages of oil generation zone can show the same value of the H/C ratio. In general, the H/C and the O/C ratios should be interpreted together, knowing that the O/C ratio is a better indicator for the kerogen type III, and the H/C ratio is a suitable maturity indicator for marine and lacustrine kerogen type of type I and II.

Speaking of the physical analysis of kerogen, the electron spin resonance (ESR) represents one of the most commonly used techniques among all the techniques used in this purpose. As a result of the bond cracking in the kerogen, there is the occurrence of free radical (or unpaired electrons), resulting in the electron spin resonance signal (*Pusey, 1973*). According to the studies of Marchand et al. (1969) where the ESR kerogen signal was investigated. These studies resulted in a conclusion that the number of free radicals is proportional to the paramagnetic susceptibility χ_p . Also, with the increase of maturity the value of the paramagnetic susceptibility increases.

Due to the investigations of the ESR signal on different types of kerogen made by Durand et al. (1977), the variation trend of this signal is the same for all types of kerogen. The results in this study have shown that the signal increases with increasing depth and temperature and reaches a maximum value at vitrinite reflectance value of 2% or more, after which it starts decreasing again at greater depths. The elimination of the alkyl chains substituted on polyaromatic nuclei was related to the initial increase of the paramagnetic susceptibility. This increase of the χ_p value corresponds to the generation of oil and wet gas, whereas the dry gas zone can be detected through a subsequent decrease of the signal, which mainly occurs due to the coalescence of the polyaromatic nuclei to form larger sheets.

When determining the thermal maturity of the source rocks by using ESR signal, there is great uncertainty, because a given ESR value can correspond to two stages of maturity evolution, i.e. one above the maximum and other below it. Also, the difference in the behavior of the kerogen types is another uncertainty in the maturation appraisal with the aid of this signal. Namely, the free radicals remain more stable on the rigid polyaromatic nuclei, that are commonly abundant in the kerogen type III and the signal has a larger value in this kerogen

type. On the other hand, the free radicals are not stable on the alkyl chains present in the kerogen type I and II, and the signal exhibits lower values. This means that certain changes in the composition can be probably misinterpreted. Additional uncertainty is the effect of time on the free radicals recombination, knowing that there is a greater chance for recombination of the free radicals.

As a final conclusion it can be pointed out that the ESR signal is a good method for thermal maturity evaluation during the stage of catagenesis in basins where the stage of metagenesis is not reached (the value of vitrinite reflectance is 2%) and the type of organic sedimentation remains constant (*Durand et al., 1977*).

Infrared spectrometry, electron diffraction, thermal analysis, and nuclear magnetic resonance represent other types of physical techniques used for thermal maturity assessment, but they are more considered as research tools used for solving some specific exploration problems.

5.4.1. Chemical maturity indicators based on bitumen

The nature of the organic matter and the degree of its thermal maturity, are the two main factors that define the chemical composition and the abundance of petroleum compounds present in the source rocks. Therefore, several methods for maturity evaluation have been developed. These methods are based on the amount or composition of the extractable bitumen as an indicator for the stage of maturity evolution. It should be kept in mind that the migration has a great impact on the chemical composition and abundance of the hydrocarbons. Certain carbonate source rocks or shale beds can be affected by short-range migration with a preferential accumulation of low molecular weight hydrocarbons, which can be detected by high bitumen:organic carbon ratio, or by relatively high transformation ratios.

a) Abundance of bitumen

Solvent extraction followed by hydrocarbon separation and weighing is the first step in the analytical process of the maturity assessment. The bitumen abundance can be defined as a bitumen ratio (total extract:total organic carbon) or as hydrocarbon ratio (hydrocarbons:total organic carbon). When a sufficient number of samples from the formation source rock are available, the generation curve can be obtained by plotting the hydrocarbon or bitumen ratio

versus burial depth. Similar procedures can be used to determine the abundance of hydrocarbons without separation, solvent evaporation, and weighing. One such procedure is the extraction followed by IR spectroscopy of the solvent in which the hydrocarbon fraction is contained (Welte *et al.*, 1981), where the hydrocarbon abundance is measured from the absorbance measurement. Another procedure involves moderate heating of the source rock (between 200-250°C) and volatilization of the hydrocarbons.

The lack of series of samples from various depths and or the changes of kerogen or the geothermal gradient in the basins suggest some limitations on the procedure of determining the stage of evolution using the amount of hydrocarbons or bitumen. For example, these changes affect the bitumen amount, which makes it difficult to trace a regular curve of hydrocarbon generation. Also, Tissot *et al.*, (1978) the changes in kerogen types accounted for, since the total organic carbon was replaced by the amount of pyrolyzable organic carbon (S2 pyrolysis signal), making the hydrocarbon ratio rather comparable to the transformation ratio. Additionally, the bitumen amount may be altered due to short-range migration and minute accumulation within the source rock.

b) General hydrocarbon composition

Due to the possible changes in the hydrocarbon abundance, their composition is rather used in most of the maturity evaluation studies. They have specific distributions. As the temperature increases, new hydrocarbons with wide distribution are generated. The newly generated hydrocarbons dilute the geochemical fossils. This is reflected by the progressive change in the hydrocarbon distribution in the source rock. Therefore, the indices that reflect the changes in the composition, can be certainly used to evaluate the maturation of source rocks. Based on the various classes of the source rock have been proposed various types of maturity parameters, whose validity depends on the uniformity of distribution of selected compounds in the different types of Recent sediments. An index based on a hydrocarbon class whose composition is the same as in the Recent sediments from any depositional environments is considered to be particularly valuable, which is the case with the light hydrocarbons (C₃-C₈). They are particularly absent in the Recent sediments, whereas the long chain *n*-alkanes distribution is also similar in many Recent sediments, but there are also some exceptions that have to be considered.

6. Oil-oil and oil-source rock correlation

Depending on the exploration and production problems, there is a great variation in the crude oil correlation's objective. Generally, most common correlations are those between oils and their source rocks, correlations of different oils with each other, correlations of gases with gases. Also, correlations of gases with oils and source rocks can be also carried out. The main concerns that the exploration geologists have is determining whether it is possible to identify various types or families of oils, condensates or gases in the sedimentary basin and if it is possible to identify the source rock of a given oil, condensate or gas. These objectives define the exploration concept.

The oil-oil source rock correlation provides information on possible communication between different productive horizons or different fault blocks in multipay oil fields or in production areas.

Based on the concept that a certain part of the organic matter is retained in the source rock, after a primary migration, where a certain proportion of the petroleum compounds generated from kerogen are released, the three principal objects of the correlation study are the insoluble kerogen of the source rock, the bitumen extractable from this source rock and the pooled hydrocarbons, possibly derived from this source rock.

In general, the main aim of geochemical correlation of petroleum with source rocks is recognition of compositional similarities or dissimilarities. Relative distribution patterns of certain compounds can be used to establish such features, although valuable information for correlation can be also provided by absolute concentration values. It is important to keep in mind that the parameters used for correlation should have sufficient quantities of characteristic compounds both in oils and source rocks, which permits differentiation between individual source rocks and oils. Also, those parameters should not be affected by any postgenerative alteration processes, such as thermal alteration, evaporative fractionation, etc.

The basic concept in these types of correlation is recognizing similar, identical, or different fingerprint patterns exhibited by the correlation parameters for kerogens, pooled hydrocarbons and bitumen. The degree of similarity or dissimilarity shows whether there is a relationship between petroleum and source rock. The determination of the oil-source rock correlation is

more reliable when using several independent correlation criteria, rather than using only one correlation parameter. For example, any correlation based on biological marker distribution, it is desirable to be consistent with bulk parameters, such as the carbon isotope values or the aliphatic/aromatic ratios.

Johns and Smith (1965) compared gross chemical differences of crude oil's distillation fractions from the Permian Basin of West Texas and New Mexico and represented the first successful correlation study. The correlation studies have been also reviewed by Koons et al., (1974), Williams (1974), Deroo (1976), Seifert and Moldowan (1978), etc.

6.1. Correlation parameters

Generally, the correlation parameters used in the oil-oil correlation studies can be selected from various classes of hydrocarbons and nonhydrocarbons that constitute the crude oil. The geochemical fossils or the biological markers provide one of the best tools used in correlation studies. Namely, the compounds of steroid and terpenoid classes and the distribution patterns of hydrocarbon molecules that have a less specific origin, i.e. the *n*-alkanes or iso-alkanes, as well as various classes of aromatics and naphthenes can be successfully utilized in correlation studies. Furthermore, some nonbiogenic compounds such as carbazole derivatives and thiophene, or porphyrin ratios, can provide useful correlation parameters.

When selecting a parameter in the oil-oil correlation studies, the wide molecular weight range is covered for any given correlation parameter. For instance, the gas chromatography record of saturated hydrocarbon fraction or the *n*-alkane distribution curve can provide valuable information. Such information can be also obtained by aromatic/aliphatic hydrocarbon ratios or isotope ratios (D/H, $^{13}\text{C}/^{12}\text{C}$), which can be also used in a more specific form by determining the isotopic composition of certain compound classes or individual compounds.

Since gases and the condensates to some extent, are related by preferential generation and accumulation mechanisms, that are different from those of the oil, the correlation between oils and condensates, or condensates and gases, represents a delicate problem. Also, the success of the correlation analysis is highly dependent on the degree of overlap between the molecular weight ranges between different products, for example between the light and gasoline range

hydrocarbons in the oil-condensate correlation. The fact that the molecular weight range of these various petroleum products is different, proves that it is quite difficult to perform a successful correlation between oils and condensates, or gases and condensates.

Since the gases are known for their simple composition, there are several limitations that have to be considered when correlating them. In general, they consist of the unspecific compounds and therefore the isotopic ratios can represent quite useful correlation parameters for their grouping (*Schoell, 1980*). On the other hand, in the correlation of light hydrocarbons and condensates, valuable information can be provided from gas chromatography analysis of the gasoline-range hydrocarbons.

Generally speaking, the correlation between pooled hydrocarbons and source rocks is more complex than the oil-oil correlations, primarily due to the accumulation of the pooled oils that occurs through processes of primary and secondary migration. Also, pooled oils consist of different hydrocarbon and nonhydrocarbon compounds generally released through series of expulsion processes and there are significant differences in the composition of the bitumen accumulated in the reservoir and the portion of bitumen that remained in the source rock. When compared to the source rock bitumen, the pooled hydrocarbons are enhanced in saturated hydrocarbons and aromatic hydrocarbons to some extent, but depleted in NSO compounds, mainly due to the migration processes. Thus, the saturated and aromatic hydrocarbons are more suitable for oil-source rock correlations than the heterocompounds.

Taking into consideration that in any type of correlation, any individual compounds should be similar to their physical properties and the groups of compounds used for correlation should be easy to isolate and characterize. these standards, it can be concluded that the steroids and triterpene's geochemical fossils represent excellent correlation parameters, as well as other hydrocarbon parameters that are suitable for oil-oil correlations.

Another possible limitation in the correlation processes is the redistribution of the bitumen present in the source rock (e.g. contamination with bitumens from an outside source), which is a reason to include the kerogen study should be included in the oil-source rock correlation. The study of kerogen actually shows that the bitumen's source rock is original and can be linked to the kerogen from which is supposed to be generated. In general, the indigenous nature of the kerogen is proved by relating the thermal maturity of the kerogen with the production index

(obtained from the Rock-Eval pyrolysis), and the amount of extractable organic matter. Knowing that the number of correlation parameters in direct correlation of bitumen with kerogen is very limited, the most commonly used technique in these correlations is the carbon isotope analysis. When performing such correlation it is important to pay attention to the fact that the bitumen derived from a certain type of kerogen should be lighter than the kerogen itself, i.e. the difference in the ^{13}C values should not be greater than 2-3%, and an oil related to certain source rock bitumen should be isotopically identical or lighter than the related bitumen. This means that when the oil is isotopically heavier than the kerogen we do not have a correlation.

Having in mind that the isotope ratios of the gases are mainly controlled by the maturity of the source material from which they originated, they isotope ratios if the pooled gases are often used to obtain information on their possible source (*Stahl and Karey, 1975*). A detailed classification of gases, based on their source origin was made by Shoell (1980) by plotting the carbon isotope values against the hydrogen isotope values (*Stahl and Karey, 1975*).

Welte (1972) suggested another method for correlation of bitumen to kerogen. The way of correlation that has been proposed by him involves pyrolysis of kerogen and is based on the fact that the extracted kerogen still has a potential for hydrocarbon generation, and during the pyrolysis will yield new hydrocarbons that have a similar pattern with those hydrocarbons that have been naturally generated. Seifert (1978) successfully applied this correlation technique by pyrolyzing the extracted kerogen and the hydrocarbon pattern of the pyrolysis product compared to the previously extracted bitumen. In this way, using GS-MS analysis and based on the match between the sterane and triterpene patterns, he proved the indigenous nature of the bitumen. Using the same concept, it is possible to correlate degraded with non-degraded oils by pyrolyzing the degraded oil's asphaltene fraction (*Rubinstein et al. 1979; Arefjev et al., 1980*).

There are several examples of oil-oil correlations. In some cases, these types of correlation can be straightforward, as in the case when a comparison of gas chromatography record of the saturated hydrocarbons clearly demonstrates an identical pattern for several groups of compounds.

Despite the basic techniques for oil correlations, there are also examples of the application of nonhydrocarbon parameters, correlations based upon aromatics and naphthoaromatics, etc. Such an example is the crude oil correlation made by Deroo (1976), who used thiophene compounds, such as benzothiophenes, dibenzothiophenes, and naphthobenzothiophenes, for characterization of the crude oils from the Alberta Basin of Western Canada. Those thiophenic compounds and the aromatic or naphthoaromatic compounds are successfully applied to oil-oil correlations considering that the crude oils become increasingly similar with maturation (*Tissot et al., 1974; Deroo, 1976*). In cases where the aromatic compounds are used for correlation, the main differentiation between different groups of oils is made based on tetracyclic molecules that are probably derived from steroids. When correlating mature oils, the tetracyclic molecules in the aromatic fraction remain stable during maturation, and therefore they are used as suitable correlation parameters for such types of oils. In general, as the maturation process proceeds further, the saturated hydrocarbons become less characteristic, as well as the geochemical fossils (or polycyclic naphthenes) due to the diminishing of their concentration, which is why the distribution patterns of the *n*-alkanes and isoalkanes tend to be more similar. Therefore, it is quite difficult to correlate older and more mature crude oils using saturated hydrocarbons (*Rullkoter and Welte, 1980*).

Additionally, the oil-oil correlation becomes more complex, when considering the biodegradation effects, that practically make the correlation impossible. In cases of slightly or moderately biodegraded oils, it is necessary to select characteristic petroleum compounds that have not experienced alteration by microorganisms. Therefore, the steranes and triterpenes are most suitable for oil-oil correlations, since it was proved that they are not affected by biodegradation in moderately degraded oils (*Welte et al., 1982*). But, it is important to consider the fact that in some rare cases those compounds can be severely affected by the microorganisms. In such cases, the triterpenes may be specifically altered, which results in ring-opening and demethylation (*Rullkoter and Wendish, 1982*). On the other hand, the steranes are preferentially destroyed (*Reed, 1972; Seifert and Moldowan, 1979*).

Compared to the polycyclic naphthenes, the polyaromatic hydrocarbons and thiophenic compounds are less affected by the processes of the biodegradation. Claret et al. (1977) presented an example of correlating oils of various degrees of biodegradation.

The correlation of the heavily degraded oils can be done by pyrolysis of the asphaltene fraction. This is the main way to reconstruct the compositional pattern of the original crude oil.

6.2. Oil-source rock correlation

The oil-source rock correlation can be made by similar methods as the oil-oil correlation. For example, the gas chromatography record of the saturated fraction of some crude oils can be compared to the equivalent gas chromatography record of the source rock. Nevertheless, the general approach of the oil-source rock correlation requires more detailed analyses due to the changes that the pooled oil might experience during migration, resulting in differences between its composition and the corresponding source rock's bitumen. Therefore, the hydrocarbon distribution pattern of specific molecules, such as steroid and triterpenoid hydrocarbons, is necessary to be included in the oil-source rock correlation parameters. Also, the oil-source rock correlation parameters should be chosen from at least two different series of molecular weight ranges, such as for example the cyclic hydrocarbons from the C₂₇₊ range and C₁₂-C₂₅ saturates and aromatics. The sulfur content, the carbon isotope ratio, the content of saturated and normal aromatics, and other gross chemical information provides additional information for the oil-oil correlation but generally is not sufficient.

The indigenous bitumen nature in these correlations should also be verified, especially if there are suspicions of oil impregnation of a rock from an outside source rock, which can be detected from the relatively high hydrocarbon:total organic carbon ratios varying in range from 150-200 mg hydrocarbons: g organic carbon, and high bitumen:total organic carbon ratios-above 200-300 mg bitumen: g organic carbon).

The most successful methods for these correlations are the Rock-Eval pyrolysis measurements presenting the free oil and gas zones, as well as the transformation ratio, or the comparison of the bitumen's maturation using a chemical maturation parameter, such as the Methyl Phenanthrene Index, with the maturity of the immobile kerogen, using the vitrinite reflectance for example (*Radke et al., 1982*).

Welte et al. (1975) presented examples for oil-source rock correlations based on several correlation parameters, such as distribution patterns of steranes and triterpenes, the isoprenoid hydrocarbons and carbon isotope ratios, etc.

The biological marker technique is also another approach used in the crude oil-source rock correlations in case of a complex geological system, as in the case of the technique presented by Sifert et al., (1980) for the Prudhoe Bay oil field (Northern Alaska), where the steranes, terpenes, and monoaromatic hydrocarbon compounds were used to fingerprint the shales extract and the crude oils.

These correlations made by the biological marker technique are considered to be a very effective tool as long as it can be assured that the original biomarker has not been affected by the postgenerative alteration processes, such as biodegradation, migration, and maturation. In general, maturation processes affect the biological markers more severely, changing their distribution, which contributes to changes in their pattern and abundance, as well. In the early phase of the maturity evaluation, the steroid hydrocarbons undergo isomerization and aromatization reactions, which causes misinterpretation of the fingerprint correlation, especially when the source rock has not reached the suitable maturation level (*Mackenzie et al., 1982*). In such cases, the triangular diagrams of carbon number distributions of regular steranes (in range C₂₇-C₂₉) can be used for correlation, since they are largely unaffected by thermal maturation compared to the isomers distribution (*Schi et al., 1982; Mackenzie et al., 1982*). The fact that these components are present in minor amounts within the hydrocarbon mixture and that they are less stable than other components in terms of thermal changes represents another limiting factor for the use of these parameters in the oil-source rock correlation.

Generally, the mature crude oils contain small amounts of biological marker compounds due to their early thermal breaking and the abrupt drop of their concentration in the stage of late diagenesis. Therefore, any later addition to a mature crude oil from a second, less quantitatively important and less mature source that is richer in biological markers and is able to give an imprint on the reservoir crude oil (which is not consistent with the more mature hydrocarbons), demonstrates the importance of using multiple parameters in the oil-oil and oil-source rock correlations.

Debroo et al. (1976) represented oil-source rock correlation using thiophenic and aromatic compounds as correlation parameters. In his study, he proved that the Rouse condensate from the Arzacq basin (France) originated from two source rocks (from Albian and Oxfordian age).

He also estimated the relative contribution of each source using the distribution patterns of the aromatics and the dibenzothiophenes, which was possible due to the fact that both source rocks were at the same maturation level.

Another characteristic example of this type of correlation is the one performed by Schaefer et al. (1978). This correlation was based on the characteristic compositional features of the light hydrocarbon fraction. As a result of his study was concluded that the oil-source rock correlation is possible when the crude oil and the source rock are at about the same maturation level. Also, the fact that the thermodynamic equilibrium of isomer distribution is not reached during natural hydrocarbon generation is an additional reason why this correlation is actually possible.

The prediction, and in some cases, if it is possible, recognition of a source rock based on certain characteristics of the reservoired hydrocarbons, represents a special application of the oil-source rock correlation. Knowing that certain petroleum are characterized by a predominance of the *n*-alkanes in the range from C₁₆ to C₃₂. The predominance of phytane over pristane is also common in these types of petroleum. Knowing that the degree and extent of these characteristics vary with the oil's type and maturity, it has been proved that petroleum from high saline, carbonate and evaporitic environment, usually show a predominance of even distribution of the *n*-alkanes, which is followed by the predominance of phytane over pristane (*Welte and Waples, 1973; Kalbassi and Welte, 1975; Dembicki et al., 1976*). Using a statistical analysis of *n*-alkane patterns of numerous crude oils and source rocks, Tissot et al. (1977) verified that crude oils with these types of characteristics are most likely derived from a carbonate or evaporite source rock.

On the other hand, the crude oils that exhibit an odd predominance of *n*-alkanes (in the range C₂₃-C₃₃) and which contain more *n*-alkanes, commonly have a slight predominance of phytane over pristane and their overall amount of isoprenoids is rather low. The crude oils that have these characteristics are derived from a source rock with a large proportion of terrestrial organic matter and higher plant origin and probably originated from non-marine source rocks, or from strata representing nearshore, marine environments.

The changes in the organic matter which light hydrocarbons originate from are related to the significant differences in their composition (*Leythaeuser et al., 1979*). It has been found

that the cycloalkanes have a tendency for higher relative proportion in the C₆ and C₇ groups, compared to the marine shales compared to coal (for the C₇ hydrocarbons). In summary, it has been concluded that the C₆ and C₇ hydrocarbon groups generated from coaly organic matter are generally enhanced in aromatics, but contain less naphthenic compounds than the C₆ and C₇ groups present in marine shales that are at equivalent maturity level. The influence of the higher plant is reflected by the predominance of the benzene and toluene (*Schaefer and Leythaeuser, 1980*).

Although the recognition of typical facies characteristic in crude oil or bitumen, has not been extensively developed yet, further research in this direction will be useful for detailed characterization of crude oils, which in turn allows prediction of the type of source rock from which it was probably derived.

In summary, the irregularities in the *n*-alkane distribution pattern in oils, or an even or odd predominance are an indication of low maturity levels, whereas the oils that exhibit smooth *n*-alkane distribution curve, have reached a higher level of maturity.

As previously mentioned, the identification of the source rock of given petroleum, or the recognition of various families of pooled hydrocarbons in a basin, are the main objectives of oil and source rock correlation. They can be of a particular when developing an exploration concept. The base of the geochemical correlation is recognition of compositional similarities between the crude oils and source beds, where the relative distribution patterns of specific chemical structures, such as compounds of steroids or terpenoid classes, or distribution patterns of hydrocarbons and nonhydrocarbons are commonly used as correlation parameters. In cases of correlating crude oils or bitumen to certain kerogen, the ¹³C/¹²C isotope ratios are also frequently utilized. In general, it is favorable to use more than one correlation parameters.

The maturation and the biodegradation of the pooled hydrocarbons, need to be considered when correlation crude oils or crude oils and source beds since they have a major effect on the compositional changes in the expelled oils. In the correlation of the mature crude oils, the aromatics, naphthenoaromatics and the thiophenic compounds have been successfully applied, whilst the aromatic hydrocarbons and the thiophenic compounds are commonly utilized when correlating biodegraded oils in addition to biological markers, such as sterane and triterpene since they are not usually affected by the biodegradation.

7. Petroleum alteration-Secondary processes affecting petroleum

Petroleum represents a complex mixture of organic compounds with high energy content. This makes petroleum thermodynamically metastable under geological conditions (*Williams and Winter, 1969; Evans et al., 1971*). Therefore, after being pooled in a reservoir, petroleum is generally susceptible to alteration.

Nowadays, petroleum alteration has been observed in numerous oil accumulations around the world. Generally, the causes for petroleum alteration can be related to the relative instability of petroleum, or to the fact that the traps are open systems that may change their level of burial due to further subsidence and erosion. Usually, the composition of the pooled petroleum can be altered by physical or chemical processes. The thermal maturation and the microbial degradation are an example of chemical alteration, whereas an example of physical alteration can represent the addition of new compounds to the reservoir due to further migration, or the preferential loss of light compounds by diffusion, etc.

As explained in the previous sections, the compositional differences in petroleums are mainly due to the origin of different source rocks. For instance, the high-sulfur crude oils are commonly related to carbonate-type source rocks, whilst the high-wax crude oils are frequently associated with source material containing a high amount of lipids of terrestrial higher plants or microbial organisms. Despite the source rock facies influence, the maturity of the source rock is also of great importance for the composition of crude oil. However, the crude oil composition is commonly affected by the alteration of the reservoir petroleum by a greater extent than it is actually affected by the character of the source rock material, which means that the crude oil alteration tends to obscure the original character of the oil. Therefore, the crude oil alteration affects the crude oil correlation studies, as well as the quality and the economic value of petroleum.

The secondary processes that are a common reason for the petroleum composition will be further discussed in the following sections.

7.1. Thermal alteration

In general, the thermal alteration occurs under the influence of heat under the subsurface. For a given geothermal gradient, as the depth of burial and the residence time at a given temperature increases, the thermal alteration also increases. Therefore, it is possible to predict the maturation effects or thermal alteration using a time-temperature relationship. It is known that with increasing depth and rising temperature, there is a tendency of the crude oils in the reservoir to become lighter, containing an increasing amount of low molecular weight hydrocarbons at the expense of high molecular weight constituents.

A more detailed examination of the changing crude oil properties with increasing reservoir temperature has been presented in the study performed on the crude oils located in the Western Canada Basin (*Evans et al., 1971*). In this study was presented a linear increase in compounds that contain less than 15 carbon atoms at the expense of the C₁₅₊ heavy constituents. Additionally, it has been noted a simultaneous exponential increase of the gases, especially methane, in relative abundance. At conditions of elevated temperatures, in the more mature zones of the reservoirs, has been detected the only presence of methane and pyrobitumen that has been generated as a result of cracking processes (*Evans et al., 1971*). The absence of the intermediate oil constituents and the presence of pyrobitumens plus light hydrocarbons in the range below C₁₅₊ in this study represent an indication of disproportional reactions during the process of thermal alteration. In this process, the ultimate stable end products from the oils of intermediate molecular weight are the low molecular weight methane and the high molecular weight carbon-rich residue. In such a way, the system follows a thermodynamic trend by adjusting towards the more stable molecules, which means that this process can be represented as a disproportionation reaction. It can be concluded that there must be a hydrogen transfer, generally from the “aromatic-type” structures to aliphatic molecules, making the aromatic structures more condensed. In the case of NSO fraction in the oils, this process is usually accompanied by desulfuration, yielding water, carbon dioxide, and hydrogen sulfide, dehydration, or decarboxylation.

However, it has to be mentioned, that it is quite difficult to distinguish between the effects of different stages of the source rock maturity at the time of oil release and the effects of the

process of thermal alteration of the pooled accumulation. In some cases, the solid residues can significantly help in the attempts to make a distinction between these two processes.

7.2. Deasphalting

The precipitation of asphaltenes from heavy to medium crude oils by the dissolution in the oil of large amounts of gas and other light hydrocarbons in the range of C₁ to C₆ represents another alteration process, known as deasphalting. It generally occurs as a natural process in heavy to medium oils whenever considerable amounts of hydrocarbon gas are either generated in larger quantities in a pool due to thermal alteration of oil due to gas injection from outside as a result of secondary migration. However, this gas is considered to be ineffective when accumulated in the separate gas cap, and therefore, it needs to be previously dissolved in the oil before it can precipitate asphaltenes. Since both the thermal maturation and the gas deasphalting occur simultaneously, and the net change in oil composition goes in the direction of lighter oil, it is difficult to distinguish them.

The thermal alteration and the gas deasphalting have been observed in the study performed on the oils from the rift-bearing area in Western Canada, done by Evans et al., 1971 and Bailey et al., 1974. According to the studies, only limited deasphalting in this area has been caused by saturation, whereas the extensive deasphalting was probably associated with the massive gas injection. This gas-injected deasphalting resulted in the formation of anomalously light oils, such as the Keg River and Devonian Beaverhill Lake oils (*Evans et al., 1971*). According to the generalized geological West-East section of this region, the reefs rest upon a platform that extends downdip towards the west into an organic facies of high thermal maturity. It has been assumed that a regional updip flow of gas from the higher temperature zone occurred through continuous porous strata, causing precipitation of asphaltenes in the reservoir that were located in the migration path of the gas. The amount of precipitated asphaltenes showed a good correlation with the amount of dissolved gas in the oils. The amount of injected gas in the oils was measured from the GOR, whereas the asphaltene content represented a measure of the oil's specific gravity. Since the investigated oils were unsaturated (with respect to gas), from the correlation of the GOR and the specific gravity of these oils was concluded that there was an inverse content of the gas and asphaltene content.

In connection with deasphalting, Evans et al., 1971, also discussed the phenomenon of gravity segregation, which is usually observed in the oils with a large vertical extent, where the temperature difference between the top and the bottom of the pool is relatively small. In reverse of what is expected from the maturation processes, the crude oil in such pool may progressively become heavier as the depth increases. In general, the oils in the deeper horizon of the reservoir contain less gas in solution than the oils from the top horizons of the reservoirs. The main reason for this is the fact that the solution of gas causes an increase in the oil's volume. When considering the pressure-volume relationship on the nearly isothermal basis, theoretically it can be concluded that the work done by a larger quantity of gas at lower pressure is nearly equal to the work done by a small quantity of gas at higher pressure, which means that the quantity of gas at the top of the reservoir should be higher than the amount of gas injected at the bottom of the reservoir. Thus, at the top of the reservoir, the GOR will be higher and the bulk density of the liquid lighter. This explanation of an inversed gravity relationship in large vertical oil pools is in most cases certainly more convincing than the process of gravity segregation. Generally, it is hard to believe that in the case of gravity segregation, the heavy compounds of oil would selectively settle through the pore structure of a reservoir that would reach the bottom zone.

Bailey et al., (1974) pointed out that the thermal maturation occurs regionally, whereas the deasphalting due to gas injection is more localized, causing oil production in the neighboring reservoirs rather than condensates and gas condensates, which represents a proper explanation why the thermal maturity and the deasphalting can be distinguished. Additionally, it was suggested that the maturation state of kerogen in the rocks can be easily measured. An exception is the pure carbonate rocks, where the virtual absence of kerogen makes this estimate impossible. In such cases, the maturation state is usually estimated by the bitumen-like organic matter. McAlary and Rogers (1971) suggested that bitumen-like organic matter, which has been subjected to thermal maturation and has reached the stage of metagenesis, is less than 2% soluble in CS₂, whereas the H/C ratio of the insoluble fraction is below 0.53, whereas the values below this indicate that the bitumen-like organic matter is produced by thermal metagenesis. On the other hand, the higher values suggest deasphalting. Also, Rogers et al., (1971) suggested that the asphaltene precipitates or the reservoir bitumens formed by deasphalting have the same isotope ratios as the original oil. On the contrary, the residues formed by thermal alteration,

i.e. the pyrobitumen have significantly higher ratios., due to the production of isotopically light methane and a high molecular weight residue, enriched in the heavier isotope, as a result of the cracking of carbon-carbon bonds.

7.3. Biodegradation

The microbial degradation, i.e. the biodegradation and the removal of water-soluble compounds, i.e. the water washing, represent one of the most commonly observed alteration processes in the oil pools located in the areas invaded by surface-derived, meteoric formation waters. In general, both of these processes are initiated by the action of sub-surface moving water, which is the main reason why are they frequently observed together. In the case of biodegradation, it is assumed that the subsurface water carries the dissolved oxygen and microorganisms in the reservoir, after which brings them in contact with the oil-water interface. In particular, the biodegradation represents a selective utilization of certain types of hydrocarbons by microorganisms and generally occurs under aerobic conditions. On the other hand, in the case of water-washing, the formation waters that are undersaturated with hydrocarbons and move along the oil-water interface, selectively extract the soluble hydrocarbons, thus changing the chemical composition of the remaining oil.

According to the documentation available in the literature, the effects of biodegradation are common in the tar mats and also widely developed at the oil-water contacts of oil producing fields, such as for instance the Burgan Field in Kuwait (*Evans et al., 1971 ; Bailey et al., 1973a ; Deroo et al., 1974*). Often, the biodegradation by aerobic or anaerobic microorganisms results in partial or total removal of *n*-alkanes, of slightly branched alkanes or possibly of low-ring cycloalkanes and aromatics. The different durations, as well as the different levels of intensity of biodegradation result, are the main reason for the crude oils that exhibit different degrees of alteration. For instance, in the bacteria introduced into an oil pool that contains oxygen-rich meteoric waters, utilizing the dissolved oxygen, preferentially metabolizes only certain types of hydrocarbons, whereas the oxygen supply of bacteria is most probably derived by sulfate ions, under anaerobic conditions. According to the evidence the selective removal of hydrocarbons by bacteria occurs in the following sequence: *n*-alkanes (below C₂), isoprenoid alkanes, low-ring cycloalkanes and aromatic. Also, Alimi and Reed (1977), showed that in cases of severe degradation there is even removal of tetracyclic steranes.

In the study of Phillipi (1977) in which were investigated crude oils of Tertiary to Cretaceous age from California, East Texas and Louisiana, USA, was presented evidence for optical activity of the investigated oils resulted from the microbial degradation. An explanation for this optical activity noted among these crude oils is the selective microbial digestion of the optical antipodes which were present in the primary paraffinic crude oils. Mainly, the optical activity was observed in a narrow boiling point fractions of saturated hydrocarbons boiling between 80 and 325°C, considering that this boiling range is well below the molecular weight range of tetracyclic and pentacyclic steranes and triterpenes, that generally are capable of exhibiting an optical activity as a feature inherited from their primary biosynthesis. Even though the chemical structure of the hydrocarbons, that is responsible for the optical activity is not known, this optical activity was interpreted as a secondary feature caused by biodegradation of previously nonrotating, racemic mixtures of hydrocarbons (*Phillipi, 1977*). The fact that the optical activity in the boiling range from 80 to 325°C was observed in different basins only at reservoir temperatures below 66°C, taking into account that above this temperature range the growth of bacteria might be inhibited, represents a strong argument in support to this interpretation.

The fate of the microbial cell material with respect to the composition of the biodegraded crude oils is pretty unclear, which is the reason why several theories have been proposed by different authors. For example, Phillipi (1977) suggested that most of the microbial cell material created during the oil's biodegradation is probably digested by subsequent generations of microbes and that part of the more stable oil-soluble compounds may be dissolved in the crude oil, whereas Bailey et al. (1973b) suggests that the protein-bearing bacterial cells may augment the nitrogen content of the asphaltenes. He also claimed that the asphaltenes are probably generated as a by-product of the biodegradation of hydrocarbons, as well as a result of an increase in the proportion of the crude oils.

Often, under anaerobic conditions, in order to satisfy their demand for oxygen, certain types of bacteria usually reduce the sulfates. The resulted sulfur reduction occurs in different forms mainly depending upon the geochemical environment (*Rogers et al., 1972*). Namely, in metal-rich environments the sulfides of iron, zinc, etc. are produced in association with the altered crude oil; in some salt domes associated with biodegraded oil elemental sulfur has been

formed, whereas in other situations, part of the sulfur extracted from sulfate may react with hydrocarbons to produce sulfur-rich oils and tars (*Connan and Orgeval et al., 1976*).

7.4. Water washing and evaporative fractionation

Unlike the microbial degradation of crude oils, the process and effects of water washing are less well described and presented in the literature. Probably, the main reason for this lack of field examples is the fact that these two processes change the crude oil in a similar direction, i.e. make the oil heavier. Also, it is considered that the water washing generally has less severe effects upon the crude oil composition. Furthermore, although both processes, biodegradation and water washing, occur independently, apparently in most cases they are parallel to each other. In particular, the water washing results in the removal of more soluble hydrocarbons from the crude oil. Therefore, individual solubilities of the hydrocarbons can represent a good measure for their water washing susceptibility. In general, it is known that the light hydrocarbons are more easily dissolved and therefore selectively removed from the pooled petroleum than the heavier ones, whereas the low-boiling aromatics, such as benzene, toluene, and xylene should be depleted. Both biodegradation and water washing are generally expected to occur in reservoirs that are close to the surface, and more accessible for surface-derived waters. Therefore, the oils seeping out at the surface are always biodegraded and in addition, oxidized by inorganic oxidation, whereas the volatile compounds are lost as a result of evaporation. Consequently, these oils become heavy oils, enhanced in NSO compounds and of tar-like appearance.

Deroo et al. (1974) presented an excellent example of progressive crude oil alteration, based on crude oil samples from Eastern Alberta in the Western Canada sedimentary basin, where have been observed systematic changes, going in an upward direction from the normal, unaltered oils in deeper pools toward the heavier oils in more shallower positions, and finally to the severely altered heavy oils positioned very close to the surface (less than 100 m of depth). The common origin of these eastern Alberta oils and their original similarity previous to alteration had been established on the basis of cycloalkanes, thiophenic compounds, and aromatics. The waters associated with the gradational alteration sequence of crude oils contained progressively less solids, which was an indication of the increased influence of the meteoric water. As compared to the unaltered pooled oils, Deroo et al. (1974) presented three

different stages of the crude oils degradation in his study. These three stages were presented in respect to the *n*-alkanes, isoprenoids and other branched alkanes and cyclo-alkanes within the fraction of saturated hydrocarbons. According to the results of his study, the Bellshill Lake oil was representative of the unaltered oils, due to its domination of the *n*-alkanes over all the other saturated hydrocarbon compounds, whereas a loss of *n*-alkanes, and hence a relative increase of isoprenoids, pristane and phytane was observed in the Edgerton heavy oils from the Mannville Formation. The Pelican heavy oils from the Wabiskaw Formation were representative of the severely altered oils. An indication for this severe alteration is the complete removal of the phytane and pristane by the microorganisms.

In this study, along with the increase of the biodegradation was also observed an increase in their sulfur content, but it was not clear whether this sulfur was added to the crude oils due to the bacterial activity, or whether the sulfur compounds were just selectively left over, and thus relatively enriched after the bacteria had eliminated certain parts of the hydrocarbon fraction.

In summary, the ultimate petroleum composition may be strongly influenced by alteration subsequent to the process of accumulation. The thermal maturation, deasphalting, and the degradation represent the three major alteration processes associated with the action of the surface-derived formation waters. According to the general scheme of alteration processes presented by Bailey et al., (1974), an original crude oil of relatively low maturity would respond to thermal maturity or deasphalting by becoming lighter. As a result of thermal maturation, it can be possibly destroyed and converted into gas and a heavy insoluble residue. When degraded by the action of formation waters, this oil increases in specific gravity and heavy NSO compounds, diminishing its economic value. Aside, from the previously described alteration processes, there are still other processes that may affect the composition of pooled petroleum. For example, in some cases, there may be changes in the composition due to selective losses from the hydrocarbon mixture via leakages. This leakage may be a consequence of a natural rupture of the sealing cap rock, due to a tectonic event, such as faulting, or in some cases, may be an informational feature of the sealing cap rock, related to its gross permeability. Phillip et al. (1963) and Smith et al., (1971) described the dependence of the losses upon the seals of the permeability. They also presented cases of diffusional losses.

However, the existence of gas fields, that have been formed during the Paleozoic time, proved that this process, in general, has low efficiency.

Generally, the losses by diffusion are gradual and increase with the closeness of the reservoir to the surface, and also with the geological duration. On the other hand, the changes due to leakages, induced by tectonic events, might be more severe and more or less instantaneous. As described by Silverman (1967), profound changes in the chemical composition of pooled petroleums can be expected by separation-migration. In case of separation migration with consecutive changes in composition, the single-phase fluids first have to be converted into two-phase systems, for instance by a pressure release due to faulting. In the case of preferential migration, the vapor phase separates from the liquid, which stays behind. As the vapor migrates into shallower trapping positions, the reduced pressure and temperature conditions may cause vapor to revert to two-phase accumulation by retrograde condensation. As a result of the continuation of this process, may be found traps with successively lighter hydrocarbon content in an upward direction. In general, there are no records about the frequency of the separation-migration in nature.

2. Practical part

8. Light hydrocarbons and application of their ratios

The light hydrocarbons-LHs represent the largest petroleum fraction in the range from C₁ to C₉. It is believed that they represent catagenic products formed in the temperature range from 75 to 140°C. However, the theories about their origin remain controversial, considering that there is little evidence that they are formed during a cracking process. For instance, it is less likely possible that the higher hydrocarbons would source light hydrocarbons at these temperatures. Knowing that most of them, except some few exceptions, have similar structural characteristics as the bio-precursors it is evident that they do not exhibit dominance in natural structures that are consistent with cracking. Reliable proof for these is the fact that generally all the isomers are found within the alkanes, cycloalkanes, and aromatics. Moreover, it is quite important that these isomers do not have a noticeable preference for natural structures, and their distribution is nearly constant from oil to oil and far from thermodynamic equilibrium.

What is certain is that the formation of light hydrocarbons requires catalytic support, which is confirmed in several studies. Also, numerous papers have supported the fact that the ratios of the isoalkanes are constant in all oils and invariant within oils that have originated from the same source. This consideration is used as a powerful constraint in any theory whose main aim is explaining the origin of the light hydrocarbons. The consistency of the fact that certain isoheptane ratios remain constant throughout the course of light hydrocarbons formation, is retained by the fact that during the catalytic process, the light hydrocarbons descend from a few precursors when the process is controlled by steady-state kinetics.

The origin of the light hydrocarbons is an object of interest in many studies and it has been detailly reviewed by many authors. However, this thesis will be mainly focused on the application of the ratios of the light hydrocarbons as reliable indicators of the effects of the alteration processes, such as biodegradation, evaporative fractionation, water washing, maturation, etc.

Application of the LHs ratios in maturity assessment

The application of the light hydrocarbons as molecular maturity parameters has been already described in chapter 6.1. In the following will be mostly discussed about the application of some light hydrocarbons ratios in the thermal maturity assessment. An example

of the application of the light hydrocarbons as maturity indicators is evident in the studies of Phillipi (1975), Johnathan et al., (1975), Du Rouchet (1978), Tompson (1978, 1983), etc. Namely, the alkane/cycloalkanes have been extensively used in their studies. It was observed in core extracts from Los Angeles and Ventura Basins, and in the Gulf of Mexico, these ratios increase with depth (Phillipi, 1975, 1977; Tompson, 1979). Also, in the core samples of the Lower Tertiary age, from Posidonia Shale, the Lower Saxony Basin in Germany, has been reported a striking correlation between the 2-MH + 3-MH/sum of DMCP ratio and the vitrinite reflectance. Tompson (1979) explained this observation by the fact that the higher polycyclic hydrocarbons, such as the steranes and triterpanes, usually crack to cyclopentanes and cyclohexanes, considering that the polycyclic hydrocarbons are less stable than the open-chain hydrocarbons, making them prone to decomposition at lower temperatures generating higher concentrations of cyclopentanes and cyclohexanes at lower maturities. Additionally, he suggested that at higher temperatures the C₇ cycloalkanes undergo ring opening, which is the reason why the ratio *n*-C₇/MCH has been proposed as a maturity index. With the increase of the subsurface temperature, this ratio increases as the methyl cycloheptane thermally undergoes ring opening. Opposite of Tompson's statement, Mango (1990a) suggested that indeed the polycyclic hydrocarbons are more stable than the open-chain hydrocarbons. In favor of his hypothesis is the fact that the light hydrocarbons are not probably sourced from the polycyclic biomarkers. According to the Mango's consideration, the alkane/cycloalkane ratio increases with maturity, even though the reason for this increase has not been properly clarified.

A variety of light hydrocarbon ratios as possible maturity indicators have been also used in the study performed by Koblova et al. (1980), in which was reported a good correlation of the ratio 2-MH/3-MH to the temperature. Also, Mango (1987) proposed the ratios 2,4-DMP/2,3-DMP and 2-MH/3-MH as useful temperature functions. Namely, the 2,4-DMP/2,3-DMP ratio is considered to be a better temperature function, considering that it was suggested as a temperature function independent of time and kerogen type (Mango, 1987, 1990b).

Application of the LHs ratios in correlation

Thanks to their broad distribution, the light hydrocarbons have found a wide application in the oil-oil and oil-source rock studies. For example, Deroo et al., (1970), used the MCP/MHC,

Tol/Benz, $n\text{-C}_7/\text{MCH}$ and $n\text{-C}_7/1,2\text{-t-DMCP}$ ratios together with other geochemical properties to place 100 oils from the Western Canada Basin into three stratigraphically distinct groups (Cretaceous, lowermost Cretaceous, Jurassic and Mississippian, and Devonian). Other examples of the use of LHs ratios in the correlation studies are the oil-source rock correlations of the oils in the Arbuckle and Ellenburger groups, Cambro-Ordovician carbonates, Kansas, Oklahoma, and Texas.

An effective technique for illustrating the LH correlations was presented by Erdman and Morris (1974). This technique requires a selection of a set of ratios and dividing each ratio R by the same ratio R' from the given set, giving a set of ratio R/R' , considering that values of 1 denote perfect match, whereas those values different than 1 reflect differences. Using this technique, they compared a North Sea oil and an oil from the Rocky Mountain Region from Utah. When attempting to correlate oils and source rocks, Philippi (1981) extended this technique using ten similarity coefficients for their comparison. These similarity coefficients are calculated to vary from 0 to 1 as the correlation increases. Even though these correlations have effectively presented the power of LHs correlations, they lack visual impact, considering that the correlations were numerically illustrated. Using this method ten pairs of oils and source rocks from the Permian Basin, Williston Basin, Texas Gulf Coast, Denver Basin, and the Los Angeles Basin were successfully correlated.

The star diagrams of the LHs ratios represent another effective display of the oil-oil correlations. This technique has a useful application in the reservoir compartmentalization. Also, in cases of detecting a behind-casing leakage or refinery contamination, the use of this method is particularly common, emphasizing its significance in the field development. An example of the use of these types of diagrams is the study performed by Halpern (1995) who employed two diagrams. In one of the diagrams were used eight ratios with considerable susceptibility to alteration processes, such as biodegradation, water washing, and evaporation, and the other diagram used five ratios indicating genetic transformations.

Application of LHs ratios that express alteration processes

In the following of this paper will be presented the means of application of the LHs ratios in the characterization of genetic affiliation, maturation, biodegradation, water washing, and evaporation. There is a broad range of LH ratios that can be used in this purpose, but here will

be used a set of 15 ratios that would characterize the above-mentioned processes. The meaning of these ratios, i.e. a detailed description of why and how each ratio represents a geochemical process will be presented in the following:

- 1) $iC5/nC6$ (i-pentane/n-hexane)
- 2) $3MC5/nC6$ (3-methylcyclopentane/n-hexane)

These two ratios are commonly used to monitor the removal of low-molecular-weight *n*-alkanes relative to branched and cyclic alkanes during the process of crude oil's biodegradation. These ratios have been originally proposed by Welte et al. (1982).

- 3) $nC7/MCYC6$ (n-heptane/methylcyclohexane)

The n-heptane/methylcyclohexane ratios are also reduced during the process of biodegradation, which is why this ratio has been also included in this study.

- 4) $BEN/nC6$ (benzene/n-hexane)
- 5) $TOL/nC7$ (toluene/n-heptane)

The above-presented ratios express the aromaticity, whereas:

- 6) $nC6+nC7/CYC6+MCYC6$
- 7) $2+3MC6/1c3+1t3+1t2-DMCYC5$, and
- 8) $nC7/2MCYC6$

are the most commonly used indices in expressing paraffinicity. These aromaticity and paraffinicity ratios are usually altered during the process of evaporative fractionation.

- 9) TOL/BEN (toluene benzene)
- 10) $3MC5/BEN$ (3-methylpentane/benzene)
- 11) $MCYC6/TOL$ (methylcyclohexane/toluene)

This ratio (toluene/benzene) reflects the extent of the water washing influence. Considering that the toluenes and the benzenes are in general partially or completely removed during the water washing, the reduced values of this ratio would represent a proper indication of this process. The other two ratios are also used with the same purpose.

$$12) k_1 = \frac{2MC7+23DMC5}{3MC7+24DMC5} \left(\frac{2\text{-methylcycloheptane}+2,3\text{-dimethylpentane}}{3\text{-methylheptane}+2,4\text{-dimethylpentane}} \right)$$

In general, this ratio is used as an indicator of whether different groups of oils have a common source. If the ratio of the sums of isoheptanes is relatively constant within a given set of oils, refers to genetically related oils. These oils are considered to be homologous oils.

$$13) 2+3MC6/\Sigma DMC5 \text{ (2+3-methylhexane}/\Sigma \text{dimethylcyclopentanes)}$$

This ratio is used in various studies as a maturity index that showed a good correlation with the vitrinite reflectance. In mature sediments, it decreases with depth.

$$14) nC7/MCYC6 \text{ (n-heptane/methylcyclohexane)}$$

Since at higher temperatures the cycloalkanes undergo ring opening this ratio is used as a maturity index.

$$15) nC7/1t2DMCYC5 \text{ (n-heptane/1-trans-2-dimethylcyclopentane)}$$

Considering that in general, the 1-trans-2-dimethylcyclopentanes are less resistant to biodegradation than the *n*-C₇, this ratio is employed when expressing a process of biodegradation.

9. Description of the geological setting

The Devonian represents a geologic period of the Paleozoic that starts at the end of the Silurian period (around 420 million years ago) and ends with the beginning of the Carboniferous period (around 359 million years ago). This geologic period is subdivided into three periods-Early, Middle and Late Devonian. The formation rocks that are used in this thesis belong to the period of Middle Devonian.

Previous works of the Geological surveys of Canada (GSC) has proved that in Southern Alberta and especially in the Devonian formations there are numerous porous and permeable reservoirs. However, only few hydrocarbon traps are revealed in this region, explaining why the drilling activities have been relatively limited. According to the previous surveys, there is proven source rock and hydrocarbon being generated in the Winnipegosis, Nisku, and

Exshaw/Lower Banff in Southern Alberta, with associated hydrocarbon production in the Lower Banff to Big Valley (Alberta Bakken), in the Nisku, and in the Winnipegosis (Mort et al., 2015).

Dr. Andry Mort of the Geological Survey of Canada performed a source rock evaluation study of selected samples from cores in the Beaverhill Lake and Winnipegosis. His study showed the presence of oil-prone source rocks within the investigated intervals. On the other hand, the evaluation of the oil samples from the Leduc, Nisku, Beaverhill Lake, and Winnipegosis revealed an evaporite related source.

The oil is produced from dolomite in the Winnipegosis in the Rich area. This area is located immediately to the south of the Big Valley Stettler Leduc platform. The Winnipegosis depositional environment in this area was located in the evaporitic interior of a carbonate platform. The salt of the Prairie Evaporite overlies the dolomite, and the trap represents a local structural closure. The oil trapped in this reservoir is slightly heavy at 25 API, whereas the geochemical analysis indicates an evaporitic algal source.

9.1. Description of the source rock formations in Western Canada

In the following will be briefly reviewed the major formation systems in the studied area.

Elk point system

This formation system is comprised of clastic dominated shoreline leading to offshore carbonate platform that is capped with evaporites. In the Rich Area exists a major oil pool with a capacity of 2.6 mmbbl OOIP and API gravity of 23. The geochemical analyses showed that the source material probably originates from basal algal laminates.

Beaverhill Lake system

According to the geological reports, the Beaverhill lake group in Southeastern Alberta was deposited as a series of prograding to the North West carbonate ramps forming the Source River Platform. This ramp complex is equivalent to the aggrading and backstepping Swanhills platform. This platform developed to the north and west of Western Alberta Ridge. The Slave Point has a salt basin deposited surrounded by evaporitic platform interior sediments at the base of the system. Although there are many indications of source rocks and proofs for the

existence of dolomitized reservoirs, there is no production from this system. According to the geochemical data, there is evidence of the evaporitic source.

Leduc system

This formation was deposited as a carbonate platform with margins propagating towards north and west. These margins are characterized by well-developed dolomite porosity. The interior of the platform is consisted of peritidal carbonates and evaporates. The presence of the vertical seals is quite evident, whereas the presence of the lateral seals is probably due to the structural events, or due to the porosity pinch out.

The Leduc system has oil and gas production, but due to the presence of diagenetic and structural traps, as well as interior barriers to flow, the production might be quite challenging. The drill stem test showed that the investigated oil samples showed a correlation with the Montana Nisku oil family, which brought up questions about the migration pathways.

Nisku system

Nisku has proven to be a productive formation in the area of Southern Alberta. In the South, an early prograding carbonate platform with a biostromal barrier is present. Also, there is a platform interior evaporitic basin present in this part of the area. Due to the syndepositional salt dissolution, the evaporitic dolomites have a variable thickness. In other words, the syndepositional salt dissolution results in the formation of structural closures filled with light oil, which is the reason for the variable thickness. Through the years, over forty million barrels have been produced from the Nisku/Arcs dolomites in the EnChant area. From the geochemical data could be assumed that most probably the Nisky area is charged from self-sourcing evaporate related algal laminates.

Wabamun system

The Wabamun Stettler member in the area is mainly constituted of tight evaporites and dolomites deposited in a platform interior evaporate basin. This member doesn't represent a reservoir, whereas the overlying Upper Wabamun Big Valley member represents a reservoir that produces oil and gas from horizontal wells. This member is merely a limestone but does become dolomitized in some areas which is the reason why it can produce oil and gas. The

overlying Exshaw formation source rock is most likely the source and this reservoir is part of the halo reservoirs around the Exshaw source rock, including the Alberta Bakken, made up of the Big Valley dolomites, the Bakken dolomitic siltstones, and finally the most productive member, the Lodgepole lower Banff sandstone to siltstone.

9.1.1. Exploration potential of the Devonian systems

It can be concluded that as a result of the development of horst and graben system, Southern Alberta has a very complex structural history. The regional dip changing from down to the west southwest to being down to the northwest results in the presence of the Sweet Grass arch (Mort et al., 2015). As a result of this event, many of the fault blocks remain open to the south. However, four-way closures have been identified and there is little information about them. Also, the occurrence of the conventional traps could be a result of pinch out porosity within the carbonate platforms (Mort et al., 2015).

Additionally, there is a potential for the occurrence of unconventional regional hydrocarbon traps that would probably develop in porous, but low permeable dolomites within the evaporitic interiors of the carbonate platforms (Mort et al., 2015). It is assumed that the dolomites could be charged from inter-bedded evaporitic algal laminates, whereas the reservoirs most probably would have to be developed using horizontal drilling, as well as completion techniques.

9.2. Summary of previous studies of family affiliation of oils

According to numerous evidences, for the majority of the Western Canada areas, the main phase of oil generation and migration mainly took place in the late Cretaceous-early Tertiary. In this section will be briefly described the characteristics of the source formations.

Keg River formation: In La Crete Sub-basin

The Upper and the Lower Keg River member in this sub-basin have thickness from 1 to 5 meters. This formation is considered to be an excellent potential source rock. The organic matter from this formation is evaluated as type II to type II-I, with a hydrogen value from 500-600. It is confirmed that the organic matter is mainly immature and mainly has algal bloom organic facies. Flower et al.,2001, confirmed that the kerogen sample from this area can be

characterized as immature to marginally mature. Its Tmax values vary in the range from 420 to 430°C.

The studies reveal different biomarker characteristics in the Upper and Lower Keg River members. The Saturated Fraction Gas Chromatogram of the Upper members shows the presence of higher amounts of C₂₀₊ *n*-alkanes, whereas the chromatogram of the Lower members shows the presence of lower molecular weight *n*-alkanes and low Pr/Ph ratio.

Beaverhill Lake

The organic matter from this formation can be categorized as type II. Its maturity ranges from 0.55 to 0.65% Ro. The source rock is mainly carbonate. Also, the source rock in the eastern part of the Southern Alberta can be considered as particularly good hydrocarbon source rock.

Slave Point formation

The depositional environment in the Slave Point formation is mainly lagoonal. Its organic matter is categorized as kerogen type II/III and Hydrogen Index from 170 to 390. According to the analyses, the Nisku oil has higher maturity than the Leduc oils. The Lower Nisku formation has a thickness from 1 to 7 meters and is mainly located in the basinal platform areas.

The depositions in the East-Central Alberta are characterized as immature oils. The organic matter of this deposition has Hydrogen Index values from 400 to 600 and is categorized as open-marine, type II kerogen. The depositional environment is marine-derived. According to the chromatograms, the presence of the C₁₅-C₂₁ *n*-alkanes is dominant, whereas the Pr/Ph ratios vary in the range 0.73-1.73. In the area of Cynthia Shale Basin, the Nisku formation is more mature with 1.0-1.1 Ro.

Camrose formation

Previous studies have confirmed the presence of four source units in this formation. The potential source rock of the first unit is type I organic matter characterized by high values of Hydrogen Index. The potential source rock of the second unit is categorized as type I organic matter and has a thickness of 1 to 2.3 m, whereas the potential source rock of the third

formation also contains type I organic matter and exists in the middle Nisku formation, with a thickness of 3 to 4m. Finally, the potential source rock of the fourth unit has an isolated type of organic matter (type I) of terrestrial-influenced organic facies. Additionally, the organic matter's maturity varies from immature (in the Eastern region) to the late oil window.

Camrose/Nisku formation

The chromatograms of the oil samples from the Camrose/Nisku formation show a dominant presence of low molecular weight *n*-alkanes, whereas the Pr/Ph ratio varies from 0.6 to 1.20, which is quite interesting since this value for most of the above-mentioned oils is less than 1. Also, similar levels of maturity between these two formations have been detected in the oils from both the Nisku and Camrose formation.

Birdbear formation

The potential source rock of the Birdbear formation is actually very thin, with a thickness of only a few millimeters. Contains an organic matter of type I and type III with TOC values similar to the values of the Camrose members, and a Hydrogen Index value of 138-802 mg HC/g. The depositional environment of this formation evolves from water lagoonal to tidal flat.

Wabamun group

In the area of British Columbia, a Basinal laminate facies exist at the base of Wabamun. This formation is rarely mentioned in reports. One of the reports in which this group has been described is the study performed by Flower et al., 2001.

10. Description of the Devonian oils compositional data

These oils originate from sources located in Devonian formations. As presented below, two data sets will be employed for the purposes of this work-the composition of the main hydrocarbons of the gasoline range, as well as the composition of the *n*-alkanes in the saturated oil's fraction.

In the following table will be presented the source formations of the investigated oils, as well as their location.

Sample	Lat	Long	Formation	Sample	Lat	Long	Formation
L00794	54.51052	-115.498	Beaverhill Lake	L02080	52.62858	-113.357	Leduc
L00858	54.54708	-116.821	Beaverhill Lake	L02081	52.64824	-113.337	Leduc
L01143	52.0215	-112.769	Nisku	L02082	52.63602	-113.346	Leduc
L01144	51.69111	-111.296	Arcs	L02084	52.51058	-113.188	Nisku
L01277	53.94367	-117.594	Wabamun	L02086	52.47948	-113.182	Nisku
L01350	53.37903	-115.27	Nisku	L02098	51.99341	-114.053	Leduc
L01354	55.64275	-118.161	Wabamun	L02099	52.38876	-113.343	Leduc/Nisku
L01420	54.01195	-116.421	Nisku	L02100	52.32724	-112.876	Leduc
L01453	54.46445	-117.745	Leduc	L02103	52.79822	-113.084	Nisku
L01556	51.66458	-111.273	Arcs	L02106	51.61418	-113.764	Crossfield
L01557	52.11556	-112.99	Nisku	L02108	51.48797	-112.746	Nisku
L01558	52.14638	-112.773	Nisku	L02109	52.25888	-114.588	Leduc/Nisku
L01559	50.96459	-112.019	Arcs	L02110	56.91252	-114.684	Keg River
L01576	52.22727	-113.331	Nisku	L02112	56.31595	-116.087	Slave Point
L01598	50.71718	-111.591	Jefferson	L02151	51.54145	-112.838	Nisku
L01638	53.17386	-115.726	Nisku	L02152	51.54145	-112.838	Leduc
L01639	53.1208	-115.789	Nisku	L02153	51.54145	-112.838	Leduc
L01641	53.04243	-115.974	Nisku	L02154	52.41677	-113.3	Nisku
L01644	53.02228	-116.209	Nisku	L02155	52.39959	-113.301	Nisku
L01645	53.10956	-115.896	Nisku	L02156	52.40738	-113.338	Nisku
L01646	53.11573	-115.698	Nisku	L02157	52.40819	-113.349	Leduc/Nisku
L01647	53.02817	-115.964	Nisku	L02158	52.32835	-113.368	Nisku
L01648	53.14161	-115.782	Nisku	L02159	51.58022	-113.278	Leduc/Nisku
L01650	53.03202	-116.091	Nisku	L02160	52.5109	-113.426	Leduc
L01651	53.18903	-115.74	Nisku	L02161	52.51126	-113.426	Nisku
L01652	53.09129	-115.868	Nisku	L02162	52.27013	-113.346	Nisku
L01654	53.12568	-115.883	Nisku	L02163	52.28353	-113.335	Nisku
L01655	53.15396	-115.87	Nisku	L02164	52.27629	-113.347	Nisku
L01656	53.15396	-115.87	Nisku	L02165	52.26258	-113.33	Nisku
L01658	53.09544	-116.067	Nisku	L02166	52.2702	-113.323	Nisku
L01664	51.50473	-112.673	Arcs	L02167	52.2914	-113.342	Nisku
L01667	51.50136	-112.668	Nisku	L02168	52.07925	-112.746	Nisku
L01676	56.71672	-114.451	Keg River	L02169	52.55221	-113.145	Leduc
L01677	56.73744	-114.383	Keg River	L02170	52.58097	-113.151	Leduc/Nisku
L01679	56.72312	-114.52	Keg River	L02171	52.54484	-113.133	Leduc

L01680	56.75265	-114.537	Keg River	L02177	51.61497	-113.764	Leduc
L01684	56.71129	-114.447	Keg River	L02178	51.62427	-113.791	Leduc
L01686	56.73082	-114.395	Keg River	L02182	52.59544	-113.169	Leduc
L01687	56.73672	-114.46	Keg River	L02183	52.75407	-113.127	Leduc
L01688	56.69365	-114.379	Keg River	L02184	52.8009	-113.086	Nisku
L01690	56.69621	-114.597	Keg River	L02190	52.83786	-113.066	Nisku
L01691	56.84899	-114.767	Keg River	L02191	52.83815	-113.062	Leduc
L01692	56.82601	-114.724	Keg River	L02192	52.33846	-112.849	Leduc
L01693	56.70099	-114.601	Keg River	L02196	51.81394	-113.586	Leduc
L01810	53.21439	-115.656	Nisku	L02197	51.83151	-113.577	Nisku
L01816	51.98092	-112.787	Leduc/Nisku	L02198	51.81826	-113.588	Leduc
L01819	51.99535	-112.788	Leduc/Nisku	L02199	51.99535	-112.788	Nisku
L01820	52.10105	-112.752	Leduc/Nisku	L02200	52.59156	-113.295	Nisku
L01821	52.19548	-112.77	Leduc/Nisku	L02201	52.61111	-113.265	Nisku
L01822	52.2029	-112.776	Leduc	L02202	52.62592	-113.265	Nisku
L01823	51.98398	-112.783	Nisku	L02203	52.64631	-113.253	Nisku
L01824	52.60546	-114.196	Leduc	L02205	52.33768	-112.864	Leduc
L01825	52.19268	-112.772	Leduc	L02206	52.33048	-112.91	Leduc
L01827	52.62012	-114.184	Leduc	L02207	53.52126	-113.723	Nisku
L01828	52.05289	-112.745	Leduc	L02208	53.54302	-113.73	Nisku
L01831	53.18291	-115.637	Nisku	L02209	53.56794	-113.729	Leduc
L01832	52.75428	-114.108	Leduc	L02210	53.56116	-113.724	Leduc
L01833	52.02095	-112.758	Nisku	L02211	53.51028	-113.741	Leduc
L01834	51.99059	-112.761	Leduc	L02212	53.5357	-113.735	Nisku
L02032	53.26003	-113.797	Nisku	L02213	53.60476	-113.704	Leduc
L02034	53.26687	-113.668	Leduc	L02215	53.48118	-113.766	Leduc
L02035	53.27047	-113.687	Leduc	L02219	52.15582	-112.77	Leduc/Nisku
L02038	53.27063	-113.765	Leduc	L02220	52.13719	-112.758	Nisku
L02039	53.27097	-113.753	Leduc	L02221	52.10469	-112.752	Leduc/Nisku
L02040	53.27406	-113.747	Leduc	L02223	52.24668	-112.794	Bearspaw
L02041	53.27409	-113.705	Leduc	L02224	52.28313	-112.835	Leduc
L02042	53.27408	-113.722	Leduc	L02225	52.28664	-112.776	Nisku
L02043	53.82364	-113.481	Nisku	L02226	52.25394	-112.788	Nisku Granite
L02044	53.82008	-113.493	Nisku	L02254	56.81703	-115.453	Wash
L02045	53.81636	-113.475	Nisku	L02255	56.8946	-115.513	Keg River
L02077	52.51099	-113.26	Nisku	L02257	52.4624	-112.167	Camrose
L02078	52.51794	-113.261	Nisku	L02290	54.77219	-116.68	Swan Hills
L02079	52.5206	-113.267	Nisku	L02291	55.10916	-117.661	Leduc

Table 2. Source formation and geographical location of the investigated oils

11. Results and discussion

In the following table are presented the components of the gasoline range that have been identified among the compositional data.

iC5	i-Pentane	MCYC5	Methylcyclopentane	3MC6	3-Methylhexane	24DMC6	2,4-Dimethylhexane
nC5	n-Pentane	24DMC5	2,4-Dimethylpentane	1c3DMCYC5	1,cis-3-Dimethylcyclopentane	223TMC5	2,2,3-Trimethylpentane
22DMC4	2,2-Dimethylbutane	223TMC4	2,2,3-Trimethylbutane	1t3DMCYC5	1,trans-3-Dimethylcyclopentane	234TMC5	2,3,4-Trimethylpentane
CYC5	Cyclopentane	BEN	Benzene	1t2DMCYC5	1-trans-2-Dimethylcyclopentane	TOL	Toluene
23DMC4	2,3-Dimethylbutane	33DMC5	3,3-Dimethylpentane	nC7	n-Heptane	2MC7	2-Methylheptane
2MC5	2-Methylpentane	CYC6	Cyclohexane	MCYC6	Methylcyclohexane	3MC7	3-Methylheptane
3MC5	3-Methylpentane	2MC6	2-Methylhexane	22DMC6	2,2-Dimethylhexane	1c4DMCYC6	1,cis-4-Dimethylcyclohexane
nC6	n-Hexane	23DMC5	2,3-Dimethylpentane	ECYC5	Ethylcyclopentane	nC8	n-Octane
22DMC5	2,2-Dimethylpentane	11DMCYC5	1,1-Dimethylcyclopentane	25DMC6	2,5-Dimethylhexane		

Table 3. Commonly identified hydrocarbons in the gasoline range fraction of oil

The normalized histograms of the chromatographic peak areas from the usual gasoline range components will be presented below.

Observing these histograms for the gasoline range can be noted that the normal octane, cyclohexane, and normal pentane are the components with the highest peak area in the Keg River Sample, whereas in the Leduc sample the components with the highest peak are the cyclohexane, 1-trans-2-dimethylcyclopentane, and the normal hexane. In the Nisku sample, the components with the highest peaks are the cyclohexane, normal heptane, and the normal octane. It can be noted that there are some variations in the other components, but generally, they carry more or less the same geochemical information.

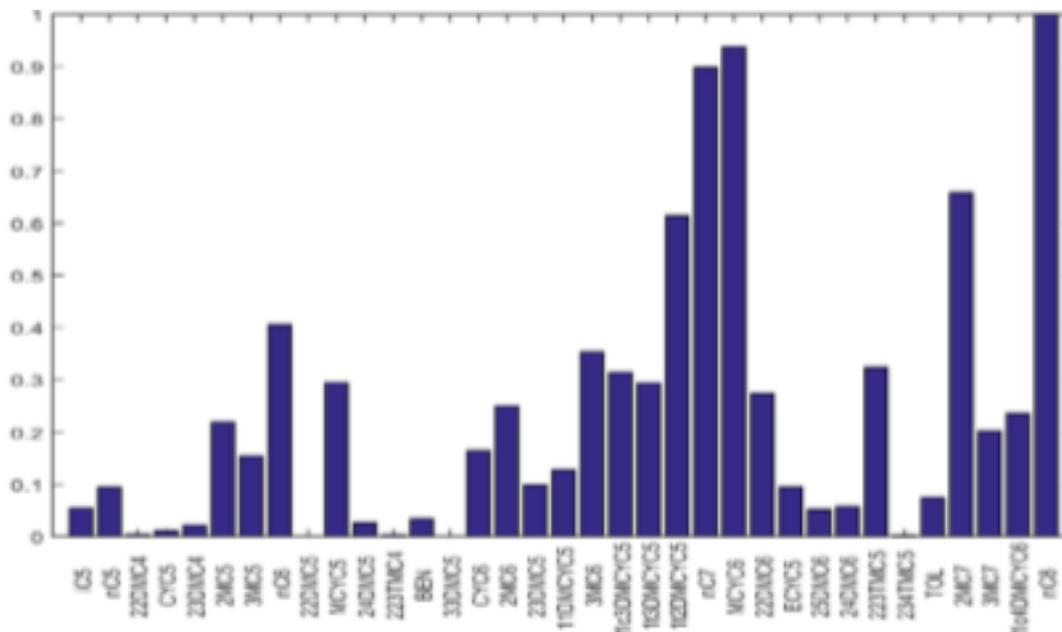


Figure 1. Normalized histogram of the chromatographic peak areas from the gasoline range of the sample L01677 sample (Keg River)

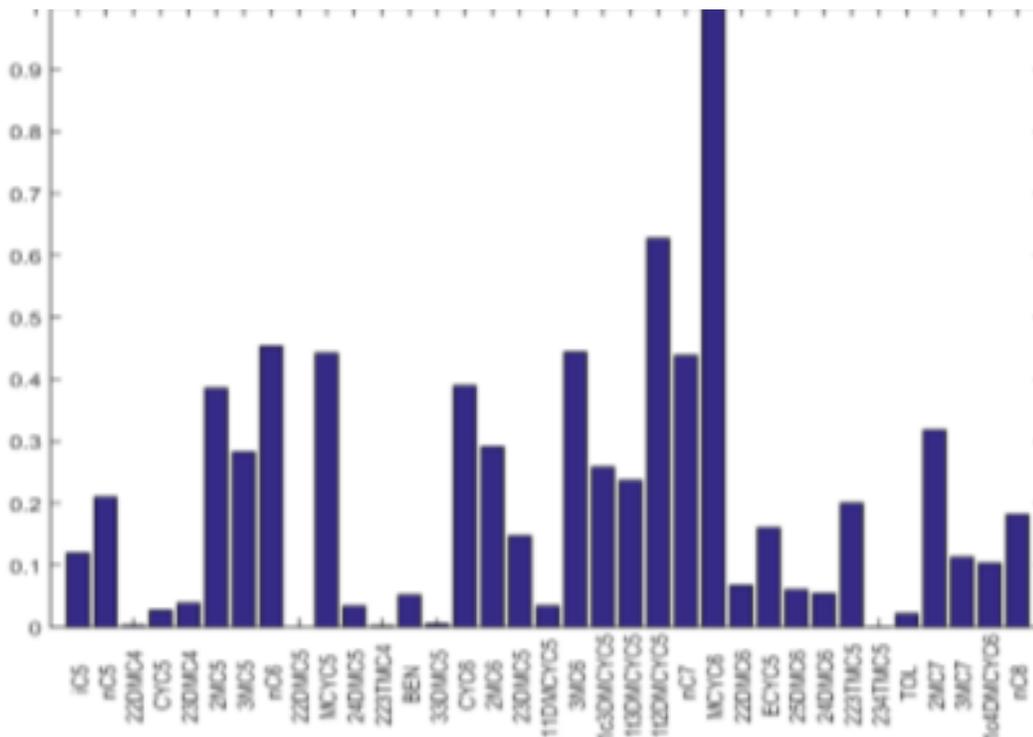


Figure 2. Normalized histogram of the chromatographic peak areas from the gasoline range of the sample L01822 (Leduc)

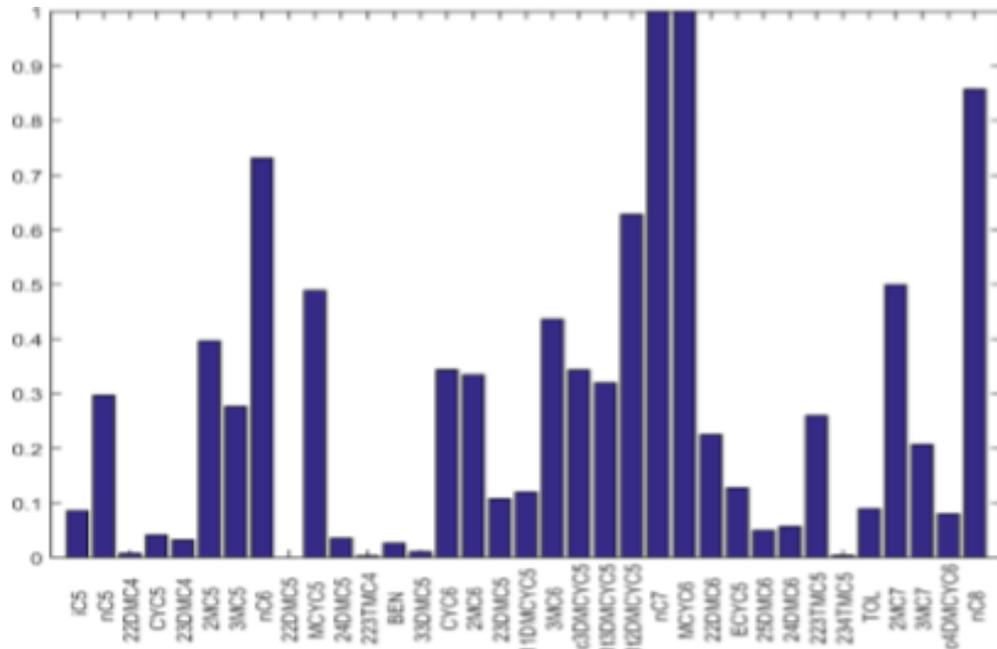


Figure 3. Normalized histogram of the chromatographic peak areas from the gasoline range of the sample L02045 (Nisku)

In general, instead of pure compositional data, the geochemical studies use ratios, often referred to as geochemical indices. They calculated based on the concentrations of the selected components. These ratios are of particular importance because they provide significant combined information about the oils. In the following will be presented how the ratios described in section 8 are applied to express maturation and alteration processes.

1) *Post-sampling evaporation*

Typically, the process of evaporation leads to reduced contents of low molecular weight hydrocarbons in oils. Therefore, it can be easily mistaken for water washing and biodegradation. In the following, the evaporation trend within the sample-sets of C-oils and Nisku oils will be checked using the distribution of C5-C8 linear alkanes.

Figure 4 represents a ternary diagram that reflects the results of the post-sampling evaporation of the family of C oils in which are included the samples from Beaverhill Lake, Arcs, Wabamun, Jefferson, Nisku/Leduc, Leduc/Nisku, Crossfield, Slave Point, Bears paw, Granite Wash, Camrose, and Swan Hills. This and similar diagrams are in general used to show organic facies differences in oils, as well as for oil-source correlation (ten Haven 1966, Oden

et al., 1998). In this case, the diagram shows evaporation trend in the direction of progressive removal of the normal hexanes due to the process of evaporation.

On the other hand, the second ternary diagram (Figure 5) shows a trend of a greater proportion of n-C₈ alkanes relative to the n-C₇ alkanes, whose proportion decreases.

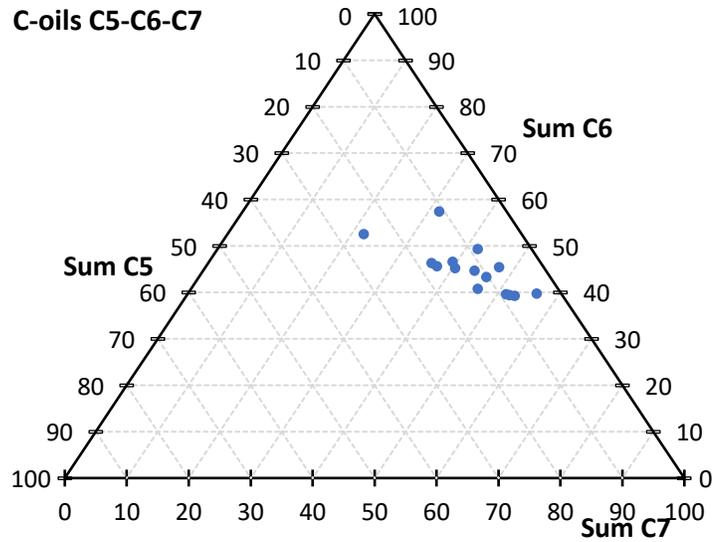


Figure 4. Post-sampling evaporation check (C-oils C5-C6-C7)

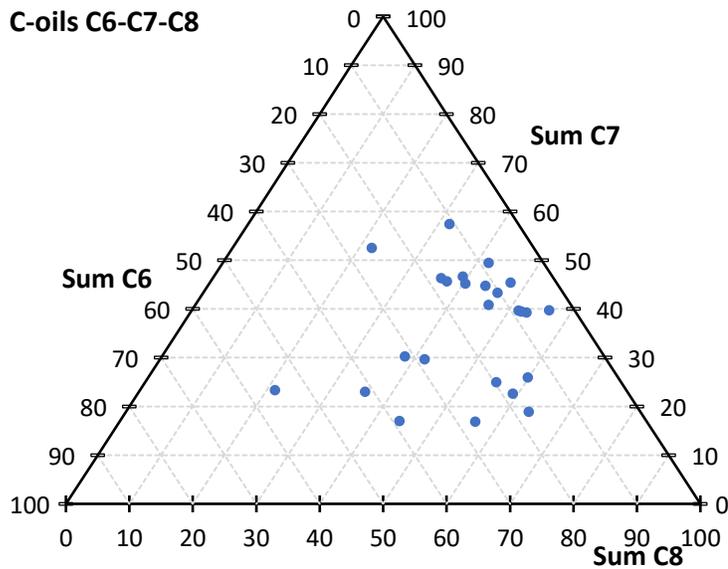


Figure 5. Post-sampling evaporation check (C-oils C5-C6-C7)

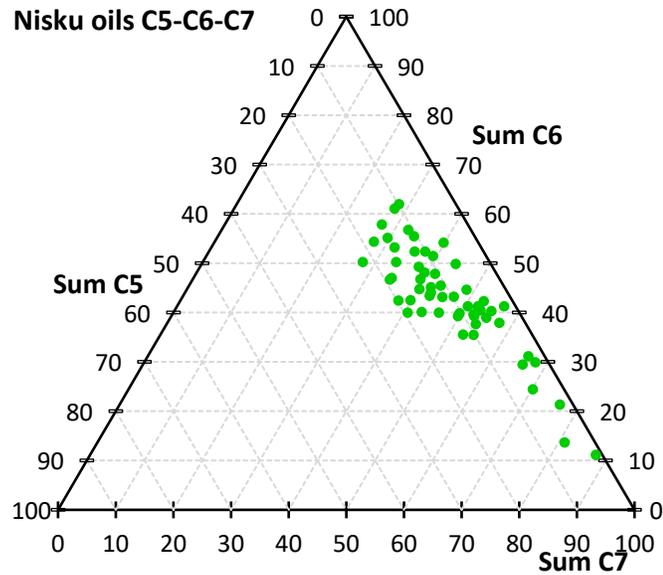


Figure 6. Post-sampling evaporation check (Nisku oils C5-C6-C7)

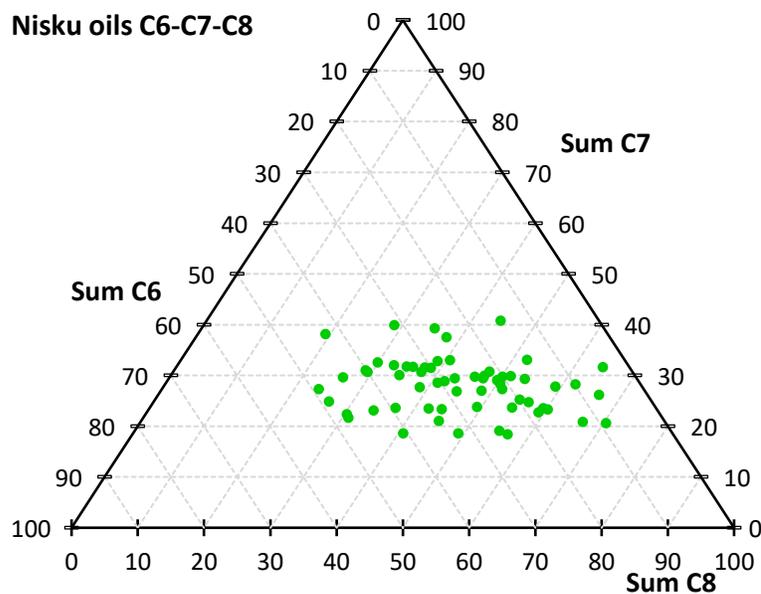


Figure 7. Post-sampling evaporation check (Nisku oils C6-C7-C8)

The ternary diagrams of the oils of family B comprised of the Nisku samples, that show the results of the post-sampling evaporation are presented below (Figure 6 and 7). The first diagram expresses depletion of the n-C₆ alkanes as in the case of the family C oils, whereas from the second diagram it can be observed that there is an increase of the n-C₈ alkanes.

This confirms that the evaporation during the post-sampling process in this oils represents a significant factor since there is constant depletion of the lower molecular weight hydrocarbons compared to the higher molecular weight hydrocarbons.

2) *Water washing*

In particular, the water washing results in the removal of more soluble hydrocarbons from the crude oil but has a less severe effect on the crude oil's composition. Therefore, individual solubilities of the hydrocarbons represent a good measure for their water washing susceptibility. In general, it is known that the light hydrocarbons are more easily dissolved and therefore selectively removed from the pooled petroleum than the heavier ones, whereas the low-boiling aromatics, such as benzene, toluene, and xylene are generally depleted, which is usually considered when checking the water washing trend.

In the following graphs will be presented the water washing check using George's technique (2002), Lafargue technique (1996).

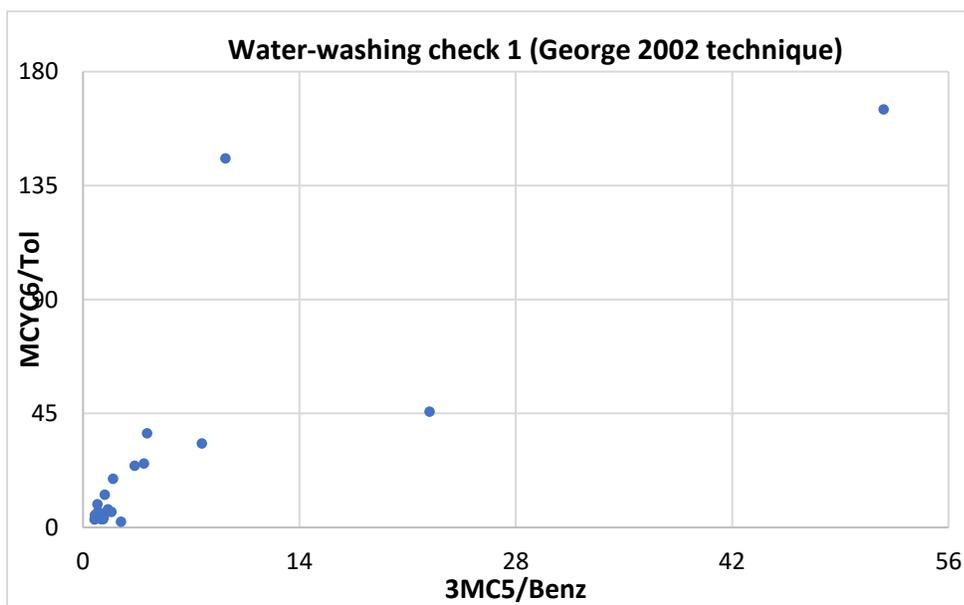


Figure 8. Water washing check (George 2002 technique)

Figure 8 represents a water washing check for the C-oils using the ratios MCYC6/Tol and 3M5/Benz. According to this graph, most of the samples in this family of oils is not considerably affected by water washing. Only two samples have undergone a severe

compositional alteration due to the process of water washing-the Wabamun sample (L01227a), and the Camrose sample (L02257).

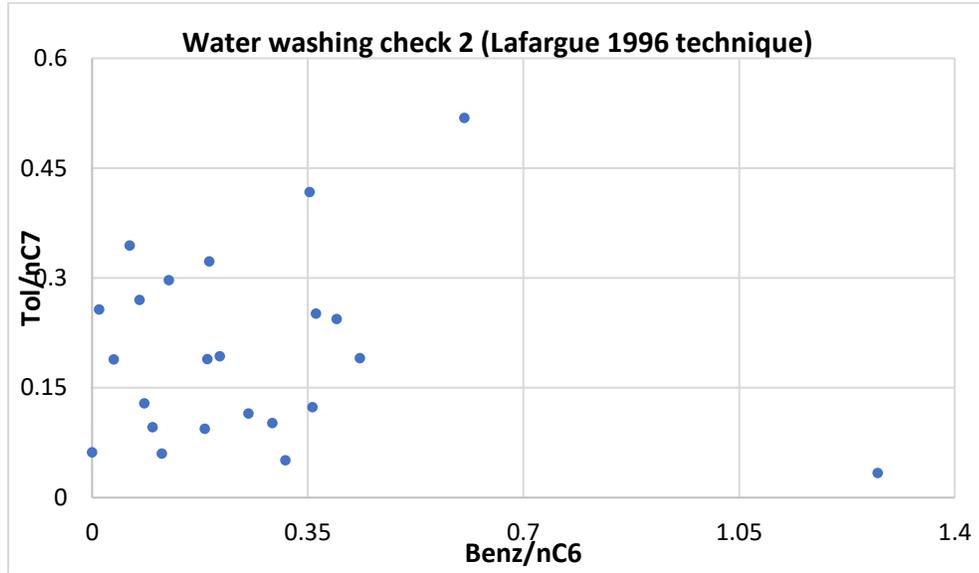


Figure 9. Water washing check (Lafargue technique 1996)

The least water washed samples in the case of the water washing check when using the Lafargue technique, the least affected samples are the oils from Granite Wash, Arcs, Crossfield and Jefferson, whereas the compositional alteration due to this alteration process is more present in the Leduc/Nisku and Slave Point samples. The most affected samples are the Nisku/Leduc samples.

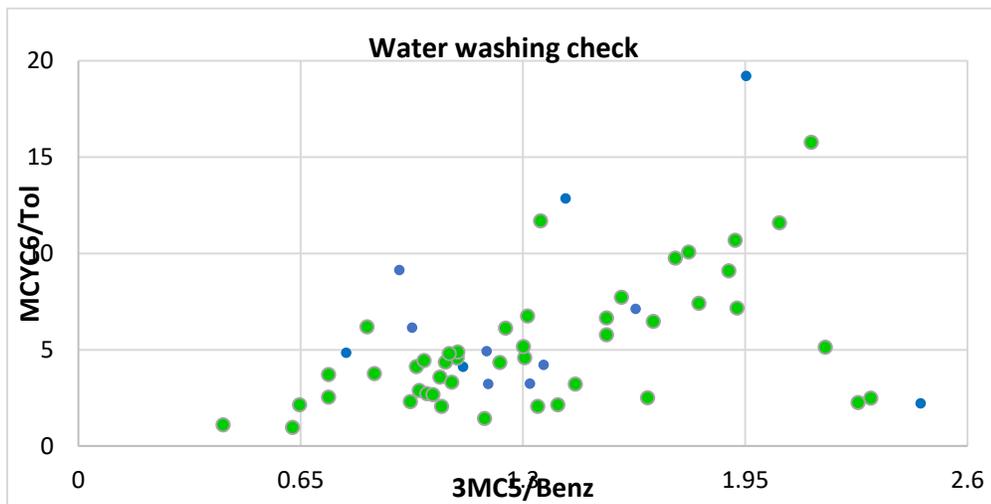


Figure 10. Water washing check (C-oils and Nisku oils)

From Figure 10, it can be concluded that the Nisku and the C-oils undergo similar compositional changes due to water washing.

3) Biodegradation

As previously explained in the theoretical part, in the case of biodegradation, it is assumed that the subsurface water carries the dissolved oxygen and microorganisms in the reservoir, after which brings them in contact with the oil-water interface. In particular, the biodegradation represents a selective utilization of certain types of hydrocarbons by microorganisms and generally occurs under aerobic conditions. Often, the biodegradation by aerobic or anaerobic microorganisms results in partial or total removal of *n*-alkanes, of slightly branched alkanes or possibly of low-ring cycloalkanes and aromatics.

The graph below represents the biodegradation check of the Leduc oils using George's technique (2002).

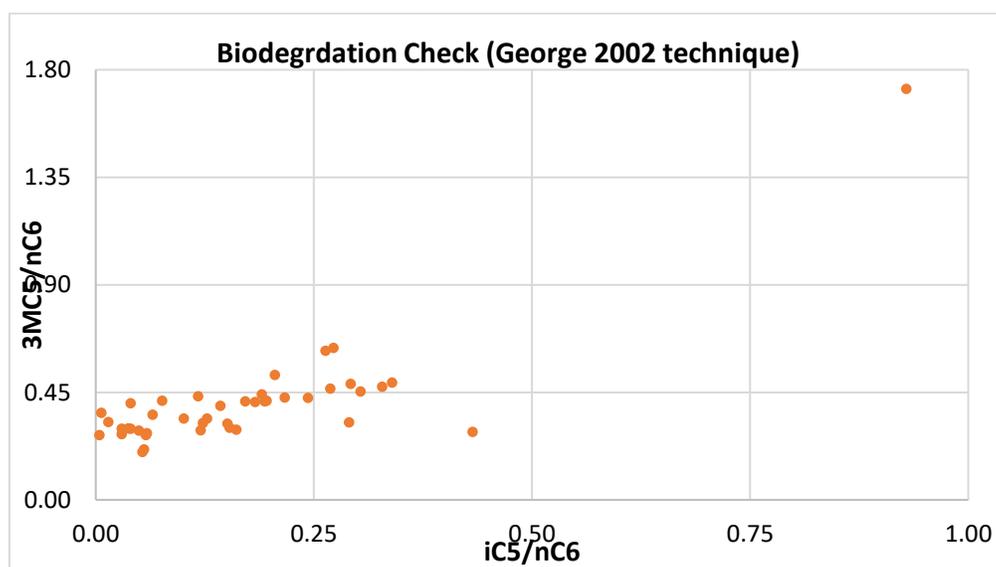


Figure 11. Biodegradation check (Leduc oils)

In this case, the biodegradation trend shows that the trimethylpentanes are less resistant to biodegradation than the methylhexanes. As suggested by Halpern (1995), the resistance to biodegradation of other C_7 skeletons can be examined using C_7 oil transformation star diagram, using P2, P3, Tr1, Tr2, Tr3, Tr4, Tr5, Tr6, Tr7, and Tr8 ratios, as it is presented below (Figure 12).

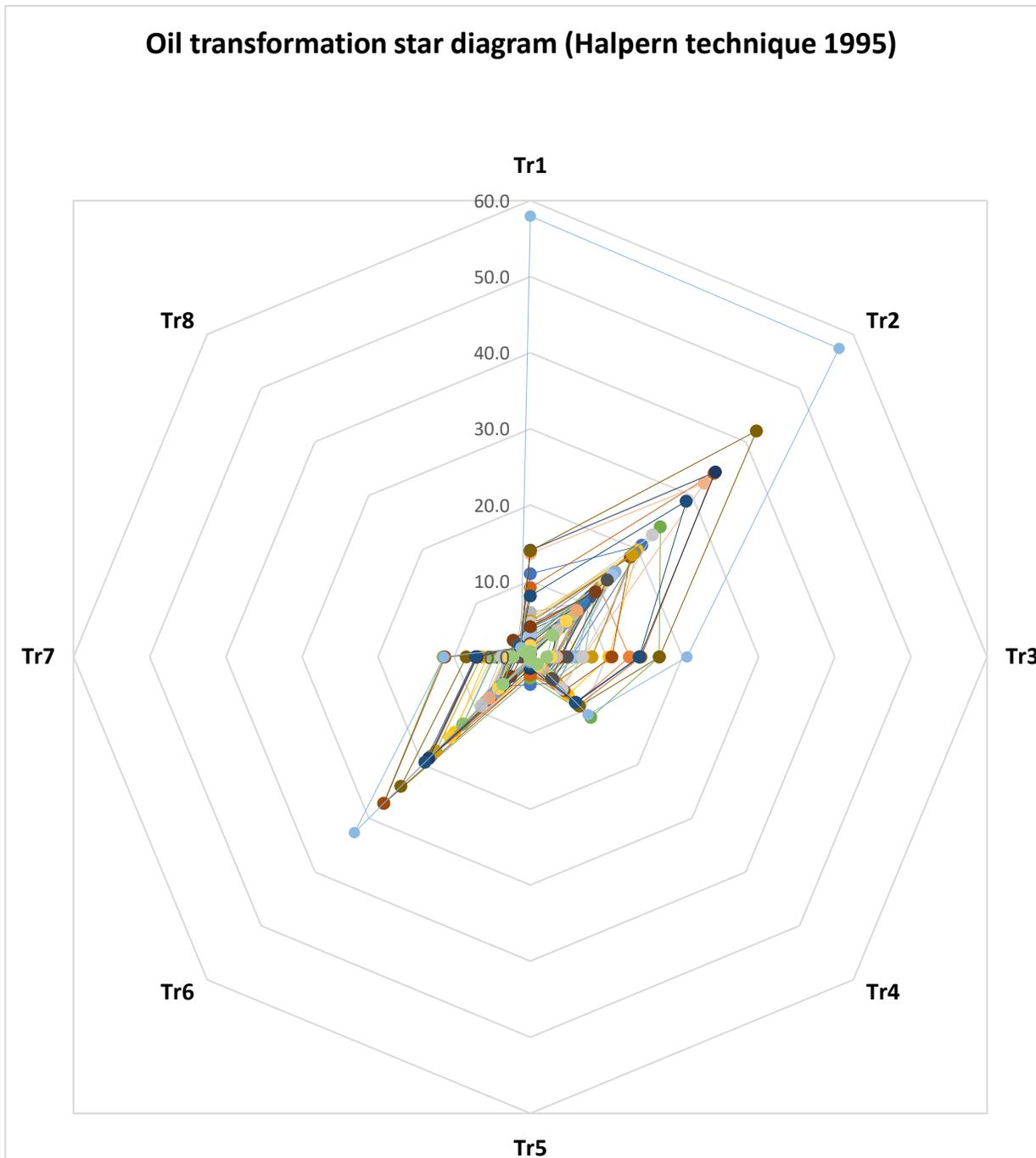


Figure 12. Oil transformation star diagram for the Leduc oils (after Halpern 1995)

$$P2 = 2MC6 + 3MC6$$

$$P3 = 22DMC5 + 24DMC5 + 33DMC5 + 23DMC5 + 1c3DMCYC5$$

$$Tr1 = Tol/11DMCYC5$$

$$\text{Tr2} = \text{nC7}/11\text{DMCYC5}$$

$$\text{Tr3} = 3\text{MC6}/11\text{DMCYC5}$$

$$\text{Tr4} = 2\text{MC6}/11\text{DMCYC5}$$

$$\text{Tr5} = (\text{CYC5} + 23\text{DMC4})/11\text{DMCYC5}$$

$$\text{Tr6} = 1\text{t2DMCYC5}/11\text{DMCYC5}$$

$$\text{Tr7} = 1\text{t3DMCYC5}/11\text{DMCYC5}$$

$$\text{Tr8} = \text{P2}/\text{P3}$$

The diagram confirms that the 1,1-dimethylcyclopentane is the most resistant to biodegradation of all C₇ hydrocarbons (Halpern 1995). On the other, the toluene and the n-C₇ are highly depleted in the Leduc sample set. Also, when comparing Tr3, Tr4 and Tr5 to Tr6 and Tr7, it can be observed that the methylhexanes are more resistant to biodegradation than the 1-trans-2-dimethylcyclopentanes, whereas the quantity of 1-trans-3-dimethylcyclopentanes did not change considerably, which also shows higher resistance to biodegradation of these components.

4) *Evaporative fractionation*

The evaporative fractionation, or also known as separation migration represents a process in which the oil's composition is altered by solution and exsolution in a gas phase. In general, this alteration process is typical in basins with vertical migration along faults and mud or salt diapirs. Usually, the oils affected by this process are less paraffinic, i.e. more aromatic and naphthenic.

In the graph below (Figure 13) is presented the evaporation check of the C-oils, using the Tompson technique (1988). According to this graph, it is evident that in the Nisku, Leduc/Nisku, Arcs and Camrose samples there is a drop in the paraffanicity index (nC₇/MC₆), whereas the evaporation trend towards the direction of the increase of the aromaticity index (Tol/nC₇) is present in the Leduc/Nisku, Nisku Leduc and the Beaverhill Lake oils.

The next graph (Figure 14) shows the evaporation check between the C-oils and the Nisku oils. It shows that the Nisku oils have undergone evaporative fractionation considerably more

compared to the C-oils. This is also confirmed by the correlation diagram (Figure 15) of these two families of oils given below.

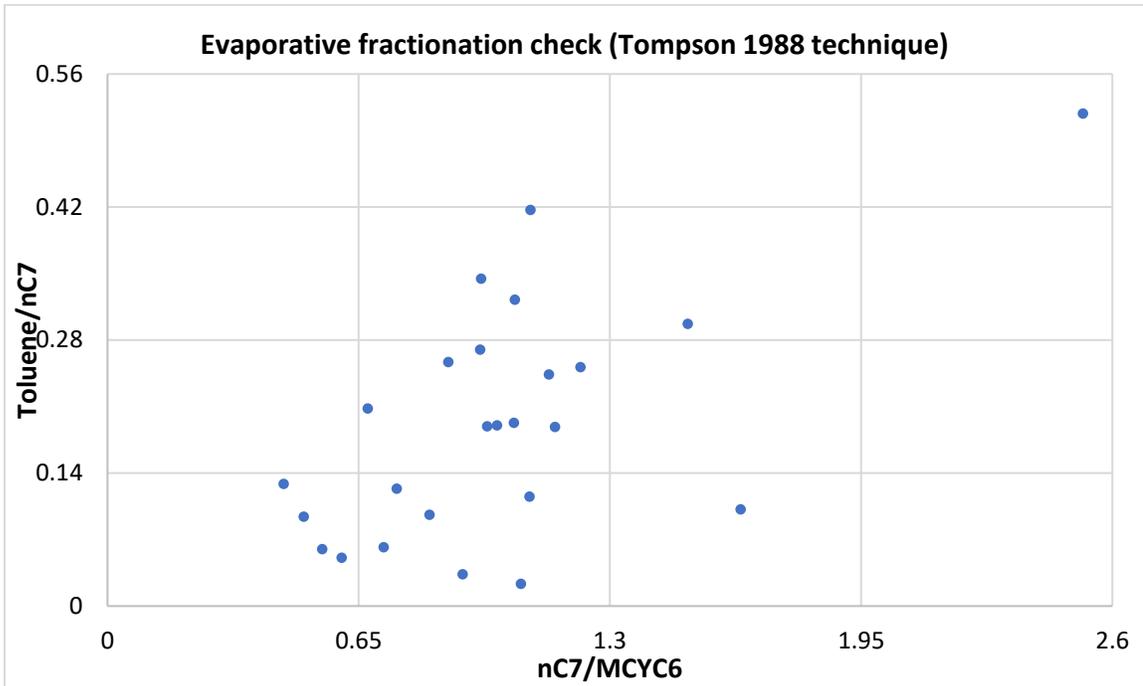


Figure 13. Evaporation check (C-oils, after Tompson, 1988)

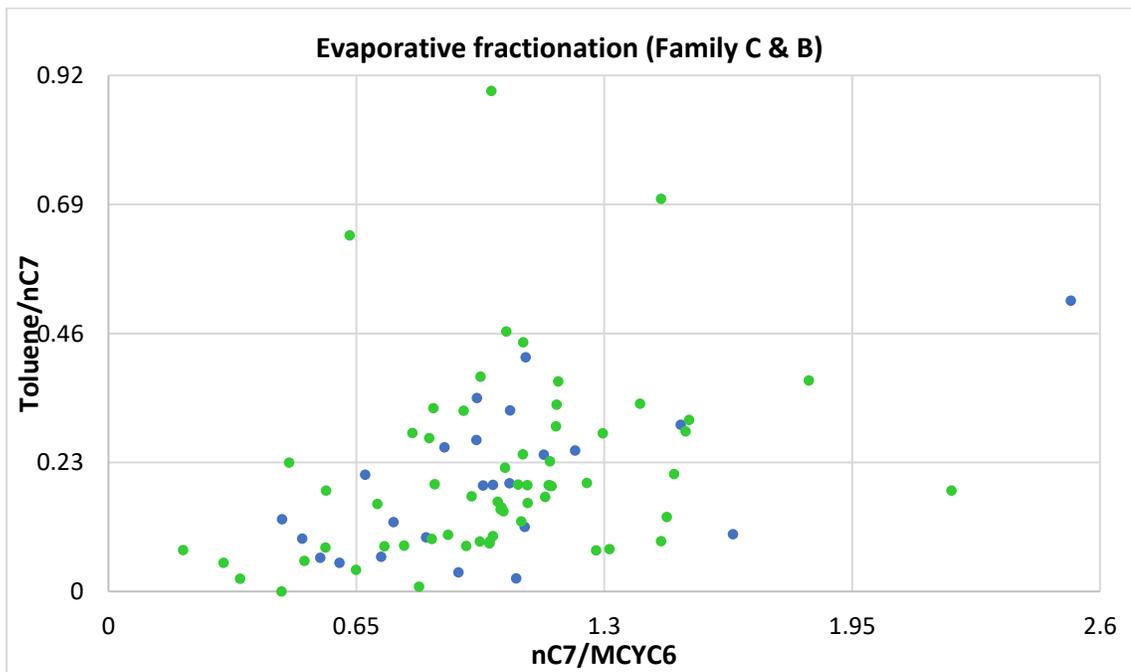


Figure 14. Evaporation check (C-oils and Nisku oils)

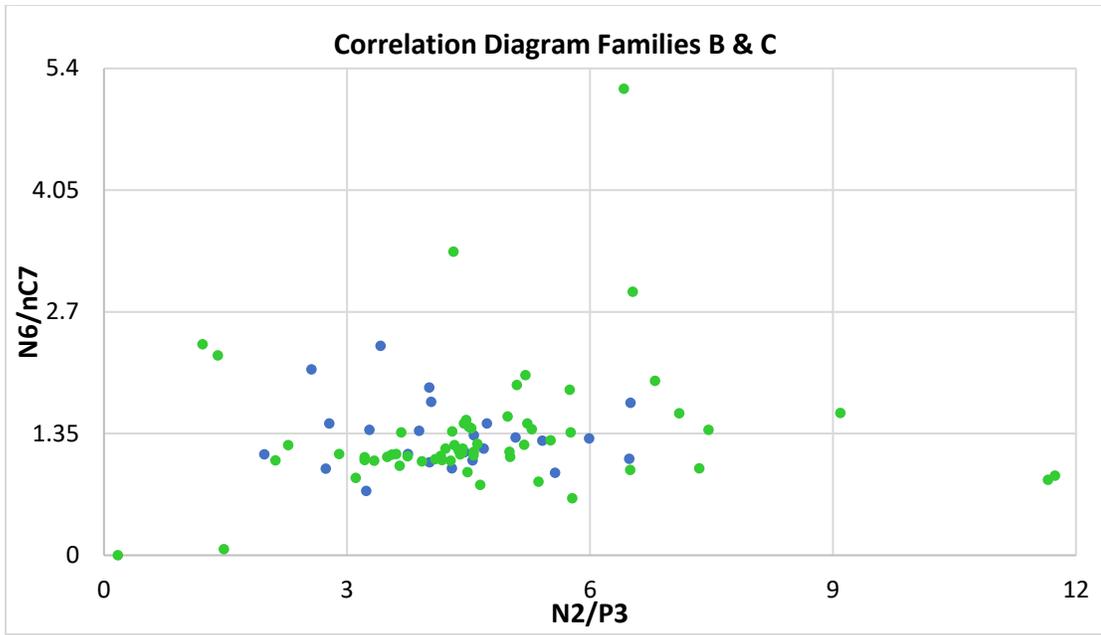


Figure 15. Correlation diagram (C-oils and Nisku oils)

5) *Application of Mango's K1*

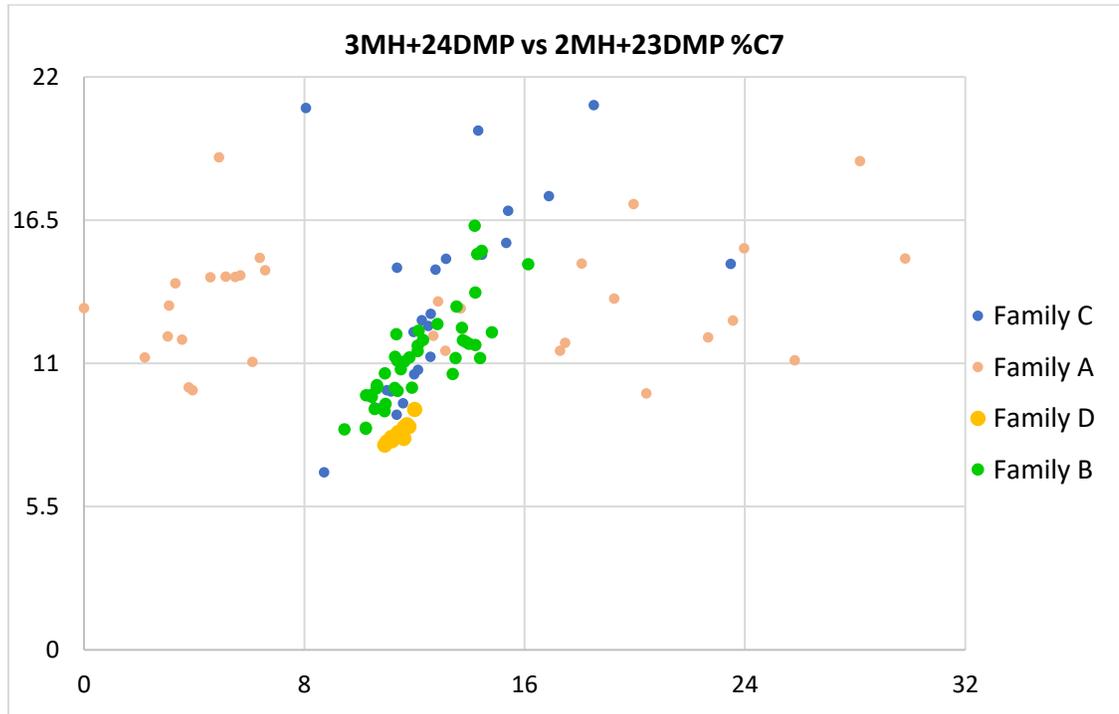


Figure 16. cross-plot of the 3MH+24DMP vs 2MH+2.3DMP

As previously mentioned, the K1 ratio ($2MC6+23DMC5/3MC6+24DMC5$) is used as an indicator of whether different groups of oils have a common source. If the ratio of the sums of isoheptanes is relatively constant within a given set of oils, refers to genetically related oils. These oils are considered to be homologous oils.

Mango showed that the variance in K1 in a given set of oils can be explained by the differences between invariant homologous sets (i.e. oils from a common source).

In the following graph (Figure 16) is given a cross-plot of the $3MH+24DMP$ vs $2MH+2.3DMP$ for all the 146 oils from the compositional data. As it can be seen from the graph the Families C, B, (Nisku) and D (Keg River) are probably originated from the same source, since their K1 is nearly constant, whereas the oils of Family A (Leduc) do not have a constant K1.

6) Application of ternary diagrams

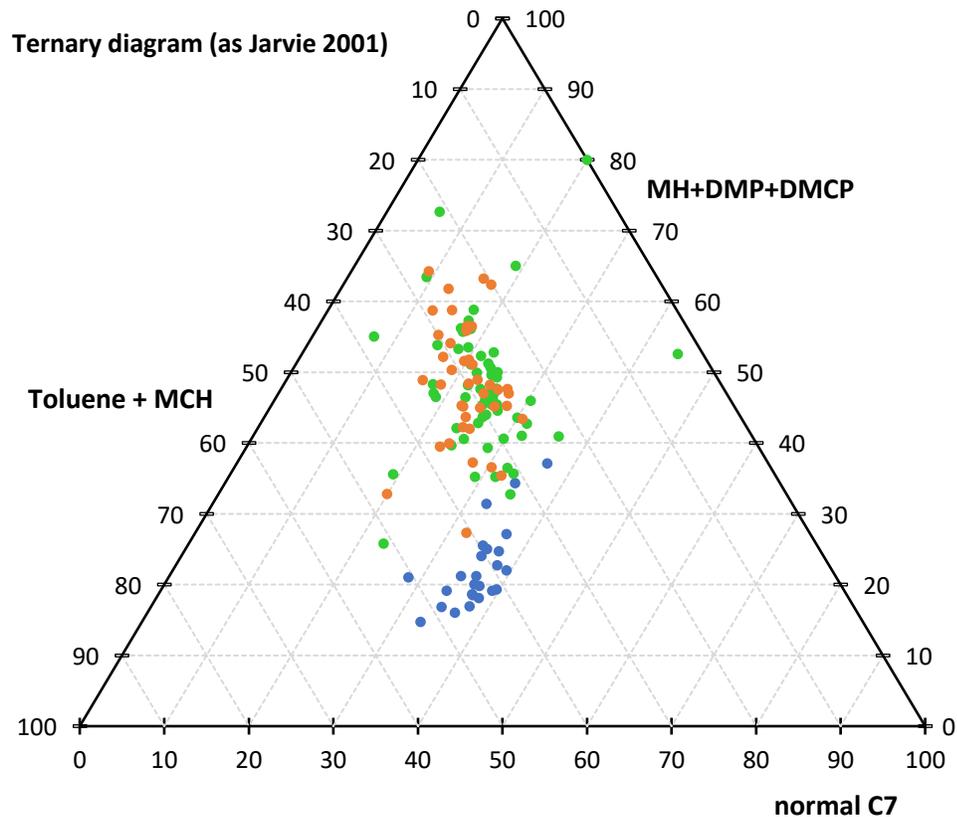


Figure 17. Ternary diagram (as Jarvie 2001)

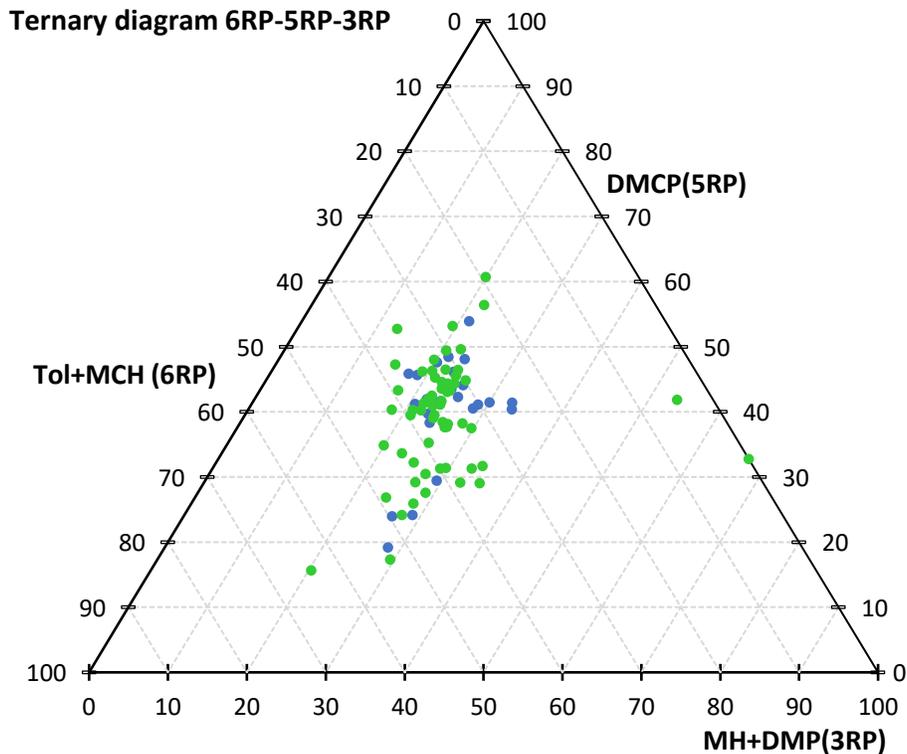


Figure 18. Ternary diagram 6RP-5RP-3RP (C-oils and Nisku oils)

In general, these types of diagrams are used to indicate the origin of the oils. For example, those oils grouped close to the 6RP apex have terrigenous origin, whereas those with the lacustrine origin, a group close to the 3RP apex, and finally, the oils of marine origin have 5RP predominance. In such a case, since it is observed a strong overlap between these two groups of oils (C-oils and Nisku oils), the application of such a triangular plot is limited.

It can be observed that in both groups of oils there is the removal of toluene, most probably as a consequence of the water washing process. Also, the overlap between these two groups of oils could be interpreted as an indication that these two families have similar characteristics.

Conclusion

As it has been presented in this thesis, the geochemistry represents a powerful tool in the field of oil production and reservoir geochemistry. The application of the oil fingerprinting in delineating reservoir compartmentalization, the wide applications of the geochemistry techniques, such in the case of predicting the flow assurance problems, identifying new exploration opportunities or missed pay zones, maximizing the waterflood efficiency, etc., has a significant contribution in the decision-making process during production. Its application also provides a significant production quality and efficient recovery.

One of the many applications of the geochemistry is the application of the light hydrocarbon ratios in characterizing the maturation, biodegradation, water washing, and evaporative fractionation.

When applying a set of light hydrocarbon ratios (such as $i\text{-C}_5/n\text{-C}_6$, $3\text{MC5}/n\text{-C}_6$, $n\text{-C}_7/\text{MCH}$, etc.) on a set of 146 oil samples from Western Canada, it can be concluded that generally, the family of C-oils, as well as the Nisku oils are affected by compositional changes due to evaporation that most probably occurred during the post-sampling process. When using the ratios $\text{MCYC6}/\text{Tol}$ and $3\text{M5}/\text{Benz}$ it can be observed that most of the samples in this family of oils is not considerably affected by water washing. Only two samples have undergone a severe compositional alteration due to the process of water washing-the Wabamun sample (L01227a), and the Camrose sample (L02257). Also, the group of the C-oils and the Nisku oils show similar compositional changes due to water washing. The $3\text{MP}/n\text{C6}$ and $i\text{C5}/n\text{C6}$ ratios are applied to observe the compositional changes due to the process of biodegradation and it is confirmed that within the group of Leduc oils the trimethylpentanes are less resistant to biodegradation than the methylhexanes. When applying the $\text{Tol}/n\text{C7}$ and $n\text{C7}/\text{MCH}$ ratios within the group of C oils, it is evident that in the Nisku, Leduc/Nisku, Arcs and Camrose samples there is a drop in the paraffanicity index ($n\text{C7}/\text{MC6}$), whereas the evaporation trend towards the direction of the increase of the aromaticity index ($\text{Tol}/n\text{C7}$) is present in the Leduc/Nisku, Nisku Leduc and the Beaverhill Lake oils. The application of the Mango's $k1$ ratio shows that probably the group of Leduc oils probably originate from a different source than group C, Nisku, and Keg River oils, whereas the ternary diagrams show that the C-oils and the Nisku oils have very similar characteristics.

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