

Edited by **Mikhail A. Varfolomeev**
Chengdong Yuan • **Jorge Ancheyta**

Catalytic In-Situ Upgrading of Heavy and Extra-Heavy Crude Oils



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About the Editors

Dr. Mikhail A. Varfolomeev graduated in chemistry (2005) from the Kazan State University. He completed his PhD thesis in physical chemistry with focus on thermodynamics of fluids in 2007, also in the Kazan State University. He is a recipient of with more than 20 different national and international awards in education, research, and innovation areas. He is a coauthor of 17 patents and more than 310 papers (H-index of 30). He was invited as a researcher and professor in University of Rostock (Germany), IFP Energies Nouvelles (France), Southwest Petroleum University (China).



Nowadays, Dr. Varfolomeev is a chair of Department of Petroleum Engineering and head of Enhanced Oil Recovery Center of the Kazan Federal University. His research interests include petroleum engineering, enhanced oil recovery, catalytic oil upgrading, in situ combustion, gas injection, chemical flooding, phase behavior, gas hydrates, thermodynamics, thermal analysis, and calorimetry. He was supervisor of more than 15 PhD students and 50 BSc and MSc theses. He actively cooperates with petroleum industry. He supervised more than 60 technical projects. A good number of them were introduced to the industrial scale. He actively participated in one of the world's first successful pilot tests of in situ catalytic upgrading of heavy oil in Russia and Cuba. Dr. Varfolomeev is an associate editor of *Journal of Petroleum Science and Engineering*, *Journal of King Saud University – Engineering Science*, and member of Editorial Boards of Petroleum and Energies. He has given more than 40 plenary, keynote, and technical presentations on international conferences.

Chengdong Yuan holds a PhD degree in oil and gas field development engineering through a combined master's-PhD program from Southwest Petroleum University, China (2016). He graduated with a bachelor's degree in petroleum engineering from Southwest Petroleum University (2011). He worked in Department of Petroleum Engineering of the Kazan Federal University as an associate professor (2019–2022), and in Department of Physical Chemistry of the Kazan Federal University as a senior researcher (2017–2022). Dr. Yuan has worked as Principal Research Scientist and Assistant Professor at Skolkovo Institute of Science and Technology since 2022. His academic interests focus on efficient hydrocarbon recovery. Specific interests include thermal methods for enhanced oil recovery including steam injection, in situ combustion (ISC), new technologies for in situ heavy oil upgrading, catalytic in situ oil upgrading, catalytic oxidation of crude oil, chemical flooding especially for interfacial phenomena (wettability of solids, interfacial tension, foams, and emulsions),



and profile control and water shutoff technologies. He has been authorized 7 patents and is author and coauthor of more than 130 scientific papers (H-index of 24), has been awarded scientific scholarship in the field of research in pharmaceuticals, chemistry, and petrochemistry, oil production, and oil and gas geology of the KFU Board of Trustees (2020). He has participated and given presentations in international conferences about 15 times since 2015, including 8 times SPE conferences presenting technical presentations. He was guest editor of the international journal *FUEL* of the special issue “In-Situ Upgrading of Heavy and Extra-Heavy Crude Oils.”

Jorge Ancheyta, PhD, graduated with a bachelor's degree in Petrochemical Engineering (1989), master's degree in Chemical Engineering (1993), and master's degree in Administration, Planning, and Economics of Hydrocarbons (1997) from the National Polytechnic Institute (IPN) of Mexico. He splits his PhD between the Metropolitan Autonomous University (UAM) of Mexico and the Imperial College London, UK (1998) and was awarded a postdoctoral fellowship in the Laboratory of Catalytic Process Engineering of the CPE-CNRS in Lyon, France (1999). He has also been visiting professor at the Laboratoire de Catalyse et Spectrochimie (LCS), Université de Caen, France (2008, 2009, 2010), Imperial College London, UK (2009), Mining University at Saint Petersburg, Russia (2016, 2017), and Kazan Federal University, Russia (2021–2024).



Dr. Ancheyta has worked for the Mexican Institute of Petroleum (IMP) since 1989 and his present position is manager of Products for the Transformation of Crude Oil. He has also worked as professor at the undergraduate and postgraduate levels for the School of Chemical Engineering and Extractive Industries at the National Polytechnic Institute of Mexico (ESIQIE-IPN) since 1992, and for the IMP postgraduate since 2003. He has been supervisor of more than one hundred BSc, MSc, and PhD theses. Dr. Ancheyta has also been supervisor of a number of postdoctoral and sabbatical year professors.

Dr. Ancheyta has been working in the development and application of petroleum refining catalysts, kinetic and reactor models, and process technologies mainly in catalytic cracking, catalytic reforming, middle distillate hydrotreating, and ex situ and in situ heavy oils upgrading. He is author and coauthor of a number of patents, books, and about 250 scientific papers (H-index of 63), has been awarded the highest distinction (Level III) as National Researcher by the Mexican government, and is a member of the Mexican Academy of Science. He is principal associate editor of the international journal *FUEL*. Dr. Ancheyta has also chaired numerous yearly international conferences since 2004, namely International Symposium on Hydroprocessing of Oil Fractions (ISAHOF) and International-Mexican Congress on Chemical Reaction Engineering (IMCCRE).

Preface

Heavy and ultra-heavy oil resources account for about 60–70% of total proved oil reserves all over the world, which are concentrated in various countries such as Russia, Mexico, Canada, and Venezuela. Due to the high viscosity and density of heavy oils, their production, transportation, and processing are much more difficult than conventional oils.

For effective development, usually thermal methods are required to reduce the viscosity for the easy flow of heavy oils in the reservoir. Currently, steam injection is the most widely used thermal method for heavy oil recovery. However, during its application, various issues have been exposed, such as

- Low efficiency with high energy and freshwater consumption for generating steam
- Environmental issues caused by the large consumption of freshwater and burning of coal or gas
- The viscosity of the recovered oil is not low enough on the ground, which increases difficulties and cost for its transportation and processing.

To solve these problems, using catalysts to initiate a catalytic aquathermolysis process for achieving a higher level in situ upgrading of heavy oils during steam injection is a promising solution, which, on the one hand, can improve the properties of heavy oils to ease the difficulties in transportation; on the other hand, can reduce the injection volume of steam, thus decreasing the consumption of energy and freshwater, reducing the cost, and improving the efficiency of steam injection.

Various efforts have been made to improve the in situ upgrading and efficiency of steam injection by using different catalysts. For these reasons, it was identified that there was the need to have a document to summarize the theoretical aspects and current advances in the main topics related to in situ upgrading of heavy and extra-heavy crude oils.

Catalytic In Situ Upgrading of Heavy and Extra-Heavy Crude Oils is organized in the following 11 chapters:

Chapter 1 describes general aspects of definition, classification, and properties of crude oils, as well as detailed experimental data of typical crude oils around the world to achieve a better understanding of their composition. Chapter 2 deals with the description of advanced characterization of heavy crudes and their fractions. Particular emphasis is put on electron paramagnetic resonance (EPR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and relaxometry, Fourier transform infrared spectroscopy (FTIR), and chromatographic and mass spectrometry methods. The methods for in situ enhanced oil recovery (EOR) methods for heavy crudes recovery are detailed in Chapter 3. Chapter 4 aims at describing the fundamentals of in situ upgrading. Chapters 5 and 6 focus on the catalyst used for in situ upgrading, liquid catalyst, and nanoparticles. Chapter 7 deals with the different kinetic models for in situ upgrading, including noncatalytic aquathermolysis, catalytic aquathermolysis, and using hydrogen. Chapter 8 is devoted to the

application of quantum chemical calculations for studying thermochemistry, kinetics, and catalytic mechanisms of in situ upgrading. A general methodology, calculation techniques, and preliminary results of applying quantum chemistry methods for studying complex physico-chemical phenomena that accompany the in situ upgrading processes are described. Chapter 9 is devoted to describing the behavior of a catalyst in porous media. A systematical investigation of the effect of pore space heterogeneity on the dynamics adsorption of catalyst dissolved in the water during a single-phase flow is studied, which allows for registering the catalyst distribution in the pore space using 4D tomography. Chapter 10 details the numerical simulation of catalytic in situ oil upgrading process, and Chapter 11 presents the novel technologies for upgrading heavy and extra-heavy oil.

It is foreseen that *Catalytic In Situ Upgrading of Heavy and Extra-Heavy Crude Oils* becomes promptly an outstanding and distinctive book, not only for researchers that conduct investigations in this area, but also for BSc, MSc, and PhD students that need detailed information and explanations on how to carry out experiments and calculations in the topic of upgrading of heavy oils.

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Properties of Heavy and Extra-Heavy Crude Oils

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1.1 Introduction

The increase in the population and continuous development of the global economy and industrialization has triggered a sharp growth in energy demand. Petroleum oil is the source of energy most used, and it is also the leading feedstock for various types of industries, among the manufacture of synthetic fibers, plastics, paints, fertilizers, insecticides, soaps, and synthetic rubber. Thus, the uses of petroleum as a source of raw material in manufacturing keep functioning the modern industry. According to the Organization of Petroleum Exporting Countries, oil demand is expected to increase by 16.4 MB/D between 2015 and 2040, reaching 109.4 MB/D by 2040. Conventionally, the energy demand has been covered by the exploitation of light oil resources. Nevertheless, petroleum is a nonrenewable resource that cannot be replaced naturally at the rate that it is consumed and is, therefore, a limited resource. Due to the decrease in light hydrocarbon reserves, it is essential to develop technologies capable of improving the production, transportation, and refinement of unconventional hydrocarbons reserves, such as heavy crude oil, extra-heavy crude oil, bitumen, among others, that represent 60–70% of the proven oil reserves around the world. The high content of high molecular weight hydrocarbon molecules with heteroatoms in their lattices (asphaltenes and resins) in this type of resource hinders their exploitation and utilization since these compounds tend to precipitate out, resulting in deposition and plugging of oil wellbores, pipelines, and surface facilities that cause various costly operational problems to oil producers. It is then of high importance to know the details of oil properties for the proper definition of the processes and catalysts that can be used for its upgrading.

The objective of this chapter is to present the definition and classification of crude oils according to their constituents, as well as to describe the main properties used to characterize them. The relevancies of some physical and chemical properties, and standardized methods used for measurement are provided together with detailed experimental data of diverse samples of typical crude oils around the world in order to achieve a better understanding of petroleum composition and its constituents.

1.2 Heavy and Extra-Heavy Crude Oils

Petroleum or its equivalent term “crude oil” covers a wide assortment of materials consisting of a naturally occurring mixture of hydrocarbons and some organic compounds derivatives containing heteroatoms such as sulfur, nitrogen, oxygen, and trace amounts of some metals such as nickel and vanadium. Crude oil is derived from organic matter (dead plant and animal material) decomposed and exposed to certain temperatures and pressure for prolonged periods. This organic matter migrated from the original source beds to more porous and permeable rocks, where it has been buried and accumulated underground at pressure (depending on the depth) in geologic structures called reservoirs. An ensemble of reservoirs within a common rock structure or in separate structures but neighboring formations is currently referred to as an oil field (Abdel-Aal et al. 2003).

Characterization of the different chemical species contained in crude oils remains a challenging task due to an immense range of moieties presented in terms of number of molecules and chemical structures. The variation of types of molecules present in petroleum is influenced by the temperature and pressure in the reservoir, the age of the oil field, as well as the origin and the relative amounts of the different constituents that form the original materials. Thus, the composition of petroleum around the world varies from one oil field to another, from one well to another in the same field, and even with the depth of an individual well. Therefore, it is possible that adjacent wells produce crude oils with diverse properties.

Under pressure and temperature conditions on the reservoir surface (i.e. at the wellhead), low boiling hydrocarbon compounds (methane, ethane, propane, and butane) emerge from petroleum as gases. Meanwhile, higher boiling hydrocarbon derivatives (pentane and higher molecular weight compounds) remain in the liquid phase. Moreover, higher molecular weight hydrocarbon derivatives occur in the solid phase (i.e. wax derivatives), remaining dissolved in the liquid phase.

The high hydrocarbons content in crude oil, with its diverse structures of alkane (paraffins), cycloalkane (naphthenes), and aromatic hydrocarbon derivatives, provides a source of usable products such as waxes, lubricants, diesel, gasoline, and various forms of petrochemicals.

Certain crude oil reserves contain high proportions of hydrogen-rich compounds with relatively short hydrocarbon chains and low boiling components (low molecular weight). On the other hand, some oil reserves have been altered by aerobic biodegradation, where meteoric water supplies nutrients, oxygen, and bacteria attack the lighter alkanes, which increase the proportions of higher boiling components (higher molecular weight). This is the case of the deposits of extra-heavy crude oil and tar sands bitumen from the Orinoco Belt in Venezuela and Alberta Basin in Canada in which the oil has accumulated in a low-temperature environment allowing for the growth of bacterial communities feeding on the crude oil. Although most heavy crude oil reserves worldwide are the result of bacterial alteration of conventional oil, other factors can be responsible for the formation of heavy crude oils. For instance, the heavy crude oils deposits of California are explained by the nature of the sedimentary organic matter from which the oil is sourced. This organic matter is thermally labile and releases petroleum at an early stage of the burial history of the source rock, which results in a viscous, sulfur-rich, and thermally immature oil.

Heavy crude oil, extra-heavy crude oil, and tar sand bitumen typically have a relatively high molecular weight fraction that comprises an assortment of different complex compounds deficient in hydrogen and with high carbon and heteroatoms (metal, sulfur, and nitrogen) content that significantly contribute to the poor fluid properties of the oil and providing low mobility. These properties hinder the extraction, upgrading, transport, and refining of these resources to produce high quality and economic value fractions, such as naphtha, kerosene, diesel, and liquefied petroleum gas (LPG).

The classification of crude oil involves an assessment of various properties as well as knowledge of diverse methods of recovery from reservoirs. Conventional petroleum is often referred to as the crude material accumulated in reservoirs that can be recovered utilizing only naturally occurring forces or resulting from the injection of water or an immiscible gas at moderate pressure (primary and secondary recovery methods). In contrast to conventional crude oils, unconventional oils present low mobility through the reservoir due to their high viscosity. Thus, the recovery of these resources may require the application of thermal stimulation techniques for more efficient recovery of the oil, along with heating and dilution methods for their transportation to refineries by pipelines. Recent studies estimate that unconventional oil reserves, including heavy crude oil, extra-heavy crude oil, and tar sand bitumen, exceed 6 trillion barrels that is equivalent to about 70% of all energy resources derived from fossil fuels in the world.

Some organizations have reported various classifications for crude oil based on certain properties such as sulfur content, API gravity, or viscosity. For instance, those crude oils with a sulfur content higher than 0.5 wt% are classified as sour oil, while crude oils with less than 0.5 wt% are termed as sweet oils (Gray 2015). Generally, the most used classification for crude oil is based on the API gravity, which is a measurement related to oil density (Section 1.3.1). The American Petroleum Institute considers light oil that type of petroleum that has higher than 31.1° API, while oil with API gravity between 22.3° and 31.1° API is classified as medium crude oils. Otherwise, a crude oil that has an API gravity less than 22.3° API is termed as heavy crude oil. Nevertheless, the criterion for oil classification based on the API degree range has not been standardized. Diverse oil organizations have adapted their own API scales considering financial aspects and the degree of technological improvement. The World Petroleum Congress and the US Geological Survey state that heavy crude oil has an API in the range of 10 and 20 and a gas-free viscosity between 100 and 10 000 mPa s at original reservoir temperature. On the other hand, Petrobras defines heavy crude oils as those in the range between 10° and 19° API (Huc 2010).

Basically, heavy crude oil has a much higher viscosity (i.e. resistance to flow) and density than conventional crude oil and generally has sulfur content higher than 2 wt%. Consequently, recovery of heavy crude oil usually requires thermal stimulation of the reservoir content (Speight 2019).

The term “extra-heavy crude oil” is used to define the subcategory of crude oil with less than 10° API and is more viscous than heavy crude oil. Nonetheless, this crude oil type has mobility in the reservoir under at reservoir temperature. On the other hand, tar sand bitumen is typically incapable of mobility (free flow) under the conditions in the tar sand deposit, presenting high viscosities (>10 000 cP). Therefore, tar sand bitumen requires more advanced methods than heavy crude oils. The mobility of extra-heavy crude oil is due to a high reservoir temperature (higher than the pour point of the extra-heavy crude oil) or other factors subject to variations and specific conditions in the reservoir.

These classifications have been suitable for achieving a general understanding of the properties of crude oils despite their inaccuracy because they do not always reflect the true nature of heavy and extra-heavy crudes (Speight 2016).

1.3 Physical Properties

The importance of certain physical properties has been highlighted for the classification of crude oil and complications of recovery from reservoirs. Therefore, a clear understanding of the significance of these properties is required to provide vital insights into the behavior, characteristics, and quality of crude oil. Physical properties such as density, viscosity, and pour point may vary widely in crude oils from different locations. Certain methods that measure the physical properties of heavy crude oil and extra-heavy crude oil can identify the quality of crude oil (Ancheyta and Speight 2007).

1.3.1 Density, Specific Gravity, and API Gravity

Density is defined as the mass of a unit volume of a substance at a specified temperature (usually expressed for oils in dimensions of grams per cubic centimeter). On the other hand, relative density or specific gravity (*sg*) is the ratio of the weight of a unit volume of oil to the weight of the same volume of water at specified temperatures, which are usually determined at the standard temperature of 60 °F (15.6 °C).

Different standardized procedures for measuring the density or specific gravity apply to heavy crude oil and may be measured utilizing a hydrometer (ASTM D287 and ASTM D1298) or using a pycnometer (ASTM D941 and ASTM D1217).

Density and specific gravity are widely used in the industry for preliminary assessment of the character of the oil. The values for density (and specific gravity) cover a narrow range considering the differences in the feedstock appearance and behavior. To introduce a more meaningful relationship between the physical properties and processability of the various crude oils, the American Petroleum Institute devised a measurement of specific gravity to determine the quality of crude oils and refinery streams by means of the following equation:

$$API = \frac{141.5}{sg} - 131.5 \quad (1.1)$$

The API gravity scale helps emphasize differences in specific gravity values between crude oil samples. For instance, crude oil samples might have specific gravities of 0.88 and 0.84, which would appear to be a small difference. However, the API gravities of these liquids are 29 and 37, respectively. The specific gravity usually ranges from about 0.8 (45.3° API) for the lighter crude oils to over 1.0 (10° API) for heavy crude oils and bitumen, which is consistent with the general trend that increased aromaticity leads to a decrease in API gravity (i.e. an increase in specific gravity). The extra-heavy crude oil and bitumen have an API gravity less than 10, which means a specific gravity higher than 1, being heavier than pure water.

The variation of density with temperature is a property of great technical importance since most petroleum products are processed, treated, and marketed based on their volume, which has fundamental application in both petroleum production and processing as well as its transportation and storage. These properties are used in the calculations related to the sizing of pipes, valves, and storage tanks, the power required by pumps and compressors, and flow-measuring devices. In addition, density oil is used in reservoir simulation to estimate the amount of oil and gas in a reservoir, as well as the amount of their production at various reservoir conditions (Ancheyta and Speight 2007; Riazi 2005).

1.3.2 Viscosity

Viscosity is the measure of the internal resistance to fluid motion because of the forces of cohesion between molecules or molecular groups. It characterizes the motion of crude oils and is typically expressed in g/cm s or Poise (1 P = 100 cP). Since viscosity varies with temperature, measured values of viscosity must be reported at specified temperatures. Generally, the kinematic viscosity of petroleum fractions is measured at standard temperatures of 37.8 °C (100 °F) and 98.9 °C (210 °F). The viscosity values of crude oils vary markedly over a wide range from less than 10 cP to many thousands of centipoises at room temperature. Moreover, this parameter depends on soil composition, pressure, and gas solubility, and it is a critical property in predicting oil recovery since viscosity reduction and thermal expansion are the key properties for increasing the productivity of heavy crude oil. As stated previously, heavy crude oils present high viscosity values (in comparison with conventional oils), being the main drawback for its production from reserves and transportation

through the pipelines turning difficult the production process. Some documents have set the maximum viscosity at 250 cSt (100 °F) and the minimum API gravity at 16° for transportation purposes.

Several standardized methods are available for the experimental determination of viscosity for different types of crude oils and petroleum products. The most used are ASTM D88, D341, D445, D2161, D2170, D2270, D7483, and E102. These methods differ concerning the type and required amount of sample, the experimental setup, the time for analysis, the operating conditions of apparatus, and the viscosity ranges in which the device can be used. Therefore, the experimental determination of the viscosity was made based on the characteristics of the sample. In practice, it has been observed that measuring the viscosity of crude oils with low API gravity is complicated due to their nature and difficulty in handling. This drawback makes the analysis time-consuming and more amount of sample to obtain reliable results is necessary (Sánchez-Minero et al. 2014; Speight 2013).

Some terms have been derived from viscosity to determine the behavior and handling of fluids. The kinematic viscosity is the ratio of viscosity and specific gravity. The unit of kinematic viscosity is the stoke (cm²/s), although centistokes (cSt) are commonly used units. On the other hand, fluidity is defined as the reciprocal of viscosity.

1.3.3 Pour Point

The pour point is referred to as the lowest temperature at which the oil flows under standard test conditions (ASTM D97). The pour point of crude oils is a critical parameter to the proper functioning of the production line and generally varies from 52 to −59 °C (125 to −75 °F).

This parameter is influenced by the content of waxes, viscosity, and even the thermal history of the sample, that is the degree and duration of heating and cooling to which the sample has been exposed. Moreover, it is emphasized that the tendency of the oil to flow is influenced by the size and shape of the container, the head of the oil, and the physical structure of the solidified oil. The pour point of the oils is, therefore, a predictor of the temperature at which flow ceases in the reservoir. This term has significant consideration since, for efficient production of unconventional oils (heavy crude oil, extra heavy crude oil, among others), additional energy must be supplied to the reservoir by a thermal process to increase the reservoir temperature beyond the pour point and improving the ability of the heavy crude oil to flow (Riazi 2005; Speight 2014).

1.4 Chemical Properties

Heavy and extra-heavy crude oils are complex mixtures of different hydrocarbon types, and their composition depends on their geological origin. These crude oils present larger amount of heavy molecular weight hydrocarbons, hindering the refining process due to the impurities content such as heteroatoms and metals. Although the number of heavy fractions is small compared with the number of countless compounds in this type of crude oils, the adverse effect that these impurities cause is high (Caumette et al. 2009; Chacón-Patiño et al. 2022; Santos et al. 2014; Tirado et al. 2022; Yadykova and Ilyin 2022).

Chemical properties are indispensable to know the quality of heavy or extra-heavy crude oils in order to evaluate the refining capacity likewise the type of products generated. Therefore, a good manner to know the complexity of a petroleum to refine is by analyzing the chemical composition since this conformation of elements will determine the nature of reactions performed in the upgrading process. In this way, the products generated during the reaction depend on the composition of the heavy or extra-heavy crude oil fed (Ancheyta and Speight 2007; Kayukova et al. 2017; Rodrigues et al. 2018; Silva et al. 2011).

Most of the heteroatoms and metals are presented in highly condensed and large molecular weight compounds such as asphaltenes and resins. A feedstock with low content of heavy fraction such as asphaltenes, and thus small number of heteroatoms and large number of light fractions, is more easily processed in a refinery than a feed with greater content of heavy molecules. The reason is because in these types of crude oils a series of complex reactions to remove the impurities takes place (such metals and heteroatoms). Moreover, these impurities tend to deactivate the catalyst employed to upgrade the feedstock into more valuable products hindering the refining process (Muraza and Galadima 2015; Yadykova and Ilyin 2022; Zhao et al. 2005).

1.4.1 Elemental Analysis (CHONS)

One of the first methods to evaluate the general quality of petroleum is the elemental analysis, which provides the percentages of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S) as the basic constituents of the heavy and extra heavy crude oils whose contents range for different types of petroleum, depending on the origin, in the following intervals: C, 83.0–87.0%; H, 10.0–14.0%; N, 0.1–2.0%; O, 0.05–1.5%; S, 0.05–6.0%. However, the quality of heavy and extra heavy crude oils depends on the heteroatoms content (O, N, and S) as well as hydrogen content since a difference in these values provokes significant changes in their properties (Ancheyta and Speight 2007; Dehkissia et al. 2004; Riazi 2005).

Most of the elemental analyzers use a similar methodology, where the sample is combusted in an oxygen atmosphere, while product gases are separated and analyzed with different detectors based on different methods (ASTM D5291, Chinese industry standard SY/T 5122, classical Pregl-Dumas method, etc.) (Li et al. 2018; Riazi 2005; Zhang et al. 2021). Generally, the oxygen content is calculated by the difference of 100 and the sum of C, H, N, and S content (Ganeeva et al. 2021; Leyva et al. 2013; Medina et al. 2022). In addition, there are some methods to analyze specific elements separately as depicted in Table 1.1 (Ancheyta and Speight 2007; Kumar et al. 2018; Quitian and Ancheyta 2016; Rana et al. 2008; Riazi 2005).

Among all the heteroatoms, which are other atoms apart of carbon and hydrogen, sulfur presents the highest quantity in heavy and extra-heavy crude oils as thiols, sulfides, thiophene, benzothio- phene, dibenzothiophene (DBT), and its derivatives that are considered as undesirable compounds. Sulfur aromatic compounds (such as alkyl-substituted DBT) are difficult to convert during the refining of heavy and extra-heavy crude oils because of their steric hindrance as they attempt to adsorb on the catalyst surface (Ancheyta et al. 2009; Santos et al. 2014). Whereas nitrogen in heavy and extra-heavy crude oils is generally present in the form of basic (pyridine) and nonbasic (pyrroles,

Table 1.1 Standard methods for elemental analysis.

Elemental analysis	Method
C	ASTM D3178, D5291, E777
H	ASTM D1018, D3178, D3343, D3701, D4808, D5291, D7171, E777
O	ASTM E385
N	ASTM D3179, D3228, D3431, D4629, D5291, D5762, E148, E258, E778
S	ASTM D129, D1266, D1552, D1757, D2622, D3177, D4045, D4294, D4952, D5453, IP 30, IP 61, IP 107, IP 243, IP 336, IP 447

Source: Ancheyta and Speight (2007)/Informa UK Limited; Garcia-Montoto et al. (2020)/Elsevier; Kumar et al. (2018)/Elsevier; Quitian et al. (2016)/American Chemical Society; Rana et al. (2008)/Elsevier; Riazi (2005)/Google LLC; Speight (2002)/Google LLC.

indoles, and carbazoles) compounds, being more stable compounds than sulfur species (Santos et al. 2014; Wei et al. 2015). Oxygen is present in low amounts as carboxylic and phenolic groups mainly, although the presence of ketones, ethers, and anhydrides has also been reported by influencing the acidity of petroleum crude oil, which is especially important during refining processes and hence affects its market price (Santos et al. 2014).

The content of different elements, such as C, H, and O, can be related to the rearrangements of the different compounds containing these elements in the petroleum during the refining process. Furthermore, the ratios of these elements provide knowledge about the quality of the heavy fractions (Ancheyta and Speight 2007; Riazi 2005). Another indicator of the quality of the petroleum is the carbon-to-hydrogen mass percent ratio (C/H) because if the C/H relationship increases, the molecular weight and API gravity of petroleum increases and decreases, respectively. Moreover, a crude oil with a low C/H ratio is a good feedstock for the refining process because of the low hydrogen requirement. This behavior is also observed with the content of sulfur and nitrogen, increasing the quality of a heavy or extra-heavy crude oil by decreasing the content of these elements (Dehkissia et al. 2004; Riazi 2005). A preliminary hint of the aromaticity in crude oils can be obtained by the hydrogen-to-oil (H/C) atomic ratio which is calculated with Eq. (1.2) since the aromaticity decreases when the H/C ratio increases. This atomic ratio supplies a quantitative estimation of the nature in petroleum, considering that the aromatic molecules such as toluene (H/C ratio of 1.14) have low values, while the aliphatic constituents like heptane (H/C ratio of 2.29) have higher values (Leyva et al. 2013; Li et al. 2022; Riazi 2005; Sullivan et al. 2007):

$$\text{H/C(atomic ratio)} = \frac{11.9147}{\text{C/H(weight ratio)}} \quad (1.2)$$

The nitrogen and sulfur atoms are usually found in aromatic compounds where sulfur species are present in a large amount. The amount of sulfur in crude oil fractions increases as the molecular weight of the compound does, where asphaltene is the fraction containing the higher amount of sulfur. There are more catalysts focused on sulfur removal than nitrogen deletion since the latter is more difficult to eliminate while only a few catalysts have been developed to remove nitrogen. Moreover, the sulfur conversion during petroleum upgrading can reach up to 99% using novel catalysts in refineries (Ancheyta and Speight 2007; Leyva et al. 2013; Shafiq et al. 2020). The content of these two atoms in the heavy crude oil enhances the production of pollutant gases such as nitrogen oxides (NO_x) and sulfur oxides (SO_x). In addition, the sulfur compounds in crude oil products like gasoline or diesel contribute to the pollution through the exhaust gases and cause rusting and corrosion of the engine. Gas emission is penalized if sulfur concentration overcomes the upper limits allowed by local laws (Ancheyta and Speight 2007; Shafiq et al. 2020).

1.4.2 Metal Content

Heavy and extra-heavy crude oils display different concentrations of metals depending on their origin. Nickel (Ni), vanadium (V), and iron (Fe) are the most abundant metals in heavy crude oils ranging between 10 and 1000 ppm. However, other elements such as lead (Pb), barium (Ba), tin (Sn), silver (Ag), cobalt (Co), copper (Cu), molybdenum (Mo), titanium (Ti), and zinc (Zn) are present as well in fewer concentrations (1–50 ppm range) in heavy crude oils depending on their quality or composition because when the API gravity of crude oil decreases, the content of metals increases (Caumette et al. 2009; Dehkissia et al. 2004; Riazi 2005; Zhao et al. 2013). Metals are commonly present as porphyrins, nonporphyrin, and naphthenic acid salts, and different methods are applied to measure their content. Hence, the following individual analyses are employed to quantify the content of metals: ASTM D1548, D2788, D3605, D4628, D4927, D5708, D5863, D6443, IP 265,

IP 285, IP 288, IP 433, and IP 465. In all these methods, the sample is burnt to ash and diluted in acid to measure the absorbance of the metal by atomic absorption spectroscopy or inductively coupled argon plasma spectrometry (Ancheyta and Speight 2007; Rana et al. 2008; Riazi 2005; Speight 2002).

The metalloporphyrins are constituted by several porphyrins bonded to a central metal (Ni, V, Fe, or Cu), and more than 50 types of porphyrins have been identified in crude oils containing Ni or V, mainly. The nonporphyrin metal compounds are less polar than metalloporphyrins and account for 50–80% of the metal species. Nonetheless, these compounds are currently hypothesized since there is not enough characterization of them. The naphthenic acid salts, which are the less abundant metal species, are linked to Ca, Mg, Zn, and Ti, but there is no evidence of the presence of V or Ni-based naphthenic acid complexes in petroleum (Caumette et al. 2009; Mironov et al. 2018). Metal compounds tend to concentrate in heavier fractions like residue, asphaltenes, or resins, and are connected by strong bonds or surrounded in macromolecular networks. Metalloporphyrins can be directly related to the type of rocks where the heavy or extra heavy crude oil is formed. Furthermore, the V-to-Ni concentration ratio provides a hint of the geological conditions of sedimentation to which the crude oil was exposed (Caumette et al. 2009; Gao et al. 2013; Mironov et al. 2018; Riazi 2005).

The content of V and Ni impacts negatively in the refining process because their dehydrogenation activity increases the amount of coke and gases that are generated, decreasing the yield of liquid. Moreover, these metals also decrease the catalyst activity due to the poisoning of the active sites (Ancheyta and Speight 2007; Caumette et al. 2009; Riazi 2005; Santos et al. 2014; Shang et al. 2016). Vanadium-based species present in diesel fuels produce corrosive compounds, which at elevated temperatures damage some engine parts; hence, magnesium-based additives are employed to avoid corrosion. Nevertheless, the presence of lead suppresses the effect of these additives enhancing corrosion. Calcium compounds do not cause corrosion and even help to inhibit the corrosive action of vanadium compounds in refineries, yet they generate deposits that cannot be easily removed (Shang et al. 2016).

1.4.3 Carbon Residue

Carbon residue is a good predictor of crude oil quality, as well as the amount of carbonaceous deposits (asphalt or coke) that can be produced by the influence of heat (Duarte et al. 2016; Rodrigues et al. 2018). There are three types of carbon residue analyses that are applied to crude oils: Conradson carbon residue (ASTM D189, IP 13, JIS K2270-1, ISO 6615:1983, GB/T268-1987), Ramsbottom carbon residue (ASTM D524, IP 14), and the Micro carbon residue (ASTM D4530, IP 398, JIS K2270-2, ISO 10370). The application of these analyses must be carried out on crude oils free of volatile compounds as they are subjected to atmospheric distillations. Care must be taken during the analyses if samples easily produce ash, owing to measurements that may be erroneously obtained. These tests can be also applied to evaluate the deposits of carbon in engines generated by fuels (Ancheyta and Speight 2007; Kumar et al. 2018; Palacio Lozano et al. 2017; Riazi 2005; Speight 2002).

Although these methods are based on the distillation of a hydrocarbon sample, differences among them arise. For the Conradson carbon residue method, the sample is burnt in a crucible for a determined period weighing the residue at the end; for the Ramsbottom test, the sample is weighed and placed into a glass bulb that has a capillary opening. Later, it is heated in a furnace at 550 °C for a fixed period, and at the end, the carbonaceous deposits are weighed. On the other hand, for the Micro carbon residue method, the sample is burnt (at 500 °C) in an inert atmosphere for a specific time. Finally, the carbon residue remaining is weighed. All these methods are expressed as a percentage (wt/wt) of carbon residue in the initial sample. Among these techniques,

the Conradson and Micro carbon residue tests can be correlated directly, whereas the Micro carbon residue is the preferred technique for analyzing carbon residue since several runs are carried out simultaneously using small amounts of sample, keeping the distillation well controlled (Duarte et al. 2016; Palacio Lozano et al. 2017; Speight 2002).

A high content of metallic compounds, as observed in heavy and extra-heavy crude oils, can interfere in the measure of carbon deposits since the metals remain in residues. Therefore, these compounds need to be eliminated from the sample or taken as ash by the complete combustion of carbons deposits after the analysis (Riazi 2005).

1.4.4 Molecular Weight

The molecular weight of a heavy or extra-heavy crude oil is the average number of the molecular weight of the complex mixture of components present (at least several thousand) or the weight average molecular weight of all constituents. There is a wide variety of methods to determine the molecular weight that is divided into those that do not require any standard and those that require calibration with a material of known molecular weight (Azinfar et al. 2018; Speight 2014).

These analyses can be classified into methods that determine an average molecular weight value and those providing a complete distribution. Among them, viscosity vapor pressure osmometry (VPO, ASTM D2503, D2878, and UOP 676-84) and gel permeation (size exclusion) chromatography (GPC, ASTM D5296, and D6579) have been widely used because methods requiring calibration are generally easier and faster to be done. The main difference between these two analyses is that in GPC, the separation depends on the size of molecules, taking more time to pass through the chromatography column for the small molecules than for bigger compounds, providing a molecular weight distribution. Whereas VPO relies on the difference in vapor pressure when a drop of solute is added to a drop of pure solvent due to the molecular weight is related to the change of the vapor pressure in the solvent. The result is reported as molecular weight average (Álvarez et al. 2019; Ancheyta and Speight 2007; Azinfar et al. 2018; Castro and Vazquez 2009; Peramanu et al. 1999; Satya et al. 2007; Zhao et al. 2005).

In addition, new methods, such as Matrix-assisted laser desorption/ionization–time of flight (MALDI TOF), have been applied to heavy crude oils to measure the molecular weight distribution. The need of a small amount of sample (liquid or solid) is a huge advantage for this analysis (Kim et al. 2016; Zhang et al. 2015; Zheng et al. 2018). The combination of methods to measure the distribution of molecular weight has been carried out for heavy crude oil, such as the use of GPC together with VPO, high performance liquid chromatography (HPLC), and several spectroscopy methods (Azinfar et al. 2018; Dettman et al. 2005; Leontaritis and Mansoori 1989).

The molecular weight is a suitable property to know the quality of heavy and extra-heavy crude oils since it provides the average molecular mass or the molecular mass distribution of the vast mixture of compounds. Furthermore, the molecular weight distribution can be beneficial for the characterization of these complex mixtures because simulations (computational thermodynamics, phase equilibria, etc.) of the hydrocarbon systems are carried out taking this distribution (Azinfar et al. 2018; Speight 2002). The molecular weight in the upgrading of heavy and extra-heavy crude oils illustrates the conversion from higher-to lower-molecular weight fractions, providing evidence of the reactions nature of these feeds (Ancheyta and Speight 2007).

1.5 Composition

Crude oil has been commonly lumped into four fractions according to the literature, and different techniques have been used for its fractionation into saturates, aromatics, resins, and asphaltenes,

which are defined in terms of their solubility in different solvents. It is considered that asphaltenes impact on deposition during production and processing of petroleum. The classical colloidal model establishes that asphaltenes are in the core of solid particles surrounded by resins and aromatic molecules. Resins and asphaltenes are formed by polar heteroatoms, but both fractions differ in their solubility in alkanes (pentane or heptane). Asphaltenes are insoluble in alkanes, while resins are miscible. Thus, asphaltenes and resins constitute the disperse phase considering the crude oil as a colloidal system, whereas saturates and aromatics correspond to the continuous phase (Ashoori et al. 2017).

The composition of crude oils based on SARA fractionation, true boiling point (TBP) curves, and characterization through elemental analysis, metals content, and carbon residue, among other properties, allows knowing the crude oil behavior during refining, particularly when obtaining different cuts through atmospheric and residue distillation. Depending on the content of heavy fractions, more or less yield of distillates is obtained. During distillation, naphtha, kerosene, diesel, gasoil, atmospheric, and vacuum residue are obtained as temperature increases. For each fraction, different characterization tests are required. For example, for naphtha fraction, it is commonly reported its density, aromatics and naphthenes content, octane number, and sulfur content. For kerosene fraction used as aviation fuel, the density, sulfur content, pour point, freezing point, and aromatic content is required, while if kerosene is used as diesel fuel precursor, then the cetane index, pour point, density, and cold filter plugging point are reported. For diesel fraction, it is required to know its density, sulfur and aromatic contents, cetane index, pour point, and cold filter plugging point. For gasoil fraction, the UOP K factor, nitrogen, and Conradson carbon content are reported since this fraction is upgraded in the Fluid Catalytic Cracking (FCC) units. For atmospheric residue and vacuum gasoil, the density, pour point, sulfur and metals content, viscosity, UOP K factor, and Conradson carbon content are determined since atmospheric residue is upgraded through FCC, while hydrocracking is used for vacuum gasoil. The vacuum residue cut is characterized by density, pour point, sulfur and metals content, UOP K factor, and Conradson carbon content (Stratiev et al. 2010). The crude oil base is characterized according to the *K* factor by which the crude oil is paraffinic base (*K* factor: 12.9–12.2), intermediate base (*K* factor: 12.2–11.5), or naphthene base (*K* factor: 11.5–10.5) (Behrenbruch and Dedigama 2007).

Taking into consideration the aforementioned fractions and properties, the API gravity for cuts at different temperature intervals is plotted in Figure 1.1 for two reference crude oils (West Texas Intermediate from the USA and Brent blend from the North Sea) and four heavy crude oils (Maya from Mexico, Lloydminster from Canada, Emeraude from Congo, and Tia Juana from Venezuela). Naphtha is mainly composed of light compounds by which its API gravity is quite high for all types of plotted crude oils. This value decreases as the temperature interval increases. However, it is observed that for the heaviest crude oil (Tia Juana), the API gravity has the lowest value in the atmospheric residue.

Another important property commonly reported for each fraction is the sulfur content, as observed in Figure 1.1 as well. In this case, the opposite behavior regarding API gravity is attained as expected, i.e. the heavier the fraction, the larger the sulfur amount since its heteroatoms are more difficult to be removed when present in heavy fractions.

If the same crude oils plotted before are divided according to their atmospheric and vacuum residues and characterization tests are carried out, it is observed in Figure 1.2 that Conradson carbon content is higher in the vacuum residue because more refractory compounds are deposited in cuts having the highest temperature interval. The same trend is observed for the metals ($\text{Ni} + \text{V}$) content. Low content of metals is observed for lighter crude oils; however, heavy crude oils display high concentration of metals in vacuum residue where Maya crude oil showed the largest ($\text{Ni} + \text{V}$) content. Asphaltene content also increases in the vacuum residue, being the Maya crude oil with

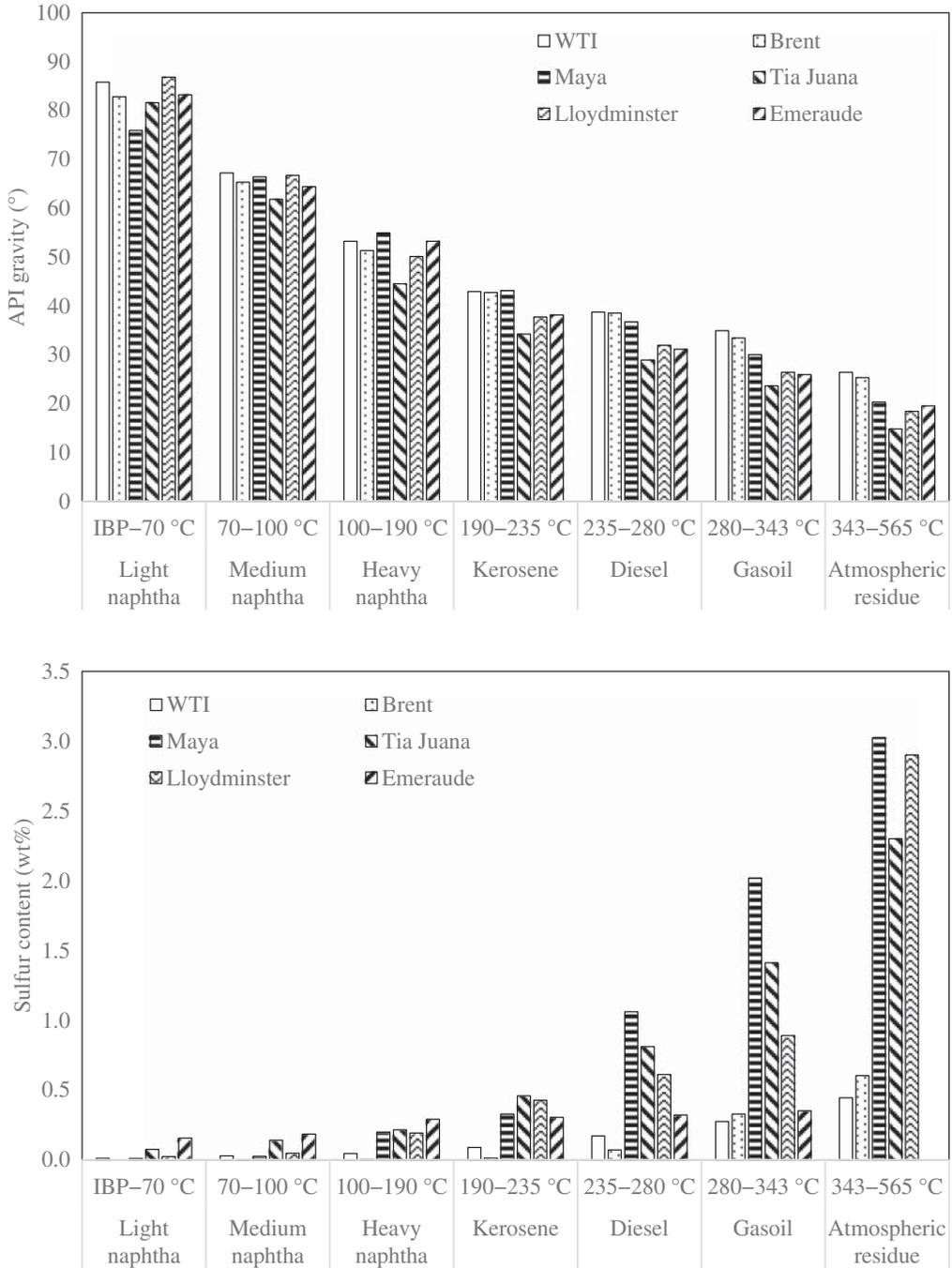


Figure 1.1 API gravity and sulfur content for different fractions based on temperature intervals.
Source: Adapted from Stratiev et al. (2010).

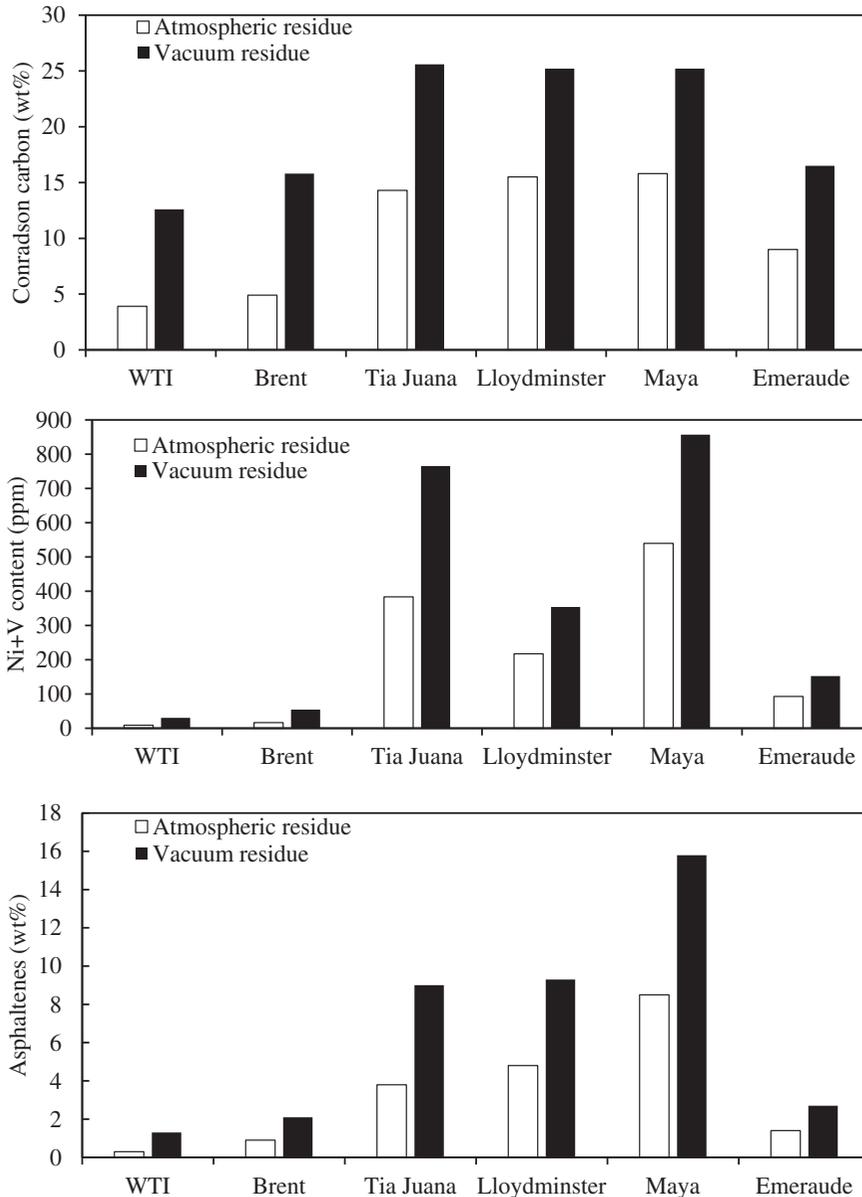


Figure 1.2 Conradson carbon, metals, and asphaltenes deposited in atmospheric and vacuum residue.

the highest content. Despite being considered as heavy, in Emeraude crude oil (12.1° API), the metal, asphaltene, and Conradson carbon contents are quite low compared with other heavy crude oils plotted in the figure.

1.5.1 SARA Analysis

Heavy and extra-heavy crude oils contain large amounts of the so-called resin and asphaltene fractions with high aromaticity and polar atoms such as nitrogen, sulfur, and oxygen. Most of the techniques used on lighter crude oils are not applicable to these crude oils by which separation based on polarity needs to be carried out as preparative method (Merdrignac and Espinat 2007).

Separation of fractions from heavy and extra-heavy crude oil involves precipitating firstly asphaltenes and then, the deasphalted oil (DAO) is passed through an open-column chromatograph by which four fractions are obtained based on the standard method ASTM D4124. Asphaltene separation includes the use of linear alkane such as pentane or heptane. The heavy crude oil and heptane are placed into a flask to be heated and stirred. Further, the sample is cooled to room temperature, and filtration is carried out to retain the solids that correspond to asphaltene fraction, while the liquid is commonly called as maltene fraction or DAO, and it is composed of saturates, aromatics, and resins. The solvent used to precipitate asphaltenes is evaporated to recover the maltene fraction, and the open-column chromatography is used to recuperate the remaining fractions in a column that is packed with activated alumina. The maltene fraction is dissolved in dichloromethane and poured into the column. Once maltenes were adsorbed in the activated alumina, different solvents are used to elute saturate, aromatic, or resin fraction. Thus, heptane is added to the column to extract the saturate fraction, while toluene separates aromatics. Furthermore, a toluene/methanol mixture is used to recover resins. Each fraction is sequentially drained from the bottom of the column and solvent used to separate the fraction is evaporated. Finally, each fraction is weighed and reported as the percentage of the whole sample. Examples of separations based on SARA analysis have been reported in the literature (Park et al. 2022). Aromaticity factor, which is a parameter related to the amount of aromatic carbon in regard to total carbon content, influences the tendency to form coke when upgrading heavy crude oil. This factor is quite low in heavy fractions such as resins and asphaltenes because aromatics in heavy and extra-heavy crude oils ranges widely (Alonso-Ramírez et al. 2021, 2020; Félix and Ancheyta 2019; Ortiz Moreno et al. 2014). Aromatic fraction is mainly composed of mono-, di-, tri-, and polyaromatics having alkyl chains. Major changes in structure and compositions are observed in asphaltene fraction.

When processing heavy or extra-heavy crude oils, resins are converted into lower molecular weight aromatics. Even distillates are formed as a consequence of cracking heavier molecules. However, resins may form condensed structures such as asphaltenes. If more asphaltenes are formed, then the resin fraction is not enough to peptize asphaltenes and colloidal stability is decreased. During crude oil upgrading, the higher reaction temperatures enhance the dealkylation reaction and formation of free radicals that condense to form coke (Wang et al. 2012).

Resins tend to associate with asphaltenes and disperse them into the crude oil. It is considered that asphaltene molecules are in the core of micelles surrounded by resins. The knowledge of SARA fractions in heavy and extra-heavy crude oils allows for predicting the relative stability of crude oils based on the nature of asphaltenes and dispersion medium. However, the stability of the crude oil depends on the interaction among all fractions. Aromatics also contribute to keep asphaltenes soluble by solvating the aromatic part of asphaltenes, while the polar section is solvated by resins. On the contrary, saturate molecules make asphaltene flocculate and precipitate. Thus, higher amounts of aromatics and resins will keep asphaltene fraction soluble in the crude oil (Ashoori et al. 2017).

Considering the SARA fractions, the colloidal instability index (CII) is used as a preliminary test analysis for stability/instability of heavy or extra heavy crude oils. This value is calculated as follows:

$$CII = \frac{\text{Saturates} + \text{Asphaltenes}}{\text{Aromatics} + \text{Resins}} \quad (1.3)$$

Below 0.7, the crude oil is considered as stable, while instability occurs when $CII > 0.9$. More stable crude oils keep asphaltene soluble and avoid its precipitation. The crude oils with values between 0.7 and 0.9 correspond to metastable with minor problems of deposition. Thus, the CII criterion may recognize potential troubles of asphaltenes deposition through SARA fractionation,

which may turn it into a screening test for preliminary examination on stability/instability of crude oils. Reports in the literature concluded that CII criterion predicts better the instability than stability of crude oils (Guzmán et al. 2017). Other indicators based on Chamkalani Stability Classifier (CSC), Stankiewicz Plot (SP), and Modified Jamal plot predict well instability of crude oils, while Stability Index (SI) and Jamaluddin plot (Jamal) are conveniently applied as stability predictors of crude oils (Ali et al. 2021).

Different SARA compositions have been reported in the literature as well as API gravity. Table 1.2 summarizes the values of saturate, aromatic, resin, and asphaltene fractions along with the API gravity of heavy and extra-heavy crude oils. Additionally, the colloidal instability index for each sample is reported and further is plotted against API gravity as shown in Figure 1.3 with data obtained from Table 1.2. For heavy and extra-heavy crude oils, the API gravity ranged from 4° API up to 21° API. Taking into consideration that crude oil stability is achieved when the CII value is below 0.7, it is observed that most of crude oils are stable according to this parameter by which stability is attained despite having a wide range of API gravity. However, the SARA composition needs to be also considered to predict the crude oil behavior during transportation and/or upgrading.

When plotting each SARA fraction and the colloidal instability index for the parent crude oil (Figure 1.4), it is observed that aromatics, resins, and asphaltenes may vary in wide interval, and stability is performed in most of cases. However, when saturate fraction and CII value are plotted, it may be stated that crude oil is stable as fewer amount of saturates is present in the crude oil. For most of plotted crude oils, stability is attained if saturate content is lower than 30 wt%. Higher concentration of saturates enhances the crude oil to be instable since more paraffinic compounds cause destabilization of asphaltenes in the micelle and precipitation occurs. Heavy crude oils may be instable not necessarily if having high content of asphaltenes as obtained from SARA fractionation. Most commonly, the higher the saturate fraction, the higher the crude oil instability. On the contrary, aromatic fraction is a good solvent for asphaltene by bridging the micelle containing asphaltene molecules and saturates, by which dispersion of all components occurs in the crude oil. Resins are associated to asphaltene in the micelle forming layers avoiding the precipitation of asphaltenes. However, this protection is broken when changes in the medium take place or when crude oil is blended with lighter crude oils (Hongfu et al. 2002).

When upgrading heavy crude oil in presence of catalysts, it is to be expected that resins do not form more asphaltene; instead, resins could be obtained from asphaltene decomposition, as well as more light ends. On the contrary, if noncatalytic processes are taking place, conversion of resins into asphaltenes is attained by elimination of aliphatic chains and aromatization reactions (Ortiz Moreno et al. 2014). Other reports have stated that the increase in lighter cuts is due mainly to transformation of residue fraction of heavy crude oils, such as vacuum and atmospheric residues (Alonso-Ramírez et al. 2020).

1.5.2 TBP Distillation

The true boiling point test consists in distilling the crude oil or hydrocarbon mixture in a fractionation column. Initially, distillation is carried out from the initial boiling point to around 210 °C under atmospheric pressure. Then, partial vacuum is applied to distillation to avoid cracking of heavier compounds in crude oil or fractions at higher temperatures. Cuts are collected at specified temperature intervals and mass and density of each fraction are able to be measured. Conversion to volumetric yield is made using the mass and density data. The vapor temperature measured at reduced pressure is converted to atmospheric equivalent temperature (AET) and distillation still continues up to 400 °C AET. TBP curve is plotted as mass or volume yield versus boiling temperature in terms of AET and its shape is dependent on composition of crude oil or fractions.

Table 1.2 SARA fractionation and colloidal instability index for different heavy and extra-heavy crude oils (fractions of saturates, aromatics, resins, and asphaltenes are expressed in wt%).

Heavy/extra-heavy crude oil	API, °	Saturates	Aromatics	Resins	Asphaltenes	CII	References
Bachaquero	9.00	25.00	33.00	29.00	13.00	0.61	Ocanto et al. (2009)
Lagunillas	15.00	30.00	26.00	32.00	12.00	0.72	Ocanto et al. (2009)
Boscan	8.00	10.00	23.00	48.00	19.00	0.41	Ocanto et al. (2009)
Sur Mediano	15.00	25.00	28.00	35.00	11.00	0.57	Ocanto et al. (2009)
Hamaca	8.00	11.00	19.00	57.00	13.00	0.32	Ocanto et al. (2009)
Merey 16	20.00	25.00	24.00	36.00	15.00	0.67	Ocanto et al. (2009)
CNS	21.00	21.00	27.00	37.00	15.00	0.56	Ocanto et al. (2009)
Mesa 30	20.00	44.00	25.00	21.00	10.00	1.17	Ocanto et al. (2009)
UD 672	21.00	22.00	30.00	44.00	4.00	0.35	Ocanto et al. (2009)
Furrial	21.00	35.00	24.00	32.00	9.00	0.79	Ocanto et al. (2009)
Carabobo	8.00	19.00	28.00	42.00	11.00	0.43	Marcano et al. (2011)
Hamaca	9.00	19.00	25.00	43.00	13.00	0.47	Marcano et al. (2011)
Boscan	10.30	12.00	36.00	38.00	14.00	0.35	Marcano et al. (2011)
Furrial	23.70	55.00	28.00	13.00	4.00	1.44	Marcano et al. (2011)
Korean VR	4.10	9.53	30.71	40.37	19.39	0.41	Park et al. (2022)
Athabasca ^{a)}	4.04	7.22	33.12	44.69	14.97	0.29	Danial-Fortain et al. (2010)
Ural ^{a)}	9.58	11.88	46.80	36.65	4.67	0.20	Danial-Fortain et al. (2010)
Duri ^{a)}	15.30	22.80	31.05	39.96	6.19	0.41	Danial-Fortain et al. (2010)
Arabian Light ^{a)}	6.95	11.69	48.99	31.55	7.76	0.24	Danial-Fortain et al. (2010)
Ku-Malooob-Zaap	12.50	16.30	25.20	39.50	19.00	0.55	Alonso-Ramírez et al. (2020)
Cold Lake	10.71	20.74	39.20	24.81	15.25	0.56	Peramanu et al. (1999)
Wolf Lake	10.50	25.18	37.40	27.33	10.09	0.54	Greaves and Xia (2004)
Heavy crude oil A	8.67	17.24	38.6	32.66	11.50	0.40	Arciniegas and Babadagli (2014)
Heavy crude oil B	10.28	19.45	45.60	25.34	9.60	0.41	Arciniegas and Babadagli (2014)
Athabasca	8.05	17.27	39.70	25.75	17.28	0.53	Peramanu et al. (1999)
Lloydminster	13.95	22.41	50.65	26.95	7.67	0.39	Khansari et al. (2014)
Liaohe	9.54	20.43	22.05	54.52	3.00	0.31	Li et al. (2007)
Liaohe	9.87	20.43	22.05	48.22	9.30	0.42	Wu et al. (2006)
Liaohe	15.20	40.98	28.79	21.25	5.50	0.93	Shang et al. (2018)
Shengli	18.00	31.90	19.30	43.80	5.00	0.58	Dolbear et al. (1987)
Xinjiang	16.00	28.09	31.45	32.86	7.60	0.55	Zhao et al. (2018)
Xinjiang	19.69	50.69	30.58	14.81	3.92	1.20	Zhao et al. (2022)
Xinjiang	16.75	35.64	20.78	28.3	15.28	1.04	Zhao et al. (2022)
Extra-heavy crude oil	6.40	13.00	16.90	49.90	20.20	0.50	Taborda et al. (2017b)
Heavy crude oil	13.00	14.79	32.39	40.51	12.31	0.37	Taborda et al. (2017a)

(Continued)

Table 1.2 (Continued)

Heavy/extra-heavy crude oil	API, °	Saturates	Aromatics	Resins	Asphaltenes	CI	References
Boca de Jaruco	14.07	17.10	40.40	22.90	19.60	0.58	Novikov et al. (2019)
Arta 4	16.20	13.71	56.83	19.19	10.28	0.32	Mohammad et al. (2012)
Azadegan	17.19	8.13	58.44	20.68	12.75	0.26	Taheri-Shakib et al. (2018)
West Paydar	18.53	14.10	58.10	18.30	9.50	0.31	Mozafari and Nasri (2017)
Heavy crude oil	15.82	10.49	9.00	64.12	16.39	0.37	Castro and Vazquez (2009)
Extra-heavy crude oil	9.17	15.00	19.11	46.78	19.11	0.52	Castro and Vazquez (2009)
Maya	21.00	18.17	28.97	41.52	11.31	0.42	Rana et al. (2008)
Ku-Maloob-Zaap	11.97	13.02	36.25	29.44	21.29	0.52	Félix and Ancheyta (2019)
Heavy crude oil	11.60	7.94	5.28	70.93	15.85	0.31	Murillo-Hernández et al. (2009)
Aguacate	12.80	10.7	3.40	62.60	23.30	0.52	Duran Armas (2021)
Aguacate	12.00	26.16	21.27	28.28	23.30	0.99	Coronel-García et al. (2021)
Gulf of Mexico	16.40	32.50	21.80	31.30	14.30	0.88	Martínez-Palou et al. (2013)
Tatar	15.00	25.40	44.70	23.70	6.4	0.46	Yeletsky et al. (2020)
Ashalchinskoye	15.10	23.10	45.60	23.80	7.50	0.44	Yadykova and Ilyin (2022)
Ashalcha	15.50	26.33	39.55	27.37	6.75	0.48	Mukhamatdinov et al. (2021)
Ashalcha	13.35	28.79	44.32	20.98	5.91	0.53	Félix et al. (2022)
Heavy crude oil	12.60	20.31	38.81	29.72	10.94	0.46	Zou (2017)

a) Normalized values.

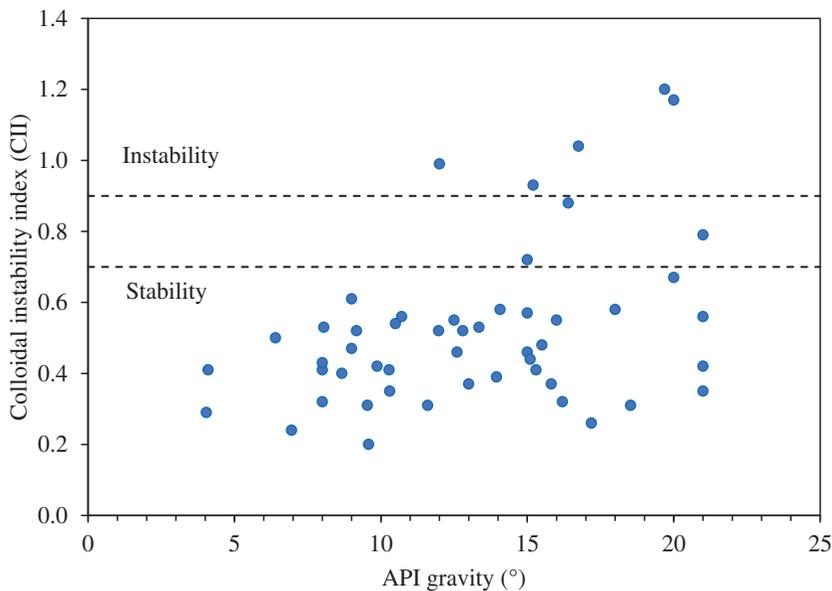


Figure 1.3 API gravity for different heavy and extra-heavy crude oils and their corresponding values of colloidal instability index.

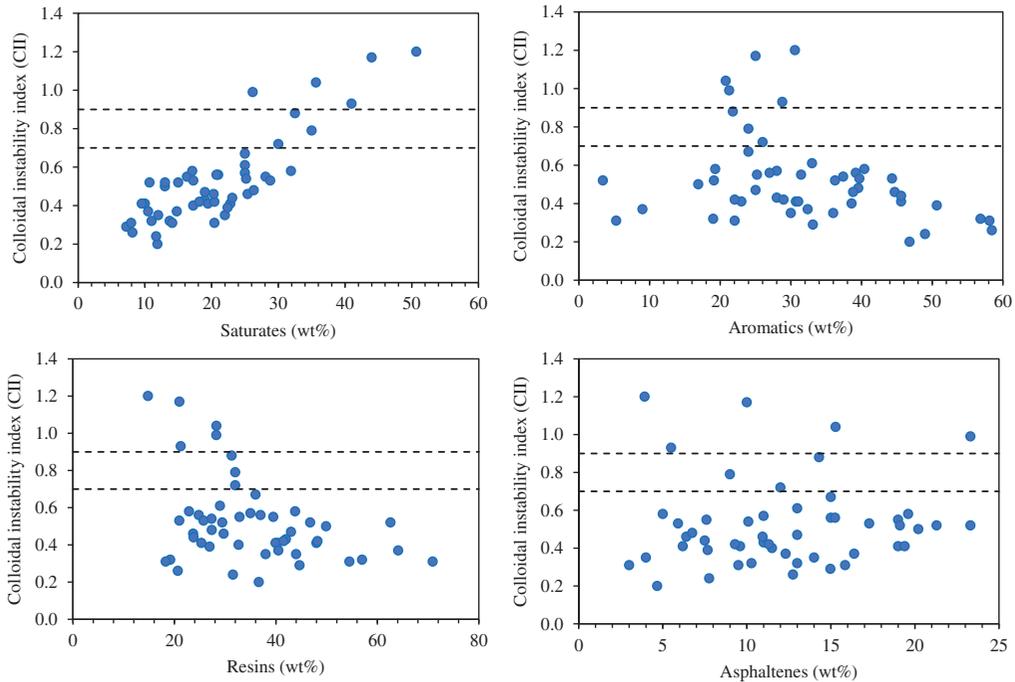


Figure 1.4 CII values for the parent crude oils and their relationship with SARA fractions.

Standardized methods to carry out TBP distillation are disclosed in ASTM D2892 and ASTM D5236 being appropriate to crude oils, petroleum fractions, and condensates; however, the methods are not able to be used in light naphtha or fractions having initial boiling points greater than 400 °C.

Each TBP curve for crude oils is unique, and it is used for refiners to marketing purposes and crude oil characterization (Behrenbruch and Dedigama 2007). In the case of heavy crude oils, the TBP curves have steeper slopes (Dhankar et al. 2019). Based on reported data, TBP curves are depicted in Figure 1.5 for selected crude oils having different composition (Equinor 2021; Stratiev et al. 2010). As a reference, the Algerian condensate considered as a low sulfur condensate (68.3° API, Algeria) is shown at the top of the figure. Then, the TBP curves of West Texas Intermediate (40.8° API, USA) and Brent (38.3° API, North Sea) crude oils commonly used as reference in the marketing of crude oil are plotted. Cabinda (31.7° API, Angola) crude oil and its TBP curve is also plotted. Depending on the refiner, the definition of light, medium, heavy, or extra-heavy crude oil is attained; however, the following intervals may be accepted to define crude oils according to their API values: light crude oil (API higher than 31.1°); medium or intermediate crude oils (API values among 22.3° to 31.1°); heavy crude oils (API values between 22.3° and 10°); extra-heavy crudes (API lower than 10°). TBP plots for heavy crude oils such as Maya (21° to 22° API, Mexico), Hebron (20.4° API, Canada), Peregrino (13.5° API, Brazil), and Tia Juana (12.1° API, Venezuela) heavy crude oils are shown in Figure 1.5. It is observed that heavier crude oils have a lower slope in the mid-region of the curve compared with lighter crude oils, and the distilled yield is low having larger yields for atmospheric and vacuum residue. The initial boiling point (IBP) for heavy crude oils starts at higher temperature since refractory compounds are found in these crude oils.

In summary, a description of some standardized methods to carry out the distillation of crude oils or fractions is disclosed. For example, the standard method ASTM D2892 is applied to stabilized crude oil with an initial boiling point of 150 °C, while the final cut temperature is 400 °C atmospheric equivalent temperature (AET). The fractionating column is considered to behave like

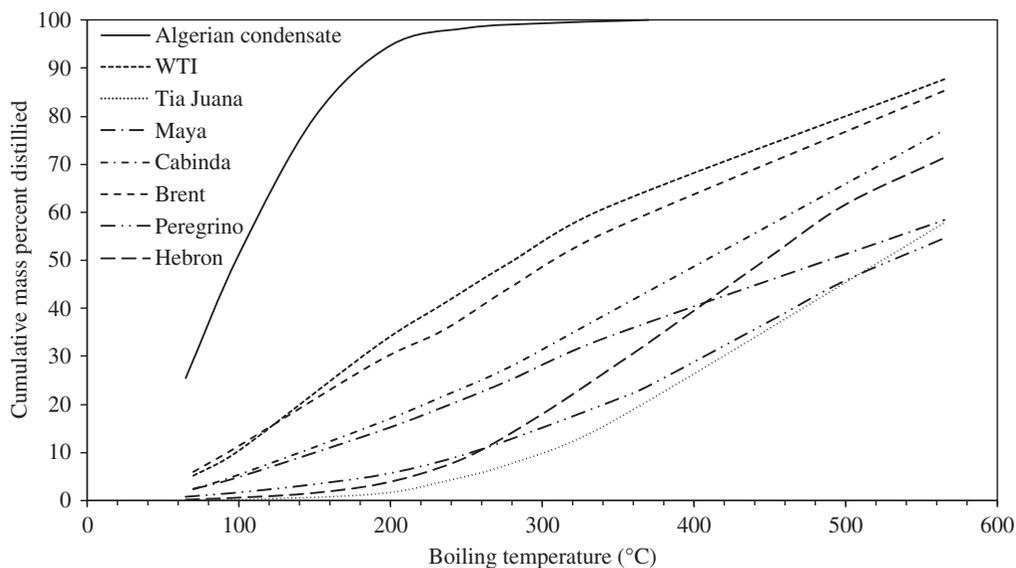


Figure 1.5 TBP curves for different crude oils.

14–18 theoretical plates with a reflux ratio of 5 : 1. During distillation, a plot of temperature against mass or volume distilled is obtained.

The standard method ASTM D5236 discloses the procedure to distillate heavy crude oils, petroleum distillates, residues, etc., in a potstill with a low pressure drop entrainment separator. The initial boiling point for hydrocarbons is greater than 150 °C, while the final boiling point commonly is 565 °C depending on the heat sensitive samples. The recommended distillation method for crude oil having ending cuts of 400 °C AET is the ASTM D2892 method; however, distillation curves obtained by these methods are not comparable among them.

The standard method ASTM D86 is applied to carry out the atmospheric distillation of petroleum and petroleum products relating its composition with energy content and boiling range distribution. It is possible to know the tendency to form deposits that cause obstruction of pipelines with this curve. For this reason, the distillation yield at different temperatures is requested, especially the temperatures at 10 vol% (T10), 50 vol% (T50), and 90 vol% (T90) of distilled volume as well as the final boiling point.

The standard method ASTM D1160 includes the determination of the range of boiling points for petroleum products at reduced pressures, which are vaporized partially or fully at a maximum liquid temperature of 400 °C. A conversion of heavy crude oil distillation data from ASTM D1160 to ASTM D5236 has been reported elsewhere. For heavy crude oils, methods based on Daubert, Edmister-Okamoto with modified coefficients gave the best correlations to convert distillation data from ASTM D1160 to ASTM D5236. The method proposed by authors also yielded good correlation (Nikolaychuk et al. 2015).

The standard method ASTM D2887 is applicable to petroleum, petroleum products and fractions having a distillation range between 55.5 and 538 °C at atmospheric pressure. The analysis time is reduced to about eight minutes, and it is available to samples having vapor pressures sufficiently low to be handled at ambient temperature.

The standard method ASTM D7169 is complementary of the ASTM D2887 because it is applied to samples that do not elute completely during simulated distillation by which it is used to determine the boiling point distribution up to 720 °C. The maximum temperature corresponds to elution

Table 1.3 Typical methods to analyze the distillation behavior of crude oils.

Analysis type	Standard method	Boiling temperature interval (°C)
Atmospheric distillation of crude oil	ASTM D2892	150–400
Distillation of heavy hydrocarbon mixtures	ASTM D5236	150–400
Simulated distillation	ASTM D2887	55–538
	ASTM D7169	Up to 720
Distillation	ASTM D86	150–350
	ASTM D1160	Up to 400

of C₁₀₀ and atmospheric residues, vacuum residues, among other heavy crude oils or cuts may be analyzed by this technique. Since capillary columns with thin films are present, incomplete separation of C₄–C₈ is attained. The aforementioned methods are depicted in Table 1.3.

1.6 Typical Heavy Crude Oils

Heavy crude oils from different origins present similar ranges of properties because they are characterized as viscous liquids with high content of heteroatoms providing low API gravity values. Different reservoirs in North and South America, as well as Middle East countries, have similar properties, such as high sulfur content (Guo et al. 2016). However, although these heavy crude oils have similar properties, there are some exceptions, where the value of some properties is outside the established range. Hence, some heavy crude oils may be atypical based on the property of interest as discussed below.

1.6.1 Properties

Mexico produces different heavy and extra-heavy crude oils with diverse physical and chemical properties as summarized in Table 1.4. One of the most known heavy crude oils from Mexico is Maya, which is characterized by the high content of heteroatoms, such as sulfur and metals, as well as heavy fractions (asphaltenes). Conversely, this oil has low viscosity and density, provoking an elevated API gravity almost similar to intermediate crude oils. Another heavy crude oil with relatively low viscosity is the Gulf of Mexico heavy crude oil, which presents a small amount of asphaltenes and high content of saturates and sulfur. The Aguacate field heavy crude oil accounts for larger concentration of sulfur and metals due to the high content of Conradson carbon along with the resins content, causing the low amount of light fractions (aromatics and saturates) and high viscosity. The Ku-Maloob-Zaap is an extra-heavy crude oil characterized by the high viscosity, amount of metals, heteroatoms content (S, O, and N), molecular weight, and Conradson carbon together with high content of heavy fractions (asphaltenes and resins) and low H/C atomic ratio.

Heavy and extra-heavy crude oils from China are characterized by the low content of sulfur and metals (Table 1.5). Xinjiang heavy crude oil has high values of H/C atomic ratio as well as O and N content. However, the low content of metals (especially V), Conradson carbon, sulfur, and light fractions (aromatics and saturates), as well as low pour point and viscosity values increase its API gravity. Shengli heavy crude oil has similar properties to Xinjiang oil since the larger amount of

Table 1.4 Physical and chemical properties of Mexican heavy and extra-heavy crude oils.

Property	Maya	Gulf of Mexico	Aguacate	Ku-Maloob-Zaap
API gravity	19.43–21.97	12.50–16.40	12.00–15.82	9.17–11.97
<i>Elemental analysis (wt%)</i>				
C	84.30–86.90		79.96–84.28	83.01
H	8.30–10.40		10.28–10.64	9.66
O	0.50		0.01	1.52
N	0.30–0.52	0.29–0.75	0.35–0.51	0.54
S	3.51–4.70	4.40–5.56	5.02–5.74	5.27
H/C atomic ratio	1.47–1.54		1.45–1.56	1.39
<i>Metals content (ppm)</i>				
V	204.00–413.00		268.80	415.00–506.68
Ni	36.00–83.00		63.35–97.20	81.00–97.82
Ni/V ratio	4.98–5.67		4.24	5.12–5.18
MW (g/mol)			378.50–486.00	486.00–507.80
Conradson carbon (wt%)	15.30		17.15	17.75
<i>Dynamic viscosity (Pa s)</i>				
At 30 °C	0.70		13.31	
At 50 °C	0.23	0.51		
<i>Kinematic viscosity (cSt)</i>				
At 25 °C			2984.97	43 233.00
At 50 °C				2082.00–15 854.80
Pour point (°C)	–30.00		–12.00	13.50
<i>SARA fractions (wt%)</i>				
As	11.31–25.20	14.30	15.85–23.3	19.11–21.29
Re	25.90–41.52	31.30	28.28–62.6	29.44–46.78
Ar	26.72–28.97	21.80	3.40–21.27	19.11–36.25
Sa	18.17–29.56	32.50	10.7–26.16	13.02–15.00

heteroatoms increases the resin fraction. Additionally, lower values of V/Ni ratios can be caused by the small asphaltenes content. Lunpola heavy crude oil is another crude oil having low sulfur and asphaltene contents as well as Conradson carbon. Nevertheless, this crude oil is defined for its high viscosity and resins amount. Depending on the extraction well, the Liaohe oil can be categorized as heavy or extra-heavy crude oil. This petroleum has elevated values of viscosity and molecular weight but low asphaltene contents, which provide larger amounts of resins and saturates. Moreover, the content of V is poor compared with the Ni content, which gives higher values of V/Ni ratio as the Chinese heavy crude oils aforementioned.

Russia has a large reserve of heavy crude oils, and the properties of these oils can be observed in Table 1.6. Ashalcha heavy crude oil is characterized by a small amount of asphaltenes and

Table 1.5 Physical and chemical properties of Chinese heavy and extra-heavy crude oils.

Property	Xinjiang	Shengli	Lunpola	Liaohe
API gravity	16.00–20.45	13.72–20.71	16.98	9.54–15.20
<i>Elemental analysis (wt%)</i>				
C	80.70–84.75	81.20–85.50	84.58	83.96–86.15
H	11.90–13.20	9.84–13.70		10.95–13.25
O	1.51–3.47	1.26		1.27–2.22
N	0.35–1.15	0.44–1.71	0.69	0.38–0.96
S	0.15–0.46	0.28–4.37	0.24	0.34–0.45
H/C atomic ratio	1.71–1.95	1.39–2.01		1.54–1.88
<i>Metals content (ppm)</i>				
V	0.20	3.40		1.91–2.10
Ni	13.90	42.30–47.60		46.80–125.00
Ni/V ratio	0.01	0.08		0.02–0.03
MW (g/mol)				482.00–624.00
Conradson carbon (wt%)	5.40	7.50–9.70	2.70	9.00
<i>Dynamic viscosity (Pa s)</i>				
At 40 °C	17.42			1.11
At 50 °C	0.27	0.27–175.00		139.80–158.00
At 60 °C	0.29–5.04			
At 80 °C				88.50–124.30
<i>Kinematic viscosity (cSt)</i>				
At 50 °C			23 455.70	
At 80 °C				3661.00
Pour point (°C)	–22.00	4.00–14.00		
<i>SARA fractions (wt%)</i>				
As	3.92–15.28	0.70–5.00	0.48	3.00–9.30
Re	14.81–32.86	43.80–44.63	41.42	21.25–54.52
Ar	20.78–31.45	19.30–29.06		22.05–38.50
Sa	28.09–50.69	23.75–31.90		20.43–40.98

low molecular weight. The wide range of V/Ni ratio is due to some samples having insignificant content of V. In addition, this heavy crude oil has a high amount of aromatics hydrocarbons and dynamic viscosity values, despite the low content of high molecular weight fractions (asphaltenes). Another heavy crude oil is Usinsk having low amount of asphaltenes as well as low molecular weight. Moreover, this oil is characterized by its decreased value of pour point. Yarega heavy crude oil displays low pour point and sulfur content, high H/C atomic ratio but large content of metals (V and Ni). Whereas the Mordovo–Karmalskoye oil exhibits larger content of heteroatoms

Table 1.6 Physical and chemical properties of Russian heavy and extra-heavy crude oils.

Property	Yarega	Mordovo–Karmalskoye	Ashalcha	Usinsk
API gravity	18.17–19.00	15.90	13.35–15.10	14.87
<i>Elemental analysis (wt%)</i>				
C	86.29	81.50	82.64–83.88	84.94
H	12.72	11.60	11.21–12.10	11.98
O	0.16	2.10	0.12–1.96	0.47
N	0.04	1.10	0.29–0.70	0.63
S	0.79–1.24	3.65–3.70	3.20–4.52	1.98
H/C atomic ratio	1.76	1.70–1.71	1.61–1.72	1.68
<i>Metals content (ppm)</i>				
V	160.00		1.26–200.00	
Ni	47.00		10.00–60.00	
Ni/V ratio	3.40		0.13–3.33	
MW (g/mol)	452.00		385.12	365.00
Conradson carbon (wt%)			9.70	
<i>Dynamic viscosity (Pa s)</i>				
At 20 °C			3.31	
<i>Kinematic viscosity (cSt)</i>				
At 20 °C		1609.00		3952.39
At 25 °C			282 500.00	
Pour point (°C)	–18.00			–22.50
<i>SARA fractions (wt%)</i>				
As	3.00–17.00	5.20	5.91–7.50	8.10
Re	20.00–32.00	24.50	20.98–27.37	18.00
Ar	35.00	45.40	39.55–45.60	
Sa	16.00	24.90	23.10–28.79	

(S, N, and O). However, this heavy crude oil presents low values of viscosity and asphaltenes content, together with high aromatics content and H/C atomic ratio.

Canadian heavy and extra-heavy crude oils are similar to Mexican oils, having high content of sulfur, metals, and an elevated viscosity value, as observed in Table 1.7. Lloydminster heavy crude oil commonly presents low asphaltenes content and high aromatics fractions besides the high values of the viscosity, H/C atomic ratio, and low sulfur content. The Cold Lake heavy crude oil displays a high molecular weight value as well as high aromatics and sulfur content, whereas the Wolf Lake heavy crude oil exhibits properties similar to Lloydminster oil (asphaltenes, aromatics, sulfur content, and H/C atomic ratio) also with high content of metals. Finally, Athabasca bitumen is an extra-heavy crude oil with remarkably high viscosity and elevated content of heteroatoms, metals, Conradson carbon, and aromatics. Additionally, the high molecular weight value and the aforementioned properties give decreased value of API gravity.

Table 1.7 Physical and chemical properties of Canadian heavy and extra-heavy crude oils.

Property	Lloydminster	Cold Lake	Wolf Lake	Athabasca bitumen
API gravity	10.90–13.95	10.71	10.50	8.05–11.00
<i>Elemental analysis (wt%)</i>				
C	82.30–83.70	83.62–84.00	83.70	83.20–83.34
H	10.60–11.80	10.00–10.50	10.62	9.70–10.26
O		0.20–0.86		1.08–1.70
N	0.20–0.40	0.40–0.45	0.25	0.40–0.53
S	3.40–4.40	4.56–5.10	4.50	4.64–5.30
H/C atomic ratio	1.53–1.68	1.42–1.50	1.51	1.39–1.52
<i>Metals content (ppm)</i>				
V			192.00	247.00
Ni			75.00	93.00
Ni/V ratio			2.56	2.66
MW (g/mol)	440.00	550.00		557.00
Conradson carbon (wt%)				12.00–12.32
<i>Dynamic viscosity (Pa s)</i>				
at 20 °C	13.44–14.60			
at 30 °C	5.26			581.00
at 40 °C	0.81–2.27			
at 50 °C				32.40
<i>SARA fractions (wt%)</i>				
As	7.12	15.25	10.09	11.67–18.60
Re	25.03	24.81	27.33	16.80–25.75
Ar	47.04	39.20	37.40	39.70–48.50
Sa	20.81	20.74	25.18	16.10–17.27

The low asphaltene content and high pour point value are properties commonly found in heavy and extra-heavy crude oils from the USA, as summarized in Table 1.8. Hondo heavy crude oil is characterized by its high sulfur, metals, and resins content and present an increased H/C atomic ratio. For the Alba and Thums heavy crude oils, the low asphaltenes content, high H/C atomic ratio, and small value of viscosity are similar properties in these oils, whereas Kern River and Coalinga heavy crude oils display low values in the S, V, and asphaltenes contents. For the pour point and Ni content, the values are high, causing a low V/Ni ratio. The Cymric and Midway Sunset heavy crude oils show alike physicochemical properties: small amount of asphaltenes, saturates, and sulfur, elevated value of pour point and similar content of V and Ni giving the V/Ni ratio close to 1.

Venezuela is a country with large reserves of heavy crude oil that have different properties, as shown in Table 1.9. Tia Juana is a heavy crude oil with high Conradson carbon and V contents, but low viscosity, pour point, and asphaltenes fraction values. Boscan is a heavy crude oil rich in

Table 1.8 Physical and chemical properties of heavy and extra-heavy crude oils from USA.

Property	Hondo	Alba	Thums	Kern River	San Joaquin Valley	Cymric	Midway Sunset	Coalinga
API gravity	13.40–19.35	19.03	8.60–17.13	9.70–14.50	13.04	8.70–11.70	10.40–10.50	9.70–10.30
<i>Elemental analysis (wt%)</i>								
C								
H								
O								
N	0.70–0.73			0.72–0.88		0.84–0.91	0.89–0.91	0.73–0.79
S	5.10			1.00		1.40–1.49	1.72–1.75	0.87–0.93
H/C atomic ratio	1.68	1.65	1.69–1.70		1.52			1.60–1.72
<i>Metals content (ppm)</i>								
V	280.00			25.00–75.00		65.00–73.00	105.00–110.00	10.00
Ni	92.00			65.00–110.00		65.00–69.00	95.00	29.00–33.00
Ni/V ratio	3.04			0.38–0.68		1.00–1.06	1.11–1.16	0.30–0.34
Conradson carbon (wt%)	10.80							
<i>Dynamic viscosity (Pa s)</i>								
At 40 °C	0.36	0.14	0.15–0.66		1.39			
<i>Kinematic viscosity (cSt)</i>								
At 50 °C				330.00–3260.00		800.00–6420.00	3200.00–3670.00	2830.00–2950.00
Pour point (°C)				20.00–50.00		20.00–60.00	60.00	60.00
<i>SARA fractions (wt%)</i>								
As	13.90–14.80	1.64	3.31–5.09	4.00–7.00	4.56	6.00–8.00	9.00	5.00
Re	20.50–40.20	10.10	12.50–18.70		19.40			
Ar				25.00–26.00		27.00–28.00	24.00	32.00–33.00
Sa				19.00–21.00		16.00–19.00	16.00	21.00–22.00

metals and sulfur content in which the great amount of V provides a high V/Ni ratio, while Hamaca and Cerro Negro heavy crude oils present similar properties where their sulfur and metals content, Conradson carbon, and viscosity are quite high.

Heavy crude oils from Middle East countries are characterized by low asphaltene fraction and high metals content, as seen in Table 1.10. Arta-4 heavy crude oil from Egypt displays high content of sulfur, metals, and aromatics, as well as high values of viscosity. The Iranian heavy crude oils (Azadegan, Gach Saran, and West-Paydar) have not only similar properties such as low viscosity, asphaltene, and saturates contents, but also large aromatic fraction. Qayarah heavy crude oil from Iraq has extremely high sulfur content besides high amount of asphaltene and Conradson carbon. Heavy crude oil from Kuwait presents a low H/C atomic ratio, small amounts of metals,

Table 1.9 Physical and chemical properties of Venezuelan heavy and extra-heavy crude oils.

Property	Tia Juana	Boscan	Hamaca	Cerro Negro
API gravity	12.58	10.10	8.50–9.10	8.88–8.90
<i>Elemental analysis (wt%)</i>				
C			83.93	
H			9.58	
O			1.42	
N	0.30	0.44	0.75–0.89	0.75
S	2.50	5.66–5.70	3.75–3.78	3.99–4.00
H/C atomic ratio			1.36–1.37	
<i>Metals content (ppm)</i>				
V	397.00	1220.00	412.00–488.00	430.00
Ni		147.00	91.90–105.00	108.60
Ni/V ratio		8.30	4.41–4.65	3.96
MW (g/mol)				
Conradson carbon (wt%)	12.30	15.00	14.20–15.80	15.20
<i>Dynamic viscosity (Pa s)</i>				
At 30 °C			500.00	
At 40 °C	0.89	1.79–7.70		
At 60 °C		1.55	6.10	4.91–15.50
At 80 °C			1.81	1.97
Pour point (°C)	–1.00	10.00	27.00	
<i>SARA fractions (wt%)</i>				
As	7.50	15.20–24.20	10.20–23.50	10.10–19.90
Re				
Ar				
Sa				

and asphaltenes as high molecular weight and sulfur content values. Two heavy crude oils from Saudi Arabia present diverse properties since the Heavy Arabian oil has low viscosity, asphaltenes, and resins values, while the other heavy crude oil presents high content of metals, sulfur, and Conradson carbon.

Latin American countries also commercialize a variety of heavy and extra-heavy crude oils (Table 1.11). Marlim heavy crude oil from Brazil is characterized by low impurities content (metals, sulfur, and asphaltenes) and low viscosity and pour point values which is suitable for refining. The Castilla and one extra-heavy crude oils from Colombia have a low H/C atomic ratio, larger amount of resins, and sulfur content as well as high values of viscosity but the extra-heavy crude oil has higher values, especially for sulfur. Whereas Boca de Jaruco heavy crude oil from Cuba presents high impurities (sulfur and metals) and aromatics content together with a high H/C atomic ratio. Ecuador has the Napo heavy crude oil, which displays a low pour point and small sulfur amount. In Table 1.12, other heavy crude oils from different countries around the world are

Table 1.10 Physical and chemical properties of heavy and extra-heavy crude oils from Middle East countries.

Property	Country							
	Egypt	Iran	Iran	Iran	Iraq	Kuwait	Saudi Arabia	Saudi Arabia
	Arta-4	Azadegan	Gach Saran	West-Paydar	Qayarah	Heavy crude oil	Heavy crude oil	Heavy Arabian
API gravity	16.20	17.19	15.60	18.53	15.28	12.20	12.60	18.08
<i>Elemental analysis (wt%)</i>								
C	80.55	85.15				86.70		
H	10.63	10.11				8.20		
O	3.04							
N	0.34	1.53	0.41			0.50	0.26	
S	4.50	3.21	2.60		8.40	4.60	4.23	
H/C atomic ratio	1.57	1.41				1.13		
<i>Metals content (ppm)</i>								
V	183.97		108.00			20.00	87.00	
Ni	113.05		36.00				28.00	
Ni/V ratio	1.63		3.00				3.11	
MW (g/mol)						411.00		
Conradson carbon (wt%)	11.34		8.80		15.60		12.60	
<i>Dynamic viscosity (Pa s)</i>								
At 20 °C		0.88				3.90		
At 30 °C						1.50		
At 40 °C						0.67		0.03
<i>Kinematic viscosity (cSt)</i>								
At 25 °C				76.87		2500.00		
At 50 °C						343.00		
At 80 °C	196.39							
Pour point (°C)	12.00							
<i>SARA fractions (wt%)</i>								
As	10.28	12.75	6.80	9.50	20.40	8.00	12.60	6.68
Re	19.19	20.68	28.50	18.30			27.50	7.46
Ar	56.83	58.44		58.10				
Sa	13.71	8.13		14.10				

shown. Van Gogh and Doba heavy crude oils from Australia and Chad, respectively, show similar properties since both have low contents of impurities (S, N, Ni, and Conradson carbon content) and decreased values of viscosity and pour point, while the Germany heavy crude oil presents a high H/C atomic ratio and low content of asphaltenes.

Table 1.11 Physical and chemical properties of heavy and extra-heavy crude oils from Latin American countries.

Property	Country				
	Brazil	Colombia	Colombia	Cuba	Ecuador
	Marlim	Castilla	Extra-heavy crude oil	Boca de Jaruco	Napo
API gravity	19.20	13.00–13.40	6.40	14.07	17.40
<i>Elemental analysis (wt%)</i>					
C		80.40	84.80	75.47	
H		9.46	7.50	10.12	
O				8.40	
N	0.49	0.47–2.30	0.88	0.41	
S	0.78	2.16–4.84	6.82	5.29–5.60	2.18
H/C atomic ratio		1.40	1.05	1.60	
<i>Metals content (ppm)</i>					
V	25.00	311.70		76.00	
Ni	20.00	78.20		26.00	
Ni/V ratio	1.25	3.99		2.92	
Conradson carbon (wt%)		15.17			
<i>Dynamic viscosity (Pa s)</i>					
At 20 °C				271.00	
<i>Kinematic viscosity (cSt)</i>					
At 20 °C	544.60				
At 50 °C		971.90			370.63
At 80 °C		144.60			
Pour point (°C)	–39.00				–7.22
<i>SARA fractions (wt%)</i>					
As	2.60	12.31–15.50	20.20	19.60	12.06
Re		40.51	49.90	22.90	
Ar	42.00	32.39	16.90	40.40	
Sa		14.79	13.00	17.10	

1.6.2 Relationship Between Properties

The physical and chemical properties of all these heavy and extra-heavy crude oils present some relationships between them. The API gravity has different correlations with physical (viscosity and pour point) and chemical (H/C atomic ratio, molecular weight, and Conradson carbon) properties as observed in Figure 1.6. The higher the H/C ratio, the higher the API gravity. Higher value of H/C relationship is particularly important when upgrading heavy crude oils due to less amount of hydrogen that is required if hydrogenolysis reactions are carried out such as hydrodesulfurization.

Table 1.12 Physical and chemical properties of heavy and extra-heavy crude oils from different countries.

Property	Country		
	Australia Van Gogh	Chad Doba	Germany Heavy crude oil
API gravity	17.10	18.80	13.03
<i>Elemental analysis (wt%)</i>			
C		86.25	86.00
H		12.10	12.50
O		1.16	
N	0.184	0.25	
S	0.38	0.14	1.25
H/C atomic ratio		1.67	1.73
<i>Metals content (ppm)</i>			
Ni	1.70		
Conradson carbon (wt%)		5.66	
<i>Dynamic viscosity (Pa s)</i>			
At 30 °C		0.56	
At 40 °C		0.28	0.239
At 50 °C		0.16	
At 60 °C		0.11	
Pour point (°C)	-17.50		
<i>SARA fractions (wt%)</i>			
As			1.50
Re			18.90
Ar			34.20
Sa			22.50

The API gravity is inversely proportional to density, which decreases as the light fraction content like saturates increases. However, some heavy crude oils (Shengli, Thums, and Azadegan) do not follow this trend. The saturates content is in agreement with the H/C atomic ratio due to it increases as API gravity increments for the same reason, except for the Azadegan and West-Paydar heavy crude oils, which have low amount of saturates at relatively elevated API gravity. On the contrary, the dynamic viscosity and pour point diminished as the API gravity increased as expected because lighter crude oils have improved mobility; however, Thums, Xinjiang, and Boscan heavy crude oils do not follow this trend. Other properties vary depending on the API gravity, i.e. the higher the API gravity value, the lower the Conradson carbon and the molecular weight values as a consequence of heavier fractions such as asphaltenes and resins are less abundant in crude oils.

The asphaltenes content is an important chemical property for heavy and extra-heavy crude oils since this fraction represents the main issue during crude oil upgrading. Thus, understanding the relationship of this fraction with other properties (Figure 1.7) is essential to screen the quality of

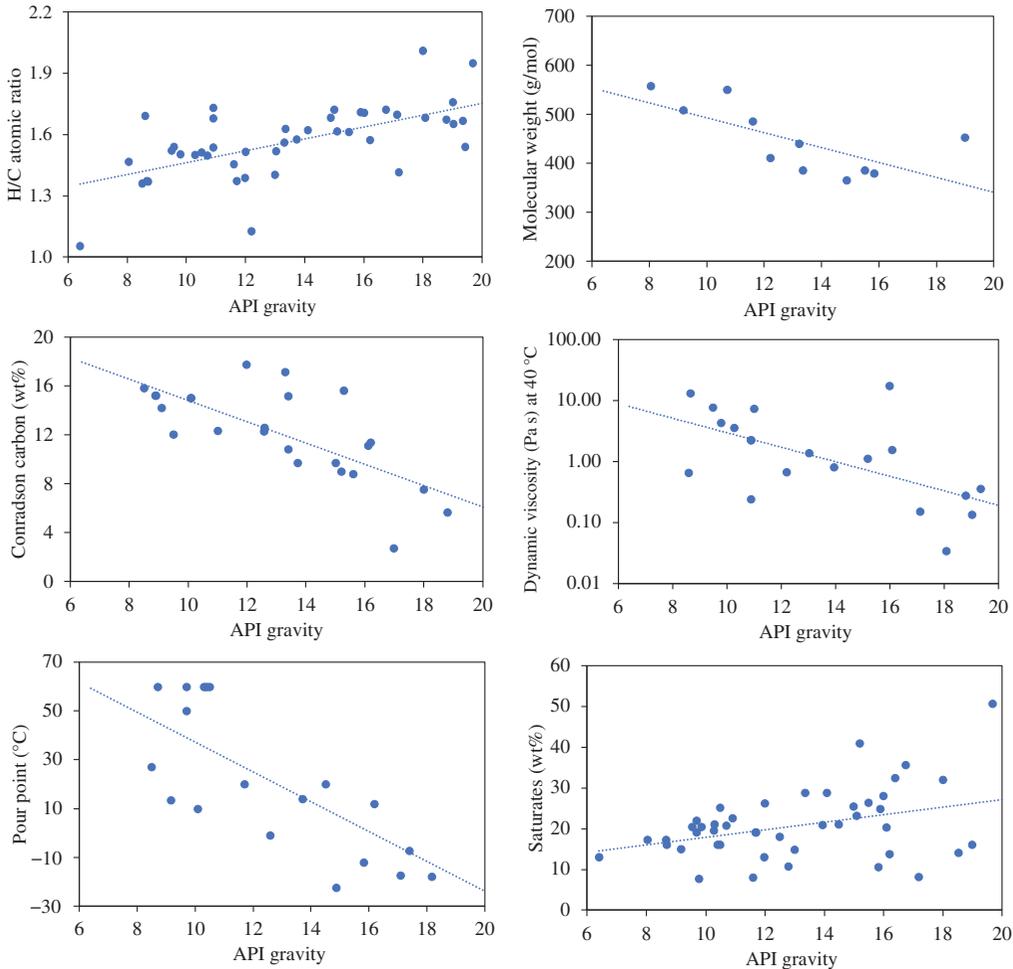


Figure 1.6 Correlations between the API gravity and other properties of different heavy and extra-heavy crude oils.

the oil preliminary. Like the API gravity does, the asphaltene fraction behaves as a function of the H/C atomic ratio and saturate fraction whose values decrease as the content of asphaltenes increases. The H/C atomic ratio varies inversely with the asphaltene content because larger values of H/C ratio imply higher content of aromatic molecules commonly contained in asphaltenes as aromatic ring clusters. Therefore, increasing the amount of asphaltene fraction heightens the aromatic nature of the oil, reaching values of H/C atomic ratio similar to toluene. In addition, values of Conradson carbon and dynamic viscosity growth as asphaltenes content increased owing to asphaltenes are carbon residue producer. Its content also influences the increase of dynamic viscosity. Other values such as V/Ni ratio also depend on the amount of asphaltene. The higher the amount of asphaltenes, the higher the amount of metals because most of them are contained in asphaltene molecules as porphyrins. Vanadium is commonly more abundant than nickel with exception of Chinese and Ashalcha heavy crude oils whose Ni content is higher than V. Sulfur content follows the same trend like V/Ni ratio because most of sulfur species are contained in resins and asphaltene fractions.

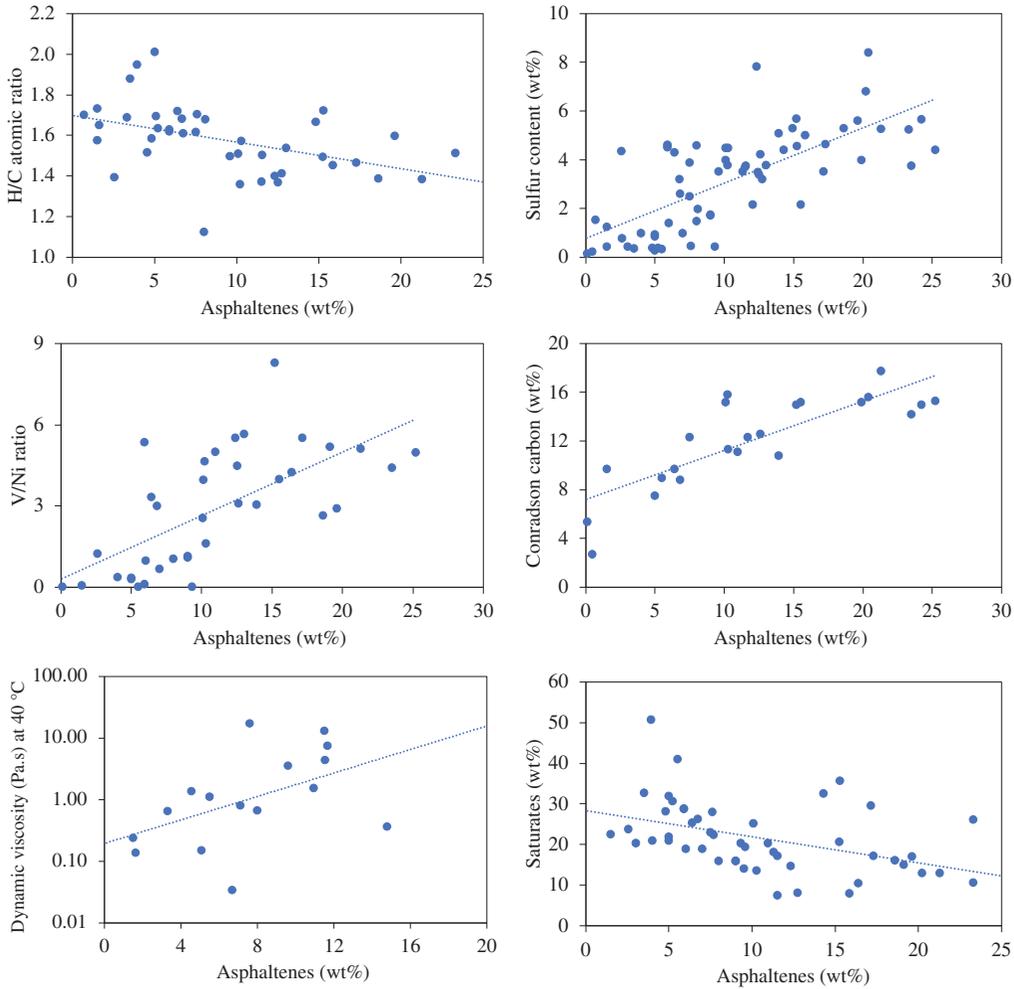


Figure 1.7 Correlations between the asphaltenes content (wt%) and other properties of different heavy and extra-heavy crude oils.

The values of Conradson carbon behave similarly to asphaltene content, as depicted in Figure 1.8. The Conradson carbon content increases as the H/C atomic ratio and saturate fraction decrease. On the contrary, values of dynamic viscosity, sulfur content, and V/Ni ratio increased. The aforementioned behavior is due to the fact that Conradson carbon depends directly on asphaltene fraction that contains most of the impurities (sulfur, metals). Moreover, the relations between SARA fractions of some heavy and extra heavy crude oils are correlated with the Conradson carbon owing to the asphaltenes-to-resins (As/Re) ratio, the asphaltenes-to-aromatics (As/Ar) ratio, and the asphaltenes-to-saturates (As/Sa) ratio also increased as the Conradson carbon content is larger as observed.

The relationships between the H/C atomic ratios with other properties are observed in Figure 1.9. The lower the sulfur content, the higher the H/C atomic ratio, which implies more aromatic crude oils as H/C ratio diminishes because sulfur species are mainly aromatic-based compounds. The saturate fraction increases as the H/C atomic ratio is larger; however, derived from SARA analysis,

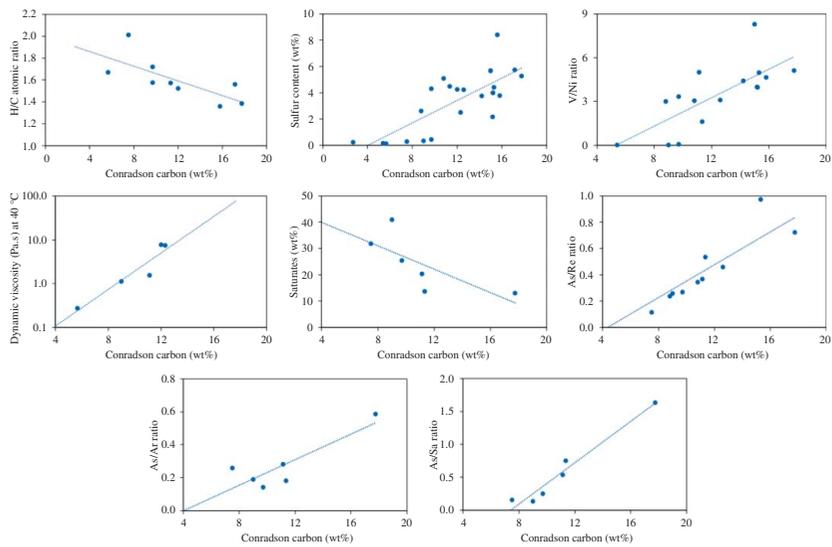


Figure 1.8 Correlations between the Conradson carbon (wt%) and other properties of different heavy and extra-heavy crude oils.

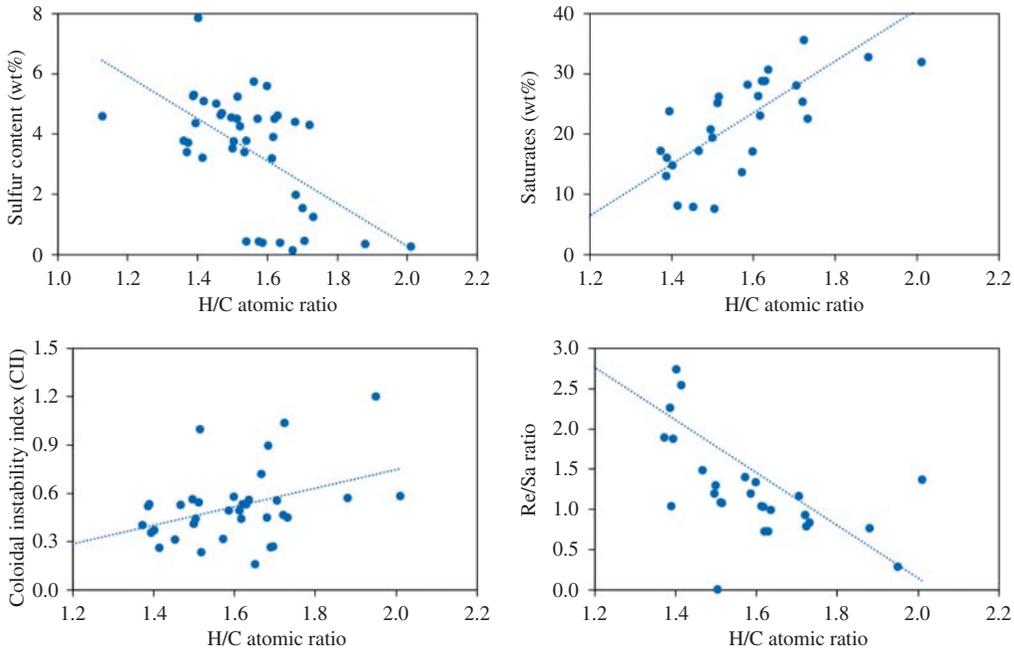


Figure 1.9 Correlations between the H/C atomic ratio and other properties of different heavy and extra-heavy crude oils.

the Re/Sa ratio decreases as the H/C atomic ratio increments. This behavior is owing to fact that the saturate fraction turns the crude oil into more aliphatic by increasing the H/C atomic ratio. Furthermore, the CII values heighten when the H/C atomic ratio increases because the aromatic fractions (resins and aromatics) have less content.

The sulfur content is another relevant property to determine the quality of heavy and extra-heavy crude oils, and different properties are dependent on its content, as observed in Figure 1.10. The V/Ni ratio increases as the sulfur content does, indicating that the sulfur and V compounds are present in heavy fractions like asphaltenes. It was observed from Figure 1.7 that the higher the amount of asphaltenes, the higher the V/Ni ratio and sulfur content since it is expected that larger amounts of sulfur and metals are contained in the heaviest fraction. However, the Ashalcha and Arta-4 heavy crude oils are the exceptions to this behavior owing to the similar amount of Ni and V in these crude oils besides having high sulfur content. On the basis of this behavior, the As/Re and As/Sa ratios heighten as the sulfur content increases. Some heavy crude oils (Shengli and Ashalcha) do not follow this trend because of their low content of asphaltenes and high amount of sulfur.

Another interesting value related to molecular weight of the crude oil is the colloidal instability index, which tends to increase as molecular weight does (Figure 1.11). This behavior is due to when the relatively low molecular weight aromatics (resins and aromatics) diminish their content, the asphaltenes fraction having the highest molecular weight compounds tend to increase its content, while the CII heightens and so does the molecular weight. Nonetheless, there are some exceptions to this behavior, such as the Ku-Maloob-Zaap heavy crude oil, which has high molecular weight and high content of aromatics and resins with low saturates content by which its CII value is low.