Edited by **Mikhail A. Varfolomeev**
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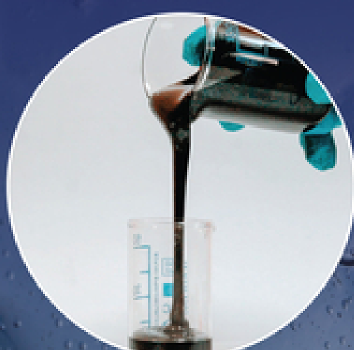
Catalytic In-Situ Upgrading of Heavy and Extra-Heavy Crude Oils



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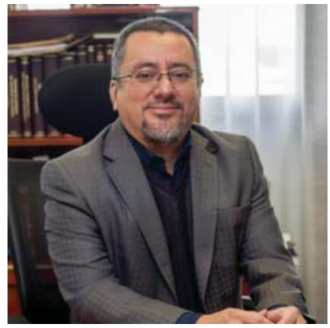
Nowadays, Dr. Varfolomeev is a chair of Department of Petroleum Engineering and head of Enhanced Oil Recovery Center of the Kazan Federal University. His research interests include petroleum engineering, enhanced oil recovery, catalytic oil upgrading, in situ combustion, gas injection, chemical flooding, 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 pharmaceutics, 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 physicochemical 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.

We would like to thank all our colleagues that contributed with the preparation of chapters and for the support of the Russian Science Foundation related to the Project № 21-73-30023 dated 17 March 2021.

June 2023

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1

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.

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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).