FUTURE TECHNOLOGY IN HEAVY OIL PROCESSING

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Contents

Summary

The change in crude oil quality around the world has impacted petroleum refining industry in such a way that current and new refineries are being re-configured and designed respectively to process heavier feedstocks, i.e. blends of various crude oils with elevated amount of heavy petroleum. This is of course due to the reduction of light crude oil and the increase of heavy or extra heavy crude oils production. These new feeds are characterized by high amounts of impurities (sulfur, metals, nitrogen, asphaltenes) and low distillate yields, which make them more difficult to process compared with light crude oils. Contrarily, the demand of light distillates for producing the so-called clean fuels (e.g. ultra-low sulfur diesel and gasoline) is increasing throughout the world. These circumstances situate not only refineries but also research centers, catalyst manufacturers and process developers in a great dilemma, which need to adapt and design future technologies for properly conversion and upgrading of heavy oils. There are various commercially available technologies to upgrade heavy petroleum, which can be classified in carbon rejection and hydrogen addition processes. Their main characteristics, advantages and disadvantages as well as some other emerging technologies are reviewed in this chapter. Special attention has been put for their application for upgrading of heavy petroleum.

1. Introduction

1.1. The Problem of Processing Heavy Petroleum

The situation of worldwide reserves of crude oils is very clear: while light crude oils production is declining heavy and extra-heavy crude oils production is increasing. Thus, in the near future, refineries will be obliged to replace light crudes by heavy/extra-heavy crude oils as feedstock. But, what is the real problem of this change in a refinery diet? Light and heavy crude oils have remarkable differences as can be observed in Table 1. Heavy petroleum is characterized by low API gravity, high amount of impurities and low yields of distillates. A summary of different crude oil properties is shown in Table 2. The samples are organized from heavy to light petroleum.

In general it is seen that the lower the API (the heavy the crude oil) the higher the impurities content and the lower the middle distillates yield. Such properties make its processing different from that used for light crude oils refining. In other words, a refinery designed to handle light petroleum cannot be totally employed to work with 100% of heavy petroleum, and some changes in the process plants or even installation of new units are mandatory. In addition, the price of heavy petroleum is lower than that of light petroleum as shown in Figure 1, which focuses on the historical price of crude oil in the last few decades and its variation with API gravity. These aspects also represent a motivation for the continuous research to develop technologies for upgrading of heavy crude oils.

	Type of crude oil			
	Extra light	**Light crude**	**Heavy crude**	**Extra heavy**
API gravity	> 50	22 - 32	10 - 22	< 10
Hydrocarbons				
Asphaltenes, wt.%	0 - < 2	< 0.1 - 12	11 - 25	15 - 40
Resins, wt. %	0.05 - 3	3 - 22	14 - 39	-
Oils, wt. %	-	67 - 97	24 - 64	-
Impurities				
S, wt. %	0.02 - 0.2	0.05 - 4.0	0.1 - 5.0	0.8 - 6.0
N, wt. %	0.0 - 0.01	0.02 - 0.5	0.2 - 0.8	0.1 -1.3
Ni+V, ppm	< 10	10 - 200	50 - 500	200 - 600

Table 1. Main properties of different types of petroleum.

Considering these forthcoming stipulation for the crude oil, it has been recognized that for processing of heavy petroleum in order to obtain more gasoline and other liquid fuels, the knowledge of the constituents of these higher boiling feedstocks is also of some importance. For instance, the problems encountered in processing heavier feedstocks can be equated to the chemical character and the amount of complex, higher-boiling constituents in the feedstock. Refining these materials is not just a matter of applying know-how derived from refining conventional crude oils but also requires knowledge of the chemical structure and behavior of these more complex constituents (Ancheyta et al., 2005).

Crude	API Gravity	N, wt.%	S, wt.%	Resins, wt.%	Asphaltenes wt.%
Algeria, Hassi Messaoud	45	-	-	3.3	0.15
France, Lagrave	43	-	-	7.5	4
Mexico, Isthmus	38	0.14	1.45	8.1	1.3
Mexico, Maya	22	1.1 [a]	3.5	87.6 [b]	12.6
Canada, Lloyminster	15	-	4.3	38.4	12.9
Qayarah, Iraq	15	-	8.4	36.1	20.4
Venezuela, Boscan	10	0.52	5.6	34	14
Canada, Cold Lake	10	1.24	7.14	25	13
Canada, Athabasca	8	1.25	7.95	14	15

[a] (N+O), [b](Resins + maltenes)

Table 2. Properties of various crude oils

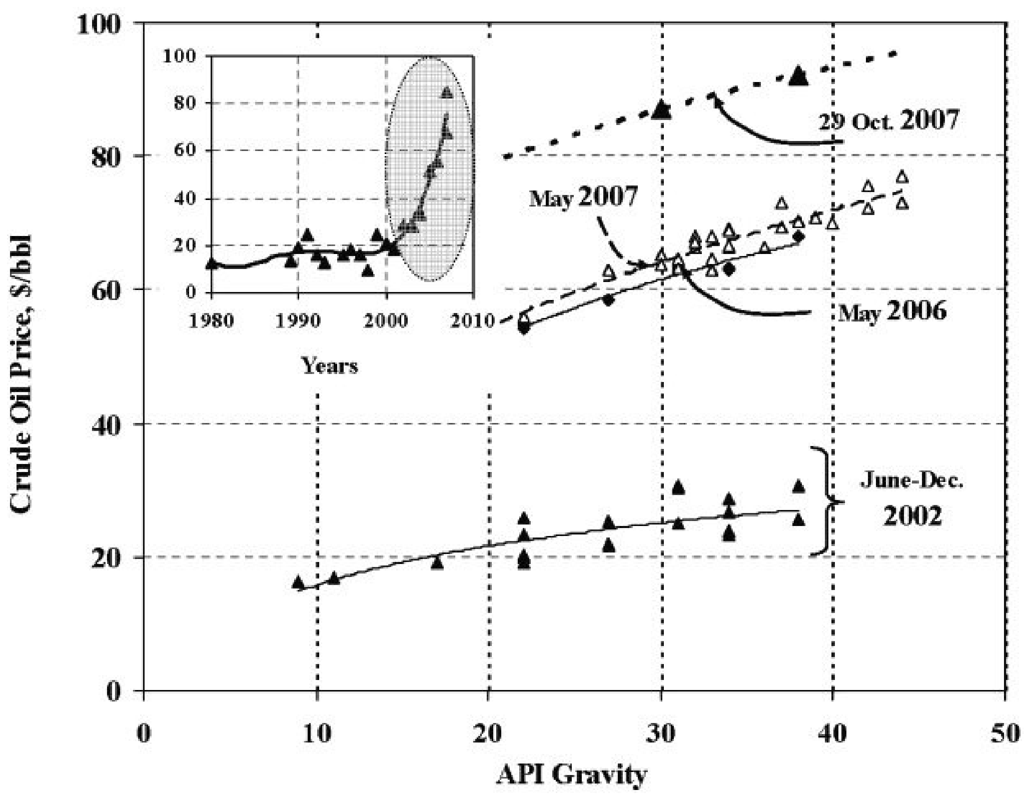

Figure 1. Fluctuation in crude oil prices and effect of crude oil quality.

There is then no doubt that for processing heavy petroleum to produce a considerable proportion of liquid fuels into the foreseeable future, refining strategies will focus on upgrading the heavy oils and residua and will emphasize the differences between the properties of the heavy crude feedstocks. This will dictate the choice of methods or combinations thereof for conversion of these materials to products (Schuetze and Hofmann, 1984).

1.2. Properties of Heavy Petroleum

Heavy petroleum exhibits a wide range of physical properties and several relationships can be made between various physical properties as shown in Figure 2. Whereas the properties such as viscosity, density, boiling point, and color of petroleum may vary widely, the ultimate or elemental analysis varies over a narrow range for a large number of samples (Speight, 2006). The carbon content is relatively constant, while the hydrogen and heteroatom contents are responsible for the major differences between petroleum. The nitrogen, oxygen, and sulfur can be present in only trace amounts in some petroleum.

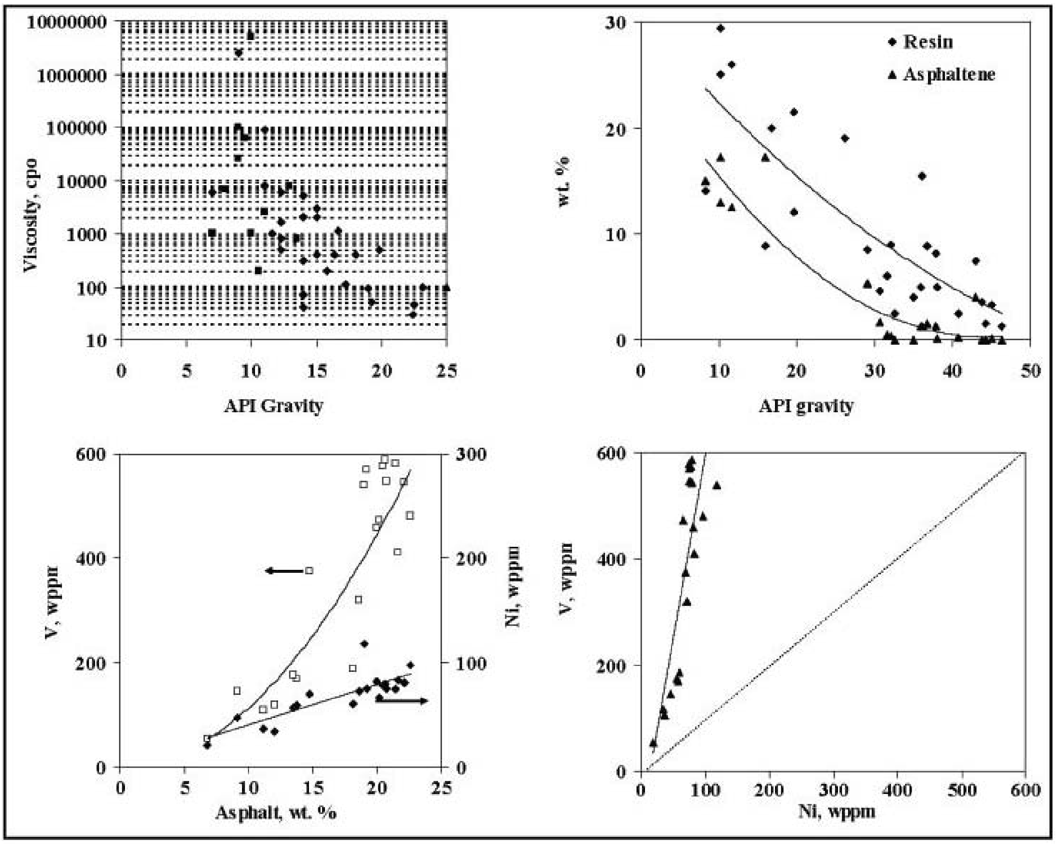

Figure 2. Relationship between various crude oil properties.

The properties of heavy and extra-heavy petroleum are comparable to those of the vacuum (565°C+ VR) and atmospheric (345°C+ AR) residua. Heavy petroleum is constituted by heavy hydrocarbons, and several metals (Riazi, 2005). Typical amounts of impurities of different petroleum are shown in Table 3. Heavy feeds contain aggregates of resins and asphaltenes dissolved in the oil fraction held together by weak physical interactions. With resins being less polar than asphaltenes but more polar than oil, equilibrium between the micelles and the surrounding oil leads to homogeneity and stability of the colloidal system. If the amount of resins decreases, the asphaltenes coagulate forming sediments. Asphaltenes are complex polar structures with poly-aromatic character containing metals (mostly Ni and V) that cannot be properly defined according to their chemical properties, but they are usually defined according to their solubility. Asphaltenes are the hydrocarbon compounds that precipitate from petroleum by addition of light paraffin in crude oil or residue. Asphaltenes precipitated with n-heptane have lower H/C ratio than those precipitated with n-pentane while asphaltenes obtained with n-heptane are more polar, have a greater molecular weight, and display higher N/C, O/C, and S/C ratios than those obtained with n-heptane.

	Maya				**Kern River**				**Arabian Heavy**			
	S	A	R	A	S	A	R	A	S	A	R	A
Crude oil												
HC [a]	20.7	26.5	29.9	20.6	21.8	28.7	37.6	5.5	20.1	31	31.2	12.2
S	0.9	24.6	39	36.3	<1	30.7	60.3	8.8	<1	29.6	46.3	23.9
N	3.3	8.2	39.6	48.9	2.7	4.2	77.2	15.8	6.7	8.4	43.8	41.1
Ni	-	0.4	17.9	81.7	-	7.5	52.8	39.8	-	3.4	25.2	71.4
V	-	3.3	17.7	79	-	4.5	63	32.5	-	10.4	28.2	61.8
345°C+ AR												
Ni	-	2.7	13	84.3	-	1.8	22.8	75.4	-	5.2	14.2	80.6
V	-	2.7	13.1	85.6	-	2.7	16.7	80.6	-	1.6	11.8	86.6

[a] HC: hydrocarbon

Table 3. Impurities content of several crude oils (composition as wt% of the total).

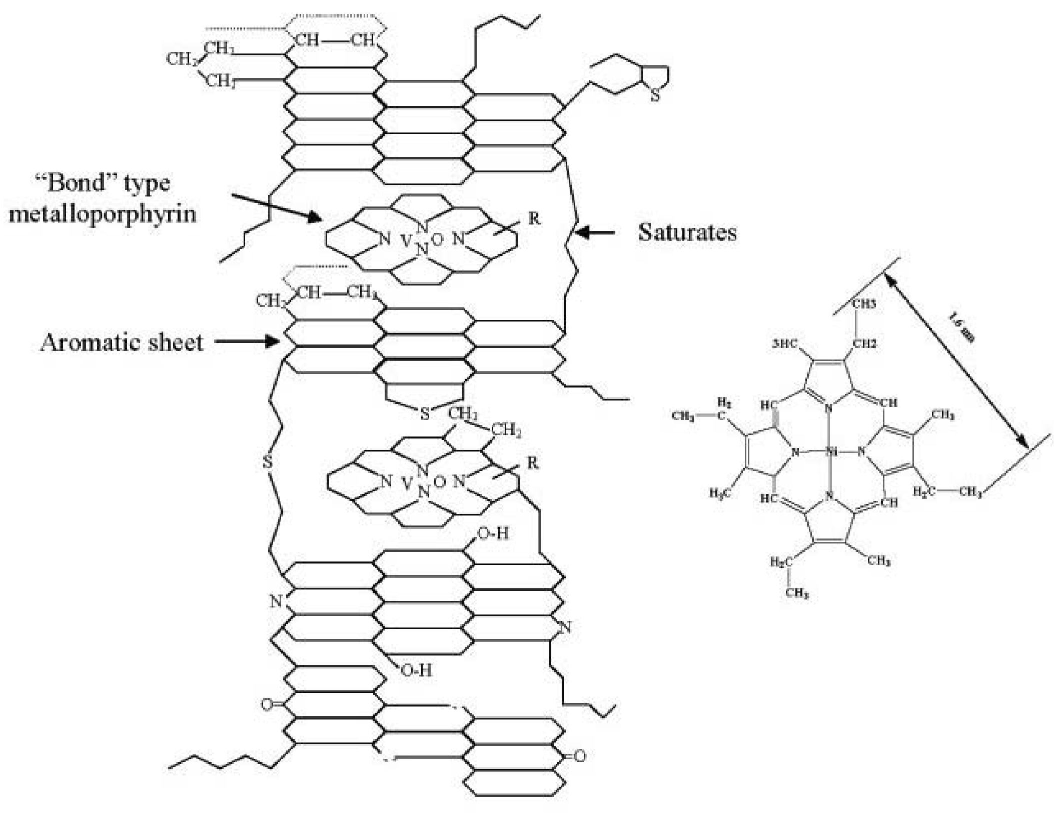

Figure 3. Hypothetical asphaltene molecule and its interaction with organo-metallic compounds.

Asphaltenes are constituted by condensed aromatic nuclei carrying alkyl groups, alicyclic systems and hetero-elements (Dickie and Yen, 1967; Tynan and Yen, 1969; Merdrignac and Espinat, 2007). Asphaltene molecules are grouped together in systems of up to five or six sheets, which are surrounded by the so-called maltenes (all those structures different from asphaltenes that are soluble in n-heptane). The exact structure of asphaltenes is difficult to obtain and several structures have been proposed for the asphaltenes present in different crudes (Beaton and Bertolacini, 1991). The length of the alkylic chains in asphaltenes has been the subject of different studies. Mojelsky et al. (1992) found chains of 3-4 carbon atoms while Speight (1999) found alkylic chains of up to 30 carbon atoms. Other studies on the structure of asphaltenes have been performed (Miller et al., 1998; Mullins et al., 1999). An asphaltene molecule may be 4 to 5 nm in diameter, which is too large to pass through micro-pores or even some meso-pores in a catalyst. Metals in the asphaltene aggregates are believed to be present as organo-metallic compounds associated to the asphaltene sheets, making the asphaltene molecule heavier than its original structure (Figure 3).

1.3. General Classification of Processes for Upgrading Heavy Petroleum

One manner to establish the quality of crude oil is with the hydrogen-to-carbon (H/C) ratio. Values of about 1.5 indicate high-quality petroleum, while poor-quality petroleum may have H/C ratio as low as 0.8. Therefore, to improve the quality of heavy petroleum its H/C ratio needs to be increased either by increasing the hydrogen content or by decreasing the carbon content. Based on this consideration, processes for upgrading of heavy oils can be classified in two groups:

1. Hydrogen addition processes: hydroprocesses such as hydrotreating and hydrocracking, hydrovisbreaking, donor-solvent processes.
2. Carbon rejection processes: coking, visbreaking, and other processes such as solvent deasphalting.

Both hydrogen addition and carbon rejection processes have disadvantages when applied to upgrade heavy oils or residua. For instance, removal of nitrogen, sulfur and metals by exhaustive hydrodenitrogenation (HDN), hydrodesulfurization (HDS), and hydrodemetallization (HDM) is very expensive (excessive catalyst utilization) due to metals and carbon deposition. The non-catalytic processes yield uneconomically large amounts of coke and low liquid yield.

Processes for upgrading of heavy oils and residua (Speight and Ozum, 2002; Speight, 2006) are evaluated on the basis of liquid yield (i.e. naphtha, distillate and gas oil), heteroatom removal efficiency (HDS, HDN, HDM), feedstock or residue conversion (FC), carbon mobilization (CM) and hydrogen utilization (HU), along with other process characteristics. Heteroatom removals and feedstock conversion are calculated from their corresponding amounts in feed and product, with the following equations:

$$HDS,\ HDN\ \text{or}\ HDM = \left(\frac{I_{\text{feed}} - I_{\text{product}}}{I_{\text{feed}}}\right)\times 100 \qquad (1)$$

$$Conversion\ (FC) = \left(\frac{[538°\mathrm{C}+_{\mathrm{feed}}] - [538°\mathrm{C}+_{\mathrm{product}}]}{[538°\mathrm{C}+_{\mathrm{feed}}]} \right) \times 100 \qquad (2)$$

where I_{feed} and I_{product} represent the amount of sulfur, nitrogen and metals in the feed and product respectively. $[538°\mathrm{C}+_{\mathrm{feed}}]$ and $[538°\mathrm{C}+_{\mathrm{product}}]$ are the petroleum fractions in the feed and in the product respectively with boiling point higher than 538°C, i.e. vacuum residue.

Carbon mobilization and hydrogen utilization are defined as follows:

$$CM = \left(\frac{[\mathrm{Carbon}_{\mathrm{liquids}}]}{[\mathrm{Carbon}_{\mathrm{feedstock}}]} \right) \times 100 \qquad (3)$$

$$HU = \left(\frac{[\mathrm{Hydrogen}_{\mathrm{liquids}}]}{[\mathrm{Hydrogen}_{\mathrm{feedstock}}]} \right) \times 100 \qquad (4)$$

High values of *CM* and *HU* correspond to high feedstock conversion processes such as hydrocracking (hydrogen addition). Since hydrogen is added, *HU* can be greater than 100%. On the contrary, low *CM* and *HU* correspond to low feedstock conversion such as coking (carbon rejection).

2. Description of Processes for Upgrading of Heavy Petroleum

Petroleum industry can be divided in two main sectors: Upstream and Downstream. The principal roles of each sector are:

Upstream:

- Exploration and development involved in the search of petroleum oils. The development includes underground or underwater oil and gas fields, drilling of exploratory wells.
- Flow assurance problems in well bores and topsides including asphaltene or wax precipitation, contaminants, corrosion, slugging, hydrates foaming, and emulsion breaking.
- Early identification of oil quality issues that allows the downstream to develop targeted solutions and prepare refineries for upcoming feedstock changes.

Downstream:

- Petroleum refineries, product quality and its distribution.
- Elaboration of products such as gasoline, diesel, jet fuel, heating oil, asphalt, lubricants, petrochemicals or even pharmaceuticals.

The focus on the downstream and upstream sectors for each country may vary depending on the quality of crude oil. Significant advances have been made in these sectors of petroleum over the last few decades. Downstream sector has been traditionally in charge of petroleum refining. However, with the increasing production of heavy crude oils upstream sector has entered into the upgrading area in order to increase the value of the produced oil. Thus, nowadays both sectors are looking for better alternatives to upgrade and refine heavy petroleum.

From another point of view, the upgrading technologies can be classified as catalytic (hydrogen addition) and non-catalytic (carbon rejection) as presented in Figure 4. The primary processes usually prepare synthetic crude oils that contain relatively large amount of heteroatoms such as nitrogen and sulfur, which must be removed in secondary processes that are able to produce transport fuels. The process technologies are principally different on the basis of the feedstock and process conditions (reactor) and catalyst used by the different licensers.

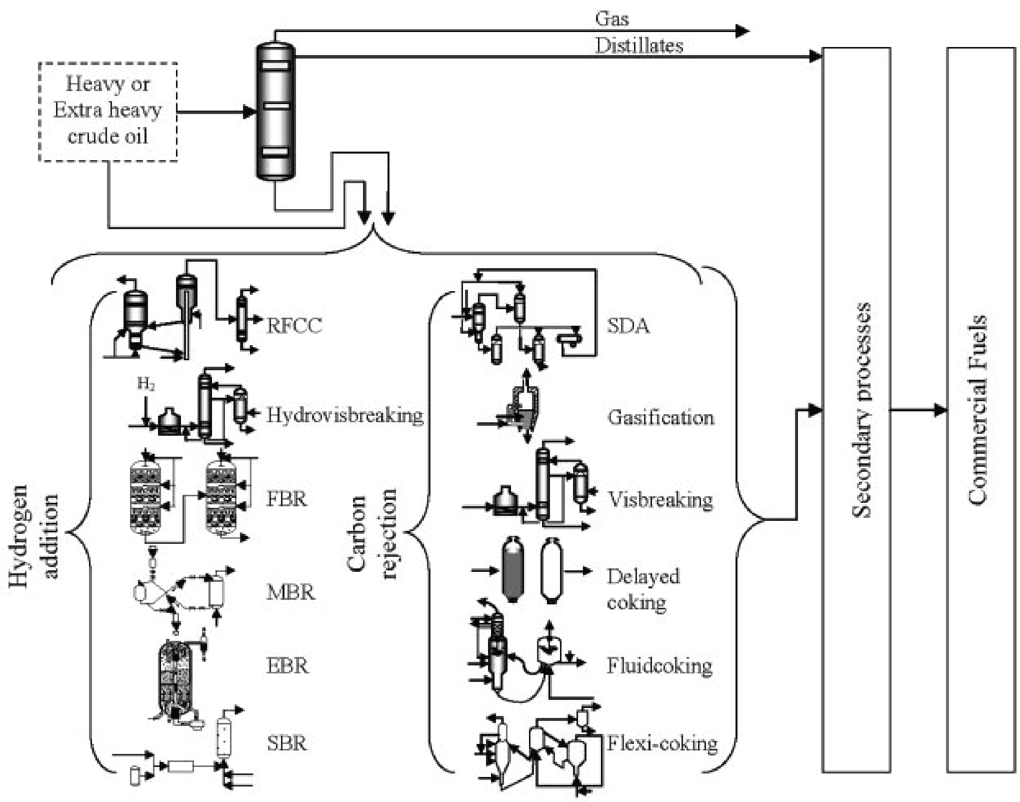

Figure 4. Hydrogen addition (catalytic route) and carbon rejection (non-catalytic route) technologies for upgrading of heavy and extra heavy crude oil and residua.

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Biographical Sketches

Jorge Ancheyta was born in Chiapas, Mexico. He graduated with a Bachelors degree in Petrochemical Engineering (1989), Master degree in Chemical Engineering (1993) and Master degree in Administration, Planning and Economics of Hydrocarbons (1997) from the National Polytechnic Institute (IPN) of Mexico, split PhD at the Metropolitan Autonomous University (UAM) of Mexico and Imperial College of Science, Technology and Medicine, London, UK (1998), and postdoctoral fellowship in the Laboratory of Catalytic Process Engineering of the CPE-CNRS in Lyon, France (1999).

He has worked for the Mexican Institute of Petroleum (IMP) since 1989 and his present position is Research and Development Project Leader. He has also worked as professor at 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 posgrade since 2003. He has been supervisor of more than seventy BSc, MSc and PhD theses.

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 heavy oils upgrading. He is author and co-authors of a number of patents, books and scientific papers, and has been awarded the National Researcher Distinction by the Mexican government and is member of the Mexican Academy of Science. He has also been guest editor of various international journals, e.g. Catalysis Today, Petroleum Science and Technology, Fuel, Industrial Engineering Chemistry Research, Chemical Engineering Communications, and chairman of international conferences.

Mohan S. Rana was born and raised in Uttaranchal (North), India. He obtained BSc. and MSc. degrees in chemistry from the University of HNB Grahwal, Srinagar, India in 1990 and 1992 respectively. He later received his doctorate degree in heterogeneous catalysis from the HNB Garhwal University (research center: Indian Institute of Petroleum, CSIR), India in 2000. He was then working for a couple of years as post doc fellow at the University of Caen, CNRS, France, on inhibition effect carried out by reaction intermediate in hydrotreating catalyst. Presently he is working as research scientist at Instituto Mexicano del Petroleo, Mexico covering different areas of work such as upgrading of crude oil by catalytic as well as non catalytic methods.

Dr. Mohan has more than 13 years of work experience in areas associated to the heterogeneous catalysis and petroleum refining processes, mainly in hydroprocessing. His research has involved petroleum oil upgrading, improvement of middle distillates, heavy gasoil and oil sands bitumen, including catalyst development, hydrotreating, mild hydrocracking, hydrocracking, catalytic cracking, and hydrogenation. He has published more than 50 papers in international Journal.