Versão do arquivo anexado / Version of attached file:

Versão do Editor / Published Version

Mais informações no site da editora / Further information on publisher's website:

https://www.scielo.br/scielo.php?script=sci_arttext&pid=S0104-66322014000300001

DOI: 10.1590/0104-6632.20140313s00001853

Direitos autorais / Publisher's copyright statement:

AN OVERVIEW OF HEAVY OIL PROPERTIES AND ITS RECOVERY AND TRANSPORTATION METHODS

R. G. Santos[1*], W. Loh[2], A. C. Bannwart[3] and O. V. Trevisan[3]

[1]Laboratory of Miscible Displacement Methods, Center for Petroleum Studies,
University of Campinas, CP 6122, CEP: 13083-970, Campinas - SP, Brazil.
Current Address: Department of Chemical Engineering, Cntr. Univ. FEI,
CEP: 09.850-901, São Bernardo do Campo - SP, Brazil.
Phone: + (55) (11) 4353 2900, Fax: + (55) (11) 4109 5994
E-mail: rgsantos@fei.edu.br
[2]Institute of Chemistry, University of Campinas, C.P. 6154,
CEP: 13083-970, Campinas - SP, Brazil.
[3]Faculty of Mechanical Engineering, University of Campinas, C.P. 6122,
CEP: 13083-970, Campinas - SP, Brazil.

Abstract - Unconventional oils - mainly heavy oils, extra heavy oils and bitumens - represent a significant share of the total oil world reserves. Oil companies have expressed interest in unconventional oil as alternative resources for the energy supply. These resources are composed usually of viscous oils and, for this reason, their use requires additional efforts to guarantee the viability of the oil recovery from the reservoir and its subsequent transportation to production wells and to ports and refineries. This review describes the main properties of high-viscosity crude oils, as well as compares traditional and emergent methods for their recovery and transportation. The main characteristics of viscous oils are discussed to highlight the oil properties that affect their flowability in the processes of recovery and pipeline transportation. Chemical composition is the starting point for the oil characterization and it has major impact on other properties, including key properties for their dynamics, such as density and viscosity. Next, enhanced oil recovery (EOR) methods are presented, followed by a discussion about pipeline and transportation methods. In addition, the main challenges to achieve viable recovery and transportation of unconventional oils are compared for the different alternatives proposed. The work is especially focused on the heavy oils, while other hydrocarbon solid sources, such as oil sands and shale oil, are outside of the scope of this review.
Keywords: Heavy oil; Unconventional oil; Transportation methods; Viscosity; EOR; Pipeline; Oil production; Oil recovery.

INTRODUCTION

The continuous increase in world energy demand driven by the economic development and the dramatic population growth recorded in recent decades has caused the decline of the availability of petroleum resources characterized by more efficient production and refining. These resources were composed mainly of conventional oil reserves with high market value and whose production and processing consist of simple and technically well-established methods. Forecasts predict that a continuous expansion in world energy consumption must extend at least until 2035, as indicated by the U.S. Energy Information Administration (See Figure 1).

The analyses of the production capacity of oil

---

*To whom correspondence should be addressed

fields have shown that the conventional oil reserves, both light and medium, reached a maximum volume around the early 1960s (Campbell and Laherrère, 1998). Since then, these reserves have followed a constant decline, so they will probably represent only a small portion of the total petroleum resources available in the near future (Figure 2). Currently, new discoveries of conventional oil are scarce and insufficient to meet the increase in energy demand. The result is a wide gap in the worldwide energy supply with global economic impacts. Filling this gap depends on the oil industry's capacity to transform potential resources into commercial exploitable reserves. In this context, the development of new technologies becomes crucial for the economical produc-

tion of unconventional resources such as heavy and extra-heavy oils (Suslick *et al.*, 2003). It should be highlighted that the term "unconventional resources" can also refer to unconventional reservoirs containing light and media oils, in contrast to unconventional oils. In this work, the term unconventional resource refers to crude oils having API gravity lower than 22 degrees.

Parallel to the decline of conventional oil reserves, it has been observed that the new discoveries are oils with a clearly distinct nature from those inherent to light oils (Lanier, 1998; Meyer and Attanasi, 2003; Suslick *et al.*, 2003; Trevisan *et al.*, 2006), thus these oils are called unconventional. The main aspect that distinguishes these two types of reserves
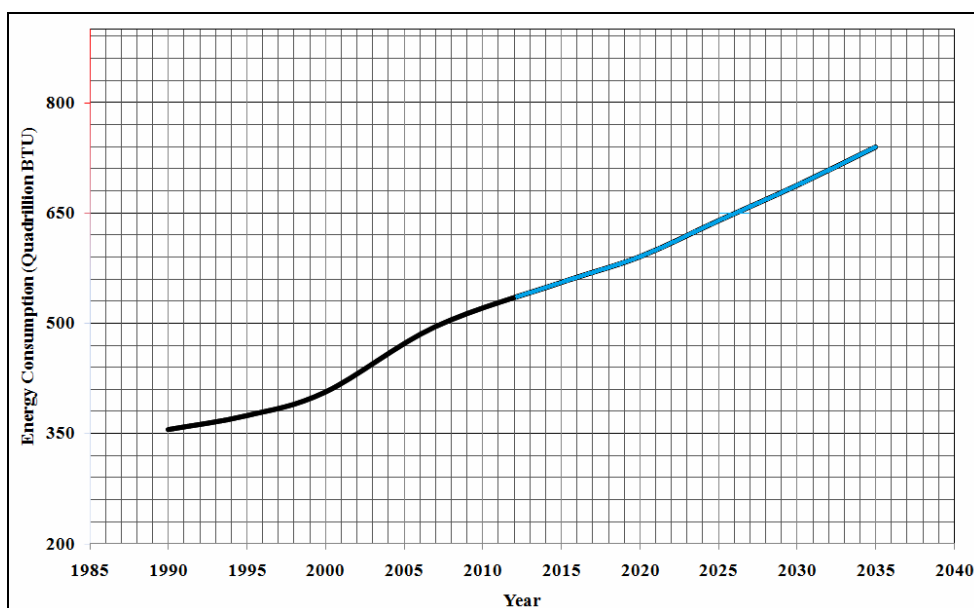

Figure 1: World market energy consumption - Forecast up to 2035. Adapted from DOE/EIA 2010 International Energy Outlook, U.S. Energy Information Administration, 2010.
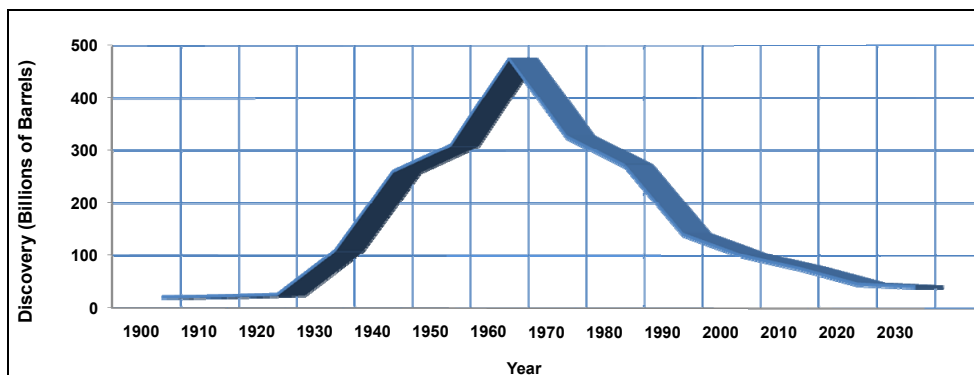

Figure 2: History and forecast of world discoveries of conventional oil (Adapted from Tverberg, 2008).

is that unconventional oils cannot be recovered in their natural state by the exclusive application of typical production methods, and further they generally require heating and dilution during transport (Speight, 1991), which increases recovery costs. Another important aspect is the high flow resistance displayed, that normally impacts their natural flow. In addition, in contrast with conventional oils, these unconventional oils present a higher density, a higher content of nitrogen, oxygen, sulfur and heavy metals and a wider quantity of heavier oil fractions. Furthermore, the refining of unconventional oils requires great specificity and produces lower proportions of

high added value products, such as liquefied petroleum gas (LPG), gasoline, kerosene, and diesel oil.

Recent studies estimate that unconventional oil reserves, including heavy oils, extra-heavy oils and bitumen exceed 6 trillion barrels. This amount is equivalent to about 70% of all energy resources derived from fossil fuels in the world (Oilfield Review Summer, 2006). Figure 3 provides an illustration of the regional distribution of proven and recoverable reserves of unconventional oils. The large sum related to North America and South America is associated with the giant reserves of heavy oils and bitumen from Venezuela and Canada, illustrated in Table 1.
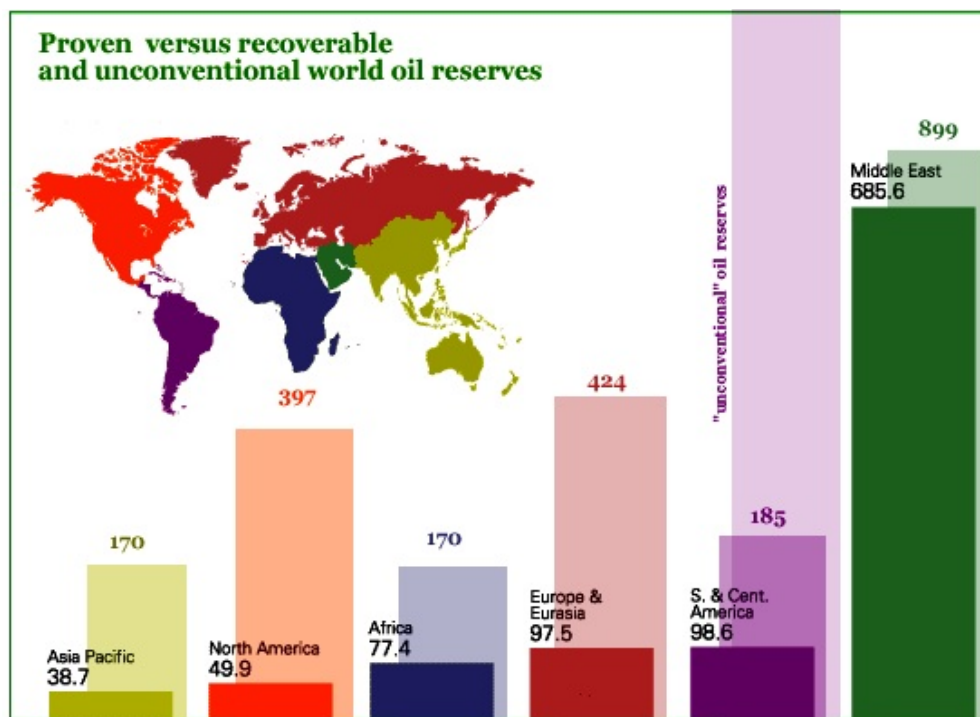

Figure 3: Proven and recoverable oil reserves distributed by region in billions of barrels (from Kovarik, 2011).

Table 1: Geographical distribution of heavy oils and bitumen reserves (Adapted From *U.S. Geological Survey*, 2003).

Region	Heavy oil		Bitumen	
	Recovery Factor	Reserve (BBO)[1]	Recovery Factor	Reserve (BBO)
North America	0.19	35.3	0.32	530.9
South America	0.13	265.7	0.09	0.1
Africa	0.18	7.2	0.10	43.0
Europe	0.15	4.9	0.14	0.2
Middle East	0.12	78.2	0.10	0.0
Asia	0.14	29.6	0.16	42.8
Russia	0.13	13.4	0.13	33.7
Total	**-**	**434,3**	**-**	**650,7**

[1] billions of barrels of oil

South America retains 61% of the recoverable heavy oil due to contributions from the Orinoco River basin in Venezuela (Meyers and Attanasi, 2003). The World Energy Outlook from the International Energy Agency projects that heavy oil and bitumen production from Canada and Venezuela together might reach 6 million barrels per day by 2030 (IEA, 2006). The low recovery factors point to the necessity for technical developments in the recovery of these resources.

Recently, the total volume of unconventional oils in Canada was estimated to be similar to conventional oil reserves in the Middle East. Athabasca oil sands deposit is the world's largest known petroleum resource, which contains more than 1.3 trillion barrels in the ground. The Cold Lake oil sands contain 200 billion barrels, and the Peace River deposit is estimated to have 155 billion barrels (Petroleum Communication Foundation, 2000). In 2005, Canadian production of heavy oil and bitumen was approximately 1 million barrels per day (BOPD), and it is forecasted to be 4 million BOPD by 2020 (National Petroleum Council, 2007).

Despite the widespread availability of heavy oils, the recorded annual production in 2000 corresponded to only 12% of the total annual production (Meyers and Attanasi, 2003). Furthermore, heavy oils with better quality in terms of composition and density are given priority in production - 66% of heavy oils produced have °API gravity higher than 15.

In Brazil, recoverable reserves totalize the amount of 2.9 billion barrels. In addition, four billion other barrels would be immediately incorporated if resources previously discovered became technically and economically feasible. Confirmed feasibility would mean that heavy oils could represent 40% of the proven Brazilian reserves in the medium term (Trevisan *et al.*, 2006). Studies by the Brazilian oil company (Petrobras) report that heavy oils corresponded to 20% of the total volume produced in the country in 2010 (Petrobras, 2010). Besides the inherent adversities for the production and transport of viscous oils, the largest reserves of heavy oils in Brazil are located in water deeper than 1500 m and usually in shallow reservoirs with temperatures between 40 and 60 °C. The rock existing in these Brazilian reservoirs is typically unconsolidated with high permeability (Capeleiro Pinto *et al.*, 2003). In fact, significant volumes of heavy oil found in recent discoveries have API gravity between 13 and 17 degrees and viscosity ranging from 20 to 400 cP under reservoir conditions (Capeleiro Pinto *et al.*, 2003). This new scenario led Petrobras to create a technology program to focus on offshore reserves of

heavy oil with the objective of developing technologies for the production of these oils.

This work is organized in four main sections: Introduction, Heavy oil properties, Methods for recovering of heavy crude oils and Methods to improve the characteristics of pipeline flow. The Introduction section discusses the significance of heavy oil in the worldwide oil reserves, as well the economic and technological aspects. The next section presents the significant characteristics of heavy oils and their classification and definition, including oil composition and flow properties. The subsequent sections introduce the traditional and emergent technologies applied to heavy oil recovery and transportation, respectively. Heavy oil properties are discussed to highlight their effects on oil flowability.

HEAVY OILS

Heavy Oil Classification

Heavy oil, extra heavy oil, oil sand, tar sands, oil shale and bitumen are all unconventional oil resources. Confusing heterogeneous denominations arise because of similar key characteristics presented by these resources. The general oil classification is related to the crude oil's ease of flow and consequently it denotes specific technical characteristics of their production, transportation and refining. Oil companies and government agencies usually adopt oil definition criteria that take into account financial aspects and the degree of technological improvement. Because they display special and temporal variations, these criteria have limited applications. In refineries and oil fields, the criteria adopted are generally related to crude oil properties, such as density and viscosity.

The most widely used definition for heavy oils is based on the API gravity[1] proposed by the American Petroleum Institute, which uses the °API scale (index that is based on the oil relative density) as the criterion for oil classification. The API degree range elected to define and classify oils has not been standardized. For instance, the World Petroleum Conference classifies heavy oil as those having

---

[1] °API gravity – Measurement unit from the American Petroleum Institute for specific gravity usually applied in petroleum systems. API gravity is related to relative density (d_r) by:

$$API = \frac{141.5}{d_r(60/60)} - 131.5$$

d_r is the relative density with respect to water, measured at 60 °F.

below 22.3 API degrees. For the American Petroleum Institute, heavy oil is defined as those having an API index equal to or smaller than 20 degrees. The North American taxation system has a similar criterion (Trevisan *et al.*, 2009). Based on the API index, the Brazilian National Petroleum Agency (ANP) identifies four different types of petroleum, as shown in Table 2. However, Petrobras defines heavy oils as those in the range between 10-19 °API (Figure 4).

Oil classification relative to properties such as viscosity and sulfur content is also found in the literature (Speight, 1991; Meyer and Attanasi, 2003). Objectively, heavy oils are characterized by a high specific gravity, elevated viscosity, low H/C ratio as well as high contents of asphaltene, resin, heavy metals, sulfur and nitrogen (Speight, 1991), often featuring a black color.

Heavy Oil Generation

The particular characteristics of the heavy oils are mainly attributed to a biodegradation process in which microorganisms on a geological time scale degrade light and medium hydrocarbons, making the reserves rich in polyaromatic compounds, resins and asphaltenes (Oliveira and Carvalho, 1993; Head *et al.*, 2003). Microbial degradation reaches optimal temperatures below 80 °C, promoting oil oxidation, reduction of the gas/oil ratio (GOR) and increasing density, acidity, and viscosity as well as the relative proportion of sulfur and heavy metals. Besides biodegradation, heavy oil formation can occur through mechanisms such as water washing and phase fractionation, which are based on the loss of a significant fraction of original mass, and removal of light petroleum fractions by physical rather than biological means (Oilfield Review Summer, 2006).

Heavy oils usually occur in giant shallow formations in marginal geological basins formed by non-consolidated sand. Heavy oil reservoirs tend to have low pressure and low GOR (exception for foamy heavy oils), resulting generally in lower recovery factors in comparison to light oil reservoirs. Although the characteristics of the heavy oil reservoirs point to more complex and expensive production processes, factors such as high permeability can make the process worthwhile (Wehunt, 2003).

Table 2: Crude oil classification by the National Petroleum Agency of Brazil (Adapted from ANP, 2000).

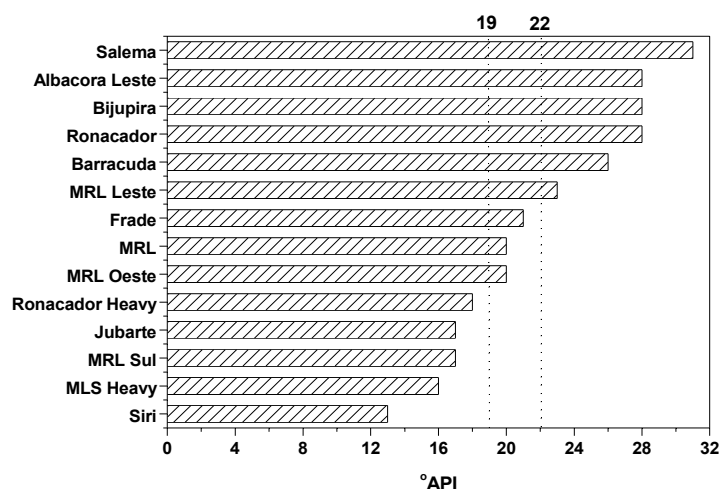| Oil Class	°API
Light	°API ≥ 31
Medium	22 ≤ °API < 31
Heavy	10 ≤ °API < 22
Extra-heavy	°API ≤ 10

Figure 4: API types of the main Brazilian oil reserves, excluding pre-salt oil. (Adapted from Petrobras, 2007).

Heavy Oil Properties

Heavy oils display a high content of high molecular weight hydrocarbons and elevated levels of heterocompounds including sulfur, nitrogen, oxygen and metals (Speight, 1991). Typically, the molecules present in heavy oil have more than fifteen carbon atoms in the chain, making the refining process more complex and costly (Trevisan *et al.*, 2006). This mixture of high molecular weight compounds generates products with a low content of high-octane gasoline and diesel at the refinery. Although the amount of compounds containing heteroatoms is relatively small, the effect of these compounds on the oil properties is usually strongly pronounced (Triggia *et al.*, 2001).

Chemical species containing sulfur atoms are often regarded as harmful for their effects on the refining process. The most common types are thiols, sulfides, thiophene and their derivatives. The nitrogen compounds are generally basic, formed by pyridine and its homologues. However, nitrogen compounds can also occur in non-basic forms, formed by species including pyrroles, indoles and carbazoles and their derivatives. Significant amounts of porphyrins may occur in the non-basic fraction of the nitrogen compounds. Metals are generally present in the form of organic salts dissolved in oil-emulsified water. Heavy oils often contain a large portion of nickel and vanadium, which form chelates with porphyrins (Speight, 1991). These metallic compounds are responsible for catalyst contamination and corrosion problems.

Oxygenated compounds appear as carboxylic and phenolic groups, although the presence of ketones, ethers and anhydrides has also been identified. The content of these compounds determines the acidity of the oil, which is particularly important in the refining process and thus affects its market price. These features can occur on the same molecular structure, further increasing the complexity and difficulty of the characterization of the compounds present in the crude oil.

Due to the impossibility of an elemental characterization of petroleum because of its complex nature, a complete characterization has been satisfactorily obtained by fractionation, based on fraction polarity and solubility (Ali and Nofal, 1994; Lundanes and Greibrok, 1994). The SARA analysis is the most widely used method to describe petroleum fractions. SARA classifies crude oils based on their fraction polarity through a chromatographic technique that divides the oil into four main fractions. These fractions provide the name for the analysis: saturates, aromatics, resins and asphaltenes. Oil fractionation by SARA is performed with regard to the polarity of these fractions by using different solvents and adsorbents (Fan *et al.*, 2002). The SARA method is reproducible and applicable to a wide variety of oils and bitumen, shale and petroleum residues.

Saturates are composed of nonpolar hydrocarbons with linear or branched chains, as well as aliphatic cyclic paraffins. Aromatics correspond to the fraction that contains compounds with one or more aromatic rings linked to aliphatic chains (Speight, 1991). Resins and asphaltenes are formed by high molecular weight compounds, which contain heterocompounds of crude oil. Resins are insoluble in propane and soluble in pentane and higher hydrocarbons, whose density is approximately equal to 1 g.cm^{-3} and molar mass varies from 500 to 2000 g.mol^{-1}. Asphaltenes are commonly defined as the crude oil fraction insoluble in n-alkenes of low molecular weight; they are soluble in toluene or benzene (Speight, 1991; Loh *et al.*, 2007) and are in a class of petroleum macromolecules composed of polycondensed aromatic rings and lateral aliphatic chains, presenting a smaller proportion of acidic and basic functional groups. Table 3 shows a typical elemental composition for SARA fractions, obtained from Venezuelan heavy oil. Since heavy oil properties often change randomly with a large number of variables, SARA composition for certain oils may be enormously different from that in Table 3. Elemental composition for crude oil asphaltenes precipitated with n-pentane from crude oil of different countries is presented in Table 4. For this asphaltene collection, the carbon/ hydrogen ratio ranges from 1.00 to 1.56, representing a wide range of aromaticity.

Heavy oils usually display a greater content of asphaltenes and resins than conventional oils (Speight, 1991), which directly impacts recovery, transport and refining processes. Colloidal properties of asphaltenes and resins have been the subject of intense debate in the literature - see for instance Loh *et al.* (2007). In many production fields and refineries, the content of asphaltene is one of the main criteria for process control. Table 5 shows the composition differences normally found in conventional oils, heavy oils and residues.

Petroleum density is generally expressed in terms of °API (Table 6). When detailed physical and chemical analyses are available, °API can be used as a rigorous quality index of the petroleum against a similar composition in its natural state without the effects of mixing and dilution. As the °API value decreases, the value of the distillation product decreases (Trevisan *et al.*, 2006). This phenomenon is

due to the higher production of petroleum fractions with a lower added value, such as fuel oil, coke and asphalt, indicating that °API is a measure of oil solvency (Buckley *et al.*, 1997). When different types of crude oil are mixed, °API cannot be used for anything other than as a measure of fluid density.

One of the most important aspects of heavy oils is their viscosity, since the high viscosity of heavy oils directly impacts the recovery and productivity of the reservoir (Wilson, 1997). Although there is no direct relationship between density and viscosity, a reduction in °API is generally accompanied by an increase in viscosity. Heavy oils display viscosities ranging from a few hundred to tens of millions of centipoises under reservoir conditions (Speight, 1991). Thus, the transport of heavy oils through pipelines and porous media almost always requires additional energy, and often requires the addition of heat or diluents to guarantee acceptable flow rates (Larnier, 1998).

Table 3: Typical elemental composition for heavy oil[1] (Gateau *et al.*, 2004).

Fraction	Weight percentage (%)	Elementary composition based on C_{20} + (%)				
		C	H	N	O	S
Asphaltene	14.1	83.8	7.5	1.3	1.7	4.8
Resin	37.3	82.8	8.9	1.5	2.0	4.3
Aromatic	37.2	84.3	10.0	< 0.3	1.1	4.0
Saturate	11.4	86.6	13.0	< 0.3	< 0.2	< 0.1

[1] From Venezuela reserve.

Table 4: Elemental composition of asphaltenes from several oil samples (Loh *et al.*, 2007).

Origin	Composition (%)					H/C Ratio
	Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur	
United States [a]	88.6	7.4	0.8	2.7	0.5	1.00
Kuwait [a]	82.4	7.9	0.9	1.4	7.4	1.14
Venezuela [a]	85.5	8.1	3.3	1.8	1.3	1.14
Mexico [a]	81.4	8.0	0.6	1.7	8.3	1.18
Brazil [b]	83	9	2	-	-	1.3
Italy [a]	78.0	8.8	Trace	3.0	10.2	1.35
Canada [a]	85.1	11.1	0.7	2.5	0.6	1.56

[a] Data from Marcel Dekker, Inc (From Speight, 1991)
[b] Total content of oxygen and sulfur is 6%.

Table 5: Composition for conventional oil, heavy oil and residue (Adapted from Speight, 1991).

Sample	Typical composition range (Wt.%)		
	Asphaltene	Resin	Oil fraction [1]
Conventional oil	< 0.1 - 12	3 - 22	67 - 97
Heavy oil	11 - 45	14 - 39	24 - 64
Residue	11 - 29	29 - 39	< 39

n.d: Not determined
[1] Correspondent to the fraction composed of saturate and aromatic.

Table 6: SARA composition, density and API gravity for heavy oil from different locations (Hinkle *et al.*, 2008).

Origin	Saturate (Wt.%)	Aromatic (Wt.%)	Resin (Wt.%)	Asphaltene (Wt.%)	Density (g/mL)	API gravity
Alaska	23	22	35	18	0.997	10.4
Canada	18	27	27	15	0.991	11.3
Texas	4	17	37	43	1.119	-5.00
Utah	19	14	46	20	1.000	8.05
Venezuela	19	32	29	18	1.013	8.05

METHODS FOR RECOVERING HEAVY CRUDE OILS

Oil is retained in the reservoir mainly due to capillary, gravitational and viscous forces. The relative interaction between these forces during the oil flow in the porous media may be measured by the capillary number and the mobility ratio (Stalkup, 1992). The capillary number (Ca) is defined as the dimensionless grouping of variables involving the ratio between capillary and viscous forces acting on the pore scale.

$$Ca = \frac{\eta \cdot v}{\gamma} \qquad (1)$$

Here η is the viscosity of the fluid, v denotes the flow velocity through the pore and γ is the interfacial tension between the fluids.

The mobility of fluids in porous media is defined on the basis of the Darcy equation.

$$u = \frac{k}{\mu} \cdot \frac{dP}{dx} \qquad (2)$$

Here u is the Darcy superficial velocity of the fluid, k is the permeability, μ is the viscosity, P is the pressure and x is the length. For a single phase, k represents the absolute permeability. For multiphase flow, k represents the effective permeability. The phase fluid mobility is given as

$$\lambda = \frac{k}{\mu} \qquad (3)$$

Then, the mobility ratio is defined as

$$M = \frac{\lambda_2}{\lambda_1} \qquad (4)$$

M represents the dimensionless viscosity ratio, given by the parameters λ_1 and λ_2, which refer respectively to the viscosity of the defending and invading fluid, respectively. M is an important parameter in displacement processes, since it affects both areal and vertical sweep and it classifies the displacement stability. M values higher than unity refer to an unfavorable mobility ratio, while M values lower than unity refer to a favorable mobility ratio (Green and Willhite, 1998).

The primary recovery of petroleum depends on the natural energy from the reservoir and how well the oil is conducted through a complex network of pores in the production well (Speight, 1991). This driving force may arise from liquid expansion and evolution of dissolved gases from the oil when the pressure in the reservoir is reduced during production (Lake, 1989). The energy accumulated in the well must be sufficient to overcome surface forces, hydrostatic pressure and the load losses of the process. Due to low efficiency to overcome that resistive forces involved in the oil flow, primary recovery may leave as much as 70% of the petroleum in the reservoir (Speight, 1991; Triggia et al., 2001). This percentage is even greater in the case of heavy oils.

To increase the recovery factor and the production rates, a supplementary recovery mechanism is required. This supplementary method must be chosen based on the characteristics of the reservoir as well as the system operating parameters and its economic viability. Supplementary recovery methods are generally termed improved oil recovery (IOR), which is a general term that represents any methods that improve the amount of oil recovered by means of operational strategies and supplying additional energy to the well (Thomas, 2008). Improved oil recovery (IOR) methods encompass the Enhanced Oil Recovery (EOR) methods, as well as new drilling and well technologies, intelligent reservoir management and control, advanced reservoir monitoring techniques and the application of different enhancements of primary and secondary recovery processes (Alvarado and Manique, 2010). The additional recovery methods used in more immediate operations involve heating and pumping and injection of material into the well to facilitate the movement of the remaining oil (Lake, 1989; Buttler, 1991; Speight, 1991; Farouq Ali, 2003).

Enhanced Oil Recovery

Enhanced oil recovery (EOR) generally refers to methods applied to reduce the residual oil saturation after primary and secondary recovery methods. EOR is considered to be the third, and sometimes the last, stage of the oil production, in the past times called tertiary production (Donaldson et al., 1985). In these processes, the oil recovery rate depends on the particular characteristics of each reservoir. In fact, reservoirs containing high viscosity oils usually do not respond at all to conventional recovery techniques (Speight, 1991).

The performance of the enhanced oil recovery method is measured by the amount of additional oil that can be economically recovered in relation to that obtained by conventional methods. Improved

recovery processes use thermal and chemical effects and phase behavior properties to reduce or eliminate the capillary forces that trap the oil, diluting it or changing its mobility (Lake, 1989). These processes include waterflooding, caustic flooding, hydrocarbon injection, carbon dioxide flooding, micelar-polymer flooding and several thermal methods, which can be ordered into four major categories - mobility control, thermal recovery, miscible displacement and chemical flooding (Green and Willhite, 1989; Donaldson *et al*., 1985; Rosa *et al*., 2006). The categorizing of these methods is not completely satisfactory since there is some overlap of mechanisms between the categories. Despite these shortcomings, this classification is deeply embedded in the petroleum engineering literature and is quite useful to guide the understanding of the EOR method (Green and Willhite, 1989).

The choice of the method depends on the properties of reservoir fluids and the characteristics of the reservoir rock. Table 7 illustrates the effect of some parameters used as criteria for selection of the enhanced recovery method. The rheological properties of heavy oils and the characteristics of their reservoirs make its production a challenge in the oil industry. For heavy oils, thermal methods are the most successfully, while non-thermal methods have had limited success in real field tests.

Thermal methods are common in technologies used for the production of heavy and ultraviscous oils (van Poolen, 1981; Farouq Ali, 2003; Shah *et al*., 2010). Thermal methods are the most advanced EOR method because of the wide experience in the test field and the technology developed during the many years (almost 6 decades) of their application.

Thermal methods are based on supplying heat to the reservoir. In this way, the improvement in oil recovery is mainly due to the reduction of the oil viscosity and, consequently, to the improvement of the mobility ratio. Besides, the heating of the reservoir induces the expansion of solid and fluid phases, steam distillation and visbreaking (Donaldson, 1985; Lake, 1989; Farouq Ali, 2003; Thomas, 2008), which affect the recovery efficiency. Heat may be supplied to the reservoir through either steam or water injection and also by means of petroleum combustion inside the reservoir (Lake, 1989; Triggia *et al*., 2001) and should ensure an economically viable oil flow. The main processes that use thermal methods for heavy oil recovery are Steam methods, like Cyclic Steam Stimulation (CSS), Steam Flooding (SF) and Steam Assisted Gravity Drainage (SAGD), *In-situ* combustion (ISC) and Hot water flood. However, there is a wide variety of these methods that includes co-injection of steam, solvents and other gases.

Table 7: Screening parameters for some EOR methods (Adapted from Donaldson, 1985).

Screening Parameters	Steam injection	*In-situ* combustion	CO$_2$ Flood	Surfactant-polymer	Polymer	Alkaline Waterflood	Hydrocarbon Miscible
1. Oil viscosity, cP	n.c.	n.c.	< 12	< 20	< 200	< 200	< 5
2. Oil gravity, API	10-25	10-45	> 30	< 25	> 18	15-35	> 30
3. Depth, ft	200-5000	> 500	> 2300	< 8500	< 8500	n.c.	n.c.
4. Reservoir temperature, °F	n.c.	n.c.	n.c.	< 250	< 200	< 200	n.c.
5. Initial reservoir pressure, psig	n.c.	n.c.	> 1200	n.c.	n.c	n.c.	n.c.
6. Net pay, ft	> 20	> 10	n.c.	n.c.	n.c	n.c.	n.c.
7. Permeability, md	n.c.	n.c.	n.c.	> 20	> 20	> 50	n.c.
8. Residual oil saturation, %	50	50	25	> 25	> 50	> 25	> 25
9. Transmissibility, md ft/cp	> 100	> 20	n.c.	n.c.	n.c.	n.c.	n.c.
10. Porosity, %	> 10	> 10	n.c.	n.c.	n.c.	n.c.	n.c.
11. Salinity (TDS), ppm	n.c.	n.c.	n.c.	< 50.000	n.c.	< 2500	n.c.
12. Hardness (Ca and Mg)	n.c.	n.c.	n.c.	< 1000	n.c.	-	n.c.
13. Operating pressure, psi	< 2500	n.c.	> 1100	n.c.	n.c.	n.c.	> 1300
14. Target oil, bbl/acre-ft	> 500	> 400	n.c	n.c.	n.c.	n.c.	n.c.
15. Lithology	n.c.	n.c.	n.c	Sandstone	n.c.	Sandstone	n.c.
16. Well spacing	< 10	< 20	n.c	n.c	n.c	n.c	n.c

n.c.: not critical.

Thermal Methods

Cyclic steam stimulation (CSS) is a strategy of thermal production in which steam is injected into the reservoir under high pressure and high temperature for a long time, which can be as long as a month. After this period, the injection is stopped, allowing the saturation and the heat distribution along of formation, and consequently the oil thinning. Then, a technique known as "huff and puff" is applied to reverse the injector well to producer well, stimulating the production from the same well where the steam was injected. The process is repeated by cycles defined for the oil production rate. Typical recovery factors for CSS are 20% to 40% OOIP with steam/oil ratios of 3 to 5 (National Petroleum Council, 2007). In Steam Flooding, steam is continuously injected into fixed well patterns and creates a hot zone that moves continuously across the reservoir, promoting an oil sweep that can represent a recovery factor of 60% OIP. Steam Assisted Gravity Drainage (SAGD) is a thermal heavy oil recovery process applied to multiple well pairs, parallel and vertically aligned. The SAGD process consists of steam injection into a horizontal well, placed above a parallel horizontal producer in the same vertical plane. After an initial period of conduction heating of both wells by steam circulation in each, steam is continuously injected into the upper injector, while the oil flows down by gravity into the lower producer (Farouq Ali, 2003). SAGD can reach recovery factors up to 55% OIP (National Petroleum Council, 2007). SAGD has received attention in countries with large resources of heavy and extra-heavy oil, especially Canada and Venezuela, owning vast oil sand resources. Many experiences with SAGD have been reported worldwide (Mendoza et al., 1999; Grills et al., 2002; Liqiang, 2006). Canadian commercial applications of the SAGD process have been reported in Athabasca (Alvarado and Manrique, 2010).

In-situ combustion (ISC) is a thermal method in development based on the downhole combustion of a portion of the oil to provide heat and mobilize it and, in some cases, to provide in situ upgrading. In ISC, gas containing oxygen is continuously injected into the reservoir and ignites by contact with the oil, creating a combustion front that propagates itself through the reservoir. Air has usually been the injection gas for production of viscous oils. The heat produced by the ISC process reduces the oil viscosity and consequently improves oil displacement (Yannimaras and Tiffin, 1994; Moore et al., 1995). The heating produces hydrocarbon cracking, light hydrocarbon vaporization and production of water vaporization,

besides the deposition of the heaviest hydrocarbons. Under controlled conditions, the oil consumed to form the combustion front represents only a minor fraction of the oil in-place. In this case, the relative amount of oil displaced and eventually produced results as of economic interesting. The residual oil undergoes changes on its physical and chemical structure and yields a solid or semi-solid material. Oil oxidation reactions are usually divided into low temperature oxidation, fuel deposition and high temperature oxidation, which encompasses different mechanisms (Greaves and Bentaher, 2007). Low-temperature oxidation (LTO) reactions are heterogeneous reactions that occur below 350°C. LTO reactions can increase the amount of fuel available for combustion in the subsequent reactions. Medium-temperature oxidation (MTO) reactions are homogeneous reactions that promote fuel formation and involve hydrocarbon cracking/pyrolysis that leads to the formation of coke. Finally, high temperature oxidation (HTO) reactions are heterogeneous and highly exothermic reactions in which oxygen reacts with the non-oxidized oil. These reactions usually occur at temperatures above 350 °C and they are the main technique responsible for the energy release that promotes the reduction in the oil viscosity and supports combustion (Sarathi, 1999; Greaves and Bentaher, 2007; Vargas et al., 2012).

Variation of the ISC process has been proposed to take into account current technological advances. THAI (Toe-to-Heel Air Injection) is an alternative ISC which integrates in situ combustion and horizontal well technology (Greaves, 2000). CAPRI is a catalytic version of THAI (Xia et al., 2002). However, both THAI and CAPRI are at early stages of evaluation and they are not expected to have an impact on EOR production in the near future (Alvarado and Manrique, 2010).

Other approaches of thermal EOR methods include downhole steam generation, electric heating or electromagnetic heating and microwave technologies (Eson, 1982; Rodriguez et al., 2008; Das, 2008; Hascakir et al., 2008; Alvarado and Manrique, 2010). However, these technologies have not been proven to be technically and economically feasible compared with traditional EOR thermal methods, and they have an insignificant or nil impact on oil production.

Miscible Displacement

Miscible solvent injection is one EOR method largely employed to extract oil from the porous medium (Lake, 1989; Gogarty, 1997) and consists of

injecting a fluid that dissolves or mixes with the oil. Among the fluids used are organic solvents (liquid or gas), surfactants, chemical additives and polymers. The first fluid causes miscible displacement processes since miscibility is the primary recovery mechanism, while the last ones cause chemical flooding that will be discussed in the next section. Carbon dioxide has been indicated as a promising solvent for light oil, mainly in supercritical conditions.

Miscible displacement refers to the recovery processes in which there is no interface between the displacing and displaced fluids (Rosa *et al*., 2006; Shah *et al*., 2010). This means that the interfacial tension between those fluids is zero. In this condition, the fluids reach miscibility and can move across the porous media similar to a homogeneous phase. Miscibility depends on the chemical affinity between the fluids, their composition, the temperature and the pressure (McCain, 1990). To assure the miscibility condition between oil and injection fluid it is necessary to maintain the system under pressure conditions higher than the minimum miscibility pressure (MMP) at a given temperature. The MMP represents the pressure at which contact between oil and injection fluid produces a multicomponent single phase. The MMP can be determined by analytical calculations (Wang and Orr, 1997; Jessen *et al*., 1998), from empirical correlations (Yelling and Metcalfe, 1980; Jonhson and Pollin, 1981; Holm and Josendal, 1982) and by experimental methods (Stalkup, 1983), which include techniques such as rising bubble, slim tube and pendant droplet.

The displacement processes can be categorized as first-contact miscible (FCM) or multiple-contact miscible (MCM). In the FCM process, the displacing fluid forms a single phase immediately after contact with the oil, in all proportions. In the MCM process, miscible conditions are developed during the fluid flow in the reservoir through composition alteration of the injected and displaced fluids (Green and Willhite, 1989; Stalkup, 1983). Miscible displacement can be categorized into three different processes. Miscible slug process, Enriched gas process and High pressure lean gas process (Donaldson *et al*., 1985; Green and Willhite, 1998). These processes use light hydrocarbons as injection fluid and hence they are usually applied in light oil reservoirs.

Besides phase behavior description, EOR methods applying miscible displacement should consider the mass transfer between the displaced and displacing phases (Ancher and Wall, 1986). Mass transfer is particularly important for miscible systems arranged after multicontact processes in which miscibility between the oil and injected fluid is attained through repeated contacts and which has been traditionally called the enriched-gas, or condensing-gas, miscible drive (Ancher and Wall, 1986; Whitson and Brulé, 2000).

Carbon dioxide (CO_2) has been employed as a useful fluid for injection in oil reservoirs because of its wide availability and its singular properties as a supercritical fluid. Although CO_2 injection is a well-established oil recovery method applied to light oil reservoirs, it can be an effective EOR technique for cold heavy oil production, including waterflooding, immiscible CO_2 flooding, and CO_2 water-alternating gas (WAG) (Mai *et al*., 2009; Nasehi and Asghari, 2010; Tchambak *et al*., 2012; Torabi *et al*., 2012). CO_2 is not expected to be miscible with heavy oil and hence the reservoir sweep efficiency is generally lower than that for conventional reservoirs. The use of foam to improve sweep efficiency during CO_2 injection seems to be a logical way to displace the CO_2-diluted oil out of the porous medium. Foam has been proven to be an efficient way to improve the sweep of the injected gas by reducing the effects of low gas viscosity and reservoir heterogeneity (Emadi *et al*., 2011).

Chemical Flooding

Chemical flooding encompasses the injection processes that use special chemical solutions as displacing fluid. These solutions are usually composed of surfactants, polymers and alkali compounds (Donaldson *et al*., 1985; Green and Willhite, 1998) and they are intended to reduce the mobility ratio and to increase the capillarity number. In chemical flooding, the oil recovery is enhanced either by an improvement in the performance of the injected water, such as by polymer addition, or by an increase in the displacement efficiency by means of the formation of surfactant micelles, for instance (Yang and Han, 1991). Emulsions, foams and microbiological agents are also employed, although their impact on EOR production is negligible (Thomas, 2008). For an effective reduction in residual oil saturation, chemical EOR methods must apply chemical solutions that reduce the interfacial tension with displaced crude oil to 10^{-2} dynes/cm (Green and Willhite, 1998).

Surfactants are surface active agents that are able to reduce the oil-water interfacial tension, improving the oil mobility and producing foams and emulsions. Surfactants can also interact with the reservoir rock, changing its wettability. Petroleum sulfonates are the most used surfactants in oilfields (Donaldson *et al*., 1985; Thomas, 2008). The polymer flooding process is based on the injection of water-soluble polymers

constituted by high molecular weight compounds. Polymers promote an increase in the water viscosity and hence increase the resistance to flow, improving the reservoir sweep efficiency, mainly in high permeability regions. Polymers may also be used in gel form for blocking or diverting flow. Polyacrylamides and polysaccharides are the polymers most often used in EOR operations, because they present better efficiency in improving the mobility ratio and reducing permeability (Kessel, 1989; Thomas, 2008).

Alkaline or caustic flooding uses alkali solutions, such as sodium dioxide or sodium carbonate, to react with the acid fractions from crude oil, producing *in-situ* surfactants (Cook *et al*., 1974). These natural surfactants are able to reduce the oil-water interfacial tension, promoting effects similar to those from surfactant flooding (Seifert, 1975; Campbell, 1981). The presence of divalent cations, such as calcium and magnesium, in the formation water can lead to hydroxide precipitation. Generally, alkaline solutions react slowly with silica in sandstones and almost always present no reactivity with dolomite and limestone (Shah *et al*., 2010). Alkaline flooding is in general applied to sandstone reservoirs and is discouraged for application in carbonate reservoirs, because there is an abundance of calcium in the brine.

Whereas polymer and alkaline flooding methods are considered to be processes of moderate complexity, surfactant flooding is among the more complex of EOR methods (Kessel, 1989).

The major limitations for using polymer flooding are the adsorption of polymer onto reservoir rock, polymer degradation and injectivity loss. Similarly to surfactants, polymers may adsorb onto the internal surface of the rock pores, leading to significant losses of chemical that can render chemical flooding prospects economically unattractive.

METHODS TO IMPROVE THE CHARACTERISTICS OF PIPELINE FLOW

Modern lifting techniques and processes of upgrading heavy oils have positively impacted the commercial value of heavy oils, as well as enabling their extraction (Browne *et al*., 1996; Oilfield Review Summer, 2006). From these innovations, many research programs were implemented by oil companies around the world to overcome the problems of transporting viscous petroleum through pipelines in order to guarantee its flow through the long distances that separate the wells from the refineries and ports.

Recently proposed technologies for the transport

of heavy oils should decrease flow resistance to low enough values that the pumping requirements and pipeline size will guarantee that the process will be economically viable (Rimmer *et al*., 1992). A series of methods is capable of providing these features in the process of transporting heavy oils, some of which proved to be promising in field trials and are currently being used, while others are still under development. The most important and current methods for heavy oil transportation can be divided into four major categories: heating, dilution, partial upgrading and lubricated transport.

While heat, dilution and partial upgrading are methods aimed at reducing oil viscosity by modifying its microstructure, lubricated flow (standard oil-in-water emulsion and annular core flow) reduces the effects of frictional pressure caused by the viscous effects produced during draining and is indicated as an emerging technology to replace the conventional processes currently used in the industry (Nunez *et al.*, 1997; Joseph *et al.*, 1997; Bannwart, 2001; Salager *et al.*, 2001; Santos *et al.*, 2011).

In an up-to-date publication, Martinez-Palou *et al*. (2011) presented an extensive discussion on conventional and emergent technologies, including viscosity and friction reduction, to displace viscous oils from the production site to the processing facilities. The authors provide a review of typical methods such as heating and dilution, and also point out innovative solutions to move heavy and extra-heavy oils, such as drag reduction additives, o/w emulsions and pour point depressants. Some of these points are complementarily discussed in a later section in this work.

Heating

Heating has been widely used to move heavy oils in various parts of the world, having its first commercial application in Nahorkatiya and Moran, in India (Chandrasekharan and Sikdar, 1970). The application of heat to improve the flow of viscous oils is based on the reduction of viscosity with increasing temperature, as shown in Figure 5 (Farouq Ali, 2003). The effect of temperature upon viscosity depends mostly on the nature or composition of the oil, but also on other factors, such as volatility (Speight, 1991). For pure compounds and single systems, the temperature effect on the global system is dictating by the solvent properties. However, for complex systems, such as crude oil, an increase in temperature affects mainly the petroleum macromolecular structures, promoting aggregate disruption and keeping monomer units scattered. Flow properties of the

dispersed system should be more favorable than those of the organized macrostructures (Szilas, 1986), improving oil flow resistance.
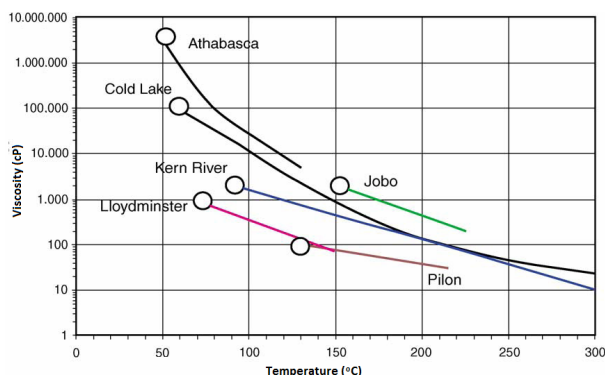

Figure 5: Relation between viscosity and temperature for heavy oils from several oilfields. Circles point to reservoir conditions. (Farouq Ali, 2003).

Equations proposed to represent the viscosity-temperature relationship are commonly of logarithmical or double logarithmical forms. Many of these equations are based on the Eyring (1936) relationship:

$$\eta = \frac{N \cdot h}{V} \cdot \exp\left(\frac{\Delta G^{'}}{RT}\right) \qquad (5)$$

where η, $\Delta G^{'}$ and V represent respectively the absolute viscosity, the Gibbs's activation energy and the molar volume. The parameters h, N and R are respectively the Planck, Avogadro and ideal gas constant parameters. Eyring's equation was the precursor for many others exponential types of viscosity and temperature relations which have been proposed. Among the large number of equations proposed, Walther's equation has been widely applied to represent the viscosity of the oil and its fractions.

$$\log(\log \eta + C) = A + B \cdot \log(T) \qquad (6)$$

where η is the dynamic viscosity, A and B are constants that depend on the nature of the liquid, C is a fixed constant for most oils ($C=0.6$ for viscosities above 1.5 cSt and varies slightly with smaller viscosities) and T is the absolute temperature.

Heat should be applied to the oil to guarantee that its viscosity reaches acceptable values for transport in pipelines. These values typically refer to a maximum viscosity of 500 cP, below which many crude oils can be economically pumped (Nuñez *et al.,* 1998; Rimmer *et al.,* 1992). Heat loss is present during oil flow and heating stations should be planned anticipating gradual cooling in the line. A project involving heated pipelines is not an easy task. It involves technical considerations regarding pipeline expansion, number and capacity of pumping stations and estimates related to heat loss. In addition, cost considerations should be taken into account to heat a large oil volume and to avoid heat loss during in the oil pipeline. Although widely diffused as a method for viscosity reduction for transportation, heating is expensive due to the high cost of heat generation, especially when applying it in cold regions.

Dilution

The mixture of two different oils or petroleum products will result in a product in which the flow properties will be between those of the initial components (Szilas, 1986). Based on this finding, the addition of less viscous crude oils and fractions of distilled petroleum such as condensate, gasoline, kerosene or naphtha to viscous oils has been proposed to reduce the viscosity to acceptable levels for pumping (Nuñez *et al.,* 1998). There is an exponential relationship between the viscosity of the resulting mixture and the volume fraction of diluent, so small fractions of diluents can cause a marked reduction in oil viscosity. Due to the addition of light oils or solvents, the loss of frictional pressure is reduced. The rate of this reduction is greater in lower temperatures (Szilas, 1986).

Limitations to the use of dilution in the transport of heavy oils are imposed by the increasing scarcity of light oils and diluents and their high market values. Diluent reuse is a way to reduce costs, but it requires a high investment to build and operate an additional pipeline system. Light hydrocarbons and natural gas condensates (C_{5+}), which are a byproduct of natural gas processing, are the most widely used diluents today (Sanière *et al.,* 2004). An additional problem is the availability of light oils close to the regions of heavy oil production, making the oil mixture even more difficult.

The scarcity of light oils and diluents and the high cost of heat generation, combined with the costs caused by environmental and climate specific issues, have discouraged the use of dilution for the movement of heavy and viscous oils. The use of diluents with a high added value, such as kerosene, is generally an expensive choice because an amount of about 20% (for bitumen, this percentage may reach 50%) is needed. Dilution with light oils is less efficient and

almost always requires heating the mixture (Yaghi and Al-Bemani, 2002). Even in situations where the viscosity is reduced to acceptable levels for pumping as by the increase in solvent polarity (Gateau *et al*., 2004), there is the need for compatibility testing between the oils to prevent solids precipitation, mostly composed of asphaltenes, and the subsequent pipeline blockage, and building a solvent recovery unit (Sanière *et al.,* 2004), which results in a cost increase.

Partial Upgrading

Upgrading is a heavy oil or bitumen improvement method that uses hydroprocessing to modify the relative proportion of the oil hydrocarbons, making the oil less viscous without altering its refining characteristics. In this process, carbon–carbon bond breaking produces smaller paraffin and olefin molecules, reducing the oil viscosity and making it lighter. Almost always partial upgrading is preferred with regard to total upgrading because the cost of the process and the extension of the upgrading depend on the cost-benefit relation (Figure 6). Hydroprocessing is a broad term that includes hydrocracking, hydrotreating, and hydrorefining.
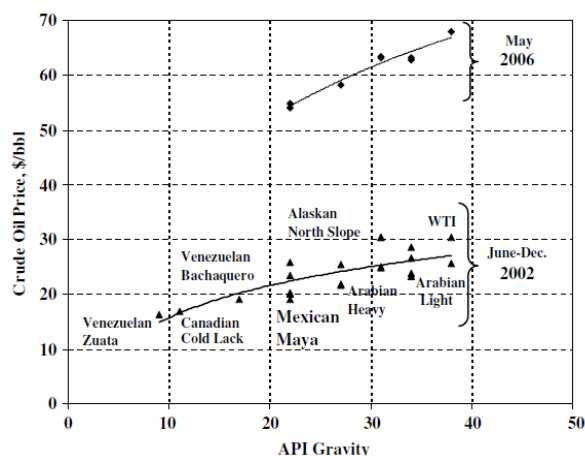

Figure 6: Relationship between crude oil price and API gravity (from Rana *et al*. 2007).

The main goal of upgrading is to improve the quality of the oil or residue, increasing its market value. Residue can represent significant portion of a crude oil barrel and its disposal treatment is not yet up to the mark (Rana *et al*., 2007; Shah *et al*., 2010). In this view, the conversion of residue into more consumable and valuable products is also an environmental issue. On the other hand, the increasing fuel oil demand makes the processing and utilization

of bottom residue from atmospheric distillation and vacuum distillation columns unavoidable.

The partial upgrading process is usually performed in two stages. In the first stage, called *hydrocracking*, the heavy oils are heated along with hydrogen under high pressure to promote molecule rupture, forming smaller and simpler chemical structures. In the second stage, called *hydrotreating*, hydrogen is added to promote hydrogenation without breaking structures and to remove impurities. In the latter stage, the saturation of olefins and the conversion of aromatic compounds into naphthenics occur (Speight, 1991). Hydrocracking of heavy oils causes the scission of macromolecular structures in the oil, changing its properties and the quality of its products. This stage increases the proportion of saturated carbons and aromatics and reduces the amount of asphaltenes and oil resins (Kirkwood *et al*., 2004; Speight, 2004).

In the upgrading process, the hydrogenation process is catalyzed by metals such as nickel, palladium and platinum and can be summarized as a process of carbon rejection and hydrogen addition (Yen, 1998). Since metal catalysts are easily poisoned by sulfur-containing compounds, the operation of the process requires a refined control technique. Carbon rejection processes include visbreaking, thermal cracking, coking, deasphalting, and catalytic cracking, while hydrogen addition processes include catalytic hydrodemetallization, hydrodesulfurization, hydrodenitrogenation, hydrogenation, and hydrocracking fixed bed, moving bed, ebullating bed, or slurry phase reactors (Yen, 1998; Rana *et al*., 2007; Joshi *et al*., 2008).

The method assembly used as the strategy for upgrading depends on the product value and the SARA fraction distribution in the oil (Reynolds *et al*., 1992; Rana *et al*., 2007). Since asphaltenes and resins are the major constituents of heavy oils, these components present the highest impact on the method selection. The implication of this is that a high resin and low asphaltene oil and a low resin and high asphaltene oil must use different upgrading processes, even though both may have the same API gravity (Ancheyta *et al*., 2005; Rana *et al*., 2007).

Lubricated Transportation

Transportation of heavy oils lubricated by water is a technology based on a natural phenomenon in which a less viscous phase migrates to the high shear region near the pipe wall, where it lubricates the flow. Once the pumping pressures are balanced by the wall shear stress, lubricated transport requires

pressures that are comparable to pumping water alone, independent of the oil viscosity (Beretta *et al.,* 1997; Joseph *et al.*, 1997). The oil and water phases can be arranged in various ways during pumping. In horizontal pipes, the most common arrangements are stratified flow based on density, oil-in-water concentrated emulsions (stabilized by surfactants) and core annular flow. The configuration of the phases depends strongly on the flow rate of each fluid (Bannwart, 2001). The arrangements of most interest for transport of heavy oils in pipelines, including elevation ducts, are core annular flow and oil-in-water emulsions.

Core Annular Flow

Core annular flow is a technology based on the formation of a flow pattern in which the oil is transported in the central region of the tube, surrounded by a thin annular aqueous film formed near the wall, lubricating the flow. This flow pattern shows great stability if the liquids have similar densities, are immiscible and do not form emulsions (Bannwart, 1999). The mechanisms of hydrodynamic destabilization of the annular flow originate from capillary forces and inertia (the difference between the interfacial velocity of the fluids), and are evidenced by the deformation of the liquid-liquid interface. Capillary instability is a consequence of surface tension and of the density difference between the liquids.

Core flow has attracted much industrial interest, being the reason for several patents for the transport of heavy oils. Among them, and probably the most important industrial application to date, is in the Shell project in California, in which a 39-km pipeline operates with 30% volumetric water with a flow rate of 24,000 barrels per day. Other examples include the lubricated pipelines in Lake Maracaibo (Venezuela), 35 km in length, and the self-lubricated pipelines of *Syncrude's Canada Ltd.* (Salager *et al.*, 2001).

The accumulation of oil at the pipe walls is one of the main problems encountered in implementing core annular flow – the gradual adherence of oil can cause a blockage in the pipe section, preventing flow. Visser (1989) revealed the tendency of the oil to adhere to the pipeline walls during tests with 9 °API oil with annular flow. Joseph (1997) concluded that, even when the annular flow is hydro-dynamically stable and able to maintain its structure through various line accidents, the oil tends to embed itself in the pipe walls by means of thermodynamic effects that are not included in the studies of hydrodynamic stability.

Although experimental studies show that it is possible to obtain hydrodynamic stability of the system by adjusting the process parameters, the stability of the system is still dependent on thermodynamic aspects (Arney *et al.,* 2001; Bannwart, 2001; Joseph *et al.*, 1997). Santos *et al.* (2006) concluded that the formation of incrustations in oil pipelines is due to the reversal of wettability of the system caused by asphaltenes and naphthenic acids found in the oil. The effects of wettability reversal over the load loss of the system can be avoided or reduced by the addition of sodium meta-silicate to the aqueous phase (Ribeiro, 1994; Liu and Buckley, 1997; Santos *et al.* 2006). These problems can be aggravated by the starting and stopping of the process, where stratification of the phases occurs, and requiring high pressures to restore the system (Sanière *et al.*, 2004).

Crude Oil-in-Water Emulsions

The flow of viscous oil in the form of oil-in-water emulsions is an attractive route for the hydraulic transport of heavy oils because emulsification can reduce viscosity to values of 50-200 cP (Rimmer *et al.*, 1992), in which it can be easily pumped (Ahmed *et al.*, 1999; Yaghi and Al-Bemani, 2002; Langevin *et al.*, 2004; Santos *et al.,* 2010). Furthermore, emulsion technology can improve residual oil removal from mature fields that are not as efficiently recovered by traditional methods that apply heat or diluents (Kokal *et al.*, 1992).

The transport of emulsified heavy oil had its technological viability clearly demonstrated by the development of the pioneer process of large-scale fuel emulsions, ORIMULSIONS®, applied for the generation of energy in thermal plants by the state-owned company PDVSA in Venezuela (Salager *et al.*, 2001; Langevin *et al.*, 2004). Another strategy for implementing the technology of oil-in-water emulsions predicts the separation of the oil and water phases at the refinery entrance, after transport, for subsequent treatment (upgrade, desalinization and distillation). In this case, the technology must take into account the oil-in-water emulsion preparation with properties that allow for crude oil recovery at the end of the pumping process in a simple and economical way.

Several field studies have supported the viability of oil-in-water emulsions as a technology for transportation of viscous oils. Emulsion flow rate tests performed with 13° API oil from a field in Shanjiasi (China), reported by Zhang *et al.* (1991), show a reduction in pressure loss by as much as 80%, which was achieved by emulsions formulated with water fractions around 0.6-0.8. This reduction in pressure

occurred especially when the tests were conducted in more drastic conditions, such as with extra-viscous oils and at low temperatures. A joint project between BP Canada and the Alberta Energy Company has developed TRANSOIL®, a technology that is comprised of the steps of oil emulsification, characterization of transport properties, and evaluation of storage and recovery conditions by de-emulsification (Stockwell *et al.*, 1988). The emulsions obtained were pumped continuously for six days at 80 m³/day and stored for six days without any sign of degradation. The demulsification produced 0.5% BSW for the heavy oil and less than 100 ppm oily contaminants in the separated water.

Finally, oil-in-water emulsions can be considered for applications in improved recovery processes of heavy oils and for the increase in the recovery factor of mature fields (Lissant, 1997), including the amounts not retrieved from the exhausted fields of light oils (Giuggioli and De Ghetto, 1995). Bertero *et al.* (1994) tested heavy oil emulsification in Sicily and the Adriatic Sea (Italy) for application in transport and production. The system was based on the injection of an emulsifying aqueous phase into the well without any modification to the existing system. Contact with the oil in the well produced oil-in-water emulsions with 70% dispersed oil. The emulsions showed a viscosity 30-50 times lower than that obtained with dilution and produced an increase four times greater in oil productivity when compared to conventional production by diesel dilution.

FINAL REMARKS

In spite of the recent discoveries of giant oilfields of conventional oils, heavy oil and bitumen still represent a large amount of the worldwide oil reserves. Heavy oil reserves may be essential to supply the global energy demand of fuels and petroleum derivatives if oil cost is favorable and if suitable technology is available to produce and transport these oils. The strategy to move these oils depends on the oil properties, such as viscosity, API gravity and asphaltene content, and its potential to yield high value products after the distillation process.

Many methods has been proposed to move viscous oils; however, many of them fail with regard to commercial application, either as a recovery method or as a method for improving pipeline flow. In the first case, thermal methods has been the most successful because of the wide experience acquired during the long period of their utilization. Among the thermal methods, cyclic steam stimulation is espe-

cially promising because it has fast payout, although the recovery factors achieved can be considered to be low in relation to other thermal methods. Today chemical flooding brings a large technical efficiency, but aspects related to its technological complexity and its high level of expertise and experience needed to successfully implement it in the oilfield should be taken into account to preserve the economic requirements. Recent technological advances and the current demand for climate issues have resulted in a renewed interest in some past enhanced oil recovery methods and future challenges can change entirely EOR characteristics.

Piping of heavy oil is expensive due to the elevated resistance encountered in the flow of these oils. Since this resistance has its origin in the heavy oil composition, the most successful methods to improve the pipeline flow properties of heavy oils aim to modify the oil microstructure. Therefore, partial upgrading has received wide attention in the last few years, though its field operation requires substantial technological improvement. Heating and dilution have been the most widely applied methods in pipeline transportation of heavy oils, even with the disadvantage of the expensive cost of heat and the scarcity of diluents and lights oils with which the heavy oil could be mixed. Lubricated pipeline methods are attractive proposals for the reduction of the maintenance and cleaning costs, besides the increase in flow rate and energy savings promoted by decreasing the flow friction losses. Despite the benefits, field tests must be carried out to evaluate aspects such as formulation and emulsifier costs, for o/w emulsions, and hydrodynamic stability, for core flow.

NOMENCLATURE

A, B and C	Constants of the Walther equation
ANP	National Petroleum Agency (Brazil)
BOPD	Barrels Oil Per Day
BP	British Petroleum
BSW	Basic Sediments and Water
Ca	Capillary number
C_{n+}	Hydrocarbon fraction containing compounds with carbon chain length higher than n
CSS	Cyclic Steam Stimulation
d_r	Relative density
EOR	Enhanced Oil Recovery
GOR	Gas-Oil Ratio
h	Planck constant

IEA	International Energy Agency
IOR	Improved Oil Recovery
ISC	*In-Situ* Combustion
LPG	Liquefied Petroleum Gas
M	Viscosity ratio
MMP	Minimum Miscibility Pressure
N	Avogadro constant
ºAPI	American Petroleum Institute for oil gravity
OIP	Oil in Place
R	Ideal gas constant
SAGD	Steam Assisted Gravity Drainage
SARA	Saturate, Aromatic, Resin and Asphaltene Fractions
SF	Steam Flooding
V	Flow velocity through the pore
V	Molar volume
γ	Interfacial tension
η	Absolute viscosity
$\Delta G'$	Gibbs activation energy

REFERENCES

Ahmed, N. S., Nassar, A. M., Zaki, N. N. and Gharieb, H. Kh., Formation of fluid heavy oil-in-water emulsions for pipeline transportation. Fuel, 78, 593-600 (1999).

Ali, M. A. and Nofal, W. A., Application of high performance liquid chromatography for hydrocarbon group type analysis of crude oils. Fuel Science and Technology International, 12, 21-33 (1994).

Alvarado, V. and Manrique, E., Enhanced oil recovery: An update review. Energies, 3, 1529-1575 (2010).

Ancheyta, J., Sanchez, S. and Rodrıguez, M. A., Kinetic modeling of hydrocracking of heavy oil fractions: A review. Catalysis Today, 109, 76-92 (2005).

ANP, Portaria Nº 009 de 21 de Janeiro de 2000. Agência Nacional do Petróleo, Rio de Janeiro (2000). (In Portuguese).

Arney, M. S., Ribeiro, G. S., Guevara, E., Bai, R. and Joseph, D. D., Cement-line pipes for water lubricated transport of heavy oil. International Journal of Multiphase Flow, 22, 207-221 (1996).

Bannwart, A. C., A simple model for pressure drop in core-annular flow. Revista Brasileira de Ciências Mecânicas, 21, 233-244 (1999).

Bannwart, A. C., Modeling aspects of oil–water core–annular flows. Journal of Petroleum Science and Engineering, 32, 127-143 (2001).

Beasley, C., Castel, B., Zimmerman, T., Lestz, R., Yoshioka, K., Long, A., Lutz, S. J., Riedel, K., Sheppard, M. and Sood, S., Mining heat. Oilfield Review, 21, 4, 4-13 (2010).

Beretta, A., Ferrari, P., Galbiati, L. and Andreini, P. A., Horizontal oil-water flow in small diameter tubes: Pressure drop. International Communications in Heat and Mass Transfer, 24, 231-239 (1997).

Bertero, L., Dilullo, A., Lentini, A. and Terzi, L. An innovative way to produce and transport heavy oil through dispersion in water: Laboratory study and field test results. 69th Annual Technical Conference and Exhibition, New Orleans, LA, September 25-28 (1994).

Browne, G. E., Hass, G. R. and Sell, R. D., Downhole emulsification: Viscosity reduction increases production. The Journal of Canadian Petroleum Technology, 35, 25-31 (1996).

Buckley, J. S., Liu, Y., Xie, X. and Morrow, N. R., Asphaltenes and crude oil wetting - the effect of oil composition. SPEJ, 107-119 (1997).

Butler, R. M., Thermal Recovery of Oil and Bitumen. Prentice Hall, New Jersey USA (1991).

Campbell, C. J. and Laherrère, J. H., The end of cheap oil. Scientific American, March (1998).

Campbell, T. C., The Role of Alkaline Chemicals in Oil Displacement Mechanisms. In: D. O., Shah, Ed., Surface Phenomena in Enhanced Oil Recovery. Plenum Press, New York, NY, p. 293 (1981).

Capeleiro Pinto, A. C., Branco, C. C., de Matos, J. S., Vieira, P. M., da Silva Guedes, S., Pedroso, C. J., Decnop Coelho, A. C. and Ceciliano, M. M., Offshore heavy oil in Campos basin: The Petrobras experience. OTC 2003, Houston, May (2003).

Chandrasekharan, K. P. and Sikdar, P. K., Here's how waxy Indian crude is prepared for pipeline transit. Oil & Gas International, 10, 85-95 (1970).

Cook, Jr. C. E., Williams, R. E. and Kolodzie, P. A., Oil recovery by alkaline waterflooding. Journal of Petroleum Technology, 1, 1365-1374 (1974).

Das, S., Electro-magnetic heating in viscous oil reservoir (SPE-117693). In: Proceedings of International Thermal Operations and Heavy Oil Symposium, Calgary, AB, Canada, 20-23 October (2008).

Donaldson, E. C., Chilingarian, E. V., Yen, T. F., Enhanced Oil Recovery I – Fundamentals and Analyses. Elsevier Sci. Pub., Armsterdan (1985).

Emadi, A., Sohrabi, M., Jamiolahmady, M., Ireland, S. and Robertson, G., Mechanistic study of improved heavy oil recovery by CO_2-foam injection. Society of Petroleum Engineers - SPE Enhanced Oil Recovery Conference 2011, EORC v. 1, p. 67-85 (2011).

Eson, R. L., Downhole Steam generator – field tests

(SPE-10745). In: Proceedings of SPE California Regional Meeting, San Francisco, March 24-26 (1982).

Fan, T., Wang, J. and Buckley, J. S., Evaluating crude oils by SARA analysis. In: Proceedings of SPE/DOE Improved Oil Recovery Symposium, 13-17 April 2002, Tulsa, Oklahoma (2002).

Farouq, A., Heavy oil - evermore mobile. Journal of Petroleum Science and Engineering, 37, 1-2 (2003).

Gateau, P., Hénaut, I., Barré, L. and Argillier, J. F., Heavy oil dilution. Oil and Gas Science and Technology, 59, 503-509 (2000).

Giuggioli, A. and De Ghetto, G., Innovative technologies improve the profitability of offshore heavy oil marginal fields. International Meeting on Petroleum Engineering, Beijing, November, 14-17 (1995).

Gogarty, W. B., Oil Recovery with Surfactants: History and a Current Appraisal. In: Improved Oil Recovery by Surfactant and Polymer Flooding. Shah, D. O. and Schechter, R. S., (Eds.) Academic Press, UK (1997).

Greaves, M., Bentaher, A. H., Exothermicity characteristics of wolf lake heavy oil, Athabasca tar sand and clay medium heavy oil. J. Can Petrol. Technol., 46, 16-19 (2007).

Greaves, M., El-Sakr, A., Xia, T. X., Ayasse, A. and Turta, A. T., Thai—new air injection technology for heavy oil recovery and in situ upgrading. Journal of Canadian Petroleum Technology, 40(3), 1-10 (2000).

Green, D. W. and Willhite, G. P., Enhanced Oil Recovery. SPE Textbook Series, Soc. Petroleum Eng., Houston, USA (1998).

Hascakir, B., Acar, C., Demiral, B., Akin, S., Microwave assisted gravity drainage of heavy oils (IPTC-12536). In: Proceedings of International Petroleum Technology Conference, Kuala Lumpur, Malaysia, December 3-5 (2008).

Head, I. M., Jones, D. M. and Larter, S. R., Biological activity in the deep subsurface and the origin of heavy oil. Nature, 426, 344-352 (2003).

Hinkle, A., Shin, E. J., Liberatore, M. W., Herring, A. M. and Batzle, M., Correlating the chemical and physical properties of a set of heavy oils from around the world. Fuel, 87, 3065-3070 (2008).

Holm, L. W., Josendal, V. A., Effect of oil composition on miscible type displacement by carbon dioxide. Journal of Petroleum Technology, 87-98 (1982).

IEA, Energy Technology Perspectives: Scenarios and Strategies to 2050. Beijing, China. July (2006).

Jessen, K., Michelsen, M. L., Stenby, E. H., Global approach for calculation of minimum miscibility pressure. Fluid Phase Equilibria, 153, 251-263 (1998).

Joseph, D. D., Lubricated pipelining. Powder Technology, 94, 211-215 (1997).

Joshi, J. B., Pandit, A. B., Kataria, K. L., Kulkarni, R. P., Sawarkar, A. N., Tandon, D., Ram Y. and Kumar, M. M., Petroleum residue upgradation via visbreaking: A review. Ind. Eng. Chem. Res., 47, 8960-8988 (2008).

Kessel, D. G., Chemical flooding - status report. Journal of Petroleum Science and Engineering, 2, 81-101 (1989).

Kirkwood, K. M., Foght, J. M. and Gray, M. R., Prospects for biological upgrading of heavy oils and asphaltenes. Studies in Surface Science and Catalysis, 151, R. Vazquez-Duhalt and R. Quintero-Ramirez (Eds.), 113-143 (2004).

Kokal, S. L., Maini, B. and Woo, R., Flow of emulsions in porous-media. In: Advances in Chemistry Series, 231, 219-262 (1992).

Kovarik, B., The Oil Reserve Fallacy. Proven Reserves Are not a Measure of Future Supply. <http://www.radford.edu/~wkovarik/oil.html> (Accessed: April 10, 2011).

Lake, L. W., Enhanced Oil Recovery. Prentice Hall, Englewood Cliffs (1989).

Langevin, D., Poteau, S., Hénaut, I., Argillier, J. F., Crude oil emulsion properties and their application to heavy oil transportation. Oil & Gas Sci. and Technol., 59, 511 (2004).

Lanier, D., Heavy oil - a major energy source for the 21st century. UNITAR Centre for heavy crude and tar sands, No. 1998.039 (1998).

Lissant, K. J., Emulsification and Demulsification in Oil Recovery. In: Improved Oil Recovery by Surfactant and Polymer Flooding. Shah, D. O. and Schechter, R. S., Eds. Academic Press, UK (1997).

Liu, Y. and Buckley, J. S., Evolution of wetting alteration by adsorption from crude oil. SPEFE, 5-11 (1997).

Loh, W., Mohamed, R. S. and Santos, R. G., Crude Oil Asphaltenes: Colloidal Aspects. In: P., Somasundaram, (Org.), Encyclopedia of Colloid and Surface Science. New York: Taylor & Francis (2007).

Lundanes, E. and Greibrock T., Separation of fuels, heavy fractions, and crude oils into compound classes: A review. J. High Res. Chrom., 17, 997-202 (1994).

Mai, A. and Kantzas, A., Heavy oil waterflooding: Effects of flow rate and oil viscosity. Journal of

Canadian Petroleum Technology, 48(3) 42-51 (2009).

Martínez-Palou, R., Mosqueira, M. L., Zapata-Rendón, B., Mar-Juárez, E., Bernal-Huicochea, Clavel-López, J. C. and Aburto, J., Transportation of heavy and extra-heavy crude oil by pipeline: A review. Journal of Petroleum Science and Engineering, 75, 274-282 (2011).

McCain, W. D., The Properties of Petroleum Fluids. PennWell Pub. Co. Tulsa, Oklahoma (1990).

Meyer, R. F. and Attanasi, E. D., Heavy oil and natural bitumen: Strategic petroleum resources. United States Geological Survey USGS (2003).

Moore, R. G., Laureshen, C. J., Belgrave, J. D. M., Ursenbach, M. G. and Mehta, S. A., In situ combustion in Canadian heavy oil reservoirs. Fuel, 74, 1169-1175 (1995).

Nasehi, M. and Asghari, K., Use of CO_2 in heavy-oil waterflooding. SPE International Conference on CO_2 Capture, Storage, and Utilization, p. 474-486, November 12 (2010).

National Petroleum Council, Heavy oil, extra-heavy oil and bitumen unconventional oil. NPC Global Oil and Gas Study, July (2007).

Nuñez, G., Guevara, E. and Gonzalez, J., Highly viscous oil transportation methods in the Venezuela industry. Proceeding of the 15th World Petroleum Congress, 495-502 (1998).

Oilfield Review Summer, Highlighting heavy oil. Schlumberger Oilfield Review Summer, 18, 2 (2006).

Oliveira, R. C. G. and Carvalho, C. H. M., Influência do tipo de emulsão sobre a reologia do petróleo de Marlim. I Seminário de Tecnologia de Produção. Petrobrás (1993). (In Portuguese).

Petrobras, <http://www2.petrobras.com.br> Petroleum Communication Foundation, Canada's oil sands and heavy oil. April (2000). (In Portuguese).

Rana, M. S., Sámano, V., Ancheyta, J. and Diaz, J. A. I., A review of recent advances on process technologies for upgrading of heavy oils and residua. Fuel, 86, 1216-1231 (2007).

Reynolds, B. E., Brown, E. C. and Silverman, M. A., Clean Gasoline via VRDS/RFCC. Hydrocarbon Process, 43 (1992).

Ribeiro, G. A. S., Topics in the transport and rheology of heavy crude oils. PhD Thesis, University of Minnesota (1994).

Rimmer, D. P., Gregoli, A. A., Hamshar, J. A. and Yildirim, E., Pipeline Emulsion Transport for Heavy Oils. In: Emulsions: Fundamentals and Applications in the Petroleum Industry. L. L. Schramm, Ed. American Chemical Society, Washington, DC, USA (1992).

Rodríguez, R., Bashbush, J. L., Rincón, A., Feasibility of using electrical downhole heaters in Faja heavy oil reservoirs (SPE-117682). In: Proceedings of International Thermal Operations and Heavy Oil Symposium, Calgary, AB, Canada, 20-23 October (2008).

Rosa, A. J., Carvalho, R. S. and Xavier, J. A. D., Engenharia de Reservatórios de Petróleo. Interciência. Interciência, São Paulo (2006). (In Portuguese).

Salager, J. L., Briceno, M. I. and Brancho, C. L., Heavy Hydrocarbon Emulsions. In: Encyclopedic Handbook of Emulsion Technology, Sjöblom, J. (Ed.), Marcel Dekker, New York (2001).

Sanière, A., Hénaut, I. and Argillier, J. F., Pipeline transportation of heavy oils - a strategic, economic and technological challenge. Oil & Gas Science and Technology, 59, 455-466 (2004).

Santos, R. G., Bannwart, A. C. and Loh, W., Physico-chemical properties of heavy crude oil-in-water emulsions stabilized by mixtures of ionic and non-ionic ethoxylated nonylphenol surfactants and medium chain alcohols. Chemical Engineering Research and Design, 89, 957-967 (2011).

Santos, R. G., Mohamed, R. S., Bannwart, A. C. and Loh, W., Contact angle measurements and wetting behavior of inner surfaces of pipelines exposed to heavy crude oil and water. Journal of Petroleum Science and Engineering, 51, 9-16 (2006).

Seifert, W. K., Carboxylic Acids in Petroleum Sediments. Prog. Chem. Nat. Prod., Springer, NY, p. 1 (1975).

Shah, A., Fishwick, R., Wood, J., Leeke, G., Rigby, S. and Greaves, M., A review of novel techniques for heavy oil and bitumen extraction and upgrading. Energy Environ. Sci., 3, 700-714 (2010).

Speight, J. G., Chemical and Physical Studies of Petroleum Asphaltenes. Yen, T. F., Chilingarian, G. V., Eds. 1st Ed., Asphaltenes and Asphalts. Elsevier Science B. V., Amsterdam, The Netherlands, 7-65 (1994).

Speight, J. G., The Chemistry and Technology of Petroleum. Marcel Dekker, Inc. (1991).

Stalkup, F. I., Miscible Displacement. SPE, Richardson, TX (1992).

Stockwell, A., Sit, S. P. and Hardy, W. A., Transoil technology for heavy oil transportation. results of field trials at wolf lake. Paper SPE 18362 presented at SPE European Petroleum Conference, October 16-19, 249, London, UK (1988).

Suslick, S. B., Schiozer, D. J., Nepomuceno, F. and Furtado, R., Forecasting the development of heavy-oil reserves in ultra-deep waters using technological risk models. SPE Hydrocarbon

Economics and Evaluation Symposium, 5-8 April, Dallas, Texas, USA (2003).

Szilas, A. P., Production and Transport of Oil and Gas. Gathering and Transportation. Elsevier, New York (1986).

Tchambak, E., Oyeneyin, B. and Oluyemi, G., Heavy oil recovery: A cold process using CO_2-EOR technique. Advanced Materials Research, 367, 421-429 (2012).

Thomas, S., Enhanced oil recovery – an overview. Oil & Gas Science and Technology – Rev. IFP, 63, 9-19 (2008).

Torabi, F., Jamaloei, B. Y., Zarivnyy, O., Paquin, B. A. and Rumpel, N. J., The evaluation of variable-injection rate waterflooding, immiscible CO_2 flooding, and water-alternating-CO_2 injection for heavy oil recovery. Petroleum Science and Technology, 30(16), 1656-1669 (2012).

Trevisan, O. V., Lisboa, A. C. L., França, F. A. and Trindade, W., Oil production in offshore fields: An overview of the Brazilian technology development program. World Heavy Oil Conference, 1-7, Pequim, China (2006).

Triggia, A. A., Correia, C. A., Filho, C. V., Xavier, J. A. D., Machado, J. C. V., Thomas, J. E., Filho, J. E. S., Paula, J. L., Rossi, N. C. M., Pitombo, N. E. S., Gouveia, P. C. V. M., Carvalho, R. S. and Barragan, R. V., Fundamentos de Engenharia de Petróleo. Rio de Janeiro: Interciência (2001). (In Portuguese).

van Poolen, H. K., Fundamentals of Enhanced Oil Recovery. Pennwell Publishers, Tulsa, Okla. (1981).

Visser, R. C., Offshore production of heavy oil. Journal of Petroleum Technology, 41, 67-70 (1989).

Wang, Y. and Orr, F. M., Analytical calculation of minimum miscibility pressure. Fluid Phase Equilibria, 139, 101-124 (1997).

Wehunt, C. D., Burke, N. E., Noonan, S. G. and Bard, T. R., Technical challenges for offshore heavy oil field developments. Offshore Technology Conference Proceedings, Paper 15281 (2003).

Xia, T. X., Greaves, M., Werfilli, W. S., Rathbone, R. R., Downhole conversion of Lloydminster heavy oil using THAI-CAPRI Process (SPE-78998). In: Proceedings of SPE International Thermal Operations and Heavy Oil Symposium and International Horizontal Well Technology Conference, Calgary, AB, Canada, 4-7 November (2002).

Yaghi, B. M. and Al-Bemani, A., Heavy crude oil viscosity reduction for pipeline transportation. Energy Sources, 24, 93-102 (2002).

Yannimaras, D. V. and Tiffin, D. L., Screening of oils for *in-situ* combustion at reservoir conditions by accelerating-rate calorimetry. SPE/DOE Symposium on Improved Oil Recovery held in Tulsa, April 17-20 (1994).

Yellig, W. F. and Metcalfe, R. S., Determination and Prediction of CO_2 Minimum Miscibility Pressures. Journal of Petroleum Technology, 32, 160-165 (1980).

Zhang, J., Chen, D., Yan, D., Yang, X. and Shen, C., Pipelining of heavy crude oil as oil-in-water emulsions, SPE 21733. SPE Production Operations Symposium, 7-9 April, Oklahoma City, Oklahoma (1991).