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# Chapter

# Flow of Heavy Oils at Low Temperatures: Potential Challenges and Solutions

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#### **Abstract**

Global demand for non-conventional heavy and extra-heavy oil has been marginal until the end of twentieth century because of their composition complexity and high viscosity that cause many operational difficulties in the production with decline of their economic viability. However, growing energy demands in the beginning of the twenty-first century motivate many countries to handle such non-conventional resources. Heavy extra-heavy crudes usually have higher pour points due to high content of high molecular weight components, such as waxes, asphaltenes, and resins. The structural changes for these components cause abrupt rise in oil viscosity and simultaneous deposition of wax and asphaltene on the inner walls of pipelines. This can cause clogging of pipes accompanying oil flowability reduction with extra burden on the pumping system and consequently increases its power requirement and cost. This chapter presents technological challenges in transportation, describing the different mitigation strategies that have been developed to improve the low-temperature flow properties of heavy crude oils (heating, dilution, oil-in-water emulsion, and upgrading and core annular flow).

**Keywords:** heavy crude oils, cold flow, heating, dilution, oil-in-water emulsion, upgrading, core annular flow

#### 1. Introduction

The continual global demand for petroleum fuels led to the decrease in supply from conventional reservoirs. Where, the conventional light oils had typically been produced at a high rate and a low cost. Therefore, the plateau in conventional oil production and the corresponding increase in the demand for liquid fuels have motivated markets to respond with higher oil prices and subsequently have stimulated in the global oil industry the advancement in technologies for the exploitation of reservoirs of transitional and unconventional oils [1, 2]. An array of these new oils including oil sands, tight oil, heavy oils (including extra-heavy oils and bitumen), deep water oil, and eventually oil shale are projected to fill the gap through the next few decades and that could continue to be revised upward as new technologies are developed so that they could dominate the liquid-fuel supplies through the endings of the twenty-first century especially regarding the global abundance of these new oil supplies.

The oil industry is expected to invest huge sums in petroleum production and oil infrastructure in the years ahead, up to an estimated \$1 trillion over the next decade alone. Without a concerted policymaking effort, these investments will likely continue to flow disproportionately toward unconventional oils. The involvement of unconventional crude oils in the international energy markets faces serious difficulties that need certain technological developments in the production, refining and transportation [3].

As conventional crude oil supplies have peaked and leveled off globally in recent years, oil has begun to transition, the makeup and geography of the new or tomorrow's oil, however, will be dramatically different from the current ones. Generally, the International Energy Agency defines conventional oil as "a mixture of hydrocarbons that exist in liquid phase under normal surface conditions". Meanwhile, unconventional oils are defined as those oils obtained by unconventional production techniques because they cannot be recovered through pumping in their natural state from an ordinary production well without being heated or diluted. By other words, unconventional oils require new, highly energy intensive production techniques and new processes to deal with their inaccessible placements or unusual compositions. In this context, the U.S. Department of Energy divides unconventional oil into four types: heavy oil (HO), extra-heavy oils (EHO), bitumen, and oil shale. Moreover, some analysts include oils produced from natural gas or coal using gas-to-liquids (GTL) processes and coal-to-liquids (CTL) processes in the unconventional oil category. These unconventional oil-processing techniques broaden the feedstock of unconventional oils to include unconventional natural gas, such as tight gas, shale gas, coal-bed methane, and methane hydrates [4] (**Figure 1**).

These new oils are an abundant untapped potential energy source, which is expected to be a large contributor to the world's energy needs in the future.

Conventional Oils	Transitional Oils	Unconventional Oils	
	All Oils		
Crude oil			
Natural gas liquids (NGLs)			
Condensate			
	Heavy oil		
	Ultra-deep oil		
	Tight shale oil		
		Extra-	
		heavy oil	
		Oil sand/	
		bitumen	
		Oil shale/	
		kerogen	C 4-
			Gas-to- liquids
			Coal-to-
			liquids

Figure 1.
Transformation of liquid fuels.

However, these oils tend to be less valuable than conventional crude in addition to the technological costs per barrel that are currently much higher than for conventional resources, which is readily transformed into the most marketable petroleum products by today's standards.

# 2. Physico-chemical properties of new crude oils

Crude oil is a mixture of different compounds consisting of hydrocarbons, heteroatoms, and metals. The various compounds can differ widely in molecular structure, volatility, density and viscosity. These compounds are usually divided into fractions: saturates, aromatics, resins and asphaltenes (SARA). The saturate fraction is non-polar and includes linear, branched and cyclic alkanes. Long-chain linear alkanes ( $>C_{20}$ ) are known as waxes, or paraffinic waxes, and can make oil recovery challenging as the wax becomes solid at low temperatures. Aromatics are slightly more polar and consist of one or more aromatic rings connected by double bonds. Saturates and aromatics constitute the majority of the crude oil. Resins and asphaltenes are the most polar heavy molecules and complex components in crude oil. The majority of heteroatoms and metals are found in these fractions. Conventional oils are hydrogen-rich compounds with relatively short hydrocarbon chains, fewer carbon atoms (C<sub>1</sub>–C<sub>60</sub>), and lower molecular weights than most unconventional oils (around 200) where hydrogen packs all of the energy while carbon goes along for the ride [5]. The physical properties and grade of oil depends on the dominance of one of the hydrocarbons or its fractions in its composition. The light conventional crude oil has low density where several of the molecules are volatile, while the unconventional heavy oils have high density and high viscosity where resins, paraffins and asphaltenes are found at a higher amount than those in light crude oil [6, 7]. These oils require special treatments for their extraction and transportation according to their content of these compounds. Regarding the close relation between the physical properties of crude oil with these content, it is worthy to mention that the crude oils can be categorized based on the paraffin content into; less paraffin-oils (paraffins < 1.5%), paraffinic or waxy oils (paraffins = 1.5–6%) and high paraffin- oils (paraffins > 6%). Also, the crude oils can be categorized based on their content of resins into; less resins-oils (resins < 8%), resinous oils (resins = 8-25%) and high resins-oils (resins > 25%). Additionally, sulfur and vanadium are present in high concentrations in heavy oils and lead to reduce its quality and cause many problems through extraction, transportation, storage, and refining of these oils as a result of the side reactions of these compounds causing the corrosion effects on pipelines, boilers, and storage tanks. In this context, the crude oils can be also categorized based on their content of the sulfur compounds into; sweet oils (total sulfur level < 0.5%), sour oils (total sulfur level > 0.5–1.9%) and highly sour oils (total sulfur level > 1.9%). These sour crude oils containing larger amounts of the impurity sulfur, an extremely corrosive element that is difficult to process, and deadly when released hydrogen sulfide gas.

Generally, transitional oils have compositions comparable for that of conventional oils; however, they are extracted by unconventional means. As conventional oils become less accessible, new, more technical, energy-intensive methods are being developed for their recovery, from ultra-deep wells drilled miles below the sea to fracturing shale rock in order to tap oil trapped in low-permeability siltstones, sandstones, and carbonates deep in the earth. Meanwhile, heavy oils are tricky to extract, requiring gas injection and other invasive techniques due to their high, molasses-like viscosities that approach those of unconventional oils. On other hand, the unconventional oils are typically much heavier and sourer than even the

Location	High Quality Range	Low Quality Range
Africa	Nigeria (Agbami Light) 47°, 0.04%	Angola (Kuito) 19°, 0.68%
Asia	Indonesia (Senipah Condensate) 54°, 0.03%	China (Peng Lai) 22°, 0.29%
Australia	Bayu Undan 56°, 0.07%	Enfield 22°, 0.13%
Europe	Norway (Snohvit Condensate) 61°, 0.02%	UK (Alba) 19°, 1.24%
Middle East	Abu Dhabi (Murban) 39°, 0.8%	Saudi Arabia (SA heavy) 27°, 2.87%
North America	US (Williams Sugarland Blend) 41°, 0.20%	Canada (Albian) 19°, 2.1%
Latin America	Columbia (Cupiaga) 43°, 0.14%	Venezuela (Bascan) 10°, 5.7%
Central Asia	Kumkol (Kazakhstan) 45°, 0.81%	Russia (Espo) 35°, 0.62%

Benchmark Crudes: Brent 38°, 0.37%; WTI (West Texas Intermediate) 40°, 0.24%; Dubai 31°, 2.0%.

**Table 1.**The composition of crude barrel originating from various regions.

lowest-quality conventional oil, where the heavier oils such as, oil sand (bitumen) and oil shale (kerogen), are the more carbon laden, higher in sulfur, and filled with toxic impurities. And therefore, conventional light oils tend to deliver more productivity with less waste than unconventional oils.

Crude oil make-up is highly dependent on the origin and depth of reservoir. Whereat no two sources are alike, no two crudes are exactly alike or have the same make-up. However, there can be a great deal of variation within a range. The natural resources range from high-quality "light, sweet" crudes to lower-quality "heavy, sour" crudes based on their region (**Table 1**).

The physical properties of crude oils are highly related to their make-up. Furthermore, the technological conditions applied during exploration, drilling, transportation and storage of these oils can affect strongly their physical properties. On the other side, the physical parameters have to be in the allowable ranges to achieve the highest potential yield technologically and economically. Density and viscosity are the most important physical properties affecting the flowability of the crudes. Such flowability has a great and clear impact through the transportation and storage of these liquid hydrocarbons, especially for new unconventional ones. Where, some of these new hydrocarbon resources are effectively solid and must be removed through mining or heated in place (in situ) until they flow. Extra-heavy, impure oils also require very large energy inputs to upgrade and preprocess into synthetic crude oil that is then processed by a refinery (known as feedstock). Therefore, such key properties determine the economics of a heavy oil field development. Generally, heavy oil sells at a lesser price than lighter hydrocarbons, as it will have to go through an energy intensive upgrading process before use. On the other hand, high viscosity values lead to lower production and more expensive enhanced oil recovery (EOR) investments.

The density of the oils is measured on a scale known as API gravity developed by the American Petroleum Institute and the National Bureau of Standards developed a scale of the density of liquid petroleum products. The gravity scale is calibrated in terms of API degrees, which equals:

$$(141.5/\text{Specific gravity (SG) at }60^{\circ}\text{F}) - 131.5$$
 (1)

The lighter crudes have the higher API gravity. If the API gravity is greater than 10, the oil is lighter and floats on water; if less than 10, it is heavier and sinks. Generally, API gravity of light crudes exceeds 38°. However, it is commonly below 22° for heavy crudes. Intermediate crudes fall between 22 and 38°. Extra-heavy oils are below 10; the API gravity of bitumen approaches zero.

Viscosity is measured in centipoises (cP) that represents the oil's resistance to flow; the higher the value, the higher the viscosity. Viscosity is the property that most affects production and recovery operations where it complicates its production and pipeline transportation, due to its poor fluidity and high pressure differentials generated with values between 20 cP and more than  $1 \times 10^6$  cP [8, 9]. The heavy oil in terms of viscosity was defined as the class of oils ranging from 50 to 5000 cP. Among the different compounds of crude oil, asphaltenes are usually most responsible for the high viscosities in HO and EHO.

The high viscosity restricts the easy flow of oil at the reservoir temperature and pressure [10]. The viscosity of heavy crudes is strongly affected by temperature variations. For this reason, thermal recovery methods are commonly used in heavy oil production. **Figure 2** shows the relationship between viscosity and temperature for two Athabasca bitumen samples. There is no universal relationship between oil density and viscosity. However, oils are generally found to be more viscous when density increases. This relation can be greatly attributed to the presence of asphaltenes, which are high molecular weight polycyclic hydrocarbons that tend to aggregate. Indeed, it has been shown that the viscosity of oils increases exponentially with asphaltene content [11].

**Figure 3** is a graph relating viscosity and API ratings and it can be observed that the heavy oil region lies in the high viscosity range.

The high density and viscosity of unconventional oils at atmospheric conditions has traditionally made their recovery very energy demanding compared to lighter crudes and has resulted in very low recovery factors, which means that these oils tend to result in higher carbon emissions and other societal impacts. Mnemonically, when other factors being equal, the lower the API gravity, the oil will be more expensive to extract and process, and simultaneously the obtained oil will have lower price.

The rheological properties are highly controlling all processes in which fluids are transferred from one location to another such as in, the migration of crude oil within the oil reservoir and transportation of the crude oil from oil wells and the refining units. Therefore, the unconventional oils are required to have the fluid viscosity of the migrating conventional oils [13]. The viscosities of the unconventional crude oils (i.e. heavy oil and bitumen/tar sands) at 25°C might reach more than 10<sup>5</sup> cP. The extremely low flowability due to high viscosity at reservoir

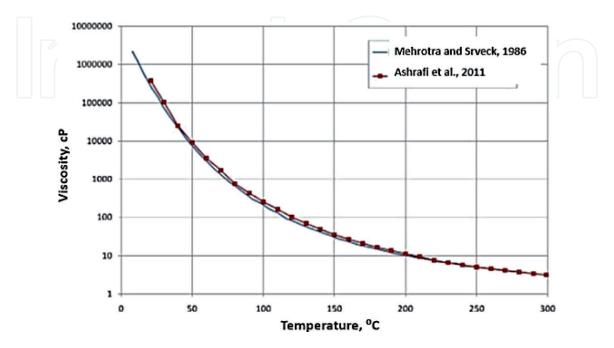


Figure 2. Viscosity—temperature relationship of an Athabasca bitumen [12].

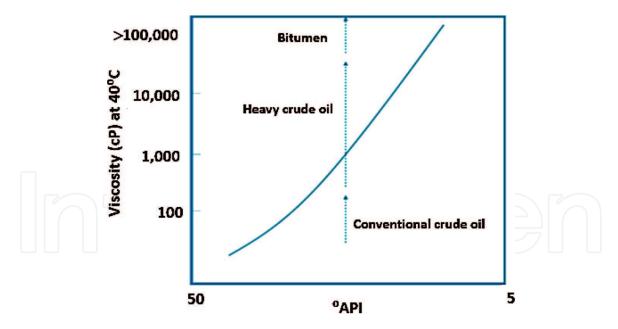
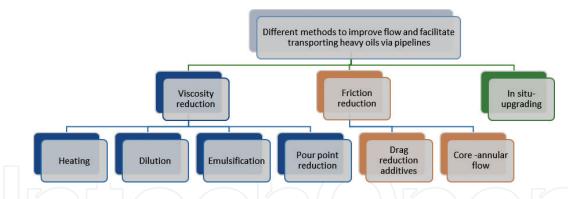


Figure 3.
General relationship of viscosity to API gravity [2].

conditions, especially in offshore conditions alongside asphaltene deposition, heavy metals, sulfur and brine or salt content making these kinds of oils more challenging to produce, transport as well as refine by conventional means without firstly upgrading them to meet conventional light crude oil properties [14, 15]. It is well known that pipelines are the most effective means of transporting crude oil from the producing field to the refinery because of their low expense and environmentally convenient. As such, transportation of the heavy crude oil via pipeline is a major challenge for petroleum industries, where conventional pipelining is not adequate because of the huge energy (i.e. high pumping power) is required to overcome the high pressure drop in the pipeline, owing to their high viscosity. Therefore, to transport heavy oils economically, the pressure drop in the pipeline must be lowered to minimize the pumping power via reducing the viscosity [16]. Furthermore, the pumping temperature is an important affecting factor of the flowability and consequently the pipeline transportation of crude oil. Heavy crudes usually have higher pour points due to high content of high molecular weight components, such as waxes, asphaltenes and resins. Under conditions in which the atmospheric temperature is below the pour point, gelation of the crude oil occurs lowering its flow completely and causing severe transportation problems. Especially in the cold offshore environment, waxes and asphaltenes deposit over inner surfaces of pipelines and eventually clog the pipelines, which decreases the accessible cross-sectional area for oil flow that causes reduction in flow rate and rise in pressure drop and multiphase flow, may occur resulting to further increases in the pumping cost [17, 18]. Here, it is worthy to mention that the desired pipeline viscosity of crude oils might not exceed 400 cP at 25°C [19–21]. However, it should be less than 200 cP at 15°C [22]. On the other side, the presence of brine or salt in the heavy crude stimulates corrosion problems in the pipeline [17]. In some cases, the formation of emulsion such as the oil-water mixture produced from the reservoir poses transportation difficulty.

# 3. Mitigation technologies for low flowability

Sync of the ever-growing world energy demand with the decline of conventional middle and light crude oil reserves and the limited supply and rising price



**Figure 4.**Schematic diagram presenting different methods for improving flow of heavy crude oil and bitumen and facilitating their transporting via pipelines.

of crude oil led to attract the interest the petroleum industry growingly in heavy crude oil and bitumen/tar sands exploitation. Nevertheless, the exploitation of these crudes is still low because of the technical challenges that face it at all stages from recovery/production from the reservoir to transportation and refining [23, 24]. To reduce this high-pressure drop and cost of transportation, several technologies have been proposed to improve the flow properties of the heavy crude oil and bitumen through pipelines and thus to meet the production volumes projected by the market. Generally, these different technologies can be divided into three categories (**Figure 4**) including (1) viscosity reduction [e.g. preheating of the heavy crude oil and bitumen and subsequent heating of the pipeline, blending and dilution with light oils or organic solvent, emulsification through the formation of an oil-in-water emulsion and lowering the oil's pour point by using pour point depressants (PPDs)]; (2) drag/friction reduction [e.g. pipeline lubrication through the use of core-annular flow, drag reducing additive]; and (3) in situ partial upgrading of the heavy crudes to produce synthetic crudes with lower viscosity [23, 25].

In this chapter, various technologies available for transporting heavy crude oil and bitumen from the production site to the processing facilities including viscosity and friction reduction and in-situ upgrading are reviewed with extensive discussion. The author provide a review of typical methods such as heating and dilution, and also point out lubrication solutions to move heavy and extra-heavy oils, such as core-annular flow and o/w emulsions. The advantages and disadvantages of each technology are highlighted with the view that the chapter will provide direction for improvement and development of novel economically viable technologies to improve the transportation of heavy oils via pipelines. Other approaches as drag reduction additives and pour point depressants (PPDs) may be complementarily discussed in a later section in this work.

## 4. Heating

Heating technique is commonly utilized to overcome the difficulties related to the transportation of the heavy crude oil. This technique involves preheating the heavy crude oil followed by subsequent heating of the pipeline. Such thermal treatments are based on the strong viscosity-temperature relationship, since the viscosity of the heavy oils and bitumen is reduced by several orders of magnitude with increasing temperature and subsequently the flowability of such oil is improved and it will be easier to pump. The response of viscosity to changes in temperature for some heavy oil and bitumen is illustrated in **Figure 5** [26]. Heat should be applied

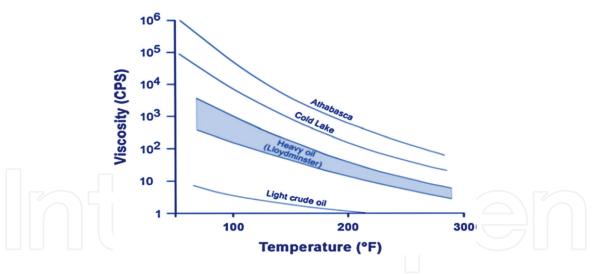


Figure 5.
Response of viscosity to increase in temperature [26].

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 [27, 28].

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 relationship that has been proposed in 1936:

$$\eta = \frac{N.h}{V} \cdot \exp\left(\frac{\Delta G'}{RT}\right) \tag{2}$$

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

$$Log (log \eta + C) = A + B \cdot log (T)$$
 (3)

where,  $\eta$  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 (cP/SG) and varies slightly with smaller viscosities) and T is the absolute temperature.

The effect of temperature upon viscosity relies greatly on the composition or volatility of the oil [29]. 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, a raise in temperature affects mainly the petroleum macromolecular structures, promoting disruption of their aggregate and maintaining monomer units scattered. Therefore, the dispersed system should be more favorable than those of the organized macrostructures because these organized structures of the latter system enhancing its flow resistance [30]. A well-documented example is the pipeline Alyeska in Alaska, which transports the crude oil at approximately 50°C. A project involving heated pipelines is not an easy task. However, there are many considerations have to be taken into account on the design of a heated pipeline including; (a) instability in the flow of oils as a result to change of their rheological properties that may be possibly induced by heating the pipeline, (b) many number of heating and pumping stations are required over long

distances of pipelines posing an additional cost, and (c) the heat losses along the pipeline because of the low flow of the crude oil i.e., heat loss is present during oil flow (the cooling effect). Therefore, heating stations should be planned anticipating gradual cooling in the line where, the pipeline is often insulated to maintain an elevated temperature and reduce the heat losses to the surrounding water as well as the earth lowers the efficiency of the technique. In such case when the pipeline is vulnerable to shut-in, a heated diluent has to be injected to restart flow in the pipeline [27]. In warmer climates where the ambient temperature does not bring the heavy oil below the pour point, electrical heating may be used to boost production without the need for special restart procedures. This has been demonstrated on shorter production lines in Colombia [31]. 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. Therefore, this technique might not be viable for transporting crude oil when it comes to subsea pipelines, sudden expansion and contraction along the pipeline may induce challenging problems, as well as the high rate of corrosion inside the pipeline due to the high temperature. Consequently, the capital and operating costs will be significantly high especially over long distances of pipelines from the oil field to the final storage or refinery on the high side [32]. The costs of insulated pipelines or installing heaters are less than that of dilution or upgrading.

#### 5. Dilution

Dilution/blending of heavy crude oil and bitumen with light hydrocarbons or organic solvents is the most commonly used oldest and preferred technique to reduce viscosity and to improve their transportation via pipelines almost five decades ago. The cost-effective diluents used to enhance the transportability of heavy crude oils in pipelines are relatively cheap and readily available. The widely used diluents include light crude oils and light to medium products from the upgrader or refinery processes such as naphtha, kerosene, etc. as well as light natural gas condensate, by-product of natural gas processing. However, the use of organic solvents such as alcohol, methyl tert-butyl ether (MTBE), tert-amyl methyl ether (TAME), and dimethyl ether (DME) has been investigated [33]. Generally, it is well known that blending the fluids or diluents with the lower viscosity produce the blended mixture of heavy crude and bitumen with the lower viscosity which is easier to pump allowing transportation of a large quantity or volume of these oils at reduced cost [34]. Furthermore, dilution helps the desalting and dehydration operations downstream. The viscosity of the resulting blends depends on the viscosities and densities of the heavy crude oil and bitumen and the used diluent, the dilution rate, heavy oil/diluent ratio and also the operating temperature. It is worthy to mention here that heavy crude oil and bitumen can have a viscosity of more than 10<sup>5</sup> mPa s. However, viscosity of the diluted or blended oil must be less than 200 mPa s to transport heavy crude oils conveniently via the classical pipelines [22]. In this sense, large volume of diluents is required to achieve this pipeline viscosity specification where, the amount of diluents required for bitumen is higher than that for heavy crude oil where, the ratio of diluents/heavy oils in their exported blends ranges from 0 to 20%, while it is in the range of 25-50% for diluents/bitumen blends. The method also suffers certain disadvantages. The dilution of heavy crude oils is employed to enhance pipelining using two pipelines, one for the oil and another for the diluents via two main strategies depending on whether, the diluent is recycled or not. In both cases, a larger pipeline diameter is needed. This demands considerable capital and operational investment in pumping and pipeline

maintenance. Moreover, the difficulty in prediction of solvent/oil ratio required for achieving a reduction in viscosity owing to the large and inconsistent number of governing parameters leads to ineffectiveness of simple mixing rules and therefore, the diluent will command a significant hold-up. The non-recycling strategy is based on the availability that secure the steady supply for the diluent. As the light hydrocarbons (i.e. diluent) may be acquired from neighboring conventional oil fields that the company owns, or from a competitor which could prove costly, something that may not be the case at peripheral heavy oil fields. In case of recycling strategy, the project economics are less of a subject to the price of diluent. However, this strategy is required, as recycling facilities and constructions required to return of diluent to the production site pose an additional capital expenditure.

Also, the oil composition has to be considered on selection of the solvent. This consideration is due to the compatibility issues between the asphaltenes and paraffins present in the oil with the solvent. If due care is not taken, deposition of asphaltenes and paraffins can cause further problems as, the light condensate recovered from natural gas (C<sub>5</sub>+ or "Pentane Plus"), a low-density and less viscous mixture of hydrocarbon liquids, has been used to dilute the heavy crude oil and bitumen in order to enhance their transportation using pipeline in Canadian and Venezuelan oil fields. Though the efficiency of this condensate in reducing the viscosity of the heavy crude oil and bitumen significantly, instability during transportation and storage is observed as a result to precipitation, segregation and aggregation of asphaltenes [35]. These findings are because of insolubility of asphaltenes in most of condensate components involving alkanes such as n-pentane and heptanes. Besides, asphaltenes have the tendency to interact and aggregate in the oil-condensate blended mixture, as the condensates are known to be paraffin rich light oil. This may result in flocculation which leads to partial plugging of pipelines. Furthermore, the availability of condensates based on natural gas demand is one of the important limitations to its use as a heavy oil thinner where, the production of condensate is not sufficient to sustain the demand due to the growing production of heavy crude oil and bitumen [27]. Thus, light crude oils with API gravity between 35 and 42 have also been employed for dilution of the heavy ones, but it is less efficient than the condensate in lowering their viscosity [36]. Because of decline of the reserves of conventional light crudes, these oils suffer similar disadvantages as condensates like availability and compatibility with asphaltenes. Also, the light hydrocarbons such as gasoline and kerosene as distillates have been found to be effective owing to their good solvent properties. Gasoline also helps to improve the octane number in downstream processing. Thus, it has been shown that 15% kerosene mixed with heavy oil at 50°C achieves the same viscosity reduction achieved by 20% kerosene at room temperature [37]. Another common diluent used is naphtha, hydrocarbons ranging from  $C_6$  to  $C_{12}$  from naphtha fraction of crude oil distillates. Naphtha has high API gravity (low density) which leads to efficient dilution of crude oil and shows good compatibility with asphaltenes owing to the presence of aromatic content in it. It is easily recyclable and reusable. However, the mostly used light hydrocarbons for dilution of heavy crude oils are expensive and are not readily available in large quantities. Therefore, the recycling is essential in despite of the required large investments and subsequently additional operating cost.

As previously mentioned, employing of organic solvents including MTBE, TAME and DME in thinning the heavy crude oils have been considered [33]. Recovery of DME is easier than the other solvents. Indeed, alcohols have been found to be more effective in reducing the viscosity where, the addition of ethyl alcohol at 10% led to reducing viscosity of the crude oil by almost 80% at 25°C [38]. This can be due to interaction between the hydroxyl groups and

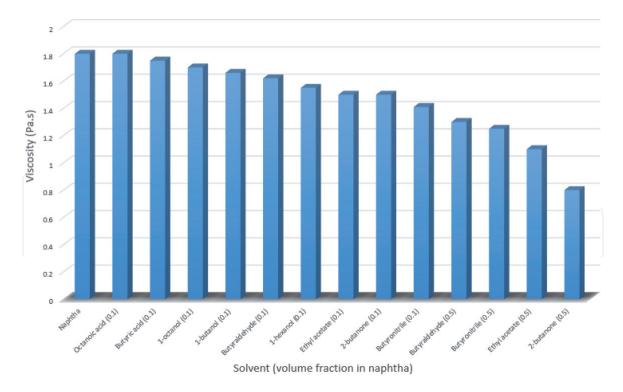


Figure 6.

Effect of naphtha/organic solvent blend at different volume fraction on the viscosity of the diluted heavy crude oil.

asphaltenes [39]. The use of these solvents is prompted based on their use in improving the octane number of gasoline. Subsequently, a mixture of hydrocarbons and organic solvents bearing polar groups onto their molecular structure has slightly exhibited efficacy in viscosity reduction of heavy crude oil at constant dilution rate [34]. Therefore, it has been proposed that a blend of naphtha and organic solvent would reduce the amount of diluents needed to lower the viscosity of heavy oil-to-pipeline transportation specifications [34]. The relative viscosities of the blend of heavy oil diluted with mixtures of naphtha and organic solvents are shown in **Figure 6**. The reduction of viscosity for resulting diluted heavy crude oil is attributed to the increasing polarity or hydrogen bonding of the solvents and the ability of the polar solvent to solubilize the asphaltenes components present in the heavy crude oil [34]. In that case, high polarity of solvents enhances their dilution efficiency causing greater reduction in viscosity of the heavy crude oil. However, the solvent can be easily recycled when its viscosity is comparable for that of the hydrocarbon as well as their boiling point.

Recently, the effect of carbon dioxide on the heavy crude oil has been studied. The findings of this studies have showed that crude oil saturated with carbon dioxide undergoes significant reduction in viscosity at a given temperature and pressure [40].

#### 5.1 Prediction of resultant viscosity of the crude oil-diluents mixture

Generally, 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 noticeable decline in oil viscosity. The addition of light oils or solvents resulted in lowering the frictional pressures. The rate of this reduction is greater in lower temperatures [30]. Up to date, a number of correlations have been developed for prediction of resultant viscosity of the blended mixture of heavy crude oil and diluents. But the accuracy of these relations is limited owing to the number of parameters involved in them. A few relationships have been discussed by Gateau and others [34]. In essence, viscosity of the resulting diluted heavy crude oil can be

calculated from a modified correlation developed by Lederer [41] that is similar to the classic Arrhenius expression as follows:

$$\log \mu = \left(\frac{\alpha V_o}{\alpha V_o + V_d}\right) \log \mu_o + \left(1 - \frac{\alpha V_o}{\alpha V_o + V_d}\right) \log \mu_d \tag{4}$$

Where,  $V_o$  and  $V_d$  are the volume fraction of the heavy crude oil and diluents,  $\mu_o$  and  $\mu_d$  are the viscosity of the heavy crude oil and the diluents, respectively, and  $\alpha$  is an empirical constant ranging from 0 to 1. Thus, an empirical formula for determining the constant  $\alpha$  for the blend of heavy crude oil diluted with light hydrocarbons has been proposed by Shu [42]. This relation depends on the differences in densities of oil to diluents (i.e. light hydrocarbons) and their viscosity ratio.

$$\alpha = \frac{17.04 \left(\rho_o - \rho_d\right)^{0.5237} \rho_o^{3.2745} \rho_d^{1.6316}}{\ln\left(\frac{\mu_o}{\mu_d}\right)}$$
(5)

where,  $\rho_o$  and  $\rho_d$  are densities of oil and solvent, respectively.

Currently, partial upgrading and dilution may be used in different stages of heavy crudes production. In the Orinoco field developments in Venezuela, the heavy oil is diluted at the production site for pipeline transport to a centralized refinery. At the refinery, the heavy oil goes through and upgrading process for further transport, while the diluent is separated from the blend and returned to the production site for recycling.

# 6. In-situ upgrading

In situ upgrading has been employed at surface conditions to locate the heavy crude oils and bitumen in viscosity conditions required for its production and transportation. In general, partial upgrading is often preferred with regard to entire upgrading because the cost of the process and the extension of the upgrading depend on the cost-benefit relation. This partial upgrading uses hydroprocessing to modify the relative proportion of the oil hydrocarbons (the composition of heavy oils) into a field refinery to make them less viscous and subsequently more suitable for pipeline transport without altering its refining characteristics. Hydroprocessing is a broad term that includes hydrocracking, hydrotreating, and hydrorefining. Where, 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 the scission of macromolecular structures in the oil molecule rupture, forming smaller and simpler chemical structures as smaller paraffin and olefin molecules that change the properties of oil and the quality of its products as the viscosity of oil that reduce and it become lighter. In the second stage, called hydrotreating, hydrogen is added to promote hydrogenation without breaking structures and to remove impurities [29]. The hydrogenation process is catalyzed by metals such as nickel, palladium and platinum. Since metal catalysts are easily poisoned by sulfur containing compounds, the operation of the process requires a refined control technique. In this stage, the saturation of olefins and the conversion of aromatic compounds into naphthenics occur wherefore, the proportion of saturated carbons and aromatics increases with reducing the amount of asphaltenes and oil resins [43, 44]. Hereby, the upgrading process produces a large unwanted byproduct of coke that has to be handled and deposited. The potential advantage of upgrading over other techniques is to improve the quality for both of the oil and the residue, simultaneously with 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 [45, 46]. 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. Moreover, the partial upgrading has the advantage of lower pipeline investments, limited restart issues and no particular corrosions. Nevertheless, the investments associated with a field refinery demands a large production.

Summarily, upgrading can be considered as a process of carbon rejection and hydrogen addition [47]. Carbon rejection processes include visbreaking, thermal cracking, coking, deasphalting, and catalytic cracking, while hydrogen addition processes include catalytic hydrodemetallization, hydrodesulphurization, hydrodenitrogenation, hydrogenation, and hydrocracking in fixed bed, moving bed, ebullating bed, or slurry phase reactors [45–48]. Hereof, it was indicated that the partial upgrading is a hybrid approach involving a simultaneous use of several of these technologies. The assembly used as the strategy for upgrading depends on the product value and the SARA fraction distribution in the oil [45, 49]. Since asphaltenes and resins are the major constituents of heavy oils, these components present the highest impact on the method selection. So the heavy oils containing whether high resin and low asphaltene or low resin and high asphaltene even when both have the same API gravity, different upgrading processes must be employed [45, 50]. Farther, other considerations beside the properties of the oil have to be taken into account through choice of the upgrading treatments assembly such as, regional logistics between the well-head and the refining site, operational concern, transport distance, cost, environmental concerns and the legislation.

Example of the proper upgrading treatments developed by Association for the Valorization of Heavy Oils (ASVAHL) are deasphalting process Solvahl, thermal treatment Tervahl process and catalytic hydrotreatment Hyvahl processes [51]. Recently, many studies at Institut français du pétrole (IFP) aim to associate these different processes to optimize the heavy crude conversion. The combination of thermal cracking, solvent deasphalting and hydrocracking processes are commonly used for the processing of heavy oils. Furthermore, the present strategy in the petroleum industry is to integrate in situ upgrading to thermal enhanced oil recovery (EOR) methods for achieving the cost, environment and energy effectiveness. The Syncrude operations in Canada are an example of this, where surface mined 8° API bitumen is upgraded to a 30-32° API synthetic blend. It has also been practiced in Venezuela to export extra-heavy oil from the Orinoco belt. In situ upgrading technologies which can be achieved during thermal recovery methods include ISC, SAGD, CSS and subsequently the novel THAI and its add-on catalytic upgrading process in situ (CAPRI), collectively called THAI-CAPRITM [15, 24, 52]. These processes rely on the reduction of heavy crude oil viscosity by heat to improve its flow from the oil reservoir to the production well. This in situ thermal cracking process reduces the viscosity of the heavy oil and bitumen to a high order of magnitude, thereby improving flow and production. However, of all these processes, the THAI-CAPRI process integrates a catalytic upgrading process into the recovery. Details of the above-mentioned in situ upgrading technologies for during heavy oil recovery have been presented in a review article involving the novel extraction and upgrading technologies for heavy oil and bitumen by Shah and others [46].

# 7. Coverage of heavy oils by water

Coverage of heavy oils by water to facilitate their transportation via pipelines is a technology based on a physical 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, covered transport requires pressures that are comparable to pumping water alone, regardless the viscosity of oil [53, 54]. The oil and water phases can be configured in various ways during pumping. In horizontal pipes, the most common configurations are stratified flow based on the two phase's density, oil-in-water emulsions (stabilized by surfactants), and core annular flow, which are the most approaches employed in transport of heavy oils via pipelines including elevation ducts. These configurations depend strongly on the flow rate of oil and water [55].

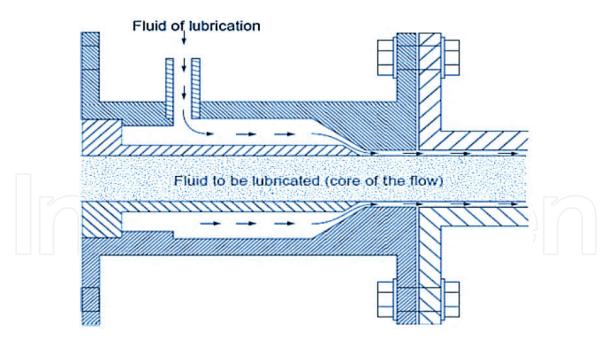
#### 7.1 Core-annular flow

Core-annular flow (CAF) is a technology to facilitate the flow of heavy crude oil and bitumen through pipeline by reducing the pressure drop in the pipelines owing to the friction. Where, this friction caused by the high viscosity of these fluids can make their flow in a single-phase is so difficult or undoable. This technique was first reported by Isaacs and Speeds in 1904 for the possibility of pipelining viscous fluids through the lubrication of pipe walls with water [56]. However, a commercial pipeline dedicated to transportation of heavy oil through annular flow was not in operation until the 1970s [57, 58]. Commercial establishing for core-annular flow systems involves not only technical questions but also operational methodologies to increase their feasibility and flexibility. The effectiveness of the commercial implementation of core annular flow is related to its adaptability to existing pipeline systems, in particular its capacity to share with other types of fluids that are not incorporated in the core flow regime. Core flow has attracted much industrial interest, being the subject of many patents to facilitate the pipeline transportation of heavy oils [59]. Almost, the most important industrial application among them up to date is employed in the Shell project in California, in which a 38.6 km pipeline from North Midway Sunset reservoir to the central facilities at Ten Section (California) operates for 12 years with 30% volumetric water with a flow rate of 24,000 barrels per day. Other examples include the 55 km lubricated pipelines from San Diego to Budare (Venezuela) used for transporting Zuata heavy crude oil (9.6 API°) and the self-lubricated pipelines of Syncrude's Canada Ltd. [60].

The core-annular flow technique is based on exploiting the low viscosity of water and high density of heavy oil to form a concentric flow pattern, where thin film of water or aqueous solution formed onto the inner wall of the pipe, "lubricating" the flow of core fluid consisting of heavy oil. Lining the pipe with an aqueous film is done by injecting water into the pipeline at its head (**Figure 7**). Accordingly, the core-annular flow is considered one of the regimes based on flow of two-phase via pipelines. Somewhere further down the pipeline, formation of an aqueous coating around the core of heavy oil will stabilize the flow with reducing the friction pressure loss. Where, the reduced longitudinal pressure gradient and a total pressure drop are similar to that of volumetrically equal pure water flow [57, 58, 61]. The typical fraction of water required in this approach (10–30%) implies that the pressure drop along the pipeline depends very closely on the viscosity of water, but weakly on that of the heavy oils [23, 62]. Furthermore, the pressure drop reduction exceeds 90% when the flow of water as an annulus near the pipe wall surface is done around the core of heavy crude oil comparing with that without water lubrication [57].

If the core-annular flow is assumed to be perfect and well centered, then the pressure drop can be calculated from the following equation:

$$\frac{\Delta P}{L} = \frac{Q}{\frac{\pi}{8} \left[ \frac{R^4}{\mu_w} + R_s^4 \left( \frac{1}{\mu_0} - \frac{1}{\mu_w} \right) \right]}$$
 (6)

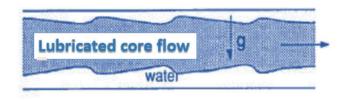


**Figure 7.** *Illustration of the core annular flow injector configuration* [57].

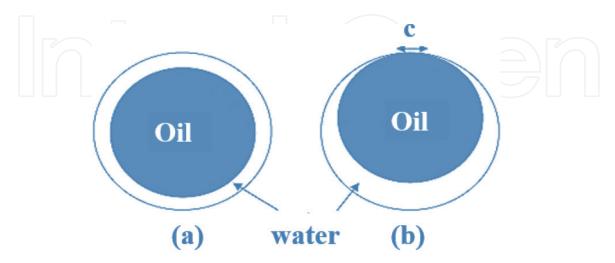
where  $\Delta P/L$  is the pressure drop of the centered core-annular flow (Pa/m), Q is the total flow rate (m<sup>3</sup>/s), R is the radius of the pipe (m),  $R_s$  is the core radius (m), and  $\mu_w$  and  $\mu_o$  are the dynamic viscosities of water and oil, respectively (Pa s).

Despite of core annular flow capability for reducing the pressure drop to that of moving water, achieving this perfect flow having high stability is very rare because such perfection and great stability may only accomplish with density-matched and immiscible fluids. i.e., have similar densities and do not form emulsion [57, 63]. Whereas, the mechanisms of hydrodynamic destabilization of the annular flow originate from capillary forces and inertia (the difference between the interfacial velocity of the fluids), are evidenced by the deformation of the liquid-liquid interface. These flow velocity and capillary instability arising from surface tension and the density difference between the liquids break the inner core into slugs at low velocity and stratification occurs in the system. Hereby, several flow regimes may occur depending on the properties of the oil such as density, surface tension, and shear rate of the flow and fluid injection flow rate. Where, wavy core-annular flow, in which waves are created at the water and oil interface can occur (Figure 8). This flow regime is more likely to be present in the core fluid through the core annular flow process [64]. Furthermore, a radial movement of the oil core to the upper wall of the pipe by act of a buoyancy force can occur when the density difference between the oil and water is large (**Figure 9**). On the other side, increasing the velocity enhances the core flow stability.

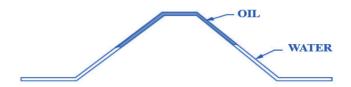
Still, there are significant problems encountered in the commercial application of annular flow for heavy oil transportation as instability of the flow regime, fouling and corrosion of the pipe walls. These problems emerge the moment flow rate drops or the pipeline is shut-in (**Figure 10**) where, the liquids will segregate into two horizontal layers (stratification of the phases). If the pipeline has an elevated section; this could lead to a permanent heavy oil plug blocking the flow. Knowingly, many potential interruptions may occur in any normal pumping operation of crude oil due to mechanical failure, power interruptions, and ruptures in the pipeline or climate concerns. Ditto, interruptions occurring in the core annular flow-based pipelining even for relatively short periods of time can lead to the stratification of the two phases. This stratification of the two phases can be aggravated by the difficulties of restarting the flow in case of unscheduled downtime, where high



**Figure 8.**Schematic diagram of wavy Core annular flow [54].



**Figure 9.**Radial position of the oil core: A perfect core-annular flow and b with density difference. C is the contact perimeter between the oil phase (core) and the pipe wall.



**Figure 10.** Shut-in issues occurred in core-annular flow.

pressures are required to restore the system [23]. This high pressure can cause major failures in the pipeline as it may exceed the maximum allowable pressure. A basic process has been proposed for restarting core flow with heavy oils after a long standstill period in which a flow of a low viscosity fluid, water, is pumped first into an inlet portion of the pipeline with increasing the flow gradually until reaching the critical velocity required to develop annular flow in a steady state condition. Then, the heavy oil is injected into the inlet portion of the pipeline, and similarly its flow is gradually increased either by adjusting a variable speed motor to the pump or by adjusting a control valve in a viscous oil bypass line. An increase of pressure due to the pumping of heavy oil is much smaller than the pressure peaks observed during the low viscosity fluid build-up stage.

Fouling as one of the main problems in implementing core annular flow caused by the gradual adherence and accumulation of oil at the pipe walls that can cause a blockage in the pipe section, preventing flow. The tendency of the oil to adhere to the pipeline walls exhibited during annular flow of 9°API oil [65]. Even in the hydro-dynamically stable annular flow which is able to maintain its structure through various line accidents, the oil tends to embed itself in the pipe walls by means of thermodynamic effects. Although the hydrodynamic stability of the system can be achieved by adjusting the process parameters, the stability of the system is still dependent on thermodynamic aspects [54, 55, 66]. In addition, formation of

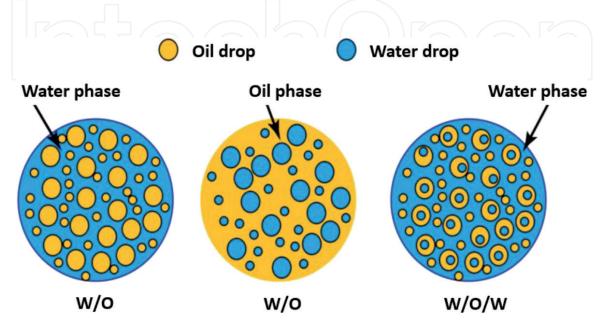
the incrustations in pipes can occur due to the reversal of wettability of the system caused by asphaltenes and naphthenic acids present in the oil [81]. The effects of wettability reversal over the load loss of the system can be avoided or reduced by the addition of sodium meta-silicate to the aqueous phase [67–69].

#### 7.2 Emulsification

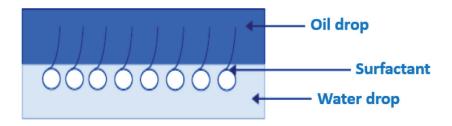
Several methods have traditionally been proposed to enhance the mobility of heavy crudes for pipeline transportation; these include heating crude oils or diluting them with lighter fractions of hydrocarbons. However, each of these methods has economic, technical and logistical drawbacks especially when it comes to transportation of heavy crude oil through offshore pipelines.

Emulsions naturally occur in petroleum production and pipelining, mainly those of water-in-oil (W/O) and more complex (double) emulsion like oil-in-waterin-oil (O/W/O) emulsions (Figure 11). Such emulsions are detrimental for oil production since oil's viscosity raises, increment corrosion issues and are difficult to break in desalting and dehydrating units before refining. Nevertheless, O/W emulsion reduces the viscosity of heavy crude oils and bitumen and may provide an alternative to the use of diluents or heat to reduce viscosity in pipelines [70]. Thereby, emulsification of heavy oils with water with aid of active surface additives is considered to be one of the newest and most economical alternative techniques to overcome flow assurance problems associated with transportation of heavy crude oil through pipelines under the cold offshore environments. This technology is hydraulically transporting heavy crude oil via pipeline in form of oil-in-water (O/W) with the drop sizes in micron range can reduce the viscosity to values of 50–200 cP at 15°C [23, 25, 28], in which it can be easily pumped [37, 70–72]. The methods used to generate the oil droplets to create the different possible emulsions includes use of devices such as dispersing machines, mixing with rotor-stator, colloid mills, high-pressure homogenizers applying high shearing stresses, emulsification by membrane and ultrasonic waves [39, 73, 74].

These oil-in-water emulsions are thermodynamically unstable where they can be subjected to several breakdown processes like Ostwald ripening, sedimentation and creaming due to density difference and coalescence of the drops [70]. Therefore, a surfactant (or mixture of surfactants) suitable for varying conditions have to be



**Figure 11.**The several emulsion forms used to transport heavy crude oils.



**Figure 12.** Surfactant-stabilized emulsion.

added forming a strong interfacial film to enhance the kinetic stability of these emulsions and consequently improve their transportability by pipelines [75]. Besides, in some cases additional substances as stabilizing agents (high molecular weight) to avoid phase separation. Accordingly, cost of the surfactant, its ability to maintain the emulsion stability during pipeline transportation and the ease of its separating from the crude oil at the final destination (since the density of heavy oil is close to that of water) are major challenges associated with the emulsification technology for transporting heavy crude oils. Monolayer of the surfactant molecules settles onto the oilwater interface to prevent drop growth and phase separation during transportation. As shown in **Figure 12**, such interfacial monolayer is formed by directing the polar region (i.e. hydrophilic head) of the surfactant toward the water phase and nonpolar tail (i.e. hydrophobic region) toward the oil phase. Hereof, the efficiency of the surfactant based on the properties of this adsorbed layer (the polar hydrophilic head and the non-polar hydrophobic tail) of surfactants that stabilize the oil-water surface against shear and decrease the interfacial tensions, and subsequently control the flow behavior of the emulsion [70]. However, heavy crude oil emulsion exhibits either Newtonian behavior at high shear rate or a shear thinning rheological behavior at low shear rate [25, 76].

Pointedly, properties of the emulsion including the rheological characteristics and stability depend mainly on many parameters such as, drop size and their polydispersity, temperature, salinity and the pH of the water, the components of the heavy crude oil, mixing energy and oil/water volume ratio [39, 77]. Drop size and their polydispersity depends on surfactant type, energy of mixing and pressure. The use of a dynamic mixer as a rotor-stator mixer, may cause the formation of small droplets with a diameter of less than 10  $\mu$ m which can cause a significant increase in the viscosity of O/W emulsion and emulsion inversion to an oil continuous emulsion that are detrimental to pipelining.

The use of surfactants and water to create a stable oil-in-water emulsion with heavy crude oil has been a topic of several investigations with a series of patents. Stabilizing the O/W emulsion from Egyptian Geisum crude oil using an anionic surfactant for pipeline transportation has been studied. The findings exhibited that stability and viscosity of surfactant-stabilized O/W emulsion increased with increasing concentration of the anionic surfactant that reduces the O/W interfacial tension and size of dispersed droplets [78]. Similar results were found in a nonionic surfactant stabilized O/W emulsion [37]. Triton X-114 is one of the commonly used non-ionic surfactants based on their ability to withstand the salinity of the produced water, they are also cheap, their emulsion is easy to separate, and they do not form undesirable organic residues that affect the oil properties [79]. However, the use of anionic and non-ionic surfactants produced a synergistic effect that allows a lower viscosity and more stable O/W emulsion. The preferred water soluble nonionic chemical surfactants for viscous crude oils are the commercially available ethoxylated alkyl phenols and ethoxylated alcohols; while the preferred water-soluble anionic chemical surfactants are ethoxylated alcohol sulfates. On the

other side, as a water-soluble chemical surfactant, or, together with a bio-emulsifier can absorb onto the hydrocarbon/water interfaces. Hence, "surfactant packages" composed of water-soluble chemical and/or biological co-surfactants have been proposed to transport viscous hydrocarbons by pipeline through the formation of low-viscosity bio-surfactant-stabilized oil-in-water emulsions, or the so-called hydrocarbosols. Here, hydrocarbon droplets dispersed in the continuous aqueous phase are substantially stabilized from coalescence by the presence of biosurfactants (Bio-emulsifiers), in particular, microbial surfactants [80]. Generally, bio-emulsifiers act by orienting their molecules at the oil/water interface, avoiding the coalescence of the oil droplets and stabilizing the resulting emulsion with maintaining their reduced viscosity over time. The hydrocarbosols viscosities were reduced by at least a factor of 10. Bio-emulsifiers, specifically extracellular microbial polysaccharides ("emulsans") produced by different strains of the *Acinetobacter* bacteria have been extensively researched [81, 82]. Among the preferred bio-surfactants are heteropolysaccharides produced by bacteria of the genus *Acinetobacter* and the genus Arthrobacter, and in particular, those produced by strains of Acinetobacter calcoaceticus. Still some heavy oils were not successfully emulsified with the surfactant packages studied. Here, it is worthy to mention that fresh water, sea water or even formation water may be available for emulsification and thus, these are very efficient oil-in-water emulsifiers possessing a high degree of specificity in both fresh water and sea water for emulsifying hydrocarbon substrates which contain both aliphatic and aromatic or cyclic components. Here, the use of formation water instead of fresh water resulted in a lower interfacial tension between crude oil and formation water and a more viscous O/W emulsion because of the formation of smaller crude oil droplets [71].

In this context, the heavy crude oil is a complex mixture of hundreds of thousands of compounds that include the asphaltenes which act as natural emulsifiers as well as other active surface components such as naphthenic acids, resins, porphyrins, etc. [70]. The presence of these component increases the complexity of crude oil emulsion, as they can interact and reorganize at the oil-water interface. On the other hand, the presence of natural hydrophilic particles such as clay and silica in the crude oil may cause instability in the emulsion [70]. Additionally, the O/W emulsion system may sometimes contain solids and gas, which increases the complexity of the process. In general, it is worthy to mention that the behavior of heavy crude oil-in-water emulsion is complex due to the interaction of several components within the system and many other factors mentioned hereinabove. By the fact that the use of surfactants can significantly increase the cost of emulsification, the activation of surfactants naturally occurring in heavy and extra heavy crude oils is a reliable option. The ionization of acidic groups present in fatty and naphthenic acids as well as asphaltenes with a strong alkali can make these surfactants more hydrophilic causing a reduction of the interfacial tension [70]. Thus, the activation of the natural molecules present in bitumen with amines serves as natural surfactants to form a bitumen-in-water emulsion or Orimulsion® (Orimulsion® is a bitumen-in-water emulsion and simultaneously the technology developed to facilitate the transportation of Cerro Negro bitumen) [83]. Moreover, some works refer to the use of the natural surfactants present in crude oil with particles such as silica, clay, iron oxides, etc., more stable emulsions can be obtained by saturation of surface of these particles by asphaltenes [70]. There are still many unresolved questions related to the peculiar behavior of these emulsions as result to the complexity of the molecular composition of oil having a wide range of chemical structures and molecular weights, the hydrophilic-lipophilic balance (HLB) values of the surfactants, the multiple interactions oil-water-surfactant and the possible molecular rearrangements at the oil/water interface.

Economically, pipelining of oil in form of O/W emulsion must transport as much oil as possible and as little water as possible (high O/W volume ratio). Notwithstanding, when the oil content in O/W exceeds 70%, the viscosity may become too high or inverse to W/O emulsion. Meta-stable and easy-to-break O/W emulsions should be produced with the minimum quantity of cost-effective surfactant and other additives where, strategy of implementing the technology of oil-inwater emulsions to transport heavy crude involves three stages such as producing the O/W emulsion, transporting the formed emulsion and separating the oil phase from the water phase. However, recovering the crude oil entails breaking the oil in-water emulsion. Hereby, different techniques including thermal demulsification, electro-demulsification, chemical demulsification, freeze-thaw method, pH modification, addition of solvent and demulsification by membranes have been developed to achieve the separation stage [73, 84].

In this technology, the surfactants should allow at the same time a simple but efficient rupture of the O/W emulsion before crude oil refining and the separated water should be treated in order to comply with environmental and industrial regulations for water discharge or recycling. The demulsification produced 0.5% BS&W for the heavy oil and less than 100 ppm oily contaminants in the separated water. Nonetheless, O/W emulsions can be considered for applications in improved recovery processes of heavy oils and for the increase in the recovery factor of mature fields [85], including the amounts not retrieved from the exhausted fields of light oils [86]. Furthermore, such emulsification technology can improve residual oil removal from mature fields that are not as efficiently recovered by traditional methods that apply heat or diluents [87]. Also, restarting a pipeline after an emergency shutdown and re-emulsification of oil may not pose major problems [88].

The potential of this technology to enhance pipeline transportation of heavy crude oil has been demonstrated in Indonesia in 1963, as well as in a 13-mile distance using 8 in. diameter pipeline in California [71]. Field-tested pipeline transportation of heavy crude oil as oil-in-water emulsions containing high fractions of oil has been proposed by Hardy and others [89]. A large number of studies, mostly experimental in nature, have been carried out on oil-water emulsions [78, 90]. However, the results of these studies are not uniform and are sometimes contradictory and thus, the results obtained from a study on a certain crude are difficult to apply to another. This can be attributed to the complex viscosity behavior of emulsions which depends on several factors such as base sediment and water (BS&W), temperature, shear rate, type and concentration of surfactant, and the components of the crude itself. Consequently, oil companies investigate on their own the specific crude that they produce the type of emulsion that is most appropriate allowing simple and economical crude oil recovery at the end of the pumping process.

Transportation of emulsified heavy oil had its technological viability clearly demonstrated by many field studies and the development of the pioneer process of large-scale fuel emulsions, 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 [91]. The emulsions obtained were pumped continuously for 6 days at 80 m³/day and stored for 6 days without any sign of degradation. Besides, ORIMULSIONS® process has been developed for the generation of energy in thermal plants by the state owned company PDVSA (Petr oleos de Venezuela) in Venezuela in the 1980s [17] and commercialized by its filial Bitumen's Orinoco S.A. (BITOR) [60, 70]. Ditto, emulsion flow rate tests performed with 13° API oil from a field in Shanjiasi (China) showed 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 [14]. In another work, emulsification of heavy oil in Sicily and the Adriatic Sea (Italy) has been tested for application in transport and production. The trial was based on the injection of an emulsifying aqueous phase into the well without any modification to the existing system. The dispersed oil content in the well-produced oil-in-water emulsions was 70%. The emulsions showed a viscosity 30–50 times lower than that of the diluted oil and oil productivity was greater four times than obtained with the conventional diesel dilution production [92].

## 7.3 Heavy oil emulsions for transport in cold environments

Considering, handling difficulty for O/W emulsions in cold environments because of phase destabilization, freezing or an increase in viscosity to a level too high for pipeline transport, brine with a high salt content and freezing point depressants like ethylene glycol in sufficient concentration are suggested to be used to maintain the oil-in-brine emulsion in pipeline condition at 253.15 K or less, but insufficient to break down the emulsion. Here, it is worthy to consider the costs of emulsion rupture and further processing of produced water to discharge or reuse.

The emulsion is suggested to contain a small amount of 0.1–5% by weight, of a conventional surfactant to facilitate the formation and preservation of the emulsion. The use of common surfactants mixes has been proposed to form the emulsion and supplemented by use of the xanthan biopolymer to enhance the stability of the emulsion [93]. In another research, a novel surfactant, tri-triethanolamine monosunflower ester, was synthesized from fatty acids produced from hydrolysis of sunflower (Helianthus annuus) oil. The resultant surfactant was used to emulsify a heavy crude oil from the western oil field of India. The oil-in-water emulsion developed with 60% oil content and 2 wt% surfactant exhibited a decrease in viscosity of 96% and a dramatic decrease in pour point where, the prepared emulsions were found to be flowing even at 1°C. The high stability of the emulsion has been attributed to the large reduction in the equilibrium interfacial tension (IFT) between the crude oil (diluted) and the aqueous phase of emulsions, which was almost nine times lower than that of no surfactant. These results suggested that the synthesized surfactants may be used to prepare a stable O/W emulsion for its transportation through offshore pipelines efficiently [94].

Furthermore, heavy oils in cold environments can be efficiently transported through a large diameter insulated pipelines at temperature below 273.15 K in the form of oil-in-brine emulsions containing 40–70% w/w of the dispersed oil with dissolving salts in the water phase at concentration sufficient to prevent freezing. These operating conditions permit the insulated pipeline to be buried in the ground without causing thawing of the permafrost, which in turn can cause damage to both the environment and the pipeline.

#### 8. Conclusion

The plateau in conventional oil production and the corresponding increase in the demand for liquid fuels have motivated markets to respond with higher oil prices. And the current economics of oil are spurring the transformation of energy supplies, not away from oil, but toward new oils which are expected to be the dominant supplies of liquid-fuel through the twenty-first century based on the market forces. The amount of these new petroleum resources could continue

to be revised upward as new technologies are developed. In this chapter, the mitigation technologies of low mobility of heavy crude oils used to facilitate their pipelining were explored. These methods have been divided into three categories based on reduction of viscosity and friction and in situ upgrading of these heavy crudes and bitumen. Each of these treatment techniques has special advantages and drawbacks. Therefore, there are many criteria to take into consideration on choice of each technique including the chemical and physical properties of the crude, regional logistics between the well-head and the refining site, operational and environmental concerns, distance of transportation, cost, and regulatory requirements. These criteria require that the petroleum industry tailor treatment strategies to fit the circumstances of its systems in accordance with the quality requirements of the pipeline operator as well as the content and quality demands of the refinery customer. Emulsification of crudes to form O/W emulsion was an appropriate method to reduce the viscosity of oils and enhance their flow under offshore conditions. Currently, in situ upgrading can be achieved during thermal enhanced oil recovery methods because this strategy characterized by the cost, environment and energy effectiveness. Also, the introduction of bacteria and biometal nanoparticles (Bio-NPs) in the reservoir to upgrade heavy oil, extra heavy oil, and bitumen in situ is an area of active research and hold great promise for improving flow of these crudes.



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# References

- [1] Ali S. Heavy oil recovery-principles, practicality, potential, and problems. In: SPE Rocky Mountain Regional Meeting. Montana, USA: Society of Petroleum Engineers; 1974. pp. 1-10
- [2] Thomas S. Enhanced oil recovery—An overview. Oil & Gas Science and Technology—Revue d'IFP. 2008;**63**:9-19. DOI: 10.2516/ogst:2007060
- [3] Gordon D, Sperling D. Big oil can't get beyond petroleum. Cap Times. June 20, 2010. Available from: http://host.madison.com/ct/news/opinion/column/articleb1775726-9ef8-5e5a-85fb-ed56417475d8.html
- [4] International Energy Agency (IEA), World Energy Outlook 2011. London; Press Launch. http://www.iea.org/weo/docs/weo2011/homepage/WEO2011\_Press\_Launch\_London.pdf
- [5] Speight JG. The Chemistry and Technology of Petroleum. New York: Marcel Dekker, Inc.; 1999. p. 11-14, 32, 306, 322-323
- [6] Mullins OC, Sheu EY, Hammami A, Marshall AG. Asphaltenes, Heavy Oils and Petroleomics. New York: Springer; 2007. pp. 554-555, 621-622
- [7] Merino-Garcia D. Calorimetric Investigations of Asphaltene Self-Association and Interaction with Resins. København: Technical University of Denmark; 2004
- [8] Alboudwarej H, Felix JJ, Taylor S, et al. La importancia del petróleo pesado. Oilfield Review. 2006;**18**:38-39. Available from: https://www.slb.com/~/media/Files/resources/oilfield\_review/spanish06/aut06/heavy\_oil.pdf
- [9] Curtis C, Kopper R, Decoster E, et al. Yacimientos de petróleo pesado. Oilfield Review, II. 2003;**23**:32-55

- [10] Goodarzi N, Mai A, Bryan J, Kantzas A. Insights into non-thermal recovery of heavy oil. In: Presented at World Heavy Oil Conference. 2009. pp. 2006-2553
- [11] Cesar Ovalles, Estrella, Rogel, John Segerstrom, Chevron ETC. Improvement of flow properties of heavy oils using asphaltene modifiers. In: SPE Annual Technical Conference and Exhibition. Denver, Colorado, USA. October 30 – November 2, 2011
- [12] Ashrafi M, Souraki Y, Karimaie H, Torsaeter O. Experimental PVT property analyses for Athabasca bitumen. In: Presented at the Canadian Unconventional Resources Conference Held in Calgary, Alberta, Canada. November 15-17, 2011
- [13] Werner A, Behar F, de Hemptinne JC, Behar E. Thermodynamic properties of petroleum fluids during expulsion and migration from source rocks.

  Organic Geochemistry. 1996;24(10-11): 1079-1095. DOI: 10.1016/
  S0146-6380(96)00082-4
- [14] Zhang N, Zhao S, Sun X, Zhiming X, Chunming X. Storage stability of the visbreaking product from Venezuela heavy oil. Energy & Fuels. 2010;24:3970-3979. DOI: 10.1021/ef100272e
- [15] Hart A. The catalytic upgrading of heavy crude oil in situ: The role of hydrogen. International Journal of Petroleum Science and Technology. 2012;**6**(2):79-96
- [16] Ahmed NS, Nassar AM, Zaki NN, KhH G. Formation of fluid heavy oil-in-water emulsions for pipeline transportation. Fuel. 1999;78:593-600. DOI: 10.1016/S0016-2361(98)00157-4
- [17] Martinez-Palou R, Maria de Lourdes M, Beatriz Z-R, Elizabeth

- M-J, Cesar B-H, Juan de la Cruz C-L, et al. Transportation of heavy and extra-heavy crude oil by pipeline: A review. Journal of Petroleum Science and Engineering. 2011;75:274-282. DOI: 10.1016/j.petrol.2010.11.020
- [18] Eskin D, Ratuloswski J, Akbarzadeh K, Pan S. Modelling asphaltene deposition in turbulent pipeline flows. Canadian Journal of Chemical Engineering. 2011;89:421-441. DOI: 10.1002/cjce.20507
- [19] Fruman DH, Briant, J. Investigation of the Rheological Characteristics of Heavy Crude Oil-in-Water Emulsions. In: Proceedings of the International Conference on the Physical Modeling of Multi-Phase Flow. England: Coventry; 1983
- [20] Nunez G, Briceno M, Mata C, Rivas H, Joseph D. Flow characteristics of concentrated emulsions of very viscous oil in water. Journal of Rheology. 1996;40:405-423. DOI: 10.1122/1.550751
- [21] Schumacher MM. Enhanced Recovery of Residual and Heavy Oils. Park Ridge, NJ: Noyes Press; 1980
- [22] Kessick MA, Denis CES. Pipeline Transportation of Heavy Crude Oil. U.S. Patent No. 4,343,323. 1982
- [23] Saniere A, Hénaut I, Argillier JF. Pipeline transportation of heavy oil—A strategic, economic and technological challenge. Oil & Gas Science and Technology—Revue d'IFP. 2004;59(5):455-466
- [24] Hart A, Shah A, Leeke G, Greaves M, Wood J. Optimization of the CAPRI process for heavy oil upgrading: Effect of hydrogen and guard bed. Industrial and Engineering Chemistry Research. 2013;52(44):15394-15406. DOI:10.1021/ie400661x
- [25] Al-Roomi Y, George R, Elgibaly A, Elkamel A. Use of a novel surfactant

- for improving the transportability/ transportation of heavy/viscous crude oil. Journal of Petroleum Science and Engineering. 2004;42:235-243. DOI: 10.1016/j.petrol.2003.12.014
- [26] Raicar J, Procter RM. Economic considerations and potential of heavy oil supply from Lloydminster Alberta, Canada. In: Proceedings of the Second International Conference on the Future of Heavy Oil and Tar Sands. Meyer RF, Wynn JC, Olson JC, eds., New York, McGraw- Hill. 1984. p. 212-219
- [27] Guevara E, Gonzalez J, Nuñez G. Highly viscous oil transportation methods in the Venezuela oil industry. In: Proceedings of the 15th World Petroleum Congress. London: John Wiley and Sons. 1998. pp. 495-501
- [28] Rimmer DP, Gregoli AA, Hamshar JA, Yildirim E. Pipeline emulsion transport for heavy oils. In: Schramm LL, editor. Emulsions: Fundamentals and Applications in the Petroleum Industry. Washington, DC, USA: American Chemical Society; 1992
- [29] Speight JG. The Chemistry and Technology of Petroleum. 2nd ed. New York: Marcel Dekker, Inc; 1991. 760 p
- [30] Szilas AP. Production and Transport of Oil and Gas. Gathering and Transportation. New York: Elsevier; 1986
- [31] Jaimes MG et al., Efficiency of Artificial Lifting Systems in the Production of Heavy Crude, by the Use of Electrical Heating in Surface Facilities. In: the Proceedings of the World Heavy Oil Congress [WHOC13]. Aberdeen, Scotland: Instituto Colombiano del Petroleo; 2013
- [32] Chang C, Nguyen QD, Ronningsen HP. Isothermal start-up of pipeline transporting waxy crude oil. Journal of Non-Newtonian Fluid Mechanics.

1999;**87**:127-154. DOI: 10.1016/ S0377-0257(99)00059-2

- [33] Anhorn JL, Badakhshan A. MTBE: A carrier for heavy oil transportation and viscosity mixing rule applicability. Journal of Canadian Petroleum Technology. 1994;33(4):17-21. DOI: 10.2118/94-04-02
- [34] Gateau P, Henaut I, Barre L, Argillier JF. Heavy oil dilution. Oil & Gas Science and Technology—Revue de l'IFP. 2004;59(5):503-509. DOI: 10.2516/ogst:2004035
- [35] Shigemoto N, Al-Maamari RS, Jibril BY, Hirayama A. A study of the effect of gas condensate on the viscosity and storage stability on Omani heavy crude oil. Energy & Fuels. 2006;**20**(6):2504-2508. DOI: 10.1021/ef060074h
- [36] Urquhart RD. Heavy oil transportation: Present and future. Journal of Canadian Petroleum Technology. 1986;**25**(2):68-71. DOI: 10.2118/86-02-05
- [37] Yaghi BM, Al-Bemani A. Heavy crude oil viscosity reduction for pipeline transportation. Energy Sources. 2002;**24**:93-102. DOI: 10.1080/00908310252774417
- [38] Argillier J-F, Barre L, Brucy F, Dournaux J-L, Henaut I, Bouchard R. Influence of Asphaltenes content and dilution on heavy oil rheology. In: Proceedings of SPE International Thermal Operations and Heavy Oil Symposium. Vol. 69771. Venezuela: SPE; 2001. pp. 1-8
- [39] Hasan SW, Ghannam MT, Esmail N. Heavy crude oil viscosity reduction and rheology for pipeline transportation. Fuel. 2010;**89**:1095-1100. DOI: 10.1016/j.fuel.2009.12.021
- [40] Hu R, Crawshaw JP, Martin-Trusler JP, Boek ES. Rheology of diluted heavy crude oil saturated with carbon dioxide.

Energy and Fuels. 2015;**29**(5):2785-2789. DOI: 10.1021/ef5020378

- [41] Lederer EL. Viscosity of mixtures with and without diluents. In: Proceedings of the World Petroleum Congress. London. 1933;2:526-528
- [42] Shu WR. A viscosity correlation for mixtures of heavy oil, bitumen and petroleum fractions, SPE 11280. SPE Journal. 1984;24(3):277-282
- [43] Kirkwood KM, Foght JM, Gray MR. Prospects for biological upgrading of heavy oils and asphaltenes. In: Vazquez-Duhalt R, Quintero-Ramirez R (Eds.). Studies in Surface Science and Catalysis. 2004;**151**:113-143. DOI: 10.1016/S0167-2991(04)80145-9
- [44] Speight JG. Chemical and physical studies of petroleum Asphaltenes. In: Yen TF, Chilingarian GV, editors. Asphaltenes and Asphalts. 1st ed. Amsterdam, the Netherlands: Elsevier Science B.V; 1994. pp. 7-65
- [45] Rana MS, Sámano V, Ancheyta J, Diaz JAI. A review of recent advances on process technologies for upgrading of heavy oils and residua. Fuel. 2007;86:1216-1231
- [46] Shah A, Fishwick R, Wood J, Leeke G, Rigby S, Greaves M. A review of novel techniques for heavy oil and bitumen extraction and upgrading. Energy & Environmental Science. 2010;3:700-714
- [47] Yen TF. Filtration, Chapter 31. In: Environmental Chemistry: Chemical Principles for Environmental Processes. Vol. 4B. Upper Saddle River, NJ: Prentice Hall; 1998. pp. 1405-1439
- [48] Joshi JB, Pandit AB, Kataria KL, Kulkarni RP, Sawarkar AN, Tandon D, et al. Petroleum residue upgradation via visbreaking: A review. Industrial and Engineering Chemistry Research. 2008;47:8960-8988

- [49] Reynolds BE, Brown EC, Silverman MA. Clean gasoline via VRDS/RFCC. Hydrocarbon Process. Houston: Hydrocarbon Processing, International Edition. 1992;71(4): 43-51
- [50] Ancheyta J, Sanchez S, Rodriguez MA. Kinetic modeling of hydrocracking of heavy oil fractions: A review. Catalysis Today. 2005;**109**:76-92
- [51] Charlos JC, Courdec JL, Page, JF. Heavy oil processing, a synthesis of the ASVAHL results. In: Proceeding E.C. 3rd European community symposium on new technologies for the exploration and exploitation of oil and gas resources. Luxembourg. March 22-24, 1988. Vol. 2, E. Millich et al. eds
- [52] Greaves M, Xia TX. Downhole upgrading of Wolf Lake oil using THAI–CAPRI processes-tracer tests. Preprints of Papers-American Chemical Society, Division of Fuel Chemistry. 2004;49(1):69-72
- [53] Beretta A, Ferrari P, Galbiati L, Andreini PA. Horizontal oil-water flow in small diameter tubes: Pressure drop. International Communications in Heat and Mass Transfer. 1997;24:231-239
- [54] Joseph DD, Bai R, Chen KP, Renardy YY. Core annular flows. Annual Review of Fluid Mechanics. 1997;**29**:65-90
- [55] Bannwart AC. Modeling aspects of oil-water core-annular flows. Journal of Petroleum Science and Engineering. 2001;32:127-143
- [56] Isaacs JD, Speed JB. Method of Piping Fluids. US Patent 759374. 1904
- [57] Bensakhria A, Peysson Y, Antonini G. Experimental study of the pipeline lubrication for heavy oil transport. Oil & Gas Science and Technology. 2004;59:523-533
- [58] Peysson Y, Bensakhria A, Antonini G, Argillier JF. Pipeline lubrication of

- heavy oil: Experimental investigation of flow and restart problems. SPE Production & Operations. 2007;**22**:135-140
- [59] Zagustin K, Guevara E, Nunez G. Core-annular Flow Process. US Patent 4753261. 1988
- [60] Salager JL, Briceno MI, Brancho CL. Heavy hydrocarbon emulsions. In: Sjöblom J, editor. Encyclopedic Handbook of Emulsion Technology. New York: Marcel Dekker; 2001
- [61] Ghosh S, Mandal TK, Das G, Das PK. Review of oil water core annular flow. Journal of Renewable and Sustainable Energy Reviews. 2009;13:1957-1965
- [62] Wylde JJ, Leinweber D, Low D, Botthof G, Oliveira AP, Royle C, Kayser C. Heavy oil transportation: Advances in water continuous emulsion methods. In: Proceedings of the World Heavy Oil Congress. Aberdeen; Scotland. Canada Inc; 2012
- [63] Bannwart AC. A simple model for pressure drop in core-annular flow. Revista Brasileira de Ciências Mecânicas. 1999;**21**:233-244
- [64] Bai R, Chen K, Joseph DD. Lubricated pipelining: Stability of core-annular flow. Part 5 experiments and comparison with theory. Journal of Fluid Mechanics. 1992;**240**:97-132
- [65] Visser RC. Offshore production of heavy oil. Journal of Petroleum Technology. 1989;41:67-70
- [66] Arney MS, Ribeiro GS, Guevara E, Bai R, Joseph DD. Cement-line pipes for water lubricated transport of heavy oil. International Journal of Multiphase Flow. 1996;**22**:207-221
- [67] Santos RG, Mohamed RS, Bannwart AC, 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. 2006;51:9-16
- [68] Ribeiro GAS. Topics in the transport and rheology of heavy crude oils. Minneapolis, MN; PhD dissertation, University of Minnesota. 1994
- [69] Liu Y, Buckley JS. Evolution of wetting alteration by adsorption from crude oil. SPEFE (Mar. 1997) 5-11
- [70] Langevin D, Poteau S, Hènaut I, Argillier JF. Crude oil emulsion properties and their application to heavy oil transportation. Oil & Gas Science and Technology. 2004;59(5):511-521
- [71] Ahmed NS, Nassar AM, Zaki NN, Gharieb HK. Stability and rheology of heavy crude oil-in-water emulsion stabilized by an anionic–nonionic surfactant mixture. Petroleum Science and Technology. 1999;17:553-576
- [72] Santos RG, Bannwart AC, 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. 2011;89:957-967
- [73] Ashrafizadeh SN, Kamran M. Emulsification of heavy crude oil in water for pipeline transportation. Journal of Petroleum Science and Engineering. 2010;71:205-211
- [74] Lin CY, Chen LW. Emulsification characteristics of three and two phase emulsions prepared by ultrasonic emulsification method. Journal of Fuel Processing Technology. 2006;87:309-317
- [75] Jiang J, Mei Z, Xu J, Sun D. Effect of inorganic electrolytes on the formation and the stability of water-in-oil (W/O) emulsions. Colloids and Surfaces A:

- Physicochemical and Engineering Aspects. 2013;**429**:82-90. DOI: 10.1016/j. colsurfa.2013.03.039
- [76] McKibben MJ, Gillies RG, Shook CA. A laboratory investigation of horizontal well heavy oil-water flows. Canadian Journal of Chemical Engineering. 2000;78:743-751
- [77] Khan MR. Rheological properties of heavy oils and heavy oil emulsions. Energy Sources. 1996;18:385-391
- [78] Zaki NN. Surfactant stabilized crude oil-in-water emulsions for pipeline transportation of viscous crude oils. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 1997;125(1):19-25. DOI: 10.1016/S0927-7757(96)03768-5
- [79] Sun R, Shook CA. Inversion of heavy crude oil-in-brine emulsions. Journal of Petroleum Science and Engineering. 1996;**14**:169-182
- [80] Hayes M, Hrebenar KR, Murphy PL, Futch LE, Deal JF, Bolden PL. Bioemulsifier-Stabilized Hydrocarbosols. US Patent 4793826. 1988
- [81] Gutnick DL, Rosenberg E, Belsky I, Zinaida Z. Alpha Emulsans. US Patent 4395354. 1983
- [82] Gutnick D, Bach HR. Compositions Containing Bioemulsifiers and a Method for their Preparation. US Patent 6512014. 2003
- [83] Rivas H, Gutierrez X, Cardenas AE, Morales A. Natural Surfactant with Amines and Ethoxylated Alcohol. US Patent 5792223.1998
- [84] Yan N, Masliyah JH.
  Demulsification of solids-stabilized oil in-water emulsions. Journal of Colloids and Surfaces A:
  Physicochemical and Engineering Aspects. 1998;11:15-20

- [85] Lissant KJ. Emulsification and demulsification in oil recovery. In: Shah DO, Schechter RS, editors. Improved Oil Recovery by Surfactant and Polymer Flooding. UK: Academic Press; 1997
- [86] Giuggioli A, De Ghetto G. Innovative technologies improve the profitability of offshore heavy oil marginal fields. In: International Meeting on Petroleum Engineering, Beijing, November 14-17. 1995
- [87] Kokal SL, Maini B, Woo R. Flow of emulsions in porous-media. Advances in Chemistry. 1992;**231**:219-262. DOI: 10.1021/ba-1992-0231.ch006
- [88] Simon R, Poynter WG. Pipeline Oil/water Mixtures. U.S. Patent. 1970. No. 3,5 19.006
- [89] Hardy WA, Sit SP, Stockwell A. Field trials of transoil technology for emulsion pipelining of bitumen. In: Fourth UNITAR/UNDP Conference on Heavy Crude Tar Sands. Vol. 5. Edmonton, Alberta: UNITAR/UNDP; 1988. p. 222
- [90] Urdahl O, Fredheim AO, LØken KP. Viscosity measurements of water-incrude-oil emulsions under flowing conditions: A theoretical and practical approach. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 1997;123-124:623-634
- [91] Stockwell A, Sit SP, Hardy WA. Transoil technology for heavy oil transportation. Results of field trials at Wolf Lake. In: Paper SPE 18362 Presented at SPE European Petroleum Conference, October 16-19. Vol. 249. London, UK; 1988
- [92] Bertero L, Dilullo A, Lentini A, Terzi L. An innovative way to produce and transport heavy oil through dispersion in water: Laboratory study and field test results. In: 69th Annual Technical Conference and Exhibition, New Orleans, LA, September 25-28. 1994

- [93] Gregoli AA, Olah AM. Lowtemperature Pipeline Emulsion Transportation Enhancement. US Patent 5156652. 1992
- [94] Kumar S, Mahto V. Emulsification of Indian heavy crude oil using a novel surfactant for pipeline transportation. Petroleum Science. 2017;14:372-382. DOI: 10.1007/s12182-017-0153-6