CHAPTER II
LITERATURE REVIEW

2.1 Oil Production Overview

Hydrocarbon resources are very important; they are approximately estimated as 65% of the world's overall energy resources. Nowadays, crude oils are the most important hydrocarbon resources in the world, and heavy crude oils are counted for a large portion of the world's potentially recoverable oil reserves. The demand for heavy crude oil had been historically ignored because of their high viscosity and complexity in composition, which make them difficult and expensive to produce, transport and refine. The production of heavy crude oil is currently limited in Alberta, Canada and Orinoco Belt, Venezuela. Heavy and extra-heavy crude oils production has been lately introduced in several regions like The Gulf of Mexico and The Northeast China, as it will be needed over next two decades in order to replace declining production of conventional middle and light oils. Therefore, the production of heavy crudes is expected to increase in the near future as low viscosity crudes become exhausted (Abdurahman, 2012; Ashrafizadeh, 2010).

2.2 Heavy Crude Oil Transportation

Heavy crude oils are crude oils rich in asphaltenes but lean in low molecular weight components. The viscosity of heavy crude oil and extra heavy crude oil is within the range of approximately 10^3 to 10^6 cP. They may also have high contents of sulfur, salts and metals like nickel and vanadium as shown in Table 2.1.

Table 2.1 Properties and composition of medium, heavy and extra-heavy Mexican crude oil (Martínez-Palou, 2011)

Parameter	Mexican crude oils		
	Medium	Heavy	Extra-heavy
API gravity	21.27	11.9	9.17
Molecular weight (g/mol)	314.8	486	507.8
Sulfur content (%)	3.40	5.02	4.80
Water content (%)	1.80	0.05	<0.05
SARA analysis			
Saturates	26.53	7.94	15.00
Aromatics	14.74	5.28	19.11
Resins	47.60	70.93	46.78
Asphaltenes (from n-C_7)	11.13	15.85	19.11

Transportation of heavy and extra-heavy crude oils via pipelines is difficult due to low flowability of the viscous crude and wax and asphaltene deposition issues. In order to overcome the difficulties in heavy crude oil transportation, several techniques have been developed over many decades. There are three general approaches for the transportation of heavy and extra-heavy crude oil: viscosity reduction, drag minimization and *in-situ* oil upgrading.

The combination of two or more of these approaches can improve the efficiency of heavy crude oil transportation.(Abdurahman, 2012; Martínez-Palou, 2011).

2.3 Viscosity Reduction

This approach can be accomplished by four resolves; a) dilution with other substances, b) formation of an oil-in-water emulsion, c) increasing and/or conserving oil's temperature and/or d) depressing crude oil's pour point (Martínez-Palou, 2011).

2.3.1 Dilution of Heavy and Extra-heavy Crude Oils

Dilution is one of the conventional and widely applied methods for reducing the viscosity of heavy oils since 1930s. Dilution involves the addition of lighter liquid hydrocarbons to heavy oil. The light hydrocarbons typically consist in condensates from natural gas production or lighter crude oils. Dilution is not only an effective option to improve oil mobility but also facilitating certain operations such as dehydration and desalting. Dilution is the most widely used solution where condensates or lighter crude oil is available, but it may require substantial investments in pumping and pipelines due to the increase of the transport volume and the later need to separate the light components.

2.3.2 Formation of Heavy and Extra-heavy Crude Oil Emulsions in Water (O/W)

Emulsions naturally occur since crude oils are rich in natural surfactants, such as asphaltenes and resins, which are known to stabilize either the water-in-oil or oil-in-water emulsions because they carry both the hydrophobic and the hydrophilic functional groups (Oh, 2011). Moreover, water is also produced along with oil in most oil production (Couto, 2008). Water-in-oil (W/O) emulsions are mainly formed during the petroleum production but they can be more complex as oil-in-water-in-oil (O/W/O) emulsions. Nevertheless, emulsions or dispersions of heavy or extra-heavy crude oil in water (O/W) or in brine may be formed as a strategy to transport high-viscosity crudes because of the viscosity reduction upon emulsion formation (Martínez-Palou, 2011). Oil-in-water emulsion will be discussed in detail in the following section.

2.3.3 Heating Heavy and Extra-heavy Crude Oil and Heated Pipelines

The second most used method for transporting heavy oil by pipeline is to heat the pipelines. The purpose is for maintaining the elevated temperature (<373.15 K) in which the oil is produced at the well-head through insulation of the pipelines. Because heat losses cannot be avoided completely, external heating of the heavy oil is always required during oil transportation. It should be noted that the heating method needs to be combined with reheating at the pumping stations through direct-fired heaters. Insulation options include burying the pipeline to conserve heat.

Some studies indicate that the viscosity is reduced from roughly 700 to 300 cP by heating the medium crude oil from 283 to 303 K.

2.3.4 Pour Point Depressants (PPD)

PPD, alternatively known as wax crystal modifiers, are chemical additives that affect nucleation, adsorption or solubility of waxes. The modification of wax crystallization may facilitate the transportation of waxy crude oils by depressing the crude oil's pour point, viscosity and yield stress appreciably. Various polymer compounds have been described as PPD; the most extensive use for waxy heavy oils are highly branched poly-α-olefin (Martínez-Palou, 2011).

2.4 Emulsification of Heavy Crude Oil in Water

As mentioned previously, emulsions can be formed by the aid of natural surfactant, primary asphaltenes and resins. Depending on the molecular characteristics of the surface active agent, either oil-in-water or water-in-oil emulsion can be formed (Oh, 2011). Water-in-oil emulsion is commonly observed as the water cut of the production stream increases along the production. Water content contained in untreated oil may vary from a small fraction of 1% to exceed 90%.

Additionally, to overcome the high viscosity of heavy and extra-heavy crude oil for transportation, oil-in-water emulsion was formed with suitable surface-active agent and natural surfactant. This strategy of forming oil-in-water emulsion is being developed and has been published as practical viscosity reduction approaches. Abdurahman *et al.* (2012) and Ashrafizadeh *et al.* (2010) successfully prepared stable heavy crude oil-in-water emulsion using Triton X-100, nonionic surfactant, as emulsifying agent. They investigated the oil-in-water emulsion stability as a function of on oil content, surfactant concentration and operating condition of emulsion preparation, including speed and duration of mixing. It was discovered that the stability of oil-in-water emulsions decreased as oil content of emulsion increased up to the phase inversion point. The stability of oil-in-water emulsions increased as the surfactant concentration, speed and duration of mixing increase. The viscosity of oil-in-water emulsion was observed to increase with increasing the surfactant concentration, the time and speed of mixing due to high number density of oil

droplets dispersed in the water continuous phase. In addition, the phase inversion occurs when oil volume fraction in oil-in-water emulsion exceeded 70%, indicated by a drastic increase in the viscosity upon the formation of water-in-oil emulsion (Martínez-Palou, 2011).

Although the formation of oil-in-water emulsion can be a promising strategy to transport highly viscous crude oil, potential wax deposition issues can arise and should be considered when applying this strategy. Wax deposition from single phase oil flow, water-in-oil and oil-in-water emulsion as the major problem for crude oil production and transportation in subsea pipeline will be described in following sections.

2.5 Wax Deposition in Subsea Pipelines

Wax deposition in subsea oil pipeline is significant economic problem in petroleum industry because it can lead to a reduction in oil production, pipeline shutdown, and increase operating costs problems. For the worst cases, the pipeline may become completely plugged by the wax deposit, requiring the remediation of the pipeline by removing and replacing plugged pipeline in order to continue the production. In most cases, remediation processing is periodically operated in order to maintain the crude oil production and transportation. A conventional and common method technique for wax removal is "pigging", which is a mechanical technique using a pig (a solid object with smaller diameter compared with inner diameter of pipeline) is regularly launched through the inlet of the pipe. As the pig is moving along the plugged pipeline, it scrapes out the wax deposited on the inner pipeline surface. In the case of pigging, it is vital to determine a pigging frequency because the cost of pigging exponentially increases as the pigging frequency increases. An optimum pigging frequency is usually determined based on wax deposition modeling and field experiences (Huang, 2011; Singh, 2001; Zheng, 2013).

2.5.1 Wax Deposition Mechanisms

Wax deposition mathematical models have been studied for many decades and numerous wax deposition mechanisms have been proposed including 1) Molecular diffusion, 2) Soret diffusion, 3) Brownian diffusion, 4) Gravity settling,

5) Shear dispersion, 6) Shear stripping, and 7) Nucleation and gelation (Aiyejina, 2011; Azevedo, 2003). It is widely accepted that molecular diffusion is the dominating deposition mechanism. According to this mechanism, wax molecules first precipitate out of the solution to form an incipient layer of deposit, resulting in less wax dissolved at the near wall region. A concentration gradient is thus established due to precipitation. The concentration gradient drives the diffusion of wax molecules toward the wall as shown in Figure 2.1, leading to the build-up of wax deposit (Huang, 2011; Singh, 2001).

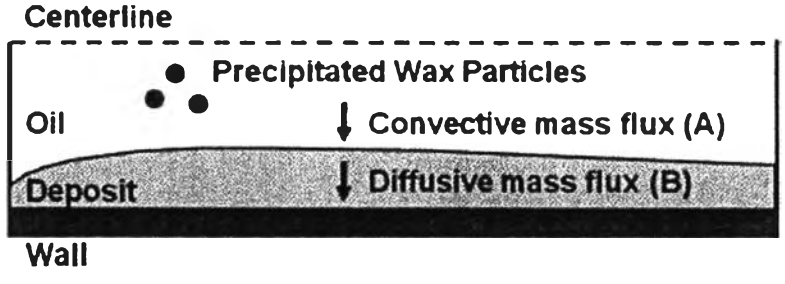

Figure 2.1 Schematic of the MWP model for wax deposition in subsea pipelines (Huang, 2011).

Although different mathematical models have been developed, most of the developed wax mechanism are only provided for single-phase flow (Aiyejina, 2011; Sarica, 2012), There are very few models that predicts two-phase wax deposition. The only currently available two-phase deposition model, such as the model developed by Apte *et al.* (2001), is a simple application of the single-phase oil deposition model with use of two-phase heat-transfer correlations to empirically account for the effect of water on wax deposition. Wax deposition in two-phase flow highly depends on the flow pattern. In an investigation by Anosike *et al.* (2007) indicated that the wax deposition merely occurred at the upper part of the wall in water/oil stratified flow as shown in Figure 2.2 (Aiyejina, 2011; Singh, 2001).

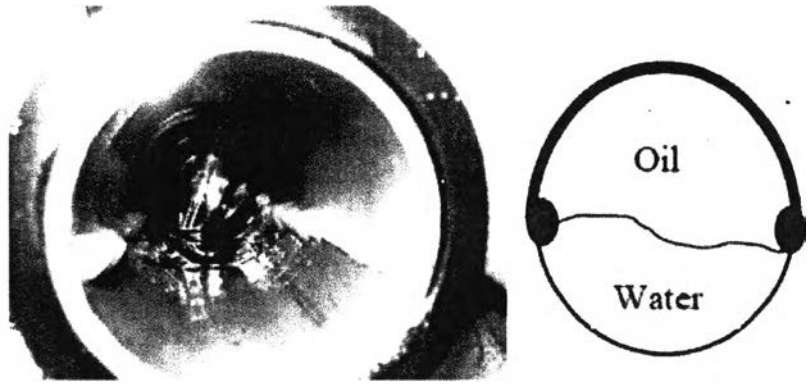

Figure 2.2 Wax deposition under oil–water stratified flow with mixing at the interface (Sarica, 2012).

In the case of dispersion of water in oil, thicker wax deposits were observed in comparison with dispersion of oil in water, which probably either occurred due to less contact between the dispersed oil droplets onto the pipeline wall. As shown in Figure 2.3, insignificant deposit thickness was observed from oil-in-water dispersed flow.

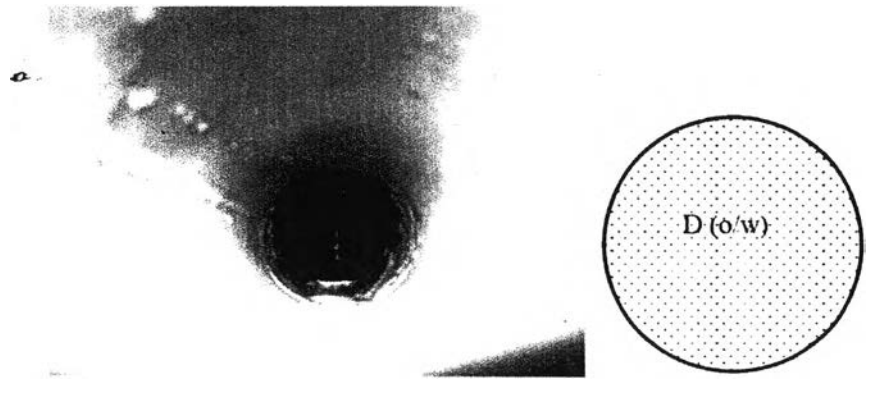

Figure 2.3 Wax deposition under dispersion of oil in water picture (left) and schematic (right) (Sarica, 2012).

More complex flow pattern such as dual dispersion, which is consisted of upper dispersion of oil in water and lower dispersion of water in oil, can occur in pipeline. Similar wax deposition characteristic was observed where upper dispersion gave thinner deposit while lower dispersion gave thicker. Figure 2.4 indicates partially dispersed oil in water flowing along with water. The deposit layer on the upper surface can be markedly seen compared with the lower surface.

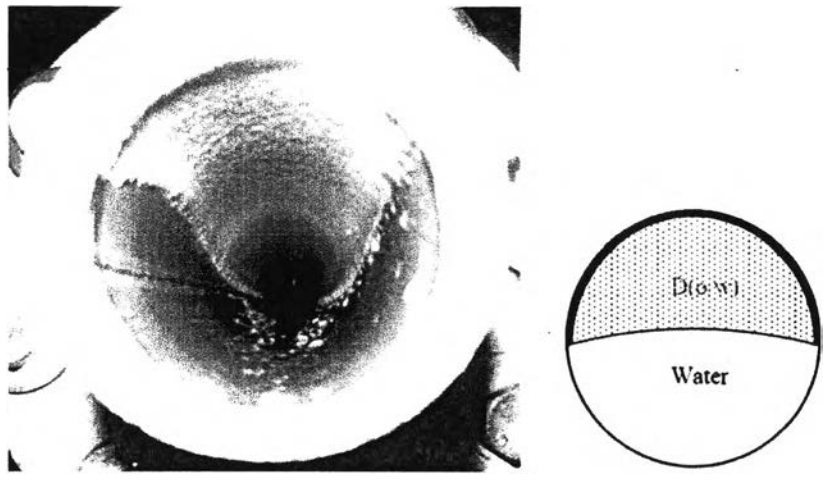

Figure 2.4 Wax deposition under dispersion of oil in water & water picture (left) and schematic (right) (Sarica, 2012).

2.6 Evidence of Wax Deposition for Oil-in-Water Dispersed Flow

Despite the previous listed studies, wax deposition from oil-in-water deposition has not been understood from fundamental perspective of views. Multiple factors can affect wax deposition from oil-in-water, e.g. the oil wettability of the pipe wall surface. In order for wax deposition to occur, it is required that the pipe surface to be oil-wetted.

Couto *et al.* (2008) investigated waxy crude oil deposition from oil/water solution using cold finger apparatus under various temperature driving forces. They observed lesser deposit mass as water cuts were increasing, regardless the

temperature differences between the cold finger and the oil reservoir as shown in Figure 2.5 below.

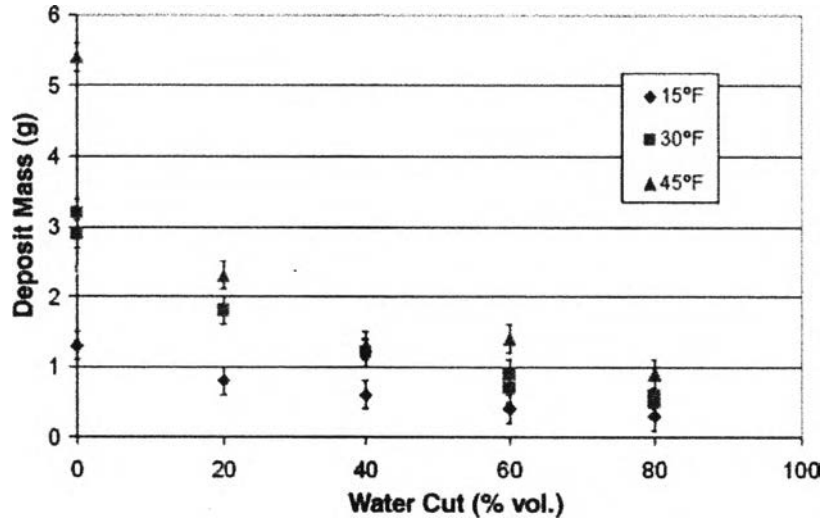

Figure 2.5 Average weight profile of deposits as a function of water cut with a test period of 24 hours (Couto, 2008).

A possible increase in the viscosity of the solution at high water cuts might be an explanation for lower wax deposition rates. Nevertheless, the phase inversion point hasn't been investigated in this literature, it is unclear whether the oil/water solution is literally oil-in-water at water cut 80% or not.

Bruno *et al.* (2008) performed the small-scale flow loop experiment using Garden Banks condensate and found that the wax deposit thickness from two-phase dispersed flow decreased as the water cut increased. The 5th test of their experiments was performed at 85% water cut which was above phase inversion point, 80.6% water cut. They observed the deposit thickness of 0.08 mm as shown in Figure 2.6.

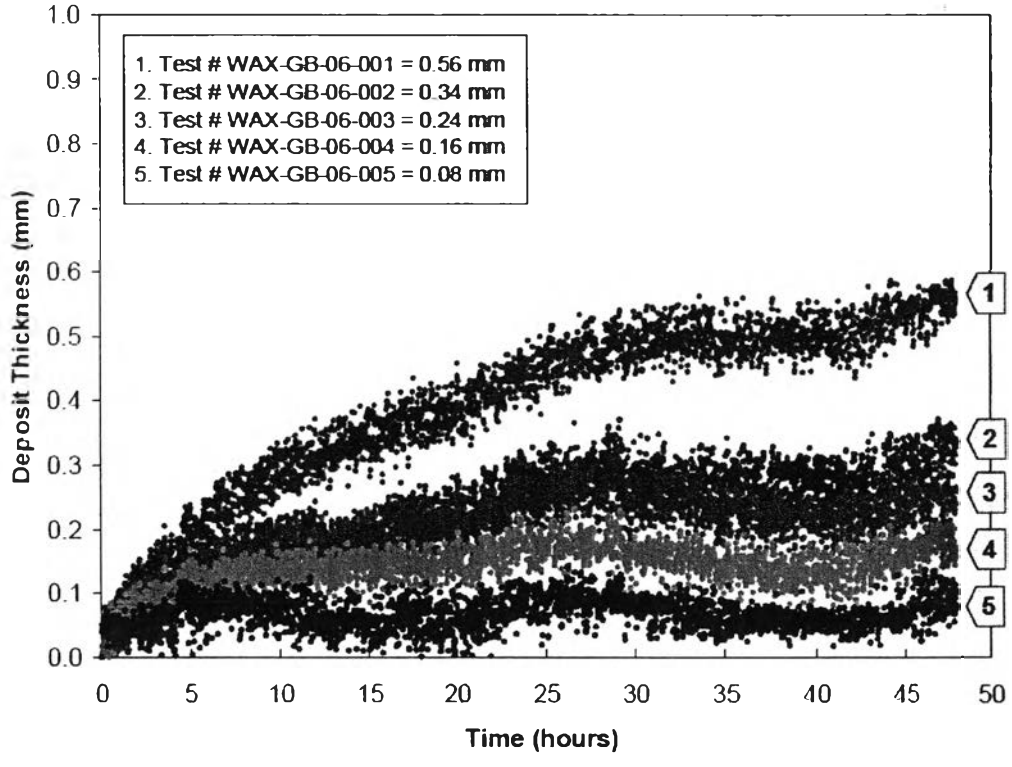

Figure 2.6 Garden Banks deposit test results (Bruno, 2008).

However, several issues haven't been fully addressed; the microstructure of bulk fluid is not well-characterized and the low wax deposition is not well-explained. Regarding to the microstructure of bulk fluid, the deposit formed on the pipeline possibly happen due to the wall wetted with un-dispersed oil layer or from expected oil-in-water emulsion. And the low wax deposition rate might occur owing to the fact that oils rarely attach to pipeline surface.

Other than those wax deposition studies, the surface characteristics of substrate are another key factor of the deposition mechanism in oil-in-water emulsion. When the substrate is exposed to the water continuum and possibly covered with water thin-film which apparently prevents the oil droplets in attaching to the pipeline wall, thus oil should not attach to the substrate surface. There are a few more studies on the effects of various parameters that are similar to oil-in-water emulsion system as following;

dos Santos *et al.* (2006) investigated the role of polar components, such as asphaltenes and naphthenic acids, on the wettability of metallic pipeline surfaces.

Known as natural surface-active agent, asphaltenes are pointed out as the primary species responsible for surface wettability alteration owing to their polar functional groups with the surface polar sites (Kumar, 2011). It was observed by dos Santos that the presence of asphaltenes converted the surface from water-wetted to oil-wetted. Consequently, a higher possibility of wax deposition from oil-in-water dispersion can be expected for crude oils with high asphaltenes content.

According to the viability of asphaltenes in oil field operations, Ajmera *et al.* (2011) also investigated the change in wettability of the substrate pre-wetted with both water and oil in oil-in-water emulsion. For the water pre-wetted surface, the surface remained hydrophilic for all solvents and pure crude oil regarding asphaltenes in both toluene and heptol and also Arab Heavy crude oil. For oil pre-wetted, the surface wettability didn't change with pure solvents but did change with additional of asphaltenes, from hydrophilic to hydrophobic. Also, the increase in asphaltenes concentration contributed hydrophobic ability of the surface. However, these results are only for Arab Heavy crude oil. Other crude oil asphaltenes might yield different surface characteristics.