

CHAPTER II

LITERATURE REVIEW

2.1 Paraffin / Wax

The wax present in petroleum crude primarily consists of paraffin hydrocarbons (C_{18} - C_{36}) known as paraffin wax and naphthenic hydrocarbons (C_{30} - C_{60}). Hydrocarbon components of wax can exist in various states of matter (gas, liquid or solid) depending on their temperature and pressure. When the wax freezes, it forms crystals. The crystals formed from paraffin wax are known as macrocrystalline wax. Those formed from naphthenes are known as microcrystalline wax.

2.1.1 Macrocrystalline Waxes (Paraffin Waxes)

Paraffin waxes are obtained from light and middle lubricating oil cuts of vacuum distillation. Paraffin waxes also include waxes from heavy lubricating oil distillates, which are intermediates between macrocrystalline and microcrystalline waxes with respect to structure and composition (intermediate waxes).

Chemical Composition: Paraffin waxes consist predominantly of mixtures of straight-chain alkanes in a typical distribution of the homologous series, whose molar masses depend on the boiling range of the lubricating oil distillate from which they are obtained. Long-chain weakly branched isoalkanes are present in a much lower proportion, along with a very small fraction of monocyclic alkanes.

Physical Properties: Paraffin waxes are insoluble in water and sparingly soluble in low molar mass aliphatic alcohols and ethers. They are more soluble in ketones, chlorohydrocarbons, petroleum spirit, solvent naphtha, benzene, toluene, xylene, and higher aromatics, especially at elevated temperature. The solubility decreases markedly with increasing molar mass (higher melting point) of the waxes.

Chemical Properties: Paraffin waxes are extremely unreactive under normal condition. Oxidation reactions occur only at elevated temperatures (e.g., on storage and processing above 100°C), particularly in the presence of oxygen and

catalytically active metals. These reactions can be recognized from the burnt odor produced and the yellow to brown coloration of the waxes. Nevertheless, under certain thermally and catalytically controlled conditions, these waxes can undergo chemical reactions, such as chlorination, oxidation, dehydrogenation, and cracking, of which chlorination and cracking are important in industry (www.waxindia.com).

2.1.2 Microcrystalline Waxes (Microwaxes)

Microcrystalline waxes originate from vacuum residues and from the sediments of paraffinic crude oil (settling waxes). Waxes that are liquid at room temperature are mostly contained in diesel oil or gas oil fractions and can be isolated from them.

Chemical Composition: Like paraffin waxes, microcrystalline waxes consist of a mixture of saturated hydrocarbons that are predominantly solid at room temperature, such as n- and isoalkanes, naphthenes and alkyl- and naphthenes-substituted aromatics. Unlike paraffin waxes, isoparaffins and naphthenic compounds predominate here. The microcrystalline structure can be explained by the presence of strongly branched isoparaffins and naphthenes, which inhibit crystallization.

Physical Properties: Microcrystalline waxes are insoluble in water and most organic solvents at room temperature. They are moderately soluble in solvents, such as chlorohydrocarbons, benzene, toluene, xylene, solvent naphtha, and turpentine oil, especially at elevated temperature. Solubility decreases markedly as molar mass increases. Solvents and oils are retained very strongly by microcrystalline waxes, and therefore jellies or floor and shoe polish is determined by this retention capacity of microwaxes.

Chemical Properties: Microwaxes are more reactive than paraffin waxes because of the higher concentration of complex branched hydrocarbons with tertiary and quaternary carbon atoms. These C-C bonds are not very thermally stable (i.e. the waxes darken and resinify) on prolonged heating. In addition, they form black tar-like substances on contact with aggressive chemical, such as concentrated sulfuric acid. The reaction of microwaxes with oxygen at elevated temperature and in

the presence of catalytically acting heavy-metal soaps is used for the production of oxidized microwaxes.

2.2 Waxy Crude Oil

A waxy crude usually consists of: (1) a variety of light and intermediate hydrocarbons (paraffins, aromatics, naphthenic, etc.), (2) macro and microcrystalline, and (3) a variety of other heavy organic (non-hydrocarbon) compounds, even though, at very low concentrations including resins, asphaltenes, mercaptans, organo-metallics, etc. when the temperature of a waxy crude oil is lowered, first the heavier fractions of its wax content start to freeze out. For a waxy crude, it is customary to measure its cloud point and pour point according to ASTM methods.

Depending on their natural occurrence and their composition, waxy crude oils are divided into: (1) clean waxy crude and (2) regular waxy crude (Mansoori, 2001).

2.2.1 Clean Waxy Crude

A clean waxy crude is defined as a crude oil, in which there exist only hydrocarbons and wax as its only heavy organic constituent. As the clean waxy crude flows through a cold pipe or conduit (with a wall temperature below the cloud point of the crude), crystals of wax may be formed on the wall. Wax crystals could then grow in size until the whole inner wall is covered with the possibility of encapsulating oil inside the wall layers. The arterial blockage problems of clean waxy crude can be efficiently controlled by insulation and heating of the pipe to a temperature above its cloud point. Most of the existing wax deposition problems of the clean waxy crudes are due to the lack of proper insulation and heating systems. As a result, application of chemical anti-foulants and frequent use of pigging operation have become necessary.

2.2.2 Regular Waxy Crude

Regular paraffinic or waxy crudes are widespread in the world and the major complex systems. The problems related to the production, processing, and

transportation of these medium-gravity fluids are not only crystallization of their wax content at low temperatures, but also the formation of deposits, which do not disappear upon heating and cannot be completely removed by pigging. Regular waxy crudes are not clean and, in addition to wax, they contain other heavy organics, such as asphaltene, resin, and etc. These other heavy organics do not generally crystallize upon cooling and, for the most part, they may not have definite freezing points. Depending on their natures, these other heavy organics will have different interactions with wax, which could either prevent wax crystal formation or enhance it.

2.3 Mechanism of Deposition

Four different effects (mechanisms) are recognized for such depositions. One or more of these mechanisms would describe the organic depositions that may occur during oil production, transportation, or processing (Mansoori, 2001).

The degree of dispersion of heavy organics in petroleum fluids depends upon the chemical composition of the petroleum. The ratio of polar/non-polar and light/heavy molecules and particles in petroleum (Figure 2.1) are the factors primarily responsible for maintaining the stability of the polydisperse oil mixture.

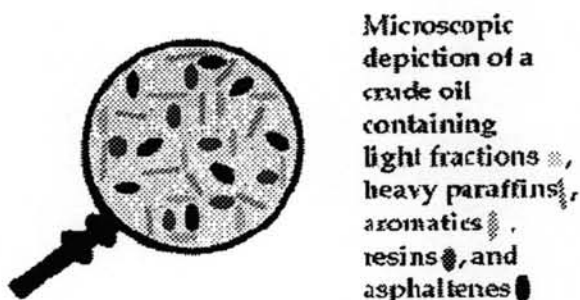


Figure 2.1 Microscopic depiction of a crude oil (Mansoori, 2001).

2.3.1 Solubility Effect

Deposition of heavy organics can be explained by an upset in the polydisperse balance of oil composition. Any change in temperature, pressure or

composition (such as addition of a miscible solvent to oil as demonstrated in Figure 2.2) may destabilize the polydisperse oil. Then, the heavy and/or polar fractions may separate from the oil mixture into steric colloids and another liquid phase or into a solid precipitate.

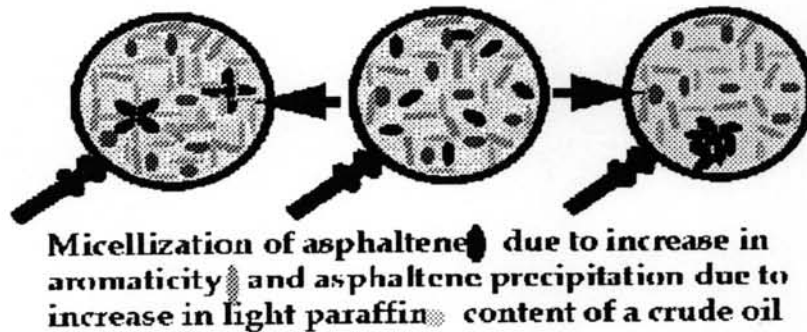


Figure 2.2 Effect of composition change on heavy organic precipitation (Mansoori, 2001).

Segments of the separated fractions, which contain sulfur, nitrogen, and/or hydrogen bonds, could start to flocculate and as a result produce the irreversible heavy organic deposits, which may be insoluble in solvents.

2.3.2 Colloidal Effect

Some of the heavy organics (specially asphaltenes) will separate from the oil phase into an aggregate (large particles) and then will remain suspended in oil by some peptizing agents, like resins, which will be adsorbed on their surface and keeping them afloat, as demonstrated in Figure 2.3.

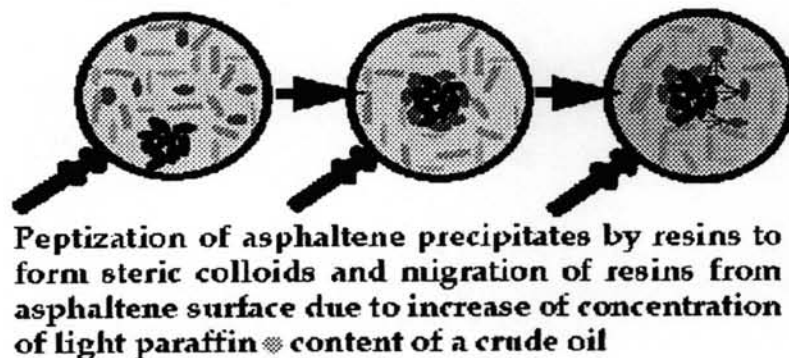


Figure 2.3 Peptization of asphaltene precipitated (Mansoori, 2001).

Stability of such steric colloids is considered to be a function of concentration of the peptizing agent in the solution, the fraction of heavy organic particle surface sites occupied by the peptizing agent, and the equilibrium conditions between the peptizing agent in solution and on surface of heavy organic particles.

2.3.3 Aggregation Effect

The peptizing agent concentration in oil may drop to a point, at which its adsorbed amount would not be high enough to cover the entire surface of heavy organic particles. This causes the potential for aggregation of heavy organic particles due to development of free active sites on their surfaces, and their eventual flocculation, as shown in Figure 2.4. This may then permit the heavy organic particles to come together (irreversible aggregation), grow in size, and flocculate. The nature and shape of the resulting aggregates will determine their effect on the behavior of the petroleum fluids.

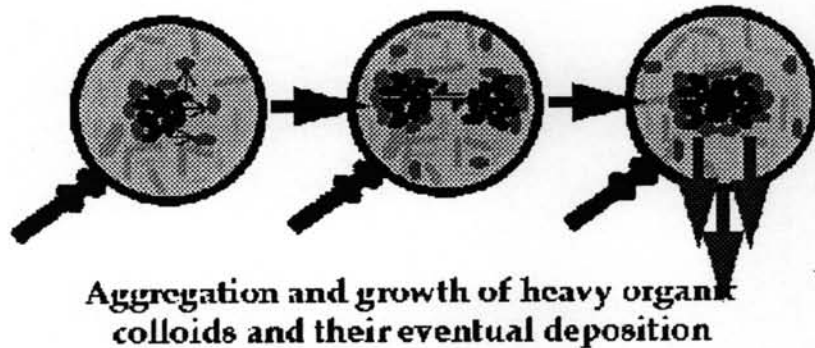


Figure 2.4 The aggregation of heavy organic particles (Mansoori, 2001).

2.3.4 Electrokinetic Effect

When a crude oil is flowing in a conduit (porous media, well, pipeline, etc.) there is an additional effect (electrokinetic effect) to be considered in the behavior of its heavy organic constituents. This is because of the development of electrical potential difference along the conduit due to the motion of charged particles. This electrical potential difference could then cause a change in charges of the colloidal particles further down in the pipe, the ultimate result of which is their

untimely deposition and plugging of the conduit, as shown in Figure 2.5. The factors influencing this effect are the electrical and thermal characteristics of the conduit, flow regime, flowing oil properties, characteristics of the polar heavy organics and colloidal particles, and blending of the oil.

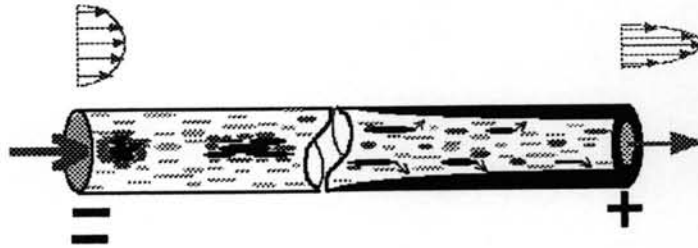


Figure 2.5 Electrokinetic deposition in an isothermal-single phase pipeline flow (Mansoori, 2001).

In 1981, Burger *et al.* studied the mechanisms of deposition of paraffin. The deposition occurred as a result of lateral transport by diffusion, shear dispersion, and Brownian motion. The temperature at the walls is less than the temperature at the center of the flow line. This leads to a temperature gradient and concentration gradient leading to molecular diffusion of the paraffin crystals toward the wall. There are many factors that can affect the rate of deposition of paraffin in flow line, such as temperature of the crude, temperature of the tube wall, flow rate, residence time, wax concentration, pipe roughness, and others.

In 1997, Li *et al.* studied the mechanisms of wax prevention in a pipeline with a glass inner layer by simulating crude oil production by a pump well, and transport of crude oil and formation water in glass and steel tubes in a laboratory. It is clearly demonstrated that the water wetting property of glass and steel is the key factor in controlling the ability of wax to be deposited on the walls of glass and steel tubes. When the water content of crude oils was more than 60%, the oils and formation water flowed as a plug and oil-in-water emulsion, and a stable water film was formed between the oil and the wall of the glass tube. The film prevented the oil from being deposited on the wall of the glass tube, and consequently, the amount of wax deposited on the wall was reduced. The mechanisms of wax deposition on the wall of glass and steel tubes are molecular diffusion and shear dispersion.

2.4 Study of The Characteristics and Properties of Waxy crude Oils

2.4.1 Wax Precipitation

In 1991, Rønningesen *et al.* studied wax precipitation in North Sea crude oils, leading to an improved thermodynamic model for prediction of wax formation. Seventeen crude oils and condensates were characterized analytically and rheologically with emphasis on properties related to the content of wax. In particular, three different methods for determination of wax precipitation temperature (WPT), namely polarization microscopy, differential scanning calorimetry (DSC), and viscometry, were discussed, and the results obtained by the three methods were compared. Microscopy invariably gave the highest WPTs, probably being the most relevant values for predicting the onset of wax deposition on cold surfaces. The WPTs from microscopy were found to depend on many factors, such as thickness of the sample film and cooling rate. DSC and viscometry are likely to underestimate the onset temperature of initial wax deposition. Finally, compositional analyses of wax precipitated from one of the oils indicated that wax crystallizing just below the WPT was richer in condensed naphthenes and poorer in isoalkanes than wax formed at lower temperatures. Isoalkanes appeared to be the most abundant class at all temperatures.

2.4.2 Wax Crystallization

In 2000, Chevallier *et al.* investigated the thermodynamic and structural formation of solid deposits in solutions that consist of a commercial multiparaffinic wax in the normal tetradecane, used as solvent. The studies were carried out by X-ray diffraction with the decrease in temperature from the liquid state, chromatography analyses of (liquid and solid) phases separated at equilibrium, and simple and differential thermal analyses. They found that the solid deposits form a single multi- C_n solid solution in the course of the crystallization of (wax+C₁₄) mixtures. The first deposits observed just below the liquidus point consist of all the C_n from C₂₀ to C₄₂ and present an average number of carbon atoms higher (around 2 carbon atoms) than the initial wax. When the temperature decreases, this average

number of carbon atoms decreases as the ratio of smaller alkanes gradually increases in the multi- C_n solid solution.

2.4.2.1 Influence of Heavy Linear Alkane

In 2000, García studied the influence of heavy linear alkane concentration on the wax crystallization tendency or wax appearance temperature (WAT) of a paraffinic crude oil, and paraffin inhibitor effectiveness was evaluated by means of polarized light microscopy. A crude oil insensitive to the addition of wax inhibitors was fractionated into its hydrocarbon class fractions. Virgin crude oil distillation, deasphaltation of the 385°C+ residue, HPLC separation of the heavy saturated hydrocarbons, and molecular sieves adduction enabled the isolation of the linear paraffins fraction with a carbon distribution of more than 24 atoms (nC_{24+} paraffins). He found that the abundance of large linear alkanes (nC_{24+}) in paraffinic crude oils increases their tendency to the wax crystallization, which can be demonstrated by a linear correlation between the concentration of this hydrocarbon family and the crude oil cloud point. The presence of flocculated asphaltenes in the bulk crude oil generates wax crystallization sites, which increase the cloud point of the crude oil and interfere the crystal inhibition mechanism of a maleic anhydride crystal modifier. This aspect should be taken into consideration in the design of paraffin inhibition treatments by the addition of asphaltene flocculation inhibitors to the formulation, when necessary.

2.4.2.2 Effect of Paraffin Class-Types

In 2000, García *et al.* studied the effect of paraffin class-types on the wax crystallization tendency in oils and the activity of paraffin inhibitors for waxy crude oils. Oil enrichment with isolated paraffin fractions allowed the assessment of the influence of their molecular weight on the cloud point and the behavior of crystal modifiers. An insensitive crude oil without response to wax inhibitors was separated into its (normal/cyclo+branched) paraffin fractions. Reduced pressure distillation, *n*-heptane asphaltenes precipitation from the residue, high performance liquid chromatography (HPLC) of maltenes, and molecular sieve inclusion of the saturates were the separation techniques used for the isolation of the (cyclo+branched) paraffin fraction. (Cyclo+branched) paraffins, also known as (naphthene+iso) alkane isomers, were added to the selected crude in order to

investigate their effect on the cloud point. They found that a significant proportion of large alkanes in crude oils is responsible for the inefficiency of paraffin inhibitors. However, when the nature of these large alkanes is cyclic or branched, a complex phenomenon is observed. At concentrations below 40 wt%, the inhibitor activity is slightly reduced. Above this concentration, the inhibitor activity is significantly improved with an offset of 4°C. This effect is thought to be caused by the structural disorder introduced during the formation of wax crystals, due to the presence of the cyclo and isoparaffin fractions. In addition, they concluded that the inhibitor was more effective in depressing the pour point for wax that precipitates as mixed crystals or solid solutions, than for those precipitating as crystals of only one type of *n*-paraffin.

2.4.3 Quantification of the Wax Content

2.4.3.1 *Fractionation using various solvents*

In 1999, Thanh *et al.* investigated the traditional methods for isolating asphaltene fractions by adding 40 volumes in excess of low boiling point solvents, such as pentane, hexane, or heptane, to produce asphaltene fractions, which are contaminated with a significant amount of microcrystalline waxes (>C₄₀). The presence of these microcrystalline waxes in the asphaltene fractions has the potential to provide misleading and ambiguous results in modeling and treatment programs. They described a novel method for the preparation of wax free asphaltene fractions. Furthermore, this method provided a quantitative subdivision of the wax fraction (micro- and macrocrystalline) into pentane soluble and insoluble waxes. It might help us to explain causes of wax deposition problems because determination of asphaltene and wax contents of crude oils can play a very important role in eliminating, or at least alleviating, production problems associated with wax and asphaltene deposition. A more accurate assessment of the composition of the deposits at wellheads and in pipelines would also provide better information when protocols are developed to remediate such the problems. In addition, an accurate assessment of any deposit or precipitate in production is essential for developing an efficient clean-up procedure. A wax build-up may be prevented or minimized by the addition of light hydrocarbons. However, if the build-up resulted predominantly from the addition of

asphaltenes, then addition of light hydrocarbons would worsen the situation, leading to the build-up of additional asphaltene deposits.

2.4.3.2 Acetone Precipitation Techniques

In 2000, Elsharkawy *et al.* studied the measurements of wax content by acetone precipitation techniques, as well as wax appearance temperature (WAT), by viscosity measurements and differential scanning calorimetry (DSC) of eight different stock-tank crude oils from the Middle East. Comparison of WAT measured by DSC and viscosity indicated that the viscosity method overestimates the WAT. They indicated that the WDT is somewhat higher than the WAT for all of the crudes. However, enthalpy of precipitation of wax during cooling is always lower than the corresponding dissolution enthalpy during the heating process.

2.4.3.3 Differential Scanning Calorimetry

In 2004, Chen *et al.* created a new method to measure the wax content of crude oil, which was developed by the use of differential scanning calorimetry (DSC). The wax content of a crude oil is proposed and proved to be the Q (total thermal effect of wax precipitation in sample) ratio of the crude oil and its corresponding wax obtained by using standard acetone method, i.e. Q_{oil}/Q_{wax} . In addition, two empirical correlations have been established on the basis of good linear relations between Q_{oil} and the wax contents determined by both standard acetone method and Q_{oil}/Q_{wax} method. Those made it easier to determine the wax content of crude oils.

2.5 Wax Deposition Problem

One of the major unsolved complex problems confronted by the petroleum and natural gas industries at present is the untimely deposition of heavy organic compounds present in the oil. The production, transportation, and processing of petroleum, bitumen, and other heavy-organic-containing hydrocarbons could be significantly affected by flocculation and deposition of asphaltene, resin, paraffin wax, diamondoid, organo-metallics, etc. Typical deposits not only consist of normal, branched, and cycloparaffins, but also may include varying amounts of oil, sand, scale, asphaltenes, corrosion products, water, and etc., which are trapped or act as

nucleation sites when the wax is deposited. Initially, deposits may range from soft to hard, but typically over time the deposit becomes harder and more difficult to remove.

In the case of waxy crudes, when the temperature is lowered, the wax crystallizes gradually in the form of needles and thin plates. Upon further crystallization, these needles and thin plates turn into three-dimensional networks and cause solidification of crude during production and transportation in the reservoir rock tubulars, oil well, pumps, storage vessels, transfer pipelines, refinery and upgrading equipment with devastating economic consequences (Groffe *et al.*, 2001).

2.5.1 Processing

2.5.1.1 *Reservoir or Oil Well*

Paraffins tend to precipitate when the temperature of the crude falls below the cloud point or the Wax Appearance Temperature (WAT). As the crude flows up the wellbore, its pressure drops cause solution gas to liberate. This leads to a fall in temperature, an increase in viscosity, and a change in oil composition. All these factors aid in the precipitation of paraffin (Weingarten and Euchner, 1986).

2.5.1.2 *Pipeline*

Crude oil production under deep water presents serious operational problems, due to possible obstruction of flow pipes or production lines. Such lines are in permanent contact with very cold sea water, and the sharp temperature decline of oil production lines provokes the crystallization of some heavy oil fractions. The separation of such fractions, constituted mainly by paraffin and waxes, produces solid deposits responsible for the reduction of the cross-section of flow lines (Carnahan, 1989). Since its early stages, off-shore oil production at the Campos basin (RJ, Brazil) has faced constant problems due to wax deposition (Marques *et al.*, 1997).

2.5.2. Production

Paraffin deposition downhole and in surface equipment is one of the most serious problems being faced in oil production operations. Changes in

physicochemical equilibrium due to a decrease in temperature below the paraffin melting point cause crystallization, losses in components' solubility, and a sequence of accumulation (Misra *et al.*, 1995). In some cases, paraffin deposits have caused reservoir plugging during stimulation treatment and interfered in low temperature oil pumping. The most significant causes for the paraffins crystallization include cooling by gas expansion, heat loss to the surroundings, and intrusion of hot water producing evaporation of light components.

2.5.3 Transportation

2.5.3.1 *Pipeline*

Wax can precipitate on surface, such as tubulars and pipewalls. Over time, build-up of the solid deposit will reduce the internal diameter and eventually will block the line. A second effect, which will most likely cause operational problems much earlier, is that the solid deposit increases the surface roughness of the pipewalls. This causes an increase in the pressure drop at high flow rates, which can result in higher pumping costs or reduced throughput (Groffe *et al.*, 2001).

2.5.3.2 *Storage Tank or Wagon*

The extent of deposition can be manifested as damaged zones in the formation, in plugged tubing, flow lines, and in sludge deposits at the bottom of the tank. These deposits in the well can lead to restricted flow line pressure and decreased production, and can cause mechanical problems. In addition, when wax deposition precipitates in storage tanks, the volume of crude oil is reduced due to the remaining on board (ROB). Consequently, the amount of crude oil supplied to the destination becomes less and less.

As a result, the formation of solid deposits during transportation and refining process of paraffinic crude oil is a major issue for the petroleum industry. The removal of the undesirable solids costs the industry billions of dollars annually, in terms of cost of treatment, reduced production, wells shut-in, inefficient use of production capacity, choking of flow lines, premature abandonment, and increased manpower.

2.6 Techniques to Solve Wax Deposition

A number of techniques have been devised to combat the paraffin deposition problem. In general, these methods can be classified into five categories (Towler *et al.*, 2004).

2.6.1 Mechanical Treatments

The oldest methods, where scrapers that cut the deposit are run-down the tubing, such as pigging, paraffin knife, paraffin hook, and corkscrew, are in general used. At the moment, mechanical methods are still in use, and when the paraffin deposits are soft, they are the most effective way to deal with paraffin problem. However, it is a cumbersome process because the recovery and disposal of the deposit usually cause difficulties.

2.6.2 Thermal Treatments

The principle of this method is addition of heat to maintain the temperature of crude oil above its cloud point or adding heat to existing wax deposits. Steam injected to melt the wax already deposited is a popular method. However, some of the fluid injected goes into the formation, and hence, particulates and chemicals in the fluid have potential to damage the formation. Moreover, hot oiling tends to cause deposits of very hard wax to build-up in the formation.

2.6.3 Bacterial Treatments

Bacterial treatment is a recent technique, where especially cultured microbes are introduced into the wellbore to produce chemicals that inhibit wax production and to break down the produced waxes. However, because the microbes require water to survive and cannot tolerate high temperatures, the method is limited to wells that produce water and has a bottom hole temperature below 93°C.

2.6.4 Electromagnetic Treatments

Electromagnetic treatments are also relatively new. In this method, the oil is constrained to pass through powerful magnets. This polarizes the wax

molecules orienting them in the direction of flow and inhibiting their ability to migrate to the walls to deposit. The effectiveness of this method has not been fully investigated.

2.6.5 Chemical Treatments

In the last couple of decades, considerable effort has been devoted to developing chemical methods for inhibiting paraffin deposition. The chemical inhibitors can be broadly classified into three categories:

2.6.5.1 *Wax Crystal Modifiers*

Wax crystal modifiers are polymeric compounds constituted by a hydrocarbon chain, which provides the interaction between the additive and paraffin, and a polar segment that is responsible for the wax crystal morphology modification necessary to inhibit the aggregation stage. For this reason, it is known as wax crystal modifiers (Machado *et al.*, 2001). Furthermore, crystal modifiers are substances capable of building into wax crystals and altering the growth and surface characteristics of the crystals. One effect utilized in oil production is the reduced tendency of the crystals to stick to metal surfaces, such as pipe walls. Besides, the crystal modifiers will have the effect of reducing the tendency to form a three-dimensional network, thereby lowering the pour point, as well as the viscosity. Hence, the name "pour point depressants" are also used for this class of chemicals. Although the exact way, in which wax crystal modifiers operate, is not absolutely clear, they all basically modify the crystal morphology and the way the crystals interact. They thereby reduce the tendency of crystals to interlock and form three-dimensional networks (Pedersen *et al.*, 2003)

2.6.5.2 *Solvents*

Solvents are normally used for dissolving the wax deposit. They mostly consist of high aromatic compounds.

2.6.5.3 *Paraffin Dispersants*

The function of paraffin dispersants is to inhibit the particles from uniting and depositing.

The last two groups are primarily surface-active agents, such as polyesters and amine ethoxylates. These may act partly by modifying the surface of the pipe wall, but primarily by keeping the crystals dispersed as separate particles, thereby reducing their tendency to interact and adhere to solid surfaces.

The use of chemical inhibitors to reduce the paraffin problem has become popular in the industry. Although a number of chemicals are known to possess paraffin inhibition properties, it has been observed that no single chemical is equally effective in all wells.

2.7 Chemical Additives for Wax Deposition Inhibition

In 2003, Pedersen *et al.* investigated the viscosity, pour point, and wax appearance temperature of a stabilized, waxy North Sea crude oil treated by 12 different commercial wax crystal modifiers, all of which may potentially act both as wax deposition inhibitors and pour point depressants. The viscosity data cover the temperature range from 40 to 5°C. In general, the studied chemicals only marginally influence the wax appearance temperatures, whereas the majority has a pronounced effect on pour points and apparent viscosity. The viscosity data suggest that the inhibitors, probably by some kinds of steric hindrance, “inactivate” wax components within a certain range of molecular weight by preventing them from building of network structures. In addition, at all temperatures, the wax forming from the treated oil mixture has a higher molecular weight than the wax forming from the untreated oil mixture, suggesting that a lower temperature is required to solidify wax molecules of a given molecular size in the presence of an inhibitor. However, some inhibitors do not completely prevent the pertinent carbon number range of molecules from precipitation, but only shift the precipitation toward a lower temperature.

2.7.1 Ester-Type Chemical Additives

In 1991, Sawhney *et al.* investigated the modification of wax crystals when Geleki crude oil was doped with ester-type chemical additives. Properties such as pour point depression data, inhibitor efficiency, melting point of the deposit, and average carbon number data were studied to extend understanding of wax crystal

modification. They found that the ester-type pour point depressants have the capacity to modify n-alkanes in the C₁₁-C₂₀ range.

2.7.2 Paraffin Inhibitor

In 2004, Towler *et al.* studied a laboratory simulation of paraffin deposition using a specially designed flow-tube apparatus. This was used to determine the deposition from the Dakota crude oil obtained from the wells of the Fourteen Mile field in the Big Horn basin. Two paraffin inhibitors were obtained for this Dakota crude and used to mitigate the wax deposition in these experiments. The inhibitors were tested at different concentrations, and the deposition rates were obtained for each of the inhibitors. Based on these experiments, it was observed that the paraffin deposited at faster rate initially and then slowly increased to some maximum, and the use of one of the inhibitors resulted in a 35% reduction in wax deposition. However, it was also determined that this solvent was not effective in removing wax once it had already deposited. Furthermore, the crude appeared to become waxier and more viscous with time after it has been exposed to air.

2.7.3 Pour Point Depressants

In 2003, Zhang *et al.* studies the addition of pour point depressants (PPD) to lower the Cold Filter Plugging Point (CFPP) of diesel fuels and showed that it is an effective and economic way to improve the cold flow properties of the oils. EVAP, a copolymer of ethylene, vinyl acetate, and propylene, is a new type of PPD and has an excellent effect in lowering the CFPP of most Chinese diesel fuels. To further develop this PPD product, its performance mechanism was studied using four kinds of diesel fuels, each with a different response. Differential scanning calorimeter and X-ray diffraction methods were selected as the research measures. According to the experimental results, it is shown that the EVAP molecules have taken effect by co-crystallization.

2.7.4 Polymeric Inhibitor

Pipelines for heavy crude oils have recurrent clogging situations due to paraffin deposition that may lower production rates and be responsible for

leakages. Quintella *et al.*, (2006) evaluated the effect of three polymers on crude oil wettability and on paraffin deposition inhibition: polypropylene (PP), high-density polypropylene (HDPE), and a vinyl acetate copolymer with 28% oxygen content (EVA28). They concluded that the low polarization obtained for flows on EVA28 was attributed to a stronger interaction with the crude oil due to the crude oil oxygen content, as well as its surface being covered with adsorbed on polycyclic aromatic hydrocarbon crude oil. Both the static and flow evaluations of interfacial interaction showed that the interaction was smaller for PP than that for HDPE and EVA28. For HDPE, the flow polarization was smaller than for PP. This confirms the emphasis of the molecular effects over the fluid effects when the liquid has a high flow rate. As both HDPE and PP are linear polymers, the PP's smaller interaction with crude oil and the higher tendency to inhibit paraffinic depositions were attributed to its branches of surface methyl groups that reduce the surface density of hydrogen atoms and hinder the interaction between the crude oil alkyls and the surface. Thus, PP was proved to be better in inhibiting paraffin deposits than HDPE and EVA28.

2.7.4.1 Ionic Surfactants Blending

In 2001, Groffe *et al.* mentioned that wax inhibitors /dispersants and anti-sticking agents are effective solutions to remediate the deposition problem. These chemicals can act as either crystal modifiers or products that reduce the rate of wax build-up on pipe walls. Novel and generic wax dispersant and anti-sticking agent have been developed and tested, which have proven to be effective for retarding the deposition mechanism significantly. The chemical is a synergistic blend of ionic surfactants, which has an ability to adsorb onto bare surfaces of tubings and equipment making them oleophobic. They described some novel chemistries, which suggest that such chemistry is effective in significantly reducing the wax deposition process. In addition, they found that when the temperature is below the wax precipitation temperature, these waxes tend to form interacting three-dimensional structures and can cause congealing to occur. Chemistry, described here, can provide a single monolayer coating and change the wax crystal surface by adsorbing onto the crystals and keeping the entire system dispersed. Furthermore, the crystal size was diminished by the addition of the commercial inhibitor (P5), and the strength of the three-dimensional network was

also diminished as observed by the reduced pour point and the improved flow characteristics of crude oils. In one case, the chemical was able to lower the WAT by almost 10°C. Furthermore, the chemical has been shown to display anti-sticking properties by drastically reducing the amount of wax deposited onto adhering metal surfaces.

2.7.4.2 *Poly(Ethylene-co-Vinyl Acetate)*

Several techniques have been used to minimize the problems caused by the wax deposition, and the continuous addition of polymeric inhibitors is considered as an attractive technological alternative. The addition of copolymers, like polyacrylates, polymethacrylates, or poly(ethylene-co-vinyl acetate) (EVA), permits to inhibit the deposition phenomenon; nonetheless, this effect is specific, i.e. similar copolymers present different performances depending on their physical-chemical properties in solution. Machado *et al.*, (2001) studied the influence of the EVA vinyl acetate content on the viscosity, and the pour point of a Brazilian crude oil was evaluated. The phase behavior and the solubility parameter of EVA copolymers, with different vinyl acetate contents, were investigated in various solvents together with an evaluation of the efficiency of these copolymers as pour point depressants for two different samples of crude oil. The results obtained from viscosity measurements showed that only below the temperature, at which wax crystals start forming, the copolymer exhibited a strong influence in the reduction of oil viscosity, at an optimum concentration. The pour point results revealed EVA 30 to be the most efficient. Not only the solubility parameter and the vinyl acetate content, but also the molecular weight and polydispersity have an important influence on both phase behavior and pour point depression. Furthermore, in order to be efficient, an additive must present a cloud point close to the oil WAT, which has been pointed out by various authors. Bilderback and McDougall (1969) suggested three alternative mechanisms for wax inhibitors. Firstly, the additive may come out of solution at a temperature slightly higher than the oil WAT and cause nucleation and small wax particles. Secondly the additive may come out of solution at the oil WAT and co-crystallize with the wax, forming weak and deformed aggregates. Finally, if the additive comes out of solution at a temperature slightly lower than the

oil WAT, it adsorbs on the wax crystals, inducing the dispersion of the wax crystals. These effects may reflect the lack or excess of polymer precipitation at the oil WAT.

2.8 Previous Works on Phet Crude's Wax Deposition

In 2005, Numura studied the influence of wax inhibitors on Thai crude oils. A chemical method was used to minimize wax deposition problem by adding 7 different wax inhibitors (100-1,000 ppm) and 3 different solvents, i.e. n-pentane, n-hexane, and n-heptane (0-50 wt%) in three Thai crude oils, i.e. Phet, U-thong, and Fang. The results indicated that Fang crude oil had lower physical properties, e.g. pour point and wax content, than U-thong and Phet crude. In addition, the results from chemical treatment showed that maximum pour point reduction by solvent was about 40°C, and the increase in hydrocarbon chain length showed slight effect on pour point reduction. In the case of wax inhibitors, the non-polar part of wax inhibitors played more important role on pour point reduction than polarity, and the maximum pour point reduction by wax inhibitor was about 20°C at operating temperature of 80°C.

In 2006, Malikhow studied the wax inhibitor and inhibiting stability for Phet crude oil. In this study, three solvents and ten polymers were investigated (0-10 wt% for the solvents and 100-1,000 ppm for the polymers). Three solvents, n-heptane, o-xylene, and toluene, showed slight effect on pour point reduction, i.e. when 5% wt/wt of each solvent was added, the pour point of crude decreased only 5°C. While the addition of polymer, poly(ethylene-co-vinyl acetate), could decrease the pour point of crude from 33 to 17°C at 1,000 ppm. The effective polymers acted as a wax dispersant by preventing wax crystal agglomeration in the bulk crude.