CHAPTER II

LITERATURE REVIEW

2.1 **Waxy Crude Oil** (Mansoori, 2001)

Waxy crude oil usually consists of a variety of light and intermediate hydrocarbons (paraffins, aromatics, naphthenic, etc.), wax (macro and microcrystallines) and a variety of other heavy organic compounds, such as resins, asphaltenes, diamondoids, mercaptans, organo-metallic, etc. For the non-waxy heavy organic compounds, they do not generally crystallize upon cooling and, for the most part, they may not have definite freezing points. In addition, depending on their nature, the heavy organics will have different interactions with wax that could either prevent wax crystals formation or enhance it.

When the temperature of waxy crude oil is lowered, first the heavier fractions of its wax content start to freeze out. For waxy crude, it is customary to measure its cloud point and pour point according to ASTM methods. Generally, the waxy crude oil can be separated into 2 major groups. First type is called clean waxy crude which exists only hydrocarbons and wax as its only heavy organic constituent. The plugging problems of clean waxy crude can be removed by insulation and heating of the pipe to a temperature above its cloud point. The second type is regular waxy crude that dose not contain only hydrocarbons but also contain heavy organic compounds such as asphaltene, resin, etc. The heavy organic compounds do not generally crystallize upon cooling and, for the most part, they may not have definite freezing point.

2.2 **Paraffin Wax** (Mansoori, 2001)

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 crystalline wax from paraffin is known as macrocrystalline wax and those from naphthenes are known as microcrystalline wax.

Individual wax properties are determined by molecular size and structure, chemical composition and oil content. Paraffin wax consists mostly of straight chain hydrocarbons with 80 to 90% normal paraffin content and the balance consists of branched paraffins, (iso-paraffins) and cycloparaffins (Figure 2.1).

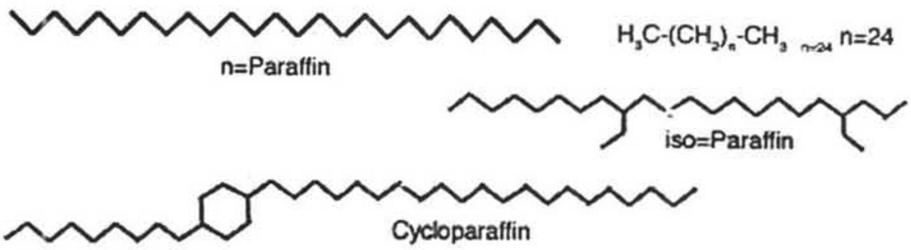

Figure 2.1 Molecular structure of n-paraffins, iso-paraffins and cycloparaffins. (The international group, INC. (IGI) website, www.igiwax.com)

2.3 Wax Deposition (Misra *et al.*,1995)

Paraffin deposition downhole and in surface equipment is one of the most serious problems facing in oil production operations during production, transportation and storage. 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 causing solution gas to liberate. This leads to a fall in temperature, increase in viscosity and a change in oil composition.

Moreover, other authors suggested the factors that can affect deposition of paraffin. Burger *et al.* (1981) indicated the deposition occurred as a result of lateral transport by diffusion, shear dispersion and Brownian motion. The temperature at the wall 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. In addition to diffusion, small particles of previously precipitated wax can be transported laterally by Brownian motion and shear dispersion. Other factors are flow rate, residence time, wax concentration, pipe roughness, etc (Towler and Rebbapragada, 2004).

This problem costs the petroleum 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 (Yong, 1996).

2.4 Study of The Characteristics and Properties of Waxy Crude Oils

The characteristics and properties of waxy crude oils, such as viscosity, solidification and thermal properties are usually determined in order to understand their behavior or explain interaction among crude properties.

2.4.1 Viscosity (Al-Zahrani and Al-Fariss, 1998)

Viscosity is a measure of the resistance of a fluid to deformation under shear stress. Normally behavior of crude is non-Newtonian fluid which is defined as those exhibiting a non-linear propotionality between shear stress and shear rate. High viscosity reduces transport to cold surfaces resulting in an increase of deposition and also harder deposits. Al-Zahrani and Al-Fariss (1998) studied a viscosity model and suggested a generalized viscosity model which predicted the viscosity as a function of shear rate, temperature, and wax concentration as shown in equation (2.1).

$$\mu = \frac{B_1}{\gamma}\left[\left(\frac{\gamma + A_1}{A_1}\right)^n - 1\right]^{\left(\frac{1}{n}\right)} e^{\left(\frac{C}{T} + DxW\right)} \tag{2.1}$$

μ = viscosity (Pa.Sec)

γ = shear rate (sec-1)

T = Temperature (K)

W = wax concentration (wt.%)

A1, B1, C, D, and n = the model parameters

Wax concentration affects the viscosity, when wax concentration increases the viscosity of crude also increases. Moreover, another predicting model of wax deposition was also developed to evaluate the waxing tendencies of Nigeria crude oil and gas condensate system (Adewusi, 1997).

2.4.2 Cloud Point and Pour Point (Machado *et al.,* 2001)

Cloud point and pour point are important parameters used to determine the efficiency of wax inhibitor or design the mechanical facility dealing with waxy crude. For example, Machado *et al.* (2001) used the pour point of crude after adding inhibitor to evaluate the efficiency of each inhibitor. The cloud point of a waxy crude oil is the temperature when the oil appears as haze when the oil is slightly cooled (ASTM D2500 and ASTM D3117). As cooling is continued, the pour point of a waxy crude oil is the lowest temperature at which the oil pours or flows under prescribed conditions when it is cooled without disturbance at a standard rate (ASTM D97).

2.4.3 Thermal Properties of Petroleum Wax by Differential Scanning Calorimetry (DSC) (Letoffe *et al.*, 1994)

The phase transition phenomena is a topic that is widely studied by using spectroscopic and thermo analytical methods, although these techniques do not provide much information on solid-solid and solid-liquid phases transition energies which depends on the composition of the waxes. The differential scanning calorimetry is another thermal technique in which difference in heat flow into a substance and a reference is measured as a function of sample temperature. The basic difference between differential scanning calorimetry and differential thermal analysis is that the former is a calorimetry method in which differences in energy are measured, whereas, in differential thermal analysis, differences in temperature are recorded. The temperature programs for the two methods are similar. Differential scanning calorimetry has by now become the most widely used of all thermal methods. It is used to measure phase transition temperature and associated energies for petroleum waxes of different melting points.

Letoffe *et al.* (1994) used differential scanning calorimetry and thermomicroscopy techniques to characterize wax precipitate on cooling. Thus, thermomicroscopy is useful for correlating morphological or structural changes with the thermal effects observed by DSC. The wax content is determined by using DSC and standard acetone method. They estimated wax content by using Q_{oil}/Q_{wax} ratio to propose the amount of wax (Chen *et al.*, 2004).

2.4.4 X-ray Diffraction (Dirand *et al.*, 1997)

X-ray diffraction techniques provide information about the structural qualities of organic materials. Dirand *et al.* (1997) studied eight commercial and industrial waxes and a heavy crude oil which were studied in pure alkanes, binary and ternary mixtures by X-ray diffraction analysis. From the result, the multicomponent paraffin waxes form a single orthorhombic solid solution that pack along the crystallographic C-axis to equivalent carbon atom number ($\bar{n}_c$). This orthorhombic phase is identical to an intermediate solid solution β'_n or β''_n of binary and ternary mixtures of carbon consecutive (C_n). However, as in these binary and ternary systems where phase domains of two or three phases appear with varying the concentration which it is possible that two, three or many crystalline phase coexist in other multicomponent mixtures with different composition and distributions of C_n.

Chevallier *et al.*, (2000) studied solid deposition of multi-paraffin wax in normal tetradecane, during the cooling from the liquid state to the solid state, by using X-ray diffraction and chromatography analyses. The result showed that the first deposits observed just below the liquidus point (onset crystallization temperature) consist of all the C_n from C_{20} to C_{42} and present an average number of carbon atoms higher (around 2 carbon atoms) than the initial wax; as 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. Imai *et al.* (2001) used X-ray diffraction method to observe the crystal formation on n-paraffin binary mixture, then this information was used to predict the hardness of oil-wax gel.

2.5 Quantifying The Amount of Waxy Deposit

2.5.1 Filtration and Centrifugation (Burger *et al.*, 1981)

Filtration and centrifugation are the methods typically used for determining solid wax content versus temperature for crude oil systems even though the results are influenced by occluded oil and difficult for high-pressure applications. The standard method is used to find wax content, that is UOP method 46-85. This method is for estimating the paraffin wax content of petroleum oils and asphalts. Wax content is an empirical value dependent upon the conditions under which the wax is separated from the original material. In this method paraffin wax content is defined as the mass-percent of material precipitated when a solution of asphalt-free sample in methylene chloride is cooled to –30°C. The lower limit of detection is 5 mass percent. Another method the determined wax content is by using filtration concept, i.e. Chinese petroleum standard SY/T 7550-2000, modified standard acetone method (Chen *et al.*, 2004).

2.5.2 Enthalpy or Heat Content by Differential Scanning Calorimetry (Coutinho *et al.* 1999)

The enthalpy or heat content can be observed by calculation of area below DSC curve that is depicted in Figure 2.2 (Chen *et al.*, 2004). The data obtained from the DSC measurement such as melting enthalpy, cloud point etc. were calculated from the amount of solid forming by thermodynamic approach during cooling process. Method to find the fraction of crystallized solution in hydrocarbon solution was proposed by Coutinho *et al.* (1999). The proposed calculation presents a very good agreement with data obtained by other method as shown in Figure 2.3. Moreover phase diagram of binary system investigated was faster and cheaper, although this method is a bit less accurate than the conventional method for detection of the phase boundaries.

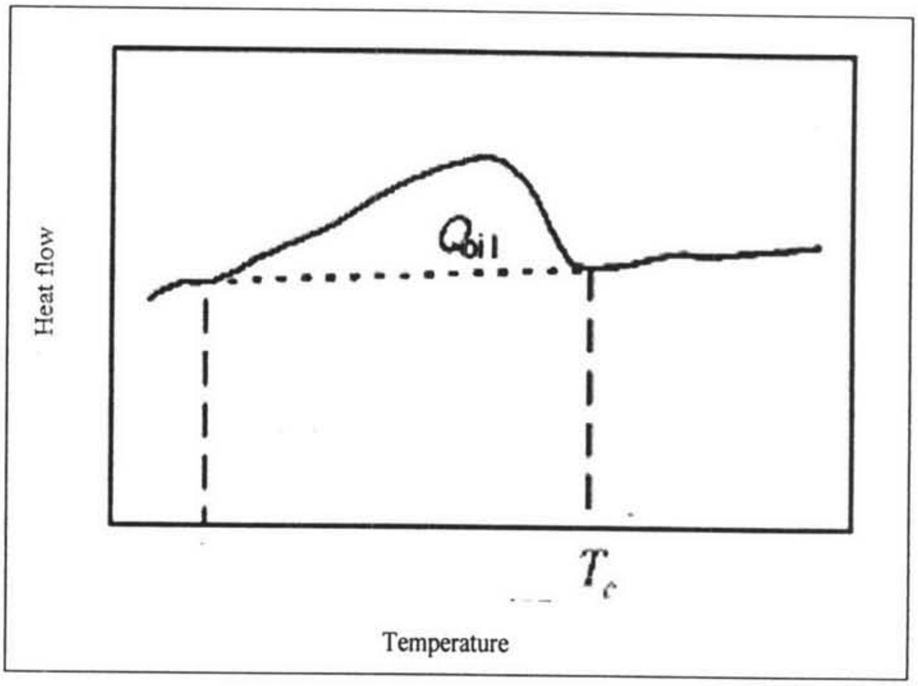

Figure 2.2 A sample of DSC curve of crude oil (Chen *et al.*, 2004).

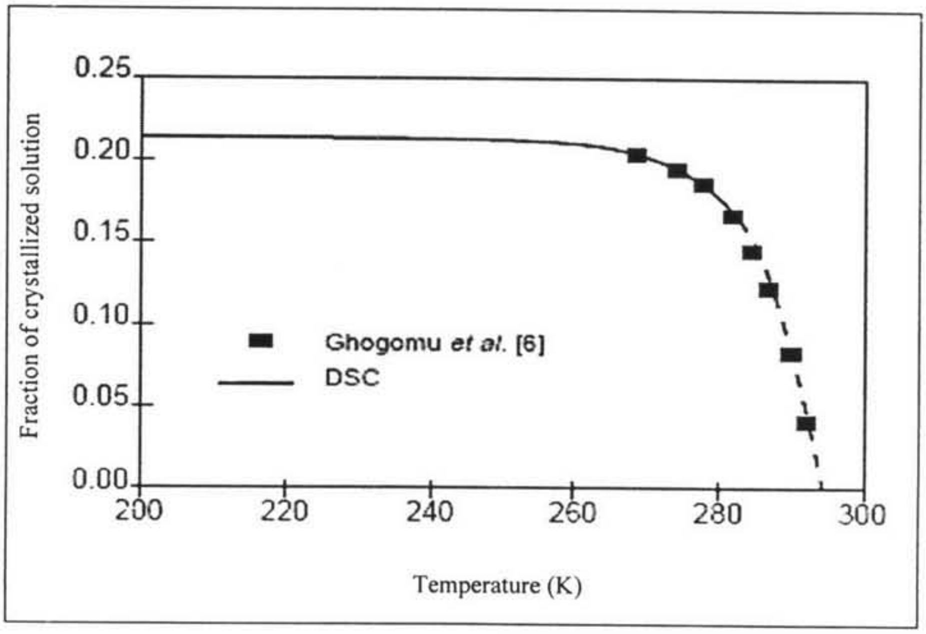

Figure 2.3 Comparison between the fraction of crystallized solution measured by the proposed method and the data by another method (Coutinho *et al.*, 1999).

2.5.3 Gas Chromatography (Guehenneux *et al.*, 2002)

Composition of a petroleum crude is unique and characteristic. The gas chromatography such as high temperature gas chromatography (HTGC) or simulation distillation gas chromatography (Sim-dist GC) are used to analyze the components in crude oil. Crude oil or production oil was separated into various fractions at high temperature. This technique can predict the wax precipitation at an early stage of the reservoir characterization and process production. For example, comparison of produced oil and its associated separator wax deposit can conclude their relative content, and is very different in C_{52} range as shown in Figure 2.4. The presence of wax deposit suggests that the produced oil might have lost a substantial amount of its initial content in high molecular weight hydrocarbon (HMWHC).

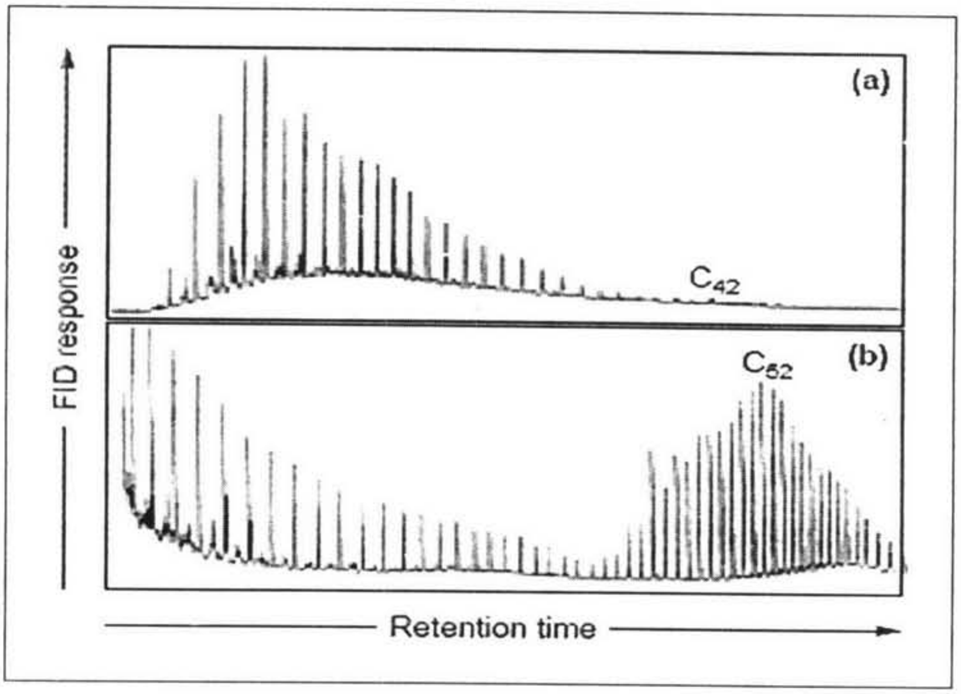

Figure 2.4..HTGC chromatogram of produced oil (a) and its associated separator wax deposit from oil field (b) (Guehenneux *et al.*, 2002).

2.6 Wax Deposition Solution

There are mainly three methods to prevent and control wax deposition problems.

2.6.1 Mechanical Methods

2.6.1.1 Pigging

Pigging has been used for many years to clean larger diameter pipelines in the oil industry. however, the use of smaller diameter pigging systems is now increasing in many continuous and batch process plants as plant operators search for increased efficiencies. The pig is driven down the pipeline by compressed gas, fluid and the machanically scrapes off the wax and redisperses in the bulk crude in front of the pig to give a clean line ready for reuse. Pigging is become a successful chioce of cleaning up the wax depostion in pipeline due to cost effective method for control the wax accumulatied in pipiline.

2.6.1.2 Wireline Cutting

Wireline cutting is employed when the deposition problem become violent trouble and the several kinds such as spheres pig, foam pig or very aggressive pig cannot clean up it. Although the wireline cutting is more effective method to solve problem, this method is uneconomical way because of operation time consuming.

2.6.1.3 Through Flowing Cutting

In this method the cutting tool is pumped down through the flowline into the well bore in order to cut wax deposits. TFC is not a common practice in the industry, although the method has the advantage which can treat the wax deposition on distant position from production station or platform such as sub sea flowline.

2.6.2 Thermal Methods

2.6.2.1 Keeping the Temperature of Crude Oil Above Cloud Point

As we know the crude oil will become semi-solid or solid when the ambient temperature is lower than the cloud point of crude. In this method heat is added to maintain the crude temperature above the cloud point. There are several methods to maintain the crude temperature such as installation of heating coil, circulation of the hot water in the annular space, or insulation the storage facility by insulator.

2.6.2.2 Applying Heat to Melt The Existing Waxy Deposits

This method is employed with the existing wax deposition. Heat is supplied to remove waxy deposition in a flowline. In some case, steam is injected into existing waxy deposit to melt them. Then, the condensate of steam is separated and the melting wax is a waste which can be used as fuel for furnace or raw material in other process such as wax purification.

2.6.3 Chemical Methods

2.6.3.1 Inhibiting of The Formation of Waxy Deposits

Commercial wax inhibitors are dosed into crude oil which has function to co-crystallize with the wax molecules to prevent formation of wax crystal structure on inside pipewall. Often chemical dispersant will cover the wax crystal to prevent wax from agglomeration. The surfactants or detergents have a potential prevention of the adhesion of wax crystal on pipewall, so they act to water wet the wax crystal.

2.6.3.2 Pour Point Depression

Pour point depressant or wax crystal modifiers, which are high molecular weight polymers can modify the structure of wax crystal. The part per million concentration of polymer can significantly reduce pour point and viscosity. However these chemical may not decrease the rate of wax build up on the pipe.

2.6.3.3 Solvents to Dissolve Wax Deposits

Hydrocarbon solvent has a potential to dissolve the wax after that heat is added to speed up the process. Hot oiling method is a traditional process to solve the wax deposition problem especially for downhole application. This method uses hydrocarbon solvent that is mixed with crude oil then the mixture is heated and sent down into the well in order to melt accumulation wax. After treatment the melted wax has tended to re-agglomerated again. Thus the dispersants or wax inhibitor should be also sent to downhole in order to prevent agglomeration of melted wax.

2.6.3.4 Chemical to Induce Heat

Wax deposition can be treated by applying the heat to melt it. The concept of this method is to apply the heat to melt accumulated wax by using a strong exothermic reaction of both chemical mixing. Petrobras suggested process to induce heat by using two salt solutions that is;

Ammonium Chloride + Sodium Nitrite = Heat* + Sodium Chloride + Nitrogen. The both salt solution are sent into flowline. This mixing process performs ideally at the point in a flowline where there is the wax deposit. After the both salt solution are mixed, the strong exothermic reaction occur and the heat* is released as shown in above chemical reaction to melt the wax deposit. Although in the practical application, this method is quite difficult in very long flowline.

However, mechanical and thermal methods are not easy to apply due to high capital cost and high investment. The chemical methods become more influence because they are easy to use and reasonable investment. The well-known chemicals used to solve wax deposition problem are called "wax inhibitors". The wax inhibitor improves low temperature flow properties of crude oil. Basically, the chemicals inhibitor can be broadly classified into three categories: (Towler and Rebbapragada, 2004)

- Solvents: They are used for dissolving paraffin
- Wax crystal modifiers: these are polymers that inhibit or alter wax crystal growth
- Paraffin dispersant: it inhibits the particles from uniting and depositing

The recent works that studied on wax problem in crude oil are the performance of wax inhibitor, the factors that effect to crystallization of crude oil, polymer flow improver, etc. Garcia (2000) studied the effect of heavy linear paraffin concentration on wax appearance temperature (WAT) of paraffinic crude oil by use of polarized light microscopy (PLM) method, and the maleic anhydride copolymer derivative paraffin inhibitor. Moreover the effect of flocculated asphaltenes on the paraffin crystal growing is also evaluated. The result showed that the linear alkanes (nC24+) in paraffin crude oil increase tendency to wax crystallization and the presence of flocculation in crude oil bulk, which increases the cloud point and interferes with the crystal inhibition mechanism of maleic anhydride crystal modifier.

The effect of a pour point depressant to phase transition parameter is studied by Srivastava *et al.* (1995). The Bombay middle distillation was used in this experiment by using differential scanning calorimetry (DSC) to observe the thermal behavior of sample. The result indicated that the additive have influence to reduce solid – liquid transition energy and increase the solid – solid transition energy. Both results can describe the effect of additive to pour point lowering of bulk system.

The wax inhibitor was not equally effective in all wells. There was instance when a particular chemical performed well in one well but failed in another well in the same basin. Towler and Rebbapragada (2004) studied by using 2 commercial chemical inhibitors. The Dakota crude was tested by 2 commercial chemical inhibitors so that one of inhibitor is match with Dakota crude and another is not. The result indicated that the commercial one is not matched with the Dakota crude oil and cannot decrease the deposition of wax.

Machado *et al.* (2001) investigated EVA as a wax inhibitor for Brazilian crude oil. They found that the appropriate vinyl acetate in EVA is 30% for crude oil obtained from Albacore and Badejo fields. Moreover, the effective evaluation of wax inhibitor studied by Qian *et al.* (1995) suggested that the new flow parameter, Q, has been developed to assess the efficiency of flow improvers for china waxy crude oil. In this work, 5 kinds of polymer improvers were used; 1) poly (ethylene-co-vinyl acetate) (EVA), 2) poly (EVAgraft-octadecyl acrylate) (EVA-g-POA), 3) poly (ethylenepropylene grafted maleic anhydride) (EP-g-MAH), 4) poly (ethylene-co-octadecyl acrylate) (EOA) and 5) poly (ethylene oxide-co-propylene oxide) (EO-co-PO). The new flow parameter, Q, calculated by dilute solution viscometry and depends on the interaction parameter for polymer-wax and polymer-resin-asphaltene. The new flow parameter proposed in this work can be used to assess the rheological improvement of doped crude oil, such as the reduction of apparent viscosity, pour point and temperature of wax crystallization.