

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Paraffin/Wax

Monsoori *et al.* (2002) indicated that wax present in petroleum crudes primarily consists of paraffin hydrocarbons ($C_{18} - C_{36}$) known as paraffin wax and naphthene ($C_{30}-C_{60}$). 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 large crystals of paraffin wax known as macro-crystalline wax, while those formed from naphthenes known as micro-crystalline wax.

Hydrocarbons in pure state have definite boiling and freezing (or melting) points which can be measured in Laboratory. By knowing the intermolecular energy parameters or critical properties and acentric factor and/or refractive index of hydrocarbons, one can predict their boiling points using vapor pressure correlations with various degrees of accuracy. However, such methods are not capable of predicting pure hydrocarbon freezing points. There are other methods which can be used to predict hydrocarbon and wax freezing (melting) points which include but not limited to:

- 1) Variation statistical mechanical theory
- 2) Density functional theory
- 3) Dislocation theory

2.2 Waxy Crude Oil

Monsoori *et al.* (2002) indicated that waxy crude oil usually consists of:

- 1) A variety of light and intermediate hydrocarbons (paraffins, aromatics, naphthenic, etc.,)
- 2) Wax as defined above
- 3) A variety of other heavy organic (non-hydrocarbon) compounds, such as resins asphaltenes, diamondoids, mercaptans, organo-metallic, etc.,

For the 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 natures the heavy organics will have different interactions with wax that could either prevent wax crystal formation or enhance it.

2.3 Wax Deposition

It is indicated that compounds found in paraffin deposits are dependent upon the characteristics of the crude oil (Wright, 1951). Oil is mostly mechanically trapped in the deposits, held between wax grains. If a large amount of oil is present, the paraffin deposits are hard and less plastic. In this case an increase in the temperature does not have much effect on the plasticity until the melting point of the wax is approached. Other solid depositions such as asphaltenes, resins, etc., are normally very small. Essentially, the wax crystal behavior is dependent on the crude oil itself, the rate of cooling, and the degree of agitation during cooling.

Problem related to crystallization and deposition of paraffin waxes during production and transportation of crude oil cause losses of billions of dollars per year to the petroleum industry worldwide through the costs of chemicals, reduced production, extra horse power requirement, and blocking of flowlines.

2.4 Study The Characteristics and Properties of Waxy Crude Oil

The majority of crude oils and crude oil products contains substantial amounts of petroleum wax. Depending on the kind of, the composition of the wax may range from the predominantly low molecular weight *n*-alkanes (C₂₀ - C₄₀) to high proportions of high molecular weight *iso*- and *cyclo*-alkanes. The former type of wax is termed paraffin or distillate wax and generally crystallize as large needles and plates while the latter type is termed micro-crystalline or amorphous wax.

Fundamental issues related the wax crystallization process, crystal morphology, and physical properties of petroleum wax have been studied in detail. The study of wax deposition in hydrocarbon mixtures and the crudes requires measuring techniques which are able to deal with the solid phase behavior.

Ronningsen *et al.* (1991) studied the wax precipitated from North Sea crude oils. By compositional analyses of wax precipitated from one of the oils indicated that wax crystallizing just below the wax precipitation temperature (WPT) was richer in condensed naphthenes and poorer in *iso*-alkanes than wax formed at lower temperatures. *Iso*-alkanes appeared to be the most abundant class at all temperatures.

There are numerous research that study the separation and the composition of hydrocarbons in crude oil that are composed of saturates, asphaltenes, resin, and aromatics. However, the traditional methods to isolate asphaltene fractions by adding excess of low boiling point solvents such as *n*-pentane, *n*-hexane, *n*-heptane, etc., can produce asphaltene fractions which are contaminated with a significant amount of micro-crystalline wax. Nguyen *et al.* (1999) described a novel method for the separation of wax-free asphaltene fraction. This method can provide a quantitative subdivision of wax fraction into pentane soluble and pentane insoluble waxes. Nevertheless, while the term micro- and macro-crystalline waxes have been used for many years to differentiate wax types on the basis of their carbon number distributions and other properties, detailed molecular characterization of waxes rarely undertaken in the past due to the lack of suitable analytical techniques.

The cloud point measurement is also investigated (Al-Ahmed *et al.*, 1997). An empirical correlation based on upper position technique is developed to predict the cloud point phenomenon. The correlation is a function of the type of oil and its viscosity as well as the type of wax. Experimental data on phase equilibria is important to understand the crystallization of paraffins and for the development of thermodynamic models used to describe it.

An equipment that is used to study wax deposition is differential scanning calorimeter. It can be used to determine wax appearance temperature (WAT) and wax disappearance temperature (WDT). Elsharkawy *et al.* (2000) studied the stock tank crude oil from Middle East by using DSC. It is concluded that the measured WAT by DSC compared very well with that predicted from the model.

In the part of crystallization, Chevalier *et al.* (2000) studied the solid deposits in solution that consist of a commercial multiparaffinic wax in the normal tetradecane, used as a solvent, were studied by x-ray diffraction. The result shoed

that the first deposits formed a single orthorhombic multi-C_n solid solution that consisted of all the alkanes of the commercial wax from C₂₀ to C₄₂.

2.5 Quantifying the Amount of Deposit Wax

Determination of the amount of solid wax precipitated at the temperatures below wax appearance temperature is critical for understanding crude oil rheology and solids deposition. Experimental data on wax precipitation are normally limited to determining the cloud point temperature and total wax content of each oil. Detailed characterization of wax content as a function of the temperature is very important for establishing thermodynamic models of wax formation in crude oils with good predictive capability. Burger *et al.* (1981) indicated that 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.

Pulse NMR and DSC have also been used, but are problematic and ineffective for low wax of crude oils (Ronningsen *et al.*, 1991). For most oils investigated, except for some biodegrade and asphaltenic oils, the NMR estimated solid content at -40 °C correlated well with the amount of wax determined by acetone precipitation at -25 °C. The later work by Coutinho *et al.* (1999) indicated that the formation obtained from DSC measurements can be used to assess the amount of solid forming when a fluid is cooled and also to make faster measurements of phase diagrams for binary systems where no solid solutions exist.

Guehenneux *et al.* (2002) suggested a way for predicting wax precipitation at an early stage of the reservoir characterization and process production. In this respect, reservoir core extracted and production oil saturated fractions have been analyzed by high temperature gas chromatography (HTGC) in order to quantify the high molecular weight hydrocarbon (HMWHC) at the origin of wax deposits in the tubing and surface facilities.

In addition, a novel FT-IR spectroscopy method is described for the determination of the wax precipitation temperature (WPT), and the estimation of the amount of precipitate solid wax material (both crystalline and amorphous) present in

petroleum crude oils. Rohner *et al.* (2001) showed that the precipitated wax which is determined by FT-IR spectroscopy compared well with other experimental data.

Thermodynamic models can be used to calculate WAT and the amount of solid deposit versus temperature. Provost *et al.* (1998) used simple expressions Gibbs molar energy to calculate a mixture of heavy components including two *n*-alkanes and a solvent. Chodoba *et al.* (2001) moreover, showed that a heat transfer method that provided the film heat transfer coefficients in the heat transfer equation can be used to calculate wax thickness formed accurately.

2.6 Investigating Ways to Solve Wax Deposition

Hunt (1996) indicated that there are conventionally three methods to solve wax deposition problems, i.e.

2.6.1 Mechanical Method

Wright (1951) mentioned that pigs, the paraffin knife, paraffin hook, corkscrew, and swap were 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.

2.6.2 Thermal Method

The principle of this method is addition of heat to maintain above the temperature of crude oil cloud point or adding heat existing wax deposits. Spitzer (1987) patented an annular plug which fits on the string. It slows passage of hot oil down the annulus so that heat is more efficiently transferred to the tubing string. There were also reports that the hot oil process was applied in the field of very high paraffin content near Vernal, Utha.

2.6.3 Chemical Method

The principles of this method to solve deposit wax are to prevent formation of wax crystal masses (reduce the effective cloud point) by decreasing the

pour point of crude oil, to use the solvents to dissolve wax, and to use the chemical that induce and melt wax.

Although, there are numerous research concerning with the solution of wax deposition, almost all of them are interested in chemical method since this method is easy to work on the laboratory scale and low cost. A number of novel and generic wax dispersants and anti sticking agents have been developed and tested, and proved to be effective in retarding the deposition mechanism significantly.

A well-known group of chemicals to solve wax deposition problem is called wax inhibitors or wax crystal modifiers (Pedersen *et al.*, 2003). They are sometime added to waxy crude oils to minimize transport problems. Basically three main groups of chemicals are used:

- 1) Wax crystal modifiers
- 2) Detergents
- 3) Dispersants

The last two groups are primarily surface-active agents, as for example polyesters and amine ethoxylates. These may act partly by modifying the surface of pipe wall, but primarily by keeping the crystals dispersed as separate particles, thereby reducing their tendency to interact and adhere to solid surfaces. Pedersen *et al.* (2003) studied the effect of the twelve wax inhibitors to North Sea crude oil. The viscosity data suggested that the inhibitors, probably by some kind of steric hindrance, “interactive” components within a certain range of molecular weight by preventing them from building network structure.

Moreover, a chemical that is poly (ethylene-co-vinyl acetate, EVA) copolymers as pour point reducer and organic deposit inhibitor is also studied, and it is found that the copolymer with the highest vinyl acetate content exhibited the best performance as organic deposits inhibitor can be suggested that the EVA copolymer acts on the morphology of the wax crystal (Andre *et al.*, 1999). The structures which have responded well to chemical treatment include poly alkyl acrylates and methacrylates, esters, ethylene-vinyl acetate copolymers, naphthenes derivatives is also used as wax inhibitors.

Sawney *et al.* (1991) studied ester type chemical additives to modify the wax crystal in Indian crude oil. It shows that the ester-type chemical in the $C_{11} - C_{19/20}$

range have the capacity to modify *n*-alkanes, but for the crude oil containing higher carbon atom number, i.e. C₂₀ – C₃₅ or above, respond very poorly to chemical treatment.

Furthermore, the traditional methods of solvent-based removal are time consuming, expensive and can create traditional problems of re-deposition and dehydration facilities upsets. Brown *et al.* (1999) showed that if chemicals added can generate exothermic reaction that melts and disperses paraffin wax and asphaltene deposits, the reaction product can be a powerful paraffin dispersant that prevents re-deposition after the temperature returns to normal.