CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 Waxy Crude Oils (Mansoori, 2001)

A waxy crude oil usually consists of

1. A variety of light and intermediate hydrocarbons (paraffins, aromatics, naphthenic, etc.)

2. Wax consists of macro and microcrystallines (as defined below)

3. A variety of other heavy organic compounds, such as resins, asphaltenes, diamondoids, mercaptans, organo-metallic, etc. When the temperature of a waxy crude oil decrease the heavier fractions of its wax content start to freeze out.

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

Vazquez and Mansoori (2000) identified and measured petroleum precipitates. A method is used to measure the precipitates that result from petroleum fluids. This method composed of 1) analysis of suspended materials in a crude oil by microscopy 2) analysis of total asphaltenes content in the a crude oil by using different normal paraffin hydrocarbon solvents, 3) analysis of precipitated asphaltenes from a crude oil by gel permeation chromatography (GPC), 4) SARA (saturates, aromatics, resins, asphaltenes) separation and 5) separation and characterization of diamondiods. The above experimental procedures provide an understanding of the overall behavior of the species that precipitate as well as the interactions among them. The result of each procedure is used for predictive and preventive measures for heavy organic deposition from petroleum fluid.

2.2 Nature of Waxy Paraffins (Mansoori, 2001)

Waxy paraffins are a continuum of high molecular weight alkanes

(C_nH_{2n+2}) saturated   hydrocarbons that exist in crude oils. Size can exceed C_{100} with either a normal or branched structure. Normal paraffins exhibit higher melting points than equivalent-sized branched structures. The longer the paraffin (higher carbon), the higher the melting point. This means the larger molecules come out of solution first, so the deepest downhole deposits would be the higher molecular weight paraffins.

The temperature at which paraffins begin to crystallize out of solution is defined as a cloud point. (Cloud points of a crude from different wells within a field can vary as much as 30 ^{O}F). Pour point is defined as a temperature where the crude sample becomes solid. Solid deposition can contain paraffin as high as 60% or more of oil. Paraffins (generally linear hydrocarbons) float on water and are soluble in xylene, n-heptane and crude.
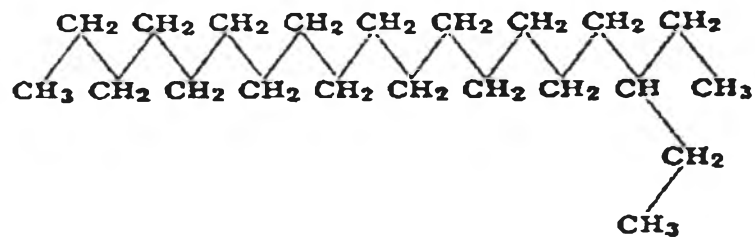
Monsoori *et al.* (2002) indicated that hydrocarbon components of wax can exist in various states of matter (liquid or solid) depending on their temperature and pressure. When the wax freezes it forms large crystals of paraffinic wax known as macrocrystalline wax, while those formed from naphthenics known as microcrystallines wax (Figure 2.1).

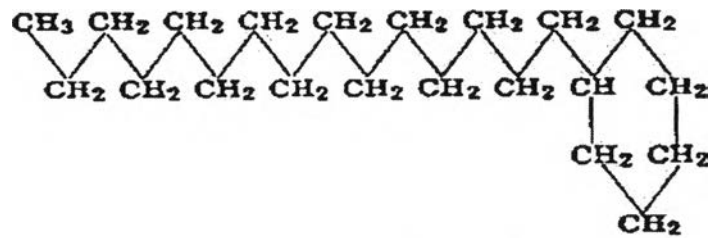## 2.3 Wax Deposition Problem (Speight *et al.*, 2002)

Paraffin deposition is a thermally driven process. Reducing the temperature during production causes wax to precipitate as temperature drops below the cloud point. The percentage of paraffin alone in a crude oil is not an indicator of potential paraffin problems, rather it is the cloud point and the percentage of paraffin that indicate the magnitude of potential problems. Viscosity and flow rate can also effect paraffin deposition. High viscosity reduces transport to cold surfaces, thus increase deposition. High viscosity also results in harder deposits. Paraffins cause problems through deposition (perforlation, tubing, flowline, pipeline), settling (tank bottom, interfaces), and solidification (the problems are related to restarting or requiring very high pressures to pump).

CH₃ CH₂ CH₂ CH₂ CH₂ CH₂ CH₂ CH₂ CH₂ CH₃

CH₂ CH₂ CH₂ CH₂ CH₂ CH₂ CH₂ CH₂ CH₂

NORMAL PARAFFIN

CH₂ CH₂ CH₂ CH₂ CH₂ CH₂ CH₂ CH₂ CH₂

CH₃ CH₂ CH₂ CH₂ CH₂ CH₂ CH₂ CH₂ CH CH₃

CH₂

CH₃

ISOPARAFFIN

CH₃ CH₂ CH₂ CH₂ CH₂ CH₂ CH₂ CH₂ CH₂

CH₂ CH₂ CH₂ CH₂ CH₂ CH₂ CH₂ CH CH₂

CH₂ CH₂

CH₂

CYCLOPARAFFIN

| Macrocrystalline | Microcrystalline | Wax system |
| (n-paraffin) | (iso- and cycloparaffin) | |
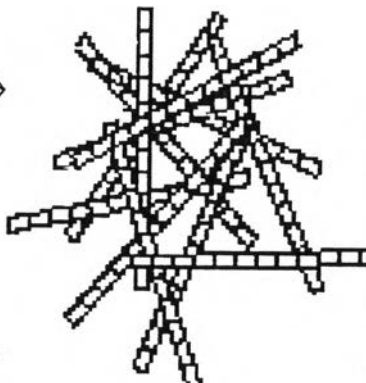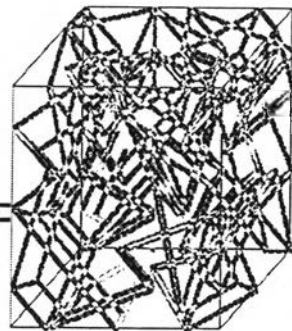
Figure 2.1 Paraffin structure (Monsoori *et al.*, 2002).

Paraffin problems are the results from (1) natural causes (temperature loss, high volumes of production even if paraffin content is relatively low, gas expansion, pipe cooling due to ground- water aquifers, and low surface temperature) , (2) solvent loss (dropping below bubble point, gas production, gas separation, hot oil treatments, and heater treaters), and (3) well maintenance operations (temperature driven, water injection, cooling equipment, gas lift, acid/free jobs with cold fluids.)

Wright (1951) indicated that the components found in paraffin deposits are dependent upon the characteristics of crude oil. 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 or solid deposits. Essentially, the wax crystal behavior is dependent on the crude oil itself, the rate of cooling, and the degree of agitation during cooling. Paraffins deposition in a downhole and on surface equipment is one of the most serious problems in oil production operations. Change in physico-chemical equilibrium due to a decrease in temperature to below the paraffins melting point causes crystallization, losses in component solubility and a sequence of accumulation. In some cases, paraffinic deposits have caused reservoirs plugging during 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 surrounding and intrusion of water producing evaporation of light components (Ritchie *et al*, 1979). The above problems cause losses of billions of dollars per year to the petroleum industry worldwide through the costs of chemicals, reduced production, extra horse-power equipment and blocking of flowlines.

2.4 Study of the Characteristics and Properties of Waxy Crude Oils (Speight *et al.*, 2002)
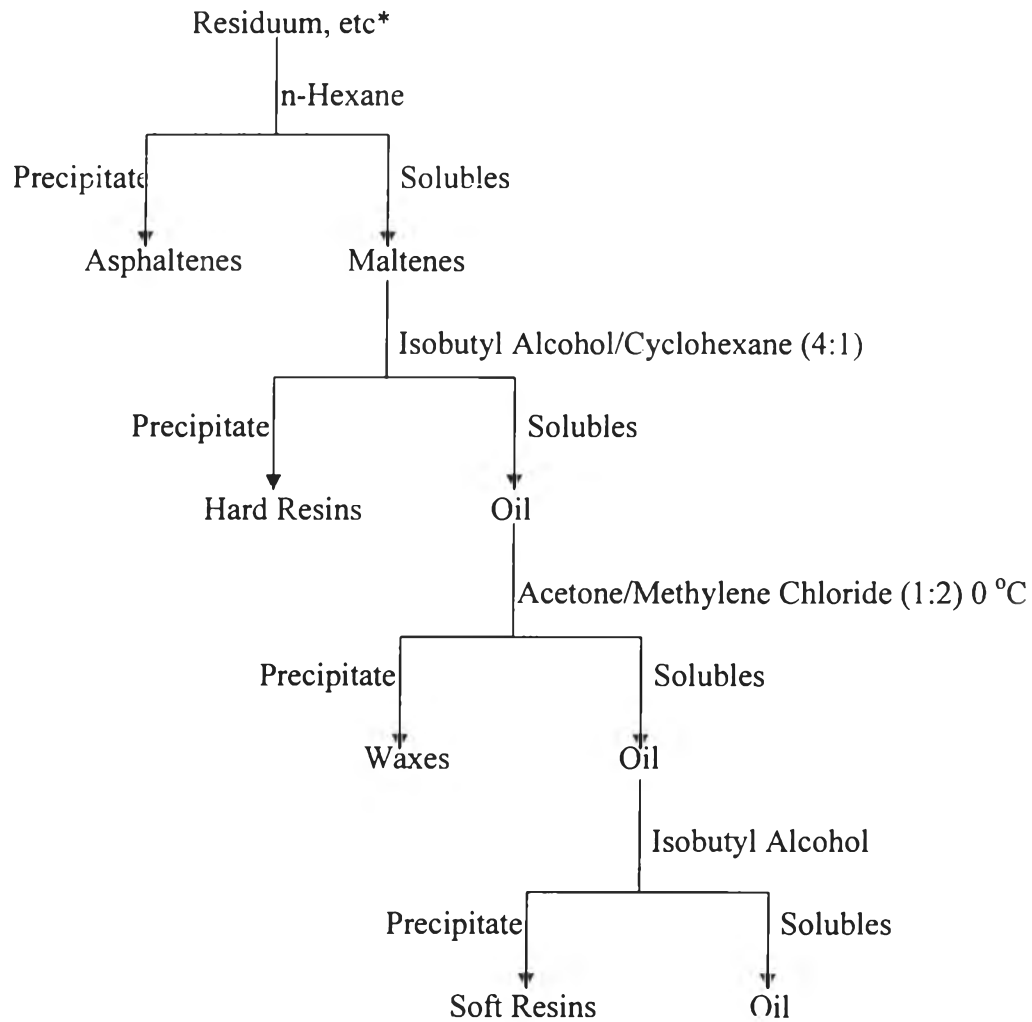
Crude oils appear as liquids of varying viscosity. Their color can range from green (crude from Moonie, Australia) to dark brown (crude from Ghazi, Saudi Arabia). Their chemical compositions are very complex and depend essentially on their ages, that is, the phase of development of the kerosene, regardless of the origin

of the crude (Speight, 1981). Some crude oils and crude oil products contain substantial amount of petroleum wax. The major components of wax are paraffins of which generally crystallize as a mixture of large needles and plates with amorphous wax. Fundamental issues related to 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 crudes requires measuring techniques which are able to deal with the solid phase behavior. Knowledge of crude oil physical and chemical characteristics will determine what kind of initial treatment will be associated with separation and stabilization at the field for production, transport and storage.

There are numerous researchers that study the fractionation of the four hydrocarbon chemical forms in crude oils which are saturates, asphaltenes, resins and aromatics by using different solvents. For example, pentane, hexane, heptane and n-butanol lead to fractionation of the meltenes and asphaltenes. (as shown in Figures 2.2-2.5). Methods used to fractionate crude oil can provide a quantitative subdivision of the wax fraction into pentane-soluble and insoluble waxes. Nevertheless, while the terms 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 was rarely undertaken in the past due to the lack of suitable analytical techniques (Nguyen *et al.*, 1999).

2.4.1 Viscosity (Speight *et al.*, 2002)

It is the force in dynes required to move a plane of 1 cm area at a distance of 1 cm from another plane of 1 cm area with a viscosity of 1 cm/s . It is the most important single fluid characteristic governing the motion of waxy crude oils and crude oil products and is actually a measure of the internal resistance to motion of a fluid because of cohesion forces between molecules or molecular groups. In the early days of the petroleum industry viscosity was regarded as the body of an oil, a significant number for lubricants or for any liquid pumped or handled in quantity. Variations of viscosity with temperature, pressure and shear rate are needed, not only in lubrication but also for other engineering problem such as heat transfer.

Residuum, etc*
|n-Hexane

Precipitate   Solubles

Asphaltenes   Maltenes

                   Isobutyl Alcohol/Cyclohexane (4:1)

          Precipitate   Solubles

          Hard Resins   Oil

                            Acetone/Methylene Chloride (1:2) 0 °C

                   Precipitate   Solubles

                   Waxes   Oil

                               Isobutyl Alcohol

                   Precipitate   Solubles

                   Soft Resins   Oil

*Residuum, asphalt, bitumen, or petroleum

Figure 2.2 Fractionation using various solvents (Nguyen *et al.*, 1999).

Residuum, etc
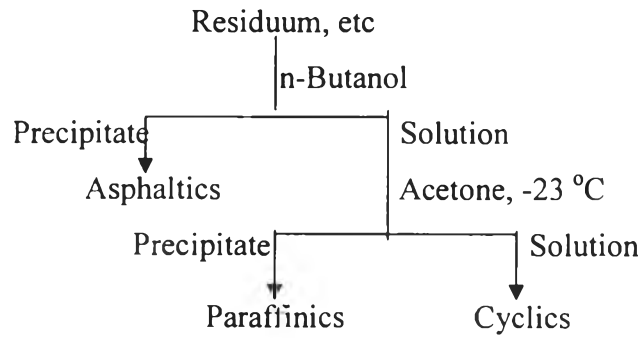|n-Butanol

Precipitate   Solution

Asphaltics   Acetone, -23 °C

Precipitate   Solution

Paraffinics   Cyclics

Figure 2.3 Fractionation using n-butanol and acetone (Hpiberg, A.J.(ed.) 1964).

Residuum, etc
|n-Pentane

Precipitate   Solution

Asphaltenes   Maltenes

Propane

Precipitate   Solution

Resins   Oil

Methyl Isobutyl Ketone

Aniline   Precipitate   Solution

Wax   Oil

Precipitate   Solution   Acetone, -23 °C

Hard Resins   Soft Resins   Precipitate   Solution

Paraffinic Oils   Naphtenic Oils
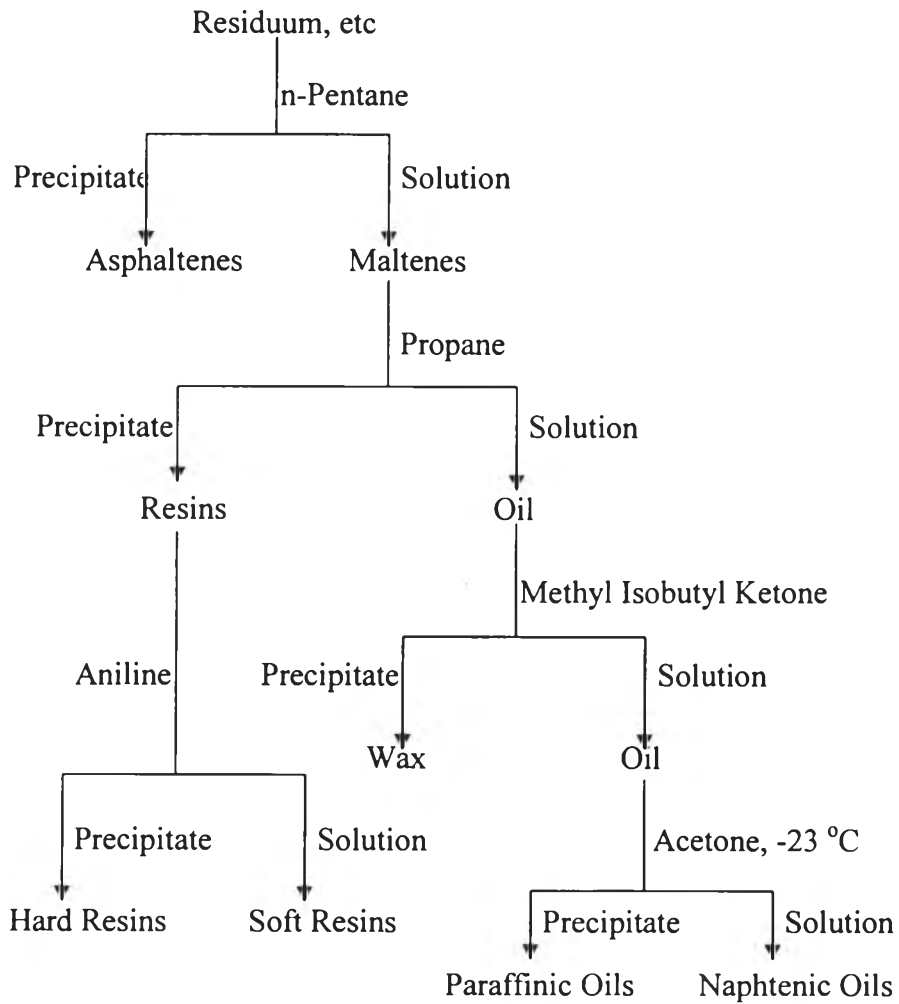
Figure 2.4 Fractionation using n-pentane (Nguyen *et al.*, 1999).

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                    Feedstock
                        |
                        | n-Heptane (or n-Pentane)
            _____|_____
           |                         |
     Precipitate                 Solubles
           |                         |
           ▼                         ▼
     Asphaltenes              Deasphaltened Oil
                                     |
                                     | Acetone
                          _____|_____
                         |                       |
                    Precipitate              Solubles
                         |                       |
                         ▼                       ▼
                      Resins                    Oils
                                                 |
                                                 | Dimethylformamide
                                      _____|_____
                                     |                       |
                                Precipitate              Solution
                                     |                       |
                                     ▼                       ▼
                                 Aromatics                Saturates
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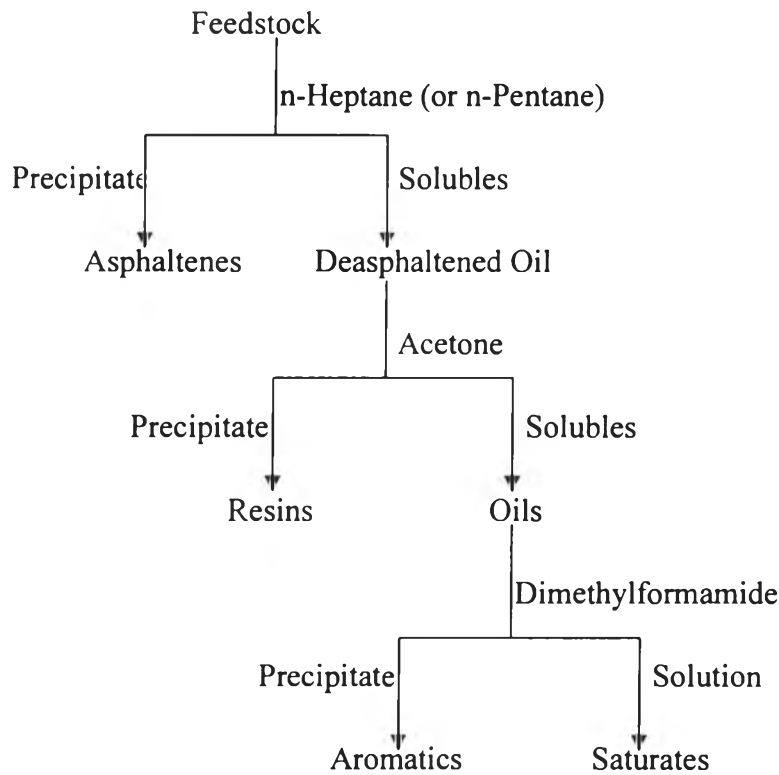
Figure 2.5 Fractionation by solvent procedure (Nguyen *et al.*, 1999).

Because of the importance of viscosity in determining the transport properties of waxy crude oils, recent work has focused on the development of an empirical equation for predicting the dynamic viscosity of low molecular weight and high molecular weight hydrocarbons vapor at atmospheric pressure (Gomez, 1995). The equation uses molecular weight and specific temperature as the input parameters and offers a means of estimating viscosity for wide range of petroleum fractions. Other work has focused on the prediction of wax deposition potential of hydrocarbon systems from viscosity-pressure correlations (Vercier *et al.*, 1979) and the prediction of the viscosity of blends of lubricating oils from the viscosities of base oil components (Al-Kashab *et al.*,1976).

2.4.2 Properties Relating to Solidification (Speight *et al.*, 2002)

Waxy crude oils and the majority of petroleum products are liquid at ambient temperature, and problems that may arise from solidification during normal use are not common. Nevertheless the melting point is a test (ASTM D-87 and D-

127) that is widely used by suppliers of wax and by the wax consumers; it is particularly applied to the highly paraffinic crystalline waxes. The melting points of the normal paraffins (Table 2.1) agree well with the data for the lower crystalline paraffin waxes when the materials are compared on a molecular weight basis, and this furnishes some of the best evidence for the chemical constitution of microcrystallines petroleum wax.

Although the melting of waxy crude oils and petroleum products has a limited usefulness, except to estimate the purity or perhaps the composition of waxes, the reverse process, solidification has received attention in petroleum chemistry. In fact, solidification characterization of waxy crude oil and petroleum products has been differentiated into four categories, namely, freezing point, congealing point, cloud point, and pour point.

Table 2.1 Melting point of n-paraffin (Al Ahmed *et al.*, 1997)

Number of carbon atoms	Melting point	
	°C	°F
1	-182	-296
2	-183	-297
3	-188	-306
4	-138	-216
5	-130	-202
6	-95	-139
7	-91	-132
8	-57	-71
9	-54	-65
10	-30	-22
11	-26	-15
12	-10	14
13	-5	23
14	6	43
15	10	50
16	18	64
17	22	72
18	28	82
19	32	90
20	36	97
30	66	151
40	82	180
50	92	198
60	99	210

Waxy crude oil becomes more or less plastic solid when cooled to sufficiently low temperature. This is due to congealing of the various hydrocarbons that constitute the oil. The cloud point of a wax crude oil is the temperature at which paraffin wax or other solidificable compounds present in the oil appear as a haze when the oil is chilled under prescribed conditions (ASTM D2500 and ASTM D3117). As cooling is continued, all wax crude oils become more and more viscous and flow becomes slower and slower. 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 chilled without disturbance at a standard rate (ASTM D-97). Cloud and pour points are useful for predicting the temperature at which the observed viscosity of an oil deviates from true (Newtonian) viscosity in the low-temperature range. They are also useful for identification of oils or when planning the storage of oil supplies, as at low temperatures many handling difficulties occur with some oils. Some work has focused on correlating the type of oil its viscosity as well as the type of wax (Al Ahmed *et al*, 1997).

2.4.3 Thermal Properties Differential Scanning Calorimetry (Speight *et al*., 2002)

A few attempts have been made to study phase transition phenomena in petroleum waxes using spectroscopic and thermo analytical methods. However these studies are very limited and do not provide much information on solid-solid and solid-liquid phase transition energies and their dependence on the composition of the waxes. Phase transition temperature and associated energies for petroleum waxes of different melting point were measured by differential scanning calorimetry. A general description of this technique has been given recently. The thermal analysis of petroleum products in general has been reviewed by Weinberg *et al*.,(1981) while DSC in particular has been used to characterize and study the thermal effects of different types of waxs, crude oils, and other petroleum products. More specifically, in a series of papers. Bouquet *et al*. (1982) studied synthetic oils consisting of n-alkanes in dewaxed gas oils to obtain information on the effect of wax composition on crystallization enthalpies and precipitation temperature. In a

similar study of the thermal behavior of crude oils, Hanson, *et al.* (1991) described the characterization of seventeen North Sea crude oil by DSC in the temperature range of +70 to –140 ^{O}C. Apart from two biodegraded oils, oil 1 and oil 11, these oils range from light paraffinic/ waxy condensates (oils 4, 10, 12, 13 and 15) over intermediate paraffinic (oils 2, 7, 8, 16 and 17) to heavier waxy crudes (oils 5, 3, 5, 6, 9 and 14). For all oils both the glass transition temperature (Tg), wax appearance (precipitation) and wax disappearance (dissolution) temperatures (WAT and WDT) have been studied together. Elshzkawy *et al.* (2000) studied the stock tank crude oil from Middle East by using DSC. It is concluded that measured WAT by DSC compares very well with that predicted from a model. Al-Ahmed *et al.* (1997) characterized lubricating and fuel oils by DSC and cloud point methods. These methods can measure also the oil with a pour point depressant additive (MEK). Other work determined phase transition temperature and energies of petroleum waxes derived from Bombay high middle distillate and investigated the effect of iso- and cyclo paraffins and aromatics ; From the result, the temperature and energies depended on the fractions composition in the crude oil (Srivastava, 1995).

    2.4.4 <u>Structural Properties Using X-ray Diffraction Techniques</u> (Speight *et al.*, 2002)

        X-ray diffraction techniques also provide information about the structural qualities of organic materials, but the data provide information about the spatial periodicity within a solid substance. However. there is one necessary assumption in the application of this method and it requires that, the longer portion of the molecules contain within and among themselves certain repeated structural fractures, such as sheets of condensed aromatic rings. The X-ray diffraction patterns of petroleum features are diffuse compared to those of the well-ordered graphite carbon, and it is usually very difficult to extract information from the diffraction patterns. However, it must be remembered that the X-ray diffraction technique is, by necessity, used for solid materials, such as waxes and asphaltenes. Early investigations indicate the presence of a band corresponding to 3.5 C in the X-ray diffraction pattern of an asphaltene fraction and compared the similarity of this feature to that of amorphous carbon while evidence of crystallinity (molecular order)

in asphaltene was also indicated. Later work shows that heavy petroleum fraction have an X-ray pattern characteristic of amorphous substances. X-ray diffraction used at very small angles, small angle scattering (SaS), has been also used for the characterization of heavy fractions of petroleum. The range of small angle scattering is in the molecular dimension from 20 to $2000A^{\circ}$. Other investigations studied the solid deposits in a solution consisting of a commercial multiparaffinic wax in normal tetradecane, used as a solvent, by X-ray diffraction. The result showed that the first deposits formed a single orthorhombic multi-Cn solid solution that consisted of all the alkanes of the commercial wax from C_{20} to C_{42}. Dirand *et al.*, 1997 studied eight commercial and industrial waxes and a heavy crude oil 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 atoms number (n_c) and this orthorhombic phase is identical to an intermediate solid solution B_n' or B_n" of binary and ternary mixtures of carbon consecutive (Cn). However these two systems appear or half concentrations and have been used to develop models that represent the behavior of petroleum cuts with heavy hydrocarbons.

2.5 Quantifying the Amount of Waxy Deposit (Speight *et al.*, 2002)

Determination of the amount of solid wax precipitated at temperature 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. A detail characterization of wax content as a function of temperature is very important for establishing a thermodynamic model of wax formation in crude oils with good predictive capability. Many techniques are used to quantify the amount of waxy deposit.

2.5.1 Filtration and Centrifugation (Speight *et al.*, 2002)

It is 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 (Burger *et al.*, 1981).

2.5.2 <u>Enthalpy or Heat Content by Differential Scanning Calorimetry</u> (Speight *et al.*, 2002)

Differential scanning calorimetry (DSC) is not only used to study wax precipitation of crude oils by measuring glass transition temperature (tg), wax precipitation (appearance) temperature (WAT) and wax dissolution (disappearance) temperature (WDT) but also measuring wax precipitation and dissolution enthalpy with respect to physical characteristics. Enthalpy is the heat energy necessary to bring a system from a reference state to a given state. Enthalpy is a function only of the end states and it is the integral of the specific heats with respect to temperature between the limit state, plus any latent heats of transition that occur within the interval. The usual reference temperature is 0 C (32 F). Enthalpy data are easily obtained from specific heat data by graphic integration, or, if the empirical equation given for specific heat is sufficiently accurate, from the equation (2.1)

$$H = \frac{1}{D(0.388 + 0.000225t^2 - 12.65)} \tag{2.1}$$

H = enthalpy

t = temperature

D = latent heat

• Generally, only differences in enthalpy are required in engineering design, that is, the quantity of heat necessary to heat (or cool) a unit amount of material from one temperature to another. Coutinho *et al.* (1999) indicated that the information obtained from DSC measurements can be used to assess the amount of solid forming when a fluid is cooled and also to make faster measurement of phase diagrams for binary systems where no solid solution exists. Other work also indicate by DSC measurement of the phase transition temperature and associated energies for petroleum waxes of different melting points. From the result, the existence of a solid

phase transition is dependent on the composition of the wax and the transition energies are related to the solid state properties of the waxes. (Handoo *et al.*, 1989).

2.5.3 <u>Pulse Nuclear Magnetic Resonance</u> (Speight *et al.*, 2002)

Nuclear Magnetic resonance has frequently been employed for general studies and for the structural studies of petroleum constituents. This techniques essentially identifies and counts hydrogen atoms according to their chemical and physical environments.

In fact, proton magnetic resonance (PMR) studies (along with infrared spectroscopic studies) were, perhaps, the first studies of the modern era that allowed structural inferences to be made about the polynuclear aromatic systems that occur in the high molecular weight constituents of petroleum. In general, the proton (hydrogen) types in petroleum fractions can be subdivided into three type (Brown and Ladner, 1960) or into five types (Yen and Evdman, 1962). The Brown and Ladder approach classifies the hydrogen types into (1) aromatic ring hydrogen; (2) aliphatic hydrogen adjacent to an aromatic ring; and (3) aliphatic hydrogen remote from an aromatic ring. The Yen and Erdman approach subdivides the hydrogen distribution into (1) aromatic hydrogen: (2) substituted hydrogen next to an aromatic ring; (3) naphthenic hydrogen; (4) methylenic hydrogen ; and (5) terminal methyl hydrogen remote from an aromatic ring. Other ratios are also derived from which a series of structural parameters can be calculated. However, it must be remembered that the structural details of the carbons backbone obtained from proton at peripheral positions can be obscured by intermolecular interactions. This, of course, can cause an error in the ratios that can have a substantial influence on the outcome of the calculation (Ebert *et al.*, 1987; Ebert, 1990). Other applications of this field have also been used, but are problematic and ineffective for low wax crude oils (Ranningsen et al., 1991). For most oils investigated, except for some biodegraded and asphaltenic oils, the NMR estimated solid content at -40 correlated well with the amount determined by acetone precipitation at –25. Polar signal of some organic compounds are shown in Table 2.2.

Table 2.2 NMR Proton signal for organic compound (Speight, 1970)

Signal T		Assignment
2.00	N-H	Pyrrole
2.19	⇨-H	Naphthalene
2.54	ß-H	Naphthalene
2.58	2-H	Furan
2.73	Ar-H	Benzene
2.81	Ar-H	Thiophene
2.89	Ar-H	Ethylbenzene
2.91	Ar-H	Toluene
3.03	Ar-H	Tetralin
3.36	Ar-H	Mesitylene
4.43	Olefinic H	Cyclohexene
6.08	⇨-CH_2	Diphenylmethane
6.19	CH_2	Fluorene
7.09	⇨-CH_2	Indane
7.13	⇨-CH_2	Dibenzyl
7.30	⇨-CH_2	Tetralin
7.38	⇨-CH_2	Ethylbenzene
7.66	CH_3	Toluene
7.77	CH_3	o-Xylene
7.86	CH_3	Durene
7.96	ß-CH_2	Indane
8.04	Allylic CH_2	Cyclohexene
8.21	CH_2	Adamantane
8.27	ß-CH_2	Tetralin
8.30	3-CH_2	2-Phenylbutane
8.40	H(eq.)	Trans-Decalin (strong)
8.46	CH_2	Methylcyclohexane
8.47	CH_2	Cycloheptane
8.47	CH_2	Cyclooctane
8.49	CH_2	Cyclopentane
8.54	CH_2	Cyclohexane
8.59	CH_2	cis-Decalin
8.75	CH_2	n-Hexane
8.75	CH_2	n-Octane
8.77	1-CH_3	2-Phenylbutane
8.80	CH_3	Ethylbenzene
9.08	CH_3	Methylcyclohexane
9.10	CH_3	n-Hexane
9.11	CH_3	n-Heptane
9.12	CH_3	N-Octane
9.12	H(ax.)	trans-Decalin (weak)
9.20	4-CH_3	2-Phenylbutane
10.00	CH_3	Tetramethylsilane

2.5.4 Infrared Spectroscopy (Speight *et al.*, 2002)

Conventional infrared spectroscopy is an excellent method for providing detailed information about the chemical constitution of organic materials. It is one of the most widely used techniques for examining the chemical constitution of organic materials. Whether the material being examined is a single compound or a mixture, infrared absorption spectroscopy offers valuable information about the hydrocarbon skeleton and about the functional groups in petroleum (Wen *et al.*, 1978). When properly prepared and scanned with suitable instruments, the infrared spectra of petroleum fractions show a number of well-defined bands (Table 2.3) For the purpose of structural groups analysis, however, the bands at 1380 cm^{-1}, 1965 cm^{-1}, 2880 cm^{-1} and 2920 cm^{-1} are usually employed. This allows an estimation of the number of methyl and methylene groups present in the sample.

Table 2.3 Infrared Spectra of petroleum fraction (Wen *et al.*, 1973)

Band		Assignment
cm^{-1}	μ	
3030	3.30	Aromatic C-H stretching
2920	3.42	Methyl C-H stretching
2880	3.47	Methylene C-H stretching
1735	5.76	Carbonyl C=O
1700	5.88	Carbonyl C=O
1600	6.25	C=C and C=O (hydro-bonded)
1465	6.83	C-H bending
1380	7.25	C-H bending in methyl groups
1130	8.85	Sulfur-oxygen functions
1020	9.80	Sulfur-oxygen functions
865	11.56	Aromatic C-H bending (out of plane)
815	12.27	
760	13.16	
735	13.61	

With the recent progress of Fourrier transform infrared spectroscopy, a quantitative estimate of the various functional groups can also be made. This is particularly important for application to the higher molecular weight solid constituents of petroleum (i.e. the waxy fraction). A novel FT-IR spectroscopy method is described for the determination of wax precipitation temperature (WPT), and the estimation of the amount of precipitated solid wax material (both crystallines and amorphous) present in petroleum crude oils. Rohnev and Hanson. (2001) estimated the amount of solid wax material in crude oils by novel FT-IR spectroscopy compared with conventional analysis methods.

2.5.5 High Temperature Gas Chromatography (Speight *et al.*, 2002)

The evaluation of petroleum must necessarily involve a study of its composition. This technique is successfully used to evaluate feedstock or petroleum products by separation them into various fractions at high temperature. The knowledge of the components of a feedstock before and after refining has been a valuable aid to process development (Rostler, 1965; Riediger, 1971; Algelt and Gouw, 1979; Gary and Handwork, 1984). Application of high temperature gas chromatography can predict wax precipitation at an early stage of the reservoir characterization and production. In this respect, reservoir core extracts 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 (Guehenneux *et al.*, 2002).

2.5.6 Other Techniques (Speight *et al.*, 2002)

Thermodynamic models can be used in order to calculate the wax apperance temperature and the amount of solid deposit versus temperature. Provost *et al.*, (1998), used simple expressions of Gibb molar energy to calculate a mixture of heavy components including two n-alkanes and a solvent. Chodolz *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 accurately wax the thickness of the wax formed.

2.6 Ways to Solve Wax Deposition

There are conventionally three methods to prevent and control wax deposition problems, i.e.

2.6.1 Mechanical Methods

2.6.1.1 Pigging

There are numerous pig designs ranging from simple spheres, to foam pig, to bristle pigs, to very aggressive pigs used for cleaning out severe deposits. Pigging is the most commonly used method for removing wax deposits that have accumulated in flowlines and pipelines. The pig is set down the line, carried along by the crude flow, and mechanically scrapes off the wax and redisperses it in the bulk oil in front of the pig. Pigging can be a successful, cost effective method for managing paraffins deposition in flowlines and pipelines providing that a regularly scheduled pigging program is initiated upon commissioning

2.6.1.2 Wireline Cutting

There are numerous pig designs ranging from single spheres for liquid removal, to foam pigs, to bristle pigs, to very aggressive pigs used for cleaning out severe deposits. Wireline cutting may be used to receive cuttings,washings and transport them when certain organic deposition problem are so severe that they can make production of some oil fields uneconomical but the method causes time-consuming fishing operations.

2.6.1.3 Through Flowing Cutting (TFC)

TFC pumps a cutting tool down the flowline and into the well bore to cut wax deposits. TFC is not yet a common practice in the industry; however, it has the advantage of being able to remediate sub sea flowlines and well bores from a distant platform

These three methods are mechanical methods that are used to prevent and manage wax deposition and oil gelling. Wright. (1951) mentioned that pigs, the paraffin knife, the paraffin hook, the corkscrew, and the swap were in general use. Other work focused on handling Prinos a field floating slop in Greece in early 1974. It used a slop system to receive "dirty" fluids from other clean-up

operation systems. It concluded that this method has been useful and successful in mitigating costs of wax deposition and maximizing production in Prinos (Kosta J. Leontaritis., 1996).

2.6.2 Thermal Method

2.6.2.1 Adding Heat to Stay Above Cloud Point

Heat may be added by mehods such as induction heating to guarantee the produced oil stays above the cloud point. Also some flowlines may be "bundled" where there is an external line surrounding the main transportation line. Hot water, for example, may be circulated in the annular space to keep the main fluids flow hot enough to avoid any wax formation. "Passive" insulation is another approach. If the produced fluids start relatively warm at the wellhead, sufficient insulation on the flowline can prevent the fluids cooling, to below the cloud point before reaching the processing platform.

2.6.2.2 Adding Heat to Melt Existing Waxy Deposit

Any of the "active" ways to heat a flowline has potential to remove waxy deposits once formed. Spitzer, 1987, patented an annular plug, which fits on the string. It slows the 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 a field of very high paraffins content near Vernal in Utah. Other work focused on the traditional methods of treatment, such as hot oiling and hot watering to solve the problem of wax building up in production areas, pipelines and refinery. These methods are still used by many companies although negative effects of hot oiling and hot watering exist when compare of with solvent treatment and crystal modifier applications because they are efficient and safer method (Becker, 2002).

2.6.3 Chemical Method

They can be divided into 4 types

2.6.3.1 Prevent or Slow the Formation of Waxy Deposits

Commercial wax inhibitors co-crystallize with the wax to prevent wax crystal structures from forming on the pipewall. Often dispersants coat wax crystals to keep them from agglomerating and detergents or surfactants act to

water wet the wax crystals so that they do not adhere to each other or to the pipe wall.

2.6.3.2 Decrease the Pour Point

High molecular weight polymers called "pour point depressant" or "wax crystal modifiers" can be used at ppm concentration levels to modify the wax crystal structure. In some cases, these chemicals can significantly reduce the pour point, viscosity, and yield stress, but these chemicals may not reduce rates of wax build-up on pipe walls.

2.6.3.3 Solvents to Dissolve Wax Deposits

It is possible to soak a wax deposit with a hydrocarbon based solvent to dissolve the wax and then add heat to speed up the process. A traditional method (especially for downhole applications) is the so-called "hot oiling" method. Some crude oil is heated and then sent down the well to melt accumulated wax. One disadvantage is that the crude oil used may itself deposit more wax as it cools. Purer (and more expensive) solvents can be used. Chemical "packages" will include dispersants to keep the melted wax particles from agglomerating.

2.6.3.4 Chemical to Induce Heat

There is a commercial process (SNG) used by Petrobras in which two salt solutions are mixed together and produce a strong exothermic reaction.

Ammonium Chloride + Sodium Nitrite = Heat + Sodium Chloride + Nitrogen.
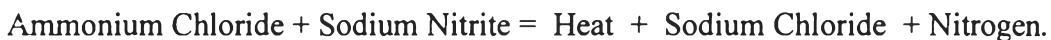
This mixing process is formed ideally at the point in a flowline where there is the wax deposit. The practical application of this is of course quite difficult in a very long flowline.

Remediation is normally performed by mechanical pigging or through solvent washing or with hot oils. All have their advantages and limitations. Addition of wax inhibitor/dispersants is an effective solution to remediate the deposition problem. The development of additives (wax inhibitor/dispersants) to improve the low temperature flow properties and wax deposit problem of waxy crude

oils involves major difficulties due to the complex composition of waxy crude oils thus many researchers have tried to find novel and practical additives and a universal mechanism to explain the change of the wax crystals in form and particle size when added to the different crude oils.

The well-known chemicals which soive wax deposition problem are called "wax inhibitors". Basically three main groups of chemicals are used :
- Wax crystal modifiers
- Detergents
- 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 the pipe wall, but primarily by keeping the crystals dispersed as separated particles, thereby reducing their tendency to interact and adhere to solid surfaces. The former groups are special chemical structures produced synthetically to interact with forming wax aggregates. The modifiers have structures with segments that interact with the forming wax crystals. These products act at a molecular level to alter the tendency of wax molecule to accumulate on each other, thereby reducing the capacity of paraffinic wax network in oil. Gracia *et al.* (2000) studied the influence of flocculated asphaltenes in bulk crude oil which could interfer with the inhibitor (maleic anhydride) by polarized light microscopy. The results indicated that asphaltene in bulk crude oil interfered with the inhibition mechanism of maleic anhydride crystal modifier that asphaltene and paraffins can generate complex solids depending on asphaltene properties. Moreover they studied the effect of paraffin class types on the wax crystallization in oils and the activity of paraffin inhibitors. They concluded that a proportion of large alkanes in crude oil is responsible for the inefficiency of paraffin inhibitor. These large alkanes are cyclic or branch which at concentrations below 40 %wt/wt making the inhibitor activity slightly reduced.

Abdel Halim *et al.*,(1985) studied the synthetic additives used to improve flow characteristics and also studied cost-benefit analysis of flow improvers injection in a 67 km long planned pipeline at different dosage rates and

costs. The flow improvers are found to be economic depending on percent weight of dosage and dosage rate and can change viscosity of oil, but, they can also create a corrosion problem.

The mechanism of pour point depressants (PPD) to lower the cold filter plugging point (CFPP) of diesel fuels was studied by differential scanning calorimeter (DSC) and X-ray diffraction (XRD) (Zhang *et al.*, 2003). The result indicated that PPD will co-crystallize with alkane molecules in the oil and performance of PPD during a nucleating process is the most important in improving the crystallinity of the oil solvent mixture.

In addition, poly(ethylene-co-vinyl acetate, EVA) copolymers as a pour point reducer and organic deposit inhibitor was also studied, and it was found that the copolymer with the highest vinyl acetate content exhibited the best performance as the organic deposits inhibitor. It is suggested that the EVA copolymer acts on the morphology of the wax crystal (Andre *et al.*, 1999). The additives that respond well to chemical treatment include poly alkyl acrylates and methacrylates, esters, ethylene-vinyl acetate copolymers, and naphthene derivatives. These are also used as wax inhibitors.

Grian *et al.* (1996) developed a new parameter to assess the efficiency of polymer flow improvers for waxy crude oils. The parameter is a flow parameter represents by Q that is related to dilute solution viscometry. They concluded that flow parameter (Q) depends on the interaction parameter of polymer flow improver with wax and resin-asphaltene (Uw and Ura respectively) and both influences can be explained by Einstein's viscosity law.

Groffe *et al.* (2001) studied a dispersant used to solve the wax deposition problem. They studied the effect of this chemical on viscosity, anti-sticking, and corrosion properties. From the result, this chemical can be used to reduce the pour point and improve the flow characteristics of crude oils. This chemical also reduces the amount of wax deposited on adhering metal surfaces (anti-sticking) and reduces corrosion rate.

Pedersen *et al.* (2003) studied the effect of twelve wax inhibitors with North Sea crude oil. The viscosity data suggested that the inhibitors, probably

by some kind of sterric hindrance effect, "inactivate" components within a certain range of molecular weight by preventing them from building network structure.

Sawhney *et al.* (1991) studied ester type chemical additives to modify the wax crystals in an Indian crude oil. They showed that the ester-type chemical has the capacity to modify n-alkanes in the C_{11} – $C_{19/20}$ range, but for a crude oil containing higher carbon atom number, i.e. C_{20} - C_{35} or above, These respond very poorly to chemical treatment.

A model for predicting the activity of addititives from physicochemical properties and from the activity of additives on the crystallization temperature of paraffinic wax was found. Cristante *et al.* (1999) showed that the additives were divided into three families and that their viscosity was modified by the nature of crude oil. This INIPAR model can be used for the multidimensional location of a new crude oil and for the choice of additive when the crude oil families are known.

The traditional methods of solvent-based removal are time consuming, expensive, and can create problems of re-deposition. Brown *et al.* (1999) showed that if an exothermic reaction is generated that melts and disperses paraffin wax and asphaltenic deposits, the reaction products being a powerful paraffins dispersant that prevents re-deposition after the temperature returns to normal.