CHAPTER-1
INTRODUCTION

1.1 Introduction

Petroleum or crude oil is a naturally occurring liquid found in earth's crust which consists of complex mixture of hydrocarbons (mostly alkanes) of various chain lengths. The word petroleum is derived from the Latin words *Petra* and *oleum* meaning rock oil which refers to hydrocarbon that occurs widely in the sedimentary rocks in the form of gases and liquids. It is usually found in black or dark brown in color, sometimes yellow or even greenish but its appearance vary greatly based on its composition. Crude bitumen is semi-solid form of crude oil found mixed with sand. Due to its high energy density, transportability and relative abundance it is world's most important source of energy since 1950s. Petroleum acts as a raw material for many chemical products which include pharmaceuticals, solvents, fertilizers, pesticides and plastics, which accounts for 16% of total which is not used for energy productions and converted into these materials.

1.2 Formation

Petroleum represents a mixture of large number of different hydrocarbons in which commonly found components are alkanes (straight chain or branched), cycloalkanes, aromatics or more complicated like asphaltene. Petroleum from different locations has a unique composition of molecules which defines its physical and chemical properties like color and viscosity. These different molecules are separated by fractional distillation technique to produce kerosene, jet fuel, gasoline and other hydrocarbons. Following two theories are proposed regarding formation of crude oil. **[1]**

1.2.1 Biogenic Theory

Crude oil and natural gas are viewed by most geologist as products of compression and heating of ancient organic material over a period of long time. Formation of oil takes place from buried remains of zooplankton and algae which get settled to sea or lake bottom in large quantities under anoxic conditions. Coal formation takes place from decomposition of terrestrial plants. Over a very long geological period this organic matter gets mixed with mud and buried under heavy layers of sediments. As a result of high levels of heat and pressure cause organic matter to chemically change during digenesis, first into waxy material known as **kerogen** which is located in various oil shale around the globe, and then with more heat into liquid and gaseous hydrocarbons by a process known as **catagenesis**. 'Oil Window' is a term often used by geologist to represent temperature range that oil forms in-below the minimum temperature oil remains trapped in the form of kerogen and above maximum temperature oil gets converted into natural

gas through the process of thermal cracking. The above mentioned process takes place at different depths at different locations around the world where 4-6 km is found to be typical depth for oil window. If formation of oil takes place at extreme depth, it may be trapped at much shallower depth, even if it is not formed over there. As most hydrocarbons are lighter than rock or water, these often migrate upward through adjacent rock layers until they either reach the surface or get trapped below impermeable rocks, within porous rocks called reservoir. However, the process is not as simple as it has impact of underground water flows and so oil may travel hundreds of kilometers horizontally or even shorter distances downward before becoming trapped in reservoir. Accumulation of hydrocarbons in a trap forms an oil field, from which liquid can be recovered by drilling or pumping. Three conditions are necessary for oil reservoirs to form: first, a source rock rich in organic material buried deep enough for subterranean heat to convert it into oil; second, a porous and permeable reservoir rock for it to collect in; and last, a cap rock or other mechanism that blocks it from moving to the surface. Within these reservoirs fluids typically organize themselves like three layered cake. Water forms the bottom layer, middle layer is of oil and top layer is composed of gases. Different layers vary in size for various reservoirs. The majority of oil that has been produced by earth escaped to the surface long ago and biodegraded by oil eating bacteria. In oil sands partially biodegraded oil is still in process of escaping but contains huge amount of migrating oil that, although most of it has escaped, vast amount are still present – more than can be found in conventional reservoirs. On the other hand, oil shale are source rocks that have never been buried deep enough to convert their trapped kerogen into oil. Reactions producing oil and natural gas are often termed as first order breakdown reactions, where breaking down of kerogen to oil and natural gas takes place by a set of parallel reactions and oil finally breaks down to natural gas by another set of reactions. **[2]**

1.2.2 Abiogenic Theory

The idea of abiogenic origin of petroleum was proposed in the western world by astronomer Thomas Gold based on Russian thoughts and studies of Nikolai Kudryavtsev. The idea proposed that hydrocarbons having geological origin exist in the planet. Density of hydrocarbons is less than aqueous fluids and tends to travel upward through deep fracture networks. Thermophilic, rock dwelling microbial life-forms are proposed to be in part responsible for the biomarkers found in petroleum.

This theory is less popular, with some takers among western geologist; oil companies in west don't explore for oil based on this theory, although Russian used this theory with some success. [2]

1.3 Composition of Petroleum: [3]

The composition of crude oil represents large variety of hydrocarbon molecules but variation in proportion of elements found to be within narrow limits. Significant variation in properties is found from lightest crude oil to highly asphaltenic crudes. The carbon content is between 83 to 87% in which hydrogen content varies from 10 to 14%. In addition, smaller proportion of nitrogen, oxygen, sulfur and metals (Ni and V) are also found. Due to complex composition of crude oils, characterization of individual molecule is not possible and elemental analysis is less informative due to constant elemental composition. Hence analysis of hydrocarbon group is commonly employed. Information about major structural classes of hydrocarbons and its distribution in crude oil is needed in various fields of petroleum industry. Examples are: studies relating reservoir evaluation, migration and maturity, degradation process, processing and environmental effects. The SARA separation technique is one such example for analysis where the crude oils are being separated into four main chemical classes based on differences in solubility and polarity. The four main SARA fractions are saturates (S), aromatics (A), resins (R), and the asphaltenes (A) as shown in Figure 1.1.
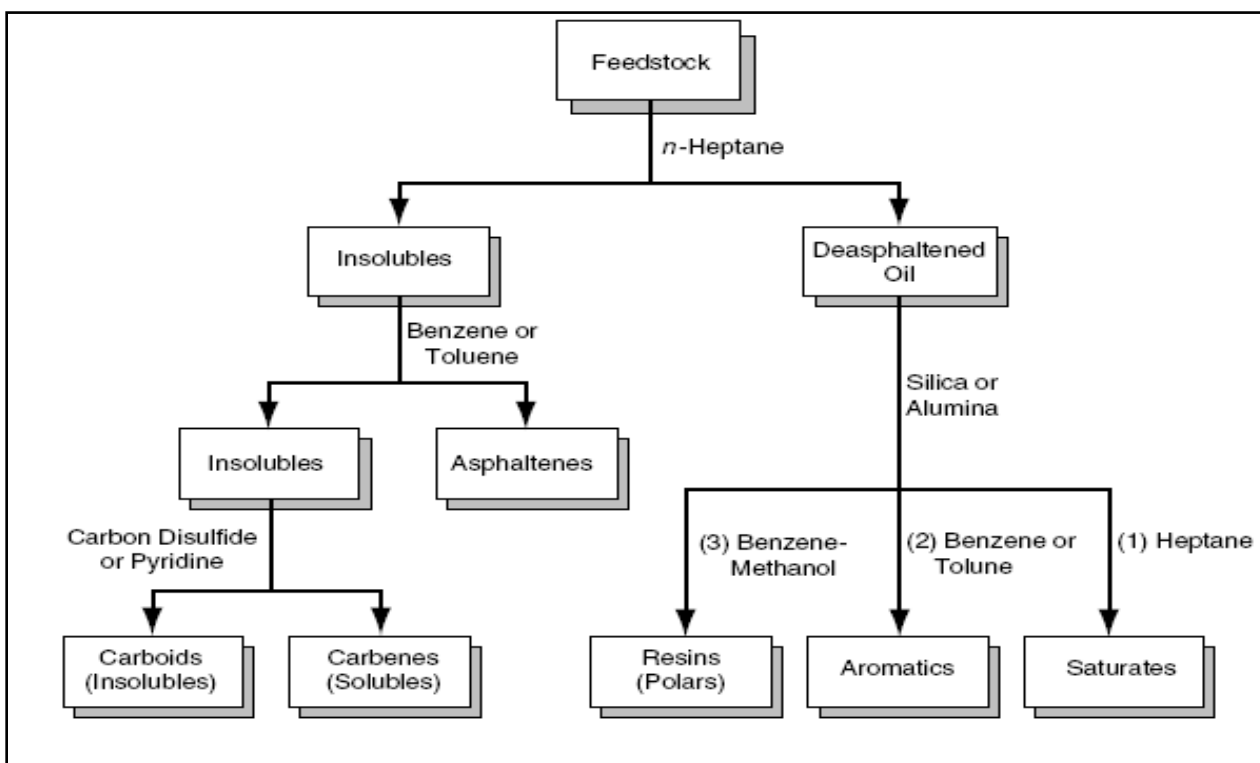

Fig 1.1: Simplified Representation of Fractionation of Petroleum

1.3.1 Saturates

The saturates (aliphatic) are non-polar hydrocarbons, having straight-chain and branched alkanes as well as cycloalkanes (naphthenes) without any double bond. Cycloalkanes contains one or more rings with several alkyl side chains. The proportions in a crude oil normally decreases with increasing molecular weight fraction, thus the saturate generally are the lightest fraction of the crude oil. A subclass of saturates is Wax which mainly consist of straight chain alkanes, ranging from C_{20} to C_{30}. Paraffin waxes have orthorhombic, hexagonal, monoclinic and triclinic structures. Wax tends to precipitate at low temperature in the form of particulate solid and found to affect emulsion stability properties of crude oil systems. **[3]**

1.3.1.1 Structure of Wax Crystal:

Waxes are n-paraffin hydrocarbons containing iso-paraffin branched paraffin. The basic structure of n-paraffin crystal is shown in figure 1.2. The crystal is very thin diamond shaped plates. Figure 1.2 shows that the plates consist of layer of n-paraffin molecules. In each layer, the n-paraffin molecules are staked side by side with their long axis parallel to the Z-axis of the crystal**. [3]**
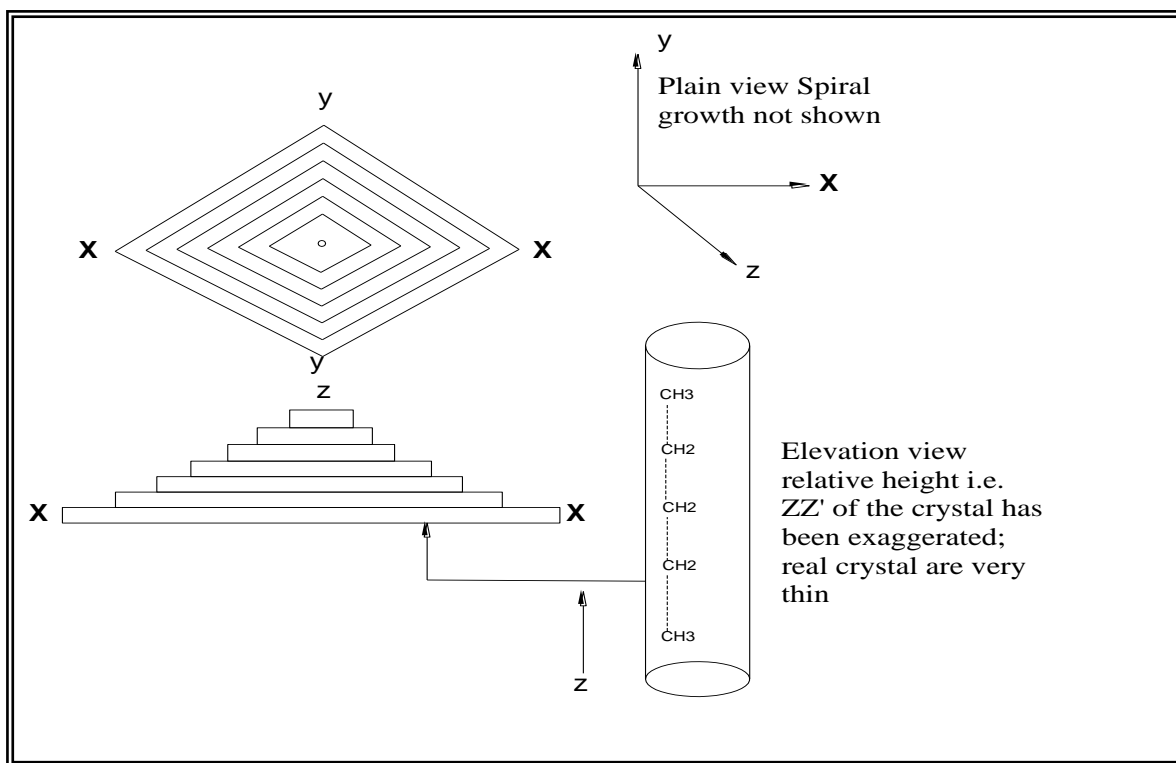

Fig 1.2 Structure of Wax Crystal

The petroleum industry differentiates four types of waxes:

1. **Paraffin Wax**

   It is recovered by chilling and pressing the light viscosity distillates and sweating the wax so that oil gets separated if present. The waxes have melting point in the range of 49-60 ^{o}C. Individual n-alkanes would range from C_{18} to C_{32} with melting points ranging between 27 to 69 ^{o}C**. [4]**

2. **Slope Wax:**

   It is found in high viscosity distillates and cannot be pressed. In this category of wax carbon number ranges from C_{26} to C_{43} and melting point ranges between 56 to 83 ^{o}C.

3. **Petroleum or Microcrystalline wax:**

   This type of wax is found in residual stocks. Microcrystalline wax with 5-20% oil have molecular weight of 450 to 1000 (possible upto 1200) and have melting point in the range of 60 to 88 ^{o}C (possible upto 93°C). A typical composition is found to have nC_{34} to nC_{43} with melting point range from 71°C to 84°C, with iso-alkanes and possibly cyclic alkanes concentrating in this fraction.

4. **Rod Wax:**

   Rod wax separates from crude oil in the well around the sucker rod and it might be characterized as paraffin wax of very high melting point.

1.3.2 Aromatics:

The Aromatics consist of benzene and its derivatives. Aromatics are commonly found in all petroleum and majority of aromatics contain alkyl chains and cycloalkane rings, with additional aromatic rings. Based on the number of aromatic rings present in the molecule these are often classified as mono-, di- and tri- aromatics. Polar, higher molecular weight aromatics may fall in the resin or ashphaltene fraction**. [3]**

1.3.3 Resins:

This fraction consists of polar molecules often containing hetroatoms such as nitrogen, sulphur or oxygen. Its operational definition is the fraction soluble in light alkanes such as pentane and heptanes but insoluble in liquid propane. With reference to crude oil properties resin fraction is very important however little work has been reported on the characteristics of the resins, compared to for

instance the asphaltenes. H/C ratio in resins is 1.2-1.7 which is higher than 0.9-1.2 for the asphaltenes. Structurally resins are similar to ashphaltene but lesser in molecular weight (<1000 g/mole). Naphthenic Acid is commonly regarded as a part of the resin fraction. [3]

1.3.4 Asphaltene:

The ashphaltene fraction is defined as the fraction of the crude oil precipitating in light alkanes like pentane, hexane or heptanes. These precipitates are soluble in toluene or benzene. The ashphaltene fraction contains largest percentage of hetroatom (N, S or O) and organometallic constituents (Fe, Ni or V) in the crude oil. The structure of ashphaltene consists of polycyclic aromatic clusters, substituted with varying alkyl side chains. Figure 1.3 shows a hypothetical monomer molecule of ashphaltene. Tendency of ashphaltene to self aggregate makes molecular weight determination difficult but molecular weight in the range 500-2000 g/mole are believed to be reasonable. Monomer molecule of ashphaltene size ranges from 12 to 24 Å. [3]
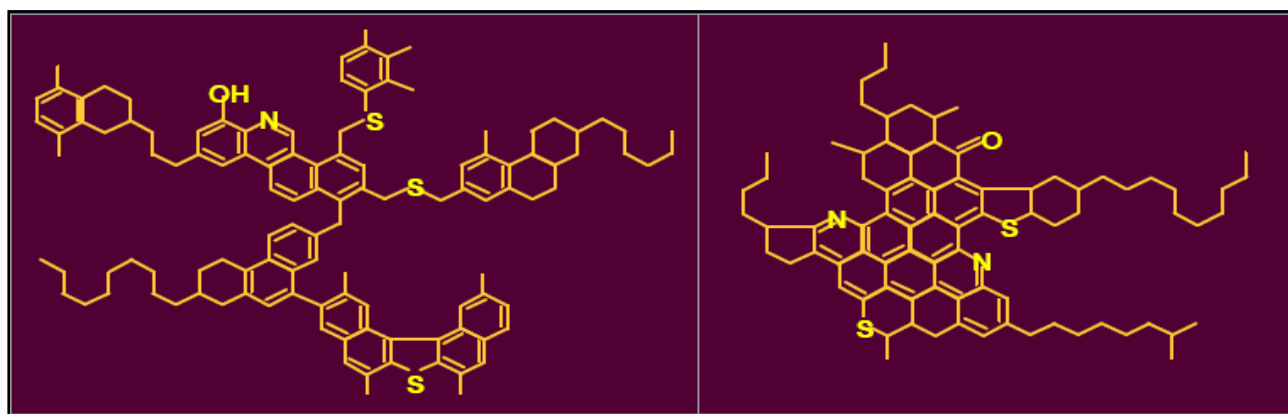

Fig 1.3 Hypothetical ashphaltene molecules

1.3.4.1 Structure of Asphaltene:

Asphaltene has H/C ratio in the range 0.8-1.4 and its molecular weight depends on solvent and concentration, monomer (500-1000), micelles (1000-5000). Hetroatom acting as polar functional group are S= 0.5 to 10 wt %; N=0.6 to 2.6 wt %; O= 0.3 to 4.8 wt % and metal elements like Ni, V and Fe.

Asphaltenes are believed to be suspended in the form of micro colloid in the crude oil, consisting of particles of about 3 nm. Each particle is made up of one or more aromatic sheets of ashphaltene monomers, with adsorbed resins behaving as surfactants to stabilize the colloidal suspension. Π-bonds, hydrogen bonds and electron donor-acceptor bonds keep the molecules together. Using suitable solvent resins desorb from the asphaltenes which brings about increase

in ashphaltene aggregate size and eventually leads to precipitation. This ashphaltene aggregation model is termed as stearic stabilization model developed by Nellensteyn and others. Based on this model it can be said that resins are necessary to suspend the ashphaltene aggregate, thus aggregate represents ashphaltene-resin complex. Figure 1.4 shows a model of an ashphaltene aggregate stabilized by resin molecules. [5][6]
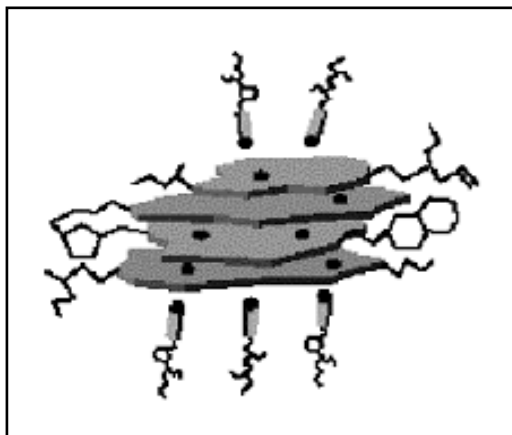

Fig 1.4 Model of an Ashphaltene aggregate stabilized by resin molecules

Alternative model for Ashphaltene stabilization exists, termed as thermodynamic model and first reported by Hirscberg et al. In this model resins are not considered explicitly but are treated as integrated part of the solvent medium. This view implies that the ashphaltene monomers and aggregates are in the thermodynamic equilibrium, solvated by the surrounding medium. Thus the critical distinction between the thermodynamics and stearic stabilization models lies in whether the ashphaltene colloids are solvated or suspended in the hydrocarbon media. Main advantage of using the thermodynamic approach when modeling ashphaltene aggregation is that it utilizes conventional thermodynamic methods for phase equilibrium like equation of state. Since, the resins are not considered explicitly it does not sufficiently take into account the resin-ashphaltene interactions, which is based on experimental observations. Different thermodynamic ashphaltene aggregation models have been reviewed by Andersen and Speight, with the conclusion that they are lacking in several respects and are not quantitatively correct. **[7][8]**

1.4 Types of Crude Oils:[9]

Variation in appearance and viscosity is observed from field to field for different crude oils. They range in color, odor and in the properties they possess. While all crude oils are essentially hydrocarbons, the difference in properties, especially the variations in molecular structure, mean that crude is more or less easy to produce, pipeline and refine. The variations may even influence

its suitability for certain products and the quality of those products. Crudes are roughly classified into three groups, according to the nature of the hydrocarbons they contain.

[1]Paraffin Based Crude Oils

They contain high molecular weight paraffins which are solid at room temperature, but little or no asphaltic matter. They can produce high-grade lubricating oils.

[2]Asphaltic-Base Crude Oils

Contains little or no paraffin but have large proportions of asphaltic matter. Some are predominantly naphthenes so yield lubricating oil that is more sensitive to temperature changes than the paraffin base crudes.

[3]Mixed-Base Crude Oils

Both paraffins and naphthenes are present along with aromatic hydrocarbons. Most crude lie in this category.

1.5 Characteristics of Crude Oil

1.5.1 Density, Specific Gravity and API Gravity [10]

In the petroleum refining industry, density and specific gravity data were used to

1 To indicate crude oil quality.

2 Correlate with aromatic character, naphthenic character and paraffinic character.

The specific gravity is highest for aromatics and lowest for paraffins. The API gravity is reverse. Hence the preliminary assessment of crude oil's character was done on the basis of density and specific gravity. In the beginning of petroleum industry, density was principal parameter for petroleum and refinery products; it was used to give approximate estimation of the gasoline and more particularly kerosene present in the crude oil. This derived relation between density of petroleum and its fractional composition were applicable to a certain type of petroleum and becomes insignificant to different types of petroleum. Still density is used to give rough estimation of nature of petroleum and its products. Density is defined as mass of a unit volume of material at a specified temperature and has the dimension of grams per cubic centimeter.

Specific Gravity is defined as the mass of a unit volume of any substance at a specified temperature compared with the mass of an equal volume of pure water at a standard temperature.

API Gravity

This is an expression of the density of oil. Unless stated otherwise the API gravity refers to density at 60 ^{o}F (15.6 ^{o}C). Its relationship with specific gravity is given by the expression

$$API^o = (141.5/specific\ gravity) - 131.5$$

ASTM D70, ASTM D71, ASTM D287, ASTM D941, ASTM D1217, ASTM D1298, ASTM D 1480, ASTM D1481, ASTM D1555, ASTM D1657, ASTM D4052, IP 235, IP 160, IP 249 AND IP 365 methods were used to determine density, specific gravity and API gravity.

Density	API Gravity	Classification
<0.8550	>34	Light
0.8550-0.934	34-20	Medium Heavy
>0.9340	< 20	Heavy

1.5.2 Distillation [11]

Distillation is a means of separating chemical compounds usually liquids through differences in their vapor pressures. Simple distillation is effective only when separating a volatile liquid from a non-volatile substance or when separating two liquids that differ in boiling point by 50 ^{o}C or more. The modern processes of distillation are as follows:

1.5.2.1 Fractional Distillation [12]

Fractional distillation is the separation of a mixture into its component parts or fractions based on their boiling point by heating them to a temperature at which several fractions of compounds will evaporate. It is a special type of distillation. This type is employed when temperature difference between different components is less than 25°C under 1 atm. pressure. If the difference in boiling points is greater than 25°C, simple distillation technique is being deployed.
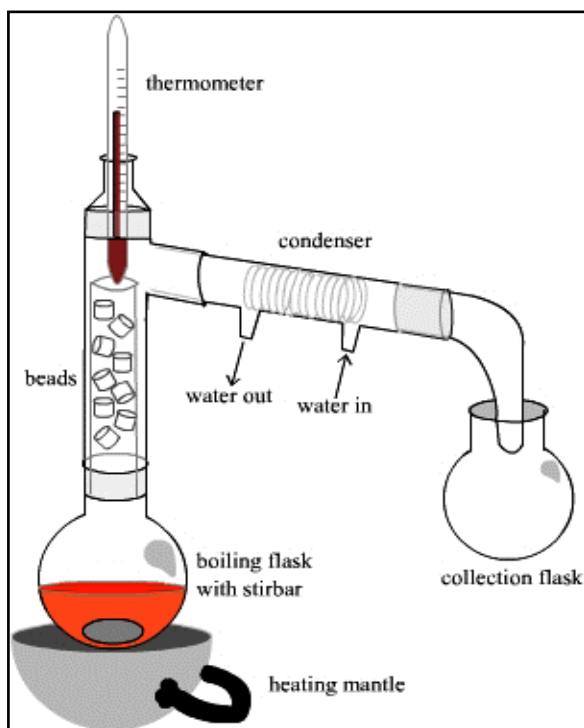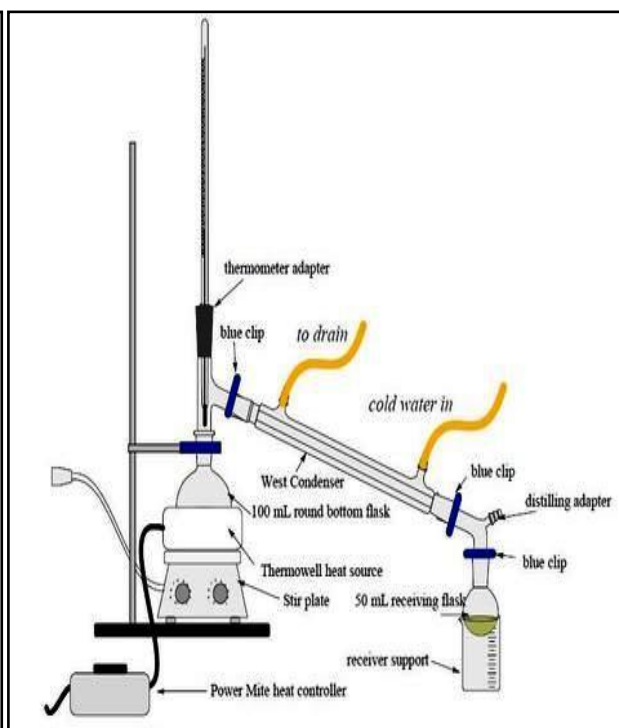
Fig 1.5 Fractional Distillation   Fig 1.6 Simple Distillation

1.5.2.2 Continuous Distillation [13]

The principle for continuous distillation is same as that of simple distillation: when a liquid mixture is heated up to boiling point, the composition of the vapor above the liquid differs from the liquid composition. If this vapor is then separated and condensed into a liquid, it becomes richer in the lower boiling components of the original mixture.
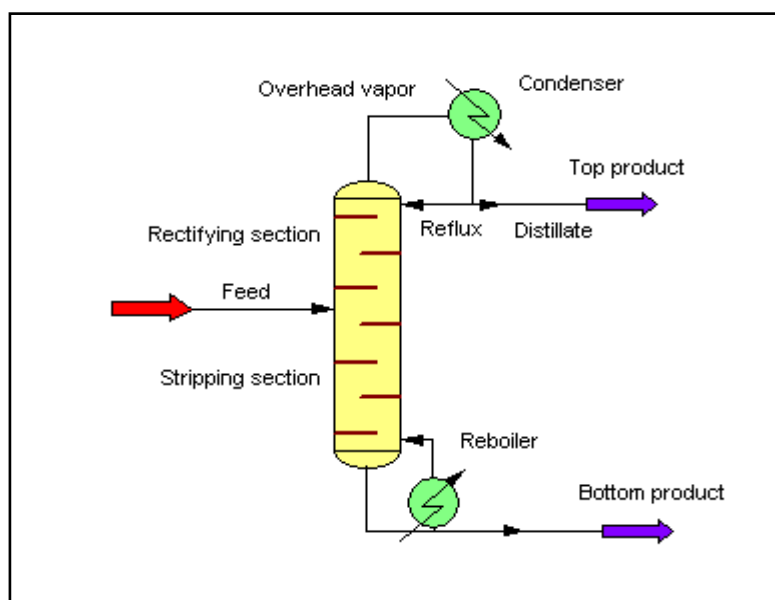

Fig 1.7 Flow sheet diagram for Continuous Distillation

1.5.2.3 Vacuum Distillation [14]

Vacuum distillation is method of distillation whereby the pressure above the liquid mixture to be distilled is reduced to less than its vapor pressure (usually less than atmospheric pressure) causing evaporation of the most volatile liquids (those with lowest boiling point). This distillation method works on the principle that boiling occurs when the vapor pressure of a liquid exceeds the ambient pressure. Vacuum distillation is used with and without heating the solution.
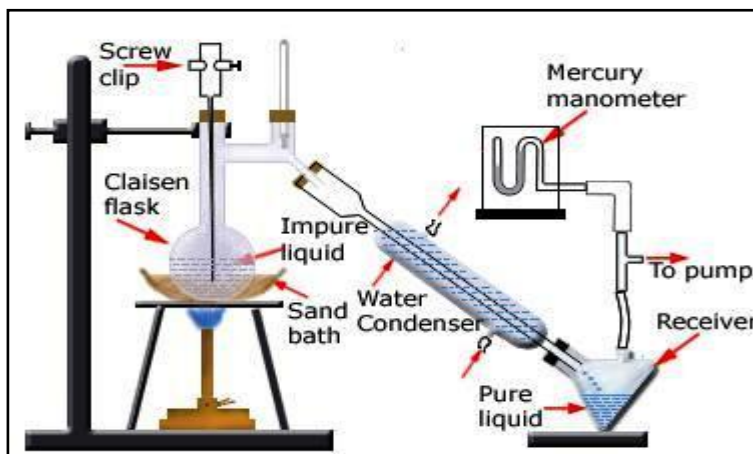
Fig 1.8 Laboratory set up for Vacuum Distillation

1.5.2.4 Azeotropic and Extractive Distillation

It is often possible to separate compounds that have very close boiling points by means of azeotropic distillation. A process by which liquid mixture is separated into pure components with help of a additional substance or solvent. In chemical engineering, azeotropic distillation usually refers to specific technique of adding another component to generate new lower boiling azeotrope that is heterogeneous. Extractive distillation is defined as distillation in presence of a high boiling, miscible, relatively less volatile component and the solvents which don't form azeotropic mixture with any component in the mixture. This method is applicable to mixture having low volatility. Simple distillation technique cannot be applied since components have very less boiling point difference with high volatility. The method of extractive distillation uses separation solvent which is non-volatile, having high boiling point and miscible with mixture but doesn't form azeotropic mixture. Components of mixture undergo change in volatilities as solvent interacts differently. This makes three part mixture separate out as top product. The bottom part consists of other components including solvent which can be easily separated as

solvent doesn't form azeotrope with it. The bottom product can be separated by available various methods. **[15]**
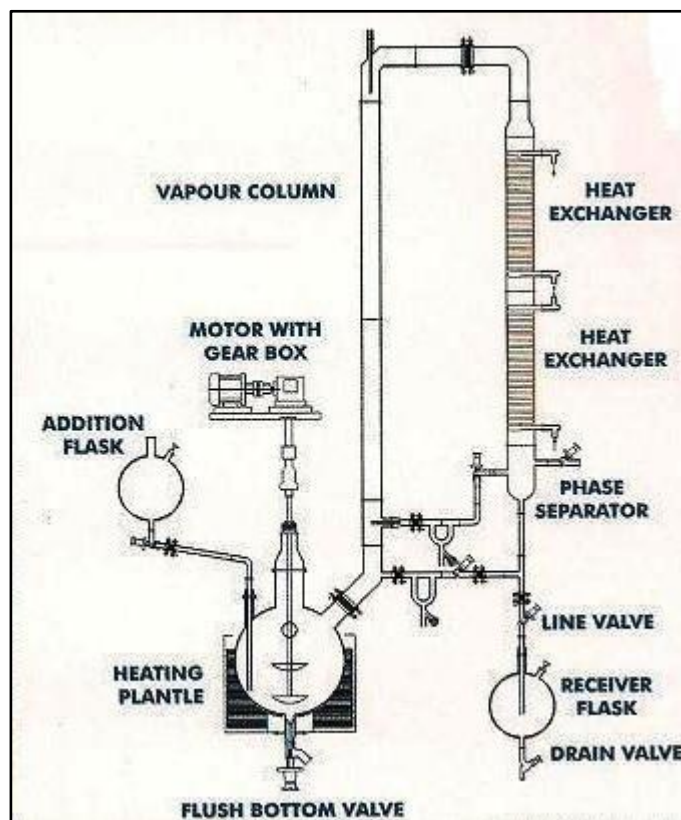

Fig 1.9 Azeotropic Distillations

1.5.3 Water Content, Salt Content and Bottom Sediment

The proportions of aqueous contaminants like water **[16]** and bottom sediment **[17]**, present in the crude either originally or picked up by the crude during handling and storage. Sometimes water and salt content of crude oils produced are very high, forming its major part. Separation of salt and water at the field is usually done by settling, draining and use of surface active agents or sometimes by electrical emulsion breaker. Although the centrifuge methods are used (ASTM D96, ASTM D 1796, ASTM D2709) many laboratory employ Dean and Strark Adaptor as shown in Fig. 1.10 [18]. The apparatus consist of a round bottom flask of capacity 50 mL connected to a condenser by a receiving tube of capacity 25 mL, graduated in 0.1 mL. A weighed amount, corresponding to approximately 100 mL of oil is placed in the flask with 25 mL of dry toluene. The flask is heated gently until the 25 mL of toluene has distilled into the graduated tube. The water distilled with the toluene, separates to the bottom of the tube where the volume is recorded as mL, or the weight as mg, or percent. To determine the sediment in petroleum or in petroleum product, the methods involve solvent extraction using Soxhlet

extractor. The Karl Fisher titration method (ASTM D1744) and the colorimetric Karl Fisher titration Method (ASTM D4298) still find wide application in many laboratories for the determination of water in liquid fuels, specifically the water content of the aviation fuels. Higher the bottom sediments and water content, higher the sludge and deposit formation rates that can be expected in the stored crude oil.
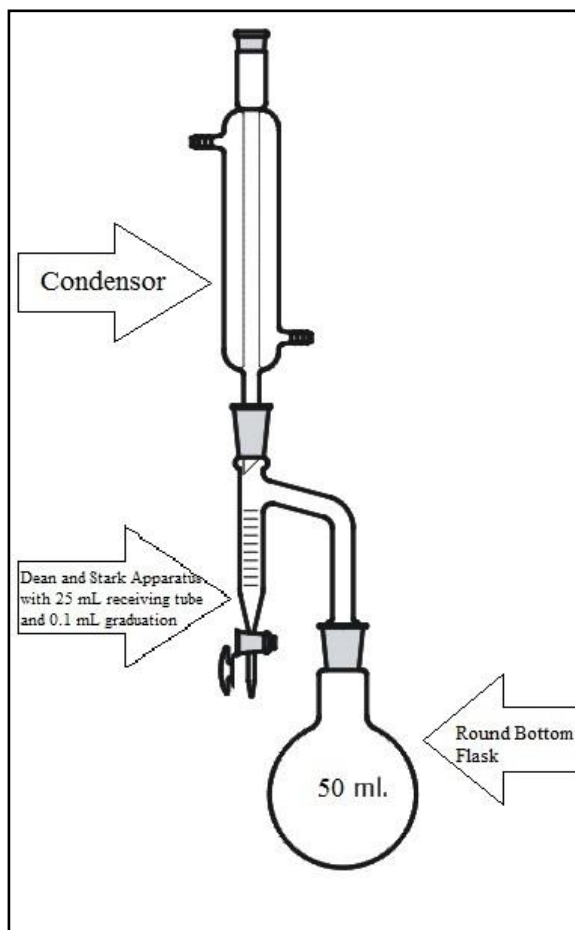

Fig 1.10 Water content determination using Dean and Stark Adaptor

1.5.4 Wax Content

Methyl ethyl Ketone (MEK) or Acetone precipitation technique is used to determine wax content of the crude oil. In this method oily fraction of crude oil separated (by dissolving ashphaltene and resin by acid treatment) and precipitating the wax with the help of ethyl alcohol and methyl ethyl ketone and cooling the mixture at -20 ^{o}C. The precipitated wax is filtered out, washes thoroughly, dried and weighed accurately. The wax content is determined by filtration. The oil is crystallized at given temperature and treated with a dewaxing solvent (MEK, dichloroethylene, butanol) for ease of the filtration. The wax residue is repeatedly washed with solvent (maintained at same temperature) until any color in wax has been removed. A low

temperature is chosen (-21°C) for getting maximum amount of wax likely to crystallize under operating conditions and to minimize the dissolution of the wax by the washing solvent however no solvent completely rejects wax and hence each method would give different wax content result depending on temperature, solvent and degree of washing. Dewaxing solvents may also precipitate asphaltenes. [19]

1.5.5   Ashphaltene Content

Ashphaltene represents organic molecules with highest molecular mass and hydrogen–carbon ratio normally occurring in crude petroleum and petroleum products containing residual material. They may give problems during storage or handling if the suspension of ashphaltene molecules is disturbed through excess stress or incompatibility. They are also the last molecules in a product to combust completely and thus may be one indicator of black propensity. Their composition normally includes a disproportionately high quantity of the sulphur, nitrogen and metals present in the crude petroleum or petroleum product. [20]

1.5.6   Pour Point

The pour point is the lowest temperature expressed as multiple of 3°C at which the oil is observed to flow when cooled and examined under prescribed condition. High wax containing crude oil shows high pour point and exhibits Non-Newtonian viscosity behavior below cloud point temperature. Wax and Ashphaltene content greatly influence pour point of crude oil. [21]

1.5.7   Cloud Point

The temperature at which lubricant becomes hazy due to wax formation, on cooling under standard condition. Cloud point indicates tendency of oil to plug filters or small orifices at cold operating temperature. [22]

1.5.8   Viscosity

Viscosity is measure of resistance to flow for a given fluid. Fluids have the tendency to resist relative motion of immersed objects as well as motion of layers with difference in velocities between them. Formally, viscosity (symbol 'η' eta) is ratio of shearing stress (F/A) to the velocity gradient ($\Delta V_x /\Delta Z$ or dV_x /dz) in a fluid. Newton's equation states that the resulting shear of a fluid is directly proportional to the force applied and inversely proportional to its viscosity.

$$\frac{F}{A} = \eta \left(\frac{\Delta V x}{\Delta Z}\right) \qquad \text{or} \qquad \frac{F}{A} = \eta \left(\frac{dV x}{dZ}\right)$$

$$\frac{F}{A} = m \left(\frac{\Delta V}{\Delta t}\right) \qquad \text{or} \qquad \frac{F}{A} = m \left(\frac{dV}{dt}\right)$$

There are two quantities that are called viscosity. The quantity defined above is sometimes called dynamic viscosity, absolute viscosity or simple viscosity to distinguish it from the other quantity, but is usually just called viscosity. The other quantity called kinematic viscosity (symbol 'v' nu) is the ratio of the viscosity of a fluid to its density. [23]

$$\nu = \frac{\eta}{\rho}$$

Kinematic Viscosity is a measure of the resistive flow of a fluid under gravitational influence. Newtonian fluid possesses properties of viscosity. Apparent viscosity is the ratio of shear stress to shear rate. It has been used to describe the viscous properties of non-Newtonian fluid; the apparent viscosity of Newtonian fluid is the same as its viscosity. [24]

1.6 Effect of temperature on viscosity of crude oil [25]

Viscosity of crude oil is markedly affected by temperature. With increase in temperature, viscosity decreases. On heating a non-Newtonian crude oil, the apparent viscosity at particular shear rate starts decreasing and stage comes when the ratio if shear rate is constant and oil shows Newtonian behavior.

1.7 Rheology [26]

The rheology of waxy crude oils is influenced greatly by their complex primary components such as wax, resin and asphaltenes as well as by external factors including thermal and shear history. Rheology is concerned with the flow and deformation of material experiencing an applied force. Two extremes of rheological behavior are:

1. Elastic Behavior- e.g. perfectly rigid solids- on removal of applied force any deformation reverses spontaneously. System stores energy and performs work.
2. Viscous (or Plastic) Behavior- e.g. Ideal Newtonian liquids- are those where any deformation ceases when the applied force is removed. Energy performs work on the material.

Viscoelastic material behaves in between the above two behaviors. In rheology, key to understanding flow behavior and structure lies in shearing of a substance. A sheared flow is achieved through flow between parallel planes, rotational flow between co-axial cylinders where one cylinder is stationary and other is rotational, telescopic flow through capillaries and pipes and torsional flow between parallel plates. To enable study of the viscosity of a material, the shearing must induce stationary flow of the material. Flow of oil is due to deformation and rearrangement of constituent particles by breaking of bonds in the structure of the material. The velocity gradient at right angle to the flow is called the shear rate (also called strain rate) and the force per unit area creating or produced by the flow is called shear stress.
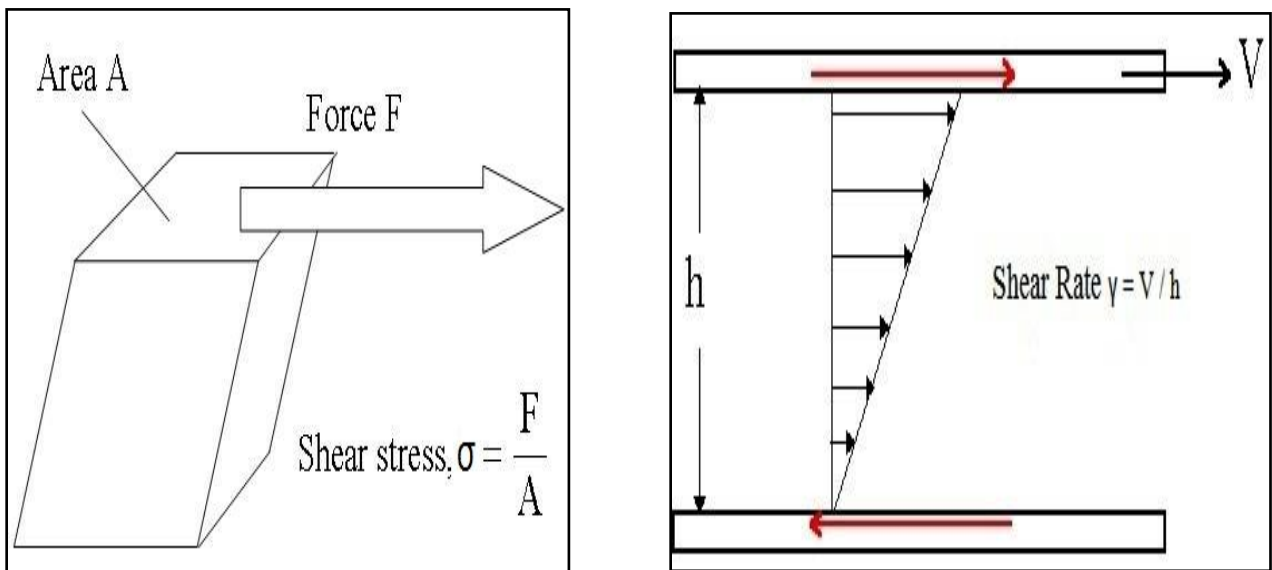

Fig. 1.11 Shear Stress and Shear Rate based on shearing between plates

The shear rate has the units of velocity divided by distance i.e. meters per second/ metres, leaving us with the units of reciprocal (i.e. one over Seconds, or s^{-1}). Shear stress-force per unit area-has the units of Newton per square meter, Nm^{-2} but in the SI system, stress like pressure, it is given in units of pascals, Pa in the honor of French Scientist. In a liquid, shear stress produces sliding of one layer over another resulting in a stack of card type flow as shown in figure 1.12.
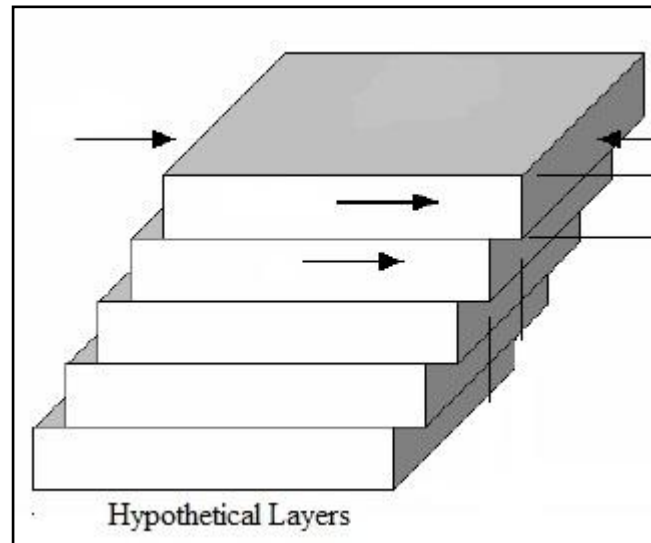
Fig. 1.12 Hypothetical layers in Shear Flow

1.7.1 Types of Flow Behavior [27]

Fluids exhibit several types of rheological behavior. The various types of behavior can be broadly divided into two classes: Time Independent and Time Dependent flow as shown in figure 1.13.
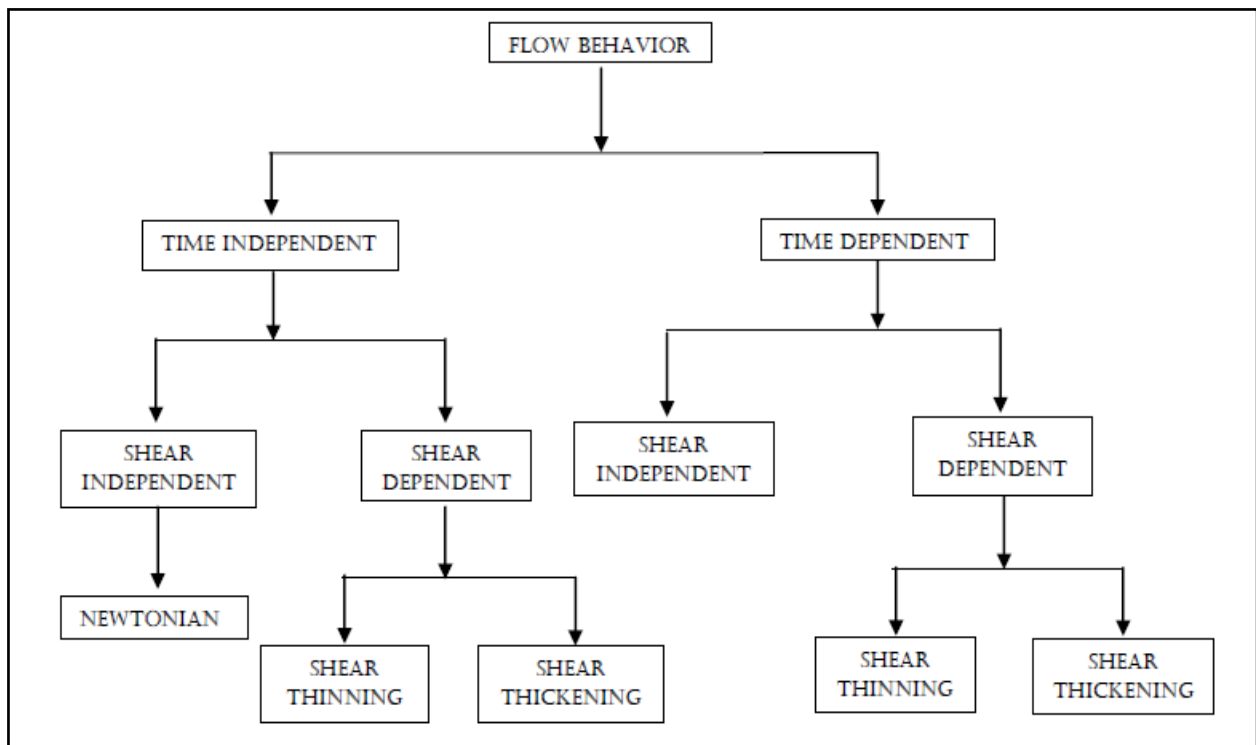

Fig.1.13 Time Dependent and Time Independent Flow Behavior of Fluid

1.7.1.1 Time Independent Flow [28]

1.7.1.1.1 Newtonian Flow - Newtonian model describes an idealized type of flow. For Newtonian fluid shear stress is directly proportional to shear rate as shown in figure 1.14.
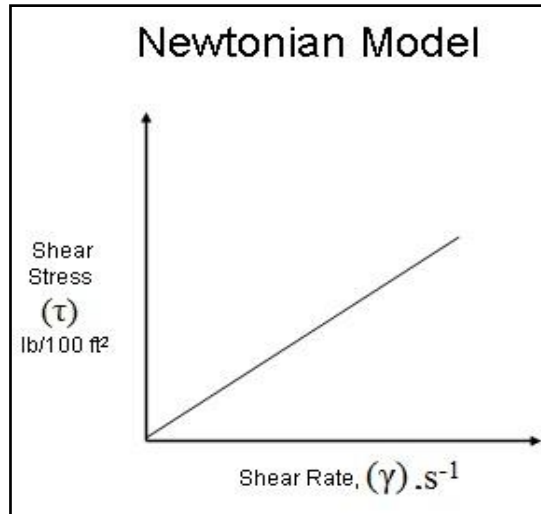
Fig. 1.14 Newtonian Flows

1.7.1.1.2 Shear Thinning (Pseudo plastic) Flow – A second type of time independent flow is the decrease of apparent viscosity with shear rate. This is known as Shear Thinning behavior or pseudoplasticity.
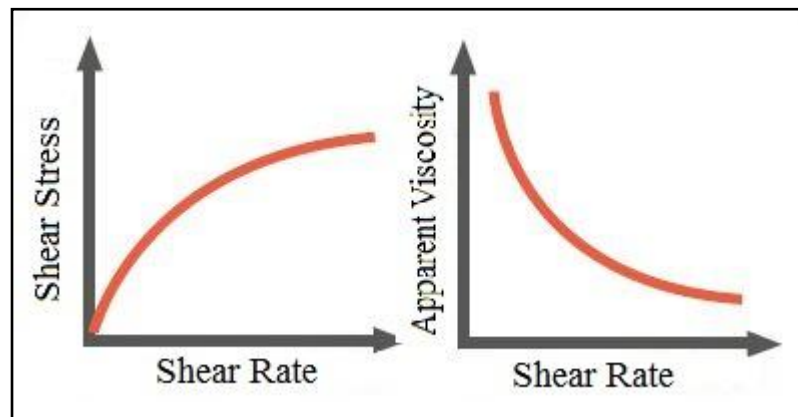

Fig 1.15 Shear Thinning Flow

It is noticed in figure 1.15 that the slope of the shear stress- shear rate curve (or the apparent viscosity) increases rapidly as the shear rate approaches zero. In many cases, extrapolation of the curve to zero shear rate results in a positive intersection on the

shear stress axis. This intercept is known as the yield stress. Bingham fluid exhibits linearity of this flow curve while viscosity decreases with increase in shear rate (shear thinning) also they require finite shear stress called yield stress to initiate flow as shown in Figure 1.16. Mathematically they can be expressed as,

$$\sigma = \sigma_y + \eta_p \left(\frac{du}{dr}\right)$$

Where σ = shear stress (Pa), σ_y = Bingham Yield Stress, η_p = Plastic Viscosity (Pa-S), $\frac{du}{dr}$ = shear rate (s^{-1}). This model has been applied to many waxy crude oil.
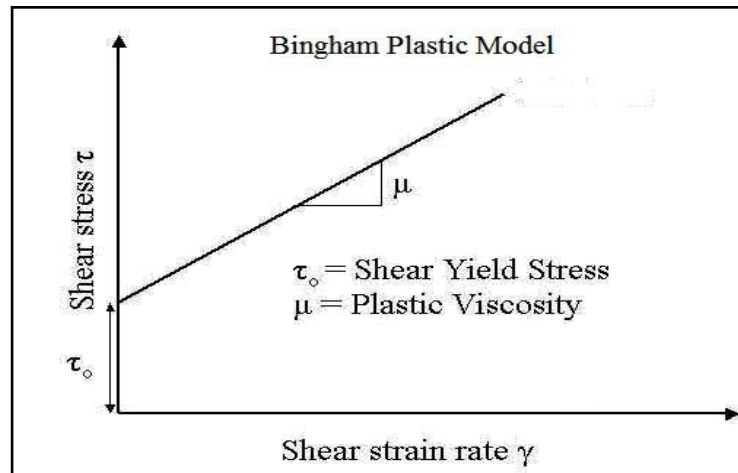

Fig 1.16 Bingham Body Flow

1.7.1.1.3 Shear Thickening (Dilatant) Flow – A third type of time independent flow behavior is that exhibited by the Shear Thickening (or Dilatant) fluid. In this case, the apparent viscosity increases as the shear rate increases as shown in Figure 1.17. Such behavior is not as common as shear thinning and it is incorrectly believed by some that the fluid must dilate when it flows. (Hence dilatant).
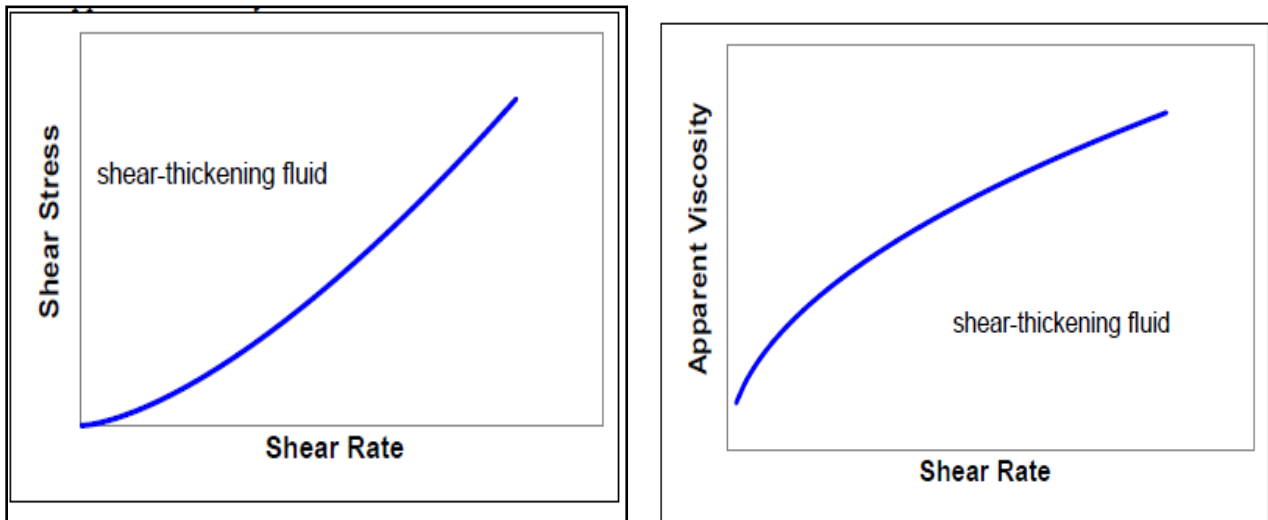
Fig 1.17 Shear Thickening Flow

1.7.1.2 Time Dependent Flow [29]

1.7.1.2.1 **Thixotropic Flow** –If the apparent viscosity is measured under steady shear conditions and it decreases with time to an equilibrium value, the material is said to be Thixotropic. On cessation of shearing, the apparent viscosity of a thixotropic fluid increases with time. Thixotropy is usually associated with the presence of a yield stress (Fig. 1.18). In some cases, the yield stress may be unaltered by shear and in others, it may be lowered.
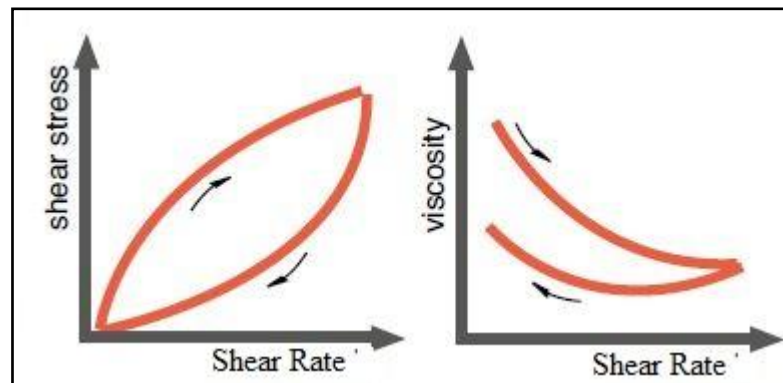

Fig 1.18 Thixotropic Fluids

1.7.1.2.2 **Rheopectic Flow** – The second type of time dependent flow is rheopexy. While being subjected to steady state shear, a Rheopectic fluid exhibits more resistance to flow with passing time. These system show viscosity decreases with increasing shear but viscosity increases with time at constant shear rate.

1.8 Blockage Of Crude Oil Pipelines Due to Wax Precipitation

For oil producers transportation and handling of crude oil presents a major challenge (Fig.1.19) Deposition of paraffin causes loss worth billions of dollars per year worldwide. Wax deposition leads to reduced production, well shutdown, pipeline replacement and increased manpower needs.
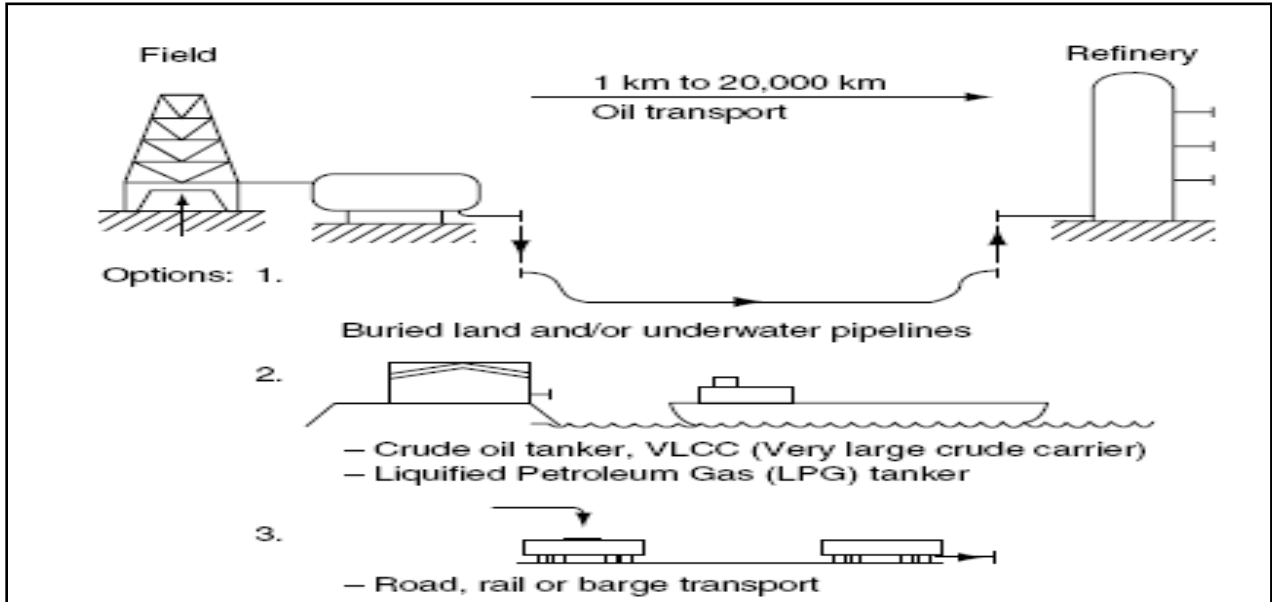

Fig 1.19 Crude Oil Transportation

On storing waxy crude oil in the tank, a part of oil comes in contact with cold portion of the tank wall and gets cooled and becomes stiff. This deposition of wax decreases flow rate of oil and creates hurdles in transportation. At lower temperature, wax separates out from crude oil and deposits on wall of the pipelines and tanker. Because of this, the effective diameter of the pipeline transporting the crude reduces and the pressure drop between the two ends of the line increases. (Fig 1.20 and Fig. 1.21) This results in the reduction of flow and extra burden on the pumping systems. **[30] [31]**
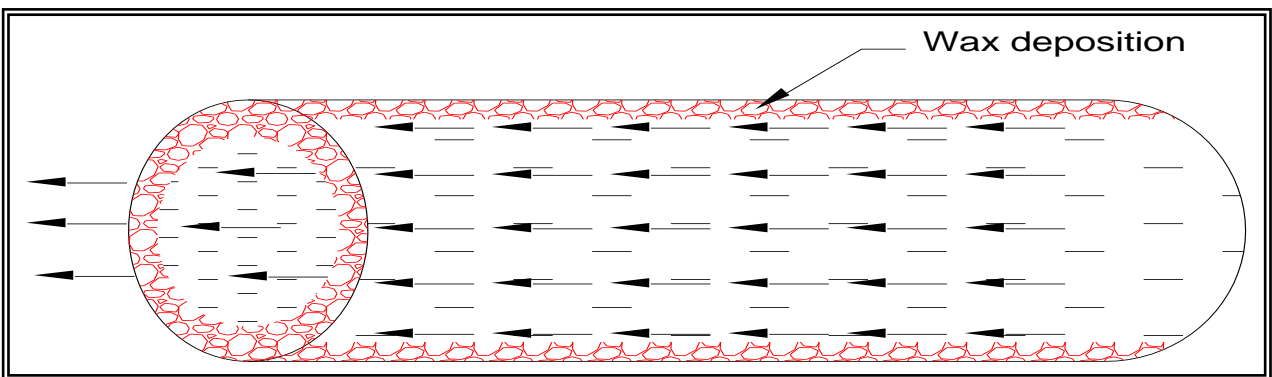

Fig 1.20 Reduction in pipeline diameter due to wax deposition

Fig 1.21 Blocked pipelines

1.9 Phenomenon of wax deposition in crude oil

The waxes generally crystallize as an interlocking network of fine sheets, thereby entrapping the remaining oil in cage-like structures and cause the blockage of pipelines. The wax crystallization phenomenon can be split into three stages. Firstly nuclei formation takes place. Second is the growing of nuclei, where mass gets transported from solution towards nuclei. Third is the aggregation- where growing crystals combine to form large crystals. **[32]**

There are two theories proposed for crystal:

1.9.1 Gibb's Theory

According to this theory, each crystal face grows layer by layer in an essentially discontinuous fashion. In figure 1.22, in stage (a) crystal waiting for nucleation to occur on any of its faces. Once nucleation has occurred, a growth step is formed and layer development proceeds rapidly. When the new layer has grown to the edges of crystal, growth has eliminated itself and so the growth stops until the nucleation on the top of the newly formed layer occurs and a new cycle begins.
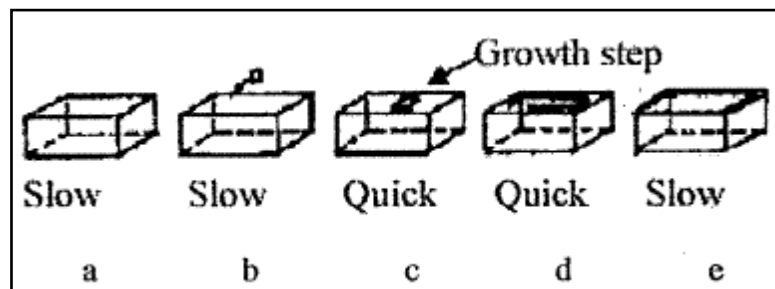

Fig 1.22 Gibb's Theory: Discontinuous Layer Addition

1.9.2 Frank's Theory

According to this theory, crystals are not perfect and contain fault. The figure 1.23 shows stacking fault due to n-paraffin molecules. They are not lining up properly. The diagram shows hypothetical crystal surface built up of block like molecules. The crystal surface is not smooth because each block is slightly out of line with some of its neighbors in the crystal surface. The addition of more blocks causes continuous propagation of fault with simultaneous growth of crystals. Thus according to this theory n-paraffin crystal are not made up of discrete terraces, but consist of extremely shallow solid spirals. **[33]**
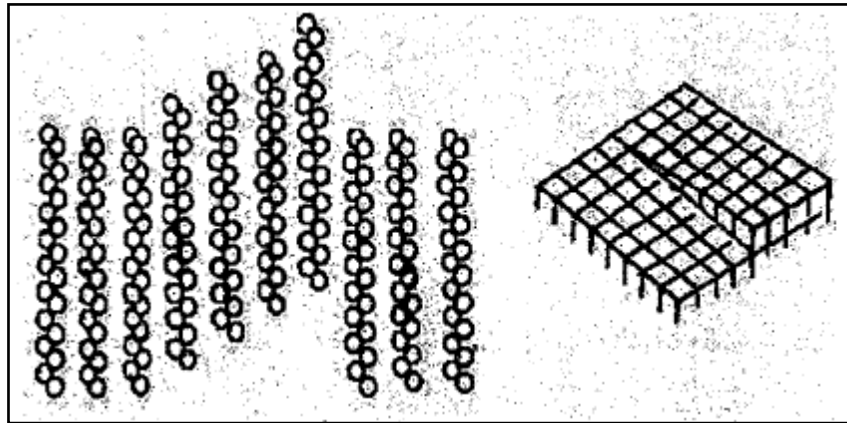
Fig 1.23 Frank's Theory: Continuous Growth via dislocation

1.10   Factors Affecting Rate of Wax Deposition [34]

The level of wax deposition depends on factors like rate of production, pipeline size, gas to oil ratio, chemical composition of crude oil, geological conditions and depth of pipeline. Two main factors governing the rate of wax deposition are as follows:

1.10.1 Flow Rate: From actual field experience and flow loop experiments it is concluded that when flow rate is minimum wax deposition is maximum and vice-versa. When flow rate is high, rate of heat transfer is higher due to which interface temperature approaches cloud point rapidly deposits observed is less in thickness.

1.10.2 Wall Temperature:

At lower temperature, deposition of wax increases due which internal radius of pipelines decreases. If wall temperatures are kept high final thickness of deposits is less.

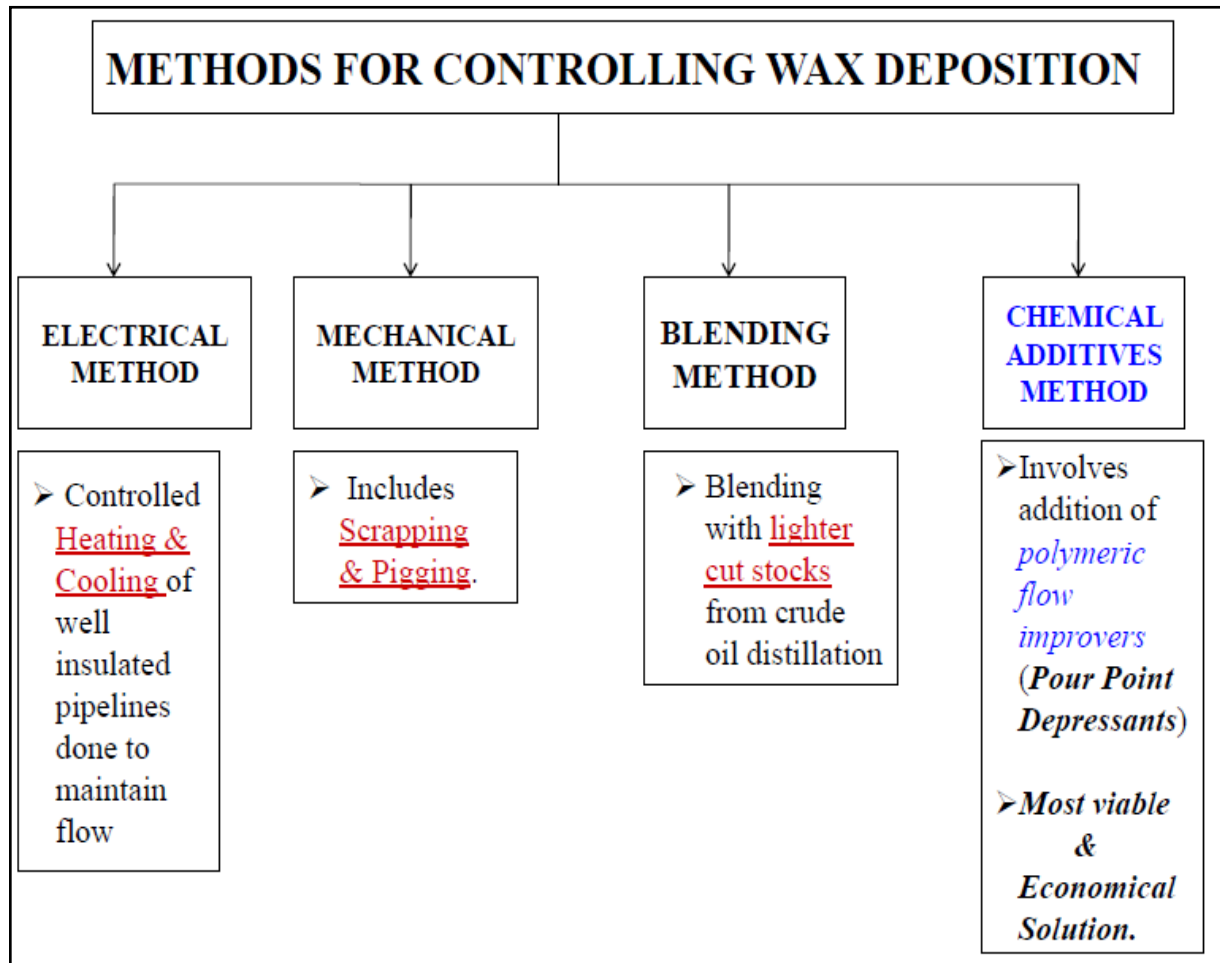## 1.11 Methods for Controlling Deposition of Wax [35]

Fig. 1.24 Different Methods for Wax Deposition Control

1.12 Chemical Additives (Polymeric) for crude oil

Chemical or polymeric additives are mixed with crude oil to improve its flow ability, conductivity and viscosity. These polymeric compounds are made up of hydrocarbon chain that interacts with paraffin of the crude oil and brings about wax crystal modification necessary to inhibit aggregation stage thus lowering pour point. Such inhibitors are known as Pour Point Depressant Additives (PPD).

Varieties of PPD are commercially available. e.g. polymers of n-alkyl acrylates and methacrylates with α-olefins or long chain alcohols, polyvinylethers, a copolymer of olefins and vinyl esters particularly, ethylene vinyl acetate (EVA) copolymers are used in the oil field in large quantity. Comb shaped polymers like copolymers of maleic anhydride with styrene or α-olifins or vinylic esters, poly-α-olefins and terpolymers like styrene/dodecyl methacrylate/octadecyl methacrylate having different monomer ratios have been evaluated as

PPD. Some diblock copolymers e.g. polyethylene-polyethylenepropylene (PE-PEP) and poly (ethylene-co-butene) (PEB) are also reported as good PPD. **[35]**

Recently, efforts are being made to introduce new additive which can disperse effectively wax of distillate fuels treated with traditional flow improvers. This type of additive is known as wax dispersant flow improver (WDFI) or wax anti-settling flow improver (WAFI). These are used with traditional flow improvers to further modify size and shape of treated wax crystal. The size of wax crystal can reach to extent of 5 to 20 pm when treated with flow improvers but with wax dispersants it is found to be in the range of 1 to 3 pm. However they tend to interact with each other to form sizeable aggregates. When both wax dispersant and flow improvers work together the size of wax crystal reduces to as less as 0.5 to 2 pm (which is upper limit of colloidal range). **[36]** Thus, the morphology of treated wax crystal is modified drastically due to combined effect of both additives. The composition and structure of wax dispersants is similar to traditional flow improvers in some aspects while different in others. They often possess highly polar functional groups which is very essential feature for dispersant potential. Polar nitrogen containing polymers can function as wax dispersant and flow improvers simultaneously in one component additive. The one component multipurpose additive shows complete compatibility between the two restrictive functions. When an additive having two components is used, one component acts as traditional polymeric flow improvers while other component comprising of hydrocarbon oil soluble chain and polar dispersant group functions as wax dispersants. The component of lesser solubility acts as a nucleator while other acts as wax growth arrestor. **[37][38]**

1.13 Types of Pour Point Depressants [39]

1.13.1 Natural Pour Point Depressants

Some natural pour point depressants such as asphaltenes having heteroatom such as nitrogen, sulphur and oxygen are found in crude oil itself. Several limitation associated with these additives are low oxidation stability, carbon forming tendency, foul odor makes it undesirable to use in finished products. The efficacy of natural PPDs is low as compared to synthetic one.

1.13.2 Synthetic Pour Point Depressants

These are either completely synthetic or obtained by modification of naturally occurring polymeric materials.

1.14 Mode of action of wax crystal modifier for waxy crudes

When a waxy fluid is cooled below its cloud point, the wax crystal begins to form and agglomerate. On further reduction of temperature crystals aggregate to form loose gel structure. The wax crystal habit depends on crude source, rate of cooling and degree of agitation during cooling. On addition of crystal modifier in minimum concentration, crystal habit size and crystal adhesion gets modified. The change in crystal habit, size and reduction in its tendency to adhere to one another, act to reduce the temperature of gel formation. This phenomenon can be well understood from following figure 1.25. **[40]**
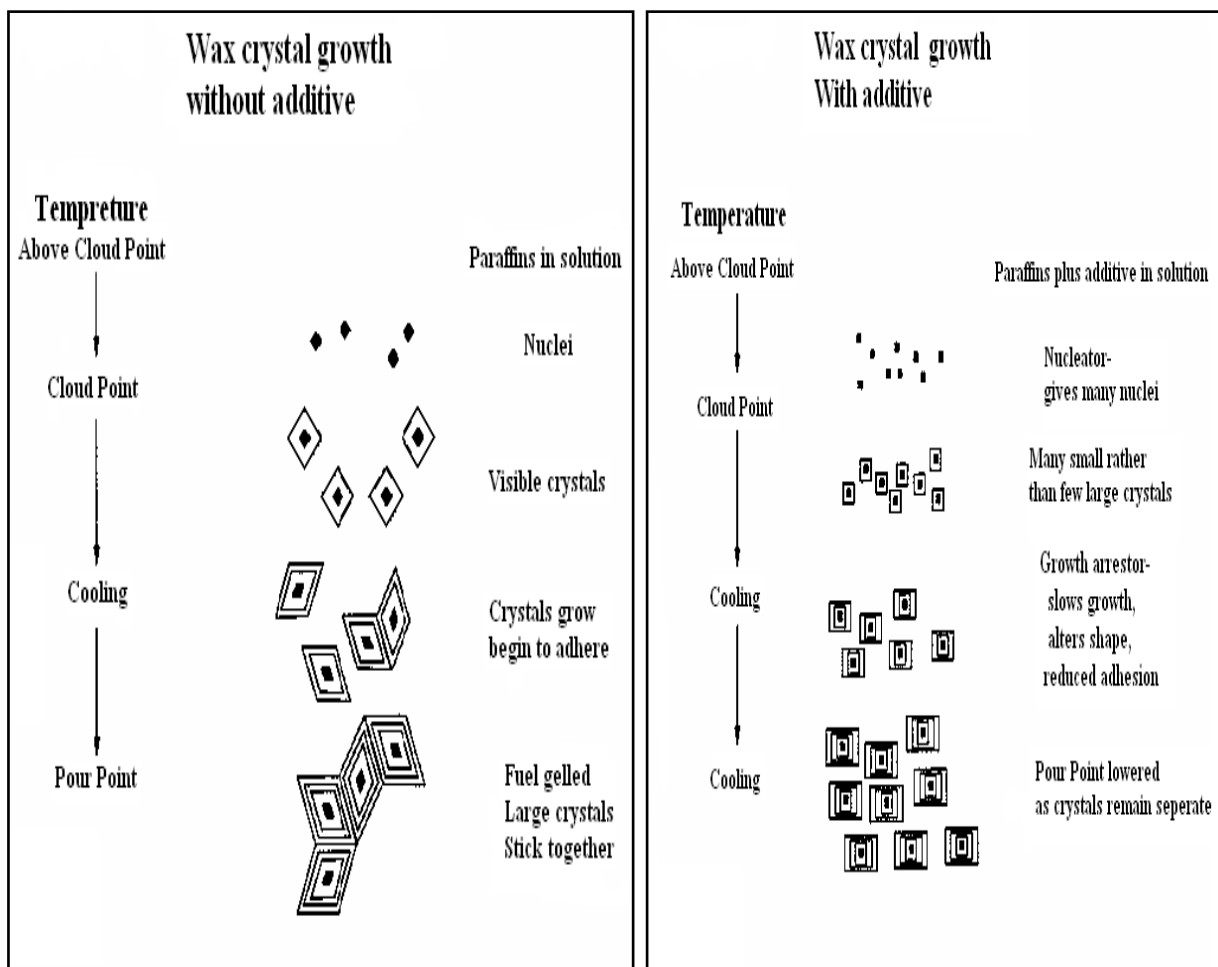

Fig. 1.25 Mechanism of wax crystal growth without and with additives

1.15 Mechanism of pour point depression [41,42]

There are two possible mechanisms of pour point depression. In the first mechanism, the additive molecules interact with n-paraffins and acts as a cover preventing addition of paraffin molecules to the crystal by limiting the dimension of existing crystal. In the second mechanism, the additive functions as nucleator to promote the growth of smaller size crystal thereby improving flow properties of crude oil.

The flow improver in the crude oil blocks the crystallization of wax by introducing polymer molecules at the fastest growing edge or dislocation. However the growth is observed only in Z-direction because n-paraffin molecules come out of the solutions. The new layers are formed according to Gibb's mechanism. Thus wax crystal habit changes from thin interlocking plates to more compact crystals. Thus pour point of the oil decreases and oil can easily flow below its pour point.
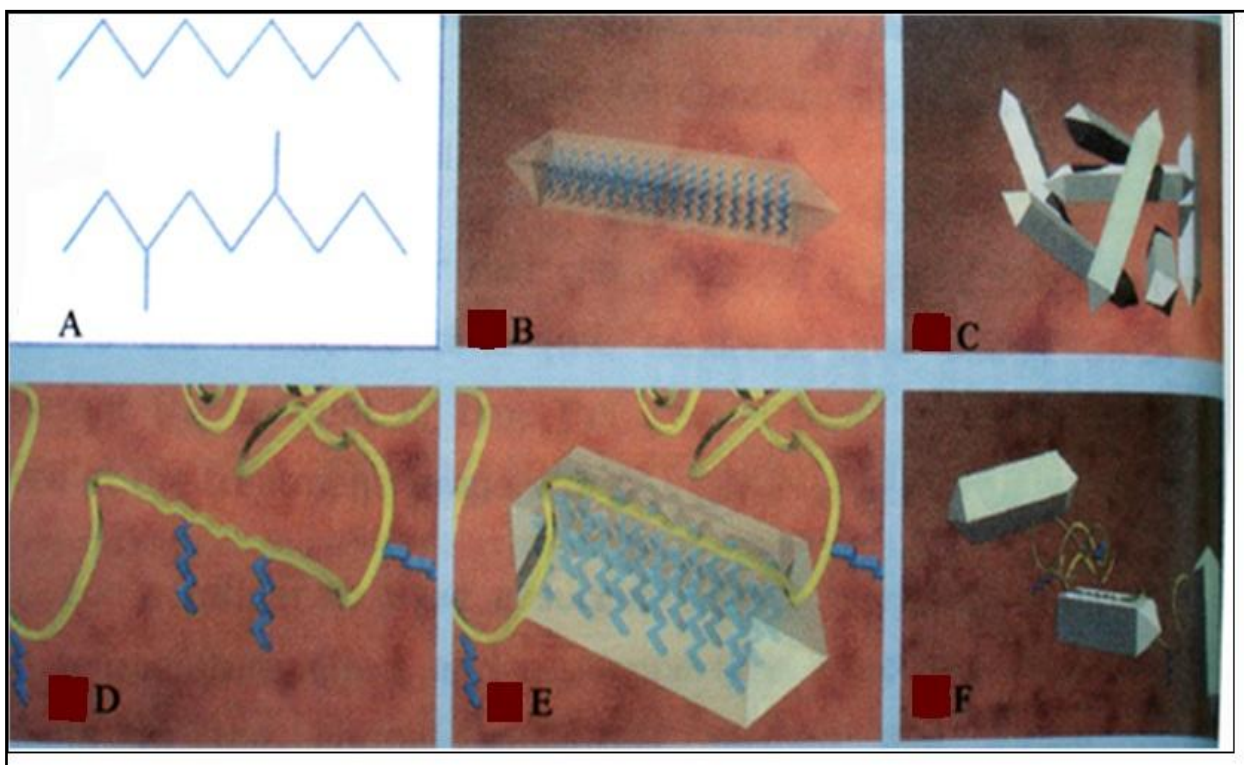

Fig. 1.26 Mechanism of Pour Point Depression

The mechanism is shown in figure 1.26 (A to F). Figure A represents wax crystal which crystallizes into needle shaped structures which is clearly indicated by figure B. These needle shaped structures associate with each other to form larger aggregates as shown in figure C. Figure D shows a polymeric additive which co-crystallize with wax molecules (Fig. E) and creates stearic hindrance for growth of wax crystals which is evident from figure F.
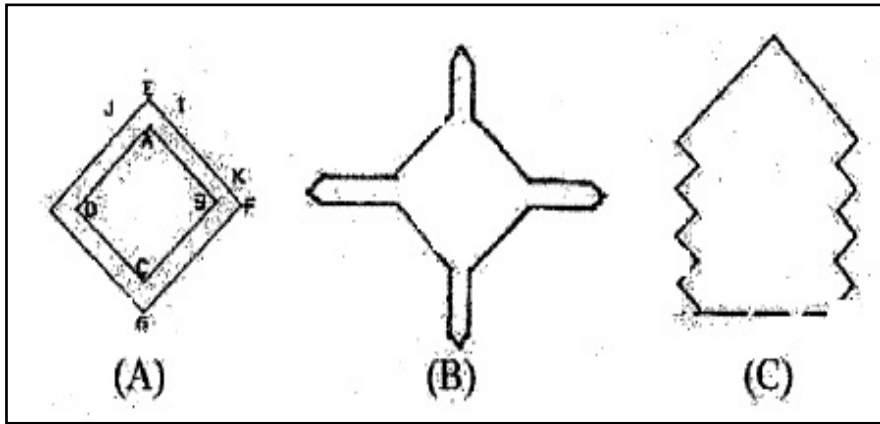
Fig. 1.27 Mechanism of formation of Dendrite Crystals

The PPD mechanism can also be explained by theory of crystal growth and dendrite growth. The theory proposes that with number of crystal faces growing, poisons present in the solution will accumulate around the faces. Due to this, growth of crystal takes place where impurity concentration is at minimum. In figure 1.27 (A) indicates growth of crystal nucleus from ABCD to size EFGH. Deposition of poison is found more on EF, FG, GH and HE then at the corners E, F, G and H. Hence accordingly growth observed is faster at the corners. At later stage formation of crystal as shown in figure B having needle like projections developing from corners of a crystal is seen. Figure C shows enlargement of one of the projections of figure B. So if each needle is seen then it is made up of projections which are true crystallographic faces. These projections are points for further growth. The end result is development of branches at regular intervals with rapid growth of corners i.e. dendrite structure formation.
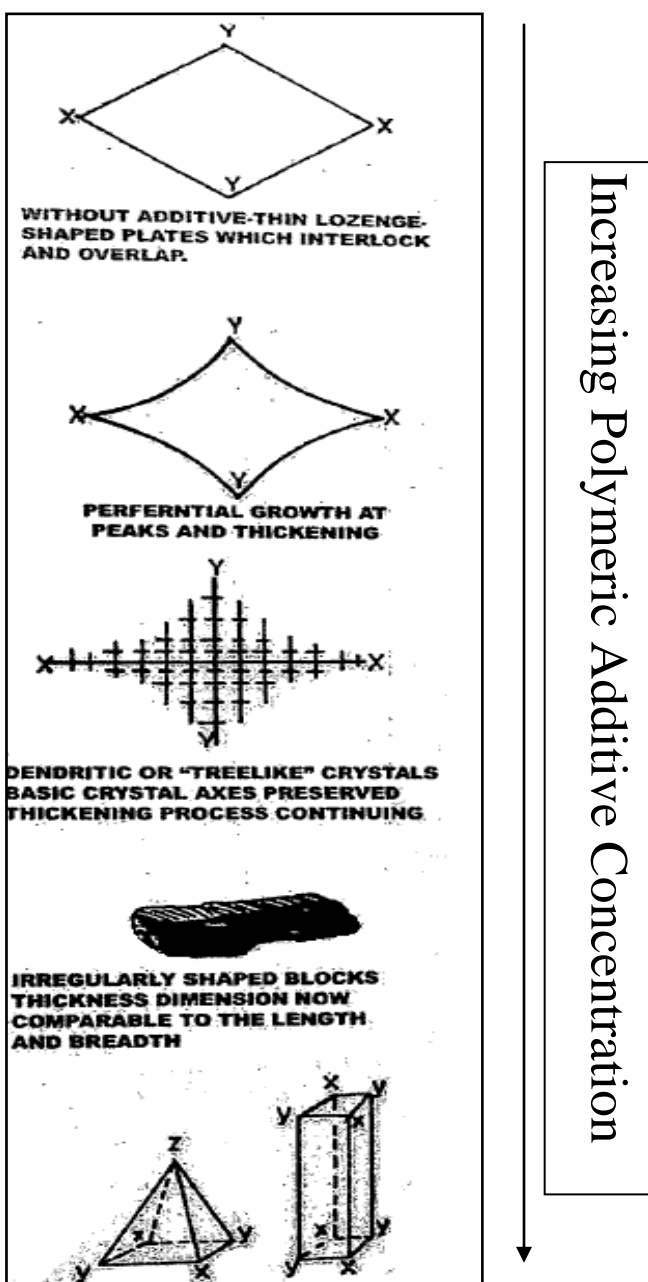
Fig. 1.28 Stages of Crystal Size Modification

1.16 Role of Polymeric Additive and Temperature in Changing the Viscosity of Crude Oil

The efficacy of polymeric additive to modify the viscosity with temperature depends on additives solubility in crude oil. The solubility of polymeric additive having moderate molecular weight increases with increase in temperature. At times polymeric molecule changes from closed to open structure as temperature increases resulting into higher volume and thus causes rise in viscosity

of the oil. It has also been found that with rise in temperature the three dimensional gel structure formed due to precipitated wax gets broken gradually which causes viscosity to drop. **[43]**

1.17 Factors affecting performance of Pour Point Depressants

1.17.1 Influence of Pendant Alkyl Chains

The solubility of polymeric additives in oil depends on its molecular weight while the length of alkyl side chain controls the adsorption of polymer on the wax. Long alkyl chain polymers are effective in reducing the pour point of high pour oils while short alkyl chain polymers are effective in low pour oils. If the lengths of alkyl chains are very short, they adsorb on the wax below the pour point which makes them ineffective and if lengths of alkyl chains are very long then chains will crystallize the polymer from the oil solution at a temperature above pour point of the oil. The working of additive is found to be best when its pendant chains matches perfectly well to the paraffin distribution in crude. **[44]**

1.17.2 Polymer Backbone

The polymer backbone does not play a significant role in pour point depression. It only acts as structure from which important pendant chains are suspended.

1.17.3 Stability of Flow Improver

Polymeric additive treated crude oil undergoes high shearing stress during transportation. In such situation it should not undergo degradation or splitting into fragments else it will lose its activity.

1.17.4 Molecular Weight of Polymers

Higher the molecular weight higher the polymer volume in an oil solution. The high molecular weight polymer provides high viscosity than low molecular weight polymers of the same chemical type.

1.18 Aims and Scope of work

At lower temperature, paraffin molecules crystallize out from crude oil and form aggregates of wax crystal. In order to control above problem pour point depressants were used which modify the flow properties of crude oil. These polymeric additives modify wax crystal habit, size, and shape via nucleation, adsorption, co-crystallization and improved wax solubility. Hydrocarbon chain of polymeric additive interacts with paraffin while polar segment is responsible for wax crystal morphology modification. It has been proved that combination of two different wax

crystal modifiers enhances the working of flow improvers, one of them acts as wax growth inhibitor and other as nucleating agent. These often have polar groups which possess surfactant features and behave like wax dispersant. This invention relates to synthesized N containing pour point depressants which act as wax dispersants and flow improvers simultaneously and to study their impact on rheology of three different crude oils from Kosamba (South Gujarat) and Bombay High (Mumbai, Maharashtra).

Two main objectives of the present investigation are:

[1] Synthesis of new polymeric flow improvers for the crude oils from different location of India and evaluating their effects on rheological properties of crude oil.

[2] To find correlation of the extent of pour point depression, viscosity and yield value with that of the molecular structure of basic polymeric unit.

Chapter-II of the thesis describes about synthesis and characterization of additives.

The summary of synthesized additives is as follows:

[1] Poly (Octyl Cinnamate-co-octadecyl maleimide-co-alkyl Cinnamate)

[2] Poly (Octyl Oleate-co-octadecyl maleimide-co-alkyl Oleate)

[3] Poly (Octyl Ricinolate-co-octadecyl maleimide-co-alkyl Ricinolate)

[4] Poly (Octyl Undecylinate-co-octadecyl maleimide-co-alkyl Undecylinate)

The above synthesized additives were purified and characterized by FT-IR and GPC.

Chapter-III deals with the application of synthesized PPDs on three different oils. The pour points of the untreated and treated crude oil at various concentrations were found as per ASTM D97-66 method. Yield stress and viscosity of various crude oils at different temperatures and concentrations of additive were evaluated by zero friction advanced rheometer AR-1500ex of TA instrument.