CHAPTER-I

INTRODUCTION

Crude oil is called petroleum as directly it comes from below the earth's crust. It is remarkably valued substance both in its use and composition; it can be string colored liquid or tar black solid red green and brown hues[1,2]. Petroleum is one of our most versatile natural resources. Petroleum has become important in every sphere of life. It is most clear fuel with high calorific value. Now a days it has been used almost in all industries and every sphere of life. Its use starts from the house for cooking and reaches to every part in the world with transportation, industries with small and big applications. Research is continued since last century for the exploration, production and uses of crude oil. Petroleum is one of the most important fuels on a global basis. There are many different opinions on the extent of remaining oil reserves, but it's fairly certain that they will be running out - or at least getting considerably more expensive - before 2050. Talk of crude oil oozes with the superlatives. Not only crude oil is the lifeline of modern industry but also is the largest amenity of the worlds. There is not something surprising that even stock markets of every country works according to crude oil prices. And it employs most of the world's commercial shipping tonnage. Crude oil may not be the panacea that snacks oil claimed to be. But for 20th century industrialized nations, it has proved to be more than good medicine. Crude oil has become the basis of worlds first Trillion – dollar industry and it is the largest items in the balance of payments and exchanges among the nations. It can be said correctly that modern society is moving towards high growth on crude oil wheels.

It was quote by Ernest Bevin at the British parliament during a heated discussion concerning the Middle East [3].

"The kingdom of Heaven runs on righteousness but the kingdom of earth runs on oil".

1.1. India's Emergence towards Self –Sufficiency in Hydrocarbons[4, 5]

Oil and Gas contributes about 60% of energy requirement in India. While the indigenous production is only about 30% of the demand and the rest is being imported especially from Middle east countries, which is draining out the major chunk of foreign exchange and vulnerable to security of supply also. Hydrocarbon Vision-2025 envisages the projected production not keeping pace with the growing demand. The present oil production is only about 32-35 million tones per annum (MMtpa) against the demand of 96 MMtpa while the Gas production is about 65 million cubic meters per day(MMm^{3}pd) against the demand of 125 MMm^{3}pd.By 2025,demand of oil and gas is projected at around 368 MMtpa and 200MMm^{3}pa respectively which will be met through imports mainly.

However scenario has changed with the encouraging recent new discoveries of oil & gas from deep water by the companies like Cairn Energy, ONGC and Gaint field by Reliance. Latest very big discovery of oil and gas field done by OVL in Iran (Economic times of India 14th may 07).Many more Hydrocarbon discoveries are expected to come in near future with the opening of new blocks in deep water, shallow offshore and on land areas through New Exploration Licensing Policy(NELP) of Indian Government. Only one tenth area of the 29 sedimentary basins comprising about 3.14 million sq.km (MMkm^2) has been explored, leaving behind major part still unexplored. Of these, about 0.40 MMkm^{2}area lies in shallow offshore (<200m isobath), 1.35 MMkm^2 in deep water (<200m isobath) and the rest 1.39 MMkm^2 in onland. Established oil & gas reserves at present are around 1.5 billion tones (MMMt), while the hydrocarbon resources are about 6 MMMt. Additional 6MMMt are envisaged to be accreted by ONGC in midterm. While DGH has forecasted accretion of 12 MMMt along east coast (7MMMt) and west coast (7MMMt).Of these (9MMMt) are expected to be accreted both from onland and offshore areas. Thus total about 30 MMMt of Hydrocarbon resources will be available by 2025 as per the estimate by present study.

Recent field discovery in India are **Hazira, Tapti, Laxmi** (by Cairn in Gulf of Cambay), **Vasai** (by ONGC) and **Dhirubhai** (discovered giant field in deep water along east by Reliance) are the best indicators of future potential gas discoveries. Further, the Gas being environment friendly fuel will be find its increasing utilization in power generation and fertilizers besides domestic and industrial fuel. Though indigenous gas exploration and production (E&P) activities will be enough to meet growing gas demand ,notwithstanding, various projects are being taken up simultaneously for import of gas in the form of LNG to the tune of around 32 MMtpa which may be able to supply about 135 MMm^{3}pd.Even gas import through cross border pipeline(Iran-Pakistan-India & Mynmar-Bangladesh-India) is also on the cards. Domestic exploration activities for unconventional gas resources like low permeability tight gas sands,coalbed methane,gas shales,underground coal gasification and gas hydrates will be able to provide additional gas production to bridge the demand supply gap.

Similarly OVL an overseas wing of ONGC has lined up new international opportunities of oil equity from countries like Iraq (10MMtpa),Sudan(4MMtpa) and Sakhalin(5MMtpa) which will be additional potential besides the domestic increase in production. Further indigenous unconventional resources of oil shale of north-eastern states, heavy oil stands and bituminous dolomite of Rajasthan will also be able to meet some oil production requirement. With integrated E&P approach, India is definitely poised to become self sufficient in Hydrocarbon supply in near future.

Crude oil and Natural Gas being the primary energy resource will continue to play dominant role in meeting the requirement of growing economy of the country. How ever the indigenous production is only about one third of the demand at present. Therefore domestic production has to be enhanced to ensure security of supply as well as conservation of foreign exchange reserves. India is aggressively perusing development activities of hydrocarbon sector with the opening up of new blocks through New Exploration Licensing Policy (NELP). So far, three rounds of international competitive bidding have taken place, resulting in award of 73 blocks to national public sector and consortiums. Hydrocarbon Vision-2025 brings out the growing demands of oil to around 368 MMtpa, more than ten times the present production of about 32 MMtpa while the gas demand is projected at about 200MMm^{3}pa which is more than eight times the present production of nearly 24 MMm^{3}pa.However, envisaged production levels are not expected to keep pace with the phenomenal increase in demand. Hence, majority of demand was expected to be met with imports.

1.1.1 E&P Efforts by PSU's [6]:

Mumbai offshore, Cambay, Upper Assam, Tripura-Cachar, krishana-Godavari, Cauvery and Jaiselmer basins are the Oil & Gas producing Basins in India with the exploratory efforts of national oil companies like ONGC and OIL Exploration trust is being given to bring other basins also on production stream.ONGC has intensified its E&P activities with the country as well as by acquiring equity abroad. An integrated approach is being adopted for reserve accretion and production enhancement from the known oil&gas

fields, developing isolated pools/fields and exploring frontier basins. Improved oil recovery from heavy oil belt of north Cambay basin(Balol-Lanwa-Santhal) by in-situ combustion, Enhanced recovery by water and polymer injection in other fields, Accelerated development of newly discovered fields like Vasai gas and satellite structures around Mumbai High, Intensified exploration in deep water areas along east coastal and Andaman sea. Renewed thrust of exploration in frontier areas like Himalyas, Gondwana basins and Vindhyan sequence. All such effort will be helpful in bringing self sufficiency in crude oil sector in India.

1.1.2 Uses of Crude Oil[7]:

The word 'Crude oil' itself explains its meaning as naturally occurring unprocessed oil which has got very little value as such. But when it is refined and distilled to valuable products for the use in daily life, becomes the biggest source of energy .In present scenario, Technology has gained revolutionary change and has put the Human life on a very fast track which is directly related to the establishment of fast transportation system and that is directly related to the crude oil. Crude oil is refined to the products like Petroleum gas used for heating, cooking, making plastic, etc. Gasoline-that is nothing but motor fuel, kerosene used as fuel for jet engines & tractors starting material for making other products, Gas-oil or Diesel distillate used for diesel fuel and Lube relating oil used for motor oil, grease, other lubricants. Heavy gas or fuel oil used for industrial fuel and residual it coke, asphalt, tar, waxes.

Firstly crude oil was refined to the only product kerosene for lightening. Gasoline and other products made during refining were thrown away because people did not know the use of them. This changed when Henry ford began producing automobiles, and they all run on gasoline. Crude oil is useful now from one end to another, Oil and its derivatives are used for a multitude of different tasks. Over half of the crude oil used for energy that is used in the transportation sector. Prior to the invention of internal combustion engines by August Otto in 1876, mechanized transportation was provided by steam engine run by coal or wood for ships and trains but they were too large and cumbersome for use in smaller applications. The gasoline powered internal combustion engine was able to deliver much more power from a compact design making an ideal match for many types of vehicle, including the automobile and later the aeroplane. At the present time oil provided the energy for over 95% of the world transportation needs.

When the oil was cheap it was often used to generate electricity especially in remote locations where hydroelectricity is not accessible. But after the oil crisis of 1973 oil has been an increasing expansive fuel for generating electricity.

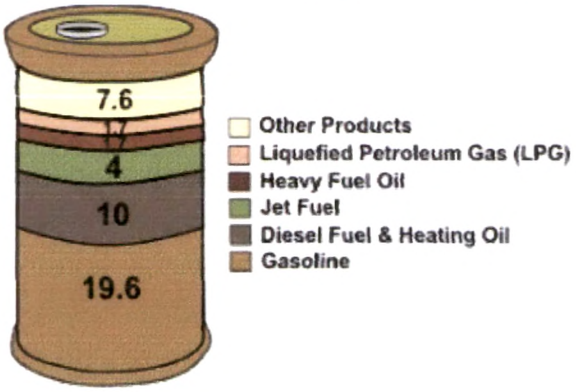
Once the crude oil is refined by refinery operations different products of oil are used for different application. Main petroleum products are gasoline, kerosene, fuel oil, Gas oil , wax distillate and bottom residue. Gasoline has been mainly used for engine. The gas oil fraction is a heavy relatively slow burning non-volatile fuel it is frequently used as light lubricating oil. This fraction can be used as a fuel, if this fraction is hydro processed, it can be made in to white oil (sewing machine oil) of high quality oil for use in domestics and Pharmaceuticals.

Wax distillation is a valuable source of lubricating stock and paraffin. By removing the wax or paraffin one of the basic components of lubricants is produced (neutrals). Neutral can be further refined through distillation and hydro processing (Catalysation) to produce a series of specialized components used in the manufacture of engine oils, gears lubricants and greases. Paraffin's are use in many different aspect of our daily life like candles, cosmetics paper coating, ink, fabrics and even in our foods.

The bottom fraction is also distilled and micro waxes is extracted which is suitable for plastic, candy and building materials. Resins extracted from bottom fraction are good for temperature insulations to under coating of fuel for ocean going barges. Oil portion from it is used in heavy duty gear oil applications and many industries lubricants.

The residue left after the distillation are very asphaltic and very good for making road tar so we can see that products of crude oil ate not just limited to auto motor industries but are important components in almost every modern convenience manufactured today so the crude oil now is used 78% mainly for transportation and rest 22% in industry and other commercial uses[8].

Products Made from a Barrel of Crude Oil (Gallon) Figure: 1



1.1.3 History of Crude Oil [9] :

The mysterious oil which exists thousands meters under the earth crust stated somewhere in time of Mesopotamia around 4000 B.C., bitumen-a tarry crude was used as caulking for ships, a setting for jewels and mosaics and adhesive to secure weapon handle. Ancient Persian 10th centaury Sumatrans and pre-cambia Indians all believed that crude oil had medicinal benefits and called it as ' Snake oil ' Marco polo found it used in the Caspian sea region to treat camels for mange and the first oil exported from Venezuela (in 1539) was intended as gout treatment for the holy roman emperor Charles.

Until the late 19th century an oil find often was met with disinterest or dismay. Pioneer who settled the America west dug wells to find water or brine a source of salt, they were disappointed when they stuck oil.

Petroleum was prized mostly for its yield of kerosene. Until the turn of the century gasoline was burned off and bitumen and asphalt the heavier parts of crude oil were discarded. But gradually rising in importance with the invention of internal combustion engine which runs on gasoline. The Drake well in Titusville, PA was the birthplace of the oil industry

1.1.4. Essentials in creation of crude oil [10,11] :

1. Source Rock- whose geologist history allowed the formation of crude oil this is usually a fine grained shale rich in organic matter. Fossil fuels formed from ancient organisms that died and were buried under layers of accumulating sediments. The additional sediment layers built up over organic deposits and most organic debris is destroyed at the earth's surface by oxidation or by consumption by microorganisms. Organic material that survives to become buried under sediments or deposited in other oxygen-poor environments begins a series of chemical and biological transformations that may ultimately result in petroleum, natural gas, or coal. Sediments may accumulate to depths of several thousand feet in a basin, exerting pressures up to one hundred million Pascals (tens of thousands of pounds per square inch) and temperatures of several hundred degrees on the organic material. Over millions of years, these conditions can chemically transform the organic material into petroleum, natural gas, coal, or other types of fossil fuels

2. **Reservoir rock** -migration of the oil from the source rock to the reservoir rock usually a sandstone or limestone that's thick and porous enough to hold a sizable accumulation of oil a reservoir rock that's a few feet thick may be commercially producible if it is at a relatively shallow depth and near other field. However to warrant the cost of producing in work challenging regions (the Archaic North Slope, ex) the reservoir may hole to be several hundred feet thick.

3. **Entrapment**:- The earth is constantly creating regular geologist structures through both sudden and gradual movements earthquakes volcanic earphone and erosion caused by wind and water uplifted rock for example, can result in dome like structures or arched folds called anticlines. The probability of discovering oil is greatest when such structures are formed near a source rock. In addition an overlaying impermeable rock must be present to seal the migration of oil in the structure .The oldest oil-bearing rock date back more than 600 millions years, the youngest about 1 millions. However most of fields hue been found in rocks between 10 millions and 270 millions years oil. Subsurface temp which is the depth is a critical factor in the creation of oil petroleum hydrocarbon are rarely formed at temperature less than 150 °C and generally are carbonized and destroyed at temperatures greater than 500°C. most HC's are found at moderate temperatures ranging from 15 to 50 °C.

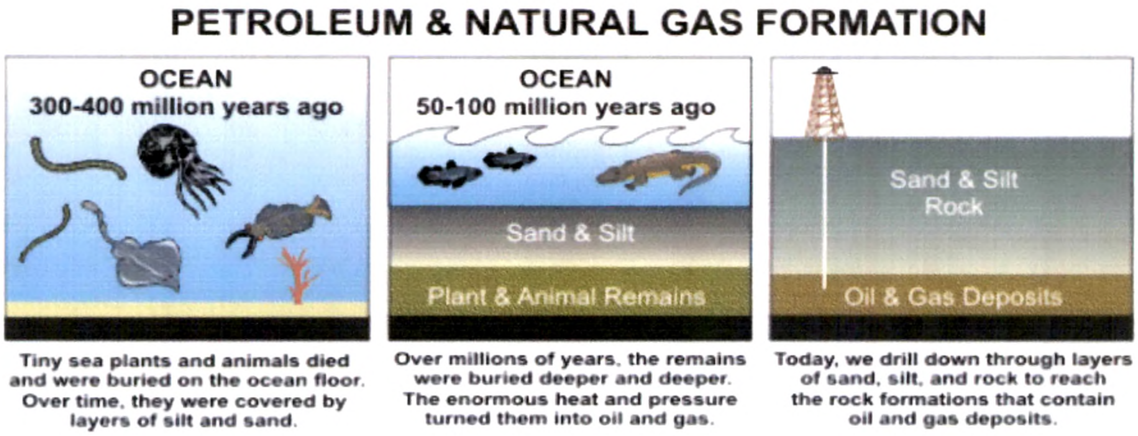


Figure: 2

1.1.5 Technical and Economic Risks in Exploration:

There are a number of technical and economic risks involved in the exploration effort, such as the ability to recover the petroleum and the quality of the oil or gas. Less than 60%, and sometimes as low as 10% of the oil in the ground (oil-in-place) and 70% to 90% of the gas-in-place has proved economically recoverable by modern technology.

At this point, the task may seem overwhelmingly difficult, but it is important to remember that Nature follows rules and does not randomly distribute this petroleum beneath the earth's surface. Our understanding of these rules is based on numerous past lessons learned from the drilling of many successful wells and many dry holes. It is the application of these rules, to a situation that are always somewhat unique, that is the "art" within the science of petroleum geology.

1.1.6 Production of crude oil[12]:

Crude oil reserves are estimated by Reservoir Engineers. Locations are released on the basis of different studies, analysis of results and discussions. Wells are drilled at these locations and successful wells are then put on to production. Production Engineers have to take care of production and measurement of crude on daily basis. When the number of wells increases in one field than group gathering station is made where the crude from all the wells is collected and come across different processing units before sending to refinery by pipeline. Now a days numerous techniques are employed for production purposes also

1.1.7. Transportation of crude oil :

In the conditions, nature helps oil field workers bring their find to the surface. But now a days first the well is drilled using advanced technology, firstly as Exploratory and once the oil is found in the place and the oil reserve is estimated and for the future use the well is put on to production. Then the production engineers have to play a big role i.e producing oil from the well with the naturally occurring ingredients like water and natural gas [13]. For the storage of crude oil huge storage tanks are installed near the oil fields. As it is highly inflammable proper care is required to be taken while storing the oil so that constant temperature and pressure check is maintained. The processing installations, different plants have to be prepared to separate water, sediments and natural gas from crude oil. Waste products are discarded and the natural gas is compressed at one end and stored for further use. The crude oil from here has to be transported to the refinery.

Transportation: Crude oil produced from the field through oil wells has to be transported to the refinery to convert it into the valuable products. Crude oil is transported by any of the following means [14,15]

(1) Tankers
(2) By pipelines

Crude oil production is done on a large scale and the oil fields are scattered via a huge area so the known best way to transport crude oil is through pipeline. Though the installation of pipeline is an highly expensive procedure but once it is layer down it became cheaper with time and is safe method. Transportation by pipeline is used throughout the world as it has got its own advantages. It is most suitable and secure way to transport the oil from field to the refinery at a long distance. Further maintenance cost is very low than the transportation by the Tankers, moreover the transportation of the huge quantity of oil is not possible for long distances. In the field in India like Akholjuni it is feasible by tankers because the refinery at Baroda is at small distance but from the other fields it is not possible. The oil produced is stored in storage tanks and demulsified to decant the water produced with the oil. From this end the crude is sent to refinery mainly by Tankers and Pipeline. As production is mostly in high quantities i.e MMt's, it is difficult to store it and transport it by tankers only so preference is given to transport it through pipelines. Pipeline installation also requires huge money investment. Firstly pipelines are designed by Design Engineers as per requirements and several phenomenon are kept in mind like environment, length of pipeline i.e distance to be covered, diameter of pipeline and how much quantity of oil is to be transported through it on daily basis. The fields selected have the facility to store the oil at Ankleshwar field nearby and from here after demulsification is sent to refinery end. For all these processes other than facilities a highly qualified brain is also required to develop and handle expertise processes. So oil industry is very expensive from one to another end. Pipeline transportation system on a distance scale began in 1897. It is the best-protected system against environmental conditions. Crude oil containing a large amount of wax possesses high pour point and exhibit non-Newtonian viscosity behaviour below the cloud point temperature. Above pour point, the viscosity of waxy crude is not very much sensitive to temperature variation. If the wax present in crude is of macro-crystalline waxes than it starts depositing even at well head and if it is micro crystalline in nature it take even longer time to deposit. Further the quantity of inorganics and water produced with the oil are also contributing factors for creating problems during transportation. For this reason it becomes necessary to study and analyses the deposits available in particular pipe line. It will be more helpful in finding out the solution for specific problems. Main problems associated with the transportation of waxy crudes are can be summarized as follow,

1. Wax deposition
2. Restartability after prolong shut down

The pipeline shown below carries up to 2 million barrels of oil per day from the Arctic coast to the Gulf of Alaska[16].

Figure 3 An Overview of an Australian pipeline

1.1.8 Refining of crude oil:

Crude oil transported through such pipelines to refinery end where it is converted into valuable products like diesel, petrol, asphalt, waxes by using different processes like fractional distillation[17]. These refinery are also very specific in the processes. Crude oil varies from light to heavy in density so special care need to be taken to convert it into different products. To know the commercial value of any crude oil it is distilled in laboratory. Through distillation it could be find out easily that which component has how much percentage in particular oil. After refining different products are further finished with different processes to add value and to improve quality of products[18,19,20]. The simplest form of a distillation column of a refinery is given under by which conversion of crude into different useful product could be understood easily.

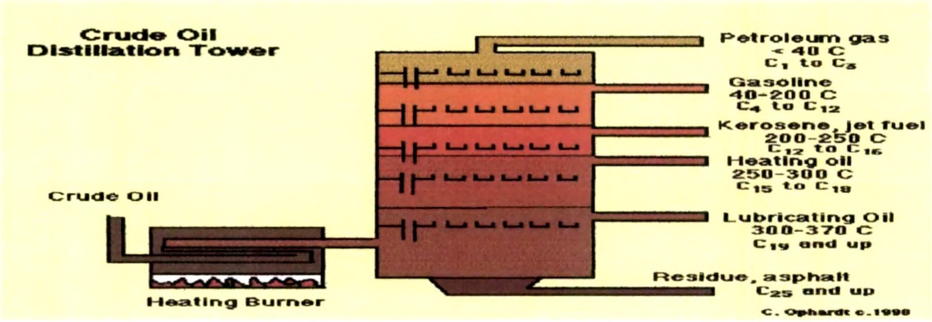


Figure :4 Simple column for refinery

Refinery also require huge money investments for installation and further maintenance. In Jamnagar , Gujarat refinery it special taken care that its structure could bear an earthquake of 8 on ricter scale and in 2001 jan' an earthquake hit the area was of the scale 7.8 . So the refinery escaped in such a condition also. Refining is very costly process. Every step requires huge technical knowledge and experience in this field [21].

Conventions of Fuel Names and their chemical composition [22,23]

Name of Fuel	Chemical composition
Fuel Gas	$C_1 - C_2$
LPG	$C_3 - C_4$
Gasoline	$C_5 - C_{12}$
Naphtha	$C_8 - C_{12}$
Kerosene	$C_{11} - C_{13}$

Diesel	$C_{13} - C_{17}$
Middle Distillates	$C_{10} - C_{20}$
Soft wax	$C_{19} - C_{23}$
Medium wax	$C_{24} - C_{35}$
Hard wax	C_{35+}

1.1.9 Gross Character of Petroleum [24,25,]:

Petroleum is composed of two principal fractions:

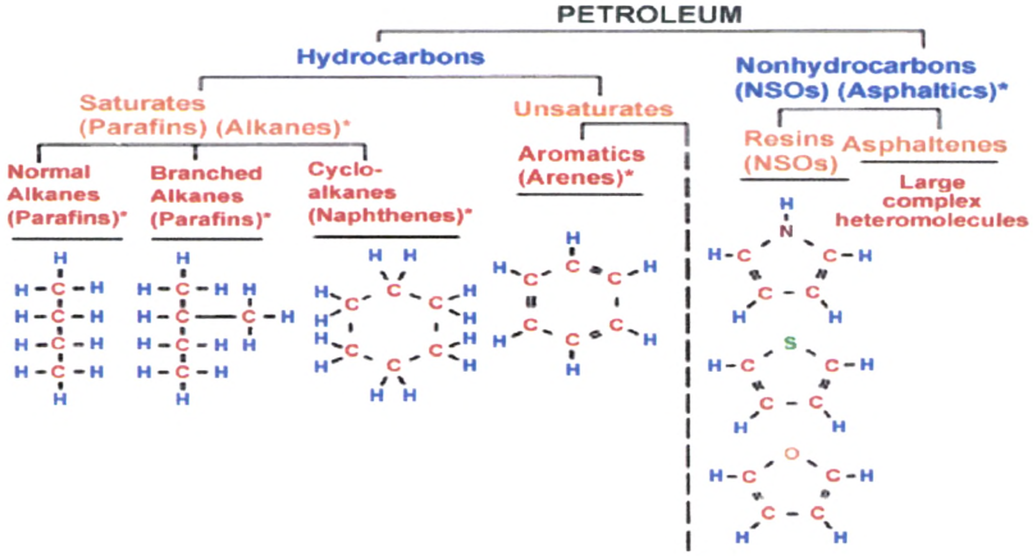


Figure: 5 Hydrocarbon compounds and Nonhydrocarbon compounds[26]

The first of these consists of molecules that are combinations of hydrogen and carbon atoms only, hence their name. The molecules of the other fraction also contain high percentages of hydrogen and carbon atoms; nonhydrocarbons, however, also have additional atoms bound into the molecules. The most common of the additional atoms, or heteroatoms as they are designated, are nitrogen, sulfur, and oxygen. Because these three elements are the most common heteroatoms, the names NSO compounds, or just NSOs.

The nonhydrocarbon fraction can have molecules which contain heteroatoms besides nitrogen, sulfur, and oxygen. Typically these heteroatoms consist of metals such as nickel, vanadium, magnesium, and copper. In some heteromolecules the metals represent trace elements originally taken in by biotic processes. In others, metals have been incorporated in organic compounds as a result of post depositional alteration and migration processes. Hydrocarbons generally make up more than 84-88% by weight, hydrogen 11-14 % by weight, sulfur 0-2 % by weight, nitrogen 0.2 % by weight, oxygen 0.5 % by weight and metals 0.02 % by weight[7]. (Tissot and Welte, 1984);

1.1.10 Constituents of Petroleum:

Alkanes (n-alkane and iso-alkane)

These are having the general formula C_nH_{2n+2} and boiling point and density increase with increasing the percentage of carbon atoms. The branched alkanes (iso-alkanes) are very small in quantity. Boiling points of straight chains are greater than iso-alkanes with the same percentage of carbon [27]. The number of hydrogen atoms associated with a given skeleton of carbon atoms may vary. When the chain or ring carries the full complement of hydrogen atoms, the hydrocarbon is said to be "saturated". Such hydrocarbons are known as paraffin's, paraffinic hydrocarbons, or alkanes/cycloalkanes. Straight-chain structures are "normal paraffin", branch-chain structures are "isoparaffins", and ring-type structures are "cycloparaffins" or naphthenes present in the crude oil. The branch-chain creates Isopentane. Naphthenes having the general formula C_nH_{2n} for one ring compounds. Alkenes or Olefins are unsaturated aliphatic hydrocarbon (ethylene or propylene). They are present in very small amounts in crude oil, produced during refining. Aromatics hydrocarbon (cyclic and polyunsaturated hydrocarbons containing conjugated double bonds) Alkylaromatics have very high octane number in gasoline for environmental regulations and health effects due to its high toxicity. The aromatic containing more than one ring is called as polyaromatic hydrocarbons e.g. naphthalene (2 rings), Anthracene (3 rings), Pyrene (4 rings) (very toxic).

NSO compounds [28,29]

The most common occurring non hydrocarbons are sulphur, nitrogen, and oxygen. There may also be small amounts of vanadium, nickel, sodium, and potassium. Sulphur is common in crude oils but it varies from 0.2% by weight to 6% by weight in crude oils. Sulfur compounds are present in inorganic and organic forms. In crude oils, sulfur concentration can range from 0.1 to more than 8 weight percent. The dibenzylthiophene (2 benzene rings separated by one S atom) is most difficult to release. The sulfur, oxygen compounds are responsible for petroleum acidity.

There are corrosive and non-corrosive sulphur compounds. One corrosive compound is Hydrogen Sulphide. The sulphides have a highly intolerable smell which gives some warning of their danger. If one of the hydrogen atoms is replaced by a hydrocarbon group, the compound is called a mercaptan or thiol. Such compounds are formed during the distillation of crude oils. If both of the two hydrogen atoms are replaced by hydrocarbon groups, the compound is called a sulfide or thioether e.g. thiophene (C_4H_4S). Thiophenes have a relatively pleasant odour, comparable to benzene, are relatively stable, and may even be beneficial. They cause serious corrosion of engines and furnaces, reduce the effect of antiknock additives in gasoline, cause charring and deposits when burned, for example in a kerosene lamp, give a bad odour to dry cleaning solvents and may dis-colour paints.

Nitrogen Compounds [30]

Nitrogen compounds are complex and produced from distillation. These may cause discolouration in gasoline and kerosene, or may produce a "lacquer" quality and reduces the effectiveness of lubricating oils e.g. Carbazole is a neutral compound. Quinoline is a basic compound.

Oxygen Compounds

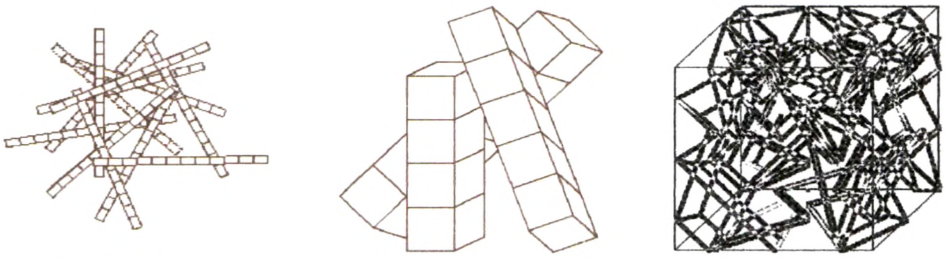
Some crude oils contain oxygen compounds. Their structure has not yet been established but on distillation of the crudes, the oxygen compounds decompose to form ring compounds with a carboxylic acid group in the side chain. These compounds are known as "naphthenic acids" having first been found in large quantities in the distillation of Russian naphthenic crudes. Phenolic compounds occur in some crude and are formed during cracking. Derived from aromatic hydrocarbons, the simplest member is the phenol.

Other Compounds

Several other organic and inorganic compounds occur in crude oils. One example is the metal vanadium which is sometimes present. Vanadium is an important component in the manufacture of speciality steels and can be recovered from the residue of the refining process. Porphyrins contain Ni, V, or Fe.

1.1.11 Crude oil waxes

Waxes are complex mixtures of high molecular weight alkanes of three structural types as straight chain, branched chain and cyclic. Waxes are solid or liquid at room temperature. According to IP, ASTM or API methods, conventional wax determination in crude oils involves cooling the oil to a specified temperature, precipitating the waxes, collecting and weighing them. This normally results in compounds containing 22 or more carbon atoms being precipitated. The wax present in petroleum crudes primarily consists of paraffin hydrocarbons (C_{18}-C_{36}) known as paraffin wax and naphtenic hydrocarbons (C_{30}-C_{60}). Hydrocarbon components of wax can exist in various states of matter (gas, liquid or solid) depending on their temperature and pressure. When the wax freezes it forms crystals [31,32]. The crystals formed of paraffin wax are known as macrocrystalline wax. Those formed from naphthenes are known as microcrystalline wax.



Macrocrystlline, Microcrystalline, and Crystal Deposit Network of Wax

Figure: 6 wax crystals

Various crystal forms have been observed in petroleum waxes. Simple solid solutions of *n*-paraffin can occur as plates or needles. Although branched chain and ring-containing impurities have been identified as ingredients in the needle crystals, it is agreed that the needles are simply plastic plate crystals that are tightly rolled up. Another form commonly observed is the so-called "mal"-crystal, also including highly branched or ring-containing impurities. Waxes that occur naturally during production and pipelining is rod waxes and those derived in refining processes ie refinery wax. Rod waxes are of high melting point ranging from 74-83 °C and found to comprise nC_{35} to nC_{41} together with larger isoalkanes and cyclic alkanes. Refinery waxes comes from refining processes. It is of low melting point ranging from 27-72 °C and comprises n-alkanes from nC_{18} to nC_{32}.

1.1.12 Nature of waxes[33]

The exact composition of wax can not be determined because it varies with oil well origin, distillation fraction from which wax is separated, the separation temperature and the degree of solvent refining of the sample. Waxes are complex mixtures of high molecular weight alkanes of three structural types as straight chain, branched chain and cyclic. The physical properties of the wax depend upon the composition of waxes, molecular weight distribution and the relative proportion of n-alkanes, iso- and cyclic alkanes

Straight chain alkanes (n-alkanes)

It contains approximately nC_{43} carbon chain length. n-alkanes have the highest melting point because of the highest molecular weight. Majority of n-alkanes found in the wax because they readily forms mixed crystal due to easy of alignment of molecules of different lengths. All other substances tends to held in solution by their small concentration and freezing point depression effect exerted by all the other substances present in the oil. Therefore it is difficult to separate n-alkanes from each other.

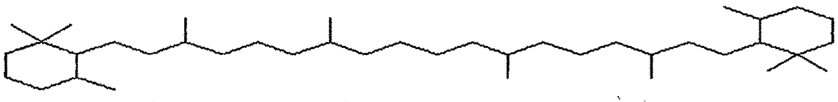
Branched chain alkanes (Iso Alkanes)

These alkanes having slightly branching with varying proportions. The terminally branched iso alkanes are very difficult to separate from the n-alkane with the same chain length. They are having melting point 5 °C lower then the n-alkanes, with a slightly greater solubility and a slightly lower density, refractive index and viscosity. Beside that the centrally branched iso-alkanes passes melting point at least 20 °C lower than n-alkane, with greater solubility, density, refractive index and viscosity. The iso- alkanes found in microcrystalline waxes and lower melting point waxes

Cyclic alkanes[7,34] Cyclic alkanes contain the naphtenic and aromatic molecules with long alkyl side groups. These are found in waxes of higher boiling fractions.

a C_{29} normal alkane or wax

botryococcane a C_{34} branched alkane or wax



β carotene a C_{40} cycloalkane or wax

Figure :7 Chains in crude waxes

1.1.13 Classification of Waxes [35] :

Classification is based on their physical appearance. It provides information about actual property, composition and the effect on rheology.

Rod Wax: These are found around the sucker rod of a producing well and come out of the solution before oil reaches the surface. It possesses the high melting point. The wax comes out of solution during production, transportation and storage is termed as rod wax.

Paraffin waxes : It is produced from low viscosity vacuum distillate. Solvent dewaxing and pressure filtering of the distillate produces slack wax (a semi-solid contains 10-15% oil). Sweating (repeated melting and crystallization) produces sweating wax contains 1-3% oil with melting point of 43-60 °C (maximum range 32-60 °C). This wax percolated through clay gives fully refined wax with oil content less than 0.5% and a melting point of 49-60 °C. Individual n-alkanes would ranges from nC_{18} to nC_{32} with melting points between 27 to 69 °C. Pressure filtering operations are severely restricted to particular oil fractions that produce large wax crystals. Fractions of small crystals are not suitable as they plug the filter cloth.

Solvent dewaxing process produces slack wax with very low oil content. The most common process used is Methyl Ethyl Ketone (MEK)-benzene mixture in repeated crystallization, filtering and washing steps and produces a large range of slack waxes. Light paraffin distillate produces hard paraffin wax contains large crystals having melting point between 30 to 70 °C. Heavy paraffin distillate produces small crystals having point between 60 to 90 °C, termed as dark raw wax. Intermediate paraffin distillate gives pale raw wax, further treated to improve colour and odour.

Slop wax: Slop wax is obtained from high viscosity distillates. It is not filter press able or centrifuged so further refinement is not carried out. In the slop wax, carbon number ranges from C_{26} to C_{43} and melting point between 56 to 83 °C.

Microcrystalline wax: It possesses very fine and distorted wax crystals and produced from vacuum residue. Solvent dewaxing and centrifuging may comprise 10% of the total wax content of the crude with very high oil content because of the higher affinity of these wax crystals for the oil. Further solvent treatment produces the microcrystalline wax (amorphous wax) with 5%-20% oil with molecular weight of 450 to 1000 (possibly upto 1200) (nC_{32} to nC_{71}) and a melting point of 60 to 88 °C (possibly upto 93 °C). A typical composition is nC_{34} to nC_{43} (mp 71 to 84 °C) with iso-alkanes and possibly cyclic alkanes concentrating in this fraction. The 'petroleum jelly' is simply the treated microcrystalline wax form highly paraffinic crudes, the waxes found in storage tanks and crude oil pipelines are sometimes referred to as microcrystalline waxes.

1.1.14 Wax crystal morphology

The morphology of wax crystals related with the behaviour of wax on a molecular level during the crystallization process. This tells the solubility relationship (quantity of wax crystallized) and the crystal shape (shape and size of the wax crystals).

n-alkanes shows considerable degree of order in the liquid phase. Due to this pre-existing order, the nucleation occurs. Several solid phase transitions occur at temperatures slightly below the melting point which relate to the relative alignment of the n-alkanes molecules. Odd and even number of carbon numbers shows different morphology[36]. The different physical properties because of opposing end groups of an even carbon number molecules are parallel (lie in the same plane) allowing them to align in a more dense (most stable) structure, while end groups of an odd carbon number molecule are not parallel thus preventing the tighter packing structure.

Because of the long thin molecules of n-alkanes can align, complete molecular disorder in the liquid state only occurs near the boiling point. At lower temperatures the molecule is likely to align parallel to each other with the backbone fully stretched, in a square packing arrangement. The ends do not align and methylene groups are free to rotate. This freedom to rotate prevents the ordered liquid state in n-alkanes.

The transition from the non-aligned to the aligned state appears to occur relatively quickly in melts according to diamagnetic susceptibility measurements (indication of degree of ordering)[37].

1.1.15 Nucleation and growth of the solid phase

The nucleation requires ordering and ability of aggregation of chain segments to form nuclei, forming smaller super saturation. Unforced nucleation occurs near the melting point so super cooling is possible. Simultaneously, heterogeneous nucleation occurs which reduces further super cooling need. So the crystal nucleation rate is high.

Crystal growth is most rapid in the axis of molecular backbone because the additional molecules align parallel to molecules within the structure. Thus very thin plates grow rapidly in outward direction and thicken by addition of successive layers. The solid crystals are held together by Vander Waal forces[38,39]. In C_n n-alkane, each layer is held together by n such bonds and successive layers held together by only one bond per molecule. So cleavage of layers occurs more rapidly than the breaking of a single layer. In the final solid form, the plate crystal may be flexible and mechanical strength of the crystal increases as molecular weight of the joining n-alkanes increases[40].

Solid-solid transition[41]

The parallel arrangement in a square configuration occurs due to order in the liquid state. The carbon-carbon bonds are fully stretched in zig-zag manner and free to rotate. When methylene groups allow the conversion of square packing structure to hexagonal structure, crystallization occurs. The end groups are aligned in a single plane having minimum energy. Rotation of methylene groups is still possible. It gives flexibility and thinness to the solid phase. This phase is known as alpha (α_H) or rotator phase and persists about 5 °C below the melting point.

Further cooling of α_H phase restricts the methylene group rotation until they lie in a single plane. The isothermal transition to non-rotator phase can occur and dense packing of the methylene groups occurs. It results in an opaque and less flexible structure.

The least dense β phase and all odd carbon number n-alkanes (except nC_9) and n-alkane mixture having the orthorhombic structure. In orthorhombic structure, the backbones of the molecule are aligned at right angles to the end plane. Even carbon number n-alkanes above nC_{24} are able to form this kind of intermediate solid phase[42].

In even n-alkane, carbon-carbon bonds at opposing ends are parallel, the even number n-alkanes forms more dense structure. It takes place by two carbon atoms forming the monoclinic structure and by one carbon atom forms triclinic structure (lowest energy). The even carbon number n-alkanes below nC_{22} go directly to the triclinic form. For nC_{24} and above, the orthorhombic and monoclinic forms are stable intermediate phases with isothermal transition occurring between each[43]. Above nC_{26}, the transformation from monoclinic or orthorhombic to triclinic form is difficult as energy requirement for displacement is more .

Needle Crystals[44]

Needle shape crystals consist of rolled up plate crystals and forming either as a plate and subsequently folding over and rolling up or growing in this distorted pattern by the growth of outer edges giving rise to successive spirals (thickening the needle) and increasing the needle length. Needle shape is characteristics of the high temperature α_H crystal form. The flexibility of α_H form would enable the sheet crystal to roll up into the shape of a needle. The formation of needle crystals due to the presence of impurities is explained as a depression of the transition point to below the crystallization temperature. Holder and Winkler studied the mixtures of pure n-alkanes and stated that the plate crystals are more likely to be seen edge on, rather than face on ands hence appear as needles [45].The successive layers that could quite possibly be plate layers, rolled around a hallow core. The thin black line run through the centre of needle crystals has often interpreted as hallow core, even though such a line could be a light diffraction effect. .

The ability of a plate crystal to form into a rigid curved shape and ultimately into a needle has been attributed to the distorting effect of iso-alkane or cyclic alkane impurities which put a wedge shape into an otherwise flat crystal . On the other hand the nC_{18} in hexane solution obtained both needle and plate crystals if the cooling rate was high enough[46]. According to Buchler and Graves and Ferris and coworkers, plate crystals were formed slowly and from dilute solutions.

Plate Crystals[47]

The plate crystal grows only in two dimensions. They perfectly form the diamond shape crystals. The plates bear uneven edges and truncated points. Regular wax crystals are only likely to be formed from dilute solutions that are cooled very slowly. Growth occurs predominantly by the addition of molecules by their long axis, to the edge, so that the thickness of a plate layer is equivalent to the chain length of the wax molecule. The superposition of layer gives pyramid type structure. The growing crystal fronts unite to form a single sheet crystal. Crystal growth is an irregular process giving distorted plates with irregular edges.

Mal –formed crystals (Microcrystals)

These are all distorted crystal shapes other than plate and needle crystal shapes. The malformed crystals are dendritic crystals and spheroids and microcrystalline forms[48] .The mal-formed crystals are of orthorhombic crystal shape and predominantly consist of n-alkanes. The properties of microcrystalline wax are similar to the iso-alkanes having one ethyl or methyl group in the centre of the main chain. Mal crystals having the size less than 1 μm and little affected by the cooling rate.

1.1.16 Mechanism of wax crystal modifier [49]

The various explanations of crystal habit modification can be summarized as follows. The action takes place by the additive is by,

(1) Suppression of the solid transformation from α_H phase to the β phase.

(2) Inhibition of the rapidly growing edge of the plate crystal.

The modification of the crystallization process alters the flow properties by,

(1) Changing the aspect ratio of the crystals and hence their ability to entrap oil and gel the fluid.

(2) Altering the kinetics sufficiently to allow the action of shear to break down the microscopic structure.

(3) Altering the kinetics or the thermodynamics to an extent that the total quantity of precipitated wax is reduced.

The mechanisms of pour point depression can broadly classified as

(1) The pour point depressant co-crystallizes with the wax and hence acting only after crystallization has occurred (i.e. the concentration of the modifier in the liquid influences the crystallization process but not the crystal modification process).

(2) The pour point depressant adsorbs onto the crystal surface either permanently or temporarily and hence acts from the bulk liquid.

Inhibition of solid transition

The additive inhibits the transition from weaker α_H crystal form more rigid β crystal. The pour point depressant do not alter the cloud point (i.e. they do not alters the formation of α_H phase. The conclusion is that α_H form is unstable to form a strong gel, whereas the more rigid β phase crystal readily forms a strong three dimensional structure throughout the fluid at very low solid concentrations.

Inhibition of the growth of the crystal edge [50,51]

The additive inhibits the growth of the crystal. Inhibition of the growing edge of the crystal is brought about by adsorption/absorption or co-crystallization of the crystal habit modifier onto the fast growing crystal edges. This forces the crystal to grow from the plate surfaces resulting in a thicker and more three dimensional shape. According to Holder and Winkler the mechanism is described in five stages as below,

(1) Orthorhombic, thin, diamond shaped plate crystals (No additive).
(2) Preferential growth at the tips.
(3) Dendritic (tree-like) crystals.
(4) Distorted, three dimensional blocks.
(5) Tetragonal pyramids and rhombic prisms.

The series from stage (2) to (5) is brought about by increasing the concentration of the flow improver. The concentration required to achieve (4) or (5) is several times greater than that normally used in commercially additives. The improvement in the flow properties is assumed to be the result of the change in shape from plates to smaller, more spherical particles. It does not necessarily follow that the flow properties of slurry consisting of many small more regular particles will be superior to slurry containing fewer, larger plate like particles. The same quantity of wax comes out of the solution regardless of the concentration of flow improver since the quantity of crystallized wax is determined by thermodynamic concentrations.

Below the cloud point the handling and transporting of the crude oils is very difficult task. For this problem various additives are added to improve the properties.

1.1.17 Asphaltenes

Asphaltenes are high molecular weight, complex aromatic ring structures containing O,N,S and heavy metals. It give crude oil its colour. Heavier, black oil crudes will typically have higher asphaltene content. The investigation of the chemical constitution of petroleum heavy fractions such as resins and asphaltenes is hindered by their complex nature. The word asphaltene was invented in France by J.B. Boussingault in 1837. Boussingault described the constituents of some bitumen (asphalts). He named the alcohol insoluble, essence of turpentine soluble solid obtained from the distillation residue "asphaltene", since it resembled the original asphalt[52]. The classic definition of asphaltenes is based upon the solution properties of petroleum residuum in various solvents.

Marcusson in1945 classified asphaltenes and resins as follows : (i) Neutral resins are defined as the insoluble fraction in alkalis and acids and it is completely miscible with petroleum oils, including light fractions; (ii) Asphaltenes are defined as insoluble fraction in light gasoline and petroleum ether. In contrast to resins, the asphaltenes are precipitated in the presence of excess ether; (iii) Asphaltogenic acid is defined as the soluble fraction in alkaline solutions and in solvents like benzene.

Recently, asphaltene is defined by chemists as the part precipitated by addition of low boiling paraffin solvent such as normal-pentane and benzene soluble fraction. In nature, asphaltenes are formed by oxidation of natural resins. On the contrary, neutral resins and asphaltenes are hydrogenated into polycyclic aromatic or hydroaromatic hydrocarbons.

On heating above 300-400°C, asphaltenes are not melted, but decompose, forming carbon and volatile products. They react with sulfuric acid forming sulfonic acids as they possess the polyaromatic structure of these components. Asphaltenes are dark brown to black friable solids. The colour of crude oils and residues is due to the combined effect of neutral resins and asphaltenes. The black color of some crude oils and residues is related to the presence of asphaltenes which are not properly peptized[53].

1.1.18.Structure and Chemistry of Asphaltenes

Asphaltenes are not crystallized and cannot be separated into individual components or narrow fractions. The neutral resins are strongly adsorbed by asphaltenes and probably can not be quantitatively separated from them. Asphaltenes are soluble in aromatics forming highly scattered colloidal solutions[54]. Specifically, asphaltenes of low molecular weight are insoluble in paraffin like pentanes and petroleum crudes. A number of investigators have attempted to postulate model structures for asphaltenes, resins, and other heavy fractions based on physical and chemical methods.

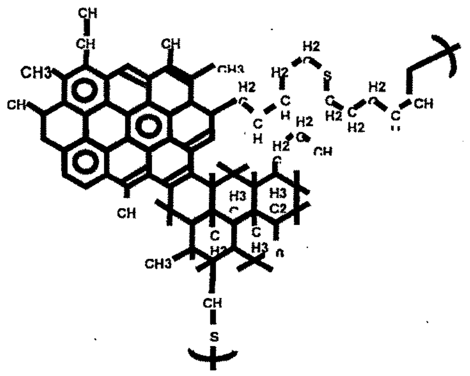


Figure: 8 Generalized Chemical structure of Asphaltene molecule

Physical methods of investigation include IR, NMR, ESR, mass spectrometry, x-ray, ultracentrifugation, electron microscopy, VPO, GPC, etc. and chemical methods involve oxidation, hydrogenation, etc.

Prof. T.F. Yen in 1974 had done microscopic and macroscopic analysis and suggested asphaltene structure shows micro and macro molecular bonding. From chemical methods, Yen postulated the micro-structure of asphaltene in which the aromatic nuclei of petroleum asphaltene are of a peri-condensed nature and various structural parameters such as aromaticity, substitution extent, etc. can specify a given asphaltene structure with hypothetical empirical formula $C_{74}H_{87}NS_2O$. By physical approaches such as dissociation-association, charge transfer, excitation, defect center, etc., Yen also postulated the macrostructure of asphaltene[55]. One of the properties of peri-condensed polynuclear aromatic systems is the attraction between the p-electron systems. For petroleum asphaltenes, the stacking is around five layers as found by x-ray diffraction.

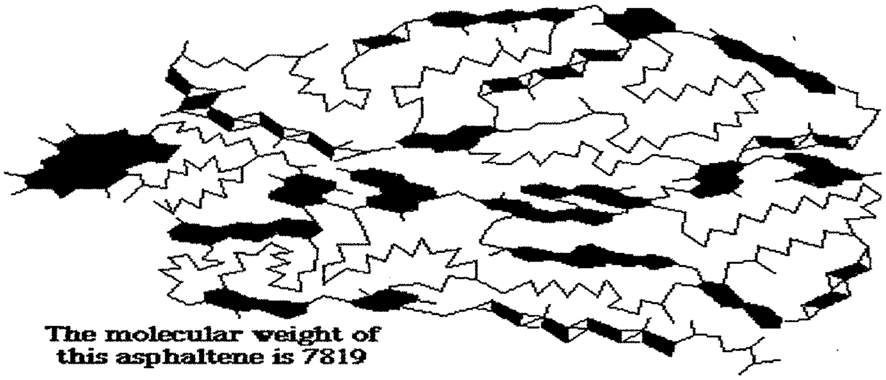


Figure: 9 Generalised Asphaltene Structure

There is no implied genetic relationship between resins and asphaltenes- resins may polymerise to form asphaltenes and asphaltenes may break down into resins.

The physical and physico-chemical properties of asphaltenes are different from those of neutral resins[56]. The molecular weight of asphaltenes is very high ranging from approximately 1,000 to 2,000,000. A major concern in reporting molecular weights is the association or aggregation of asphaltenes which can exist at the conditions of the method of measurement. Vapor pressure osmometry (VPO) has become the common method for determining asphaltene molecular weights. However, the value of the molecular weight from VPO must be weighed carefully since; the measured value of the molecular weight is a function of temperature, the solvent molecular properties. The ultracentrifuge and electron microscope studies show high molecular weights and solution viscometry and cryoscopic methods show low molecular weights.

In 1968 Dickie and co-workers had done electron micrography with rapid lyophilization and showed the size of asphaltene to be 20-30 µm. According to Dwiggens (1965) and Pollack and Yen (1970) in native oil and solutions, the asphaltene particle size can be doubled.

Resins[57]: Whereas asphaltenes, when isolated, as appear as black friable solids, resins are red-brown viscous liquids. On heating, asphaltenes do not become liquid but rather intumesce (swell) and decompose leaving a carbonaceous residue. They therefore do not possess a latent heat of fusion. Resins, however, can crystallize (probably due to the presence of microcrystalline waxes) thus giving rise to a measurable latent heat. Resins remain in solution when the oil is treated with n-pentane but are precipitated in commercial propane and butane de-asphalting processes and by dewaxing solvents. (eg. alcohols and ketones).

1.1.19 The Physical Interaction of Asphaltenes, Resins, Waxes and the Oil Medium:

To be in a fully disassociated state, the asphaltene molecule needs to be surrounded by a full complement of satirically bonded resin and/or aromatic molecules. The removal of all or part of the surrounding layer allows the planer aromatic centers of the asphaltene molecules to approach one another and become satirically bonded[58]. As the process continues, and irregular and open macroscopic structure develops throughout the system which entraps fluid and result in a gel.

The role of resins in solvating the asphaltenes is known to be crucial and that indeed resins must be present to enable the salvation of asphaltenes in the oil medium obtained from the same crude [Speight, 1980], but the mechanism is not entirely understood. It is know, for –instance, that resins from one crude oil will not solvate asphaltenes from another crude to the same extent thus indicating that the resin 'keys-in' to the asphaltene in a unique manner[59]. This is know to relate to the aromatically of each part by means of an electron donor- acceptor process and hydrogen bonding both of which relate to the heteroatom content.

It has been shown that optimum resin content enable complete salvation of asphaltenes and that in many cases this optimum coincides with the natural resin/ asphaltenes fraction in the crude or may be 10% less than this value. An interesting observation is that treatment of the oil fraction to produce a resin material enhances the dissolution of asphaltenes[60].

The role played by the lighter oils surrounding the asphaltene – resin combination is also unclear and largely a matter of definition. In general, however, the more aromatic the nature of the heavy oils the greater the ability to solubilize the asphaltenes. The oil medium would also have an effect on the rate of coagulation dissociation of the asphaltenes micelles[61]. As in other colloidal systems, the viscous the oil medium, the lower the rate of coagulation. At least one study considers that the salvation envelope extends some distance out from the asphaltene – resin micelle and that the degree if ordering (anisotroph) that occurs in this envelope is critical in determining the nucleation of occluded n-alkanes. Another study indicated that the specificity of crystal habit modifying chemicals is due to their interaction with the asphaltenes and resins, which are themselves capable of modifying wax crystals habbit[62] .

Two adverse concepts are there about asphaltene. Firstly it is noted that if ashphaltene is removed from a crude oil sample than the wax crystal formation increases tremendously and secondly it is well known that asphaltene particle serves as nuclei for paraffin crystal, thus affecting the initial formation of paraffin crystal or structure[63]. Further maltene has 2 main rheological effects on one hand they keep the asphaltenes in solution by their peptizing influence and on the other hand by getting adsorbed on paraffin crystal they may inhibit the formation of larger paraffin crystals and there by the formation of a coherent three dimensional network.

1.1.20 Mechanism of deposition in crude oil [64,65]

The degree of dispersion of heavy organics in petroleum depends upon the chemical composition of the petroleum. The ratio of polar/non-polar and light/heavy molecules and particles in petroleum are primarily responsible for maintaining the stability of the polydispersed oil mixture.

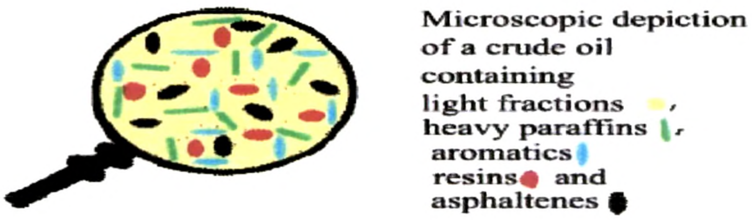


Figure:10 Microscopic depiction of crude oil

Solubility Effect

Deposition of heavy organic is explained by polydispersed oil composition. Any change in temperature, pressure or composition (addition of a miscible solvent to oil) may destabilize the polydispersed oil. Then the heavy and/or polar fractions may separate from the oil mixture into steric colloids, micelles, and other liquid phase or into a solid precipitate.

Micellization of asphaltene ● due to increase in aromaticity 🔵 and asphaltene precipitation due to increase in light paraffin 🟡 content of crude oil

Figure:11 Micellization of asphaltene

Effect of composition change on heavy organic precipitation[66].

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

Colloidal Effect in deposition[67]

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

Peptization of asphaltene precipitation by resins to form steric colloids and migration of resins from asphaltene surface due to increase in concentration of light paraffin 🟢 of crude oil

Figure: 12 Asphaltene precipitations by resins

Stability of such steric colloids is considered to be a function of concentration of the peptizing agent in the solution, the fraction of heavy organic particle surface sites occupied by the peptizing agent, and the equilibrium conditions between the peptizing agent in solution and on surface of heavy organic particles. The amount of peptizing agent adsorbed is primarily a function of its concentration in the oil. A concentration variation of a peptizing agent (resins) in oil will cause its adsorbed amount on surface of heavy organic particles to change. Migration of peptizing molecules from the surface of heavy organic particles could take place due to the change in their chemical-potential-balance between the bulk oil phase and the surface phase as shown in above figure.

Aggregation Effect in deposition[68]

The peptizing agent concentration in oil may drop to a point at which its adsorbed amount would not be high enough to cover the entire surface of heavy organic particles. This causes the potential for aggregation of heavy organic particles due to development of free active sites on their surfaces, and their eventual flocculation[69]. This may then permit the heavy organic particles to come together (irreversible aggregation), grow in size, and flocculate. The nature and shape of the resulting aggregates will determine their effect on the behavior of the petroleum fluids.

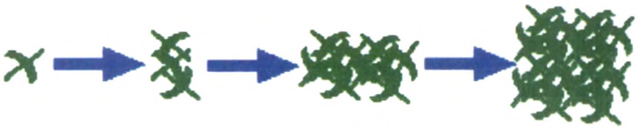


Figure: 13 Aggregation and growth of asphaltene

Various aggregating macromolecules follow different aggregation patterns. For example, the irreversible aggregates of asphaltene are considered to follow an aggregation growth pattern shown below

Electrokinetic Effect in deposition[70,71]

When a crude oil is flowing in a pipeline there is an additional effect (Electrokinetic effect) to be considered in the behavior of its heavy organic constituents. This is because of the development of electrical potential difference along the pipeline due to the motion of charged particles. This electrical potential difference could cause a change in charges of the colloidal particles further down in the pipe, the ultimate result of which is their untimely deposition and plugging of the pipeline. The factors influencing this effect are the electrical and thermal characteristics of the pipeline, flow regime, flowing oil properties, characteristics of the polar heavy organics and colloidal particles, and blending of the oil.

Figure: 14 Electrokinetic deposition in an isothermal-single phase pipeline flow

1.1.21 Review of deposition in crude oil[72,73,74]

Being a polar molecule, asphaltenes absorb to formation surfaces, especially with clays. As explained above asphaltenes are a colloidal dispersion. Paraffin deposition is a thermally driven process. Cooling during production, such as occurs from the loss of gas during production, causes wax to precipitate as temperature drops below the cloud point. The % paraffin in a crude oil is not an indicator of potential paraffin problems, rather it is the cloud point and % paraffin that indicates the magnitude of potential problem. Viscosity and flow rate affect paraffin deposition. High viscosity reduces transport to cold surfaces reducing deposition. High velocity results in harder deposits. Paraffin cause problems through deposition (formation, tubing, flowline, pipeline), settling (tank bottoms, interfaces), and solidification (high viscosity can cause problems restarting or require very high pressures to pump). These depositions of paraffin in pipeline reduces the diameter of pipeline. Sometimes choke the pipeline and overall transportation comes to an halt. In these situations restarting becomes a very big difficulty. Many different steps are taken to overcome these problems. Pigging is always used, but it is very costly process. As surface of pipeline is the most the colder part of the pipeline where deposit starts first grows towards the centre of the pipeline. Deposit is always more harder towards the surface of pipeline and softer towards the centre. It is necessary to study the deposit of the well or pipeline where the problem occurs. So whenever any chemical solution is tried to overcome the problem, the deposits from pipeline surface should be studied to know the hardness and chemical composition of the deposit. Further physico-chemical characterization of crude oil is necessary to find out good chemical solution.

1.1.22 Rheology- A Detailed study

Rheological studies are used to know the flow behaviour of any crude oil. It is an important property of any oil and is very useful in determining the problems creating during transportation of particular crude oil. It is also used in designing the pipelines and to sort out the deposition problems[75],[76]. Rheology is the science of the deformation and flow of matter. It is concerned with the response of materials to mechanical force.

The terms and descriptors associated with rheology are explained in detail below.

Deformation is the relative displacement of points of a body. It can be divided into two types: Flow and elasticity. Flow is irreversible deformations; when the stress is removed, the material does not revert to its original position. This means that work is converted into heat. Elasticity is reversible deformation, the deformed body recovers its original shape and the applied works is largely recoverable. A liquid is a material that continuous to deform as long as it is subjected to a shear stress. The shear stress is a force applied tangentially to the material[77]. In a liquid, shear stress produces a sliding of one layer over another, resulting in a stack-of card type flow show in below Figure 15.

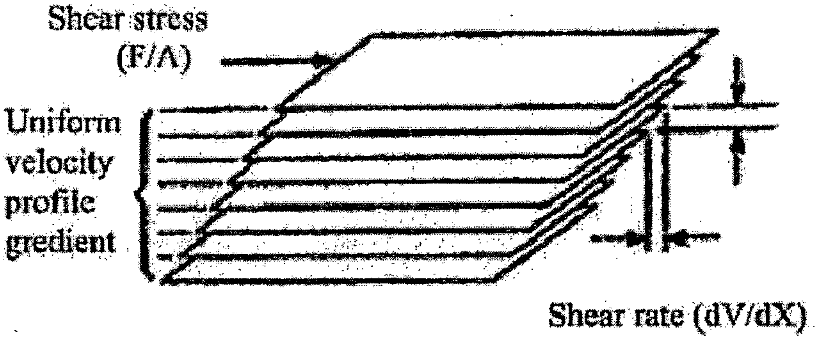


Figure: 15 Laminar flow in simple shear

$F / A = 1JdV / dX$, where F is the force acting on area A, V the velocity and X the thickness of the layer, and TJ the coefficient of viscosity or the Newtonian viscosity.

For a liquid under shear the rate of deformation or shear rate is a function of the shearing stress. The original exposition of this relationship is Newton's law, which states that the ratio of shear stress to the shear rate is constant, i.e. the viscosity. Under Newton's law, viscosity is independent of shear rate[78]. This is true for ideal or Newtonian's liquids, but the viscosities of many liquids are not independent of shear rate. These non-Newtonian liquids may be classified according to their viscosity behaviour as a function of shear rate. Many exhibit shear thinning, where others gives shear thickening. Some liquids at rest appear to behave like solids until the shear stress exceeds a certain value, called the yield stress, after which they flow rapidly.

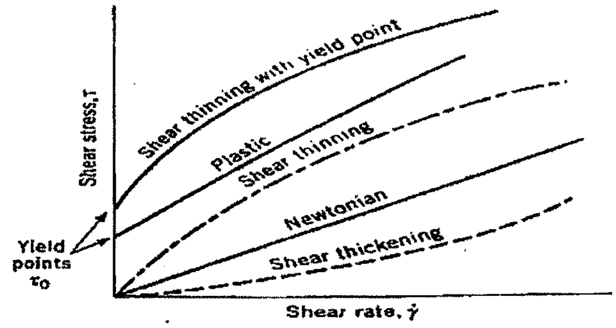


Figure: 16 Flow curves (Shear stress Vs shear rate) for different types of flow behaviour.

Some commonly observed types of flow behaviour are shown in Figure15 in which shear stress is plotted against shear rate. These plots are called flow curves and are frequently used to express the rheological behaviour of liquids [79-82]. Newtonian flow is shown by a straight line, and shear thinning and thickening by curves.

Yield stress, τo, are shown by intercepts on the stress (y) axis. Viscosity is equal to the slope of the flow curve, $\eta = d\tau/d\gamma$. The quantity τ/γ is the viscosity η for a Newtonian liquid and the apparent viscosity η_a for a non-Newtonian liquid.

When Newtonian liquids are tested by means of capillary viscometers such as ubbelohde or cannon fenske, viscosity is determined in units of kinematic viscosity. The force of gravity is acting as the force driving the liquid sample through the capillary. Thus, kinematic viscosity is the viscosity co-efficient divided by the density, $v = \eta/p$. The common unit for viscosity, dynes second per square centimeter (dyne.s/cm^2) or gms per centimeter second (gms/cm.s) called poise which is replaced by SI unit of Pascal second pa.s The SI unit for kinematic viscosity are cm^2/s i.e. stockes and mm^2/s i.e. centistokes.

In addition to non-ideal behaviour, many fluids exhibit time dependant effects. Some fluids increase in viscosity (rheopexy) or decrease in viscosity (thixotropy) with time when sheared at constant shear rate[83]. Rheopexy[84] is a rare phenomenon but thixotropic fluids are common. Examples of thixotropic materials are starch paste, gelatin, drilling mud and latex-paint. The thixotropic effect is shown in figure. Where the curves are for a compound exposed first to increasing and then to decrease in viscosity with time and with shear rate, the up and down curves do not superimpose. Instead they form a hysteresis loop, often called a thixotropic loop.

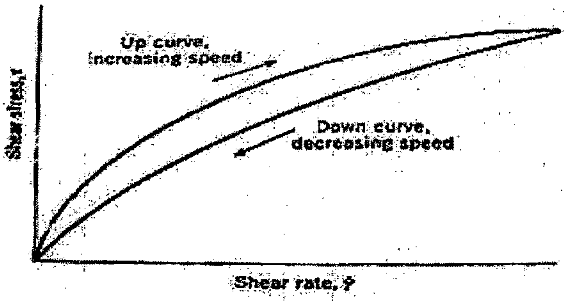


Figure:17 Flow curves (up and down) for a thixotropic material: hysteresis loop.

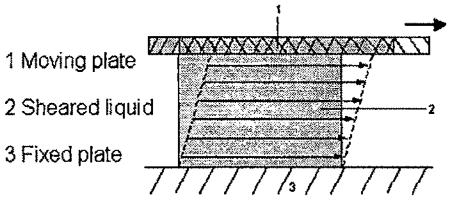
Because flow curves for thixotropic or rheopectic liquids depend on the shear history of the sample, different curves for the same materials can be obtained, depending on the experimental procedure.

1.1.23 Types of rheological behaviour[85,86]

Newtonian and non-Newtonian flow

Consider two parallel plates of area A.
The distance between these plates is x.
The space between the plates is filled with a liquid, which can be regarded as a series of very thin plates sliding one over another.

To move one plate with velocity v, some Force F has to be applied



F / A is called the shear stress, τ [Pa], while **v / x** is termed the shear rate, D $[s^{-1}]$.

$\tau / D$is called the **viscosity** of the liquid in between, η [Pa·s].

In earlier times, the unit of viscositiy was poise, **P**, or centipoise, **cP**.

1 mPa·s = 1 cP.

ηrapidly decreases as temperature increases.

If $\eta$is independent of D, the liquid is said to behave Newtonian

Yield Value

Yield value is very important calculation of any rheological behaviour. Shear rate is determined or plotted againast certain shear stress values. After giving some shear stress any oil behaves like a Newtonian oil. Like above 10°C the cloud point most of the oil behave like Newtonian oil. Earlier calculation was difficult but now with computer calculated programme it is very easy to calculate. The values are easily calculated with the given model. As such whenever waxy crudes gets solidify there is a requirement of some external restart pressure to make the crude to flow. This pressure is known as yield value. For waxy crude yield stress is inverse function temperature.

$\tau o = P_0 D/4L$

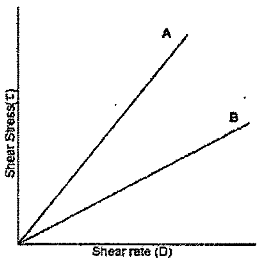
i.e τo= Yield stress (Dyne/cm^2)

P_0= Pressure at which the first flow was observed (Dyne/cm^2)

D= Diameter of the pipe(cm)

L= Length of the pipe(cm)

Newtonian Fluids Fluids for which the shearing stress is linearly related to the rate of shearing strain are designated as Newtonian Fluids.



Rheogram for Newtonian liquids. A - high viscosity, B - low viscosity

Newtonian materials are referred to as true liquids since their viscosity or consistency is not affected by shear such as agitation or pumping at a constant temperature. Fortunately most common fluids, both liquids and gases, are Newtonian. Water and oils are examples of Newtonian liquids.

Shear Thinning Fluids or **Thixotropic Fluids** reduce their viscosity as agitation or pressure is increased at a constant temperature. Ketchup and mayonnaise are examples of thixotropic materials[87]. They appear thick or viscous but are possible to pump quite easily.

Shear Thickening Fluids or **Dilatant Fluids** increase their viscosity with agitation. Some of these liquids can become almost solid within a pump or pipe line. With agitation, cream becomes butter and Candy compounds, clay slurries and similar heavily filled liquids do the same thing[88].

Bingham Plastic Fluids have a yield value which must be exceeded before flow will start flow like a fluid. From that point on the viscosity will decrease with an increase in agitation. Toothpaste, mayonnaise and tomato catsup are examples of such products.

1.1.24 Flow Models[89]

Various flow models have been proposed and are useful for treatment of experimental data or for describing flow behaviour. It is probable that no given model fits the rheological behaviour of a material over an extended shear rate range. Nevertheless, these models are very useful for summarizing the rheological data.

i. Newtonian

ii. Bingham

iii. Power Law

iv˙ Power Law with yield value

v. Casson model

vi. Williamson model

vii. Exponential model or Herschel-Bulkey Model

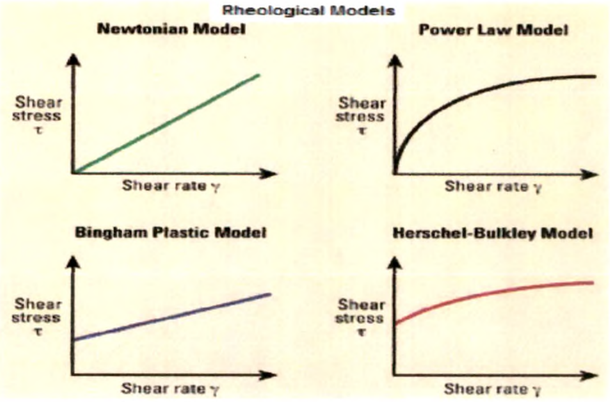


Figure: 18

1.1.25 Viscometers employed to measure viscosity[90].

The most simple instruments are :

a. capillary viscometers
b. falling sphere viscometers
c. falling sphere viscometers

capillary viscometers;

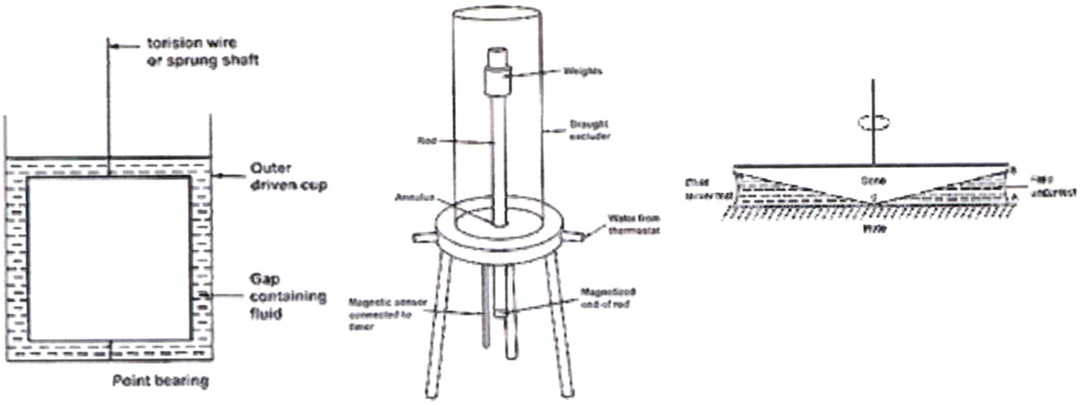
The flow of a liquid through a small capillary is recorded. Marks are given on both the ends of capillary. Standard amount of fluid can be filled in that. Flow rate is measured by eluting the fluid on normal rate. The measurement results in $\eta / \rho = \delta$, which is called the kinematic viscosity. Its unit is $m^2 \cdot s^{-1}$; out of date, but still in use are the stoke **[St]** and the centistoke **[cSt]**.

falling sphere viscometers;

A ball sinks through a liquid, its velocity is recorded. The result again is a kinematic viscosity.

flow cups;

A standardized cup with a hole in the bottom is filled by immersing it into the liquid. The time until it is empty again is recorded .Fan VG meter is one example. Kinematic viscosity is recorded with them.



rotational viscometer **falling rod viscometer** **cone & plate viscometer**

Figure: 19 Types of Viscometers

For the present work TA AR 500 Rheometer is used. It is equipped with fully temperature controlled plate and computer run software. The instrument is very sophisticated as able to sense a single wax crystal present in the crude.

Figure: 20 TA AR 500 Rheometer

The picture shows Peltier Plate and Geometry part of the Rheometer[89] with the sample platform. It requires optimum air pressure as the geometry head hangs freely in air only, so optimum pressure control is required for good results. Further water bath and computer is also attached with for other processes.

Generally, Crude oil shows Newtonian behaviour at about 10 °C above the pour point. Non-Newtonian behaviour may start at and below such temperature and increases with further decrease in temperature. Pseudo plasticity and thixotropy can also be found in the behaviour of crude oil. Non-Newtonian behaviour is due to the development of a network structure in the liquid phase and to some extent to the crystallization of waxy components at lower temperature. Thixotropic behaviour breaks down rapidly with time under sustained shear and the crude oil behaves as normal pseudoplastic, pseudoplasticity approaches Bingham plastic behaviour upon initiation of shear stress. Particularly in crude oils, which have been cooled from higher temperatures, mild dilatency observed.

1.1.26. Effect of temperature on the viscosity of crude oil with polymeric additives[91,92]

The behavior of the additive molecules decides the performance of an additive in changing the viscosity with temperature. Polymer solubility, molecular weight and resistant to shear degradation are the most important factors. As temperature increases, polymer solubility increases because polymer molecules changes from tight coils to an open structure of the greater volume. This increase in volume increases the viscosity of the oil, which affects the normal reduction in viscosity with increasing temperature. Polymers behave as thickeners when it alters solubility very little with temperature. They do not effectively improve the viscosity as they are poorly soluble at low temperature but good at high temperature[93].

The increase in molecular weight of polymer increases polymer volume in an oil solution. The high molecular weight polymer gives high viscosity than low molecular weight polymers of the same chemical type.

Polymers used as flow improvers have be stable to bring chain scission under higher shear rates. Shearing causes the deterioration of viscosity improving properties. The molecular weight of the polymer drastically reduces by shearing. The shear stability of polymer depends on polymer molecular weight[94]. Shear stability increases with decreasing polymer molecular weight. The shear stability and viscosity improvement requires divergent molecular weights. Due to this, low molecular weight polymers are generally preferred[95].

1.1.27 Chemical Additives[96]

Additives are the substance added to crude oil to improve its flow property and viscosity. A number of polymeric additives have been synthesized and reported as pour point depressant or viscosity improvers

1.1.28 Pour point depressants: The practical use of flow improvers is reported since so many years[97]. For getting the optimum additive dose, laboratory studies with field conditions must be done. It is necessary to study the treatment temperature and treatment residing temperature for choosing the best additive.

Depending upon the source of crude oil, they are in having' wax contents and concentration, so a single flow improver is not effective on all the crude oils[98]. An effective flow improver should match the crude's paraffin chain length. The chain length should effectively co-crystallize on the wax surface and improve the flow by depressing the pour point.

The flow improver classically having three characteristics as,

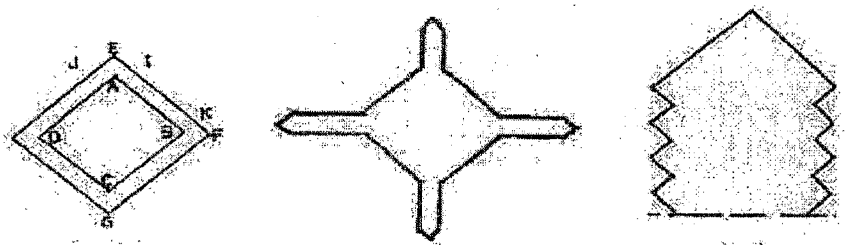
1. Mixture of linear alkyl chains of 14 to 25 carbon atoms, which co-crystallizes with wax like paraffin part.
2. A polar component which limits the degree of co-crystallization.
3. These are often polymers or copolymers which attached to the growing wax crystals statically hinder the growth, resulting in small crystals.

Specific examples of flow improvers are Ethylene Vinyl Acetate (EVA) copolymers, polymethacrylates, polyacrylates[99], alkyl esters of styrene-maleic anhydride copolymers

1.1.29 Mechanism of pour point depression [100-104]

When waxy crude is cooled down, the paraffinic wax starts to crystallize in the form of thin plates, needles or mal-crystals, with the needles the most problematic. As wax components come out of solution, the needles compact into a three dimensional network. Plates coils on their edges forming hollow needles which can then form cage like structure. Studies have shown that the wax crystals modifiers reduce the interlocking three dimensional wax networks.

According to Holder and Winkler the additives have little effect on the weight and composition of wax precipitated from the middle distillate but it affect the size and shape of the wax crystals. The explanation of PPD mechanism can be given by the theory of crystal growth and dendrite growth. The basic premise around the theory is that as many crystal faces grows, 'poisons' present in the solution will accumulate around the faces. As a result, the crystal will tend to grow as rapidly as possible where the impurity concentration is at a minimum. In figure 21 (A) shows how the crystal nucleus ABCD increases in size to EFGH. Naturally, more poison would be accumulated to the faces EF, FG, GH and HE than at the corners E, F, G and H. Accordingly, growth will be occurring relatively faster at the corners. Thus a later stage in crystal growth would be the formation of crystal such as that in figure 21(B) which shows needle like projections developing from corners of a crystal nucleus. If we see each of the needles, it is not smooth but it is made of projections which are true crystallographic faces. These projections are the source of further growth. The end result is that there is a development of branches at regular intervals with the rapid growth of corners i.e. dendrite structure is formed.



(A) (B) (C)

Figure: 21 Mechanism of formation of dendritic crystals
(C); Enlargement of one of the projections of (B)

Thus, the additive in the oil acts as a poison and it mount up around the faces of the wax crystals at cloud point. So the growth of the four faces of the wax crystals become restricted and it grow relatively quicker at the corner and also it become thick. At the later stage typical dendrite is formed. At the higher additive concentration, the side ways growth of crystal also becomes difficult and even dendrite can not be formed. Now the crystal becomes so thick that the growth of crystal in the XY direction is retarded and it grows only along the Z axis. As a result the blocks like or pyramid crystal resulted. Thus, the shape of the crystal is changed from orthorhombic to pyramidal shape because of this reason, the ability of wax crystals to inter-grow and interlock is greatly diminished. The combination of these two effects lowers the pour point the oil. All the stages of this mechanism are shown in the figure with photographs.

It is already mentioned that crude oils of different oil fields have different wax composition and the precipitation waxes of different oils have also different structure. It is good evidence that response to pour depressant is a function of the structure of precipitating crystals than of the chain length of n-paraffin molecules of which crystals are made. So to understand the mechanism of pour point depression, it is first necessary to describe both the lattice structure and growth of n-paraffinic crystals.

The basic structure of n-paraffinic crystals is shown in the following Figure 22,

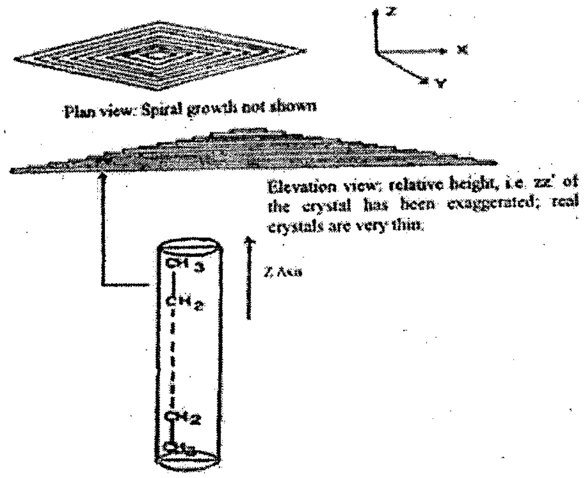


Figure:22 Diamond shaped wax crystal

As can be seen from the figure, the crystals have the appearance of very thin diamond shaped plates. These each plates arranged layer upon layer which can be seen from elevation view. Now if we consider each layer, the n-paraffin molecules are stacked side by side with their long axis parallel to the Z-axis of the crystal.

There are two theories of crystal growth (1) Gibb's theory (2) Frank's theory

Gibb's theory

According to this theory, each crystal face grows layer by layer in a discontinuous fashion. Following figure illustrates this type of crystal growth.

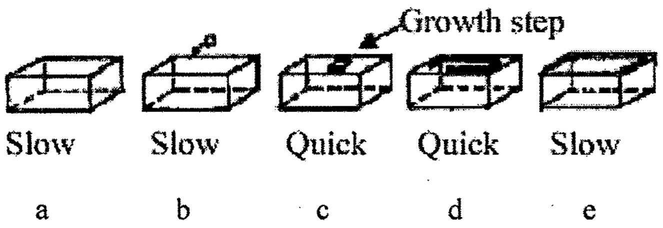


Figure:23 Gibb's Theory: Discontinuous layer addition

A crystal is waiting for nucleation to occur on any of its faces (Figure 23,a). At once, the nucleation has started (Figure 23,b), growth step forms and the development of a layer form very rapidly (Figure 23,c and 23,d). When the new layer has grown to the edges of the crystal, growth has eliminated itself and so the growth stops until the nucleation on the top of newly formed layer occurs and a new cycle begins.

Frank's theory

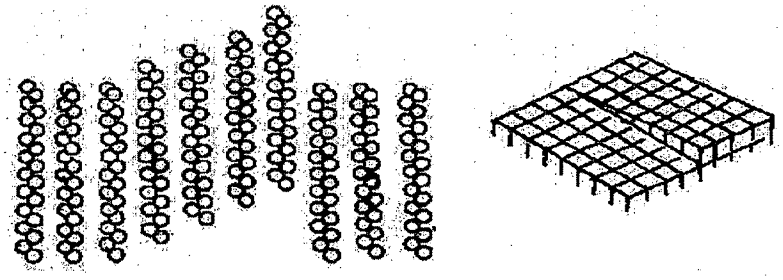


Figure:24 Frank's Theory: Continuous growth via dislocations

According to this theory, crystals are not perfect but contain faults. The first part of the figure shows stacking faults due to n-paraffin molecules which are not lining up properly. The second part describes the effect of stacking fault on the crystal growth. The diagram shows a hypothetical crystal surface built of block like molecules. The crystal surface is not smooth since each block is slightly out of lines with some of its neighbours in the crystal surface. Further, the addition of more blocks would results in the continuous propagation of the fault, along with simultaneous growth of the crystal. Thus, n-paraffin crystals are not made up of discrete terraces but consist of extremely shallow solid spirals.

The additives are incorporated in the crude oil to enhance the flow of crude oil at low temperature. These additives are operated under either or both mechanisms discussed below [105].

In the first mechanism, the additive molecules interact with the n-paraffin molecules at the growing edges of the paraffin crystals. The interacting additive molecule acts as a cap to prevent additional paraffin molecules from adding to the crystal by limiting the dimensions of the existing crystal. The ability of the additive to limit the dimensions of the growing paraffin crystal is evaluated.

In the second mechanism, the flow modifying additive may improve the flow properties of crude oil at low temperatures by functioning as a nucleator to promote the growth of smaller size crystals. This modified crystal shape permits improved flow by altering the n-paraffin crystallization behaviour.

The flow improver in the crude oil hinders the crystallization of the wax molecules by incorporation of the polymer molecules of the fastest growing edge or dislocation. The growth inhibited by further addition of n-paraffin molecules. The spiral growth is inhibited. However, the growth observed only in Z-direction because n-paraffin molecules come out of the solutions. The new layers are formed according to Gibbs mechanisms. 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.

The simulated mechanism is shown in following figure 25 A-F. Wax crystals (A) tend to crystallize first into discrete needle like structures (B) that associate with larger structure (C) Further polymeric additives (D) co-crystallize with wax molecules (E) and sterically hinders the growth of wax molecules.

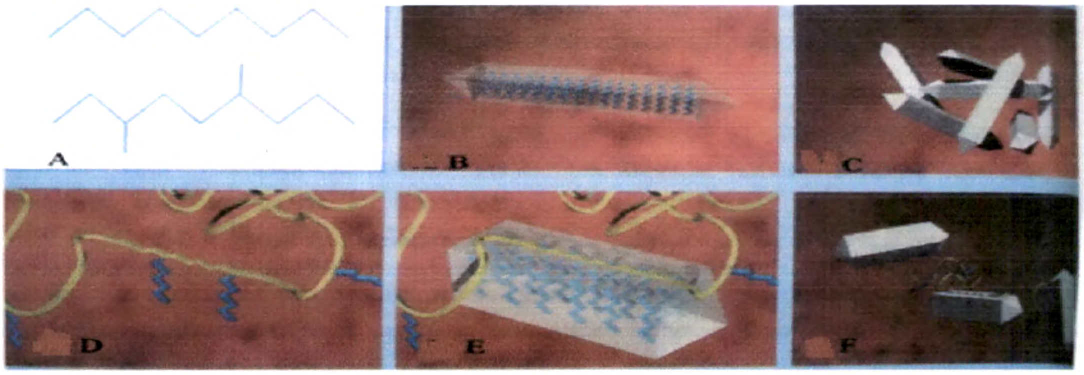


Figure:25 Mechanism of pour point depression

1.1.30 Testing of Performance of PPD's[106-109]

Several testing methods are employed to evaluate the low temperature performance of crude oil with and without additives. Widely accepted method is ASTM D-97 (Pour point of petroleum products) and ASTM D 5853 (Pour point of crude oil). According to ASTM method the sample should be preheated before measuring the pour point. However, preheating conditions in standard test methods do not match the field conditions to which the oil will be handled. The most commonly verified parameter in the test is treatment temperature, which should simulate the field temperature at whish the wax modifiers are added. A profound temperature effect is observed in many crude oils and the resulting pour point value depends upon the temperature at which the wax modifiers are added to the oil.

The other parameter that can affect the result to pour point value is the resident time which represent the time treated crude or oil stored at the treatment temperature.

The flow improvers have significant role on decreasing the pour points and are effective with a range between 25 to 1500 ppm (v/v). Above this level the cost of additive increases.

An additional but related pour point test involves the examination of reversion effect. The British Admiralty Test usually examines reversion effects and involves heating, cooling and reheating the treated crude to evaluate the tendency of the additive to loss its effectiveness after prolonged storage at cycling temperatures.

Generally, the reversion phenomenon occurs with heavier crude oils. In reversion phenomenon the pour point reduction occurs, but on cooling and reheating the pour point increases. The cyclic temperature does not give the original state to the wax modifier and the paraffin wax and thus additive becomes less effective. The reversion effect depends upon the crude oil and additive used. This effect is difficult to predict and also requires the laboratory confirmation.

Other tests are designed to more accurately ideal field conditions and use of small pipeline systems. Several laboratories have in house flow and deposition loops where crude is pumped through narrow tubes at different temperatures, simulating pipeline transportation. Pressure difference between inlet and outlet ports are then monitored to give an indication of the amount of wax deposition in the pipeline.

Commercial Flow Improvers[110]

Most of flow improver used are the polymeric compounds such as copolymers of maleic anhydride and alkyl methacrylate[111], styrene-alkyl acrylates copolymers, copolymers of fatty acid esters and maleic anhydride[112] ionic polymers, polyalkyl methacrylates, branched polyalkyl methacrylates with nitrogen containing functional group, sulfone copolymers, copolymers of alpha olefins and maleic anhydride[113] and maleic anhydride esters. Generally, copolymers of maleic anhydride and esters[114,115] amides, imides[116] are used. Generally, high molecular weight esters are synthesized using long chain alcohols, polyolefin epoxide, fatty acids. These products vary from thick liquids to hard solids and used as dilute solutions.

These products are preliminary evaluated using the ASTM D-97 IP-15 method. The rheological study starts with laboratory evaluation and then evaluates on a model pipeline having the actual field conditions

1.1.31 Types of crude oils [117-120]

Crude oil appears as brownish mobile liquid to black viscous and some times semi-solid product. The composition and properties differ from different oil fields and oil well to well. Petroleum classification depends upon the density measured at 15 °C. The classification is given below,

Types of crude oil

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

1.1.32 Physico-chemical Characteristics of crude oil[121] :

There are different physical properties of crude oil which gives us the idea of chemical composition. Every oil is unique in its properties. These properties also changes with well to well and even aging as lighter components get evaporated and solidification of heavier parts. Main physical properties of crude oil are summarized below

Bottom sediments and water content

Smaller quantities of water and sediments lead difficulties in processing and possessing irregular behaviour in the distillation units and also it blocks the heat exchangers. Sediments are the dirt and organic matter which remains suspended in the crude oil.

The method involves centrifuging the equal volumes of samples and toluene in a graduated tube and then recording the insoluble matter with water, if present, collected at the base of the tube. The reading is recorded only when constant volume of water and sediment is obtained

Water content by Dean and Stark method

The centrifuge method does not measure the water content accurately. Dean and Stark method is used to determine the accurate water content[106].

A measured volume of sample is refluxed with an equal volume of liquid carrier, preferably toluene. The carrier liquid distills into a graduated receiver carrying with the water. The separated water is measured for water content. This water is separated essentially from the crude oil sample by demulsification method to get proper results in further studies.

$$\textbf{\% Water Content} = \frac{\text{Vol of water in trap}}{\text{Wt. (or Vol) of Sample}} \times 100$$

Salt content

Crude oil contains small amounts of chlorides of sodium, calcium and magnesium due to contact with oil field brines.

The salt content is determined by extraction of the sample with water in presence of a solvent and demulsifying agent in TEL extraction apparatus. The sample is refluxed with benzene, ethyl alcohol and acetone and freshly distilled water and water phase is allowed to separate out. The chlorides in the extracts are determined volumetrically as NaCl.

Present Nacl by wt = 9.35[(V1-V2) N(V3-V4)n]/W
Present Nacl per Liter = 9.35X10 G[(V1-V2)N-(v3-V4)n]/W

V1 - vol of silver nitrate solution used to sample
V2 - vol of silver nitrate solution used in blank
V3 - vol of thiocyanale solution used to titrate the sample
V4 - vol of thiocyanale solution used to titrate the blank
N - normality of the Silver nitrate solution
n - normality of the thiocyancl solution
W - weight of sample in gms.
G - relative density of the sample at 15deg C.

Density and specific gravity

The standard method for testing density in laboratory i;e IP-160 is using a glass hydro meter, Petroleum products are normally handled as liquids having a ried vapour pressure of 18 bar (179k/pa) or less. Values are measured on a hydro meter at convenient temperatures, reading of density being reduced to 15deg C and of specific gravity and API gravity to 60 deg F by means of international standard tables.

Density is the mars of liquid per unit volume at and reported as gm/ltr at 15deg c. Relative density is the ratio of mass of a given volume of liquid at 60deg F to the mass of an equal volume of pure water, at the same temperature API is a specific function of relative density 60/60deg F is represented by

$$\text{Degree API} = \left(\frac{141.5}{\text{Specific gravity at } 15^{\circ}\text{C}} \right) - 131.5$$

No statements of reference temperature is required as 60deg F is included in the definition procedure is as under transfer the sample to a clean hydrometer cylinder avoiding evaporation of lower boiling constituents of more volatile sample. If the oil is sticky then heat is to the temp, for free flowing, ensure that the temperature of the sample does not change appreciably during the time necessary to complete the test lower the hydrometer aside in the sample, As soon as a steady reading is obtained, record the temp, using standard international tables the density is obtained at 15°C similarly specific gravity and API gravity, As the density is the most important parameter required for any further use of crude oil, a great precision is required.

Pour point[122,123]

Pour point is measured for determination of the flow behaviour of crude oil. Standard determination method is IP-15. It is a temperature expressed in a multiple of 3°C under which the oil no longer moves when the plane of its surface is held vertically for 5 sec. The pour point is then taken as 3°C above the temperature of cessation of flow. However this test is carried out under static conditions. Pour the sample into the Test jar to the level mark Heat the oil into the fluid close the Test Jar by cork and thermometer should immersed in sample. After the oil cooled enough to allow the formation of paraffin wax networking, take great care not to disturb the mass of oil, any disturbance of the spongy network of wax crystals will lead to low and fictitious results, Beginning at a temperature 8-9 °C above the expected pour point bring out the test jar from the gasket and lilt it just enough to ascertain whether there is a movements of oil within 5 sec replace the list pour does not flow as soon as the oil in the Test jar in horizontal when tilted hold the test jar in horizontal position for 5 sec and observed carefully if there is no movement record the temperature of thermometer, Repeat the procedure for further confirmation , Add 3 °C for the recorded temperature, and report as pour point of crude oil.

Distillation :

The standard method used in IP-24 this method determined the distillation characteristics of small qualities of crude oil which gives us that how use full part, crude oil is. A 100 ml dehydrated oil sample is taken into the flask and distilled in specific glass apparatus under prescribed condition of heat input and rate of distillation the flask is fitted with the thermometer of range 0 to 35°C, One side tube of the flask goes to condenser circulating ice water which condenses the distillates and are colleted in the marked cylinder, flask is heated constant heat and when the first drop come out of condenser and fall into the cylinder and the temperature recorded is called Initial boiling point of that particular crude oil, Then at every 25deg C temperature difference the volume of distillate colleted is measures by the marked in cylinder, without interrupting till 300deg C, stop hating the flask and allow the condenser to drain into the receiver, Record the total volume in cylinder as distillate, Allow the residue in flask to cool, then weight determine the relative density of continent record the volume of residue at 15 °C.

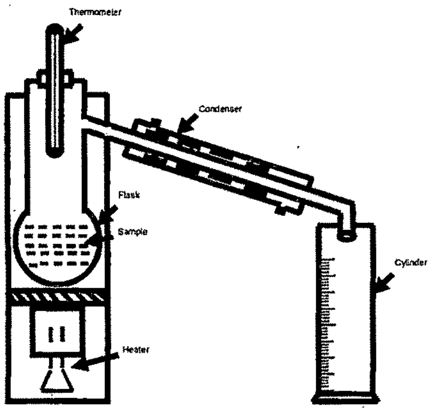


Figure:26 Small assembly for carrying out distillation in laboratory

Wax content[123]

For the present work mainly used method for determination of crude oil waxes is UOP 46-85. Here the waxes are precipitated by acetone and kept at -21°C for 16 Hrs.The quantity is measured as percent weight. To study rheology[89], measurement of solid wax content of crude oil is necessary. High content of wax in crude oil affects the fluidity of oil. The wax content in the crude oil is determined by Methyl ethyl ketone (MEK) or acetone precipitation technique. In this method, oily fraction of the crude oil separated (by dissolving asphaltene 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°C. The precipitated wax is filtered out, washed 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 easy of the filtration. The wax residue is repeatedly washed with solvent (maintained at same temperature) until any colour in the wax has been removed. A low temperature is chosen (-21°C) for getting maximum amount of wax lightly 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.

Asphaltene Content

The standard method used to determine asphaltene content is IP-143, Asphaltene is the percentage by mass of wax free material insoluble in heptanes but soluble in hot benzene heptane is added to the sample in the flask in the ratio 30ml to each 1g of less than 25%. Boil the mixture under reflux for one hour, cool and store in a dark cupboard for 90-150 minutes, place the filter paper folded in eth funnel and trough the residue in the flask to the filter paper remove the filter paper with contents and place it in a reflux extractor, reflux with heptane at a rate of 2-4 drops for one hour . Replace the flask with another having 30-60ml of toluene or benzene and continue refluxing until all the asphaltenes have been dissolved from the paper transfer the contents of flask to a clean evaporating flask already weighed Dry the dish and content in a having over at 105+50deg C for 30ml cool in the desicator weigh again the dish with asphaltene and celanlate as mars percentage.

Melting point of waxes

Selection of the proper melting point method depends upon the characteristics of the wax. Drop melting point (ASTM D127) is suitable for amorphous waxes, e.g., microcrystallines, but is not reliable for higher viscosity synthetic waxes, for which ring-and-ball softening point (ASTM D36) should be used. ASTM D87 may evaluate waxes whose time-temperature cooling curves exhibit plateaus, e.g., paraffin wax. Open or closed capillary tubes are used to measure the melting point of many of the natural waxes. The congealing point (ASTM D938) is the temperature at which a melted wax ceases to flow, and is more consistent than melting points for some waxes.

Column chromatography:

Different constituents of crude oil dissolve in different solvents and chemist takes the advantage of this property of crude oil and separate the different parts of crude oil by column chromatography. Main constituents separated by column chromatography are saturates aromatic and resins. As already explained saturates are lower number of hydrocarbons normally which in colour, waxy in nature and of low melting point, aromatics are ringed hydrocarbons yellow to brownish in clolur and liquid oil room temperature resins are high molecular weight hydrocarbon with N, S, O and are dark are brownish in colour actually this is liquid phase chemical gravity. A glass column of standard length and width are taken and are packed with silica dried at 120deg C for over night. The packed column is charged with weighted amount of 210deg C residue and first is run by hexane or petroleum ether saturate part is colleted in a flask then the column is run by benzene and the aromatic part is colleted then it is run by method and resins or N S O's are colleted this parts are colleted dried and weighted and the percentage of each part is calculated. This parameter is very important for knowing the nature of the crude oil.

Viscosity [88]

Dynamic (absolute) Viscosity

Viscosity is a very important property of oils because it affects all the processes one end to other in oil industry. Viscosity is a measure of a fluid's resistance to flow; the lower the viscosity of a fluid, the more easily it flows. Like density, viscosity is affected by temperature. As temperature decreases, viscosity increases. The SI unit of dynamic viscosity is the millipascal-second (mPa·s). This is equivalent to the former unit of centipoise (cp).

In the SI system the dynamic viscosity units are $N.s/m^2$, Pa·s or kg/m.s where

1 Pa·s = 1 N·s/m2 = 1 kg/m·s

The dynamic viscosity is often expressed in the metric CGS (centimeter-gram-second) system as g/cm.s, $dyne.s/cm^2$ or poise (p) where

1 poise = dyne.s/cm^2 = g/cm.s = 1/10 Pa.s

For practical use the Poise is to large and it's usual divided by 100 into the smaller unit called the centiPoise (cP) where

1 p = 100 cP

Viscosity measurements may be absolute or relative (sometimes called 'apparent'). Absolute viscosities are those measured by a standard method, with the results traceable to fundamental units. "Absolute viscosities are distinguished from relative measurements made with instruments that measure viscous drag in a fluid, without known and/or uniform applied shear rates. An important benefit of absolute viscometry is that the test results are independent of the particular type or make of viscometer used. Absolute viscosity data can be compared easily between laboratories worldwide.

Kinematic Viscosity

There are several ASTM Standard Methods for measuring the viscosity of oils. For this measurement, glass capillary kinematic viscometers and will produce absolute measurements in units of centistokes (cSt) only for oils that exhibit Newtonian flow behaviour (viscosity independent of the rate of shear).

CentiPoises (cp) = CentiStokes (cSt) x Density
SSU[1] = Centistokes (cSt) * 4.55
Degree Engler[1] * 7.45 = Centistokes (cSt)
Seconds Redwood[1] - 4.05 = Centistokes (cSt)

In the present studies dynamic viscosity is studied in Pa.s

Rheology[124]

As explained earlier rheology is the study of flow behaviour of any crude oil. In this work AR 500 Rheometer is used to carry out the studies. Graph between Shear rate verses shear stress were drawn at different temperatures and simultaneously viscosity values are taken at that temperature. In this instrument this facility is available that with the rheological behaviour viscosity at that temperature can be find out. Through out the studies Bingham model is used for the comparison at different temperatures. Studies are carried out exactly on the pour point of the neat crude and exactly at the pour point of crude oil with the pour point depressant. In neat oil studies are also carried out below pour point of the crude oil which is very difficult by any other instrument.

Crude oil is heated above cloud point of the crude oil for 30 minutes without stirring and pour point is noted with the method explained earlier. This crude is again heated above cloud point to make the crude oil to forget its shear history which is very important to know the correct results. After that with pour point depressant the pour point is taken and the crude is taken for rheological studies. Instrument used is very sophisticated and is able to sense a single wax crystal present in the sample. So even differences of very small numbers are also significantly seen in the studies. Comparison is done between neat and treated crude with PPDs not only in pour points but also in viscosity and rheology. Extensive studies were carried out at specific temperature. In whole of the studies the crude taken for comparison is of same physical properties i.e with same crude

Cold Finger Test[118]:

A cold finger test is normally conducted at the temperature of equipment surface where deposition occurs. Oil is circulated through the cold probe simulating the conditions of shear rate in the well. The oil treated with additives maintained at a constant temperature near the cloud point of the oil. A second bath was used to maintain anticipated well head temperature around the cold finger probe. Test was conducted for 3 hours after which the probe was flushed with diesel and allowed to dry overnight. After that the probe was cleaned with acetone to flush non entrapped oil.

The cold finger uses a cooled probe and oil temperature is maintained at application temperature. Oil is then circulated through the cold probe simulating the temperature conditions in the well. This test was performed to understand the potential of paraffin deposition under controlled temperature dynamic conditioned. This tool is useful to evaluate the amount and hardness of deposit likely to form during the production of crude oil. Cloud point and pour point and data concerning the field operations have been used to set the test parameters. The oil treated with additives was maintained at a constant temperature nor the cloud point of respective crude oil. A second bath was used to maintain anticipated well head temperature around the finger probe(copper coil 5.5 ft long, ID= 5mm, OD=8mm).

The cold finger test is normally conducted at room temperature is maintained at the temperature of the surface equipment where deposition occurs. If this is not known ,the next system lower temperature is used. For testing PPD for application in down hole, the well head temperature is used to maintained the temperature of cold surface. The test was conducted for 3 Hrs duration after which the finger probe was flushed with diesel and allowed to dry overnight. After that probe was flushed with chilled acetone to flush non entrapped oil if any remaining oil. The weight of paraffin deposit was determined for blank and after the chemical treatment to determine the percentage inhibitions.

1.1.33 Techniques for control of Paraffin deposits[125,126]:

The different methods of handling paraffin deposition are in use now a days. Some of them are as under:

Control methods: There are broadly two types of methods being followed to control paraffin in oil industry.

(a) Conventional methods- Thermal, Chemical and Mechanical

(b) Non Conventional methods- Magnetic, Nitrogen gas generating systems, Bio, insulation and wave form emulsification. These are not very frequently used

All these methods can be further classified as under

Preventive and Corrective

(I) Corrective
- Thermal (Hot oiling, steaming& heating)
- Mechanical (Scrapping & Pigging)
- Chemical (Inhibitors, Dispersants, Crystal Modifiers, Cloud Point extenders)
- Bio (Application of selective wax degrading bacteria)
- N_2 heat generating system
- Blending with light oils or solvents
- Reverse Emulsions

(II) Preventive
- Thermal(Heat Tracing, Bottom hole Heaters)
- Chemical(Continous inhibition by crystal modifiers)
- Magnetic

Thermal Methods: Although thermal method assures trouble free transportation of waxy crudes at any time but these are very expensive as it requires excellent pipeline insulation as well as heating arrangements with very high and low temperature controls. If temperature control is not there and crude get heated and lower fractions of crude may create lots of pressure on pipeline's wall so high risk is also involved. These method require extra energy so extra cost. As such these methods are useful for short pipeline.

- In most cases where these methods are used ,includes heating of crude oil, heating of pipeline by hot water circulation and insulation.

Mechanical Method: It includes Scrapping and pigging. It comes in picture when the pipeline is choked with the deposition of waxes and other parts of crude oil. It is the best suited method for early removal of the problem. But it requires lots of mechanical labour. Many cases it is not feasible also.

Bio and N_2 treatment programme: In both the methods lots of preparation requires. These two methods are more feasible in well. In case of pipeline these are not of much use.

Chemical treatment programme

Chemical methods of paraffin removal/inhibition include:

- Those in which solvent is used to dissolve the deposit once it has formed.
- Use of crystal modifiers, cloud point extenders, paraffin dispersants & inhibitors which inhibit wax crystal growth or inhibit its adherence to the tubing/ flowline.

Chemical Dispersants

These chemicals are used in batch or continous to remove paraffin that has already deposited. These chemical disperse large deposit of paraffin into microfine particles which has carried through the system by the production stream. While a dispersant may diffuse several times its own weight of paraffin, it does not have the widespread application of solvents; however, in well where dispersants are applicable. Present research work has significantly taken account the flowline and storage problems in the selected field.

Blending with light oil or solvent:

Blending is very common method for transportation of waxy and viscous crude oils. In this method waxy or viscous crude oil is mixed with light oil (having low wax content) or with organic solvents. These methods are useful when diluents are easily available at low cost.

Reverse Emulsion:

This method is very useful in heavy and viscous crude oils. In this case crude is mixed with water with the use of some surfactant and made emulsions which is very light in nature and is of very low viscosity. It is then transported as such and at the receiving point the emulsion is again converted into water and oil.

1.1.34 Outline of the Thesis [127,128]:

Exploration, production and transportation are very costliest and risky processes. Three fields from the South Gujarat were selected which are having crude oils of very high waxy in nature. These fields are facing main problems in transporting and storing the crude oil during winter season. Because of this problem there is a loss of huge money every year. Mechanical scrapping i.e pigging, solvent solutions are in use to overcome this problem. But these solutions are not cost effective. So chemical solution has been tried in this work. Fields selected are Kosamba, Nada and Gandhar, predominant oil and gas producing fields in South Gujarat, India. Physico-chemical characterization of the crudes of the selected fields was carried out in the laboratory. Four series from different studies are prepared in laboratory and tested on the crude oils from above mentioned fields. Extensive studies are carried out to reach at right conclusion. Main tests carried out are pour point, rheology and cold finger before and after treating with the prepared polymers. Results are outlined. Pour point of Kosamba field oil has been decreased from 36 to 15°C, Gandhar from 33 to 15°C and Nada from 33 to 21°C. If implemented in the field in the prescribed conditions can help in reducing the problem to a great extent.

The present work is emphasized mainly on the problems encountered during production and transportation of crude oil , So it is necessary to know the uses, history, exploration, physico-chemical characteristics and problems encountered while production and transportation of crude oils.

AIMS AND SIGNIFICANCE

As discussed earlier in the introduction that in today's world crude oil is the lifeline of any country's economy. Crude oil as such is of not of much use. So to convert it into useful products it has to be transported to refinery. For this process mainly pipelines are feasible. Pipeline itself is very costly process. Lot of hard work and latest technologies are also required for its transportation from well head to the refinery. But as per studies and practical experience of oil companies, pipeline is the most economically viable way of crude oil transportation. The most important studies carried out before installing pipeline is the type of crude oil of the field which is to be transported. Secondly how much quantity per day has to be transported and the distance to be covered from the field to the refinery end. Depending upon all these parameters engineers design the pipeline.

Main problem associated with the transportation is waxy and asphaltic crude of any field. If the crude oil is of light density than there is not much problem in transportation. But if the crude oil is of high density and viscous in nature than it creates lots of problem during transportation. Second biggest parameter governing the transportation is pour point of the crude oil. Even if crude oil is light but pour point is high it will chock the pipeline on sudden changes of external and internal temperatures and there will be lot of problem during restartability after prolonged shut downs.

To handle the above problem there are lot many methods available in literature and are in use practically. Main methods available are thermal, mechanical and chemical. Chemical method is found to be most economically viable. But for this treatment lot of research work is required as it is not universally effective in all the fields. It is very much dependent on the type of crude oil so becomes specific to the particular oil field. But once it is found to be effective for a particular field it is highly cost effective. These chemical additives are in high use now a days. Taking care of all techno-economic aspects the work is proposed on three selected fields. The crude oils are highly waxy in nature and pour points are also in higher range.

The work is elaborated to every aspect of the existing facilities in the fields undertaken. Survey carried out on crudes and solutions were searched out. Few series of selective chemical additives were prepared and tested on the selected fields crude oils. Main significance of the work is as under:

- To find out better solution with chemical additives for the selected fields and to under stand the chemistry behind the chemical solution.
- To prepare suitable pour point depressants i.e chemical additives for the South Gujarat oil fields to cut down extra costs in transportation of the crude oil.
- To study the working mechanism of these chemical additives on crude oils selected and find out their effectiveness.
- To optimize the required doses of the effective flow improvers to increase the cost effectiveness of these additives by extending the work with various studies.