

INTRODUCTION

I- INTRODUCTION

One of the greatest challenges of the petroleum industry is the phenomenon of paraffin deposition, which is the result of the transport of paraffin petroleum in a cold environment. Transportation of paraffinic crude in a cold environment can result in wax depositions, which are solid deposits, on the pipe wall. The formation of paraffin in the bulk of the petroleum is a crystallization process in solution. Such phenomenon occurs along the pipe connected to offshore wells and even onshore. Its main implication is a paraffin blockage with serious economical consequences. Crude oil production under deep water presents serious operational problems, due to possible obstruction of flow pipes or production lines. Such lines are in permanent contact with very cold sea- water and the sharp temperature decline of oil production lines provokes the crystallization of some heavy oil fractions. The separation of such fractions, constituted mainly by paraffin and waxes, produces solid deposits responsible for the reduction of the cross-section of flow lines [1].

A number of techniques have been devised to combat the paraffin deposition problem. In general, these methods can be classified into five categories:

1. Mechanical treatments**2. Thermal treatments****3. Bacterial treatments****4. Chemical treatments****5. Electromagnetic treatments**

A combination of any of these techniques is usually used. Many hidden costs are involved in most of these procedures such as down time, lost production, wasted oil and possible damage to producing equipment.

Mechanical methods are the oldest of the methods where scrapers that cut the deposit are run-down the tubing. It is a cumbersome process because the recovery and disposal of the deposit usually causes difficulties. Thermal treatment, where hot oil is injected down the wellbore, is a popular method, but studies by Sandia National Laboratories have indicated that some of the fluid injected goes into the formation, and hence, particulates and chemicals in the fluid have potential to damage the formation. Moreover hot oiling tends to cause deposits of very hard wax to build-up in the formation. Bacterial treatment is a recent technique where specially cultured microbes are introduced into the wellbore to produce chemicals that inhibit wax production and to break down the produced waxes. However, because the microbes require water to survive and cannot tolerate high

Introduction

temperatures, the method is limited to wells that produce water and has a bottom hole temperature below 200 °F (93 °C). Electromagnetic treatments are also relatively new. In this method, the oil is constrained to pass through powerful magnets. This polarizes the wax molecules orienting them in the direction of flow and inhibiting their ability to migrate to the walls to deposit. The effectiveness of this method has not been fully investigated.

The use of chemical inhibitors to reduce the paraffin problem has become popular in the industry. Although a number of chemicals are known which possess paraffin inhibition properties, it was observed that no single chemical was equally effective in all wells. There were instances when a particular chemical performed well in one well but failed in another well in the same basin. Therefore, it is required to find the best inhibitor for each well individually.

In the last couple of decades, considerable effort has been devoted to developing chemical methods of inhibiting paraffin deposition. The chemical inhibitors can be broadly classified into three categories:

- a. **Solvents** which are high aromatic compounds used for dissolving paraffin.
- b. **Wax crystal modifiers** which are polymers that inhibit or alter wax crystal growth.

c. **Paraffin dispersants**, which inhibits the particles from uniting and depositing.

1.1. CHARACTERISTICS OF WAXY CRUDE OILS: -

Crude oils are generally complex chemical systems containing from hundreds to thousands of individual components in the range from low molecular weight to high molecular weight paraffin and asphaltenes [2]. Crude oil occurs in many different parts of the world, and its structure and composition varies according its source to such an extent that each producing area, and field, and reservoir bears its own profile just as individually as fingerprints identify man. Crude oils contain a mixture of light and heavy hydrocarbon. Typically, stabilized oil may contain paraffinic, naphthenic and aromatic component as heavy as high carbon number C-60. In addition, polar and asphaltenes may also be present. The lighter components in the crude oil solublize the heavier components in solution. This Solubility depends very strongly on the temperature. If the temperature of the oil is decreased, the solubility of the heavy hydrocarbons may be sufficiently reduced to cause precipitation of these components in the form of solid wax crystals. The polars and asphaltenes may also co-precipitate with wax crystals [3].

Some of the crude oils and diesel oils contain a large amount of wax or paraffin, and have high pour points. As the temperature of crude oil is dropped, the wax will crystallize and accumulate, increasing the viscosity of the crude oil and making it more difficult to flow in pipeline at a given velocity [4].

Many crude oils throughout the world contain significant quantities of wax, which can crystallize during production, transportation and storage of the oil, resulting in an increase in viscosity by several orders of magnitude and oil gelation. This may cause major difficulties in pipeline transportation. A thorough understanding of rheology of waxy crudes is therefore, necessary for taking problems in pipeline transportation, particularly at low temperatures [5]. The rheology of wax crudes is believed to be influenced by wax, resin and asphaltenes presence [6-10], as well as by thermal and mechanical history of the crude [11, 12]. However, the nature, the type and the quantity of wax, as well as its crystallization habits, influence flow properties to a large extent.

The presence of wax crystals changes the flow behavior of the crude oil from Newtonian to non-Newtonian [13]. The pour point will decrease when a pour point depressant (PPD) is injected into the crude oils.

The wax crystals usually lead to higher viscosity with increased energy consumption for pumping and a decreased capacity. In addition, if the oil is cooled during transportation, the wax crystals tend to deposit on the colder pipe wall, if these deposits get too thick, they can reduce the capacity of the pipeline transportation and cause problems during pigging [14]. Wax deposition in process equipment may lead to more frequent shutdowns and operational problems. In extreme cases, wax crystals may also cause oil to gel and lead to problems of restarting the pipeline.

Paraffin crystallization depends on crude oil composition, temperature, and pressure conditions. The temperature at which the first crystal appears, called Wax Appearance Temperature (WAT), is an important parameter [15]. Special attention has been given to the wax crystallization in the oil production industry and several techniques have been developed to minimize the problems caused by wax crystals deposition/aggregation. Chemical methods, using polymeric additive to inhibit the deposition, are considered an interesting alternative, specially in off-shore production [16].

1.1.1. The Origin of Wax Problem:-

When waxy crude oils are exposed to lower temperatures below their cloud point, the hydrocarbon fluid can undergo a number of changes:-

Introduction

- i- Solidification,
- ii- Solidification with the formation of a precipitate of macro crystals of paraffins, and
- iii- Solidification with the formation of microcrystals which swell giving a crystal-line structure which traps the remaining hydrocarbon fluid.

The circumstances under which this occurs are dependent on the thermal history, the cooling rate, shear effect, and the composition of the hydrocarbon fluid [2]. All these changes lead to wax formation which gradually crystallizes and separates from the crude oil. These wax crystals agglomerate and form a gel structure that impedes oil flow. A small content of 2-3% of crystallized paraffins is able to form a solid interlocking network of fine sheets, thereby entrapping the remaining oil in cage like structure, and inhibiting the flow of the liquid crude/fuel [3]. Paraffin problems are generally easier to handle in onshore than offshore which are more hazardous and urgent. The solubility of paraffin in crude oil depends on the chemical composition of the crude, the temperature, and pressure of the production system. Paraffin will begin to crystallize in oil as soon as the equilibrium temperature and pressure, (i.e. the cloud point) is attained [4].

The wax deposition inhibitors are polymeric compounds constituted by a hydrocarbon chain which provides the interaction between the additive and paraffin, and a polar segment that is responsible for the wax crystals morphology modification necessary to inhibit the aggregation stage. For this reason, such inhibitors are known as wax crystal modifiers. Several polymers have been evaluated as wax crystal modifiers and poly(ethylene-co-vinyl acetate) (EVA) copolymers are among the additives that can be used since they present a good efficiency as crude oil flow modifiers and wax deposition inhibitor [17].

Paraffin crystallization depends on temperature and pressure conditions [15]. Special attention has been given to the wax crystallization in the oil production industry and several techniques have been developed to minimize the problems caused by wax crystals deposition/aggregation. Chemical methods, using polymeric additive to inhibit the deposition, are considered an interesting alternative, specially in off-shore production.

A number of factors that can affect the rate of deposition of paraffin in flow lines has been identified in the literature. Some of these factors are temperature of the crude, temperature of the tube wall, flow rate, residence time, wax concentration, pipe roughness and others.

1.1.2. Wax Crystallization:-

Wax crystallization is governed by three successive phenomena: nucleation, wax growth, and agglomeration.

a- Nucleation:-

A solution of paraffins mixed in a solvent can be described as an isotropic medium with interactions between the paraffin and solvent molecules. The heaviest paraffin is solubilized by hydrocarbons. As the temperature decreases, interaction between paraffin molecules increases. When the intermolecular forces of attraction reach a point where they are greater than solvent-paraffin interactions, the paraffin molecules combine to form a crystal nucleus [13,14].

b- Crystal Growth:-

Crystal growth occurs on the sites where the surface energy of cohesion between the crystal and the free paraffin is the greatest. So, growth is fastest on the lateral faces, at a rate increasing sharply with supersaturation [5]. Paraffins can crystallize in different ordered structures in mono or multimolecular layers, in which the aligned parallel to each other, so that the terminal methyl groups belong to parallel planes, perpendicular or oblique to the chain axis.

c- Agglomeration:-

When the product is cooled to a temperature lower than the crystallization temperature, the crystal size increases strongly

modifying rheological properties of the solution, and finally the crystals agglomerate into particles that are deposited or get entangled in rigid lattices, leading to the pour point. The different morphologies of paraffin crystals are mostly:

- i- Platelets or lamellae, lozenge-shaped, appearing especially when cooling is low.
- ii- Needles, mainly obtained by fast cooling and if n-paraffins contain impurities.
- iii- Other forms of crystals often encountered in complex media: dendrites, long crystal, parallel-pipedic pyramidal blocks.

Wax crystal modifiers generally have a specific in one or several steps of crystallization [6].

1.2. TRANSPORTATION PROBLEMS OF PETROLEUM CRUDE OIL: -

With increasing demands being placed on decreasing the production costs of crude oil much research has been devoted to the development of the transportation techniques of petroleum crude oils. Pipelining is the most convenient means for transportation of crude oils and products continuously and economically. However, high pour point, non-Newtonian flow behavior and wax deposition on pipeline wall surfaces are controlling factors defining the

reliability of such means for transferring waxy petroleum products. Waxy crudes are characterized by high pour point and difficult flow properties. Most of Egyptian western-desert crudes are waxy in nature. The amount of the wax constituent in these crudes may reach 20 wt% [18]. Crude oil additives are chemical compounds added to the base oils to impart specific properties to the oils. Some additives impart new and useful properties to the crude oil and others enhance properties already present. It is desirable that the viscosity of the crude oil changes with the production and transportation temperature range. Moreover, all waxy crude oils contain some dissolved wax which begins to separate as crystals that interlock to form a rigid structure which traps the oil in small pockets and keeps it from pouring or flowing at low temperature [19]. Low pour points may be achieved by intensively dewaxing the oil during refining which decreases the oxidation stability of the oil and increases the tendency toward carbon deposits. Thus, to lower the pour point of oils still containing even small amounts of paraffin and resins, it is desirable to add a pour point depressant. This depressant may act as anti-settling and improves the flow ability [20].

The structure and composition of wax dispersants are similar to those of flow improvers in some aspects but different in others. Hence, one chemical structure may provide the

function of the two additives by holding extra specific polar groups, but still in most cases two- or even three-component additives are used for improving flow ability [21-23].

One of the most important polymeric additives, among the various types employed in petroleum industries, is the pour point depressant. When an additive comprising two components is used as pour point depressant, one component serves as the conventional polymeric flow improver while the other component, including mainly a hydrocarbon-oil-soluble nitrogen-containing compound, acts as wax dispersant. Due to current environmental legislation, research is directed towards additives free of nitrogen dispersant groups, such as alkoxyated alcohols or phenols [24].

The transportation of crude oil from production site to refineries, especially through sub-sea pipelines, has different problems [19-21]. Pressure problems during the production of crude oil result in considerable trouble and expense to the producer. It is known that crude oils may contain substantial quantities of waxy materials. When such oils are subjected to temperatures below their pour points, the waxy constituents tend to deposit on cold surfaces or crystallize and agglomerate into a solid gel. The gelling or stiffening of the oil introduces rheological problems that interfere with normal oil production or pipeline transportation and cause handling

problem [22]. The high wax crude oils are characterized by high pour point, high viscosity, high gel strength, and abundant wax deposits. A variety of mechanical, physical, and chemical treatments have been applied to alleviate these deposition and pumping difficulties. Asphaltenic crude oils contain little paraffin, and the Asphaltenic components are amorphous i.e. they do not form crystal structures upon cooling. Asphaltenic crude becomes more viscous at lower temperature and it ceases to flow. Each problem area has key features differentiating it from the other causes of high pressures. The tests used to identify these key factors include cloud point, pour point, viscosity, yield value, solubility parameters, pumping studies, and various deposition and removal test. The main factors that cause transportation problems for crude oils are reported as paraffin and asphaltene depositions.

1.2.1. Flow Properties of Waxy Crude Oils: -

The viscosity of crude oil is perhaps its most important physical property. For most crude oils, at sufficiently high temperature, the viscosity at a given temperature is constant and the crude is a simple Newtonian fluid although it is chemically very complex. As the temperature is reduced, however, the flow properties of a crude oil can readily

change from the simple Newtonian to very complex flow behavior due to the crystallization of waxes and the colloidal association of asphaltenes. The presence of wax crystals changes the flow behavior of the crude oil from Newtonian to non-Newtonian [21-31]. The wax crystals usually lead to higher viscosity with increased energy consumption for pumping and a decreased capacity. In addition, if the oil is cooled during transportation, the wax crystals or asphaltene tend to deposit on the colder pipe wall.

1.2.2. Wax Deposition: -

Waxy crude is allowed to cool to the temperature below the wax will precipitate, agglomerate and entrap the liquid oil in to its structure; and the crude will become a two-phase dispersion with wax solid particles dispersed in the liquid hydrocarbons [5].

Wax deposits consist of a mixture of linear and branched chains hydrocarbons in the range of $C_{18} H_{38}$ to $C_{60} H_{122}$; generally mixed with other organic and inorganic materials such as crude oil, gums, resins asphaltenic materials, salt, sand, and water. Wax deposits can lead to increase pipeline roughness, reduced effective diameter, more frequent pigging requirement and potential blockage [28]. If these deposits get too thick, they can reduce the capacity of the pipeline and

cause problems during pigging. The solubility of paraffin in crude depends on the chemical composition of the crude, temperature, and pressure. Paraffin precipitates from the crude oil at an equilibrium temperature and pressure defined as cloud point [29].

Precipitation of wax significantly increases crude viscosity and will gradually change the flow properties of the crude from Newtonian to non-Newtonian behavior. The crude begins to show non-Newtonian flow behavior at temperature called the abnormal point [30], which is generally a few degree Celsius below the wax apparent temperature (WAT). On further cooling, more and more wax crystals precipitate out and interlock to form a wax crystal lattice. This results in gelation of the crude and loss of flowability. Researches [7, 31, 32] have shown that only 2-4 wt% precipitated wax is sufficient to cause oil gelling.

Paraffin depositions were explained by three mechanisms. When the oil is cooled, a concentrating gradient leads to the transport, precipitation, and deposition of wax at the wall by molecular diffusion. Additionally, small particles of previously precipitated wax can be transported laterally by Brownian diffusion and shear dispersion [33, 34]. Wax deposition in process equipment may lead to more frequent

shutdowns and operational problems. In extreme cases, wax crystals may also cause oil to gel and lead to problems of restarting the pipeline. Great potential saving can be derived from accurate prediction of wax formation. The knowledge of the magnitude of wax deposition can lead to reduction of insulation requirements for production and transportation systems [35]. Conversely, problems with wax can be addressed in an early stage of a project so that sufficient thermal insulation is planned instead of expensive chemical injection and loss in capacity or loss of availability.

1.2.3. Factors Affecting of Wax Deposition:-

The deposition of wax from hydrocarbon solution in pipelines is influenced by three main factors namely: flow rate, pipe wall temperature, and chemical nature [2]. These factors are briefly discussed herein below:

i- Flow rate:-

The increase in the flow rate normally causes a decrease in the wax deposition and an increase in the strength of deposits.

ii- Temperature:-

Wax deposition increases with the increase in the difference between the solution cloud point and the pipe wall temperature.

iii- Chemical nature:-

The chemical nature of wax and solution can affect the deposition process by modifying the adsorption forces holding deposits in place.

1.3. PUMPABILITY CHARACTERISTICS OF WAXY CRUDE OILS: -

The pumping and restarting conditions of the pipeline require some knowledge on physical properties of the oil, which should represent the actual conditions in the pipelines. These properties should be easy to determine and have good reproducibility. In the past in many pipelines, this was controlled by the pour point of the crude oil. Normally, the specification stated that the pour point should not exceed the prevailing ground temperature. It has long been known that this is not a satisfactory test. The reasons for this are [36]:

- 1) The repeatability and reproducibility of the pour point test are bad, and

2) The pour point test only measures the temperature at which oil will flow under a small but indeterminate shear stress. It gives no indication of the higher shear stress, which is available in a normal pipeline.

In addition to the properties of the crude oil itself, two other factors exert a major influence on the Pumpability in any particular pipelines. These are:

1. Ambient temperature conditions in the locality of the pipeline, and
2. Whether the pipeline is buried or above the ground.

Where there is a choice of whether the pipeline should be buried or above ground, it is sometimes argued that there is an advantage in having it above the ground so the use may be made of the heat effect of the solar radiation to assist degelling in the pipeline. If this argument is true it will most usually be found that, unless the pipeline is lagged, the night ambient temperature conditions will often be such as to cause a marked reduction in throughput or in extreme cases even stop the pipeline completely. For the judgment of the physical conditions of the pipeline and the behavior of the waxy crude oil, the oil temperature in the pipeline has to be known during normal operation and the part of static cooling.

For a pipeline already in operation, the temperature distribution dynamic cooling could be measured at the different locations over a period of time [37]. At the time of restart of the pipeline because of very high viscosity, the flow rate is expected to be low. This, however, depends on available shear stress as compared to the yield stress. In any case, the minimum flow conditions of the pumps have to be investigated if a pump is operated at very low rate, additional wear due to unbalanced flow is expended. Further, due to the poor efficiency, the oil will be heated and, after as short while, the allowable maximum temperature will be exceeded. This will limit the allowable time for the operation of the pumps with low flow [38]. If the restart flow rates do not meet the pump requirements, special pumps with appropriate characteristics (high head, low flow) have to be used for restart of the pipeline.

1.4. POUR POINT DEPRESSANTS (PPD_s): -

Pour point depressants (PPDs) are used as chemical additives when transporting crude oil and operating diesel engines at temperatures below their wax appearance points. There have been developed many kinds of polymers that are used as PPDs to influence the behavior of the paraffin crystallites formation [39]. If the waxy crude oil is allowed to cool, wax

will crystallizing, agglomerate and entrap the oil into its structure. This phenomena often happens if the ambient temperature of the place is below the pour point of the crude oil [10]. Pretreatment of the crude oil is necessary for transportation of these waxy crudes through the pipeline. Pretreatment of the crude oil with flow improver is one method by which the rheological character of the gelled waxy crude is changed for easier transportation.

Flow improver (FI) additive, alternatively known as pour point depressant (PPD)/wax crystal modifier, can reduce the growth of the wax crystal and forms smaller crystals of a higher volume to surface ratio. Owing to this change in crystal shape the ability of wax crystals to intergrow and interlock is greatly diminished. The combination of these two effects lowers the pour point, viscosity and yield stress appreciably, and it becomes easier for the transportation of waxy crude oil [31, 40]. But wax is not the only component in a crude oil. Other constituents in the crude oil i.e. asphaltenes, resins, lighter distillates, polar aromatics etc. should also be considered as important factors while ascertaining the flow behavior of a crude oil. Asphaltenes are very large heterogeneous molecules with condensed aromatic nuclei, [41] which may associate to form colloidal sized

particles that strongly influence the viscosity of the oil medium and affect the crystallization of the wax [42,43].

1.4.1. Chemicals Used as PPD:

Pretreatment of the crude oil with polymeric additives, known in the oil industry as flow improver or pour point depression has received the greatest acceptance due to its simplicity and economy [44, 45]. More recently pour point depressants and flow improvers have been developed that, in small concentration, affect the crystal growth, and as a result improve the flow properties. The use of pour point depressants and flow improvers is found to be more attractive among the various methods. The main attraction of this method is its relative cheapness and variability of dosage with respect to the temperature and desired viscosity requirements [46]. The use of chemical additives flow improvers, pour point depressants to help cure these difficulties in crude oils and residual fuel oils is a logical extension of the technology developed in lubricant oils and middle distillate [44]. The structure of these flow improvers is mostly polymeric and their essential role is to slow down or to modify the crystallization of the paraffin constituent in the crude [17]. Chemically pour point depressants and flow improvers are ashless polymeric additives which when added

into the crude oil at 300-600 PPM level reduce the pour point and viscosity of the crude oil [36]. Polymeric materials widely used as pour point depressants flow improvers are alkyl acrylate polymers and copolymers [19, 47-51], vinyl ester polymers and copolymers [52-54] and alkylated polystyrene [55]. Normally the average molecular weight of the commercial available pour point depressants for crude oil is 2000 to 20,000. These polymers and copolymers are easily soluble in crude oil at temperature ranged from 40 to 45°C and should be non-corrosive to metal of petroleum equipments [56]. They are used in pipelining of wax crude [57].

The goal of successful treatment of high pour crude with polymeric pour point depressants is to reduce the temperature of congealing, inhibit waxes from precipitating out of solution, and reduces the yield strength of the congealed crude and decreases the viscosity of the crude. Significant reduction in the yield stress and effective viscosity can be achieved by doping waxy crude oils with flow improvers [58]. The viscosity of waxy crude is highly complex due to the transition from Newtonian to non-Newtonian pseudoplastic with thixotropic character below pour point [59]. Yield value is also an important parameter characterizing the cold flow behavior of waxy crude.

However, the rate of shear while cooling has only a mirror influence on values obtained. Evaluation of flow via pour point test is inadequate for pipelining, since it is performed at too small-undefined shear effect far below that applied in field conditions. Flow improvers and shear effect act in the same sense for improving the cold flow properties of waxy crude but in a different manner. While flow improvers function by adsorption, nucleation, co-crystallization and/or thermodynamic change of solubility of wax constituent in the crude oil heterogeneous system, the shear rate acts through the breakdown of the secondary interparticle bonds formed among flocculated wax crystals during cooling [11].

1.4.2. Mechanism of Pour Point Depressants: -

When a waxy crude oil is cooled below its cloud point, the wax crystal form and begin to agglomerate and, with further temperature reduction crystal agglomerate reaches a point at which a gel structure is formed below the pour point due to interlocking of the growing crystals. The wax crystal formation depends on the crude oil constituents like resins, asphaltenes, paraffin and microcrystalline waxes. Their molecular weight, structure and quantity are based on the rate of cooling and degree of agitation during cooling. Attempts have been made [57, 60- 62] in the past to determine the

temperature, at which crystallization of wax starts, in petroleum fluids from their viscosity temperature behavior under specified dynamic cooling conditions. This temperature is obtained in terms of the sharp inflexion point when viscosity or log viscosity is plotted as a continuous function of temperature and is quite close to the cloud point as determined by ASTM D- 2500 procedure [61]. When the additives or flow improvers are added, the shape of the wax crystal change [63]. Many postulated mechanisms have been put forward to explain this phenomenon and to PPD product design. Among the mechanism theories, adsorption, co-crystallization, nucleation, and improved wax solubility are widely accepted by mechanism researchers [41, 64-66]. Although the theory of the mechanism is still disputed by researchers, the above four theories can all be used to explain the function mechanism of the PPDs. Therefore, many theoretical and experimental studies are continually being performed in order to further this study [4, 67-75]. Many researchers have tried to find a universal mechanism to explain the change of the wax crystals in habit and particle size, from which the product design of PPDs according to different kinds of crude oils would benefit. Now adsorption, co-crystallization, nucleation, and improved wax solubility

have been accepted as the most widely used theories in explaining the mechanism [76, 77].

Researchers studying the performance mechanism of PPDs have also found some powerful tools from computational chemistry, which would help them to conduct research in new fields. Duffy and Rodger have carried out much effective work these years in the field of the mechanism study with computational chemistry methods. The comb-shaped poly(octadecyl acrylate) molecule was selected as the additive, which had long side chains. With the analysis of the results, it was found that the polymer mixed well with the heptanes to produce an additional, strongly ordered layer that would provide a kinetic barrier to any subsequent wax deposition [78, 79]. Their series results have given some useful concept of the performance mechanism of the additives with long side chains, but little have been done to mechanism of PPDs of other types in their study. Jinli Zhang et al., [76] have studied the mechanism of PPDs with density function theory (DFT) and molecular mechanism (MM) in vacuo to study the interaction between normal alkane molecules and PPDs. $C_{20}H_{42}$ was selected as the wax molecules, which will be more close to the mean carbon number of wax crystal molecules in crude oils.

Ethyl vinyl acetate (EVA) with molecular weight of 2000 and 25% of vinyl acetate content was selected as the PPD. EVA is more widely used as crude oil additive in the world and has quite different structural character with poly(octadecyl acrylate).

1.5. RHEOLOGICAL MEASUREMENTS:-

The Rheological behavior of a crude oil is highly influenced by its chemical composition, temperature and the current, as well as previous thermal history. High waxy crudes exhibit a non-Newtonian character, often with a yield stress at and below their pour point temperature. At a sufficiently high temperature the crude oil, although chemically very complex, is a simple Newtonian liquid [10].

The low temperature non-Newtonian flow behaviour of paraffinic crudes is strongly affected by shear strength, time of shear, cooling temperature, rate of cooling and composition of the crude oil matrix. In addition, the shear and thermal history play an essential role in identifying this flow behaviour [58]. Difficulties encountered through cold handling of waxy crudes are concentrated in the high pour point that impede the start of flow at relatively low temperatures, the high yield stress and high viscosity on restartability after prolonged shut-down and progressive wax

deposition at the pipeline downstream. Waxy crude oils place specific constraints on pipeline design because the oil temperature usually drops along the pipeline, causing increasing quantities of wax crystals to be formed in the crude oil phase. This results in the formation of a gel structure with higher viscosity levels. Under these circumstances, viscosity is strongly dependent on the shear effect and its duration. Consequently, greater pumping power expressed in shear effect is required for easy pipeline transportation [24, 80-83].

The viscosity of waxy crudes is highly complex due to the transition from Newtonian to non-Newtonian pseudoplastic with thixotropic character below the pour point [84]. It is more realistic to use the apparent viscosity for testing, since the breakdown in apparent viscosity reflects the breakdown effect on yield value is also an important parameter, characterizing the cold flow behaviour of waxy crudes. However, the rate of shear while cooling has only a minor influence on values obtained. Evaluation of flow via pour point test is inadequate for pipelining since it is performed at too small undefined shear effect, far below that applied under field conditions. However, it is utilized for screening flow improvers in waxy crudes in particular. On pipeline transportation of waxy crudes they are subjected to a cooling

effect which adversely affects their flow properties. They are additionally influenced by the shear effect that tends to ameliorate their flow behaviour [85].

Waxy-paraffinic-crude oils exhibit a high pour point and possess non-Newtonian flow characteristics at temperatures equal to or lower than the pour point due to wax crystallization and gel formation of their heterogeneous matrix. Thus a yield stress arises and an increase in viscosity occurs. The rheological properties (shear stress-shear rate relationship) are no longer constant, and viscosity varies as a function of shear rate [84, 86-90].

The crude oils pumped in pipelines generally show normal characteristics concerning pumping conditions such as viscosity and low pour point. Crude oils exhibit non-Newtonian behavior at temperatures below the pour point. The crudes are cooled to form gel or partial gel, under static conditions a rigid gel is formed, but if the crude is cooled while in motion, the apparent viscosity will increase but the material remains fluid [13]. Therefore, the rheological properties are functions of temperature; shear rate, shear stress and past history. Problems in pumping of these crudes will occur if the temperature drops and the fluid becomes non-Newtonian and if gel formation occurs after a shutdown, the pipeline facility must be designed to recover from these

problems or prevent them. A realistic approach should be developed based upon an extensive evaluation of the rheological behavior of the crude oil under representative temperature and shear conditions. The two rheological parameters of which knowledge is indispensable for transporting crude oil through pipeline are viscosity and yield stress [91]. A few relevant terms that will be frequently used are defined in the following sections. A fluid, that is, a liquid or a gas, is a substance that undergoes deformation under the action of an applied shear force or stress. In other words, when a fluid is subjected to shear, it flows. On the other hand, a solid deforms under the action of an applied shear force and retains its original shape upon the cessation of the applied shear force [92]. The manner by which fluid obeys a given shear stress- shear rate relationship determines its class within the rheological classification of a fluid.

Consider the steady flow of a fluid in a horizontal pipe of circular cross-section, the fluid flows with an average velocity of U in a pipe of inside diameter D . The pressure difference between two points 1 and 2, separated by distance L is equal $(P_1 - P_2)$. The decrease in pressure in the fluid reflects the applied force causing the fluid to flow, and if the flow is steady (i.e. no change in the flow and enhance velocity), this force must be counter-balanced by a shear

force of equal magnitude at the wall of the pipe. If τ_w is the shear stress at the pipe wall, then the force acting on the fluid at the wall must equal $(-\pi DL \tau_w)$. The negative sign indicates that this force acts in a direction opposite to the direction of flow. The force acting upon the fluid due to pressure difference is equal $(\pi D^2/4)(P_1-P_2)$. In steady state (no acceleration), the algebraic sum of these τ_w forces is zero. Therefore the τ_w can be written as following:

$$\tau_w = \frac{D(P_1-P_2)}{4L} \dots\dots\dots (1.1)$$

The above equation shows that the shear stress at the pipe wall is just another means of expression of friction loss [93]. From equation (1.1), it follows that available shear stress for particular pipeline depends on the length of the line between two-pump stations and the pressure difference. The available shear stress can be increased by increasing the initial pressure, P_1 , and/or redesign the section length of pipe.

Consider (τ_w) parallel planes of area A , separated by the differential distance (dr) the space between two planes is filled with a fluid, the lower plane is fixed. A small force (F) applied to the upper plane will give its velocity (du) in the direction of force. If there is no slip between the wall and the fluid, the fluid adjacent to the upper plane or wall will also

have a velocity (du) in the direction of the applied force and the fluid next to the lower plane or wall will have a zero velocity. Thus, a uniform velocity gradient of magnitude du/dr is set up in the fluid since the shear force (F) is uniform across the distance (dr), the velocity gradient, (du/dr), is commonly referred to as the rate of shear. The shear force per unit area, (F/A), is called the shear stress.

Viscosity of crude oil measures the ability of fluid to flow during steady state condition. It is the property of a fluid that resists a shear force. It can be thought of as the friction resulting when one layer of fluid moves relative to another. Viscosity, η mille Pascal second (m pa s) is the ratio of shear stress to shear rate

$$\eta = \tau / D \quad \dots\dots\dots (1.2)$$

Where τ is shear stress Pascal (pa).

Yield stress measures the ability of fluid to restart its flow after shutdown of the transportation system. The yield stress of oil, at a given temperature is defined, as the shear stress required for initiating flow. It can thus be directly compared with the shear stress available in the pipeline. The yield stress of crude oils is influenced by its temperature history; shear history, aging and composition [10, 19, 94].

1.6. STUDY OF THE PARAFFIN DEPOSIT FORMATION USING THE COLD FINGER METHODOLOGY

This section aims to learn about paraffin deposit formation using a cold finger methodology. The polythermal method is used in various experiments using different temperatures in both cold finger and bulk of the fluid. The experiments measure: the thickness of the deposits, as well as the deposition rates, degree of subcooling and, finally, the induction for the onset of wax. The methodology allows the evaluation of the critical time of deposition and the critical temperature difference between the hot petroleum source and the cold seawater temperature. It is shown that the deposit rate depends on this temperature difference, as well as the cooling surface, the nucleation kinetics and the growth of the crystals on the cold finger surface. The work discusses carefully the experiments design under the light of dimensional analysis. The values of critical temperature differences are relatively small and show that the encrustation is easily attained in the offshore petroleum flow. The methodology implemented is simple and allows the prediction of very important information about the mechanism of paraffin encrustation that could pave the way to avoid paraffin deposition in offshore petroleum production

due to high temperature differences between the heat petroleum sink source and the cold seawater.

The flow assurance in subsea systems requires both the prevention and the removal of the solid deposits that could block the continuous flow of the crude oils. The present work's main interest is the paraffin that may cause the blockage. However, it should be mentioned that the blockage can also happen with hydrates, asphaltenes, stains and sands [95]. Despite the enormous cost of prevention, the problem of paraffin deposition can cause a loss of millions of dollars per year worldwide, because it reduces and/ or defers the production. There is an increase of the nominal capacity loss and of the operational risks, equipment losses, loss in the treatment efficiency and environmental risks [96-98].

The formation of paraffin in the bulk of the petroleum is a crystallization process in solution, so, it is a transition phase process, and as such, it can be studied with the approach of crystallization classic theory and more particularly with the scale formation approach [96,97].

To understand the wax deposits, or paraffination, the methodology developed by Ny'vlt [97] was used to study the scale in binary mixtures, extending it for the petroleum paraffin formation.

The dimensional analysis through a static simulator, which is called cold finger, was used to determine the critical temperature of the deposition, the thickness of the deposition and the critical time for the beginning of the deposition. This study establishes an important relationship between the Ny'vlt's [97] methodology and the dimensional analysis. Here, the identification of the several dimensional parameters that can be experimentally established consolidates an applicable correlation in the field. In the laboratory, by using the static simulator, paraffin deposition in pipes can be verified, yielding an estimation of the obstruction or reduction of the internal pipe diameter in the production streams.

It is important to have in mind that several other works on the same paraffin deposition have been produced before. This includes contributions for the North Sea oil [8, 99, 100] as well as other from USA researchers [101-103]. Of course, these references cannot be ignored. As explained before, however, the present work's main contribution is to apply the Ny'vlt [97] methodology to the paraffin deposition as will be shown next.

Crystallization is a process such that a solid ordinate structure is produced from a disordered phase. The crystallization of paraffins can be divided in three stages. The

first is the nucleation stage. The formation of crystalline nuclei, nucleation, is a process that will determine the product crystal size distribution. So, when the nucleation occurs, and the temperature stays below the nucleation temperature and inside the metastable zone, in this stage, the homogeneous nuclei of crystals appear, and the crystal paraffins will increase. The second stage is the crystal growth, in which the mass transport of the solute in the nuclei direction occurs, which was formed in the nucleation stage. The third possible stage is the agglomeration, in which the junction of growing crystals occurs, creating agglomerates with larger dimensions [104, 105].

During cooling, an extremely high supersaturation can happen mainly in the cooling surfaces, generating a huge amount of small crystals by nucleation. If these crystals were not dragged by system agitation and turbulent flow, they can stick to each other and to the cold surface, causing the deposition. Once the deposition in the surface is formed, it will behave as a thermal insulation of the system. The deposition rate is a function of the temperature difference, the quality of the cooling surface (roughness) and the growth and nucleation kinetics.

As said before, the formation of paraffin deposits in heat exchange surfaces, in other words, the formation of deposits

in subsea pipelines or in the bulk of the fluid, can defer seriously the production of petroleum: Deposits not only reduce the production rate but also the need to remove deposits from time to time requires costly plant shutdown periods. To better understand this problem, the work has proposed the following experiment, where the dimensional analysis has been applied to correlate the experimental data.

The foundation of the dimensional analysis method, independent of the method that will be employed in the determination of dimensionless parameters, began listing all the parameters that affect the phenomenon.

All the relevant variables have been included in the proposed relation. If the suspicion goes strange to the phenomenon, an extra parameter π can result; however, the experience will show that it can be eliminated from consideration [106].

In order to determine the dimensionless groups, six steps will be followed:

Step 1 List and count the variables involved in the problem. (If any important variables are missing, dimensional analysis will fail.) Let the number of variables be n .

Step 2 List a group of fundamental primary dimensions relevant for the problem which are in the first case (MLT θ) respectively the dimensions of Mass, Length, Time and

Temperature. Let the number of fundamental dimension be k (which is 4 in this case).

Step 3 Express the dimensions of all variables of steps in terms of fundamental dimensions. Then construct the dimensional matrix which rows correspond to the fundamental variables and which columns correspond to the variables. Devise the rank of the dimensional matrix. This rank defines of the dimensional basis which in the case of the present work is $k=4$.

Step 4 Select in the list k convenient parameters that contain separately and exclusively the fundamental dimensions.

Step 5 Form $n-k$ dimensionless groups whose existence is assumed by the rank (in this case k) of the dimensional matrix.

Step 6 Make sure that each obtained group is dimensionless and rearrange the groups to recover groups letter known in the literature.

According to the classical point of view of deposition, the very origin of deposition is the nucleation on the cooling surface, which corresponds to the critical under-cooling, ΔT_{crit} . It should be proportional to the metastable zone width, ΔT_{max} . The critical time of paraffin formation can be obtained from the plot of thermal resistance as function of time, that is, the elapsed time from the beginning of the

experiment to the first increase of the thermal resistance. This critical time of deposition is a function of the metastable zone width [97]. Considering the method presented by [97], the conservation of energy and the heat exchange in the system was verified. The analysis of the temperature variations in the equipment can be compared with the heat transfer in agitated vessel, which depends on the agitator type and on the internal coil for the mathematical modeling. The modeling for the analysis are considered in steady state, as mentioned by Ny'vlt, for the development of the experiment [96]. The tendency of the systems to form encrustations can be tested at laboratory, using a simple apparatus to evaluate the effect of various parameters on these encrustations formation, simulating the deposition in field conditions through dimensional analysis. The heat Q_2 removed from the cooling surface is in steady state just compensated by the heat Q_1 brought to the suspension by the hot bath.

Modeling the experiment as suggested by Ny'vlt for the convection, we have Eqs. (1.3) and (1.4):

$$Q_1 = U_1 A_1 (T_H - T)t \quad (1.3)$$

$$Q_2 = U_2 A_{co} (T - T_w)t \quad (1.4)$$

Where the variables are defined in the nomenclature. In steady state, $Q_i = \text{constant}$. Then making $Q_1 = Q_2$, the result is Eq. (1.5):

$$U_1 A_1 (T_H - T) = U_2 A_{co} (T - T_w) \quad (1.5)$$

Without deposit, then Eq. (1.4) may be written as:

$$U_1 A_1 (T_H - T) = U_2 c A_{co} (T_o - T_{wo}) \quad (1.6)$$

Making the simultaneous application to conduction and convection in a steady state and making the analogy between the heat flow and the electric flow, we obtain the global heat transfer coefficient that is given by Eq. (1.7):

$$1/Uc = 1/h_i + (\sigma s/\lambda s)(dco/dcm) + (1/h_{ci})(dco/dci) \quad (1.7)$$

This is a general relationship of the global heat exchange coefficient between the coil (cold finger) and the petroleum vessel, that is, for the external part of the cold finger, with agitation with a clean surface.

And for surface with encrustations (deposit), the correct equation is given by Eq. (1.8):

$$1/Uc = 1/h_i + (\sigma s/\lambda s)(dco/dcm) + (1/h_{ci})(dco/dci) + (\sigma_i/\lambda_i)(dco_i/dcm_i) \quad (1.8)$$

Defining $T_o - T_{wo} = (U_1 A_1)/(Uc A_{co})[T_H - T_o]$ and $T - T_w = (U_1 A_1)/(U_D A_{co})[T_H - T]$, the subtraction of these last two equations yields Eq. (1.9):

$$(T - T_w) - (T_o - T_{wo}) = (U_1 A_1)/(U_D A_{co}) [T_H - T] - (U_1 A_1)/(Uc A_{co}) [T_H - T_o] \quad (1.9)$$

On the other hand, combining the global heat transfer coefficient of incrustated surface (Eq. (1.8)) from the global

heat transfer of clean surface (Eq. (1.7), the result is given by Eq. (1.10) :

$$\delta i / \lambda i + 1/Uc = 1/UD \quad (1.10)$$

Using Eq. (1.10) in Eq. (1.9), the result is Eq. (1.11) [107].

$$(T - T_w) - (T_o - T_{wo}) = [U_1 A_1 / \lambda i A_{co}] [T_H - T] \sigma i - U_1 A_1 / U c A_{co} (T - T_o) \quad (1.11)$$

or

$$\sigma i = \{ (1 + [U_1 A_1 / U c A_{co}] - (T - T_o) + (T_{wo} - T_w)) / \{ (U_1 A_1 / \lambda i A_{co}) (T_H - T) \} \} \quad (1.12)$$

Considering $T_{wo} = T_w$, the result is Eq. (1.13):

$$\sigma i = \{ (1 + [U_1 A_1 / U c A_{co}] / (U_1 A_1 / \lambda i A_{co}) \} \{ (T - T_o) / (T_H - T) \} \quad (1.13)$$

Introducing C such that

$$\{ (1 + [U_1 A_1 / U c A_{co}] / (U_1 A_1 / \lambda i A_{co}) \} = C \quad (1.14)$$

Then using Eq. (1.14) in Eq. (1.13), the result is Eq. (1.15):

$$\sigma i = C \{ (T - T_o) / (T_H - T) \} \quad (1.15)$$

Eq. (1.15) may then be used to determine the thickness of the deposition.

When the cold finger is operated continuously in isothermal conditions, Eq. (1.16) can be applied directly:

$$Q = UA\Delta T \quad (1.16)$$

When there is a difference between the temperature in the entrance and in the exit of the cold finger, the correct equation is Eq. (1.17):

$$Q = U_c A_c \Delta T_{ln} \quad (1.17)$$

where

$$\Delta T_{ln} = (T_{we} - T_{wo}) / \ln \left\{ (T - T_{wo}) / (T - T_{we}) \right\} \quad (1.18)$$

The dimensional analysis will follow step 1–step 6 in a more practical manner. We start with Eq. (1.18) [107].

$$\sigma_i = f(A_1, A_c, T - T_o, T_H - T, T_{wo} - T_w, U_1, U_c, \lambda_i) \quad (1.19)$$

Then rearranging the three temperature variables, it is possible to get two non-dimensional groups, such that the result is Eq. (1.20) [107].

$$\sigma_i = f(A_1, A_c, T - T_o / T_H - T, T_{wo} - T_w / T_H - T, U_1, U_c, \lambda_i) \quad (1.20)$$

Proceeding pragmatically once more with the other variables, the results is Eq. (1.21).

$$\sigma_i U_1 / \lambda_i = f(A_1 / A_c, U_c / U_1, T - T_o / T_H - T, T_{wo} - T_w / T_H - T) \quad (1.21)$$

In summary, since $\mathbf{n} = \mathbf{9}$ from Eq. (1.19), one gets $\mathbf{n}_k = \mathbf{5}$ yielding only five non-dimensional groups, which have been rearranged according to step 4 mentioned in Section 2.

The main result is the group $\sigma_i U_1 / \lambda_i$ which gives another consistency for Eq. (1.13) [107].

For the calculation of the film coefficients, the work should apply the experimental analysis together with the dimensional analysis. For the heat transfer coefficients, it necessary to observe that the physical properties data is necessary and the system should be designed geometrically

in a similar way to the agitated vessel for which the equations were developed.

The deposit thermal resistance is given by Eq. (1.22):

$$\sigma_i / \lambda_i = 1/UD - 1/U_c = (U_c - U_D)/(U_D U_c) \quad (1.22)$$

After the formation of the paraffin deposit layer in the pipe wall, the convective heat transfer will be established between the paraffin deposit and the fluid.

The thermal resistance due to heat conduction through the paraffin layer is directly proportional to the increase of paraffin layer in the pipe wall.

The initial steady state, established with the clean cooling surface, will be impaired when the encrustation is formed, and it will be indicated by the rise of fluid temperature difference [97].

1.7. FLOW CHARACTERISTICS OF WAXY CRUDE OILS IN LABORATORY LOOPS:

Transportation is a major aspect of heavy oil exploitation. Methods employed in the transportation of heavy and waxy crudes can be classified as conventional and nonconventional. The most common conventional methods are heating, blending with some light crudes or solvents, or slug flow [108]. Pipeline heating is not practical and slug flow is a less used technique [108]. On the other hand,

availability of diluent fluids in proximity of the production site is crucial to the success of such a method, although doing so, will affect somehow the feedstock properties. The non-conventional methods most commonly encountered are the addition of chemicals and water to the crude [108]. In Canada, before the heavy oil recovered from the Cold Lake can be pipelined, its viscosity must be reduced, at significant cost, through addition of up to 30 wt% of natural gas condensate [108]. It is important to note that for pipeline transportation of crude oils, viscosity specification recommended in Europe and North America is $25C_{St}$ at $50\text{ }^{\circ}\text{C}$ [109]. The dynamic viscosity for pipeline specification for Canadian crudes is 35 cP at $11\text{ }^{\circ}\text{C}$.

Waxy crude oils are characterized by a high content of paraffin, a mixture of heavy hydrocarbons, called n-alkanes, usually ranging from $C_{18}H_{38}$ to $C_{40}H_{82}$. The presence of paraffin can cause severe troubles during all the working processes of these oils. It is well known that, in special conditions of pressure and temperature, paraffin begins to crystallize and that, once the crystals are formed, they show a strong tendency to aggregate. The formed agglomerates can turn the oil into a highly viscous material, which can be hardly transported through pipelines. Since the temperatures at which paraffin crystallize are not extreme (usually

between 10°C and 30°C), the problem of paraffin crystallization affects most part of waxy crude oils we can find in nature.

The temperature at which paraffin starts to crystallize is commonly known as Cloud Point, whereas the temperature at which crystals begin to agglomerate is usually called Pour Point. Pour Point is typically $10\text{-}15^{\circ}\text{C}$ lower than the Cloud Point. As showed in [35, 110-113], for temperatures higher than the Cloud Point, waxy crude oils behave like Newtonian incompressible viscous fluids, while if the temperature is below the Pour Point, their behaviour becomes distinctly non-Newtonian. In the presence of paraffin crystals the oil clearly shows a Bingham behaviour, meaning that there is a yield shear stress which must be overcome in order to have the oil flowing.

The flow properties of waxy crude oils are actually more complex. The viscosity and the yield shear stress have a strong dependency on the thermal history and on the mechanical history of the fluid, and viscosity can be greatly reduced by a continued shear, indicating a kind of thixotropy. Our analysis is focused on the flow of a waxy crude oil through an experimental loop. This is essentially a straight portion of a closed cylindrical loop in which the oil is being circulated by a constant applied pressure gradient. In this

situation the oil circulating is always the same and no paraffin can be added or removed. Even though the loop system is different from real plants (where fresh oil is continuously supplied to the pipe), it actually provides a good tool for analyzing the rheological properties of waxy crude oils in dynamical conditions. In the present paper we will study the dynamics of a waxy crude oil in a non-isothermal situation, taking into account that part of the precipitated paraffin is transported to the pipe wall driven by thermal or mechanical effects. As a consequence, a solid paraffin layer grows at the pipe wall, influencing the whole dynamics. We will formulate a mathematical model for the entire process and, after performing a quasi-steady approximation, we will prove the well posedness of the corresponding free boundary problem.

Crude oils in many reservoirs throughout the world contain significant quantities of wax, which can crystallize during production, transportation, and storage [114]. This can cause severe difficulties in pipelining and storage. At sufficiently high temperatures, the waxy crude oils (i.e., oils which contain a great deal of wax), although chemically very complex, are simple Newtonian fluids. As the temperature is reduced, the flow properties of these crudes can radically change from the simple Newtonian flow to a very complex

behavior due to the crystallization of waxes [115]. The waxes basically consist of n-alkanes, which crystallize (as soon as the equilibrium temperature and pressure is reached), forming an interlocking structure of plate, needle, or malformed crystals [116]. When the oil is cooled to a temperature lower than the crystallization point (generally called pour point), the crystals, growing and agglomerating, entrap the oil into a gel-like structure. Consequently, the flow properties of the oil become distinctly non-Newtonian. A yield-stress (the minimum stress required to start the flow) can be detected. Moreover, the flow properties are complicated by their critical dependence upon their mechanical and thermal "history." The viscosity of the waxy crudes can be greatly reduced by a continued shear. This fact seems to indicate a kind of "thixotropy." The disintegration of large wax agglomerates appears to be the primary cause of the lower viscosity [11].