

CHAPTER I

**Lubricant Industry: Application of additives specially, polymers
and ionic liquids**

I.A. GENERAL INTRODUCTION

Lubrication means improving the smoothness of movement of one surface over another and the materials, having such capability of lubrication, are called lubricants or lubricating agents. Lubricants are usually liquids or semi-liquids but may be solids, gases, or any combination of solids, liquids, and gases [1]. The applications of lubricants are:

- (a) It reduces the friction between the surfaces of mated moving parts and therefore lowers energy loss due to friction.
- (b) It slows down the wear of parts by changing the type of friction, removes heat from parts, when they tend to get hot during operation and keeps grit out of the clearances between parts.
- (c) It protects parts from corrosion.
- (d) It reduces shocks between mated parts.

In automotive industry for modern engines and high-speed machinery demand of lubricants is increasing day by day and hence a great amount of research body has been engaged to develop high performance lubricating agents [2]. Especially during the last decades the demands of oils and lubricants have increased vastly [3]. Modern lubricants are formulated from a wide range of base fluids and chemical additives. It is the base fluid that provides a fluid layer between the moving surfaces to keep them apart from each other which resist the friction. It minimizes the heat evolved during operation and eliminates the wear particles. The development of modern engine and transmission technology would have been impossible without advanced lubricant additives chemistry and lubricant formulation. Modern engine oils contain a wide range of additives, which are blended with base oils to form a complete package capable of meeting demanding performance requirements [4]. Additives for the future lubricants are required to maintain oil consumption under control over the service life of the equipment and at the same time, they have to provide a high level of thermal stability with enhanced low-temperature fluidity. They are required to reduce the oxidative or thermal degradation and wear of the oil, minimize rust and corrosion, lessen the deposition of harmful deposits on lubricated parts, and

prevent destructive metal to metal contact. Many types of additives have been developed to satisfy special lubrication needs. Some additives impart new and useful properties to the lubricant; some enhance properties already present, while some act to reduce the rate at which undesirable changes such as oxidative or any other degradations, take place in the product during its service life [5]. Today, practically all types of lubricating oil contain at least one additive, and some oils contain additives of several different types as a combination [6]. Different types of lube oil additives are used such as detergents-dispersants [7], antioxidants [8], corrosion inhibitors [9], extreme pressure agents [10], viscosity index improvers [11] and pour point depressants [12]. Before going into the details about the lubricants some terms associated with lubrication and its requirement need to be discussed first here.

I.A.1. Additives

Additives are those substances which fulfill the desired properties of lubricating oil by adding some specific properties or enhancing the existing properties or sometimes resisting some. Typically they are chemical substances mostly, with a polar head group and a nonpolar hydrocarbon chain. According to requirement different types of additives are blended with the lubricating oil as stated below.

I.A.1.a. Pour Point Depressants (PPD)

The pour point of a fluid is the lowest temperature at which it will pour or flow when it is chilled without disturbance under prescribed conditions. Most mineral oils contain some dissolved wax and when the temperature decreases, this wax begins to separate out as crystal from the liquid state and gradually as the temperature lowers further it develops a 3-D wax matrix which entraps the oil and ceases its fluidity [13]. Certain high molecular weight polymers function by inhibiting the formation of a wax crystal structure that would prevent oil flow at low temperatures [14–20]. The chemical additives are synonymously referred to as pour point depressants, flow improvers, paraffin inhibitors, or wax modifiers. Pour point depressants have no effect on the crystallization temperature or the number of crystals formed. Their most widely accepted mechanisms of action include adsorption, co-crystallization, nucleation, and improved wax solubility [14, 21–24] as shown in the **Figure I.A.**

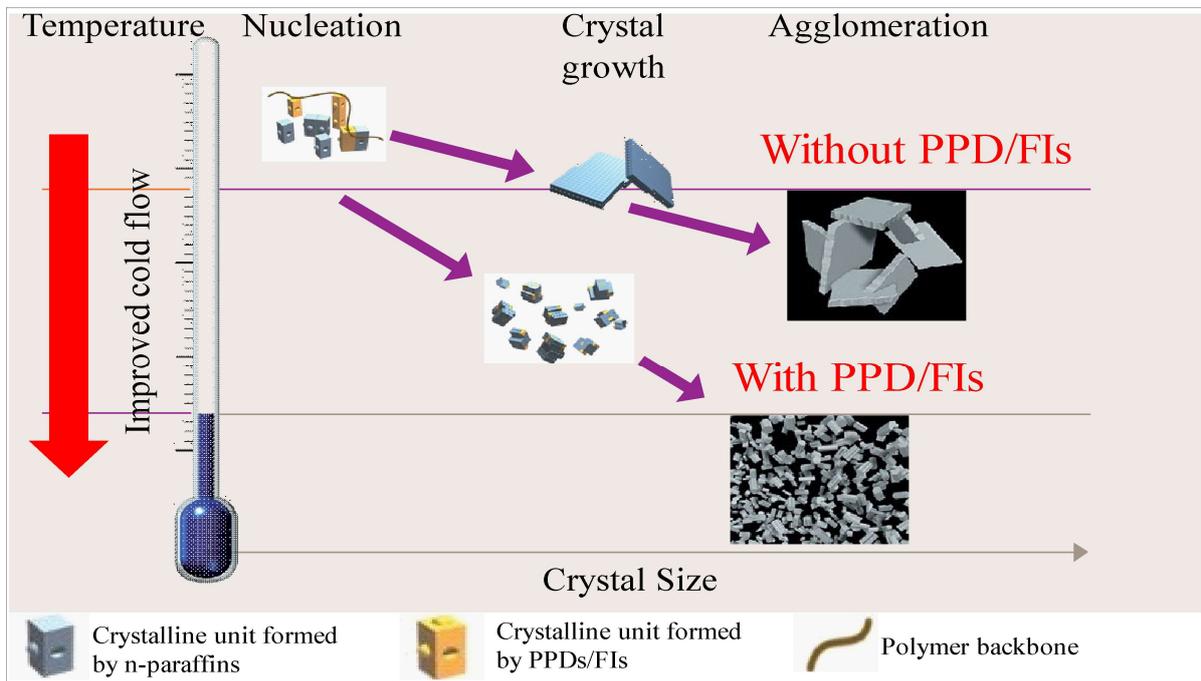


Figure I.A: Diagram showing how PPD/FI works

The effectiveness of a pour point depressant depends on the chemical composition of the polymer, its structural characteristics and the length of the alkyl side chains [25–27]. Although the removal of the last traces of wax from oils is difficult and expensive, pour point depressants provide an economical and of course effective means of facilitating the proper flow of the oil in an engine at low temperatures [28–30].

I.A.1.b. Viscosity index improver (VII)

Viscosity is one of the most important parameters of a lubricant and must be kept under limits to act accordingly. Addition of oils with lower viscosity, contamination by fuel and solvents or any lubricant degradation may cause reduction in a lubricant viscosity. On the other hand, presence of insoluble contaminants, pronounced oxidation and water contamination may increase the viscosity of a lubricant [31]. The rate at which viscosity changes with temperature is known as the viscosity index (VI) of a fluid [32]. The higher the VI, the more constant is its viscosity. In general with increase in temperature viscosity of the oil decreases but viscosity index improvers (VIIs) are those substances which when added to the oil in small amount, actually reverse this

general phenomenon which may be explained taking examples of polymers, widely used as VIIs. When polymers added in small quantity to the oil in normal temperature, they are supposed to exist as tight coils in the oil and held in colloidal suspension so that their effect on viscosity is minimized. As the temperature increases the solubility of the polymers also increases and these coils unfold themselves into open chain configuration which has larger volume and hence higher viscosity is observed at higher temperature [4, 33 & 34]. Viscosity modifiers are a key ingredient in modern lubricants. They modify the flow characteristics of lubricants and are required for most multi-grade fluids. They enable the oil to be used over an extended temperature range eliminating the need for seasonal oil changes. Performance of viscosity index improvers depends on the behavior of the polymer molecules in the oil, polymer solubility, molecular weight and their resistance to shear degradation [35].

Stability of viscosity modifiers plays a key role which is expressed in terms of **shear stability index**. Stability against mechanical shear or stress is termed as shear stability. When polymers are subjected to a high shear stress in equipment such as between piston rings and a cylinder wall, between gear teeth or across the pressure relief valve of a hydraulic system, the random coil configuration the polymer is severely distorted. In extreme cases, bond energies can be exceeded, and the polymer breaks down. Thus the polymer loses its effectiveness under shearing conditions. Resistance against such distortion at severe mechanical shear is called shear stability of a particular additive. Distortion or breaking of a polymer is associated with loss of its properties most importantly viscosity loss. When a polymer in base oil undergoes degradation two kinds of viscosity loss is observed such as permanent viscosity loss (**PVL**) and temporary viscosity loss (**TVL**), the former being mostly used for shear stability measurement and expressed as –

$$\text{PVL (\%)} = [(V_i - V_s)/V_i] \times 100$$

[Where, V refers to Kinematic Viscosity (KV) at 100°C.

V_i = KV of the oil after addition of polymer

V_s = KV of the oil doped with polymer after shearing]

Shear stability is expressed in terms of permanent shear stability index (**PSSI**) which is expressed as –

$$\text{PSSI (\%)} = [(V_i - V_s) / (V_i - V_o)] \times 100$$

[V_o = KV of the oil before addition of polymer and others represent same parameters as above.]

Shear stability under particular shearing condition depends on various factors starting from the structure, molecular weight of the polymer to its concentration in the base oil and even on the base oil used also. Some other factors also play important role here. Various studies have suggested that increasing molecular weight of the polymer also increases the polymer volume in an oil solution [36] and consequently, a polymer with higher molecular weight will impart higher viscosity index than a polymer of the same type with lower molecular weight [37]. Further, the amount of branching can also be critical to the polymer behavior. A disadvantage of long-chain branching is that it reduces the thickening efficiency and shear stability lubricating oil, relative to simple copolymer of similar molecular weight and composition [34]. On the other hand, the viscosity index increases with increase in the chain length when the degree of branching is fixed. In addition, it has been seen that the pour point decreases with increase in the degree of branching [38].

I.A.1.c. Extreme pressure (EP) additives

These are a special class of boundary lubrication additives which react with the metal surface to form compounds with lower shear strength than the metal. This low-shear compound provides the lubrication.

I.A.1.d. Friction modifiers

They can either adsorb or react with the surface to reduce friction by forming a very low shear-strength film. Without a friction modifier, the friction coefficient in the transmission would increase at low-sliding velocity where surface asperities make contact which would result in rough shifting and high-transmission in vehicles.

I.A.1.e. Anti-wear additives

In sliding contacts, physical loss of material occurs which is called wear. It occurs due to highly stressed interfacial zones where a local mechanical loss happens influenced by environmental factors. Additives which resist such loss are called anti-wear additives. Zinc dialkyldithiophosphate (ZDDP) has been widely utilised as anti-wear additives.

I.A.1.f. Detergents and dispersants

To prevent carburettor fouling and engine deposits detergent additives are required and on the other hand dispersant additives are required to combat sludge in crankcase engine oils. Polybutenyl succinimide is one of the mostly used detergent and dispersant additives. Dispersants in general are expected to be beneficial for wear protection and it has been demonstrated that succinimide dispersants can partially remove films formed by ZDDP under rubbing conditions [39]. The benefit of dispersants of different molecular weight and functionality can be seen from a number of studies but many of them are complicated by neglecting the influence of dispersant upon viscosity and hence oil film thickness.

I.A.1.g. Corrosion and rust inhibitor

Environmental effect, excessive friction between the surfaces or presence of impurities may lead to corrosion. The chemical substances which can decrease the rate of such corrosion are called corrosion inhibitors. It is assumed that the inhibitors form a coating between the corrosive substance and the metal and thus surround the metal or related object. Corrosion inhibitors are commonly found in the form of spray in combination with lubricant. Rust inhibitor is also another form of corrosion inhibitor. It has been designed to slow down the oxidization process in metals which have been exposed to oxygen and water and begun to rust. It is also obtained as anti-rust sprays in the market which can be applied to metal surfaces to stop rust from forming and create a protective barrier that lubricates the surface and prevents further rust.

I.B. LUBE OIL

During the process of crude oil refining, after removal of gas oils and lighter fractions by distillation, the remaining more viscous portion produces the base fluids of lubricating oil or lube oil. Refined petroleum base oils are the major source for formulation of lubricating oil due to easy availability, excellent performance and cheaper price. There is another class of base fluid called non-petroleum base fluid, used in special cases where petroleum base oils are in short supply or where substitution by natural products is practicable or desirable.

I.B.1. Lube oil from crude oil

To prepare the base fluids, first of all proper selection of crude oil is required since every crude oil varies from each other in terms of content, composition ratios, boiling range distribution of their components etc. Hence according to requirement thorough study is required to obtain much needed physical and chemical properties in the base fluid essential to formulate lubricant. In the refinery base oil extraction from crude involves a number of steps such as:

1. **Distillation:** To separate the desirable lube components from the bulk of the crude oil distillation is required where both the components of too low boiling point and too high boiling point are removed leaving the lubricant boiling range distillates.
2. **Removal of aromatics:** To obtain oil with better VI and stability, aromatic components are removed and the oil is made rich in saturated hydrocarbons.
3. **De-waxing:** To control low temperature properties of the base oil wax is removed as far as possible.
4. **Finishing:** To improve the colour and stability of the base oil, traces of polar components are removed.

The yield of base oil after these processes depends on the amount of desirable components in the lubricant boiling range. After obtaining an appropriate quality lubricant base stock, lubricating oil is formulated by blending required additives with it. But modern automotive engine oils and transmission fluids require additives as a package that meets certain industry-

specified testing criteria whereas in other cases, such as metalworking fluids and greases individual additives are furnished to the base stock [40]. It may be mentioned here also that lubricant additives are chemical substances mostly organic or organometallics which are added to oils or base stocks in quantities of a few weight percent to improve the lubricating capacity and durability of the oil. Lubricant additives fulfill some specific purposes such as resisting wear, improving the oxidation resistance, controlling corrosion and contamination by reaction products, reducing excessive decrease of lubricant viscosity at high temperatures, and enhancing lubricant characteristics by reducing the pour point and inhibiting the generation of foam [41]. But to meet the expectation of latest technology, multifunctional additives are in high demand which can satisfy multiple requirement single handedly.

I.B.2. Dependence of additives on base stocks and vice versa

Just like lube oils require additives to act as good lubricant, the additives also require a quality grade lube oil to act appropriately. Lubricant base stocks influence additive performance through two main functions; solubility and response. For example, performance of surface active additives depends largely on their ability to get adsorbed on the machine surface at the proper time and place. Base stocks with poor solubility characteristics may allow these additives to separate before they can fulfill their intended functions. Conversely, base stocks with very high-solubility characteristics may keep the additives in solution, not allowing them to get adsorbed on machine surface. Additive response depends on base stock composition. Natural sulfur, nitrogen, and phenolic inhibitors are removed along with undesirable materials during base stock refining. Removal of these natural inhibitors often results in reduced oxidation inhibition relative to unrefined stocks. However, the natural inhibitors, as well as the undesirable materials removed during base stock refining, often interfere with additive performance. Synthetic base oils, depending on their chemical structure, exhibit very specific solubility characteristics, additive response, and additive compatibility that are sometimes different from mineral oils. The most common synthetic base oils are synthetic hydrocarbons, such as poly-alpha olefins, and esters, such as adipate, azelate and pentaerythritol esters. Synthetic hydrocarbons exhibit excellent additive response but are poor additive solvents.

Esters vary in additive response and are excellent solvents except for additives with which they react to form precipitates. Synthetic oils can be blended with each other or with mineral oil to provide the optimum balance of solubility and additive response.

I.B.3. Problems when different additives are added together

Most modern lubricants require more than one additive to meet all performance demands. In some cases, individual additives are blended directly into the base oil. In other cases, a group of additives are blended into an additive package, which is subsequently blended into the base oil. Since most additives are active chemicals, they can interact in the package or in the lubricant to form new compounds. These interactions can decrease additive effectiveness and lead to insoluble or otherwise undesirable by-products. Additive functionalities frequently depend on their limited solubility in the lubricant. As for example, many lubricants require both an anti-wear additive like zinc dialkyl dithiophosphate (ZDDP) and a dispersant together. To act accordingly, ZDDP must be able to leave the bulk of the lubricant and adhere to the machine surface to function as a wear inhibitor. But in presence of a dispersant in the same lubricant, the action of ZDDP is prevented since the dispersant can hold the ZDDP in solution rather letting it go to the surface. Surface active additives can also compete with each other such as both wear inhibitors and some rust inhibitors function by adsorbing on metal surfaces and they compete for the same surface. The wear inhibitor can displace the rust inhibitor on the surface and be detrimental to rust inhibition. Likewise, the rust inhibitor can displace the wear inhibitor.

I.C. CRUDE OIL

Crude oil is supposed to be the biggest source of energy all over the world due to its higher and cheaper availability compared to other energy resources. In general, if the crude oil has an API (American Petroleum Institute) gravity equal to or less than 20, it is considered as heavy and if the API is 10 or less than 10 the oil is termed as extra-heavy crude oil or bitumen. Heavy crude oil and bitumen resources are considered to be more than double the conventional light oil reserves throughout the globe. Abrupt increase in population and constant industrialization result in higher demand of energy consumption which on the other hand results in declining source of lighter oil and increasing demand of the higher crude.

I.C.1. Composition of crude oil

Crude oil is basically the result of a complex combination of chemical and physical processing on the buried remains of plants and animals over millions of years. Depending on the geological background, the composition of crude oil varies a lot which reflects in its properties.

I.C.1.a. Hydrocarbons

Basically crude oil is a complex mixture of various hydrocarbons as given below:

1. **Alkanes:** Saturated linear or branched-chain aliphatic hydrocarbons known as paraffins with the general formula C_nH_{2n+2} . When $n = 13-60$, paraffins exist as solids. When the $n = 13-36$ ($C_{13}-C_{36}$), softmushy waxes are observed. This is also called paraffinic hydrocarbons or macrocrystalline waxes. Hard crystalline waxes have 30-60 or more carbons ($C_{30}-C_{60}$) in the chain. It is also called naphthenic hydrocarbons or micro-crystalline waxes. Paraffin is generally assumed to be in solution
2. **Alkenes:** Unsaturated hydrocarbons known as olefins but comparatively rare in crude oils. Certain refining processes produce large amounts of alkenes by cracking or dehydrogenation process.
3. **Alicyclics:** Saturated cyclic structures based on five and six-membered rings, known as naphthenes.

4. **Aromatics:** Cyclic structures with conjugated double bonds, mainly based on the six-membered benzene ring.

I.C.1.b. Non-hydrocarbons

Many organic compounds in crude oil incorporate other elements such as S, N, O etc, sometimes within ring structures or as functional groups attached to a hydrocarbon structure. Organosulphur compounds are generally much more prevalent than nitrogen or oxygen containing molecules. The principal oxygen containing molecules are carboxylic acids as either saturated aliphatic acids or cycloalkanoic acids (naphthenic acids). Traces of phenols and furans may also occur.

Besides heavy crudes have complex components of high molecular weight and high polarity, called asphaltenes. Asphaltenes are usually referred as the heaviest, most aromatic part of crude oil. It comprises the active surface area of crude oil [42–44], which is insoluble in light paraffin such as n-pentane, n-hexane, and n-heptane, but soluble in light aromatic compounds such as benzene, Toluene or pyridine. The structure of asphaltene is really complex. It is assumed that they have a nucleus composed of one or more poly-crosslinked aromatic hydrocarbons (PAH) attached to aliphatic chains. Asphaltenes have heteroatoms such as nitrogen, sulfur and oxygen indicating the presence of functional groups such as carboxyl, ketones, aldehydes, benzothiophenes, dibenzothiophenes, naphthenobenzothiophenes, alkyl sulphides, alkyl aryl sulphides and aryl sulphides. Some metals such as vanadium, iron, and nickel are also present there [45–47]. Presence of highly strong C=S bonds drastically increases the viscosity of the crude [48, 49]. In addition, asphaltenes are amphiphilic in nature and hence they tend to self-associate and form large aggregates which also increase the viscosity of heavy crude.

I.C.2. Handling problems of crude oil

Although heavy and even extra heavy crude oil have been considered to be the biggest source of energy required globally, their production is a bit challenging area. Especially high pour point and high viscosity are the main barriers against their high production and even transportation via pipeline to various refineries. In normal conditions paraffins are soluble in the crude, but changes

in temperature and/or pressure, loss of volatile components, etc., paraffin precipitates out as wax and adheres to the surfaces in the surrounding environment [50]. As the temperature decreases, the higher molecular weight wax becomes less soluble, solidifies, and separates out from the liquid phase. The temperature at which wax begins to precipitate out from the crude oil is called the wax appearance temperature (WAT) [51]. If sufficient wax is deposited over time, portions of the production system such as wellbores and flow lines can become partially or totally blocked thus having a significant production loss. Studies have suggested that under the most favorable conditions, the waxes form an orthorhombic lattice, but changes in conditions bring about a mixture of orthorhombic and hexagonal lattices also. In the pipelines also, wax deposition occurs as a result of lateral transport by diffusion, shear dispersion, and Brownian diffusion [52] where the temperature is very low or becomes very low seasonally.

From preheat exchangers to crude oil unit heaters, and distillation columns there occurs significant economic and operating cost penalties. Apart from increasing the cost of processing and the maintenance such problems also limit the flexibility of processing different types of crude oils. Presence of undesirable components such as asphaltenes, heavy metals and sulphur also contribute to the high viscosity of crude oil which account for the extremely low mobility of the crude in reservoir. Also in the pipelines which are the most convenient ways to transport crude oil from the production field to the refineries, moving heavy crude oil and bitumen is extremely challenging because of their inability to flow freely since high viscosity causes huge pressure drop in the pipeline and to overcome it huge energy i.e. high pumping power is required which results in increase in cost and at the same time huge production loss every year.

I.C.3. Remedies

Previously when there were enough sources of easily extractible lighter oils, heavy crude was supposed to be uneconomical to produce and process. But constant industrialization and growing demand of energy have forced the mankind to pay attention to the heavy and even extra heavy crude reserves since ever decreasing and limited source of lighter oils alone cannot quench the ever increasing thirst for energy globally. Hence variety of remedial treatments has been

employed to overcome the challenges associated with crude oil from production to transportation.

I.C.3.a. Mechanical method: pipeline “pigging”

Pigging refers to scouring action of a device to remove the wax deposited on the wall inside the pipelines. But to carry out the process, the system needs to be shut down for 1 to 3 operating days which causes severe production loss [53].

I.C.3.b. Injection of naphtha or CO₂

It is a very common and well known technique for viscosity reduction to improve the production of heavy and extra-heavy oil both at the site and at the surface [54–56]. However, these techniques may lead to precipitation of asphaltenes and their deposition in porous media through the production system [54, 55] which in turn may reduce the porosity and permeability of the system. As a result a kind of permanent damage occurs there at the reservoir condition which reflects in huge production loss in the long run.

I.C.3.c. Thermal treatment

After long period of shut down, to start up the pumps and carry the oil to the refineries thermal treatment is required by hot fluid or electric heating to remove wax for short flowlines and downhole. Having a good thermal insulator along the pipeline is required to maintain the temperature of the system above cloud point of the crude. But since it is a kind of local treatment its effectiveness is less. Besides this method is economically very costly, when large distances are to be transported [57, 58].

Catalytic cracking method may also be mentioned here under the thermal treatment for viscosity reduction. Since asphaltenes and resins are believed to be the main reason behind high viscosity of heavy crude, Yufeng et al. [59] investigated the catalytic cracking of asphaltenes and resins by converting them into lighter molecules using nickel and iron catalysts. However, each thermal process demands high amounts of energy and the use of costly agents necessary to carry out the reactions typical of each process.

I.C.3.d. Dilution method

Dilution method is probably the oldest and the most common method for viscosity reduction on surface since 1930's [54]. This method requires addition of light hydrocarbons, organic solvents like methyl tert-butyl ether (MTBE), tert-amyl methyl ether (TAME), etc or alcohols like pentanol, hexanol etc, gasoline and middle distillates like kerosene in the ratio of 0–20% for heavy crude oil and 25 to 50% for bitumen [60]. But this process comes with its own drawbacks. To carry the diluents along with the crude, there requires another parallel pipeline which itself is a cost worthy process and after the use, oil recovery is another ordeal. Moreover, determining perfect dosage of suitable diluents for a particular crude oil is essential since any mismatch with the quantity may result further deposition of asphaltene and paraffin in the pipeline. Hence hard study is needed to determine the required ratio of oil to diluents for a particular crude oil after full analysis of its composition and large variety of parameters associated with its nature. It means dilution method is not as simple as an arbitrary mixing process.

Natural gas condensates were also used as diluents, but their lower production compared to higher requirement for heavy crude production is a barrier against their use. Besides, asphaltenes are not totally soluble in these condensates and as a result flocculation occurs in the pipeline which leads to partial plugging.

I.C.3.e. Annular flow of crude oil

Another way to improve crude oil production apart from viscosity reduction is reducing pressure drop in pipelines by introducing annular flow. Isaacs and Speed [61] first reported this technique where the possibility of the channeling of viscous fluids through the lubrication of the walls of the tube with water required in the range 10–30% was cited [62, 63]. However, this technique also comes with some limitations which include the formation of waves that are created at the interface of the water and the oil and thus hinders the flow [61, 64].

I.C.3.f. Preventive method

Sometimes it is more preferable to prevent a problem or trouble before its occurrence than to find a solution after it gets happened. Hence the causes and pattern of the problems associated with

storage or transportation of crude oil have been thoroughly investigated and some preventive methods have been utilised to resist or diminish the barriers as far as possible. Some of these methods have been discussed below.

Application of additives

Versatile application of chemicals such as surfactants, scavengers, emulsion breakers, polymers, nanoparticles and other chemical additives as wax modifier and viscosity reducer for crude oil has been studied extensively [65]. So far polymers have gained prominent position among these all in this field. It has been proved in various studies that polymers having long alkyl chain and high molecular weight are good flow improvers for crude oil. Some common polymeric additives are discussed below.

I.C.3.f.1. Ethylene–Vinyl Acetate (EVA) copolymer

Ethylene–vinyl acetate (EVA) copolymer is a linear chain polymer of ethylene and vinyl acetate which has been widely used because of its ability to control the size of the wax crystals [66, 67]. Various studies have been reported about the effect of chain length of EVA on the flow properties of crude oil. As for example, according to Ashbaugh et al. [68] the efficiency of the additive to improve flow ability decreases with the carbon number of the wax crystals. Some studies have also shown the effect of addition of other active systems like methyl methacrylate (MMA), diethanolamine (DEA) etc. on the flow improvement ability of EVA [69, 70].

I.C.3.f.2. Alkyl Acrylate copolymer

Alkyl acrylate copolymers are explored extensively as pour point depressant for waxy crude oils [71]. It contains various sets of alkyl group with carbon number ranging from C₁₄ to C₂₆. Various studies have suggested that the efficiency is influenced by the alkyl chain length and the polarity of the polymer [72]. Again number of studies utilised different combinations of alkyl acrylate with the other co–monomers for further reduction of pour point of crude oil than using only alkyl acrylate polymer [73]. In another study organic nano–clay particles with polyoctadecylacrylate were utilised by Yao et al. [74] which revealed that the pour point of the Changqing waxy crude

oil was reduced by 9°C and viscosity was decreased by 33.8% at 800 mg polyoctadecylacrylate per kg of clay.

I.C.3.f.3. Maleic Anhydride copolymer

Maleic anhydride is known as one of the most active polymerising agents. Its copolymer with styrene or any alkyl esters such as acrylates and acetates have been extensively studied as effective flow improver for waxy crude oil [75–77]. Studies have suggested that longer the chain of the fatty acid in the ester higher will be the effectiveness of the copolymer for viscosity reduction of crude oil which was attributed to the fact that solubility of paraffin wax increased with increasing length of the alkyl chain [75]. Various studies have proved that apart from the alkyl chain length of the polymer, presence of polar group, molecular weight and composition of the polymer are the determining factors for its ability to act as flow improver of crude oil.

I.C.3.f.4. Other Type of Additives

Terpolymers are comparatively newer addition in this field of additives. Castro et al. reported that the viscosity of Mexican crude oil was reduced using the terpolymer consisting of high percentage of styrene and low percentage of n-butylacrylate and vinyl acetate [78]. Another copolymer, synthesized by amination of terpolymer containing monomers of octadecyl acrylate, vinyl acetate and maleic anhydride was reported to depress the pour point of Shengli crude oil by 11°C [79]. Another study suggested that incorporation of the hydrophobic part in the polymer could be effective in enhancing its viscosity reducing property due to the intermolecular association [80]. Nanotechnology also appears as a promising remedial technique in this field. It emerges as a complementary technique capable of competing in both economic and technical ground because of its high potential in improving the mobility of heavy crude by reducing the viscosity through the interaction of minute particles with asphaltenes present in the crude. In addition, the nanometric size of the particles does not represent a problem to plug the pore grooves of conventional crude oil deposits. Its surface has high affinity for the asphaltenes present in the crude, much larger than the affinity between own asphaltene aggregates and thus considerable reduction of viscosity is obtained. Several studies have reported some well designed nanoparticles as efficient viscosity reducers of heavy crude oil [61, 81]. Olusegun Peter

Akinyemi et al. successfully investigated the influence of cheaper natural chemicals, obtained from plant seeds (jatropha, rubber and castor) on the rheological properties and wax deposition tendencies of Nigerian waxy crude oil [82]. An environmentally friendly and cost effective additive for light and heavy crude oils of Oman was reported by Salam K. Al-Dawery and Saleh K. Al-Shereiqi [83]. They used waste bio materials such as fiber of palm tree, date palm kernel and walnut shell materials as viscosity reducing agents on light and heavy crude oils of Oman. In another study by Manojkumar Gudala it was found that addition of 2000 ppm potato starch to the 85% heavy crude oil and 15% water mixture at 40°C decreased viscosity of the crude by 80.24% which is an excellent and very inspiring result [84].

I.D. IONIC LIQUID

Ionic liquids are molten salts composed of large, asymmetric organic cations and usually an inorganic anion having melting point less than 100°C. Usually they are classified based on their cationic part, such as ammonium, imidazolium, pyridinium, and phosphonium [85]. The anionic part commonly consists of chloride [Cl]⁻, bromide [Br]⁻, iodide [I]⁻, hexafluorophosphate [PF₆]⁻, tetrafluoroborate [BF₄]⁻, methanesulfonate [CH₃SO₃]⁻, bis(trifluoromethanesulfonyl)imide [(CF₃SO₂)₂N]⁻, and nitrate [NO₃]⁻ [85, 86]. The physical and chemical properties of the ILs can be modified utilising varied range of cationic and anionic combinations [87].

I.D.1. Properties

Due to large shape, the charges on the ions in ILs usually remain in diffused state and hence the electrostatic force between the ions is highly diminished which accounts for its failure to acquire a regular crystalline shape and opting for the liquid state at room temperature. ILs are unique to exhibit versatile properties such as low volatility, non-flammability, thermal stability, moisture stability, miscibility with organic compounds, good electronic and ionic conductivity and its broad application in electrochemical field [88]. They are often referred to as ‘designer solvents’ due to their ability to dissolve a variety of organic, inorganic and organometallic compounds by simply choosing the proper combination of cations and anions. Some ILs possess amphiphilic structure consisting of both hydrophobic tail groups and hydrophilic head groups with surface activity. Imidazolium-based ionic liquids containing hydrophobic chain longer than four carbon atoms exhibit such behaviour. In addition ILs are considered to be more environmentally friendly in comparison to current alternative solvents and electrolytes [89] and hence are treated as green solvents [90]. Most importantly, availability of various combinations of cation and anion enriched with unique properties, ILs have attained enormous attention over the decade [91] and today variety of ILs are explored with versatile application.

I.D.2. Applications of ILs in automotive industry

Such a promising range of properties along with their potential for controlled reactivity and also their low evaporation, researchers are provoked to explore their application in corrosion

protection [92, 93] and tribology. Especially their extremely low vapor pressure, non flammability and thermal stability even upto temperatures above 200°C are accounting for their capability of lubricating even at increased temperatures and pressure. So far most of the IL based lubricants were investigated at a more fundamental level, but some studies have explored their applications such as in engine lubrication [94–97] and micro–electromechanical machines (MEMs) [98–100]. M. Anand et al have explored the high miscibility and no corrosive behaviour of two phosphonium based ILs i.e. trihexyltetradecylphosphoniumbis(2,4,4-trimethylpentyl)phosphinate and trihexyltetradecylphosphoniumbis(2-ethylhexyl)phosphate and used them successfully as additive in the fully formulated diesel engine lubricants [101]. This study provided a pathway for the used lubricants to recover their tribological performance for further use at the end of service life. Patrick Rohlmann et al. evaluated phosphonium orthoborate ionic liquid as a wear reducing additive in biodegradable oils at steel–steel surfaces in the boundary lubrication regime [102]. Again 1,4-bis(2-ethylhexyl)sulfosuccinate anion–based ILs containing different cation–imidazolium and organoammonium were synthesized and characterized as candidate lubricant additives in synthetic ester oils by Zeyun Wang [103]. Tribological tests on these synthesized ILs which were fully miscible with synthetic ester oil and noncorrosive to steel, revealed effective friction reduction and antiwear functionality. In addition, they worked well with the other typical additives, such as viscosity improver, antioxidant, pour point depressant etc. In another work, three phosphonate ionic liquids such as 1-butyl-3-methylimidazolium *O*-butylphosphonate, *N,N*-dibutylammonium *O*-butyl phosphonate and *N,N*-dibutylammonium *O*-ethyl phosphonate were used as additives in polyethylene glycol (PEG) for steel/steel contact by Yunyan Han et al. and their characterization showed that these ionic liquids improved the tribological performances of the base oil significantly owing to the competitive adsorption between the base oils and the additives and also the chemical reactions between the ionic liquids and the metal substrate [104]. V Pejakovic et al. studied the influence of temperature on tribological behaviour of a sulfate–based ionic liquid with a pyrrolidinium cation as neat lubricant and as additive for glycerol in lubrication of steel–steel contacts and showed that the ionic liquid played an important role in the friction and wear reduction, as well as in the smoothening of the worn surface [105]. Shuyan Yang et al. investigated the tribological performance of IL additives in the mixed lubrication and the

elastohydrodynamic lubrication regimes and evaluated that IL additives could reduce friction and metal wear compared to pure PEG in mild conditions [106]. In another study, ionic liquids were investigated as a possible base oil of next-generation space grease to solve mainly temperature related issues and compatibility with space environment [107]. The newly synthesized perfluoropolyether (PFPE) ionic liquid whose terminal group is an ammonium salt with a carboxylic acid has better frictional properties and has been used for magnetic tapes for about a quarter century because of their good lubricity [108]. Ammonium-based protic ionic liquids (PILs) were tested as lubricant fluids for aluminum-steel contacts by Maria Rita Ortega Vega et al. and they showed that the increase of the anion carbon chain length in the PIL structure reduced significantly the coefficient of friction value [109]. Jun Qu et al. evaluated the anti-wear behavior of an oil-miscible ionic liquid i.e. trihexyltetradecylphosphoniumbis(2-ethylhexyl)phosphate in a base oil at 1.0 wt% concentration under both room and elevated temperatures and reported that the IL and the conventional anti-wear additive, zinc dialkyl-dithiophosphate (ZDDP) worked equally well to prevent scuffing and reduce wear in the room temperature tests, but the IL significantly outperformed ZDDP in the tests performed at 100°C [110]. Patrícia M. Amorim et al. tested imidazolium-based ILs as additives to the base oil PEG to lubricate Si surfaces and found that almost all the additives (2 wt%) led to a decrease in friction coefficient as well as an increase in viscosity [111].

I.D.3. Imidazolium based ILs

Imidazolium based ILs were studied extensively owing to their higher stability than a conventional synthetic oil at 200°C [112], easy adsorption onto a surface, such as phosphonyls and esters [113, 114] and easy variation of alkyl chain length to tune up wear and friction [115–117] according to requirement. From various studies it was determined that the longer the alkyl chain length in the imidazolium group, the lower the wear [118]. Again number of studies suggested that ILs having highly fluorinated anions possess higher thermal stability. Thus imidazolium tetrafluoroborates were hugely utilised due to their ability to exhibit lower friction and wear than traditional lubricants for a number of systems [119, 120]. But ILs are very much expensive compared to mineral base oils and synthetic base oils and hence they cannot be used solely in large volume. On the other hand, they may be used as a lubricant additive where a small

amount of IL is doped into base oil, but provides a large difference to the friction and wear [121]. But there comes a problem with solubility of the IL in base oil. Generally ILs due to their polarity, are not so easily soluble in non polar base oils [122, 123] but it is seen that longer the alkyl chain length on the imidazolium group, higher is the solubility of IL in base oils [124].

I.E. REFERENCES

References for chapter I are given in bibliography section (page 114–124).