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SYNTHESIS AND EFFECT OF FLOW IMPROVER FROM ARACHIS OIL ON CRUDE OIL OF WESTERN ONSHORE OF INDIA

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Abstract: Crude oil which contains high wax content causes problem during production, storage and transportation. When temperature decreases, wax separate out from the crude oil and deposit on the wall of the tanker or pipeline, hence the flow of crude oil is Decreases. There are some techniques to minimize the problems occuring during Transportation of crude oil due to wax contain. This research aim to determine the effect of laboratory synthesized pour point depressant which improves the property of waxy Crude oil of PLD. This PPD is synthesized from ARACHIS OIL which are Polymer additives used to decrease the crystallization of wax.

***IndexTerms* -** Pour Point; Pour Point Depressant; Flow improver; Wax; Crude Oil

I. INTRODUCTION

Crude oil is naturally found in yellowish-black color liquid. In the present time it is very useful thing across the society. It is also important for the economy, politics and technology. It is refined into diversified fuels. It contains naturally occurring hydrocarbons which have different molecular weights. It also contains different organic compounds. Fractional distillation is used to separate the component of crude oil. Crude oil is separated into diversified products, which are used directly or use in manufacturing of petrol, diesel, kerosene, asphalt and chemical reagents which are used to make plastics, pesticides and pharmaceuticals. Petroleum is used to manufacture different types of material. Everyday about 100 million barrels of petroleum are consume by world. Petroleum exploitation has negative environmental effect. Mostly extraction, refining, and burning of petroleum fuels all are release large amount of greenhouse gases which contributes to climate change [28].

1.1 crude oil composition

Crude oil's elemental composition varies depending on where it comes from and what kind of crude oil it is. The elements present in crude oil are carbon (84%), hydrogen (13%), Sulphur (1 to 3%) and nitrogen, oxygen, metal and salts (less than 1%). Crude oil contains numbers of hydrocarbons, organic compounds, metals and heteroatom compounds like Sulphur, nitrogen and oxygen. There are thousands of different hydrocarbon compound present in crude oil. Paraffin's, olefins, naphthenic, and aromatics are the most common hydrocarbon found in crude oil. Aliphatic compounds, which are distinct from aromatic compounds, include paraffin's, olefins, and naphthenes. Methane is the primary component of natural gas. It is lightest hydrocarbon found as a dissolved gas in crude oil. Olefins aren't present in crude oil, but they are made through a variety of refining processes. [29] Aromatic hydrocarbons are mostly found in every crude oil from any part of the world. It is an important series of hydrocarbon found in crude oil. The simplest aromatic hydrocarbon is benzene (C_6H_6). It has three carbon-carbon double bond and it has a unique arrangement of electrons. Other simple aromatics are toluene, xylene and cumene. Benzene is unsaturated, yet it follows the principle of substitution with halogens rather than addition. Aromatics have usually high boiling point, high octane number, high viscosity and higher pour point. The naphthenes are saturated hydrocarbons with one or more carbon rings, commonly known as cycloalkanes. They have the general formula C_nH_{2n}.Cyclohexane (C_6H_1) is a typical example of naphthenes. Naphthenes have a higher boiling point and density than alkenes with the same amount of carbon atoms. Naphthenes are a key component of liquid crude oil refinery output. Naphthenic crude oil converts to gasoline more easily than paraffin rich crude oil. [31-32] **Paraffin's** are also known as alkanes.C_nH_{2n+2} are the general formula of paraffin's. Paraffin's are divided into two groups one is normal paraffin's and second is iso-paraffins. Normal paraffin's are open, straight chain saturated hydrocarbons, when iso paraffin's are branched type hydrocarbons and they begin with isobutene. It has same closed formula as n-butane (C_4H_{10}). They have 5 to 40 carbon atoms per molecule. The alkenes from C5 to C8 are refined into gasoline and

C9 to C16 are refined into diesel fuel, kerosene and jet fuel. Alkenes with more than 16 carbons are refined into fuel oil and lubricating oil. Paraffin wax is alkenes with approximately 25 carbon atoms. [28]

1.2 Paraffinic wax

Waxes are complex combination of alkanes with higher molecular weight. They have three different structural types like straight chain, branched chain and cyclic. Wax consist long chain and high molecular weight hydrocarbons. At the room temperature waxes can be solid or liquid. The aromatic rings in wax can contain more than 22 carbon atoms. The wax component present in crude oil has generally two types of hydrocarbon. 1) Paraffin hydrocarbon (C_{18}-C_{36}) and; 2) naphthenic hydrocarbons (C_{30}-C_{60}). The hydrocarbon part of wax is in different states of matter. That is depending on the temperature and the pressure. Up to 32.5% wax contents are present in the different types of crude oil present in the world. Normal paraffin accounts for up to 80% to 90% of paraffin wax, with cycloparaffins and iso paraffin's (Branched paraffin's) accounting for the remainder. Regular waxy crude oil comprises heavy organics such as asphaltenes and resins in addition to wax, whereas clean waxy crude oil has just hydrocarbons and wax as a heavy organic component. [22] The presence of paraffin wax in crude oil is known to cause flow related problem such as precipitation, wax deposition and gel formation. [2] Petroleum waxes are categorized into two groups first one is microcrystalline wax and second is macro crystalline wax. Microcrystalline wax contributes to tank bottom sludge, while macro crystalline wax causes the flow related problems in production and transportation of crude oil. [24-25] macro crystalline wax is known as paraffin wax and microcrystalline wax is known as naphthenes. Paraffin wax contain straight chin hydrocarbon which ranging from C_{18} to C_{36} and microcrystalline wax contains branched and cyclic hydrocarbons which ranging from C_{30} to C_{60}. [22] Microcrystalline wax possesses very fine and distorted wax crystals and produced from vacuum residue. Solvent dewaxing and centrifuging may comprise 10% of the total wax content of the crude with very high oil content because of the higher affinity of these wax crystals for the oil. Further solvent treatment produces the microcrystalline wax with 5% to 20% oil with molecular weight of 450 to 1000 and a melting point of 60 to 88 ºC. A typical composition is C_{34} to C_{43} with iso-alkanes and possibly cyclic alkanes concentrating in this fraction. The petroleum jell is simply the treated microcrystalline wax form highly paraffinic crudes, the waxes found in storage tanks and crude oil pipelines are sometimes referred to as microcrystalline waxes. Many types of crude oil comprise dissolved waxes, which can precipitate and deposit on the wall of pipeline, thereby restricting crude oil flow. The paraffin structure is generally weak during the regular flow. When a pipeline is completely shut down, further difficulties arise. Solid deposition is a frequent issue in production, storage and transportation of the crude oil. The solubility of the high molecular weight wax is decreases the temperature drops. As the oil is cooled below the crystallization point, nucleation would continue to occur but mass transfer limitation would restrict the size and ordered growth of the crystals. Nucleation and crystal growth are two stages of paraffin wax precipitation. When the temperature of crude oil are decrease to the wax appearance temperature (WAT) then nucleation is occur. The wax molecules in crude oil are forms clusters which causes a cloudy appearance. This temperature is called cloud point of crude oil which refers to wax appearance temperature value. Wax molecules are attached and detach until they rich a critical size. These clusters called nuclei and the formation of nuclei is called nucleation. There are two types of nucleation homogeneous and heterogeneous. Homogeneous nucleation occurs in absence of nucleating material. Meanwhile heterogeneous nucleation occurs in presence of nucleating material. The process of crystal growth is started when the nuclei are stabilized. The precipitation of wax causes increase in viscosity of crude oil. [26]

1.3 Wax deposition: The problem during production, storage and transportation

Wax deposition is one of the most common flow assurance issues in the oil industry.[23] When the temperature around the pipeline, tankers and storage vessel lowers, wax separate from crude oil and settled down on the wall. As a result of the wax build-up, the pipeline's effective diameter shrinks and the pressure drop rises. Also, producing tubing faces flow reduction due to wax deposition. To overcome this problem the pipeline is pigged regularly by mechanical pigs. The production tubing is scrapped regularly upon the severity of the deposition. Wax deposition can restrict the flow of crude oil in the pipeline which creates pressure. However, in rare circumstances, this might result in the abandonment of a pipeline or manufacturing facility. This process increases the viscosity of the crude oil by creating a 3D complex network that imprisons the remaining of the fluid inside and produces wax oil gel. [2] When the heavier Paraffin hydrocarbons precipitate as a result of temperature changes, a wax-oil gel forms. Oil gelation creates problems in the transportation and refining of crude oil. The increased viscosity caused by wax deposition decreases the flow inclinations of fluid mixes and raises the cost of pumping, which is required for fluid movement. Wax crystal precipitation can alter the characteristics of crude oil. The deposit hardened over time, a process known as ageing. Molecular diffusion is a part of the wax deposition process. Because the dissolved molecules of the waxy components are diffusing toward the vessel's wall, wax is beginning to accumulate. This occurs as a result of deep undersea circumstances influencing pipeline walls. It creates the radial temperature gradient in the crude oil flowing through the pipeline.[27] Wax crystallization occurs in the cooler religion when the temperature of crude oil approaches the cloud point. As a result of the crystallization of paraffin wax, the balance between the solid and liquid phases is disrupted. When the solubility of wax in crude oil declines with respect to heat energy, a concentration gradient appears. In the liquid phase, the cold portion that is closest to the pipe wall will have a lower concentration. This is due to the solid wax separating from the heavy crude oil. As a result, wax molecules diffuse from the bulk liquid to the pipeline wall. [19-21] Poly disperse oil composition explains the deposition of heavy organics. The Polydisperse oil can be destabilized by changes in pressure, temperature, or content. The heavy and/or polar fractions may then separate from the oil mixture, resulting in stearic colloids, micelles, and other liquid phases, as well as a solid precipitate. It results in the formation of irreversible heavy organic deposits that are sometimes intractable in solvents. The concentration of the peptizing agent in the solution, as well as the proportion of heavy organic particle surface sites occupied by the peptizing agent, is thought to affect the stability of such stearic colloids. The quantity of peptizing agent adsorbed is a direct function of the crude oil's content. In such scenario, solid wax forms a complicated network throughout the pipeline. More yield pressure is required to restart the flow correctly.[3] Moreover, throughout the process, the gel settles inside the pipeline or other manufacturing equipment [4]. With the passage of time, the gel becomes tougher, necessitating mechanical removal.[5-6] The heavy fraction, which makes up the solid phase, is mostly made up of resins, Asphaltene, and wax. To allow crude oil to flow, the structure must be disrupted. Thermal and mechanical methods such as circulation of hot water via extremely tiny diameter pipe surrounding crude oil pipes to maintain temperature and scraper or scratcher to remove deposited wax from pipelines are used to keep crude oil flowing freely. Chemical techniques have certain benefits over other approaches in terms of saving time, money, and energy. [17] We need to add polymeric additives called as flow improvers or pour point depressants (PPDs) to reduce wax crystallization. Flow improvers are commonly used to reduce crude oil's pour point, viscosity, and yield stress. [7] Different mechanisms avoid wax inhibition in flow improvers applied to crude oil. It alters the crystal's structure and inhibits its development.

1.4 Pour Point

Pour point is the minimum temperature at which the fluid can be poured. [1] Pour point is measured to determine the flow behavior of crude oil at low temperature. At this temperature liquid becomes semisolid and loses its flowing characteristics.[29] The pour point of petroleum is measured by ASTM D 97 method. The fluid pour point is related to wax gelation process. Some time it's called wax pour point.[9] It is a temperature expressed in a multiple of 3 ºC under which the oil no longer moves when the plane of its surface is held vertically for 5 sec. The pour point is then taken as 3 ºC above the temperature of cessation of flow. When the paraffin concentration of crude oil is high, it raises the pour point of the crude; this is most common in crude oil derived from a substantial quantity of plant material. Kerogen II is the source of this crude oil. Pour point of crude oil range from 32 ºC to -57 ºC. There are two types of method to determine the pour point of crude oil.

A] Manual method:

The ASTM D97 test technique for determining the pour point of crude oil is the industry standard. To facilitate the production of paraffin wax crystals, the sample is refrigerated in a cooling bath. At 9 ºC above the predicted pour point of crude oil, and for every 3 ºC the sample jar is pulled out to check the surface movement. When the sample doesn't flow when jar is tilted and hold horizontally for 5 second, then 3 ºC above the corresponding temperature is the pour point temperature of the crude oil. The failure to flow at pour point of crude oil is also be due to viscosity of sample. Therefore the pour point may be giving misleading handling properties of the crude oil. An approximate range of pour point of crude oil is deriving from the sample's upper and lower pour point.

B] Automatic method:

The standard technique for determining the pour point of petroleum products is ASTM D5949. This is the Automatic Pressure Pulsing Approach, which is a pour point test alternative to the manual method. It determines the pour point with the help of an automated device. When reporting at 3 ºC, the result from this approach is in a same format that comparable to the manual method (ASTM D97). This approach calculates the pour point in a fraction of the time it takes to do it manually (ASTM D97). This technique requires less operator time and no external refrigeration. This method is capable to determine the pour point in the range of -57 ºC to +51 ºC. This method is better than ASTM D97 method. In this method the specimen is heated and cooled multiple times. Multiple optical detectors are continuously monitoring the sample for movement in the apparatus. The lowest temperature at which movement is detected on the specimen surface is determined as the pour point. Based on its thermal history, we may obtain two pour point values that can provide an estimated temperature window. The sample seems to be liquid or solid within this temperature range. This is due to the fact that wax crystals develop less readily after it has been heated within the previous 24 hours. This results in a lower pour point.

Features and Significance of Pour Point

- It indicates the lower temperature properties of liquid.
- We can't transport oil via the pipeline if the surrounding temperature is below the pour point of the oil.
- The high value of pour point indicates the high content of paraffin wax in oil.
- It is more significant to lubricating oil.
- It determines the liquid's suitability to be used as lubricant at sub-zero temperature.
- The dissolved wax concentration in crude oil is indicated by the pour point. [30]

Factor affecting the Pour Point

- Paraffin wax content
- Flow rate
- Surface Properties
- Viscosity
- Temperature differential

Crude oil has a high pour point due to high molecular weight components such as wax, Asphaltene, and resins. Pour Point Depressants can be used to enhance the pour point of crude oil. Pour point depressant (PPDs) such as polymethacrylates, alkylated wax phenol, alkylated wax naphthalene, etc. used to lower the pour point of the crude oil. These types of PPDs modify the interface between the oil and the wax present in crude oil.[30]

1.5 Pour Point Depressant

The flow characteristic of crude oil is critical in the production, storage, and transportation of the commodity. As a result, it's critical to reduce wax's detrimental impact on crude flow characteristics. For this we can use chemical additive called Pour Point Depressant.[8] Pour Point Depressants (PPDs) are polymer which is allowing crude oil to flow at very low temperature without formation of heavy wax. It's a polymeric additive which design to prevent wax crystal in crude oil from fusing together at reduced ambient temperature.[30] The practical use of flow improvers is reported since so many years. For getting the optimum additive dose, laboratory studies with field conditions must be done. It is necessary to study the treatment temperature and treatment residing temperature for choosing the best additive. A single pour point depressant is not effective for all the crude oil because different crude oil have different wax contents, chemistry and concentration. It is depending upon the source of crude oil the paraffin chain length of the crude oil should be matched by an effective pour point depressant. By lowering the pour point, the chain length should efficiently co-crystallize on the wax surface and enhance flow. Flow improvers work by Vander Waals co-crystallizing into the paraffin structure. The pour point depressant prevents the development of big wax crystals and alters their size and shape. Crystal growth is inhibited by the addition. Adsorption, absorption, or co-crystallization of the crystal habit modifier onto the fast developing crystal edges causes inhabitation of the growing edge, forcing the crystal to form the plate surface, resulting in a thicker and more three-dimensional structure. [8] The ethylene-vinyl acetate copolymer, the maleic anhydride alkyl ester of unsaturated carboxylic acid copolymer, and the alkyl ester of unsaturated carboxylic acid -olefin copolymer are the most often utilized pour point depressants (PPDs) for crude oils. [10 – 15] The development of PPDs involves major difficulties due to complex composition of crude oil. The wax, Asphaltene and resin content in crude oil have a significant impact in assessing their cold flow properties [13]. The final crystal structure is governed by wax and Asphaltene. Asphaltene were formerly thought to be insoluble colloidal solids whose surfaces are peptized by adsorbed resin molecules. Furthermore, several theoretical and experimental investigations have been proposed to explain the interaction of crude oil components with the Pour Point Depressant. Many additional components, such as Asphaltene and resins, were present in crude oil, in addition to wax, affecting the performance and behavior of the additives. The effectiveness of the Pour point depressants (PPDs) was determined by the amount of Asphaltene present. [16] The main composition of PPD is a polymerized ester. To improve the flow, liquid hydrocarbons are mixed with a suitable additive Known as pour point depressants [18].

2. MATERIALS AND METHODS

- Arachis oil
- Ethanol
- IPA (Isopropyl alcohol)
- Catalyst

2.1 Synthesis of Pour Point Depressant

Arachis oil is prepared as pour point depressant (PPD). Arachis oil was added into round bottom flask with the addition of ethanol, the round bottom flask was equipped with condenser. The molar ratio of alcohol and oil is 6:1 (ethanol to oil). After it we have to add 1% weight of basic catalyst. The basic catalyst we used in this synthesis is sodium hydroxide. The reaction was heated to 65 c with continuous stirring for 3 hours. The reaction mixture was separated and washed with warm deionized water. Then dry the product. The other pour point depressants were synthesized in the similar condition by using methanol, IPA and 2-butanol instead of ethanol. The PPD was characterized by gel permeation chromatography (GPC). We synthesized two different PPD using Arachis oil. First PPD was synthesized using Arachis oil with ethanol and basic catalyst and second was synthesized by using Arachis oil and IPA (isopropyl alcohol).

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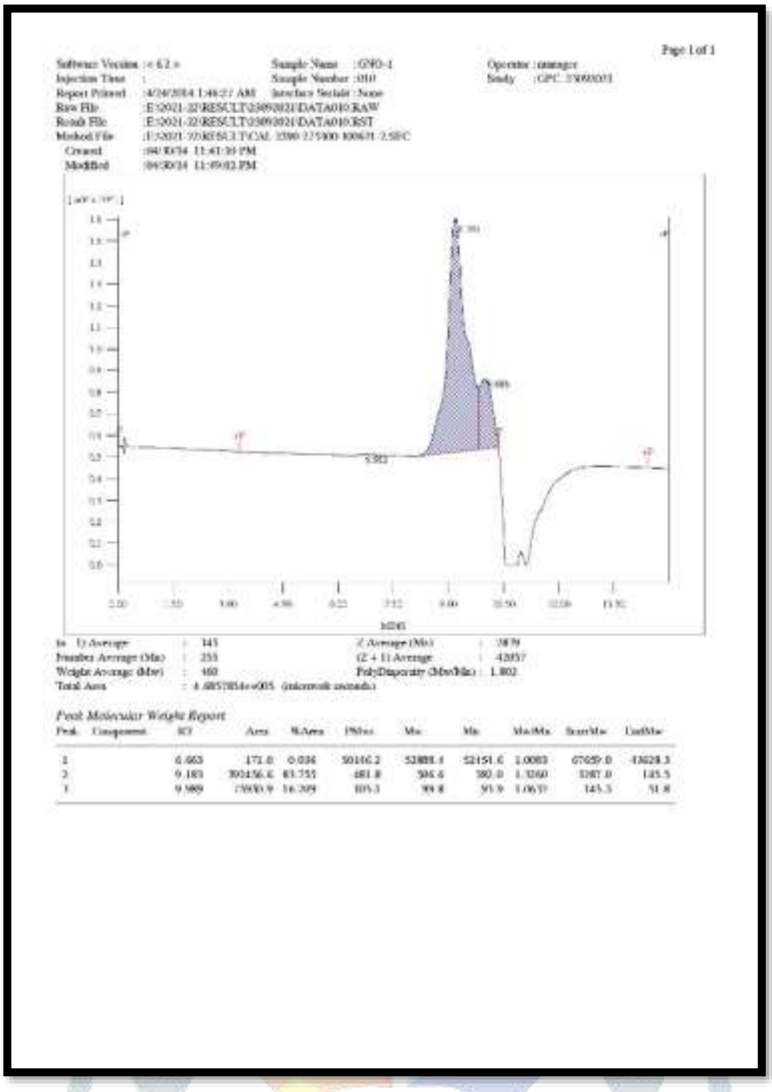

Figure 1: GPC of PPD synthesized

3. Results

Two different Pour Point Depressants (PPDs) with natural Arachis were synthesized and tested on the crude oil of western onshore of India at different ppm levels. . The pour point depressants (PPDs) were synthesized and added to PLD and LMD crude oil which shows the reduce in the Pour Point of the crude oil. The pour point of PLD crude oil was 36 ºC before which was reduced by 5º. The study identified two products which achieved pour point reduction of crude oil up to 5 to 8 ºC. which were able to improve the flow characteristics of crude at low temperature by substantially reducing Pour Point and viscosity of crude oil.

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