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EFFECT OF TEMPERATURE AND POUR POINT DEPRESSANT ON THE RHEOLOGY OF INDIAN WAXY CRUDE OIL

VIKAS MAHTO & HARVEER SINGH

Department of Petroleum Engineering, Indian School of Mines, Dhanbad, Jharkhand, India

ABSTRACT

To reduce the operating cost during production of waxy crude oil and for lowering the energy consumption and ensuring safety and cost effectiveness in pipeline transportation of waxy crude an extensive study of the rheological characteristics of crude oil is indispensible. Keeping this in view, experimental works were carried out to study the variation of rheological properties of Indian waxy crude oil without or with fatty acid ester, a pour point depressant. The dose of pour point depressants in neat waxy crude oil was varied upto 750 ppm and temperature was varied from 60^{o}C to 40^{o}C. The experimental investigations furnishes that there is significant decrease in rheological properties with the decrease in temperature and pour point as well as rheological properties decreases with the addition of pour point depressant.

KEYWORDS: Waxy Crude, Wax Deposition, Pour Point, Wax Appearance Temperature, Rheology

INTRODUCTION

The crude oils having high paraffin content are called waxy crude oils. At higher temperature, the high molecular weight paraffins (wax) are dissolved in the crude oil. But, separation of these wax molecules from the crude oil occurs as the temperature decreases. The temperature at which wax begins to precipitate out from the crude oil is called wax appearance temperature. Further decreasing the temperature, a stage is reached when crude oil ceases to flow and is called pour point. This wax precipitation makes production, transportation and storage of these crude oils difficult. This causes the reduced crude oil pumping rate and severe start up problems after pipeline shut down (Mishra et al, 1995; Khan et al, 2008; Mahto 2010).

The deposition of wax in crude oil is observed in the reservoir, well-bore, tubing, surface transportation and production facilities. These problems are causing losses of billions of dollars per year to petroleum industry worldwide through the cost of chemicals for prevention and remediation, reduced or deferred production, ceasure of the wells, less capacity utilization, chocking of flow lines, pipeline replacement etc (Mendes. and Braga 1996; Ansari et al,1998, Chang et al, 1999; Mahto et al 2010).

Several methods are used for the control and prevention of wax deposition like thermal methods, mechanical methods, biochemical methods and chemical methods Thermal methods usually involve hot oiling the well tubular and flow lines. The mechanical methods include scrapper conveyed by wire line, sucker rods and work strings on a regular basis. Chemical methods include solvents, dispersants, surfactants and wax crystal modifiers. The microbial methods involve bioproduction of surfactant and paraffin solvents to solubilise the paraffin fractions and remove paraffin based skin damage from the well bore. (Ansari et al, 1999; Banat et al, 2000; Mahto et al, 2010) Out of these, chemical methods are most convenient and economic way for the prevention of the precipitation of the wax from waxy crude oil where polymeric materials are added or mixed in the crude oil to decrease the pour point as well as rheological properties of the crude oil for increasing its flow ability at lower temperature (Deshmukh and Barambhe 2008; Mahto, 2010).

In this work, experimental works were carried out to determine the physico-chemical characteristics and SARA distribution of the Indian waxy crude oil for the study of the nature of wax deposition problems. Finally, effect of temperature and copolymer of fatty acid ester, a pour point depressant on the rheological behaviour of Indian waxy crude oil were investigated with the objective of the control of flow assurance problems in the Indian oil fields.

EXPERIMENTAL PROCEDURE

The waxy crude oil sample used under this work was collected from Ankleshwar Oil field, ONGC Ltd. To study the nature of problems, physicochemical properties of the waxy crude oil were determined using IP/ASTM methods and other literatures reported in research papers. (Kim et.al 1996; Nemirovskaya et al 2005; Khan et al 2008, Jin Jun et al 2008; Mahto 2010) The density or API gravity, water content, and pour point of the waxy crude oil sample were determined using ASTM D 1298, ASTM D 96 and ASTM D 97 respectively. The cloud point or wax appearance temperature was determined by measuring viscosity over a range of temperature and taken to be a point at which a deflection in the slope occurs due to deviation from Newtonian behaviour as wax solids begin to form in the oil. The Brooke field viscometer was used for the determination of viscosity at different temperature. For the determination of wax content, 200 ml of petroleum ether was added to 6.0990 g of crude oil taken, then heated mildly & agitated thoroughly. After that it was transferred to a flat bottom flask. To this 45 g of fuller earth (surface active agent) was added and then agitated and heated after which it was allowed to remain stand still. Then ether was evaporated from the filtrate in a steam bath. 75% (150 ml) of acetone + 25 % (5 ml) of petroleum ether were added to the residue after evaporation. The resultant solution was then kept in cold water bath (-32 ^{o} C) for 15 to 20 minutes. After this it was filtered by gravity through normal filter paper. The difference of weight of filter paper plus wax after drying for 10-12 hours and weight of dry filter paper gave us the percentage of wax content.

The characterization factor K_{UOP} (or K_W) was determined using following formula:

$$K_{UOP} = \frac{(1.8T)^{1/3}}{S}$$

Where, T being the volume average boiling temperature (Kelvin) and S being the standard specific gravity (15.6 ^{0}C/15.6 ^{0}C).

Further, SARA distribution (Saturates, Aromatics, Resins and Asphaltenes) was found using liquid column chromatography through elution using different solvents of varying polarity. In the first stage, asphaltenes and insoluble resins are separated by precipitation with n-hexane (crude oil/solvent ratio equal to 1/30 vol.).The mixture is cooled at-30^{0}C and precipitated asphaltenes are filtered out. The filtered sample (maltene fraction) is later split in a chromatographic column to obtain saturated compounds, aromatic, and polar resins. The solid asphaltenes were washed with n-heptane before drying and then weighed. The chromatographic separation of maltenes is carried out in an installation that comprises glass columns packed with silica gel. The different fractions are separated depending on their affinity to the solvent being used at each step of extraction. Trichloro-methane is used to recover resins, n-hexane is used for saturates and hot toluene is used to extract aromatics. The solvents used are extracted using Soxhlet apparatus and percentage of each fraction (weight % of crude oil) is calculated.

Finally, rheological property of waxy crude oil at different temperature was measured using Brooke field viscometer. This crude oil sample was doped with the different concentration of pour point depressant. The doping temperature and doping time of the polymeric additive were kept at 60^{o}C and 30 minutes respectively. The same rheological properties were again measured after addition of polymeric additives in the crude oil and improvement in flow behavior of waxy crude oil due to this additive was studied

RESULTS AND DISCUSSIONS

The API gravity, wax appearance temperature, pour point, characterization factor, wax content, SARA distribution (Saturates, Aromatics, Resins and Asphaltenes) are listed in Table 1-2. The crude oil sample under present study is light crude oil having API gravity of 19.12.

The Kuop value of the sample is 10.36 which as per nomographs of Universal Oil Products Company indicate that the crude oil is of intermediate base characteristics. The wax appearance temperature is +55^{o}C and the pour point of the crude is + 36^{o}C with a wax content of 17.2 wt %. The sample is predominantly rich in saturate fractions and ashphaltene is almost negligible.

Table1: Crude Oil Characteristics

Sl. No.	Properties	Observed Values
1	Density (g/cc at 15^{o}C)	0.9383
2	API Gravity (degrees)	19.12
3	Wax appearance temperature (^{o}C)	55
4	Pour Point (^{o}C)	+36
5	Wax Content (% wt)	17.2
6	Water Content	Nil
7	Characterization Factor	10.36

Table 2: SARA Distribution of Crude

Parameters	Weight Percentage
Saturates	54.9
Aromatics	36.25
Resin	7.88
Asphaltene	0.95

The Table 3 and Figure 1 show the rheological properties of the crude oil at different temperature. With decrease in temperature value of these parameters increases and it may be due to the formation of wax below the cloud point temperature. Waxy-paraffinic-crude oils exhibit high pour point and possess non-Newtonian flow characteristics at temperatures equal to or lower than the pour point due to wax crystallization.

Due to this, a yield stress arises and an increase in viscosity takes place. The rheological properties (shear-stress/shear-rate relationship) become no longer constant and viscosity varies as a function of shear rate.

Table 3: Effect of Temperature on the Rheological Behaviour of Neat Waxy Crude Oil

Shear Rate (1/sec)	Viscosity (cp) at Different Temperature		
	60^{o}C	50^{o}C	40^{o}C
90	10.1	21.2	28.6
150	9.2	14.1	18.1
225	7.4	9.2	10.4
375	5.81	7.1	7.68
450	4.19	5.15	5.7
750	2.02	2.98	3.25

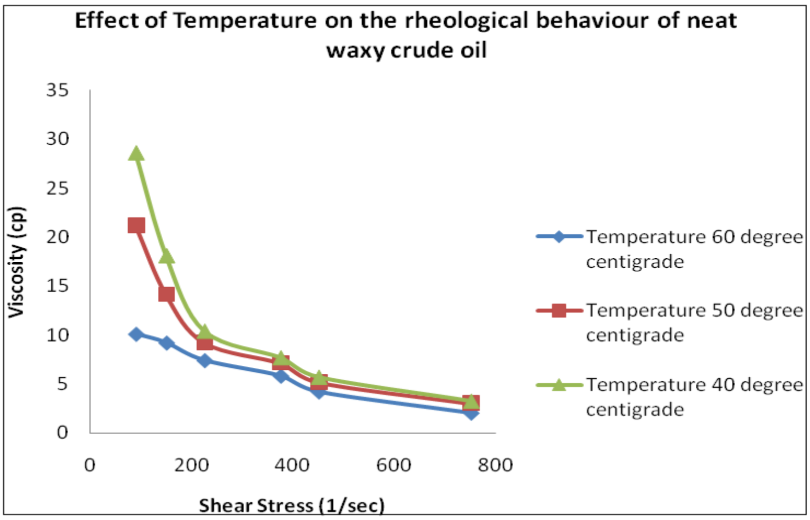

Figure 1: Effect of Temperature on the Rheological Behaviour of Neat Waxy Crude Oil

The Table 4-5 and Figures 2-3 show the pour point of the waxy crude oil and rheolgy of crude oil with the addition of pour point depressant. It has been observed that there is decrease in the pour point after addition of the additives This may be due to co-crystallisation of polymeric additive with wax present in the crude oil during cooling which causes to develop a weaker wax crystal structure and it results in decrease in pour point.

Table 4: Effect of 250 ppm Pour Point Depressant on the Rheological Behaviour of Waxy Crude Oil at Different Temperature

Shear Rate (1/sec)	Viscosity (cp) at Different Temperature		
	60^oC	50^oC	40^oC
90	5.7	8.5	18.8
150	5.1	7.12	13.7
225	4.3	6.03	9.27
375	3.57	4.07	5.28
450	2.97	3.11	4.12
750	2.01	2.37	2.68

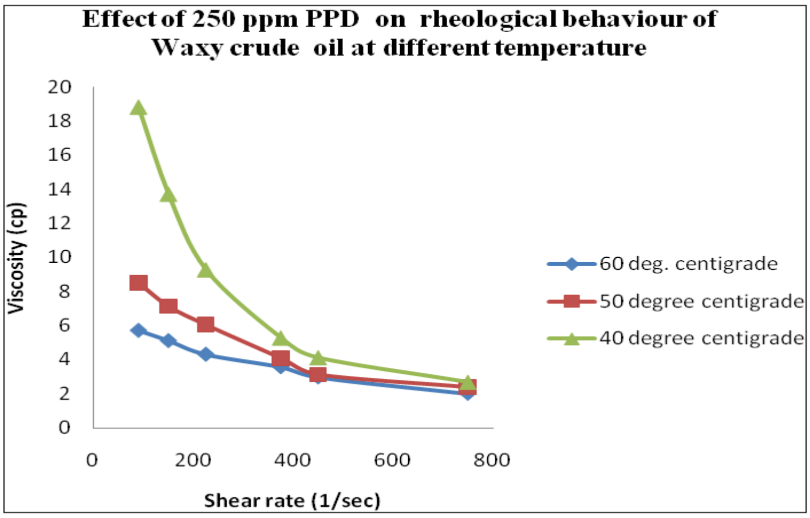

Figure 2: Effect of 250 ppm Pour Point Depressant on the Rheological Behaviour of Waxy Crude Oil at Different Temperature

Table 5: Effect of 500 ppm Pour Point Depressant on the Rheological Behaviour of Waxy Crude Oil at Different Temperature

Shear Rate (1/sec)	Viscosity (cp) at Different Temperature		
	60°C	50°C	40°C
90	6.17	13.9	18.5
150	5.23	9.71	12.4
225	4.21	6.85	7.41
375	3.29	4.58	5.37
450	3.01	4.07	4.88
750	3.01	2.36	3.98

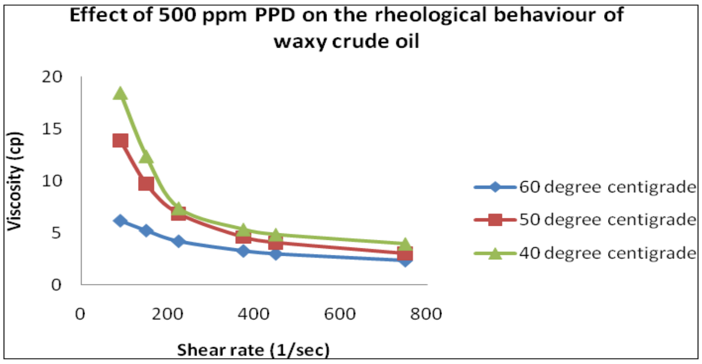

Figure 3: Effect of 500 ppm Pour Point Depressant on the Rheological Behaviour of Waxy Crude Oil at Different Temperature

There is significant decrease in rheological properties of crude oil after the addition of pour point depressant. This may be due to the disrupture of the crystal growth which ultimately reduces the apparent viscosity and yield stresses of the crude oil at lower temperature.

Table 6: Pour Point Temperature of Neat Crude Oil and PPD Treated Crude Oil

Crude Oil Sample	Pour Point (°C)
Neat crude oil	36
Crude oil treated with 250 ppm PPD	16
Crude oil treated with 500 ppm PPD	29

Table 6 help us to explain the phenomena of pour point depressant in waxy crude oil. These results show the neat crude oil has pour point36°C, it decreases sharply with 250 ppm polymeric additive concentration (shown in above table) but after with the amount 500 ppm PPD concentration it again increases. Hence, it is not effective with 500 ppm polymeric additive concentration.

CONCLUSIONS

The following conclusions can be drawn from the present investigations:

- The sample under present study is of intermediate base characteristics. It is predominantly rich in saturate fraction and the ashphaltene content is almost negligible.
- The viscosity of waxy crude oil decreases with addition of very small concentration polymeric additive at the same temperature which shows improvement in the flow behavior of the waxy crude oil through tubing, flow lines and pipelines
- The pour point of waxy crude oil decreases sharply with the addition of 250 ppm pour point depressants.

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