Studies on Paraffin Sediments

Bombay High Crude Oil

K. M. Agrawal, M. M. Mungali, G. C. Joshi, R. Krishna

The sedimentation tendency of Bombay High crude oil, having a pour point of 30°C, has been investigated using a centrifugation technique. The physical properties as well as the composition of the sediments so obtained were determined. The wax separation profile follows the expected solubility trend reflected in the melting point of these waxes. The high melting waxes which appear to exist in the dispersed phase as suspension at 40°C do not appear to influence the pour point of the crude oil.

Die Sedimentationsneigung bei dem Rohöl Bombay High mit einem Pour-Point von 30°C wurde mittels Zentrifugierung untersucht. Die physikalischen Eigenschaften sowie die Zusammensetzung der Sedimente wurden ermittelt. Die Wachs-Trennprofile folgen dem erwarteten Löslichkeitstrend gemäß deren Schmelzpunkten. Die hochschmelzenden Wachse, die anscheinend in der dispergierten Phase als Suspension bei 40°C existieren, haben keinen signifikanten Einfluß auf die Rohöleigenschaft.

Introduction

Petroleum crude oils are complex multicomponent systems exhibiting a range of properties from liquid to semi solid, almost immobile state depending on their composition and ambient conditions (temperature, pressure). At temperatures above their natural pour points they are free flowing liquids, behaving as Newtonian fluids [1]. Even at this state they are best described as colloidal systems [2]. The dispersed phase consists of high melting waxes in combination with asphaltanes and resins often associated with minor quantities of mineral matter. The continuous medium (solvent phase) is compoed of bulk liquid hydrocarbons. In high wax crudes the quantity of dispersed phase increases on cooling due to separation of wax crystals. When sufficient quantity of this wax separates out, the crystals may interlock and immobilise the whole mass.

In the fluid state the colloidal system is unstable in as much as the dispersed phase settles down slowly in crude oil storage tanks or inside the pipe lines during its transportation. The deposits in the form of sludga or sediments are commonly called paraffin or wax deposits and consist of gummy polar material, resins, asphaltic material, wax hydrocarbons, trapped crude oil, sand, silt and some times water [3]. This conglomerate has a consistency ranging from soft, semi solid slurry to firm and hard waxy mass, depending on the amount of "oil" imbibed in it.

There is considerable interest in the determination of the rate of paraffin deposition, its quantity, nature and composition from the view point of crude oil production and transportation. Studies have been carried out on the influence of flow rate, temperature, time, chemical additives etc. mainly from the view points of solving problems caused by paraffin deposits [4–7]. Such information allows schedules for periodic removal of sludge from storage tanks and "pigging" of pipelines as well as selecting effective inhibitor additives to reduce the extent of deposition. Howevar, these studies are specific for particular crudes. Besides the interest in handling and transportation, in some cases the deposits may be valuable sources of high melting point waxes (so called "tank bottom waxes") and perhaps high viscosity oils [8–9]. In the present paper we wish to report the results of an investigation carried out on paraffin deposition tendency of a waxy, offshore crude oil of intermediate character from Bombay High wells of Indian subcontinent.

Experimental

For the present study a sample of Bombay high crude oil was collected directly from the offshore platform (BHN) of production and is free of flow improver additive which is being injected in the crude oil before transportation. Physical properties of this crude oil sample is given in *Table I*.

A procedure was developed to remove the sediments present in the crude oil by centrifugation. The sediments were removed from the crude oil at a constant predetermined temperature using a high speed refrigerated centrifuge (Beckman J-21 model). The crude oil was stored under static condition in the thermostatically controlled chamber at the desired temperature (eg. 40°C) for about 4 hrs. It was then transferred to the centrifuge maintained at the same temperature. Centrifugation was done at 10 000 rpm for 30 minutes and the supernatant layer (solvent phase) separated by decantation. The weight of the sediments were determined. The process of centrifugation is then repeated at different temperatures (35°C, 30°C) with the supernatant liquid. At each stage

Table I: Physical Properties of Bombay High Crude Oil

Properties	Crude Oil
Density D_4^{15}	0.8264
API Gravity	39.6
Pour Point °C (ASTM D-97)	+30
Kinematic Viscosity, cSt @ 40°C	2.84
@ 50°C	2.33
Carbon residue (conradson) % Wt.	0.74
Wax content, % Wt. (Engler-Holde method)	11.9

Table II: Sedimentation Tendencies of Bombay High Crude Oil

Sediment	Separation Temperature		
	40°C	35°C	30°C
Yield, % wt.	2.5	5.8	7.7
Melting point, °C	60.0	52.5	48.2
Asphaltene content, % wt	1.87	0.26	0.32
Wax content, % wt	37.3	34.6	47.5
Melting point of wax, °C	81.2	69.0	64.0
Wax separated on crude oil basis, % wt	0.93	2.01	3.66
Pour point of decanted oil (after sediment removal), °C	30	27	24

the sediments and supernatant liquid were separated and characterized.

The sediments were analysed for their melting point and asphaltene content using ASTM test methods [10]. The waxes were separated from these sediments by solvent dewaxing using methyl isobutyl ketone solvent at low temperature. The waxes so separated were analysed for their melting points as well as for carbon number distribution by gas chromatography. In each case the pour points of the oils after sediment removal were determined by ASTM D-97 method. The data on the sedimentation tendencies of BH crude are given in *Table II* while carbon number distribution of the waxes separated from the sediments is shown in *Fig. 1*.

Results and Discussion

Bombay High crude oil is a high wax (Wax content 11.9%), high pour (Pour Point +30°C), low sulfur (S, 0.17%) crude oil of intermediate character ($K_{UOP} = 11.7$). At 40°C its viscosity is quite low (η_{kin} = 2.84 cSt) and it shows Newtonian flow behaviour (viscosity independent of shear rate). Centrifugation at 40°C yielded 2.5% of sediments which would have been present in the suspension at this temperature. The decanted liquid yielded 5.8% sediments on cooling to 35°C. After separation of this sediment the supernatant fluid yielded 7.7% sediments at 30°C. The cumulative yield of sediments at the natural pour point of the crude oil was 16% as against 2.5% at 40°C *(Table II)*.

Nature of Sediments

The sediments separated at higher temperatures have higher melting points. Thus sediments separated at 40°C, 35°C and 30°C had melting points of 80°C, 52.5°C and 48.2°C respectively. The concentration of asphaltenes is also highest (1.87%) in the sediments separated at 40°C. These sediments contain 37.3–47.5% waxy hydrocarbons. On the basis of the crude oil sample, 0.93% wax separates at 40°C, while 2.01% separates at 35°C and 3.66% at 30°C. Thus nearly 6.6% of wax is present in the sediment (cumulative weight) which separates at the natural pour point of this crude oil.

Properties of wax hydrocarbons

Wax separation profile (fractional separation from high to low temperatures) is an indicator of the wax solubility which in turn is related to melting point of the wax and also with its molecular weight. Thus high melting, high molecular weight waxes separate at higher temperatures. The waxes obtain from the sediments separated at 40°C, 35°C and 30°C have melting points 91.2°C, 69°C and 64°C respectively. There seems to be sharp difference in the melting point of the "40°C" wax (M. P. 91.2°C) and those separated at lower temperatures after removal of the earlier fractions.

The carbon number distribution of these waxes are shown in *Fig. 1*. The wax separated at 40°C has hydrocarbons upto C_{55} (higher carbon number could not be detected by gas chromatography due to poor volatility). The most characteristic feature is the bimodal distribution with a distinct niminum at C_{42}. The concentration of paraffins upto C_{42} and $C_{42}+$ in this wax are 79.9 and 20.1% respectively. The average chain length ($\bar{C}_n$) calculated from carbon number distribution is 29 and 49 for the lower and higher fraction of the wax. On the other hand the waxes separated at 35°C and 30°C are quite similar in their carbon number distribution. Their average chain lengths are 30.4 and 28.9 respectively. It appears that they form a solid solution. As the temperature of separation decreases, more wax separates out without much change in its composition.

An interesting observation has been made with regard to the supernatant crude oil after removal of the sediment. The supernatent liquid after removal of sediments at 40°C and 30°C has a pour point of +30°C and +24°C respectively. At 30°C temperature 6.6% of the total wax originally present in the crude oil has been removed. In fractional separation high melting point components of the wax have crystallised preferentially. It appears that

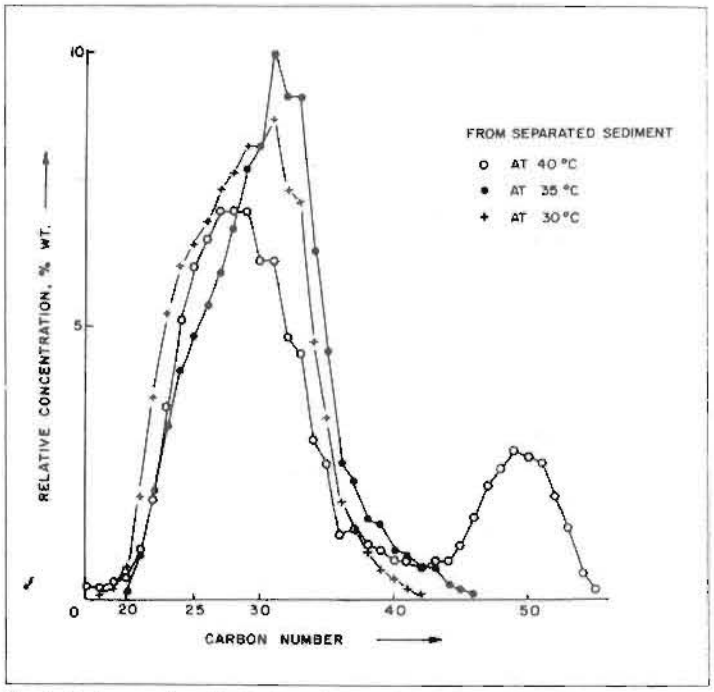

Fig. 1: Carbon number distribution of waxes present in sediments.

wax components separating at 40°C do not contribute to the natural pour point of the crude oil while those waxes which are soluble in oil at 40°C but precipitate at lower temperatures, have effect on pour point.

Conclusion

Using centrifugation technique it has been demonstrated that at temperatures well above its pour point Bombay High crude oil exists as a colloidal sol. The disperse phase consists of wax hydrocarbons, asphaltenes, resins and oil imbibed in the wax portion. The system is most likely in the form of a micelle. At 40°C very hard high melting wax is obtained from the sediments. These waxes contain considerable amount of alkanes having carbon numbers above 40. These hard waxes do not seem to contribute to the natural pour point of the crude oil. On cooling more sediments form, the cumulative yield of sediments separated at 30°C (corresponding to natural pour point of this crude oil) amount to 16%. These contain 6.6% wax hydrocarbons which is over 50% of total wax present in the crude oil

During progressive cooling high melting waxes separate out at higher temperatures while low melting (more soluble) waxes separate at lower temperatures. This technique gave the separation profile of the wax as a function of temperature gradient.

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