

Effect of Temperature and Diesel Oil on the Rheological Properties of Waxy Crude Oil

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Abstract: During low temperature conditions, crude oil which contains high amounts of paraffin shows high pour points due to paraffin deposition; that is, paraffins tend to crystallize forming wax crystals. The temperature at which deposition of wax occurs depends upon the constituents of the crude oil and the temperature is known as the pour point temperature (PPT). The deposition of wax causes numerous operation problems such as decreasing the effective diameter of the pipeline and even blockage in some situations. In order to mitigate these problems and devise a solution such as preparing a pour point depressant, we need to first understand the crude oil nature by gaining knowledge about its rheological behavior. Here, in this present work we try to study the rheological behavior of waxy crude oil sample at varying temperatures, at first without any additives, then by adding some chemicals (diesel) to understand their effect on the crude oil.

KEYWORDS: Waxy Crude Oil, Flow Curve, Rheology, Temperature, Viscosity



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I. INTRODUCTION

Deposition of paraffin occurs during production and transportation of crude oil, natural gases and condensates which is one of the main problems that affect the oil productivity especially at low temperature [1]. The composition of the waxy crudes contains high molecular weight n-alkanes (n-paraffins) which are the main components in wax deposits.[2]. The deposition of wax causes numerous operation problems such as decreasing the effective diameter of the pipeline and even blockage in some situations. Under such conditions higher Energy is required to pump oil and there is difficulty in restarting the flow of oil gels, due to high yield stress of wax gel [3]. Crude oil behavior can change from Newtonian at high temperatures to non-Newtonian at low temperatures, due to the presence of suspended solid particles such as paraffins, asphalt and other compounds [4] According to their rheological properties' fluids are classified into Newtonian and non-Newtonian fluids and can be presented by the following equation

$$\tau = K S^n$$

where,

τ = Shear stress, Pa

K= Consistency index, Pa. (sec)ⁿ

S= Absolute value of Shear rate, (sec)⁻¹

n= Flow behavior index, Dimensionless

The ratio of shear stress to shear rate is a constant, for Newtonian fluids at a given temperature and pressure, and is defined as the viscosity or coefficient of viscosity. Newtonian fluids obey Newton's law of viscosity. Non-Newtonian fluids do not follow Newton's law and, thus, their viscosity (ratio of shear stress to shear rate) is not constant and is dependent on the shear rate [5,6]. Flow improving (FI) additives, alternatively known as pour point depressants (PPDs)/wax crystal modifiers, can reduce the growth and size of wax crystals. Using these chemicals will greatly diminish the ability of these crystals to flocculate and interlock. The combination of these effects lowers the pour point, viscosity, and yield stress appreciably which facilitating the transportation of waxy crude oils [4]. The addition of pour point depressants to crude oil is adopted as a reliable and cost-effective method for the control of the formation of wax and manage the

attendant flow assurance problems [5]. Various types of PPDs can be developed such as bio based, nano composite based, oil based, water based etc. To mention few of them., oleic acid based or maleic anhydride based polymeric additives through esterification and Friedel Craft Alkylation developed by Mrs.Prabha et al.[6] ; Oil-based and water-based viscosity reducers for both low-viscosity and high-viscosity heavy oil wells developed by Fusheng et al.[7] ; Aromatic polyisobutylenesuccinimides utilized as viscosity reducers for heavy crude and extra heavy crude oils of Mexico by Tomás et al.[8] ; Maleic anhydride co-polymer and its derivatives with different polar and aromatic pendant chains synthesized by Yumin et al.[9] ; polyaminoamide(PAA) made through the process of aminolysis and polycondensation from soybean oil and canola oil by Gang et al.[10] ; poly-hydrazide (PH) prepared from vegetable oil by Qiang et al. [11] and so on. The main goal of this study is to explore the rheological characteristics of crude oil along with diesel crude oil emulsion as a function of temperature, in order to provide useful information for further design of new PPDs or other flow improving methods.

II. MATERIALS AND METHODS

A. Sample Preparation

The crude oil sample was obtained from Oil India Limited, Assam and the Physio-chemical characteristics such as density, specific gravity, API, wax and water content, pour point and SARA distribution of crude oil was found out. The characteristics of the crude oil samples are presented in Table 1.

Table 1: Physio-Chemical characteristics of Crude Oil

Sl. No.	Parameter	Method	Crude oil
1.	Density	IP 160/64	0.832
2.	API Gravity	ASTM Table	27
3.	Pour point	ASTM D-97	36.2
4.	Water Content (%; V/V)	IP 74/64	2.1
5.	Wax Content (%; w/w)	Modified UOP 46-64	15.4
6.	SARA analysis: (%; w/w)		
	Saturates:		52.1
	Aromatics:		14
	Asphaltenes:		0.5
	Resin:		8
	Resin Asphaltenes		11.5

Pycnometer was used to determine density which is a very precise method. API gravity is helpful in determining the quality of crude oil. Here the API gravity of the crude was determined using specific gravity value at 40°C. The following formula is used.

$$\text{API gravity} = \frac{141.5}{RD} - 131.5$$

(Here, RD = Relative Density)

Water content determination was by centrifuge method (ASTM D 96-58 T). Pour point temperatures of the crude oil samples were measured using the standard test method for the pour point, ASTM D97-06.11. In this method standard ASTM pour point apparatus which includes test jar, bath, jacket and thermometer was used for the pour-point determination. Pour point was obtained by interval of every 30 C. When the flow stops on tipping the test jar horizontally, that temperature was noted as pour point. Viscosity was measured using MCR-72, Anton Paar Rheometer

B. Experimental Setup

All the rheological measurements were performed by using MCR-72, Anton Paar Rheometer.

C. Methods

- **Effect of temperature on rheological behavior of crude oil:**

Two types of experiments were done in which two types of flow curves were derived.

In the first experiment, the flow curves were obtained by applying an increasing shear rate ramp from 0.1 to 100 s⁻¹ at constant temperature. This experiment was performed at five different constant temperatures i.e., 20°C, 30°C, 40°C, 50°C and 60°C. Each time a new fresh sample was used in order to avoid any irreversible evolution of the oil sample. A cumulative curve for all the temperatures was later derived out of the five curves.

In the second experiment, the flow curve was derived by decreasing the temperature from 45°C to 25°C to calculate the varying viscosity and shear stress in their respective temperatures. Here, the shear rate was kept constant at 10 s⁻¹ and each reading was taken at an interval of 0.5 min (i.e., 30 sec).

- **Effect of diesel oil on rheological behavior of crude oil**

For this study diesel oil was added to the crude oil sample at 0.1 % as an additive to improve its viscosity behavior, and both the experiments were repeated again.

III. RESULTS AND DISCUSSION

For the first experiment, the shear stress vs shear rate values are plotted in x and y axis to observe the behavior of crude oil at different constant temperatures. The curves are indicated by different color lines to indicate different constant temperature readings.

Table 2: Color lines to indicate different constant temperatures (first experiment)

 20°C	 30°C	 40°C	 50°C	 60°C
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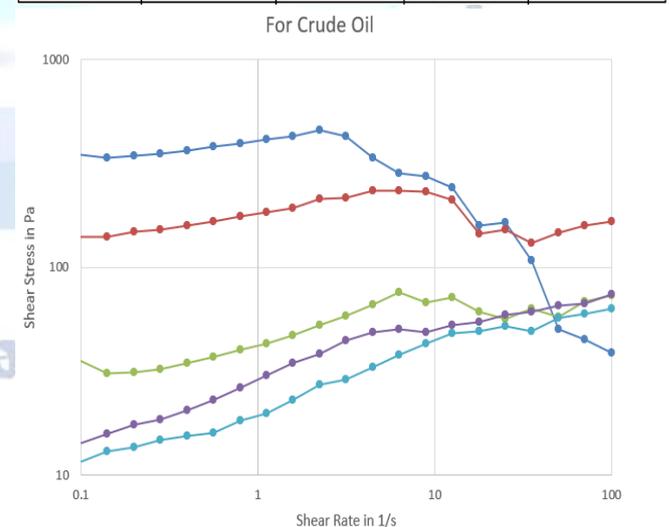


Fig. 1: Shear rate vs Shear stress curve for crude oil at different constant temperatures.

Here Fig.1 shows the change of shear stress with the change of shear rate from 0.1 to 100 s⁻¹. The different color line indicates different constant temperature curves, which show that shear stress increases with

shear rate in most of the cases, while shear stress decreases with the increase of temperature with each curve. This is likely due to the weakening of the network strength between particles by thermal motion.

The Herschel-Bulkley model is often used to describe the rheological behavior of non-Newtonian fluids, simply because it is a generalization of both the Bingham and power-law models[15]. So, we have chosen to use that model to describe the rheological behavior of the fluid being measured. The model relates the shear stress to the shear rate as follow:

$$\tau = \tau_0 + K(\dot{\gamma})^n$$

where,

- τ = measured shear stress in lb/100ft²
- τ_0 = fluid yield stress (shear stress at zero shear rate) in lb/100ft²
- K = Consistency Index
- n = Flow Index
- $\dot{\gamma}$ = Shear rate in sec⁻¹

The fitted parameters for the equation are presented in Table 2.

Table 2: Herschel-Bulkley model parameters

Parameters	Values
τ_0	-533.27
K	577.20
n	0.01
Correlation coefficient R	0.99435
Correlation coefficient R ²	0.98874

The correlation coefficient was 0.98724.

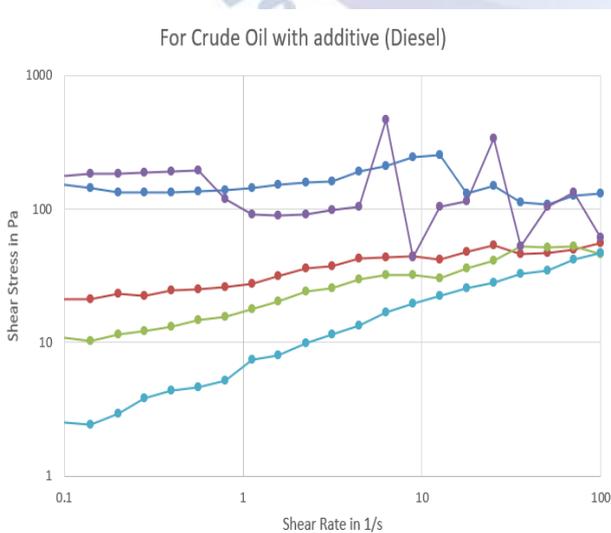


Fig. 2: Shear rate vs Shear stress curve for crude oil with additive (Diesel at 0.1%) at different constant temperatures.

In Fig. 2 Diesel is added to the crude sample and the experiment is repeated as in Fig. 1. We can observe that most of the curve comes down a few steps in the graph, indicating that the shear stress has decreased due to the addition of Diesel. Thus, the Diesel oil acted as additive which can decrease the shear stress for crude oil.

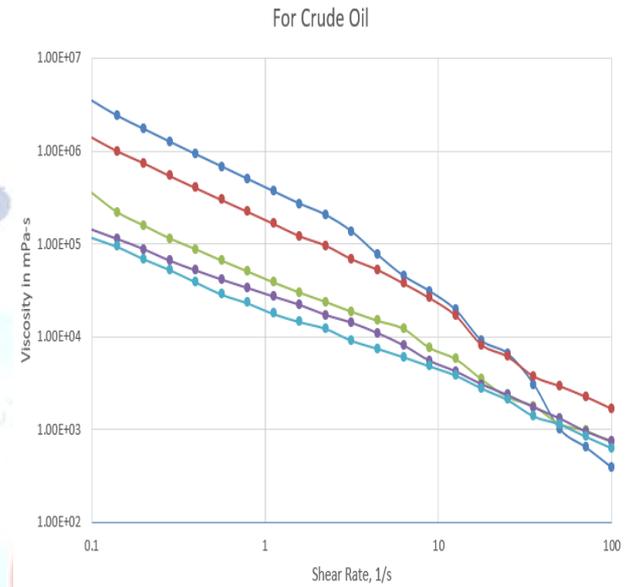


Fig. 3: Shear rate vs Viscosity Curve for crude oil for different constant temperatures.

Here, Fig. 3 shows that the viscosity decreases with the increase in shear rate for the crude oil sample.

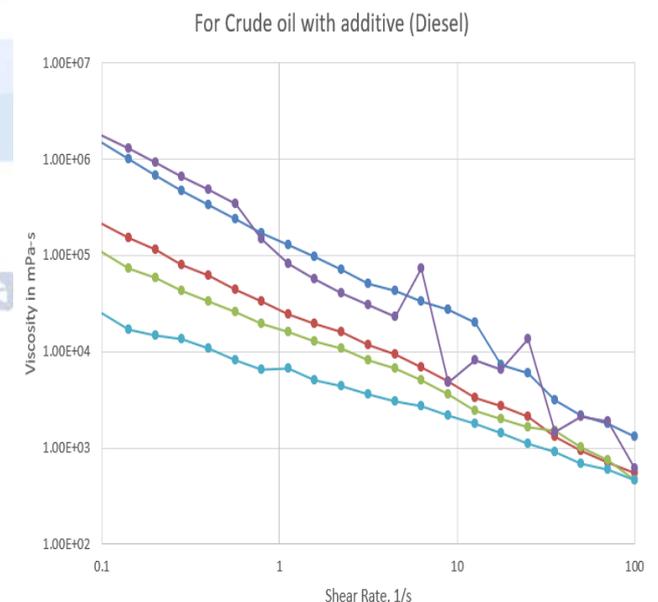


Fig. 4: Shear rate vs Viscosity Curve oil with additive (Diesel at 0.1%) for different constant temperatures.

Fig. 4 shows that the most of the shear rate vs viscosity curves comes down a step in the graph after addition of the additive (Diesel). Thus, it can be concluded that both the shear stress and viscosity of crude oil can be reduced by adding Diesel as additive.

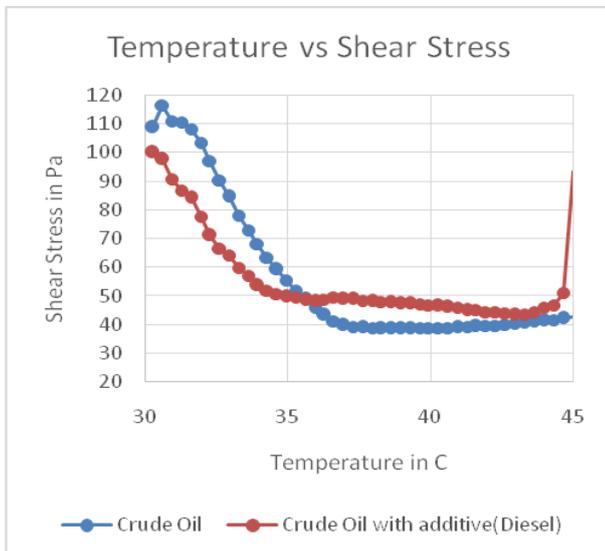


Fig. 5: Temperature vs Shear stress curve for crude oil with and without additive at constant shear rate (10 s^{-1}).

Here, fig. 5 shows the change in shear stress with the change of temperature (decreasing) with constant shear rate (10 s^{-1}). From the graph it can be seen that the shear rate of crude oil increases abruptly at around 37°C and while for the crude oil with additive (diesel) the shear rate increases abruptly at around 34°C . Thus, there is around -3°C decrease in the pour point temperature after the addition of Diesel into the crude oil sample.

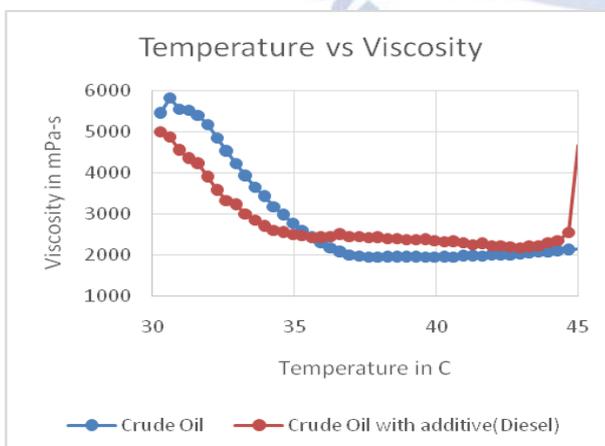


Fig. 6: Temperature vs Viscosity curve for crude oil with and without additive at constant shear rate (10 s^{-1}).

Fig. 6 shows the change in viscosity with the change in temperature (decreasing) with constant shear rate (10 s^{-1}). Similar to shear stress, the viscosity also increases abruptly at around 37°C for the crude oil and at around 34°C for the crude oil with additive (diesel). Therefore, decrease in pour point is around -3°C after addition of diesel.

Waxy crude oil behaves as non-Newtonian fluid at low temperature and there exists a temperature breakpoint of flow state transformation.

IV. CONCLUSIONS

In this study, the effect of temperature on the rheological behavior of crude oil sample from Oil India limited, Assam was studied and the effect of Diesel (at 0.1%) added to crude oil was analyzed. Two experiments were performed one with constant temperatures which was repeated five times using different constant temperatures and, another with constant shear rate and varying temperature (from high temperature 45°C to low 25°C). The results obtained from the work indicate addition of diesel in the crude oil can reduce both the shear stress and viscosity of the crude oil and change the rheology of the crude oil. The decrease in pour point was around -3°C after the addition of diesel.

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