Bulletin of Faculty of Science, Zagazig University (BFSZU)
e-ISSN: 1110-1555
Volume-2025, Issue-4, pp-171-180
https://bfszu.journals.ekb.eg/journal
Research Paper DOI: 10.21608/bfszu.2025.364256.1490

===

Rheological behavior of treated waxy crude oil under different climates using liquid copolymer pour point depressant

Ragab A. A.[1], M. A. Sayed[2], Fathy Yassin[3], Hamza Baghi[3, *]
[1]Petroleum Applications Department, Egyptian Petroleum Research Institute, Nasr City, Cairo, (EGYPT)
[2]Refining Department, Egyptian Petroleum Research Institute, Nasr City, Cairo, (EGYPT)
[3]Chemistry Department, Faculty of Science, Zagazig University, Egypt
[*]Corresponding author email: Hamzabaghi14@gmail.com

ABSTRACT: Pour point depressants are chemical products employed in waxy crude oil treatment to prevent or decrease wax precipitation and enhance its rheological properties. Thus, we studied the pour point temperature and rheological characteristics of Egyptian waxy crude oils doped with three liquid pour point depressants: LPPD-1, LPPD-2, and LPPD-3. According to the findings, the crude oil samples treated with LPPDs notably improved their pour point temperature, yield value minimization, and rheological behavior. LPPD-3 presented the greatest results by employing a 2000 ppm treatment dose. It lowered the pour point temperature of waxy crude-A from 75°F to 45°F and the pour point temperature of waxy crude-B from 65°F to 25°F. Additionally, it considerably enhanced the rheological characteristics of crude-C by decreasing its apparent viscosity; at 70 °F, an untreated crude oil sample's 30 cP viscosity was attained, whereas at 32 °F, a 1000 ppm treated sample achieved the same viscosity. LPPD-3 also reduced the yield value of crude-D at 70°F by 85% when treated with a dosage of 1000 ppm.

KEYWORDS: liquid pour point depressant, waxy crude oil, rheology, yield value.

Date of Submission: 27-02-2025 Date of acceptance:07-05-2025

I. INTRODUCTION

When temperatures drop below the wax appearance temperature (WAT), crystals of wax in the crude oil tend to develop and cluster to create a large three-dimensional network that modifies the flow of oil [1]. In addition to the high costs related to the shipment and storage of waxy crude oils, another significant problem occurs when the pipeline is being restarted following the shutdown [2]. The heavy and waxy crude oil rheology has recently received more interest from specialists in chemical engineering, rheology, the petroleum sector, and even mathematics because of conventional oil's reservoirs depletion and deep water petroleum exploitation [3]. A cooling rheological test in oscillatory mode can be used to assess the dynamic viscoelasticity, which would enable the formation of the wax crystal network to be studied as the temperature decreases [4]. Both the test temperature and the shearing condition during the cooling process have an impact on the waxy crude oil's isothermal structure formation. As a result, the effect of shear rate on the isothermal structural formation of waxy crude oil changes with test temperature [5].

The conventional methods for wax removal and prevention are summarized as follows: microbiological, thermal, chemical, mechanical, and other methods [6]. The treatment of heavy and waxy crude oil using a pour point depressant (PPD) and flow improvers (FI) is frequently employed in long-distance pipeline shipping, which has produced financial advantages [7]. In general, pour point depressants are applied to decrease crude oil's viscosity, yield stress, and pour point temperature (PPT). These additives lower additional pumping costs and increase waxy crude flowability in an oil pipeline or flowline. When it comes to the rheological manner of waxy crude oils, the flow improvers and the shear rate function similarly but differently. The shear rate acts when flocculated wax crystals cool because secondary interparticle connections between them disintegrate [8].

In light of these, the current study assesses the rheological properties and yield value reduction of waxy crude oil at various shear rates and temperatures following the addition of different pour point depressants.

II. MATERIALS AND METHODS

Crude oil characterization

Crude oil samples A, B, C, and D were gathered from KHALDA Petroleum Company (KPC) wells in the western desert of Egypt. The crude oils' physicochemical characteristics are shown in Table 1.

Table 1: Characteristics of crude oils A, B, C, and D.

Properties	Method	Sample Source			
		Crude-A	Crude-B	Crude-C	Crude-D
Zone		**AEB-3E**	**AEB-3C**	**USAF**	**AEB-3D**
Specific Gravity @ 60/60 °F	**ASTM D1298**	**0.83**	**0.808**	**0.81**	**0.82**
API Gravity @ 60 °F	**ASTM D287-92**	**39.1**	**43.6**	**43.8**	**41.0**
Wax Appearance Temperature (°F)	------	**78**	**74**	**74**	**74**
Water Content% %vol.	**ASTM D 96**	**Traces**	**Traces**	**Traces**	**Traces**
Pour Point (°F)	**ASTM D 97**	**75**	**65**	**65**	**65**
Wax Content (% wt.)	-------	**37**	**41.0**	**41.0**	**38.0**
Asphaltene Content (% wt.)	-------	**5.0**	**3.5**	**2.5**	**4.2**

Preparation and characterization of liquid pour point depressants (LPPDs)

The pour point decreasing effect, rheological characteristics, and yield value minimization were investigated on waxy crude oil samples treated with LPPD-1, LPPD-2, and LPPD-3 that are prepared as described by Ragab et. Al [9]. The structure of the prepared LPPDs was verified using different techniques.

Evaluation and characterization of prepared LPPDs and crude oil

Asphaltene and wax contents (Wt. %)

The determination of wax and asphaltene content involves a modified Burger's method. The sample of waxy crude oil is dissolved in petroleum ether, an anti-solvent mixture, and filtered. Next, hexane is used to dissolve the solid phase, followed by stirring and filtration. The beaker is then heated to evaporate hexane, and the disparity in weight is calculated. Thus, the proportion of asphaltene and wax is obtained [10].

Pour point temperature test

The standard test procedure for the pour point of petroleum products (ASTM D 97) was applied to evaluate the produced LPPDs, measuring the pour point temperatures of crude oils in the STANHOPE SETA pour and cloud point refrigerator. The analysis was conducted manually, with three separate tests for every test, and estimated errors included equilibrium and thermometer errors [11].

Various dosages of LPPD-1, LPPD2, and LPPD-3 were injected at 60 °C into crude oil samples. Then, the treated samples were subjected to ASTM D 97 pour point testing.

Rheological evaluation

Wax appearance temperature

In waxy crude oil, when wax crystals begin to develop, the slope of the viscosity-temperature curve starts to increase; this is referred to as the wax appearance temperature. Accordingly, the curves of viscosity-temperature and the numerical derivation of the test data points are employed for wax appearance temperature determination as the greatest point of slope change [12].

Viscosity against Temperature Test

The dynamic viscosity of blank crude oil samples and samples doped with the obtained LPPDs at varying concentrations was measured using a BROOKFIELD DV3T Rheometer (DV3TLVTJ0, USA) coupled with a cooling/heating system. The SC4-18 spindle, which is appropriate for such kinds of crude oils, was used for the experiments. The 132 S^{-1} shear rate was adjusted to be suitable for maintaining the torque value almost above 10%, as advised by the manufacturer. In glass bottles, crude samples were injected with different LPPDs and heated up to 140 °F for an hour before being put into the viscometer for testing. After loading the crude oil sample into the rheometer testing chamber, it is heated for three minutes at 140 °F, followed by dynamic cooling until the torque value is 100%.

Dynamic viscosity and yield value determination

The shear stresses of blank and doped samples were established through the application of different shear rates at 120, 90, and 70 °F temperatures to assess the effect of the prepared LPPDs on lowering yield value. At shear rates of 149, 100, 60, 30, and 10.5 S^{-1}, the shear stress for each sample was determined at each temperature.

Plotting the linear intercept of the y-axis shear rate-shear stress curves that could be extended to zero shear rates was used to calculate the yield values of blank and doped crude oil samples. Equations (1) and (2) can be used to determine the relationships between shear stress and shear rate for a cone and plate geometry when the conical spindle is properly positioned using the torque and cone rotational speed measurements [13].

$$\tau = \frac{T}{\frac{2}{3} \pi R^3} \qquad \text{eq. (1)}$$

$$\dot{\gamma} = \frac{\Omega}{\tan\theta} \qquad \text{eq. (2)}$$

Where: τ = shear stress
$\dot{\gamma}$= shear rate
T = torque
R = cone radius
Ω = cone speed
θ = cone angle

III. RESULTS AND DISCUSSION

Characterization of the prepared LPPDs

As described by Ragab et. Al [9], the PPD copolymer was synthesized structurally confirmed, and three different concentrations were prepared, namely LPPD-1, LPPD-2, and LPPD-3.

Asphaltene and wax contents (wt. %)

Using a modified Burger's method, the crude oil's asphaltene and wax contents were determined. Figures 1 and 2 present the asphaltene and wax contents of some evaluated crude oils, and Table 1 lists the asphaltene and wax concentrations for crudes A, B, C, and D.

Figure 1: wax content of some tested crude oils.

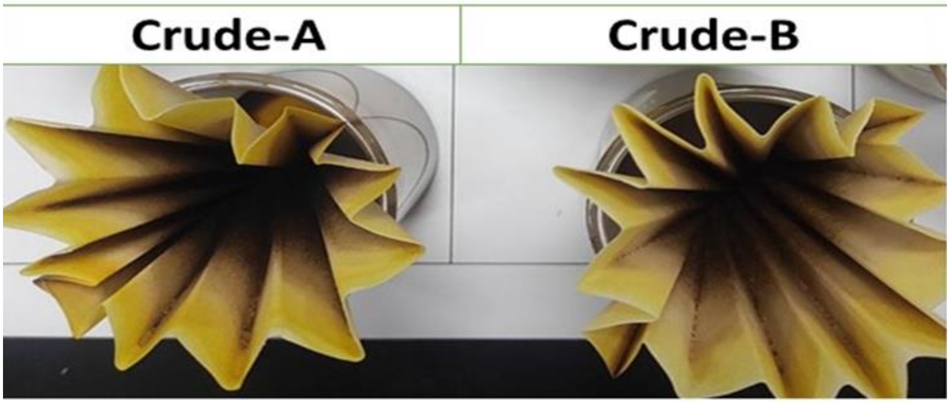

Figure 2: Asphaltene content of some tested crude oils.

Evaluation of the prepared LPPDs.

The evaluation of the prepared liquid PPDs was performed by injecting crude oils A, B, C, and D with different dosages of LPPD-1, LPPD-2, and LPPD-3. The injected doses ranged between 500 and 2000 ppm. The treated samples are then subjected to a pour point measuring test to determine their PPT and compare it with the blank sample. Table 2 displays the pour point data for both blank samples and samples that were injected with various dosages of the obtained LPPDs.

All LPPDs showed a pour point reducing effect, primarily because these additives co-crystallized with the crude oil's wax molecules during cooling, causing the wax crystals structure to become weaker and a drop in the treated samples' PPT. This solves the flow problems by preventing the paraffin molecules from interlocking and facilitating their dispersion into the oil phase.

The produced LPPDs, which contain both polar and non-polar groups, are injected into crude oil samples. As the temperature drops, the non-polar alkyl chain co-crystallizes with the wax molecules that exist in the crude oil. The inclusion of polar groups alters the characteristics of the interaction between wax crystals and inhibits bigger crystal aggregates from forming.

It was revealed that LPPD-3 exhibited the greatest effects between the synthesized LPPDs. It lowered the PPT of crude-A by 2000 ppm from 75 °F to 45 °F and crude-B by the same dose from 65 °F to 25 °F. The higher amount of LPPD solid content is crucial in changing the form of wax crystals, which reduces the PPT and enhances flow, as seen by LPPD-3's better effectiveness over LPPD-1 and LPPD-2.

Table 2: Pour point temperatures of blank and doped crude oil samples.

Chemical	Dose (PPM)	Pour Point Temperature (°F)			
		Crude-A	Crude-B	Crude-C	Crude-D
No PPD	---	75	65	65	65
LPPD-1	500	65	xx	55	xx
	1000	60	55	50	55
	1500	60	xx	50	xx
	2000	55	45	xx	55
LPPD-2	500	60	xx	55	xx
	1000	55	45	50	55
	1500	55	xx	50	xx
	2000	50	40	xx	50
LPPD-3	500	50	xx	50	xx
	1000	50	35	45	55
	1500	50	xx	45	xx
	2000	45	25	xx	45

Rheological measurements

Wax appearance temperature

The BROOKFIELD DV3T viscometer was employed to measure crude oil's dynamic viscosity under monitored cooling rate and stress. Based on viscosity-temperature curves, the wax appearance temperature of crude oils was identified to represent the largest point of slope change. Table 1 presents the wax appearance temperature values for the crude oils A, B, C, and D.

Viscosity-temperature curve

During transportation, when crude oil cools, wax crystal molecules tend to accumulate and grow on the cold pipe's inner surface. The elevated thickness of these deposits would reduce the carrying capability of the pipeline and lead to complications during pigging. To solve these problems, particularly at low temperatures, a comprehensive understanding of the rheological characteristics of waxy crude oils is necessary. The type, quantity, and wax shape, as well as its crystallizing behaviors, all of them significantly impact the flow characteristics. Process equipment with wax accumulation may suffer from increased frequency of shutdowns and other issues with operation. In extreme cases, crude oil may gel as a result of wax crystals, making pipeline restarting more difficult [14].

The impact of the prepared LPPDs on the rheological behavior improvement was evaluated on crude oils A, B, C, and D. Crude oil samples were injected with 1000 ppm of LPPD-1, LPPD-2, and LPPD-3, and the viscosity of these samples was measured against temperature using a rheometer. Dynamic viscosity versus temperature curves were plotted for all samples and compared to untreated samples. Figures 3-6 present the rheological behaviors of blank and crude oils treated with 1000 ppm of the prepared liquid pour point depressants.

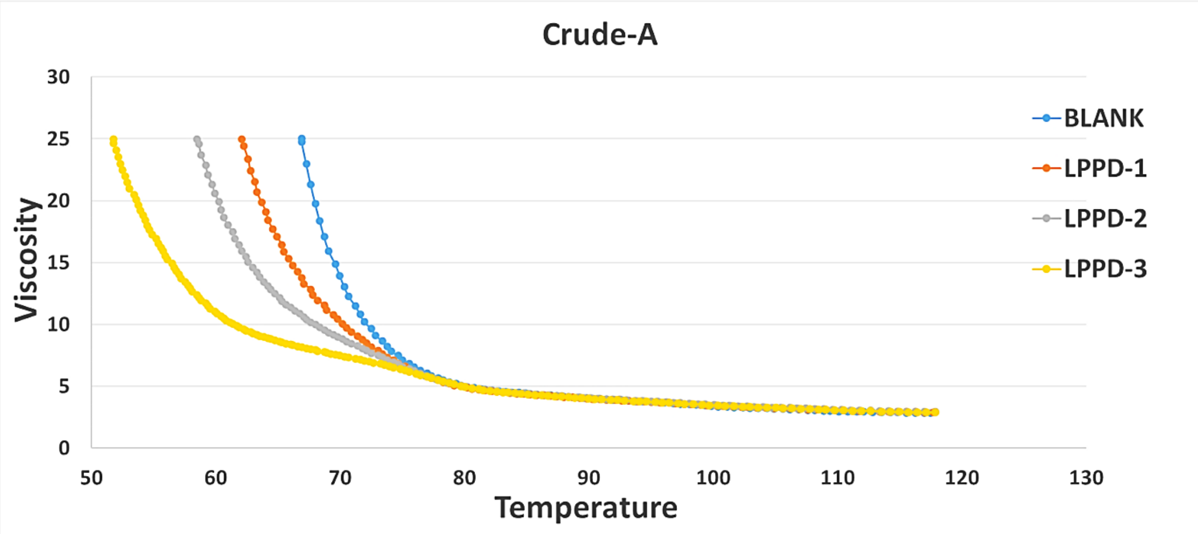

Figure 3: Rheological behavior of crude A.

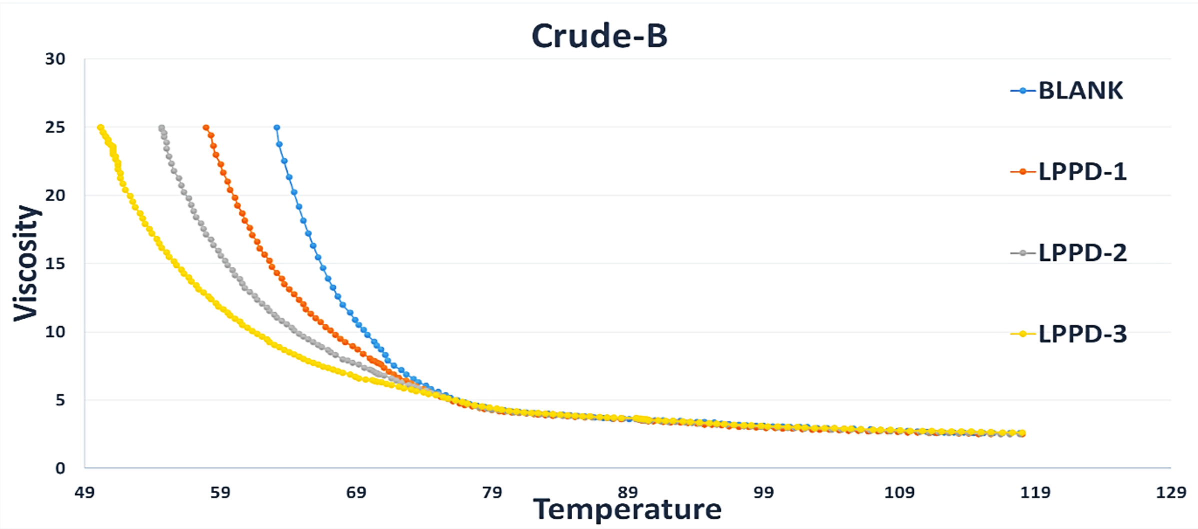

Figure 4: Rheological behavior of crude B.

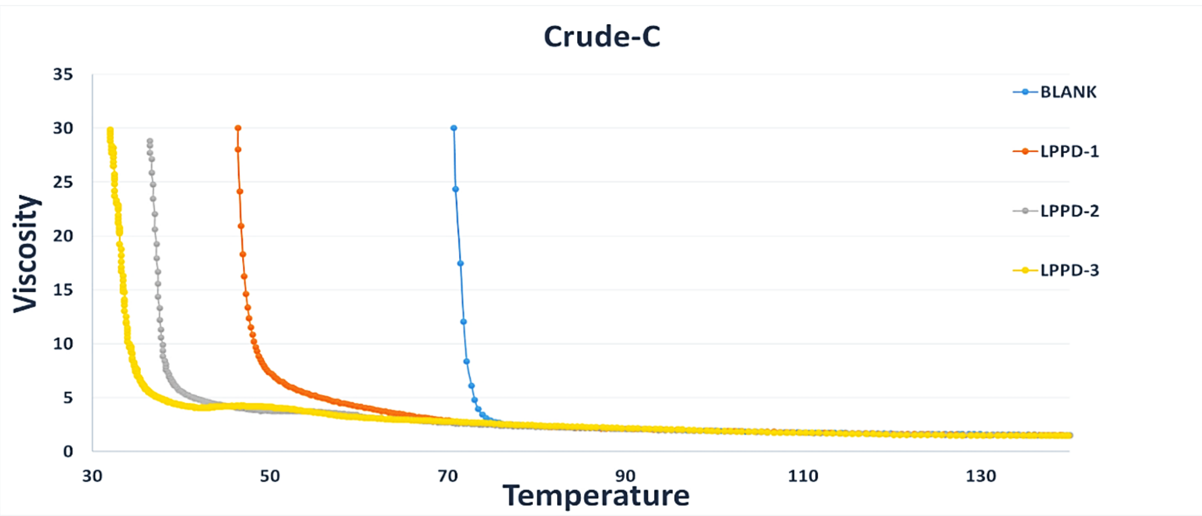

Figure 5: Rheological behavior of crude C.

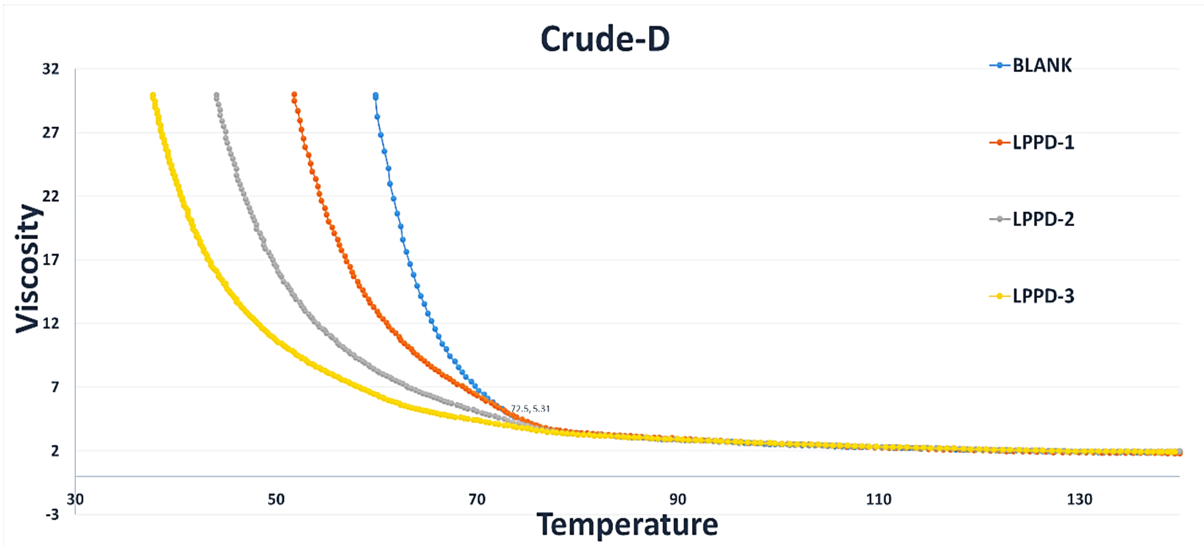

Figure 6: Rheological behavior of crude D.

Due to wax molecules crystallization, the pour point temperature of crude oils with a significant quantity of wax is high, and the rheological properties are non-Newtonian at temperatures beneath or equal to the pour point temperature [15]. In the current study, the dynamic viscosities of blank samples are rapidly rising as the temperature drops. This could be explained by the formation of wax crystals when the temperature drops below the temperature at which wax appears. However, for the treated samples, a significant improvement in the rheological behavior is achieved. This is due to the wax crystal breakdown caused by the injected LPPDs that resulted in a reduction in the dynamic viscosity and yield stress.

Dynamic viscosity and shear rate relationship

The viscosities of untreated crude oil samples decrease by increasing the shear rate. From the viscosity-shear rate curves, the slope is steep initially. However, at greater shear rates, it almost levels out [16]. Viscosity curves of blank and treated samples of crude-A at 70 °F are presented in Figure 7. At temperatures lower than WAT, which is 74 °F for crude-A, there is a sudden increase in the viscosity of blank samples at lower shear rates. For samples treated with LPPDs, the viscosity remained low even at lower shear rates.

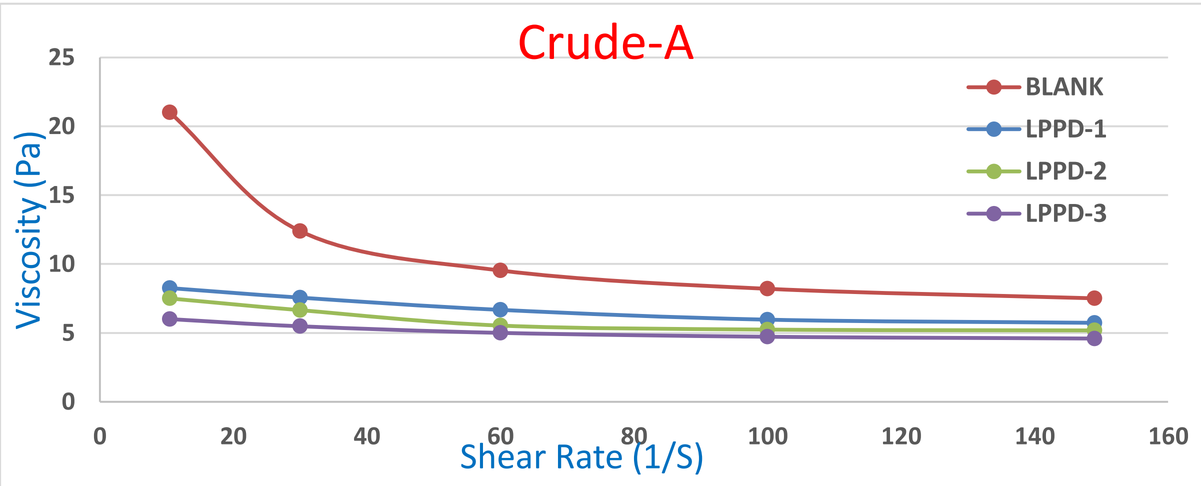

Figure 7: Effect of shear rate on Crude-A viscosity at 70 °F.

Shear stress and shear rate relationship

The deposition of wax crystals present in waxy crude oils usually affects production because of reduced rates of flow, increasing energy needs for pumps to operate, and equipment failures, including malfunctioning rod pumps and separators, plugged flow lines, shutting in producing wells, and the need for extra labor for workovers and maintenance [17]. At elevated temperatures, crude oils have a Newtonian behavior, and the shear stress is nearly the same for blank and treated samples. However, there is a clear impact on the shear stress at temperatures near or equal to the pour point for the treated samples.

By contrasting the untreated samples of crude A, B, C, and D with samples injected with 1000 ppm of LPPD-1, LPPD-2, and LPPD-3 at different temperatures, the effect of solid content percent was first investigated. The three LPPDs demonstrated a considerable decrease in crude-D shear stress, as presented by the flow curve data in Figures 8-11. The flow curves demonstrated that yield value reduction is directly impacted by an increase in the copolymer's solid content. Thus, the yield value decreasing efficiency of LPPD-3 > LPPD-2 > LPPD-1.

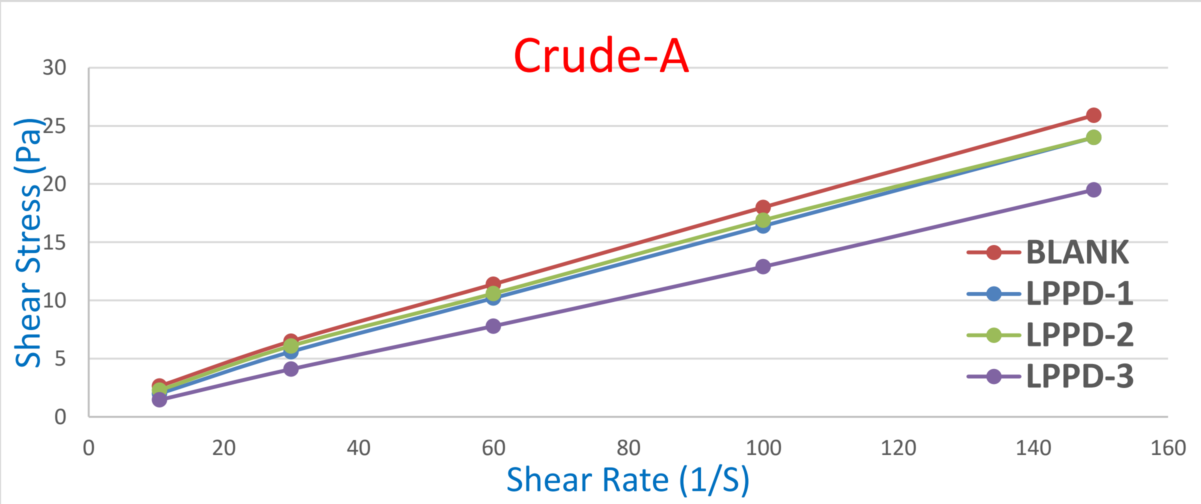

Figure 8: The flow curves of Crude-A blank and treated samples.

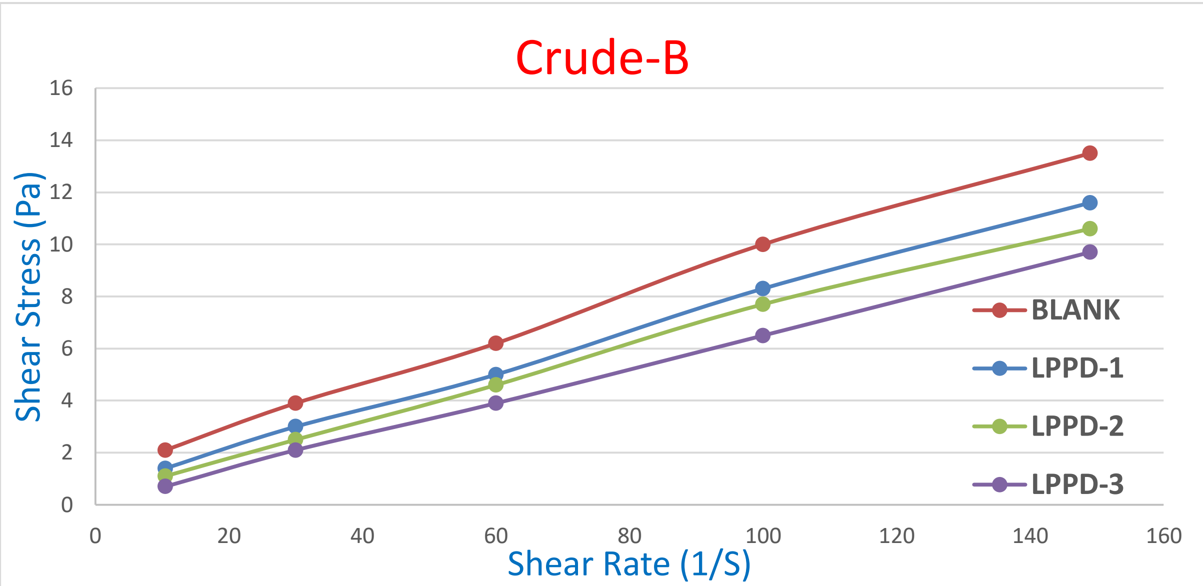

Figure 9: The flow curves of Crude-B blank and treated samples.

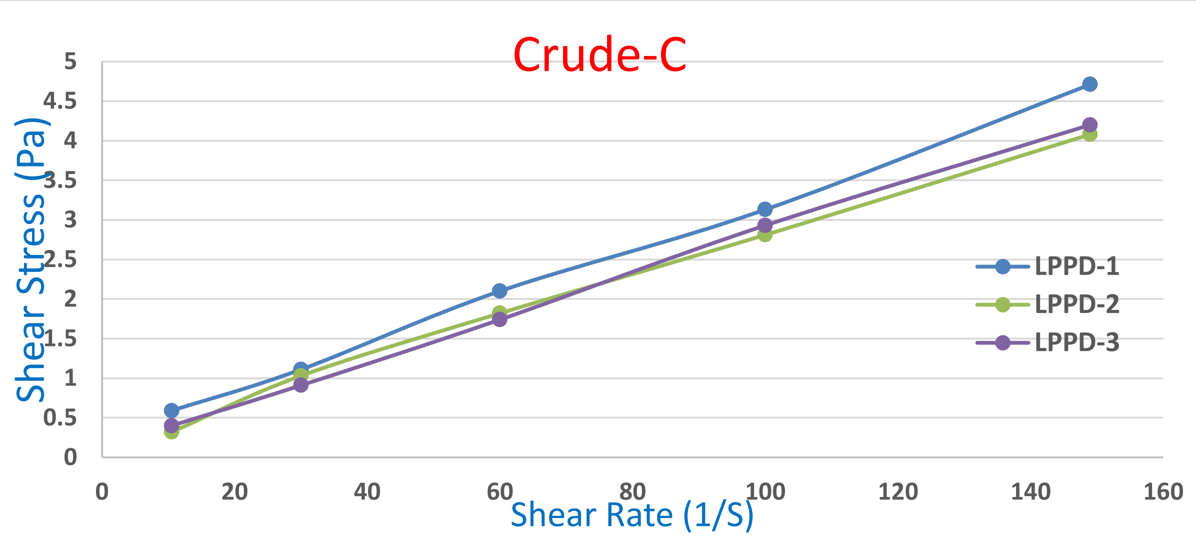

Figure 10: The flow curves of Crude-C blank and treated samples.

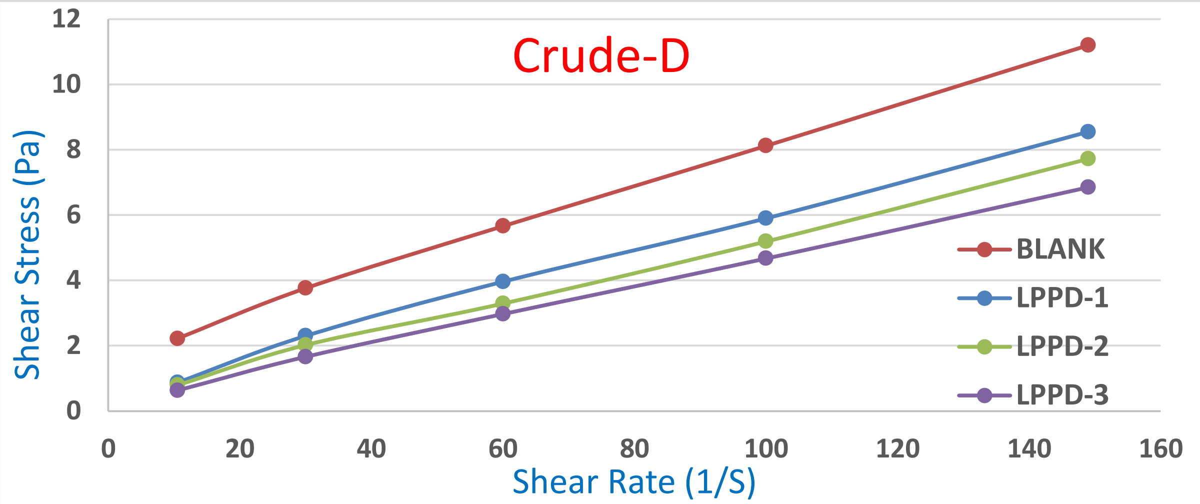

Figure 11: The flow curves of Crude-D blank and treated samples.

The yield value minimizing effect of the prepared LPPDs is confirmed by the yield value results that are presented in Table 3. When 1000 ppm of LPPD-1, LPPD-2, and LPPD-3 were injected into crude-D, the reduction of yield value was by 69, 78, and 85%, respectively.

Table 3: Effect of LPPDs on the yield value of Crude-D.

Sample	Crude-D			
	Blank	LPPD-1 (1000 PPM)	LPPD-2 (1000 PPM)	LPPD-3 (1000 PPM)
Yield value (Pa)	1.72	0.53	0.38	0.25

It is evident from viscosity-temperature curves and the flow curves that the addition of LPPDs significantly improves the rheology of waxy crude oil samples. This is primarily because the altering of crystal development caused by LPPDs eventually lowers the crude oil's dynamic viscosity and yield values at temperatures below the wax appearance temperature.

IV. CONCLUSION

Waxy crude oils' pour point temperature and rheological characteristics were assessed at different temperatures. Next, various dosages of the pour point depressants LPPD-1, LPPD-2, and LPPD-3 were added to samples of waxy crude oils. Following the doping of polymeric additives into the crude oil samples, the same PPT and rheological properties were evaluated again, and the improvement in the PPT and flow properties of waxy crude oils as a result of this addition was investigated. A summary of the evaluation's findings is as follows:

- The three LPPDs exhibit the ability to reduce the PPT. LPPD-3 provided the best outcomes by reducing the PPT of crude B from 65°F to 25°F.
- By investigating the flow behavior of both treated and untreated samples, the prepared LPPDs significantly decreased the dynamic viscosity; LPPD-3 provided the most effective results, allowing the crude-C sample treated with 1000 ppm to reach the 30 cP viscosity at 32 °F rather than 70 °F for the blank crude oil sample.
- An evaluation of yield value minimization showed that crude oils treated with LPPDs significantly improved. The percentages of yield values that were significantly decreased ranged from 69% to 85%.
- LPPD-3 outperforms LPPD-2 and LPPD-1 in PPT reduction, rheological properties, and yield value decreasing due to its ability to disrupt the wax crystals' growth.

Therefore, the rheological manner of waxy crude oil improves with the addition of polymeric additives, which indicates an enhancement in the flow characteristics of the waxy crude oil across tubing, flow lines, and pipelines.

References

1. Eke, W.I., et al., Pour point depression and flow improvement of waxy crude oil using polyethylene glycol esters of cashew nut shell liquid. Applied Petrochemical Research, 2021. 11(2): p. 199-208.
2. Elganidi, I., et al., Synthesis of a novel terpolymer of (BA-co-SMA-co-MA) as pour point depressants to improve the flowability of the Malaysian crude oil. Materials Today: Proceedings, 2021. 42: p. 28-32.
3. Zhang, J.-j. and X. Liu, Some advances in crude oil rheology and its application. Journal of Central South University of Technology, 2008. 15(1): p. 288-292.
4. Yao, B., et al., Structural properties of gelled Changqing waxy crude oil benefitted with nanocomposite pour point depressant. Fuel, 2016. 184: p. 544-554.
5. Lin, M., et al., Isothermal structure development of Qinghai waxy crude oil after static and dynamic cooling. Journal of Petroleum Science and Engineering, 2011. 77(3): p. 351-358.
6. Ragab, A.A., et al., Synthesis, evaluation and characterization of vinyl acetate/octadecyl acrylate copolymer as an energy-saving liquid pour point depressant for waxy crude oil. Journal of Molecular Liquids, 2025. 420: p. 126835.
7. Guo, W., et al., The effect of dynamic cooling on the flow properties of PPD-treated crude oil. Petroleum Science and Technology, 2018. 36(21): p. 1787-1793.
8. Sharma, S., V. Mahto, and V.P. Sharma, Effect of Flow Improvers on Rheological and Microscopic Properties of Indian Waxy Crude Oil. Industrial & Engineering Chemistry Research, 2014. 53(12): p. 4525-4533.
9. Ragab, A.A., F. Yassin, and H. Baghi, Synthesis, evaluation and characterization of vinyl acetate/octadecyl acrylate copolymer as an energy-saving liquid pour point depressant for waxy crude oil. Journal of Molecular Liquids, 2025. 420: p. 126835.
10. Himanshu, A. Majhi, and B. Behera, Prediction of wax content in crude oil and petroleum fraction by proton NMR. Petroleum Science and Technology, 2018. 37: p. 1-8.
11. A Sayed, M., et al., Effect of solid contents and the ratio of EVA/Octadecylacrylate blends on Paraffin Inhibition and pour point temperature of waxy crude oil. Egyptian Journal of Chemistry, 2022. 65(3): p. 619-625.
12. Cao, L., et al., Experiment and Application of Wax Deposition in Dabei Deep Condensate Gas Wells with High Pressure. Energies, 2022. 15(17): p. 6200.
13. Chhabra, R.P. and J.F. Richardson, Chapter 2 - Rheometry for non-Newtonian fluids, in Non-Newtonian Flow and Applied Rheology (Second Edition), R.P. Chhabra and J.F. Richardson, Editors. 2008, Butterworth-Heinemann: Oxford. p. 56-109.

14. Al-Sabagh, A.M., et al., Styrene-maleic anhydride copolymer esters as flow improvers of waxy crude oil. Journal of Petroleum Science and Engineering, 2009. 65(3): p. 139-146.
15. Mahto, V. and H. Singh, Effect of Temperature and Pour Point Depressant on the Rheology of Indian Waxy Crude Oil. International Journal of General Engineering and Technology, 2013. 2: p. 25-30.
16. Eke, I., et al., Influence of Heavy Organics Composition on Wax Properties and Flow Behavior of Waxy Crude Oils. Chemical Science International Journal, 2019: p. 1-12.
17. Elkatory, M.R., et al., Mitigation and Remediation Technologies of Waxy Crude Oils' Deposition within Transportation Pipelines: A Review. Polymers (Basel), 2022. 14(16).