RESEARCH PAPER

Investigation of styrene based terpolymers as pour point depressant for waxy crude oils

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Abstract

Paraffin deposition in the pipeline is one of the most significant challenges in oil and gas production operations, with millions of dollars spent on mitigation each year. Wax deposition in the flow line causes pumping issues, which is aggravated during the winter. The rheological characteristics of the crude oil can be enhanced by pour point depressants (PPDs) which are extensively used in petroleum industry. The current study focuses on the synthesis and evaluation of the impact of styrene-based terpolymers on the pour point and rheological characteristics of a crude oil sample. Styrene based terpolymers with different alkyl pendant chains were synthesized and then esterified with fatty alcohols to obtain esters. These esters have been characterized by various analytical techniques. The effect of the PPDs were evaluated using different analytical techniques including pour point (PP), rheology, cold finger test and microscopic techniques. The experimental investigations suggest that among all esters, the ester with a carbon chain similar to the average carbon number of wax show superior performance as PPD to improve the cold flow characteristics of fluid considered for the study.

Keywords: Cold finger test, Crude oil, Pour point depressants (PPD), Rheology, Terpolymer

1. Introduction

The world's economies are reliant on petroleum-based fuels. However, stocks of these petroleum-based fuels are rapidly decreasing, signalling the need to diversify fuel sources.[1] The rate of consumption of oil is rising in tandem with the global population.[2] To meet the demand for a renewable, sustainable, and cleaner fuel, biodiesel and hydrotreated vegetable oil or green (renewable) diesel are used as an alternatives.[3] Apart from these, unconventional reserves are also gaining attention to bridge the gap between supply and demand of fossil fuels which mainly produces highly waxy crude. The most significant tasks of the Oil and Gas industry is the shipping of such waxy crude oil to refinery from production facilities.[4] Wax crystallizes in the crude oil and impedes the flow of crude oil as it cools. Waxy crude oil poses a significant flowability problem in terms of solid deposition during production and transportation.[5] Thermal, mechanical, or chemical methods are commonly employed to avoid and remediate production difficulties caused by paraffin deposition. Among all techniques, chemical treatments are extensively used for mitigation of paraffin deposition. The utilization of chemical additives in the treatment of crude oil is a popular chemical management method that may be employed alone or in conjunction with other procedures.[6] PPDs can significantly improve the flow properties of crude oil even at low temperatures.[7] The optimum effect of additives is observed when polymeric additives have stronger resemblance with the wax components present in crude oil.[8] Numerous chemical additives viz. Ethyl vinyl acetate (EVA) copolymers, Acrylate copolymers and maleic anhydride copolymers are commonly used as PPDs.[9] The conventional PPDs contain maleic anhydride

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and acrylate monomers. Maleic anhydride and acrylate monomers have advantage of non-polar alkyl chain that interact with the wax crystals and polar vinyl bond which is extremely reactive. These two structural properties of acrylate monomers make them useful for the synthesis of acrylate polymers which are remarkable PPDs. Furthermore, the specific properties of maleic anhydride (MA) monomer including economic viability, the presence of C=C and a polar C=O functional group, render it susceptible to polymerization with other monomers to generate oil-compatible PPDs.[10] Polyacrylate polymers have polar moieties that interact with paraffin and benefit the cold flow properties of crude oil.[11] Furthermore, styrene readily reacts with other monomers and it contains polar phenyl group which effectively adsorb on the surface of wax crystals, boosting its scattering.[12] Polystyrene-maleic anhydride copolymer (PSMA) is widely employed in a variety of applications due to its excellent characteristics and affordable cost. Because PSMA may easily combine with other chemicals with unique characteristics, various useful materials based on the PSMA copolymer have arisen. Esterification of PSMA with long chain alcohols yields chemical additives which are compatible with crude oil and have a polar hydrophilic group and a hydrophobic portion which resemble surfactant.[13] Majority of Indian oil fields are mature fields and they face challenges such as economic constrain, wax deposition, low production and high viscosity of crude oil and hence, need of novel chemicals has arisen for sustainable production of crude oil from such fields. Terpolymers are gaining increasing interest as crude oil flow improvers. Elbanna and colleagues[14] reported the formation of a styrene-based terpolymer that achieved 18 °C drop in pour point of waxy crude oil. Elganidi and colleagues reported work on the production of terpolymers that resulted in a considerable improvement in apparent viscosities,[15,16] while Castro and colleagues[17] revealed an improvement in viscosity of highly viscous crude oil. Preliminary investigation into the production of terpolymers for waxy crude oils has demonstrated outstanding performance of terpolymers compared to conventional PPDs in terms of crude oil attributes such as pour point and rheological parameters. Thus, present studies were carried out for the synthesis of new terpolymers that may be employed as crude oil flow improvers. In current research, styrene, alkyl acrylates, and maleic anhydride were chosen as monomers for the synthesis of styrene terpolymers. These terpolymers, abbreviated as SAM terpolymers, were subsequently subjected to esterification with diverse fatty alcohols to produce SAM esters.

2. Experimental section

2.1. Materials

The crude oil samples required for the study were collected from Western Onshore Fields, India and abbreviated as C1 and C2. Cetyl alcohol, Stearyl alcohol, Icosyl alcohol, Behenyl alcohol, Acrylic acid, Maleic anhydride, Styrene, p-Toluene sulphonic acid (PTSA), Azobisisobutyronitrile (AIBN), Toluene and Methanol utilized for Physico-chemical analysis of crude oil and synthesis of additives were purchased from different vendors.

2.2. Physico-chemical analysis of crude oil samples

The Physico-chemical analysis of crude oil samples (Crude oil-1 = C-1 and Crude oil-2 = C-2) was done by following ASTM procedures. All the analysis were carried out on dry oil which has water content less than 0.2%. High Temperature Gas Chromatography (HT-GC) (Agilent 8890) was performed to determine the average carbon number of wax sample isolated from Crude oil.

2.3. Synthesis of polymeric additives

2.3.1. Synthesis of styrene based terpolymers

Alkyl acrylates (0.1 mol) were polymerized with styrene (0.1 mol) and maleic anhydride (0.1 mol) in 1:1:1 mole ratio by radical polymerization using Azobisisobutyronitrile (AIBN) as an initiator.[14,18–20] These terpolymers were abbreviated as SAM Terpolymers.

2.3.2. Synthesis of SAM esters

Due to poor solubility of terpolymers in crude oil, the polymers (0.1 mol) obtained in previous step were esterified with fatty alcohols (0.22 mol) in presence of p-Toluene sulphonic acid (PTSA) (1% w/w) using Dean-Stark apparatus in Toluene for 12 h under reflux condition to obtain final product. The schematic representation of chemical reactions taking place for the synthesis of SAM esters is represented in Fig. 1.

2.4. Characterizations of synthesized PPDs

The chemical structure of synthesized terpolymers was identified using FTIR (Bruker RX-IFTIR, scanning range 400–4000 cm^{-1}). ^{1}H NMR of terpolymers was obtained to confirm the presence of all the monomers (Bruker Avance Neo, Frequency: 500 MHz). Gel Permeation Chromatography (GPC) (1260 Infinity II High-Temperature GPC System) was performed to determine the molecular weight of the synthesized chemical additive.

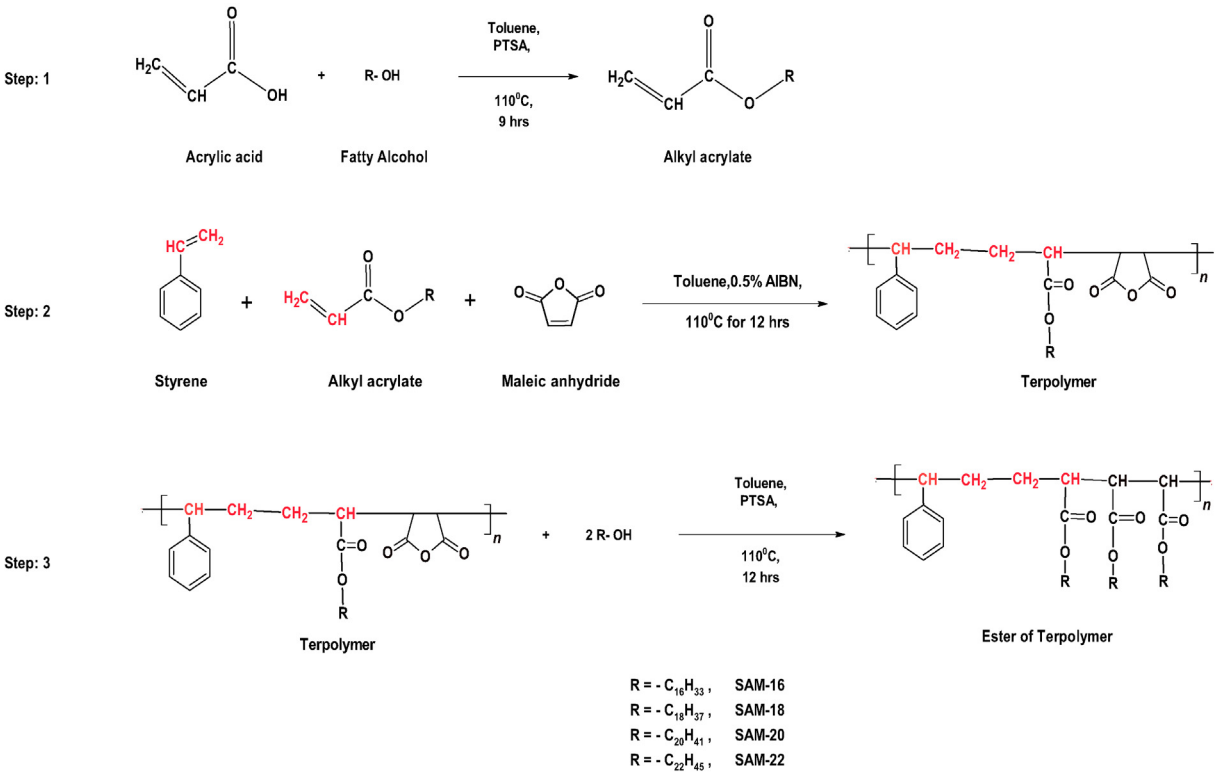

Fig. 1. Schematic representation of synthesis of SAM esters.

2.5. Studies of synthesized additives on crude oil

2.5.1. Pour point (PP) evaluation

Pour point was determined after doping the crude oil with different concentrations (100, 300, 500, 1000 and 2000 ppm) of 10% solution of synthesized additives in xylene as per ASTM D5853 (2000) method using Pour point apparatus. Before treating crude oil with additive solutions, the crude oil sample was homogenized by heating it above cloud point.

2.5.2. Viscosity measurements

Viscosity of the crude oil (treated and untreated) was determined to check the effect of synthesized additives using Rheometer (Anton par MCR-102) at various temperatures in the range of 20°C-50 °C at constant shear rate (100 s^{-1}). Rheological measurements were performed by increasing the shear rate from 10 to 300 s^{-1} at 30° and 40 °C.

2.5.3. Cold finger test

Using an in-house fabricated cold finger equipment, a cold finger test was performed to evaluate the wax deposition potential of C-1 and C-2 as well as the Paraffin Inhibition Efficiency (%PIE) of chemical additives.

2.5.4. Microscopic studies of crude oil

Microscopic studies of crude oil were performed using an optical microscope (Nikon eclipse Ci POL with linkam heating stage) at 30 °C and 45 °C at a resolution of 10 μm.

3. Results and discussion

3.1. Characterization of crude oil samples

Standard ASTM procedures were followed for characterization of the crude oil samples (C-1 and C-2). The results are given in Table 1 below:

The findings in Table 1 indicates that both the crude oils have high pour point (27 °C and 39 °C) and high wax content (18.03% and 33.61%). Furthermore, the resin concentration is moderate, whilst the asphaltene content is low. Thus, the high wax content and high pour point data suggest that the crude oil samples are waxy in nature and require chemical treatment for smooth pipeline transportation. Fig. 2 displays the absorption peaks for crude oil samples C-1 and C-2.

Peaks at 2921 and 2852 cm^{-1} in C-1 and 2920 and 2851 cm^{-1} in C-2 correspond to -CH_3 and -CH_2- groups.[21] The peak at 1461 cm^{-1} in C-1 and C-2 demonstrates the existence of an alkyl chain. The presence of alkanes with more than eight carbon

Table 1. Characterization of the crude oil samples (C-1 and C-2).

Properties	Method (Year)	Results	
		C-1	C-2
Water content (% v/v)	ASTM D4006-81 (2005)	Nil	Nil
Density @15 °C (g/cc)	ASTM D1298-12b (2017)	0.8072	0.8458
Specific gravity @15 °C		0.8076	0.8461
API (°)		43.71	35.74
Pour point (°C)	ASTM D5853 (2000)	27	39
Initial Boiling Point (IBP) (°C)		39	52
Wax content (% w/w)	UOP 46-64 (1999)	18.03	33.61
Melting point of Wax (°C)	ASTM D87	58	68
Congealing point of Wax (°C)		54	64
Saturate content (% w/w)		86.55	73.70
Aromatic content (% w/w)		10.08	17.73
Resin content (% w/w)		3.24	8.29
Asphaltene content (% w/w)	ASTM D6560 (2000)	0.13	0.18

atoms is represented by a peak at 721 cm^{-1}. This peak indicates that crude oil contains wax molecules.

The carbon number distribution of crude oil must be determined to tailor the suitable chemical additive for specific crude oil. Fig. 3 demonstrates that the average carbon number distribution for the studied crude oils.

From the chromatogram, it can be concluded that carbon distribution suggest that the chemical additives with pendant alkyl chain length resembling carbon chain with 22 carbons or nearby could be more efficient due to effective interaction of chemical additive with wax.[22]

3.2. Identification of synthesized PPDs

3.2.1. Fourier transform infrared (FTIR) spectroscopy

FTIR aids in understanding the functionality of synthesized additives. The spectra of chemical additives is given in (Fig. 4a).

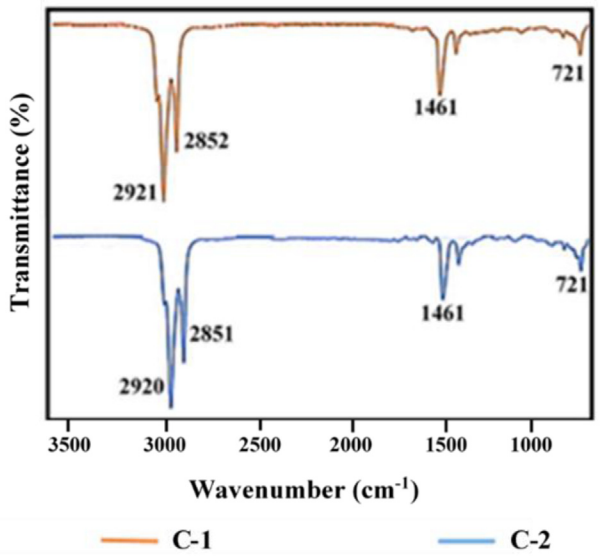

Fig. 2. FTIR spectra of Crude oil samples C-1 and C-2.

As shown in (Fig. 4a), the presence of two strong bands at 2915 and 2848 cm^{-1} represents -CH_3 and -CH_2- groups in SAM ester respectively. Similarly, bands at 2920 and 2852 cm^{-1} represents -CH_3 and -CH_2- groups in SAM terpolymer. Additionally, the absorption band at 701 cm^{-1} for $(CH_2)_n$ confirms the presence of long alkyl chain. The bands at 1827 cm^{-1} and 1745 cm^{-1} represents presence of maleic anhydride monomer in SAM terpolymer however, the absence of these bands and appearance of new band at 1729 cm^{-1} reveals the esterification of maleic anhydride in SAM esters. The absence of 1636 cm^{-1} band in final product reveal polymerization of styrene has occurred successfully in both the products.[14]

3.2.2. Proton nuclear magnetic resonance (^1H NMR) spectroscopy

Fig. 4b represents ^1H NMR spectra of SAM terpolymers which confirms presence of different monomers in synthesized products. The presence of methyl and methylene groups in the long alkyl chain of alkyl acrylates was confirmed by strong peaks at 0.87 ppm and 1.3 ppm respectively. -CH_2 group of alkyl acrylate was defined by peak at 1.6 ppm. The -OCH_2 group in acrylates was identified by peaks at 3.7 ppm and 4.1 ppm. Efficient polymerization of acrylate monomer was confirmed by the disappearance of peaks at 4.9 ppm and 5.8 ppm. The H of polymerized maleic anhydride was assigned a signal at 2.5 ppm. Furthermore, additional peaks at 3.4 and 3.7 ppm indicate the presence of -CH-CH- of maleic anhydride, demonstrating the involvement of maleic anhydride monomer in polymerization via its double bonds. The multiplate signals attributable to the aromatic protons (-CH- of the benzene ring) were detected at 7.3 ppm, confirming the presence of styrene in the polymer backbone.

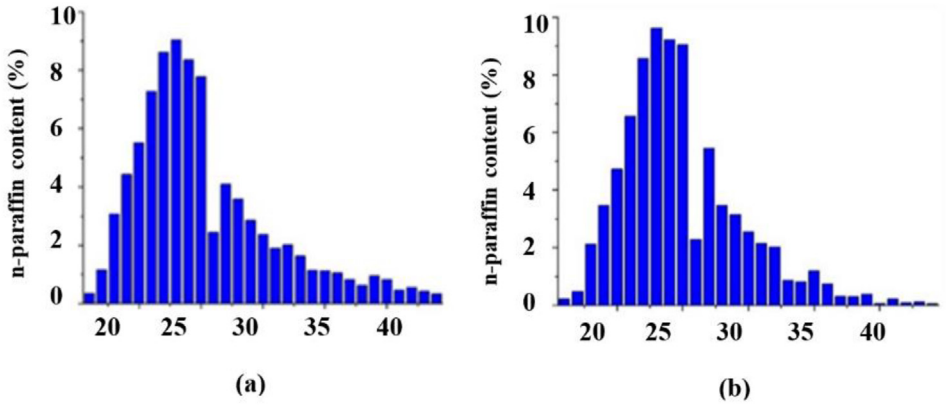

Fig. 3. Carbon number distribution for (a) wax sample isolated from C-1 (b) wax sample isolated from C-2.

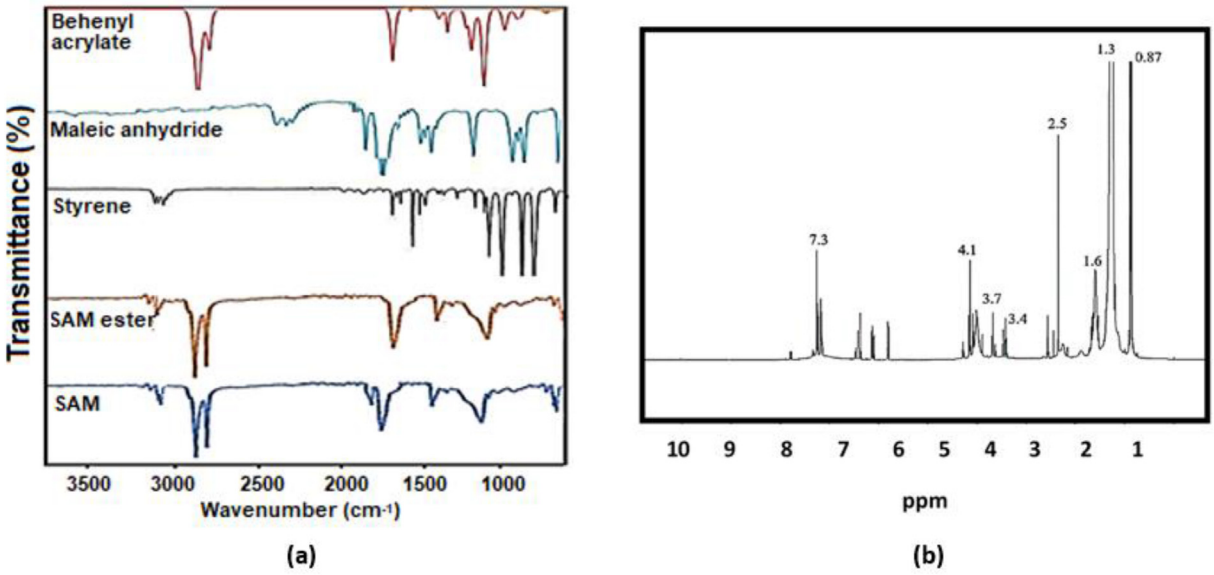

Fig. 4. (a) FTIR of Synthesized chemical additives (b) ^{1}H NMR of Synthesized chemical additives.

3.3. Effect of the synthesized polymeric additives

3.3.1. Pour point (PP) evaluation

The crude oil samples are waxy in nature and have high pour point. Thus, samples studied were dopped with varying concentrations (100, 300, 500, 1000 and 2000 ppm) of chemical additives and its influence on lowering the pour point of Indian waxy crude oil was investigated. Table 2 shows the pour points of crude oil beneficiated with and without chemical additives.

Fig. 5 depicts the influence of SAM esters on the pour point of C-1 and C-2, demonstrating that only SAM-22 depresses the pour point of C-1 and C-2 among all esters. According to the data shown in Table 2, the pour point values consistently decreased as the additive concentration increases to 2000 ppm. Thus, the optimal concentration for C-2 is 2000 ppm. On the other hand, the optimal concentration for C-1 is 1000 ppm. The pour point of C-1 increases somewhat as concentration increases. This is because the additive molecules themselves form small aggregates which restrict the side way growth of the wax crystals due to excess concentration of additives and hence, suppresses the efficacy of the additive to co-crystalize with paraffin in crude oil.[23,24] The efficiency of SAM-22 is attributed to the presence of aromatic benzene ring, pendant alkyl chains and polar functional group. The aromatic benzene ring present in SAM-22 acts as a nucleating site for asphaltenes present in crude oil and prevent the asphaltene flocculation. However, the pendant alkyl chains in SAM-22 is identical to wax present in oil samples which provides nucleating sites for wax crystals and co-crystallizes with wax resulting in structural modifications by forming small crystals.[25,26] Also, the ester group, which is polar in nature,

Table 2. Effect of chemical additives on PP of crude oil samples.

Additive	PP (°C) of C-1 = 27 °C					PP (°C) of C-2 = 39 °C				
	PP (°C) (Treated)					PP (°C) (Treated)				
	100	300	500	1000	2000	100	300	500	1000	2000
SAM-16	27	27	27	24	27	39	39	39	36	36
SAM-18	27	27	27	24	27	39	39	39	36	36
SAM-20	27	24	24	21	24	39	39	36	36	36
SAM-22	24	21	15	12	18	36	33	33	30	27

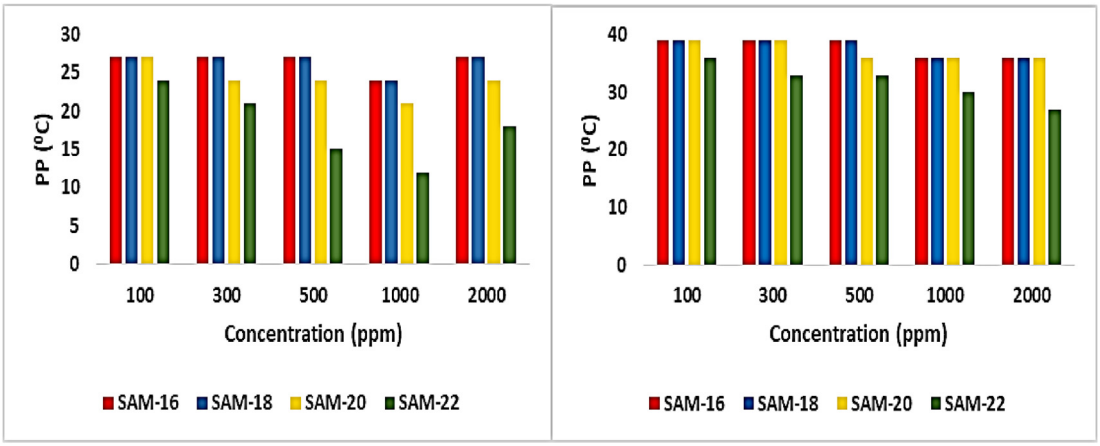

Fig. 5. Effect of synthesized chemical additives on Pour point of C-1 and C-2.

causes the formation of attracting forces that creates a barrier to the formation of interlocking wax networks, preventing the progression of waxy crystals in different directions. As only SAM-22 is showing effect as pour point depressant among all synthesized SAM ester, for further studies only SAM-22 was considered. The molecule SAM-22 was determined using GPC and the results are shown in Fig. 6 below:

	Molecular weight		
Additive code	M_w	M_n	PDI
SAM-22	32102	23923	1.34

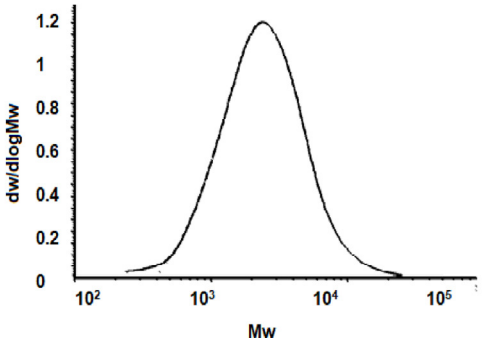

Fig. 6. Molecular weight distribution of SAM-22.

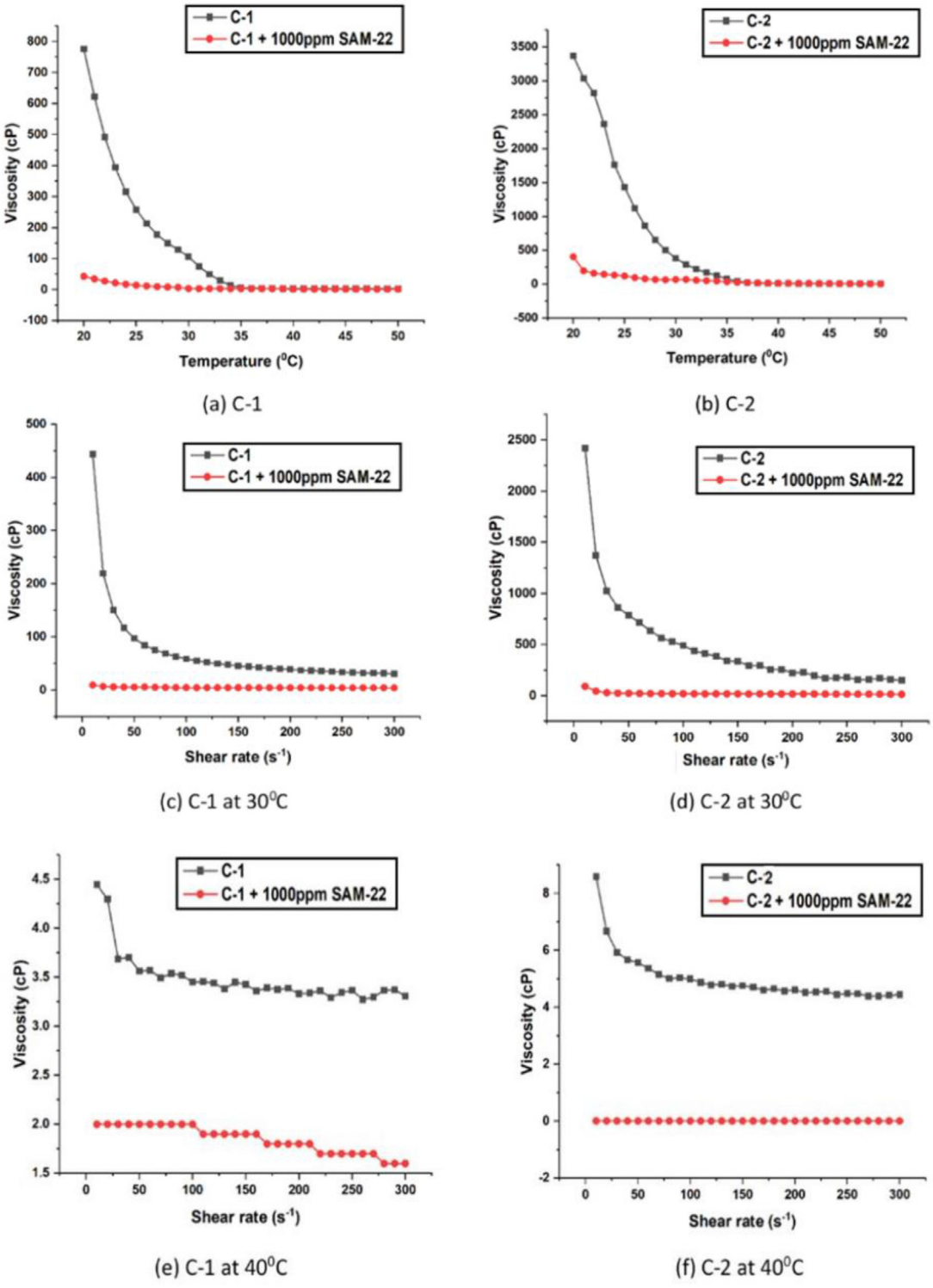

Fig. 7 Effect of SAM-22 on rheology of C-1 and C-2.

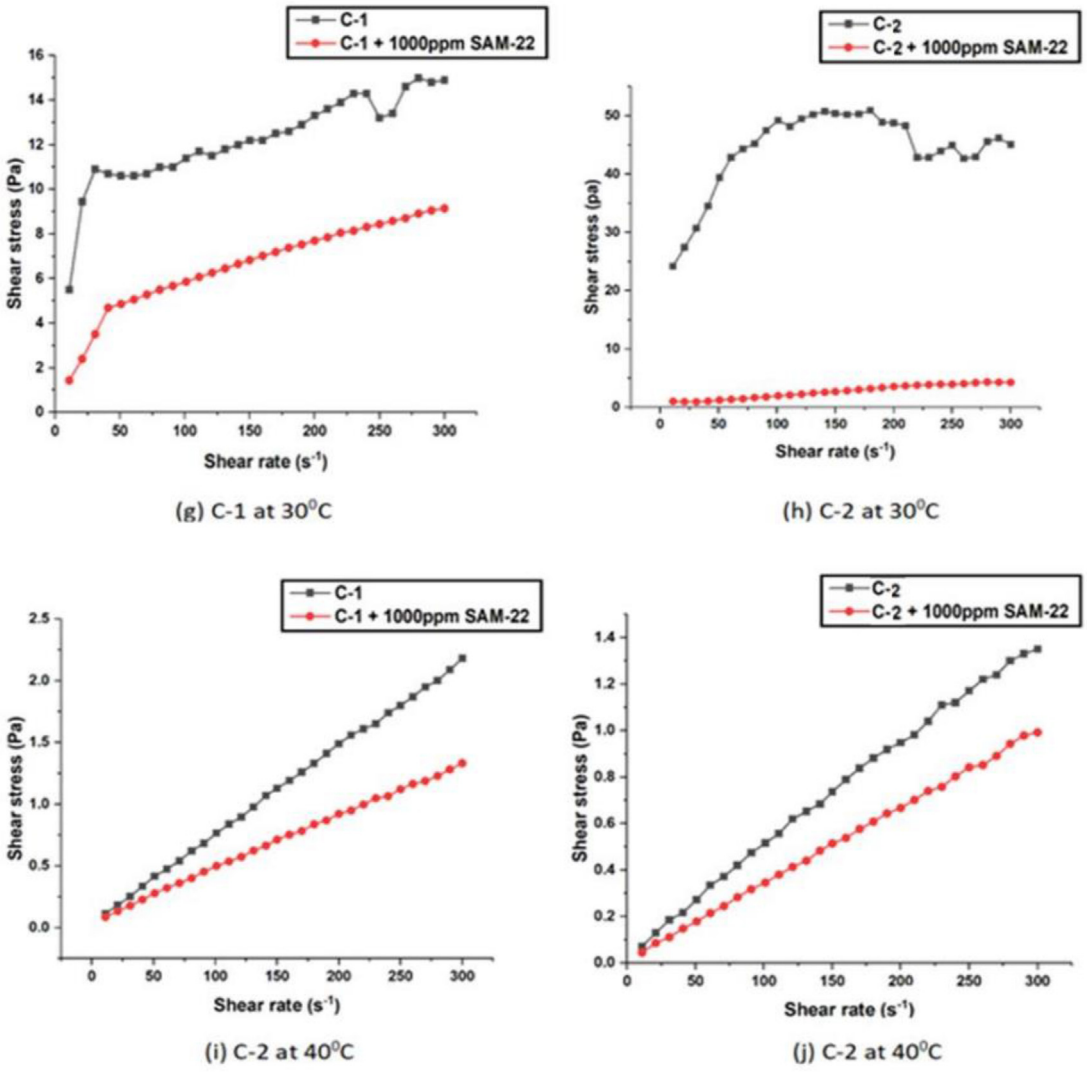

Fig. 7. (Continued)

3.3.2. Viscosity evaluation

If the temperature of oil decreases below WAT during pipeline transportation of crude oil, due to temperature gradient, wax crystals tend to deposit on inner wall of the pipeline which is at low temperature. If the thickness of wax deposit increases, they might restrict the flow of fluid by decreasing the diameter of the pipeline which makes pigging operation difficult. Furthermore, wax crystals cause gelling, complicating pipeline restarting. Thus, thorough knowledge of the rheological properties of waxy crudes is required to address these issues, particularly at low temperatures, by finding acceptable methods of wax deposition prevention.[27] The rheological tests aided in understanding the flow behaviour of neat and additive benefited crude oil samples at various shear rates and temperatures, reflecting crude oil flow in pipelines.[28] The optimal concentration of SAM-22 (1000 ppm for C-1 and 2000 ppm for C-2) was used in a rheological evaluation of additive beneficiated crude oil. To better understand the flow characteristics, flow curves of virgin and shear rates ranging from 10 to 300 s^{-1} at 30° and 40 °C.

Fig. 7a and b represent the correlation between apparent viscosity and temperature for virgin and treated crude oil, respectively. From the graphs, it can be observed that the viscosity gradually increases with decrease in temperature at constant shear rate. This is because of crystallization of wax crystals below WAT.[29] The rise in viscosity with declining temperature for treated crude oil is less than for virgin crude oil at constant shear rate. The viscosity of C-1 significantly decreased from 755 cP

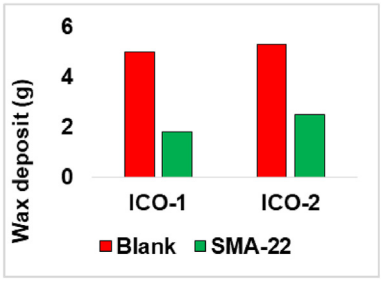

Fig. 8. Paraffin inhibition efficiency (%PIE) of synthesized chemical additives.

to 48 cP at 20 °C. On the other hand, the dramatic reduction in viscosity from 3250 cP to 470 cP for C-2 after treatment with SAM-22 solution. The typical examples in (Fig. 7c–f) show that the viscosity reduces progressively with increasing shear rate at temperatures 30 °C and 40 °C. At these temperatures (Fig. 7g–j), demonstrate a linear rise in shear stress with increasing shear rate. The figures show that virgin crude oil requires the least amount of stress for transportation at low temperatures, which represents the yield value for virgin crude oil. The yield value is significant because it measures the amount of stress required for restarting the flow. C-1 and C-2 exhibit yield values of 5.2 Pa and 23 Pa at 30 °C respectively, indicating that they act as Bingham pseudo plastics. Examination of the data represented in Fig. 7 shows that the yield value drops to 0.5 Pa and 0.3 Pa after treating crude oil with SAM-22, and the Newtonian character of the oil is evidenced by the linear nature of the rheogram passing through the origin.

3.3.3. Cold finger test

A cold finger test was performed to assess the wax deposition potential of C-1 and C-2, as well as the Paraffin Inhibition Efficacy of synthesized polymers at optimal concentration. Both the crude oils were treated with the optimum concentration of SAM-22 solution. C-1 was treated with 1000 ppm of additive solutions and C-2 was treated with 2000 ppm of additive solutions and the experiment was performed at temperatures below the pour point of virgin crude oil (25 °C for C-1 and 35 °C for C-2).

Fig. 8 shows that high amount of wax (5.0 g and 5.3 g) deposited in the tube from C-1 and C-2 respectively. The wax deposition was considerably reduced to 1.8 g after treating the C-1 with the optimal dosage of SAM-22 showing 64% PIE of the additive. SAM-22, on the other hand, displays 52.83% PIE and reduces the quantity of wax deposit to 2.5 g for C-2. The PIE of SAM-22 is attributed to the presence of a pendant alkyl chain in additive that resembles the carbon chain of wax present in crude oil and co-crystallizes with wax present in crude oil, as well as an aromatic benzene ring that provides a nucleating site for asphaltene present in crude oil, preventing wax deposition.[30]

3.3.4. Microscopic studies of virgin and crude oils benefited with synthesized PPD

Microscopic study aids in understanding the changes in morphology that occur with after addition of chemical additives. The effect of SAM-22 on wax morphology are represented in the images shown in Fig. 9.

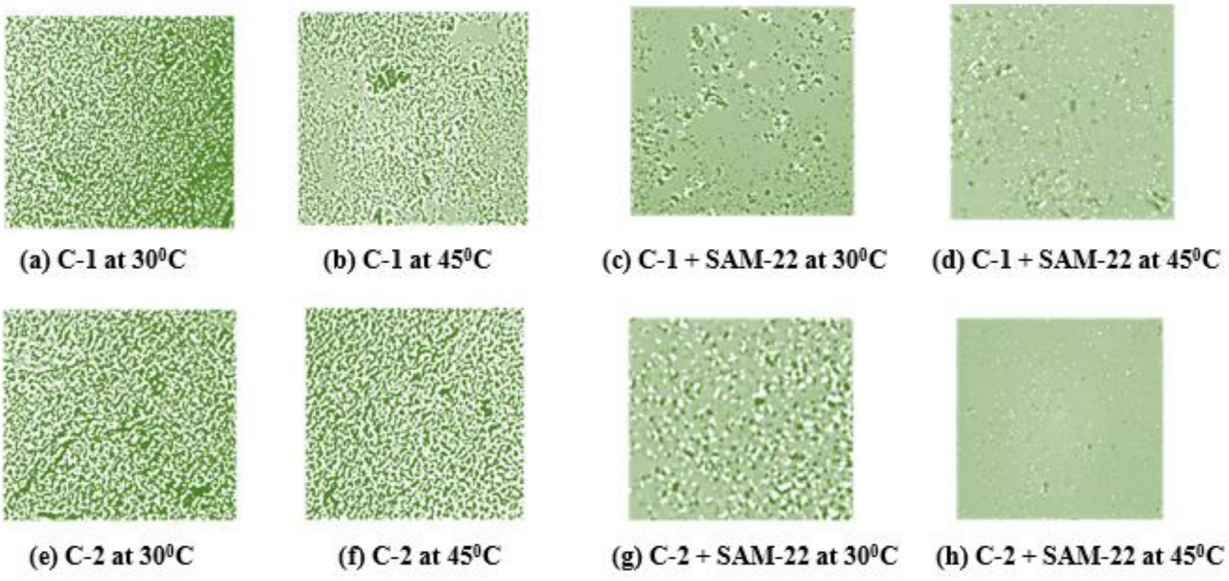

Fig. 9. Morphological analysis of crude oil.

Fig. 9a and e depict an intense network of wax crystals around asphaltene at 30 °C, which would impede crude oil flowability. As the temperature rises to 45 °C, the wax crystal network degrades due to wax solubilisation, as seen in (Fig. 9b and f). When both crude oils were treated with the additive at the optimal concentration, it seems to be the additive significantly inhibit the network formation of wax by fragmenting it even at 30 °C, representative an upgradation in the organization of the wax crystals than in virgin crude oil, as shown in (Fig. 9c and g). When the temperature is further increased to 45 °C, the wax crystals disperse completely as shown in (Fig. 9d and h). This validates the effect of SAM-22 on the morphological structure of wax crystals, which results in an improvement in crude oil flow. SAM-22 contains a benzene ring, which provides a nucleating site for asphaltene, while the pendant alkyl chain provides a nucleating site for the wax molecules present in the crude, which keeps the crystals dispersed in the crude oil by changing its morphology from feathery to spherical and limits the wax networking process. As a consequence, the intense contact between wax crystals is avoided, resulting in lower yield stress and enhanced crude oil flow.[26]

3.4. Conclusions

SMA ester were synthesized successfully by esterification of SAM terpolymers and structure of the products were elucidated by FTIR, ^{1}H NMR, and GPC. The performance of synthesized products were evaluated by pour point studies, rheological studies, cold finger analysis and microscopic studies. The key findings are:

(1) The results demonstrated that SAM-22 shows superior performance among other products and behave as PPDs and PI simultaneously. At a dosage of 1000 ppm, SAM-22 lowered the PP of C-1 from 27 °C to 12 °C (ΔPP = 15 °C) and C-2 from 39 °C to 27 °C (ΔPP = 12 °C) at a concentration of 2000 ppm.
(2) SAM-22 dramatically reduces viscosity by up to 93.6% for C-1 and 85.5% for C-2. The cold finger test demonstrated that at optimal concentration, SAM-22 prevents wax deposition by up to 64% for C-1 and 52.83% for C-2.
(3) At optimal concentration, SAM-22 significantly decreased the quantity of wax deposit by up to 64% for C-1 and 52.83% for C-2. Consequently, SAM-22 is an efficient additive for lowering the pour point and suppressing the paraffin deposition in crude oil.
(4) Microscopic examination indicated that the network of wax crystals was significantly disrupted in the presence of the SAM-22 addition.

Author contribution

Zarana Patel: Writing original draft, Jinal Patel: Writing and Ashish Nagar: Supervision.

Conflicts of interest

The author declare that they have no competing interests.

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References

1. Biswas S, Mohanty P, Sharma DK. Studies on synergism in the cracking and co-cracking of Jatropha oil, vacuum residue and high density polyethylene: kinetic analysis. *Fuel Process Technol*. 2013;106:673–683. https://doi.org/10.1016/j.fuproc.2012.10.001.
2. Sharma DK. Emerging biomass conversion technologies for obtaining value-added chemicals and fuels from biomass. *Proc Indian Natl Sci Acad*. 2015;81:755–764. https://doi.org/10.16943/ptinsa/2015/v81i4/48326.
3. Manchanda T, Tyagi R, Sharma DK. Comparison of fuel characteristics of green (renewable) diesel with biodiesel obtainable from algal oil and vegetable oil. *Energy Sources, Part A Recover Util Environ Eff*. 2018;40:54–59. https://doi.org/10.1080/15567036.2017.1405109.
4. Mahmoud T, Betiha MA. Poly(octadecyl acrylate-co-vinyl neodecanoate)/Oleic acid-modified nano-graphene oxide as a pour point depressant and an enhancer of waxy oil transportation. *Energy Fuel*. 2021;35. https://doi.org/10.1021/acs.energyfuels.1c00034.
5. Fu X, Zhu L, He B, Zhu L. Influence of monomer ratio on the performance of Poly(octadecyl acrylate-co-styrene) as pour-point depressants. *Energy Fuels*. 2020;34. https://doi.org/10.1021/acs.energyfuels.0c00174.
6. Kurniawan M, Ruwoldt J, Norrman J, Paso KG. Influence of wax inhibitor molecular weight on solution crystallization and rheology of monodisperse waxes. *Energy Fuel*. 2021;35:7666–7680. https://doi.org/10.1021/acs.energyfuels.0c04187.
7. Li W, Li H, Da H, Hu K, Zhang Y, Teng L. Influence of pour point depressants (PPDs) on wax deposition: a study on wax deposit characteristics and pipeline pigging. *Fuel Process Technol*. 2021;217:106817. https://doi.org/10.1016/j.fuproc.2021.106817.
8. Wu Y, Ni G, Yang F, Li C, Dong G. Modified maleic anhydride co-polymers as pour-point depressants and their effects on waxy crude oil rheology. *Energy Fuels*. 2012;26:995–1001. https://doi.org/10.1021/ef201444b.
9. Wen H, Zhang S, Lian Y, et al. Effect of nano pour point depressant on the flow properties of the waxy crude oil from Changqing Oilfield. *E3S Web Conf*. 2021;329. https://doi.org/10.1051/e3sconf/202132901050.
10. Kopf AH, Koorengevel MC, van Walree CA, Dafforn TR, Killian JA. A simple and convenient method for the hydrolysis of styrene-maleic anhydride copolymers to styrene-maleic acid copolymers. *Chem Phys Lipids*. 2019;218:85–90. https://doi.org/10.1016/j.chemphyslip.2018.11.011.

11. Chen Z, Wang X, Zhang H, Yang C, Shan H. A study on the interaction of crude oil waxes with polyacrylate pour point depressants by Monte Carlo simulation. *Petrol Sci Technol*. 2014;32:2151–2157. https://doi.org/10.1080/10916466.2013.769571.
12. Kulkarni AD, Wani KS. Combined effect of pour point depressants and magnetic field on the viscosity and pour point of crude oil. *Int J Creat Res Thoughts*. 2017;5:260–272.
13. Al-Sabagh AM, Noor El-Din MR, Morsi RE, Elsabee MZ. Styrene-maleic anhydride copolymer esters as flow improvers of waxy crude oil. *J Pet Sci Eng*. 2009;65:139–146. https://doi.org/10.1016/j.petrol.2008.12.022.
14. Elbanna SA, Abd El Rhman AMM, Al-Hussaini AS, Khalil SA. Development of novel Terpolymes and evaluating their performance as pour point depressants and paraffin inhibitors for waxy crude oil. *Egypt J Chem*. 2023;66:63–72. https://doi.org/10.21608/EJCHEM.2022.120528.5414.
15. Elganidi I, Elarbe B, Abdullah N, Ridzuan N. Synthesis of a novel terpolymer of (BA-co-SMA-co-MA) as pour point depressants to improve the flowability of the Malaysian crude oil. *Mater Today Proc*. 2021;42:28–32. https://doi.org/10.1016/j.matpr.2020.08.628.
16. Elganidi I, Elarbe B, Ridzuan N, Abdullah N. Synthesis, characterisation and pre-evaluation of a novel terpolymer as pour point depressants to improve the Malaysian crude oil flowability. *J Pet Explor Prod Technol*. 2022;12:2067–2081. https://doi.org/10.1007/s13202-021-01445-2.
17. Castro LV, Flores EA, Vazquez F. Terpolymers as flow improvers for Mexican crude oils. *Energy Fuel*. 2011;25:539–544. https://doi.org/10.1021/ef101074m.
18. Şimşek S, Yõlmaz E, Boztuğ A. Amine-modified maleic anhydride containing terpolymers for the adsorption of uranyl ion in aqueous solutions. *J Radioanal Nucl Chem*. 2013;298:923–930. https://doi.org/10.1007/s10967-013-2529-4.
19. Mou YL, Xia W, Wang Z, Zheng D. Synthesis and characterization of styrene. *Maleic Anhydride N-phenyl Maleimide Tripolymer*. 2016:1110–1115. https://doi.org/10.2991/ame-16.2016.180.
20. Zhang C, Chen D, Yang W. Preparation of styrene-maleic anhydride-acrylamide terpolymer particles of uniform size and controlled composition via self-stabilized precipitation polymerization. *Ind Eng Chem Res*. 2020;59:15087–15097. https://doi.org/10.1021/acs.iecr.0c02246.
21. Azeem A, Kumar R, Pal B, Naiya TK. Use of novel pour point depressant synthesized from vegetable oil for waxy crude oil. *Petrol Sci Technol*. 2020;38:185–193. https://doi.org/10.1080/10916466.2019.1697291.
22. Huang H, Wang W, Peng Z, et al. The influence of nanocomposite pour point depressant on the crystallization of waxy oil. *Fuel*. 2018;221:257–268. https://doi.org/10.1016/j.fuel.2018.01.040.
23. Machado ALC, Lucas EF, González G. Poly(ethylene-co-vinyl acetate) (EVA) as wax inhibitor of a Brazilian crude oil: Oil viscosity, pour point and phase behavior of organic solutions. *J. Pet. Sci. Eng.* 2001;32:159–165. https://doi.org/10.1016/S0920-4105(01)00158-9.
24. Wu Y. *Study of asphaltene effect on wax precipitation and deposition*. 2012:1–151.
25. El-Gamal IM, Khidr TT, Ghuiba FM. Nitrogen-based copolymers as wax dispersants for paraffinic gas oils. *Fuel*. 1998;77:375–385. https://doi.org/10.1016/S0016-2361(98)80027-6.
26. Soni HP, Kiranbala, Bharambe DP. Performance-based designing of wax crystal growth inhibitors. *Energy Fuels*. 2008;22:3930–3938. https://doi.org/10.1021/ef8002763.
27. Onwumelu DC, Onwuka MK, Nnebeana SE, et al. Crude oil and the problem of wax deposition on pipeline systems during transportation: a review. *World J Adv Res Rev*. 2022;15:781–798. https://doi.org/10.30574/wjarr.2022.15.1.0770.
28. Chandran K, Sinnathambi CM. Rheological behavior on treated Malaysian crude oil. *AIP Conf Proc*. 2016: pp. 060002-1-060002-9. https://doi.org/10.1063/1.4968129.
29. Huang Q, Li H, Zhuang Y, et al. Reducing viscosity of waxy crude oil with electric field perpendicular to oil's flow direction. *Fuel*. 2021;283:119345. https://doi.org/10.1016/j.fuel.2020.119345.
30. Sivakumar P, Sircar A, Deka B, Silviya Anumegalai A, Suresh Moorthi P, Yasvanthrajan N. Flow improvers for assured flow of crude oil in midstream pipeline - a review. *J Pet Sci Eng*. 2018;164:24–30. https://doi.org/10.1016/j.petrol.2018.01.022.