



Synthesis of a novel terpolymer of (BA-co-SMA-co-MA) as pour point depressants to improve the flowability of the Malaysian crude oil

Ibrahim Elganidi, Basem Elarbe, Norhayati Abdullah*, Norida Ridzuan

Faculty of Chemical & Process Engineering Technology, Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia

ARTICLE INFO

Article history:

Received 14 June 2020

Received in revised form 28 July 2020

Accepted 24 August 2020

Available online 6 October 2020

Keywords:

Wax deposition

Pour point depressants

Viscosity reduction

Reaction parameters

Wax inhibitor

ABSTRACT

During the extraction of crude oil, the reservoir temperature is much higher than the surface temperature especially when the oil is transported cross subsea. Therefore, the flow of virgin oil gets impeded due to the precipitation of wax on the inner wall of pipelines when the temperature decreased below the wax appearance temperature (WAT) and the flow stops if the temperature falls below the pour point. Polymeric pour point depressants (PPD) have received considerable attention as a wax control approach to enhance the flowability of waxy crude oil. The aim of the current study is to synthesize a novel PPD of benzyl acrylate-co-stearyl methacrylate-co-maleic anhydride (BA-co-SMA-co-MA) to improve the viscosity of Malaysian crude oil using free radical polymerization. The effect of polymerization parameters, such as reaction temperature, initiator concentration, experimental duration, and monomer concentration on the yield of the synthesized polymer was evaluated statistically with a one-factor-at-a-time (OFAT) approach. The performance of the prepared PPD was evaluated to determine its effects on the viscosity of crude oil using Brookfield DV-III viscometer. The experimental results showed that the optimum conditions to obtain the highest yield were at the reaction time of 8 h, initiator concentration of 1.5 wt%, reaction temperature of 100 °C, and monomers ratio of (BA:SMA: MA) 1:1:1. At the optimum conditions, the prepared terpolymer reduces the viscosity of crude oil from 7.2 mPa.s to 3.2 mPa.s at 30 °C using 1500 ppm. The significant reduction in the apparent viscosity indicated improvement in the low-temperature flow properties of the crude oil after applying the synthesized PPD.

© 2019 Elsevier Ltd. All rights reserved.

Selection and Peer-review under responsibility of the scientific committee of the International Conference of Chemical Engineering & Industrial Biotechnology.

1. Introduction

Until the end of the 20th century, domestic consumption for unconventional heavy and extra-heavy oil was negligible due to its high viscosity and complexity of crude composition, creating many technical difficulties in the supply chain that hinder their economic viability. Increase the energy demands in the early 21st century has driven some developed and developing countries such as China, Japan, the USA and India to manage their non-conventional resources which require major technical advances and thus restructuring the refining industries [1]. The low American Petroleum Institute (API) gravity and high viscosity crude oil are attributed to presence of paraffin wax, asphaltenes, and comparatively low molecular weight compounds [2]. In such waxy crudes, the structure of the wax shifts through three phases; aggre-

gation, deposition, and gelation. Such phases and rheological behavioral transitions makes the crude oil turn from basic Newtonian fluid into a complicated non-Newtonian fluid resulting in an immediate increase in the viscosity of the crude oil, and subsequent deposition of wax on the internal wall of pipeline causing flow pipelines to be blocked and high pressure drops [3].

Consequently, the decline in flowability of such heavy and ultra-heavy oils is deemed to be one of the costly obstacles which contributes to costly downtime and high-priced treatment strategies [4,5].

The wax molecules are the paraffinic component of the crude oil, including alkane, cycloalkanes, and branched-chain alkane, and the solubility of these crystals strongly related to temperature [6]. The paraffin crystals continue to be isolated from crude oil when the temperature decreases below wax appearance temperature (WAT) or cloud point which impedes the movement of crude oil and increases the oil viscosity [2,7]. Beneath the cloud point, the wax starts to crystallize as an interlocking network pulling the

* Corresponding author.

E-mail address: yatiabdullah@ump.edu.my (N. Abdullah).

remaining liquid crude in cage-like structures due to the evaporation of light hydrocarbon components [8,9]. When the crude oil reaches the pour point (the lowest temperature at which crude can flow freely at its weight) [10,11], the oily gel can be formed and crude oil movement completely stops, causing the cold flow issues, for instance, decrease in the production rate, pipeline blockage, and prolonging breakdown [12,13]. In addition to problems including enormous capital investment in the transport and storage of waxy crude oils, another serious issue takes place during the restart process after the pipeline shutdown [14]. The production shutdown causes a static cooling of waxy crude oils which leads to the transformation of the crude oil from sol to gel causing difficulty to flow through the pipeline [15].

Many mitigation and remediation techniques were established to solve the wax deposition issue and improve the flow properties of the waxy crude oil's low temperature. For instance, thermal methods, such as circulating hot water or oil through pipelines and wrapping crude pipelines for temperature maintenance, and mechanical techniques such as pigging scrape the inner walls of pipelines for the removal of deposited wax, are some methods to assure the flow in crude oil pipelines [16]. Pre-treatment by polymeric additives known as flow improvers or pour point depressants (PPD) is the most practical solution to this issue. Polymeric remediation with PPDs are commonly used in the pipeline industry in a limited dose to reduce the pour point and gelation point and improve the low-temperature flow properties of crude and promote pipeline transport [11,17,18]. These polymeric PPDs are polymerization of homo or different monomers that must be distinguished by high oil solubility and have a flexible structure comprising a wax-like paraffin element. Also, characterized by having long linear alkyl chains with a polar portion such as acetate, acrylate, and methacrylate which has a high potential to interfere with crystals wax of crude oil beneath its cloud point [15]. This possible interaction involves nucleation, co-crystallization and adsorption if such materials are available in a comb-like shape polymer, the pendant chains serve as a wax-like paraffin element that affords nucleation locations and co-crystallizes with oil's paraffin forming component. In contrast, the polar end groups obstruct the wide-ranging growth of wax matrices and restrict any crystallization. Afterward, polymers that adsorbed on the rising wax crystals sterically impeded their development, resulting in small crystals by changing morphology and growth patterns of wax crystals which are typically range from orthorhombic to a compact cubic or pyramidal shape, inhibiting wax crystals to agglomerate and creating a gel-like structure [19,20]. Therefore, from the previous researches, it is evident that the more similar the structure of the polymer to the wax component, the better its performance [21].

There are several polymeric additives with these structural properties, of which different forms are available as commercial PPDs such as alkyl acrylate polymers, alkyl methacrylate, alkyl esters, and particularly ethylene vinyl acetate polymers which are utilized in large amounts in the oil field. Comb-shaped polymers of maleic anhydride with different monomers like alkyl esters and styrene are also revealed as great PPDs. One of the long chain alkyl groups is stearyl methacrylate in particular. It is a type of acrylic monomer that has a strong association with non-polar solvents, also dispersed widely in synthesizing the PPDs. Nevertheless, poly stearyl methacrylate appears to be in the crystalline phase, and as a result, the long chain in the alkyl groups will crystallize in spite of an amorphous backbone that inhibits oil absorption [22]. Several studies have been conducted on acrylic monomers in the recent years, since the monomers are the enormous multilateral type utilized to create acrylate polymers, and shaped by acrylic-based acid-structure polymers with carboxylic acid content and vinyl groups [23,24]. Moreover, acrylic and

methacrylic ester groups are essentially among the chemicals that have been used for this purpose because of high ability to inhibit the wax deposition and flow modifiers [24]. Many of the researchers [20,25–29] have applied methacrylate and acrylate monomers in the production of PPDs polymers for their extremely reactive vinyl bonds. Such polymers may also be used to increase crude oil flowability and to lower the wax accumulation in the crude oil pipeline, such as a PPD chemical inhibitor.

Over the last few years, methacrylate and maleic anhydride polymers have received particular attention as potential performance additives owing to their highly polar functional groups [30,31]. Than et al. [32] showed that stearyl methacrylate, behenyl acrylate, vinyl acetate and AIBN as initiator decreased the pour point temperature by 15 °C and the amount of deposited wax by 70%. Behenyl acrylate has a vital role in enhancing additive performance because of the long chains of hydrocarbon and polar ends molecules. These three monomers have integrated a new-fangled terpolymer that other wax inhibition scientists have not yet invented. Soliman, et al. [1] prepared a PPD of maleic anhydride with alkyl linoleate, which led to a decrease in pour point temperature by 18 °C.

The objective of the current study is to screen and pre-evaluate a novel terpolymer of behenyl acrylate with stearyl methacrylate and maleic anhydride (BA-co-SMA-co-MA) as PPD that can prevent the precipitation of wax in crude oil pipelines. The methods for characterizing the prepared polymer through FTIR and HNMR data have been discussed in the previous paper Elganidi, et al. [33]. Polymerization parameters that can result in optimal conditions for polymerization reaction in terms of reaction yield and the highest performance were screened. The effect of operating parameters, such as reaction temperature, initiator concentration, experimental duration and monomer concentration on the yield of the synthesized polymer was evaluated statistically with a one-factor-at-a-time (OFAT) approach. Consequently, factors that influence experimental results and the optimal levels of such aspects were determined in order so that future research can be designed to achieve maximum sensitivity [34,35]. Moreover, the performance of the synthesized polymer was evaluated through viscosity measurement.

2. Experimental section

2.1. Materials

Behenyl acrylate (BA) (99%), maleic anhydride (MA) (<99%), and stearyl methacrylate (SMA) (96%) were used as monomers and were supplied by Aladdin chemicals. Toluene ($\geq 99\%$) and benzoyl peroxide (BPO) (99%) were used as a solvent and an initiator, respectively, and they were obtained from Sigma- Aldrich. The crude oil sample that tested in the current study is Malaysian crude oil, which explicitly taken from Petronas Refinery Plant, Kerteh, Malaysia.

2.2. Preparation of terpolymer

Behenyl acrylate-co-stearyl methacrylate-co-maleic anhydride was polymerized using free radical polymerization technique in a 250 mL three-necked glass flask at different ratios of monomers concentration, as shown in Table 1. The reactor was equipped with a thermometer, nitrogen gas inlet (for the first 30 min) to eradicate the presence of O₂ in the reaction, and magnetic stirrer. Under a constant stirring (400 rpm), the monomers mixture was dissolved in 50 mL of toluene at a range of reaction time from 4 to 12 h and polymerization temperature from 60 to 120 °C. Besides, benzoyl peroxide was used as the initiator for the reaction in the range of

Table 1
Effect of monomer ratio on PPD yield.

Polymer code	Monomer ratio*	Amount of produced polymer (g)	Yield wt %
PPD 1	1:1:1	14.057	86
PPD 2	1:1:0	16.654	77
PPD 3	1:0:1	10.339	72
PPD 4	0:1:1	7.063	54
PPD 5	2:1:1	15.112	84
PPD 6	1:2:1	13.802	79
PPD 7	1:1:2	10.202	74

* ratio is referred to (behenyl acrylate (BA): stearyl methacrylate (SMA): maleic anhydride (MA)).

0.5 to 2.5 wt% (of the total of monomers) and dissolved in an appropriate amount of toluene. Then, the initiator solution was added drop-by-drop to the reaction mixture every 15 min for the first hour of reaction. At end of the reaction, the solution was kept at room temperature to cool and then washed by methanol three times; after that vacuum filtered, dried, and weighed to acquire the terpolymer. The chemical reaction of the synthesis process of (BA-co-SMA-co-MA) is shown in Scheme 1.

2.3. Performance evaluation of terpolymer

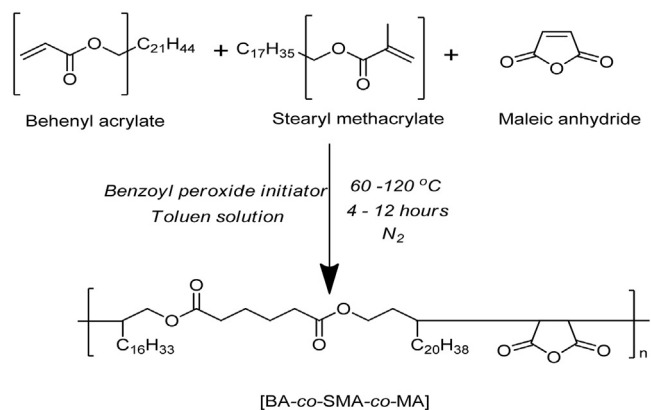
The Brookfield DV-III viscometer with Spindle model 31 was utilized to determine the apparent dynamic viscosity of crude oil with and without the addition of BA-co-SMA-co-MA. The used techniques meet the standards of ASTM D5002-99 and ASTM D445-06. Before viscosity measurement, the crude sample was heated above the WAT to ensure that all of the paraffin crystals are dissolved [36]. The 2 mL of diluted PPD in toluene and 8 mL of crude oil were transferred into a cylinder of stainless steel with casing linked to circulating thermostat water bath to study the influence of PPD on the rheological behaviour of crude oil. The viscosity was measured at a fixed shear rate 61.2 S^{-1} over a wide range of temperature from 5 to 40 °C. Besides, the degree of viscosity reduction (DVR) has been calculated using Eq. (1).

$$DVR\% = \frac{\mu_{ref} - \mu_{treat}}{\mu_{ref}} * 100 \quad (1)$$

where μ_{ref} are viscosity of blank crude oil and μ_{treat} the viscosity values of the crude oil after treatment

3. Results and discussion

The optimum condition of the polymerization reaction to acquire high yield polymer has been investigated. The polymerization of maleic anhydride-co-stearyl methacrylate-co-behenyl



Scheme 1. Synthesis of (BA-co-SMA-co-MA).

acrylate has been conducted to study the optimal reaction conditions using OFAT.

3.1. Effect of monomers ratio

A series of polymers have been synthesized at the conditions of 90 °C reaction temperature, six hours of reaction time, and 1 wt% concentration of initiator (from the total of monomers) with different monomers ratio and the yield for each PPD was calculated as shown in experimental results in Table 1.

Table 1 demonstrates that the effect of terpolymer yield is diverse when the polymerization process is achieved at various monomer ratios. Molar ratio of (BA-co-SMA-co-MA) polymer has a significant effect on the yield because of the acrylate groups which act as a feedstock for a chemical additive. As seen in Table 1, PPD 1 and PPD 5 (mole ratio 1:1:1, and 2:1:1) had a significant effect on increasing the yield of the prepared polymer due to increasing concentration of high molecular weight monomer of BA in the feed. The long hydrocarbon chains with polar ends of BA molecules are the key reasons for exhibiting better yield of the synthesised polymeric additives as per a similar result reported previously by Upadhyay, et al. [37]. The optimal condition of polymerization reaction in terms of monomer ratios was at a concentration of 1:1:1. From this result, it is evident that the equal molar ratios of behenyl acrylate, stearyl methacrylate, and maleic anhydride gives the optimal yield of the prepared polymer as similar reported by Zhu, et al. [38].

3.2. Effect of reaction temperature

At a varying range of reaction temperature from 60 to 120 °C, a series of terpolymer was prepared to investigate the effect of polymerization temperature on the yield of the terpolymer, as shown in Table 2. The other reaction conditions which were reaction time, monomers ratio, and concentration of initiator were kept constant at 6 h, (BA: SMA: MA) 1:1:1, and 1 wt% (from the total of monomers), respectively.

It can be seen from the data in Table 2, the yield of synthesized terpolymer continues to increase with increasing reaction temperature from 51% at 60 °C until it reaches 85% at 100 °C as similar reported previously by Elarbe, et al. [39]. Besides, the yield stayed stable after increasing the temperature more than 100 °C, this is possibly because of a portion of the initiating species have being destroyed at higher temperatures. As a result, the optimal condition for the polymerization temperature to be completed and achieve the highest yield of terpolymer was found to be at 85% and 100 °C.

3.3. Effect of concentration of initiator

To comprehend the effectiveness of the initiator concentration on the yield of the synthesized terpolymer, a chain of reactions was conducted with different amount of BPO between 0.5 and 2.5 wt% at 100 °C for 6 h and the BA:SMA: MA ratio of 1:1:1 as shown in the experimental data in Table 3 below.

Table 2
Effect of reaction temperature on the yield of PPD.

Polymer code	Reaction temperature (°C)	Amount of produced polymer (g)	Yield wt%
PPD 8	60	8.34	51
PPD 9	80	13.41	82
PPD 10	100	13.90	85
PPD 11	120	13.92	85

Table 3
Effect of concentration of initiator on the yield of PPD.

Polymer Code	Concentration of initiator %	Amount of produced polymer (g)	Yield wt%
PPD 12	0.5	10.623	65
PPD 13	1	14.055	86
PPD 14	1.5	14.219	87
PPD 15	2	14.100	86
PPD 16	2.5	13.892	85

As it can be seen from Table 3, the yield of terpolymer start to increase from 65% to 87% when the concentration of initiator increased from 0.5 wt% to 1.5 wt%. However, beyond 1.5 wt% the yield of reaction decreases slightly with increasing initiator concentration due to rising the number of radicals in the medium, which leads to creating more nucleation sites. Therefore, when increasing the initiator to 2 wt% the aggregation process between the monomer chains reached the point that is sufficient to react with the radicals. Besides, the higher rate of free radical initiation leads to faster initial monomer consumption, but also produces a shorter kinetic chain length and enhance the probability of chain termination by the initiator as the similar results that reported previously by Christian, et al. [40]. Consequently, the optimum condition of initiator concentration is 1.5 wt%, which the highest yield was achieved at 87%.

3.4. Effect of reaction time

Under the condition of monomer ratio of 1:1:1, at reaction temperature of 100 °C, 1.5 wt% concentration of initiator (from the total of monomers) and varying reaction time, a series of terpolymer has been synthesized, and the yield of the prepared polymer computed from experimental results is shown in Table 4.

As it can be observed from Table 4, the yield of the synthesized terpolymer increased from 70% to 90% by increasing the time from 4 to 8 h, and after that, the yield of terpolymer remained stagnant at 90%. Therefore, the optimum condition for the time of polymerization in terms of reaction yield is 8 h, which achieved the highest yield of 90%. However, after 8 h of reaction, the yield no longer increases over time. It is indicating that the polymerization process is completed after 8 h of reaction as per the similar result reported by Zhu, et al. [41].

3.5. Viscosity measurement of the PPD

Viscosity is a significant physical property of crude oil and plays an essential role to evaluate the flowability of crude oil in the absence and presence of the prepared polymeric additives. In addition, temperature is one of the factors that influences the viscosity and its observed that viscosity remains increasing with reduction in the temperature [36,42,43]. The viscosity of the crude oil was measured with and without the addition of BA-co-SMA-co-MA using the PPD14 (at the optimum condition of the polymerization reaction) at different concentrations of terpolymer (1000, 1500, 2000, 2500 and 3000 ppm) to investigate the influence of concen-

Table 4
Effect of reaction time on the yield of PPD.

Polymer code	Reaction time (h)	Amount of produced polymer (g)	Yield wt %
PPD 17	4	11.441	70
PPD 18	6	14.061	86
PPD 19	8	14.710	90
PPD 20	10	14.709	90
PPD 21	12	14.707	90

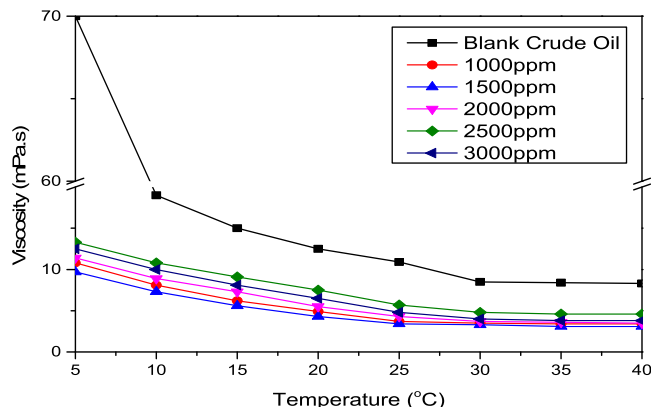


Fig. 1. Viscosity measurement.

tration on the viscosity of crude oil. Fig. 1 shows the viscosity result of the prepared terpolymers at different concentrations. Also, the figure was indicating that all of the prepared PPDs have a critical effect of reducing the viscosity of crude oil. For instance, at 5 °C, the viscosity of crude oil is decreased by 87% from 70 mPa.s for the blank crude oil to around 9.2 mPa.s after adding the PPD at concentrations of 1500 ppm. The most significant and effective viscosity reduction of the synthesized PPD was observed at the concentration of 1500 ppm which exhibited the best performance in terms of the degree of viscosity reduction from 87% to 47% as shown in Fig. 2.

Furthermore, the viscosity of crude oil with and without (BA-co-SMA-co-MA) polymer was examined to understand the viscosity movement mechanism. When BA-co-SMA-co-MA polymer was added as PPD to crude oil, molecules of copolymer interact with the molecules of crude oil, changing the original intermolecular structure of crude oil, weakening its ability to form hydrogen bonds with hydroxyl or carboxyl groups, and therefore reducing the crude oil viscosity [44]. Loss of the capacity of higher soluble inhibitors to minimize viscosity may be correlated with wax crystallization or wax inhibitor precipitation by the process of wax inhibitor nucleation [36]. As observed from NMR structural analysis that have been discussed in the previous publication [33], stearyl methacrylate and benzyl acrylate have a long alkyl chain. In this manner, when the PPD disperses the crude oil molecules, the long-chain monomers can separate oil micelles, decrease the friction, and prevent the combination of oil molecules; as a result, the viscosity of the crude oil reduces [4,41,45].

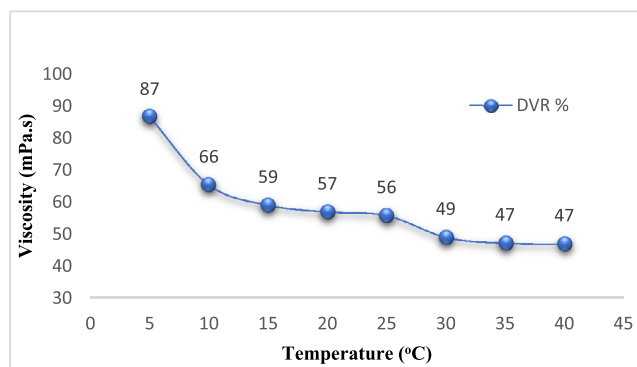


Fig. 2. Viscosity and degree of viscosity reduction (DVR) of crude oil in presence of prepared PPD at 1500 ppm and different temperature.

4. Conclusion

A novel pour point depressant of BA-co-SMA-co-MA terpolymer was synthesized as flow improver in the crude oil pipeline. The highest yield of the BA-co-SMA-co-MA was 90 wt%, which was obtained at the optimal polymerization reaction conditions of 8 h of reaction time, 100 °C reaction temperature, 1.5 wt% of concentration of initiator and monomers ratio pf (BA:SMA: MA) 1:1:1. The performance evaluation of the prepared PPD was studied for the viscosity reduction of the crude oil. When the PPD was added to the crude oil at 1500 ppm, the viscosity of the crude is reduced about 87% from 70 mPa.s for the blank crude oil to around 9.2 mPa.s at temperature 5 °C. Therefore, the new synthesized BA-co-SMA-co-MA terpolymer was successfully formulated to improve the flowability problem of Malaysian crude oil.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

Authors wish to thank the Faculty of Chemical and Process Engineering Technology at University Malaysia Pa-hang for the funding sponsorship of this study using PGRS 1903103.

References

- [1] E.A. Soliman, M.R. Elkatory, A.I. Hashem, H.S. Ibrahim, Synthesis and performance of maleic anhydride copolymers with alkyl linoleate or tetraesters as pour point depressants for waxy crude oil, *Fuel* 211 (2018) 535–547.
- [2] M.E. Mohyaldinn, H. Husin, N. Hasan, M.M. Elmubarak, A.M. Genefid, M.E. Dheeb, Challenges during Operation and Shutdown of Waxy Crude Pipelines, in: *Processing of Heavy Crude Oils-Challenges and Opportunities*, IntechOpen, 2019.
- [3] A. Japper-Jaafar, P. Bhaskoro, Z. Mior, A new perspective on the measurements of wax appearance temperature: comparison between DSC, thermomicroscopy and rheometry and the cooling rate effects, *J. Petrol. Sci. Eng.* 147 (2016) 672–681.
- [4] B. Deka, R. Sharma, A. Mandal, V. Mahto, Synthesis and evaluation of oleic acid based polymeric additive as pour point depressant to improve flow properties of Indian waxy crude oil, *J. Petrol. Sci. Eng.* 170 (2018) 105–111.
- [5] M.M. Bacon, L.B. Romero-Zerón, K.K. Chong, Determining wax type: paraffin or naphthene?, *SPE J* 15 (04) (2010) 963–968.
- [6] H.M. Meighani, C. Ghotbi, T.J. Behbahani, K. Sharifi, A new investigation of wax precipitation in Iranian crude oils: experimental method based on FTIR spectroscopy and theoretical predictions using PC-SAFT model, *J. Mol. Liq.* 249 (2018) 970–979.
- [7] A. Admiral, M. Abdullah, A. Ariffin, Evaluation of emulsified acrylate polymer and its pour point depressant performance, *Procedia Chem.* 19 (2016) 319–326.
- [8] M. Lashkarbolooki, A. Seyfaee, F. Esmailzadeh, D. Mowla, Experimental investigation of wax deposition in Kermanshah crude oil through a monitored flow loop apparatus, *Energy Fuels* 24 (2) (2010) 1234–1241.
- [9] L.Z. Hao, H.S. Al-Salim, N. Ridzuan, A Review of the Mechanism and Role of Wax Inhibitors in the Wax Deposition and Precipitation, *Pertanika J. Sci. Technol.* 27 (1) (2019).
- [10] F. Zhang, J. Ouyang, X. Feng, H. Zhang, L. Xu, Paraffin deposition mechanism and paraffin inhibition technology for high-carbon paraffin crude oil from the kazakhstan pk oilfield, *Pet. Sci. Technol.* 32 (4) (2014) 488–496.
- [11] D.W. Jennings, J. Breitigam, Paraffin inhibitor formulations for different application environments: from heated injection in the desert to extreme cold arctic temperatures, *Energy Fuels* 24 (4) (2010) 2337–2349.
- [12] M.M. El-Dalatony et al., Occurrence and characterization of paraffin wax formed in developing wells and pipelines, *Energies* 12 (6) (2019) 967.
- [13] Z. Wang, Y. Xu, Y. Zhao, Z. Li, Y. Liu, J. Hong, Role of shearing dispersion and stripping in wax deposition in crude oil pipelines, *Energies* 12 (22) (2019) 4325.
- [14] B. Yao, C. Li, X. Zhang, F. Yang, G. Sun, Y. Zhao, Performance improvement of the ethylene-vinyl acetate copolymer (EVA) pour point depressant by small dosage of the amino-functionalized polymethylsilsequioxane (PAMSO) microsphere, *Fuel* 220 (2018) 167–176.
- [15] B. Yao, C. Li, F. Yang, Y. Zhang, Z. Xiao, G. Sun, Structural properties of gelled Changqing waxy crude oil benefitted with nanocomposite pour point depressant, *Fuel* 184 (2016) 544–554.
- [16] F. Alnaimat, M. Ziauddin, Wax deposition and prediction in petroleum pipelines, *J. Petrol. Sci. Eng.* 184 (2020) 106385.
- [17] A. Aiyejina, D.P. Chakrabarti, A. Pilgrim, M. Sastry, Wax formation in oil pipelines: a critical review, *Int. J. Multiph. Flow* 37 (7) (2011) 671–694.
- [18] S. Elbanna, A. Abd El Rhman, A. Al-Hussaini, S. Khalil, Synthesis and characterization of polymeric additives based on α -Olefin as pour point depressant for Egyptian waxy crude oil, *Pet. Sci. Technol.* 35 (10) (2017) 1047–1054.
- [19] T. Liu, L. Fang, X. Liu, X. Zhang, Preparation of a kind of reactive pour point depressant and its action mechanism, *Fuel* 143 (2015) 448–454.
- [20] F. Yang, K. Paso, J. Norrman, C. Li, H. Oschmann, J. Sjöblom, Hydrophilic nanoparticles facilitate wax inhibition, *Energy Fuels* 29 (3) (2015) 1368–1374.
- [21] D. Tiwary, A.K. Mehrotra, Phase transformation and rheological behaviour of highly paraffinic “waxy” mixtures, *Canadian J. Chem. Eng.* 82 (1) (2004) 162–174.
- [22] R.K. Farag, Poly (cinnamoyloxy ethyl methacrylate-co-octadecyl acrylate) as flow improver for Egyptian waxy crude oils, *Int. J. Polym. Mater.* 57 (3) (2008) 189–202.
- [23] N. Ballard, J.M. Asua, Radical polymerization of acrylic monomers: An overview, *Prog. Polym. Sci.* 79 (2018) 40–60.
- [24] F. Yang, Y. Zhao, J. Sjöblom, C. Li, K.G. Paso, Polymeric wax inhibitors and pour point depressants for waxy crude oils: a critical review, *J. Dispersion Sci. Technol.* 36 (2) (2015) 213–225.
- [25] X. Zhu, Y. Gu, G. Chen, Z. Cheng, J. Lu, Synthesis of poly (octadecyl acrylate-b-styrene-b-octadecyl acrylate) triblock copolymer by atom transfer radical polymerization, *J. Appl. Polym. Sci.* 93 (4) (2004) 1539–1545.
- [26] A. Darvishi, M.J. Zohuriaan Mehr, G.B. Marandi, K. Kabiri, H. Bouhend, H. Bakhshi, Copolymers of glycidyl methacrylate and octadecyl acrylate: synthesis, characterization, swelling properties, and reactivity ratios, *Des. Monomers Polym.* 16 (1) (2013) 79–88.
- [27] P.K. Goswami, M. Kashyap, P.P. Das, P.J. Saikia, J.G. Handique, Poly (Glycidyl Methacrylate-co-Octadecyl Methacrylate) particles by dispersion radical copolymerization, *J. Dispersion Sci. Technol.* (2019) 1–9.
- [28] P. Ghosh, M. Hoque, G. Karmakar, M.K. Das, Dodecyl methacrylate and vinyl acetate copolymers as viscosity modifier and pour point depressant for lubricating oil, *Int. J. Industrial Chem.* 8 (2) (2017) 197–205.
- [29] F. Yang et al., Comb-like Polyoctadecyl Acrylate (POA) Wax Inhibitor Triggers the Formation of Heterogeneous Waxy Oil Gel Deposits in a Cylindrical Couette Device, *Energy Fuels* 32 (1) (2018) 373–383.
- [30] Y. Wu, G. Ni, F. Yang, C. Li, G. Dong, Modified maleic anhydride co-polymers as pour-point depressants and their effects on waxy crude oil rheology, *Energy Fuels* 26 (2) (2012) 995–1001.
- [31] M. Zhou, Y. He, Y. Chen, Y. Yang, H. Lin, S. Han, Synthesis and evaluation of terpolymers consist of methacrylates with maleic anhydride and methacrylic morpholine and their amine compound as pour point depressants in diesel fuels, *Energy Fuels* 29 (9) (2015) 5618–5624.
- [32] D.V. Than, T.H. Chuong, D.Q. Tuy, Synthesis copolymer use to reduce pour point temperature of diamond crude oil, in: *AIP Conference Proceedings*, vol. 1878, no. 1: AIP Publishing LLC, 2017, p. 020002.
- [33] I. Elganidi, B. Elarbe, N. Abdullah, N. Ridzuan, Characterization of a novel terpolymer containing maleic anhydride-co-stearyl methacrylate-co-benhenyl acrylate for wax inhibition application, in: *IOP Conference Series: Materials Science and Engineering*, vol. 702, no. 1: IOP Publishing, 2019, p. 012027.
- [34] B.S. Elarbe, N. Ridzuan, K. Yusoh, I. Elganidi, N. Abdullah, Screening of the factors for novel pour point depressant copolymer synthesis to improve the copolymer yield, *IOP Conference Series: Materials Science and Engineering*, vol. 702, 2019, p. 012028, 2019/12/07, doi: 10.1088/1757-899x/702/1/012028.
- [35] N. Ridzuan, M. Al-Mahfadi, Evaluation on the effects of wax inhibitor and optimization of operating parameters for wax deposition in Malaysian crude oil, *Pet. Sci. Technol.* 35 (20) (2017) 1945–1950, <https://doi.org/10.1080/10916466.2017.1373128>.
- [36] P.A. Subramanie, A. Padhi, N. Ridzuan, F. Adam, Experimental study on the effect of wax inhibitor and nanoparticles on rheology of Malaysian crude oil, *J. King Saud Univ.-Eng. Sci.*, 2019.
- [37] M. Upadhyay, D.K. Saha, P. Ghosh, Dodecylmethacrylate-Behenyl Acrylate Copolymers as Potential Multifunctional Additive for Lubricating Oil, 2018.
- [38] L. Zhu, X. Jing, S. Wang, J. Chen, D. Xia, A. Li, Screening and evaluation of types and ratio of monomers of oil soluble viscosity reducing agent for Shengli super heavy oil, *Pet. Sci. Technol.* 33 (4) (2015) 452–459.
- [39] B. Elarbe, N. Ridzuan, K. Yusoh, I. Elganidi, N. Abdullah, Screening of the factors for novel pour point depressant copolymer synthesis to improve the copolymer yield, in: *IOP Conference Series: Materials Science and Engineering*, vol. 702, no. 1: IOP Publishing, 2019, p. 012028.
- [40] P. Christian, M.R. Giles, R.M. Griffiths, D.J. Irvine, R.C. Major, S.M. Howdle, Free radical polymerization of methyl methacrylate in supercritical carbon dioxide using a pseudo-graft stabilizer: effect of monomer, initiator, and stabilizer concentrations, *Macromolecules* 33 (25) (2000) 9222–9227.
- [41] L. Zhu, et al., Screening of Synthesis Conditions of Polymers and the Effects on Viscosity Reduction Performance, in: *IOP Conference Series: Earth and Environmental Science*, vol. 108, no. 2: IOP Publishing, 2018, p. 022032.
- [42] A.A. Ekaputra, K.M. Sabil, A. Hosseinipour, I.B. Saaid, Impacts of viscosity, density and pour point to the wax deposition, *J. Appl. Sci.* 14 (23) (2014) 3334.
- [43] W.K. Shafi, M. Charoo, Rheological properties of hazelnut oil mixed with zirconium-dioxide nanoparticles, *Mater. Today: Proc.*, 2020.
- [44] J. Guo, H. Wang, C. Chen, Y. Chen, X. Xie, Synthesis and evaluation of an oil-soluble viscosity reducer for heavy oil, *Pet. Sci.* 7 (4) (2010) 536–540.
- [45] S. Fang, M. Wang, Z. Xu, L. Zhai, X. Wang, Y. Xiong, Preparation of an amphoteric flocculant having both high polymer content and low viscosity and its polymerization kinetics, *Chin. J. Chem. Eng.* 27 (1) (2019) 130–135.