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INHIBITING SEDIMENT FORMATION IN AN EXTRA LIGHT CRUDE OIL AND IN A HYDROCRACKED ATMOSPHERIC RESIDUE BY COMMERCIAL CHEMICAL ADDITIVES

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ABSTRACT

Extra light crude oil from Kazahstan and hydrocracked atmospheric residue from a commercial ebullated bed vacuum residue hydrocracker were investigated to reduce their sediment formation rate by employing 13 commercial chemical additives. Ten of the studied additives were based on the organic acid derivatives. Asphaltene dispersion test was applied in this study to define the most appropriate chemical additive and the optimum treating rate. The additives demonstrated different performance with the distinct oils. All organic acid derivative additives were capable of suppressing the sedimentation in the hydrocracked atmospheric residue, while not all of them were effective in decreasing the sediment formation in the extra light petroleum. The phosphoric acid and poly-iso-butylene succinimide based additives were effective in suppressing the sedimentation in the hydrocracked atmospheric residue while they promoted the formation of sediments in the extra light petroleum. The additive based on 1,2,4-trimethylbenzene was ineffective in decreasing the sedimentation in the hydrocracked atmospheric residue and slightly effective in the suppression of sediment formation in the extra light petroleum.

Keywords: *sediment formation, crude oil, residual oil, asphaltene dispersants, inhibition of sedimentation, chemical additives.*

INTRODUCTION

Crude oil is a very complex mixture, consisting of myriad components, which during changes in operating conditions such as pressure, temperature and composition of the oil can trigger deposit formation during oil production operations [1]. The deposit formation is a complex phenomenon that is mainly provoked by asphaltene aggregation and precipitation [1 - 12] and/or by precipitation of wax, also known as paraffin [13 - 19]. The asphaltenes are the most aromatic and polar fraction of the petroleum and their composition, size and structure may differ depending on their origin [20, 21]. The wax normally refers to the collection of n-alkanes in the crude oil with carbon numbers higher than 20 [14, 18]. The precipitation of asphaltenes, and waxes occurs when crude oil characteristics change as a consequence of pressure, temperature variations, and/or chemical modifications, etc. [1]. In general, these changes and their effects are relatively well understood based on experimental evidence as well as thermodynamic modeling [1, 2, 16]. However, the reason why some crude oils produce deposits while others do not, even under similar conditions, is still a matter of intense research [1]. The costs associated with cleaning of the deposition on the production equipment and the loss of profit opportunities can go beyond hundreds of millions US $ [18, 19]. Thus, there is a strong incentive to search ways for mitigation of deposit formation during crude production process. One of the most common strategies to prevent or at least reduce deposition during crude oil production is the utilization of chemical additives [8]. However, there are still several unresolved challenges associated to the utilization of these chemicals. First, the experimental conditions and results obtained in the lab are not always consistent with the field observations. Also, in some cases these chemical additives seem to worsen the deposition problem in the field [8]. Several techniques have been reported in the literature to investigate asphaltene aggregation and sedimentation: turbidymetery, automatic titration and optical microscopy [22], spot test [23], near IR spectroscopy [24], asphaltene dispersant test (ADT) [25], solid detection system (SDS) [26, 27], time-resolved ultra-small-angle X-ray scattering (USAXS) [4], image processing [28]. ADT is the most common approach to evaluate the performance of chemicals based on the dispersion efficiency of asphaltenes [29]. This method was also employed in our study to investigate the efficiency of using commercial additives to retard the process of sediment formation in an extra light crude oil. The extra light crude oil was selected based on the reports in the literature that the light oil is more susceptible to cause asphaltenes deposition [30]. In order to contrast the performance of the chemical additives with the extra light crude oil a hydrocracked atmospheric residue, obtained in a commercial ebullated bed vacuum residue H-Oil hydrocracker, which is much more susceptible to sediment formation than the light crude oil, was also treated with the same chemicals. The additives were commercial asphaltene dispersants supplied by renowned chemical companies. The additives may contain amines in aromatic solvent, poly-isobuthylene succinimide, polymer in aromatic solvent, phosponothioc acid, poly-isobutenyl derivatives, esters with pentaerythritol, alkenyl thiophosphorous ester, formaldehyde, polymers with branched 4-nonylphenol and ethylenediamine, phosporic acid, 2-ehylhexyl ester, C24-36 alkene, alpha-polymers with maleic anhydride, organic acid derivative, 1,2,4- trimethylbenzene in a different proprietary individual blends.

The aim of this study is to verify the feasibility of suppressing the process of sediment formation in an extra light crude oil by treating this crude oil with 13 commercial chemical additives, and examine their efficiency in retardation of the sediment formation in a hydrocracked atmospheric residue.

EXPERIMENTAL

The extra light crude oil (CPC) was delivered from Kazahstan. It was fractionated in a true boiling point (TBP) Euro Dist System from ROFA Deutschland GmbH, designed to perform according to ASTM D2892 requirements. The crude oil atmospheric residue from the TBP column was fractionated in a Potstill Euro Dist System according to ASTM D5236 requirements. The distillation characteristics were also determined by the use of high temperature simulation distillation (HTSD) in accordance ASTM D7169.

The hydrocracked atmospheric residue (HCAR) was sampled from the LUKOIL Neftohim Burgas (LNB) H-Oil vacuum residue hydrocracker at a conversion level of 73 %. Its distillation characteristics were measured using HTSD.

The densities of the crude oil and the HCAR were measured in accordance with ASTM D4052. Sulphur content of the oils was determined in accordance with ASTM D4294. Pour point was determined in accordance with requirements of ASTM D5853. Water and sediment content analysis were performed according to the procedures described in ASTM D4006 and ASTM D473 respectively. Method ASTM D445 was applied to measure the kinematic viscosities of the studied oils. SARA (saturates, aromatics, resins, asphaltenes) analysis of the oils was measured by employment liquid chromatography following the procedure described in [31].

Solvent power and critical solvent power of the investigated crude oil were measured by modified procedure similar to the method described in [32]. The solutions of the selected crude oil and n-heptane were prepared at varying ratios between oil and normal paraffin. One sample tube was contained 100 wt. % crude oil. The samples were thoroughly mixed and allowed to equilibrate and then centrifuged. The centrifuging process was carried out by conventional centrifuge at 5000 rpm for 30 min. Supernatant oil liquid was removed from the centrifugal tube. The sediment was subsequently washed in n-heptane and dried. The drying process was carried out at 105°C for 8 h. The recovered sediment was calculated in wt. % of the base of crude oil and plotted against the weight percent of n-heptane of the solution of the particular sample tube.

The solvent power of the oils was calculated using equation 1:

$$Sp = \frac{Kco - Khp}{Kt - Khp} * 100 \tag{1}$$

where:
Sp – Solvent power of the crude oil;
Kco – Characterization Kw-factor of the crude oil;
Kt- Characterization Kw-factor of the toluene;
Khp – Characterization Kw-factor of the n-heptane.

The Kw-characterization factors of oils are estimated by the expression of equation 2:

$$Kw = \frac{\sqrt[3]{1.8[\frac{T10+T30+T50+T70+T90}{5}+273.15]}}{d_{15}} \tag{2}$$

where:
T_{10} - boiling point of 10 % of evaporate according to the HTSD (ASTM D7169), °C;
T_{30} - boiling point of 30 % of evaporate according to the HTSD (ASTM D7169), °C;
T_{50} - boiling point of 50 % of evaporate according to the HTSD (ASTM D7169), °C;
T_{70} - boiling point of 70 % of evaporate according to the HTSD (ASTM D7169), °C;
T_{90} - boiling point of 90 % of evaporate according to the HTSD (ASTM D7169), °C.
Kw-characterization factor of n-heptane = 12.72 [33];
Kw-characterization factor of toluene = 10.15 [33].

The critical solvent power is calculated at the point of the resulting plot where asphaltenes begin to precipitate. This is done by determining the solvent power of the solution of the sample of oil blended with n-heptane where asphaltene precipitation began. The Solvent power of the solution is calculated as indicated in eq.1. The difference in the distillation curve will be in the amount of heptane recovered at 98.5°C (the boiling point of heptane). The gravity of the crude oil will also become less with the addition of heptanes [32].

The effect of the use of the additives to suppress the sediment formation was examined by employing asphaltene dispersant test (ADT) as described in [8]. The oil sample is mixed with large amounts of heptane to obtain a clear sample that allows sediment observation through it. During this study the light crude oil and the HCAR were mixed with n-heptane in amount of 93 %. The blend of 7 % oil / 93 % n-heptane was placed in graduated centrifuge tube and then centrifuged at 5000 rpm for 30 min. A sample of the oils with no dispersant was used as a control. The commercial additives were mixed with the studied oils and then homogenized in a closed beaker for a period of one hour using a magnetic stirrer at 700 rpm. Then 3 g of the blend of crude oil sample (0.5 g of HCAR) with the additive were placed in graduated centrifuge tube and mixed with 40 g of n-heptane (7 g of n-heptane for the case with the HCAR), and after that centrifuged at 5000 rpm for 30 min. Reading the volume of the sediment from the graduated centrifuge represents the amount of the sediment formed at the conditions studied. The sediment volume of pure extra light crude oil (CPC) was 0.12 mL, while that of the pure HCAR was 0.45 mL. The relative error of the measurement of the sediment volume was found to be 11.0 %.

Crude oils and the residual oils are known to contain resin fraction that acts as a natural dispersant to keep asphaltenes dispersed as approximately 40 Å in diameter particles [34]. The resins usually present in larger concentrations than the asphaltenes [35, 36], but the synthetic dispersants have been found to be much more effective than the resin fraction mitigating asphaltene fouling at concentrations of 100 ppm or less [34]. The additives employed in this study were synthetic asphaltene dispersants. Their type was discussed in our previous study [37]. They are based on amines in aromatic solvent, poly-iso-buthylenesuccinimide, polymer in aromatic solvent, phosponothioc acid, poly-isobutenyl derivatives, esters with pentaerythritol, alkenyl thiophosphorous ester, formaldehyde, polymers with branched 4-nonylphenol and ethylenediamine, phosporic acid, 2-ehylhexyl ester, C24-36 alkene, alpha-polymers with maleic anhydride, organic acid derivative, 1,2,4-trimethylbenzene. The individual additives present a blend of the chemical substances mentioned above in a proprietary confidential ratio. The 13 commercial additives employed in this study were labeled as A1 to A13.

Table 1 summarizes properties of the studied Kazahstan light crude oil, and of the secondary heavy oil from H-Oil - HCAR.

RESULTS AND DISCUSSION

The data in Table 1 indicates that CPC pertain to the group of extra light low sulfur crudes (specific gravity < 0.8017; 1.5% > S > 0.5%) [38]. The amount of sediments determined after centrifugation is 2.6 %. This level could be considered relatively high taking into account that the average level of sediments of 30 crudes from all over the world studied in LNB Research laboratory and pertaining to all crude oil types: extra light, light, medium, heavy, and extra heavy is 1.1 % [39]. Interestingly these sediments in CPC crude oil are dissolved in n-heptane when the crude oil compatible test to measure its solvent power and critical solvent power (Fig. 1). Fig. 1 displays the behavior of the extra heavy, heavy, medium, light and extra light crude oils when n-heptane is added. All crude oils after addition of some amount of n-heptane exhibit increase in the sediment content except CPC and Middle East light crude oil (MELCO). The fact that the sediments in CPC and MELCO crude oils are dissolved in n-heptane suggests that they might be predominantly consisted of waxes. However, investigations have shown that waxes can accelerate dissolution of asphaltenes [3, 40 - 42]. This phenomenon can be explained by the interaction between peripheral alkyl chains in asphaltene aggregates and waxes. The interaction increases the volume of the alkyl layers surrounding asphaltene polyaromatic cores, and the swelling improves the dissolution of the solids [3]. Moreover n-alkanes from C12 to C60 have been detected in petroleum asphaltenes [43]. Our recent study [44] indicated that lighter crude oils have lighter asphaltenes which could be easier to dissolve. Lighter asphaltenes (lower density, higher hydrogen content, and higher solubility) and possibly waxes contribute to the formation of sediments in both extra light CPC and MELCO, whose dissolution increases with augmentation of the n-heptane added to these crude oils. Irrespective of higher solubility of the sediments in both of these crude oils they may contribute to deposit formation in the process of crude oil production when pressure, temperature and composition of the oil changes occur.

Table 1. Properties of the studied extra light crude oil (CPC) and hydrocracked atmospheric residue (HCAR).

Properties	CPC	HCAR
Density at 15 °C, g cm^{-3}	0.7954	0.983
Sulphur, wt. %	0.55	0.83
TBP fraction yields, wt. %		
IBP- 110°C	17.8	
110-180°C	19.5	
180-240°C	12.7	
240-360°C	24.1	
360-500°C	18.1	
>500°C	6.8	
HTSD		
IBP	76	
5 wt. %	94	366
10 wt. %	114	395
30 wt. %	198	460
50 wt. %	273	506
70 wt. %	361	555
90 wt. %	499	634
95 wt. %	568	668
FBP	715	
SARA composition		
Saturates, wt. %	82.7	26.9
Aromatics, wt. %	16.5	58.4
Resins, wt. %	0.43	7.5
C_5 asphaltenes, wt. %	0.38	14.9
C_7 asphaltenes, wt. %	0.8	7.1
Sediments after centrifugation, wt. %	2.6	6.8
Kin. Viscosity at 40°C, mm^2 s^{-1}	1.87	1427
Kw-factor	12.22	10.50
Solvent power	22.1	88.0
Critical solvent power	22.1	100.0

It is difficult to define whether CPC is colloidally stable or unstable because the critical solvent power is determined at the point of the resulting plot (as shown in Fig. 1) where asphaltenes begin to precipitate. This is done by determining the solvent power of the solution of the sample tube (oil plus n-heptane) where asphaltene precipitation began [33]. For example in the crude oil Tempa Rossa from Fig. 1 the asphaltenes start to precipitate at a concentration of higher than 30 %. Such a precipitation result from addition of n-heptane to CPC as shown in Fig.1 is difficult to register. In this case we may assume that at zero n-heptane content in the blend CPC-n-heptane asphaltene precipitation might occur. Thus, the critical solvent power of the CPC could be assumed equal to the solvent power. In such cases where the critical solvent power equals to the solvent power the oil is considered self-incompatible [32]. It is evident from the data in Table 1 that CPC has a high saturate content and high Kw-characterization factor. According to the classification based on Kw-characterization factor CPC may be considered naphthenic since its Kw-factor falls in the range (10.5 to 12.5) [45].

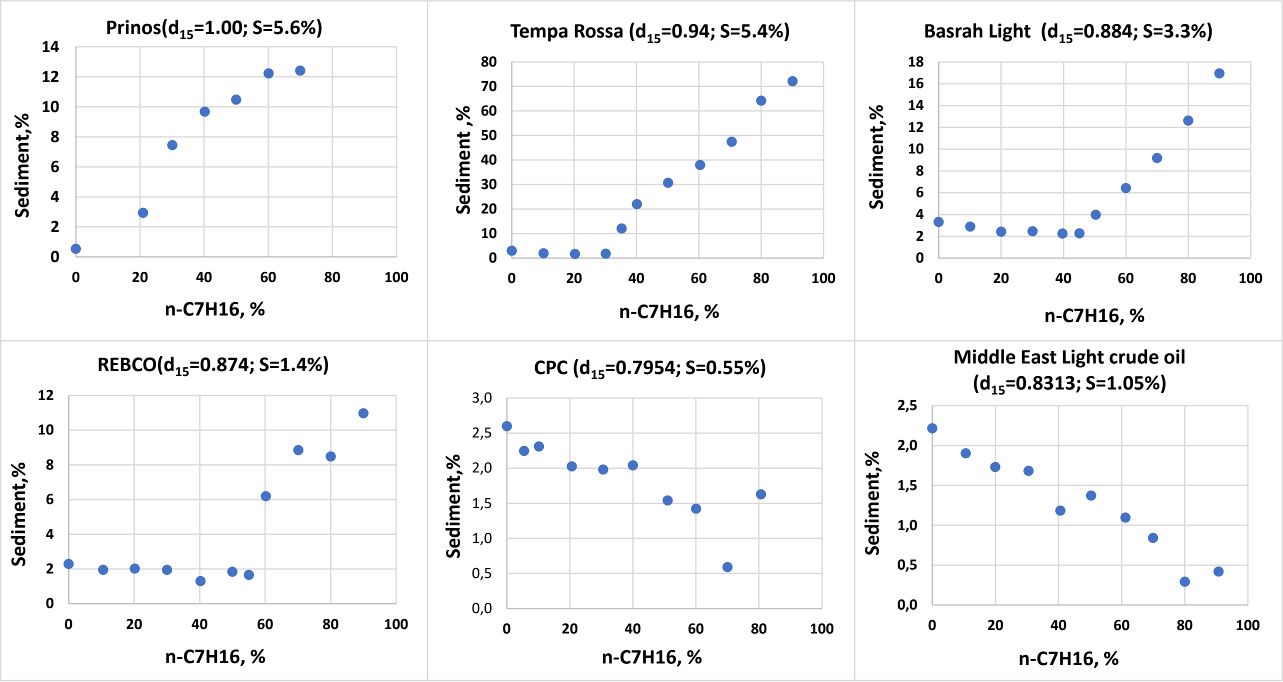

Fig. 1. Dependence of crude sediment content on the concentration of n-heptane in the blend crude oil – nC7H16 for extra heavy, heavy, medium, light and extra light crude oils.

The data in Table 1 about the hydrocracked atmospheric residue (HCAR) indicate that this oil is aromatic (Kw = 10.51) [45] and its solvent power four times as high as that of CPC. However, the critical solvent power of the HCAR is higher than its solvent power. Therefore the maltene fraction solvent power is insufficient to make the asphaltenes stay in solution and they begin to aggregate and precipitate out of the solution. Thus the HCAR may be considered colloidally unstable. Comparing the performance of the commercial asphaltene dispersants with two completely different oils may give a notion about the efficiency dependence of the additive action on the nature of the treated oil.

Tables 2 and 3 summarize the performance of the 13 commercial additives with the CPC and HCAR. It is evident from these data that the sediment formation from the colloidally unstable HCAR makes 29 times the sediment volume of the CPC. The data in Table 2 show that the additive A1 promotes the sediment formation in CPC by increasing it from 3.3 vol. % without additive treatment to 16.6 % at 1000 ppm treating rate. Whereas the same additive decreases the sediment formation in HCAR with 33 %. Obviously the containing phosphoric acid and 2-ethylhexyl ester in the commercial additive A1 promote the sediment formation in the crude oil CPC, while the same components suppress the formation of precipitate in the secondary heavy oil HCAR. This illustrates how specific is the action of the antifoulants commercially applied in crude oil production and petroleum refining.

Additive A2 has no effect on the sediment formation in CPC, while it decreases the sedimentation in HCAR also with 33 %. The containing oxidized light distillates, petroleum, and asphalt contribute to suppressing of sediment formation, while their content in the commercial additive A2 does not affect the precipitate formation in the light petroleum CPC. This is again a confirmation of the specific action of the antifoulants commercially applied in crude oil production and petroleum refining.

Additive A3 has a slight promoting effect on sediment formation in CPC and inhibiting the sediment formation in HCAR with 22 %. The combination of the components C24-36 alkene, alpha-polymers and maleic anhydride suppress the sediment formation in the secondary heavy oil HCAR, and at the same time promote the precipitate formation in the light crude oil CPC.

The data in Table 2 also indicate that the action of additives A4 - A7 is different for both studied oils. A4 initially enhances the sediment formation in CPC in the treating rate range 50-100 ppm and then decreases it at

Table 2. A1-A7 chemical additives test results.

	CPC	HCAR
A1 (phosphoric acid, 2-ehylhexyl ester), ppm	vol. % sediment of crude	vol. % sediment of HCAR
0	3.3	88
500	5.5	80
750	13.9	
1000	16.6	59
A2 (oxidized light distillates, petroleum, asphalt)		
500	3.3	88
750	3.3	
1000	3.3	59
A3(Alkene, C_{24-36}, alpha-polymers with maleic anhydride)		
500	3.3	82
750	3.9	
1000	4.4	69
A4 (1,2,4 trimethylbenzene) ppm		
0	3.3	88
50	4.2	69
100	5.0	88
300	1.9	88
A5 (Organic acid derivative), ppm		
0	3.3	88
50	3.3	78
100	5.0	69
300	1.9	69
A6 (Phosporic acid, 2-ehyl-hexyl ester), ppm		
0	3.3	88
50	3.3	88
100	3.9	78
300	2.2	69
A7 (IR analysis, see Fig.2) ppm		
0	3.3	88
50	2.8	88
100	1.9	88
300	1.9	69
500	1.1	
700	0.8	

a treating rate of 300 ppm with 42 %. With HCAR the additive A4 inhibits the sediment formation with 22 % at 50 ppm treating rate and its further augmentation has no effect on the sediment level. This behavior of the additive A4 can be ascribed to the 1,2,4-trimethylbenzene, that is the active component of this commercial antifoulant.

The action of additive A5 with CPC is analogous to that of A4 with this oil. However, A5 does not exhibit the same behavior with HCAR as that of A4 with HCAR. The treatment of HCAR with A5 inhibits sedimentation rate with 22 % by increasing treating rate up to 100 ppm and then no further inhibition improvement is registered by magnification of the treating rate up to 300 ppm. This behavior can be ascribed to the active component organic acid derivative containing in the commercial antifoulant A5. Additive A6 demonstrates sediment formation promoting effect in the treating rate 0 - 100 ppm and 33 % sediment formation inhibition at 300 ppm with CPC. With HCAR it also inhibits sediment formation at 300 ppm treating rate but no such sedimentation promoting effect is registered with this additive at the treating rate range 0 - 100 ppm when HCAR is treated. The active components in A6 are phosphoric acid and 2-ethylhexyl ester. Although the additives A1 and A6 contain the same active components their behavior is a bit different suggesting that their preparation formula, which is proprietary, should be the reason for the observed different action.

Additive A7 displays a gradual sediment formation suppressing effect in the treating range 0 - 700 ppm with CPC achieving 76 % reduction in the sediment volume. The behavior of A7 additive with HCAR is close to that with CPC showing the best inhibiting effect at a concentration of 300 ppm for the treating rate 0 - 300 ppm. The performed infrared analysis of the additive A7 (Fig.2) indicates valence oscillations in the region 3000 cm^{-1} - 2800 cm^{-1}, typical for presence of aliphatic groups. The bands at about 2960 cm^{-1} and 2870 cm^{-1} correspond to symmetric and asymmetric oscillation of CH_3 groups, whilst those at 2860 cm^{-1} correspond to symmetric oscillation of CH2 groups. The bands at around 1600 cm^{-1} and 1500 cm^{-1} are probably a result from oscillation of C-C bonds in the aromatic ring. There is a maximum at around 1770 cm^{-1} which is an indicator for the presence C=O ester, and cyclic ester. The band at around 1700 cm^{-1} is probably a result from oscillation of C=O bond participating in carboxylic group. There is a band at about 1460 cm^{-1} characterizing the asymmetric oscillation of CH3 groups. Therefore the additive A7 can be considered to pertain to the group of the organic acid derivatives like additive A5. Indeed its action is very close to that of the additive A5.

Additive A8 (Table 3) exhibits similar action as that of A7 with CPC. HCAR was not treated with this additive. The FT-IR spectra of the additive A8 (Fig. 3) shows the same valence oscillations as those of A7. However, in different ratios, suggesting a different ratio of the active components in the distinct additives. It can be also ascribed that A8 pertains to the group of the organic acid derivatives.

Additive A9 (Table 3) gradually inhibits sediment formation in CPC by enhancing treating rate up to 500 ppm with CPC reaching 76 % sediment volume reduction at 500 ppm. Further increase in treating rate up to 700 ppm does not lead to further sediment volume reduction. With additive A9 a significant reduction of sediment formation in HCAR (44 %) is registered at treating rate of 500 ppm. However, no such continual gradual reduction in sediment formation in HCAR is registered with additive A9 as was the case with CPC. As evident from the FT-IR spectra of the additive A9 (Fig. 4) there is the same valence oscillations as those of A7, and A8.

The ratios between the same valence oscillations as those of A7, and A8, are different in A9, which suggests a different ratio of the active components in the distinct additives (A7, A8, and A9). It can be also ascribed that A9 pertains to the group of the organic acid derivatives.

Additive A10 (Table 3) first displays promoting effect on sediment formation in the treating rate 0 - 100 ppm and then suppressing effect on the sediment formation with enhancement of the treating rate up to 700 ppm reaching 76 % sediment volume reduction with CPC. With HCAR A10 exhibits sinusoidal variation of sediment volume when HCAR is treated reaching 44 % sediment volume reduction at treating rate of 500 ppm.

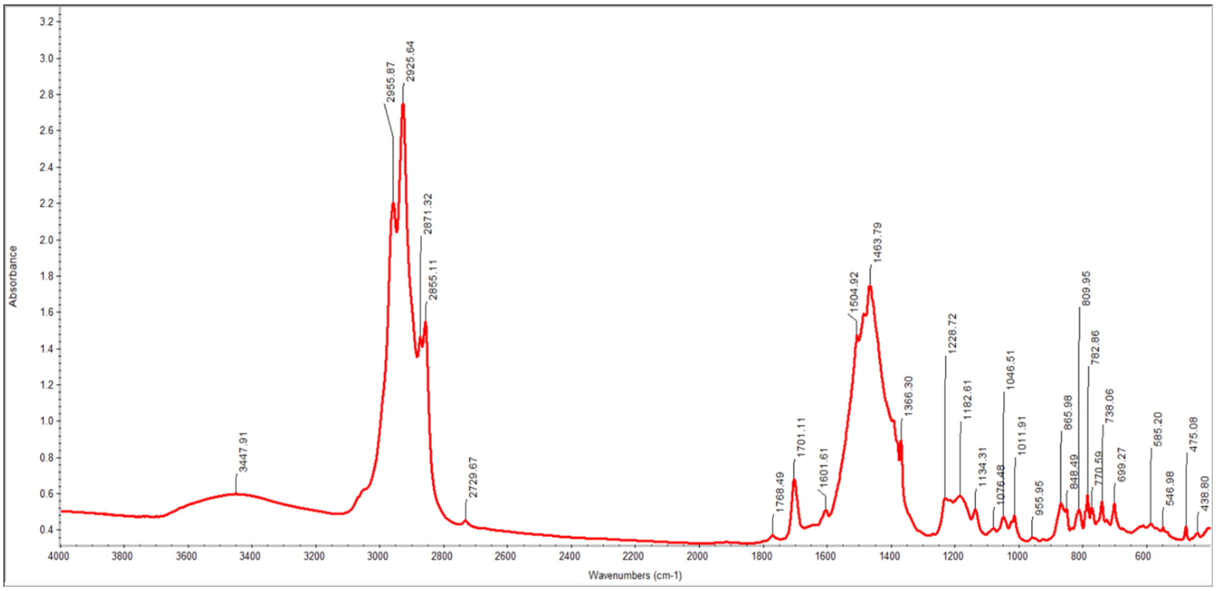

Fig. 2. IR-spectra of additive A7.

Table 3. A8-A13 chemical additives test results.

	CPC	HCAR
A8 (IR analysis, see Fig. 3), ppm	vol. % sediment of crude	vol. % sediment of HCAR
0	3.3	
50	3.6	
100	1.9	
300	1.9	
500	1.1	
700	0.8	
A9 (IR analysis, see Fig. 4), ppm		
0	3.3	88
50	2.8	72
100	1.4	88
300	1.1	
500	0.8	49
700	0.8	
A10 (IR analysis, see Fig. 5), ppm		
0	3.3	78
50	5.0	59
100	5.5	69
300	3.6	
500	1.4	49
700	0.8	
A11 (IR analysis, see Fig. 6), ppm		
0	3.3	
50	4.2	
100	3.3	
300	2.2	
500	1.1	
700	1.1	
A12 ppm (IR analysis, see Fig. 7),		
0	3.3	78
50	4.4	63
100	3.9	78
300	1.9	
500	1.1	45
700	1.4	
A13 (poly-iso-buthylene succinimide), ppm		
0	3.3	88
50	5.0	118
100	4.2	78
300	4.2	59
500	4.2	
700	4.7	

As observed from the FT-IR spectra of the additive A10 (Fig. 5) it has the same valence oscillations as those of A7, A8, and A9. Here, one can see again that the ratios between the same valence oscillations as those of A7, A8, and A9, are different in A10, suggesting a different ratio of the active components in the distinct additives. It can be also ascribed that A10 pertains to the group of the organic acid derivatives.

The additives A11 and A12 (Table 3) show similar behavior when CPC is treated. First they promote sediment formation rate at 50 ppm treating rate reaching in some cases 67 % increase in the sediment formation. Then they suppress sediment formation by augmenting the treating rate up to 500 ppm. Further increase in treating rate up to 700 ppm has no effect on further inhibition of sediment formation. The additives A11 and

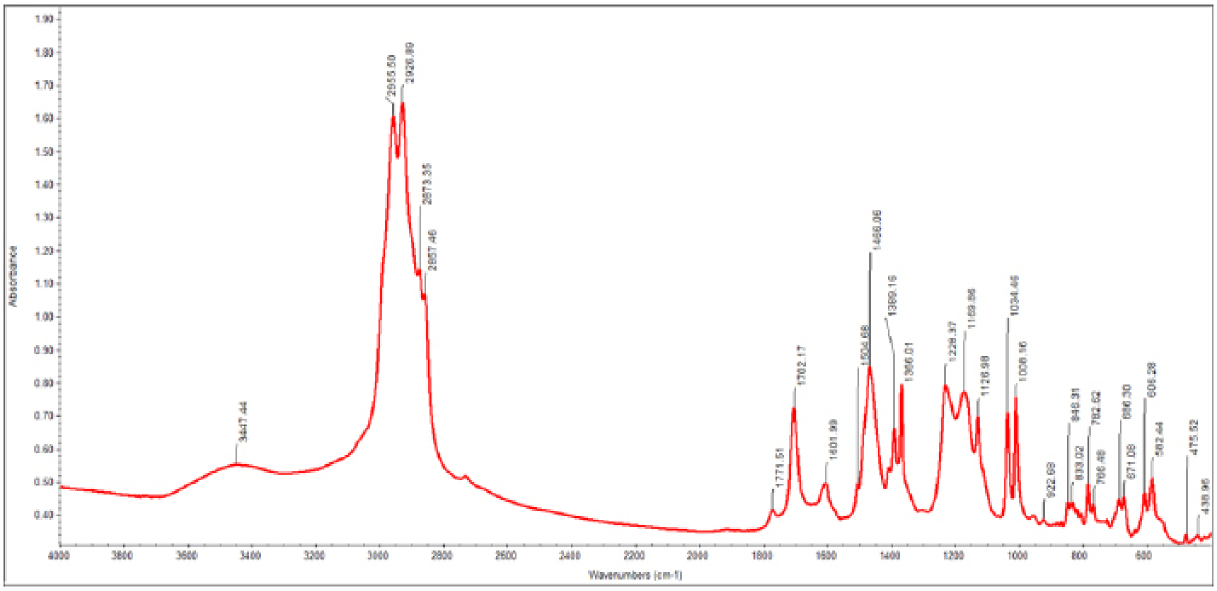

Fig. 3. IR-spectra of additive A8.

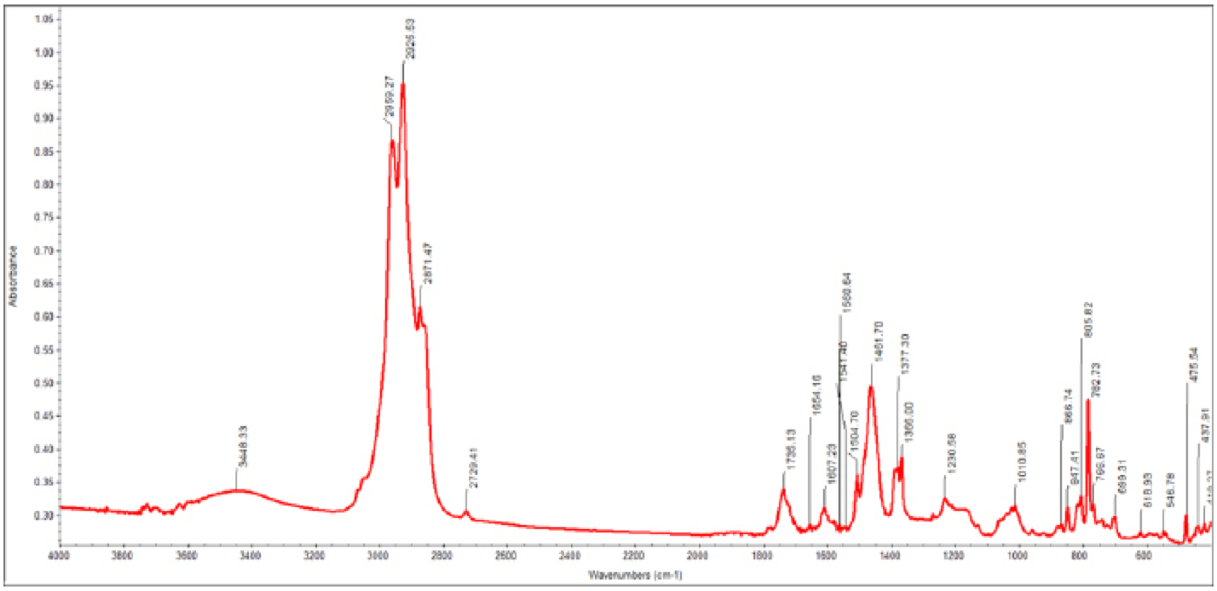

Fig. 4. IR-spectra of additive A9.

A12 also show similar behavior when HCAR is treated. The same sinusoidal variation of sediment volume with magnification of treating rates of A11 and A12, as that observed with A10 when HCAR is treated, is registered. The A11 and A12 show the best performance at treating rate of 500 ppm for the studied range of 0 - 500 ppm. As observed from the FT-IR spectra of the additives A11 and A12 (Fig. 6 and Fig.7) they have the same valence oscillations as that of A7-A10. However, in different ratios suggesting a different ratio of the active components in the distinct additives. It can be also ascribed that A11 and A12 pertain to the group of the organic acid derivatives.

Additive A13 demonstrates poor performance with CPC showing sediment formation promoting effect in all studied treating rates in the range 0 - 700 ppm. With HCAR this additive exhibits inhibition effect at 300 ppm treating rate (-33 %) with a promoting effect on sedimentation at 50 ppm treating rate (+34 %). The A13 is the only additive among 13 studied additives which contains poly-isobutylene succinimide. As was observed in the behavior of the other antifoulants investigated in this work some of them were effective in suppressing sediment formation in the secondary heavy oil - HCAR and ineffective or even promoting the sediment formation

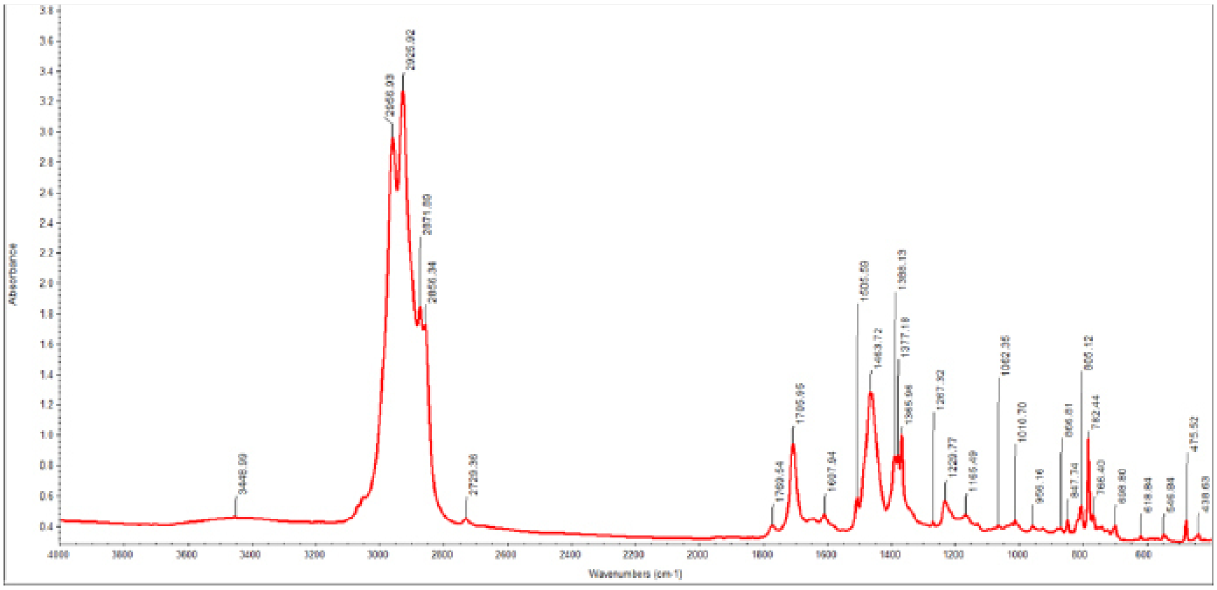

Fig. 5. IR-spectra of additive A10.

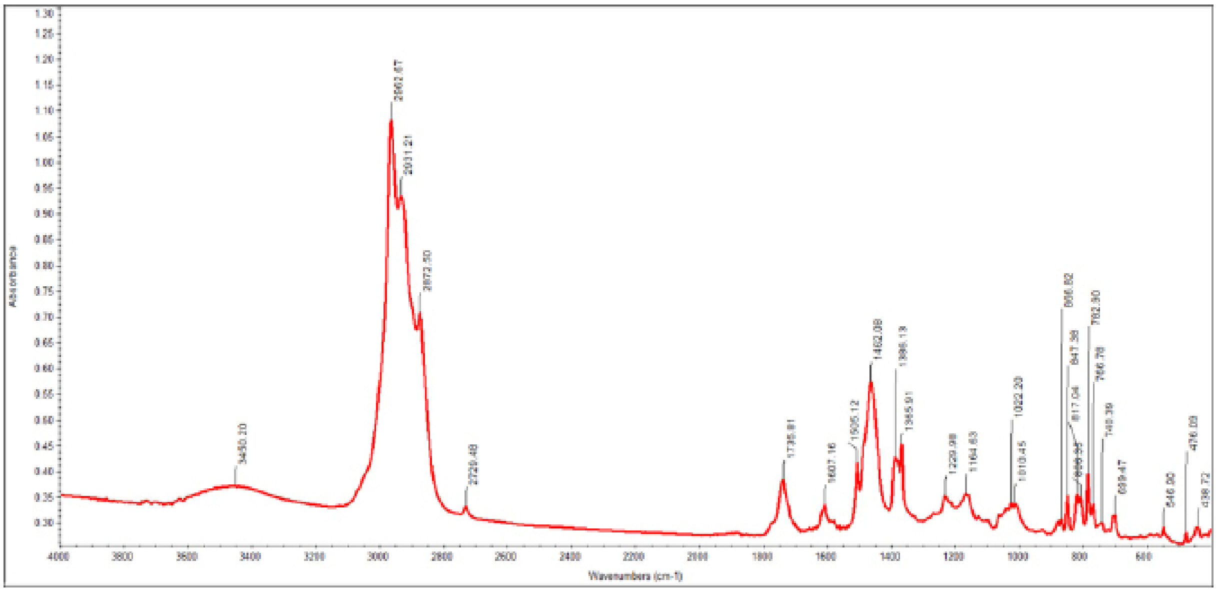

Fig. 6. IR-spectra of additive A11.

in the light petroleum - CPC. This is a clear manifestation how specific is the action additive - oil concerning sediment formation suppression and how difficult is to predict the behavior of any oil-additive combination. The laboratory test is the best approach to find the optimal additive for specific oil in the search of the way to suppress sediment formation during petroleum exploration and oil refining.

The findings in our study are in line with the reports of Melendez-Alvarez et al. [8], Barsenas et al. [46], and Madhi et al. [47] that the asphaltene dispersants can promote sediment formation depending on the oil treated, chemistry of the additive, medium, and the concentrating range. Barsenas et al. [46] showed in their study that the same asphaltene aggregation inhibitors at lower concentrations inhibited the asphaltene agglomeration while with increasing of their treatment rate their efficacy diminished significantly. They found that the same inhibitor during changing of the medium (from toluene at 50°C to o-dichlorobenzene at 90°C) from asphaltene inhibitor it turned into asphaltene aggregation promoter [46]. They suggested that inhibitor molecules (i) significantly self-associated in the more polar solvent (o-dichlorobenzene), which could be a

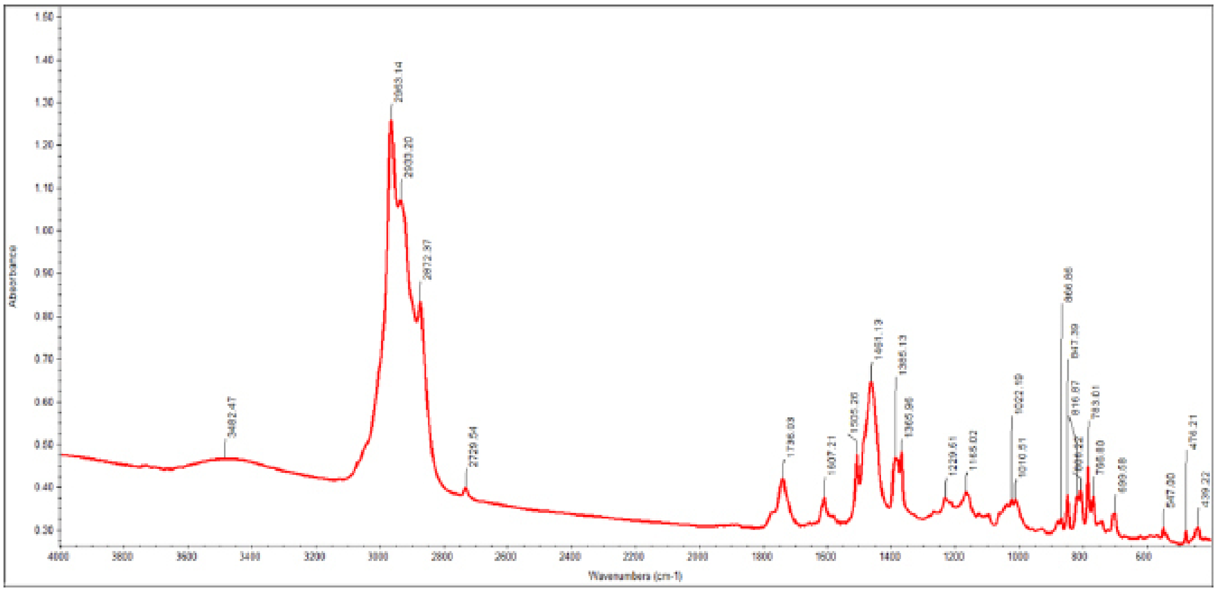

Fig. 7. IR-spectra of additive A12.

reason of the asphaltene adsorption (and enhanced agglomeration) on the surface of such inhibitor complexes; (ii) self-associate occulting their head polar part in the less polar solvent (toluene), which might be a reason of the reduced inhibitor adsorption on the asphaltene surface, and as a consequence, the worsening of the inhibition efficacy [46].

Therefore the selection of chemical additive to inhibit deposit formation during oil production or during refining operations is a delicate matter. The proper selection can provide opportunity to improve profitability by increasing cycle length of the operation equipment, reduced maintenance costs, and higher reliability in the crude oil production and oil refining outweighing the costs for the chemical additives. The improper selection, however, can have a deleterious effect on the economics of both crude oil production and oil refining.

CONCLUSIONS

A low solvent power CPC extra light crude oil and a higher solvent power but colloidal unstable hydrocracked atmospheric residues were treated with 13 commercial antifouling additives. The additive performance was evaluated in asphaltene dispersant test. Ten of the thirteen studied additives (A2, A3, A5 - A12) can be classified as organic acid derivatives with different ratio between the active components. All of them were found to be capable of suppressing the sediment formation in the hydrocracked atmospheric residue at specific treating rate. However, not all of them were capable of suppressing the sediment formation in the extra light Kazahstan CPC petroleum. The additives containing phosphoric acid, 2-ehylhexyl ester (A1), and poly-iso-buthylene succinimide (A13) succeeded to decrease sediment formation in the hydrocracked atmospheric residue but promoted the process of sediment formation in the extra light Kazahstan CPC petroleum. The aromatic additive A4, containing 1,2,4-trimethylbenzene did not suppress the sediment formation in the hydrocracked atmospheric residue and had marginal effect on decreasing the sedimentation in the extra light Kazahstan CPC petroleum. This study is a clear manifestation how specific is the action additive - oil concerning sediment formation suppression and how difficult is to predict the behavior of any oil-additive combination based on previous experience. The laboratory test is the best approach to find the optimal additive for specific oil in the search of the way to suppress sediment formation during petroleum exploration and oil refining.

REFERENCES

1. E. Rogel, T. Miao, J. Vien, M. Roye, Comparing asphaltenes: Deposit versus crude oil, Fuel, 147, 2015, 155-160.
2. A. Al-Hosani, S. Ravichandran, N. Daraboina, Review of asphaltene deposition modeling in oil and gas production, Energy Fuels, 35, 2, 2021, 965-986.

3. E. Rogel, C. Ovalles, J. Vien, M. Moir, Asphaltene characterization of paraffinic crude oils, Fuel, 178, 2016, 71-76.
4. E. Rogel, M. Witt, M.E. Moir, Effects of aging on asphaltene deposit composition using ultrahigh-resolution magnetic resonance mass spectrometry, Energy Fuels, 33, 10, 2019, 9596-9603.
5. E. Rogel, Effect of inhibitors on asphaltene aggregation: a theoretical framework, Energy Fuels, 25, 2, 2011, 472-481.
6. M. Ismail, Y. Yang, W. Chaisoontornyotin, C. Ovalles, E. Rogel, M. E. Moir, M. P. Hoepfner, The effect of chemical inhibitors on asphaltene precipitation and morphology using ultra-small-angle X-ray scattering, Energy Fuels, 33, 5, 2019, 3681-3693.
7. H. Firoozinia, K.F.H. Abad, A. Varamesh, A comprehensive experimental evaluation of asphaltene dispersants for injection under reservoir conditions, Pet. Sci., 13, 2016, 280-291.
8. A.A. Melendez-Alvarez, M. Garcia-Bermudes, M. Tavakkoli, R.H. Doherty, S. Meng, D.S. Abdallah, F.M. Vargas, On the evaluation of the performance of asphaltene dispersants. Fuel, 179, 2016, 210-220.
9. B. Otzisk, H. Kempen, Stabilisation of asphaltenes, Pet. Technol. Q., 14, 1, 2009, 31-36.
10. S.M. Hashmi, A. Firoozabadi, Self-assembly of resins and asphaltenes facilitates asphaltene dissolution by an organic acid, J. Colloid Interface Sci., 394, 2013, 115-123.
11. Y.-F. Hu, T.-M. Guo, Effect of the structures of ionic liquids and alkylbenzene-derived amphiphiles on the inhibition of asphaltene precipitation from CO2-injected reservoir oils, Langmuir, 21, 18, 2005, 8168-8174.
12. L. Goual, A. Firoozabadi, Effect of resins and DBSA on asphaltene precipitation from petroleum fluids, AIChE J., 50, 2, 2004, 470-479.
13. A.M. Sousa, H.A. Matos, L. Guerreiro, Wax deposition mechanisms and the effect of emulsions and carbon dioxide injection on wax deposition: Critical review, Petroleum, 6, 3, 2020, 215-225.
14. J. Yang, Y. Lu, N. Daraboina, C. Sarica, Wax deposition mechanisms: Is the current description sufficient?, Fuel, 275, 2020, 117937.
15. M.M. El-Dalatony, B.-H. Jeon, E.-S. Salama, M. Eraky, W. B. Kim, J. Wang, T. Ahn, Occurrence and characterization of paraffin wax formed in developing wells and pipelines, Energies, 12, 6, 2019, 967.
16. M. Obaseki, P.T. Elijah, Dynamic modeling and prediction of wax deposition thickness in crude oil pipelines, J. King Saud Univ. Eng. Sci., 2020, (in press).
17. N. Ridzuan, M. Al-Mahfadi, Evaluation on the effects of wax inhibitor and optimization of operating parameters for wax deposition in Malaysian crude oil, Petrol. Sci. Tech., 35, 20, 2017, 1945-1950.
18. M. Al-Yaari, Paraffin Wax Deposition: Mitigation & Removal Techniques, Paper presented at the SPE Saudi Arabia section Young Professionals Technical Symposium, Dhahran, Saudi Arabia, March 2011, SPE-155412-MS.
19. M.A. Theyab, S.Y. Yahya, Introduction to wax deposition, Int. J. Petrochem. Res., 2, 1, 2018, 126-131.
20. P. Zuo, S. Qu, W. Shen, Asphaltenes: Separations, structural analysis and applications, J. Energy Chem., 34, 2019, 186-207.
21. D. Stratiev, I. Shishkova, I. Tankov, A. Pavlova, Challenges in characterization of residual oils. A review, J. Petrol. Sci. Eng., 178, 2019, 227-250.
22. K. Kraiwattanawong, H.S. Fogler, S.G. Gharfeh, P. Singh, W.H. Thomason, S. Chavadej, Effect of asphaltene dispersants on aggregate size distribution and growth, Energy Fuels, 23, 3, 2009, 1575-1582.
23. G.L. Oliensis, A qualitative test for determining the degree of heterogeneity of asphalts, ASTM Proceeding, 33, 1933, 715-728.
24. I.H. Auflem, Influence of Asphaltene Aggregation and Pressure on Crude Oil Emulsion Sability, PhD Thesis, Department of Chemical Engineering, Norwegian University of Science and Technology, Norway, June 2002.
25. S.S. Schantz, W.K. Stephenson, Asphaltene Deposition: Development and Application of Polymeric Asphaltene Dispersants, Paper presented at the SPE Annual Technical Conference and Exhibition, Dallas, Texas, October 1991, SPE-22783-MS.
26. H.H. Ibrahim, R.O. Idem, Interrelationships between asphaltene precipitation inhibitor effectiveness, asphaltenes characteristics, and precipitation behavior during n-heptane (light paraffin hydrocarbon)-induced asphaltene precipitation. Energy Fuels, 18, 4, 2004, 1038-1048.
27. E.F. Ghloum, M. Al-Qahtani, A. Al-Rashid, Effect of inhibitors on asphaltene precipitation for Marrat Kuwaiti reservoirs, J. Petrol. Sci. Eng., 70, 1-2, 2010, 99-106.

28. K. Safaie, A.R.S. Nazar, Evaluation of asphaltene inhibitors effect on aggregation coupled sedimentation process, J. Dispersion Sci. Technol., 35, 3, 2013, 329-337.
29. S. Enayat, M. Tavakkoli, A. Yen, S. Misra, F.M. Vargas, Review of the current laboratory methods to select asphaltene inhibitors, Energy Fuels, 34, 12, 2020, 15488-15501.
30. R. Xiong, J. Guo, W. Kiyingi, H. Feng, T. Sun, X. Yang, Q. Li, Method for judging the stability of asphaltenes in crude oil, ACS Omega, 5, 34, 2020, 21420-21427.
31. D. Stratiev, I. Shishkova, R. Nikolova, T. Tsaneva, M. Mitkova, D. Yordanov, Investigation on precision of determination of SARA analysis of vacuum residual oils from different origin, Pet. Coal, 58, 1, 2016, 109-119.
32. S. Nemana, M.R. Kimbrell, E. Zaluzec, Predictive crude oil compatibility model, US7618822B2, 2009.
33. F. Gharagheizi, A. Fazeli, Prediction of the Watson characterization factor of hydrocarbon components from molecular properties, QSAR Comb. Sci., 227, 6, 2008, 758-767.
34. I.A. Wiehe, T.G. Jermansen, Design of synthetic dispersants for asphaltenes, Petrol. Sci. Tech., 21, 3-4, 2003, 527-536.
35. S.I. Andersen, J.G. Speight, Petroleum resins: separation, character, and role in petroleum. Petrol. Sci. Tech., 19, 1-2, 2001, 1-34.
36. M.R. Yakubov, G.R. Abilova, S.G. Yakubova, N.A. Mironov, Composition and properties of heavy oil resins, Petrol. Chem., 60, 6, 2020, 637-647.
37. V. Toteva, D. Stratiev, I. Shishkova, E. Nikolaychuk, K. Stanulov, D. Yordanov, Effect of commercial additives to reduce sediment formation in the ebullated bed vacuum residue H-Oil hydrocracking, J. Chem. Technol. Metall., 55, 6, 2020, 2040-2048.
38. D. Stratiev, I. Shishkova, A. Nedelchev, K. Kirilov, E. Nikolaychuk, A. Ivanov, I. Sharafutdinov, A. Veli, M. Mitkova, T. Tsaneva, N. Petkova, R. Sharpe, D. Yordanov, Z. Belchev, S. Nenov, N. Rudnev, V. Atanassova, E. Sotirova, S. Sotirov, K. Atanassov, Investigation of relationships between petroleum properties and their impact on crude oil compatibility, Energy Fuels, 29, 12, 2015, 7836-7854.
39. I.K. Shishkova, D.S. Stratiev, M.P. Tavlieva, R.K. Dinkov, D. Yordanov, S. Sotirov, E. Sotirova, V. Atanassova, S. Ribagin, K. Atanassov, D.D. Stratiev, L. Todorova-Yankova, S. Nenov, Evoluation of the different compatibility indices to model and predict oil colloidal stability and its relation to crude oil desalting, Resources, 10, 8, 2021, 75, https://doi.org/10.3390/resources10080075.
40. M.C. Garcia, L. Carbognani, Asphaltene−paraffin structural interactions. Effect on crude oil stability, Energy Fuels, 15, 5, 2001, 1021-1027.
41. F.G. D'Avila, C.M.F. Silva, L. Steckel, A.C.S. Ramos, E.F. Lucas, Influence of asphaltene aggregation state on the wax crystallization process and the efficiency of EVA as a wax crystal modifier: A study using model systems, Energy Fuels, 34. 4, 2020, 4095-4105.
42. E. Joonaki, A. Hassanpouryouzband, R. Burgass, A. Hase, B. Tohidi, Effects of waxes and the related chemicals on asphaltene aggregation and deposition phenomena: Experimental and modeling studies, ACS Omega, 5, 13, 2020, 7124-7134.
43. Y.M. Ganeeva, T.N. Yusupova, G.V. Romanov, Waxes in asphaltenes of crude oils and wax deposits, Pet. Sci., 13, 2016, 737-745.
44. D. Stratiev, S. Nenov, I. Shishkova, B. Georgiev, G. Argirov, R. Dinkov, D. Yordanov, V. Atanassova, P. Vassilev, K. Atanassov, Commercial investigation of the ebullated-bed vacuum residue hydrocracking in the conversion range of 55–93%, ACS Omega, 5, 51, 2020, 33290-33304.
45. M.J. Kaiser, A. de Klerk, J.H. Gary, G.E. Handwerk, Petroleum Refining: Technology, Economics, and Markets, Sixth Edition, Boca Raton, Florida, CRC Press, 2020.
46. M. Barcenas, P. Orea, E. Buenrostro-González, L.S. Zamudio-Rivera, Y. Duda, Study of medium effect on asphaltene agglomeration inhibitor efficiency, Energy Fuels, 22, 3, 2008, 1917-1922.
47. M. Madhi, R. Kharrat, T. Hamoule, Screening of inhibitors for remediation of asphaltene deposits: Experimental and modeling study, Petroleum, 4, 2, 2018, 168-177.