



Full Length Article

Mitigating paraffin wax deposition by dispersants and crystal modifiers in flow testing

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ABSTRACT

Functional molecules such as dispersants and crystal modifiers can be effective in mitigating wax deposition from crude oils and gas condensates. Both chemicals reduce the average wax particle size to sub-micron and change the crystal morphology. Water has a further significant effect on size reduction in dispersants. This work focuses on the effectiveness of these two additives in flow condition in a stainless-steel capillary tube. Unlike conventional flow loop systems, a simple open flow system is used to ensure constant wax content to avoid large fluid volume handling. Capillary tubes of 1- and 2-ft long are used to investigate effectiveness of dispersants and crystal modifiers in the laminar flow regime for a light shale oil with saturate content of 80 wt%. The effect of flow rate, concentration of the chemical additives (dispersant, crystal modifier), tube length, and brine on wax deposition are studied. An optimum concentration of chemical additives is found in flow tests, above which the effectiveness of additive decreases. Without aqueous phase, the crystal modifier is more effective than the dispersant. However, with 4% volume brine (of 5 wt% NaCl), the dispersant becomes more effective than the crystal modifier. Both additives are more effective at a higher flow rate; the influence of flow rate is more pronounced in the crystal modifier system than the dispersant. Wettability alteration to hydrophilic state is induced by adsorption of the dispersant backbone chains onto the stainless-steel (and wax molecules). Our results reveal that water improves dispersant effectiveness even in small amounts. A major observation in this work is pronounced pressure fluctuations in dispersants which relate to adhesion.

1. Introduction

Hydrocarbon production from shale and offshore formations often carries the risk of flow assurance from paraffin wax deposition and gelation [1–5]. Wax deposition commonly occurs along pipe walls below the wax appearance temperature (WAT) [3,4]. The wax gelation phenomenon in a crude oil depends on morphology of wax molecules which may occur even at low wax contents, especially for wax crystals with a high aspect ratio [6–8]. Wax precipitation and deposition from crude oils depends on operating conditions such as temperature and flow rate, and on crude oil properties such as carbon number distribution, viscosity, and asphaltenes, resins, and wax contents [9]. In recent review papers on wax deposition, the focus has been on: 1) subsea pipelines [10], 2) anti-wax pipeline coatings [11], 3) fundamental mechanisms of formation, deposition, and inhibition [12], 4) operating condition

effects [13], and 5) biomass-derived solvents for inhibition [14].

Crystal modifiers and wax dispersants are two major classes of chemical additives in wax mitigation. Crystal modifiers are functional polymers and co-polymers that co-crystallize with wax particles through change in morphology; they hinder the wax network growth, and therefore reduce the extent of wax deposition [15–19]. Wax dispersants are surfactants that are used for wax deposition mitigation (WDM). They hinder the wax crystal deposition by adsorbing onto the surface of wax crystals and onto the pipe inner wall, altering the wettability to become more hydrophilic [20]. In general, the optimal dosage of chemical additives for the WDM depends on crude oil composition [21,22]. The crude oil polar components such as asphaltenes and resins affect the wax deposition process. For example, the asphaltene-resin-wax interactions change upon asphaltene precipitation [23]. Co-deposition of asphaltenes and waxes is rarely reported, but wax deposition is reported to be

Abbreviations: ID, inner diameter; OD, outer diameter; PPD, pour point depressant; PV, pore volume; PV_b, pore volume passage before blockage; V_b, total volume passage before blockage; WAT, wax appearing temperature; WC, water cut; WDM, wax deposition mitigation.

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affected by asphaltene precipitation from interfacial rheology measurements [23–25].

The effectiveness of chemical additives for WDM is commonly studied by cold finger and flow tests. The latter accounts for the hydrodynamic effects and is therefore superior to the cold finger tests. One shortcoming of the conventional flow tests is that the outlet oil circulates through a supply vessel. Because of deposition of wax and adsorption of WDM chemicals onto the pipeline, and the co-precipitation of wax and WDM chemicals, the composition of inlet oil mixture may change with time.

Mechanisms of wax deposition in flow tests include molecular diffusion, thermal diffusion, Brownian diffusion of the particles, nucleation kinetics, gravity settling, shear dispersion (Taylor dispersion), shear stripping and flow pattern in multi-phase flow [3]. Molecular diffusion is often thought to be the controlling mechanism in wax deposition from external cooling [5,26–31]. There are extensive studies on wax deposition from crude oils and condensate liquids in flow conditions [5,32–36]. The effect of aqueous phase on wax deposition is largely unknown. Water-to-oil ratio (WOR) may affect thickness of wax deposition, wax content of the deposited medium, and WAT. However, the effects are not conclusive [33,34,36].

In several experimental studies, the efficiency of chemical additives in WDM has been assessed in flow tests. In 1970, Mendell and Jessen [37] have conducted single-phase flow loop tests, using five crude oils and five different crystal modifiers. The tests are conducted in turbulent flow conditions with additive volumes to 2%; a varying degree of effectiveness is observed with a maximum reduction of 40–85% in wax deposition [37]. Flow in turbulence condition decreases the wax deposition because of the shear removal and the shear thinning [38]. Bello et al. [39] evaluate the effectiveness of three commercial chemical additives in single-phase flow for three crude oils. They find a wax deposition reduction of 12–88%, depending on chemical additive and crude composition. They observe that addition of up to 50% xylene to the chemical additive maintains additive effectiveness while reducing the cost [39]. Lashkarbolooki et al. [40] investigate the effectiveness of ethylene vinyl acetate (EVA) and mixtures with chloroform, acetone, *p*-xylene, and petroleum ether, in single-phase flow loop in laminar regime. Among all combination of additives, a maximum reduction of 53% is observed in wax deposition at 800 ppm EVA / acetone / *p*-xylene (50%, 25% and 25%, respectively) [40]. Hoffman and Amundsen [41] conduct single-phase and two-phase (gas-oil) flow tests to investigate the effectiveness of a commercial crystal modifier in a gas condensate. They find an optimum concentration of 125 ppm at turbulent flow conditions, beyond which the enhancement stays the same. In flow tests, the wax deposited layer is 60–90% thinner with the chemical additive, but the deposited layer is harder, making the removal more difficult [41]. Venkatesan et al. [42] use single-phase flow in the loop test and study effectiveness of four commercial chemical additives (at 500 ppm) in a crude oil; they observe a maximum reduction of 60% in thickness of wax deposition. Adeyanju and Oyekunle [43] investigate the effect of acrylate ester copolymers with long alkyl chains as pour point depressants (PPD) at concentrations of 1 to 5 wt% and report a reduction of 15–35% in thickness of wax deposition, in single-phase flow in a crude oil [43]. Thayeb and Diaz [44] study wax deposition in a crude oil, using a polyacrylate polymer (C₁₆-C₂₂) at concentrations of 250–2000 ppm in single-phase flow; they report a maximum wax inhibition of 40–100% by varying temperature difference between the coolant and oil [44]. Jafari Ansaroudi et al. [19] employ flow loop tests to investigate wax deposition from a mixture of refined paraffin wax and kerosene and investigate the effect of a chemical additive on the morphology of the wax crystals formed in the flowline. They report that without the additive, the wax crystals are initially plate-like. At 100 ppm EVA, the wax crystals have smaller size mal-shape with a smaller aspect ratio [19]. The mal-shaped crystals are under-developed and agglomerate [45]. Recently, Chi et al. [46] investigate effectiveness of EVA and two different copolymers of alkane-maleic anhydride (MAC, a comb-like

copolymer) with short and long alkane chains in a gas condensate from Azerbaijan [46]. They report that after 72 h, EVA decreases the thickness of wax deposits by 55% while MAC with short and long side alkane chains decrease wax thickness by 66% and 85%, respectively [46]. The additive application leads to a thinner deposition of higher wax content. Without additive, the wax content of the deposit is 19%, which increases to 28% with EVA, and to 21% and 44%, by MAC with short and long side alkane chains, respectively [46].

The objective of this work is to investigate the effect of two types of additives on wax deposition from a shale oil in laminar regime. One crystal modifier and one dispersant are used in this investigation. The two chemicals are found promising in our earlier research using wax particle size measurements in vials [49]. The effect of the aqueous phase (brine) on deposition is part of this investigation. Most authors quantify the chemical effectiveness in terms of reduction in wax deposition thickness [18,37–39,41,43,44,46–48]. In this work, the effectiveness is quantified in terms of cumulative volume of oil that flows in the capillary tube before a pressure drop threshold is exceeded. Our simple method does not require an assumption about the deposit and provides a practical measure of blockage. The focus is on laminar flow regime as flow assurance by wax deposition is less severe at high flow rate. Experimental.

1.1. Materials

A shale oil is used with 80 wt% saturate content, 6.7 wt% wax content and a low concentration of asphaltenes (0.2 wt%). The measured wax appearance temperature (WAT) for the oil is about 40 °C [49]. The shale oil sample is kept at 55 °C before flow tests to avoid wax precipitation prior to fluid flow. The relevant oil properties are presented in Table 1.

In vial tests, a total of nine chemical additives (provided by Lubrizol Corporation) are screened, including six crystal modifiers and three dispersants. The most promising dispersant (D) and the most promising crystal modifier (CM) are selected. The dispersant D is a polyalkylated phenol with 50 wt% active components in an aromatic solvent. The crystal modifier CM is a copolymer ester with 37 wt% active components in an aromatic solvent. The molecular structures of these two polymers are sketched in Fig. 1.

The additives are identified with the tag names (D for dispersant and CM for crystal modifier) and the concentration, appearing in the subscript (in ppm). For example, D₅₀₀ is 500 ppm dispersant and CM₅₀₀ is 500 ppm crystal modifier. An aqueous phase of 5 wt% NaCl in water is used in this investigation.

1.2. Experimental procedure in flow tests

Wax deposition tests are initially conducted in flow tests without the additives to establish a baseline. From the tests, total injection before blockage (by wax deposition) is measured. After introducing the additive to the oil phase, enhancement in the total volume passage before blockage is measured from dynamic pressure drop measurements in the tube. The outlet is open to atmospheric pressure.

Flow tests are conducted, using the oil, with and without the aqueous phase. The effects of flow rate, water-to-oil ratio (WOR), chemical additive type, additive concentration, and tube length are investigated as

Table 1
Relevant properties of the shale oil.

Property measured	Value
Viscosity at 25 °C (cP)	14.8
Density at 25 °C (g/cm ³)	0.83
Asphaltene content (wt%)	0.22
Wax content (wt%)	6.67
Wax appearance temperature (°C)	40.5

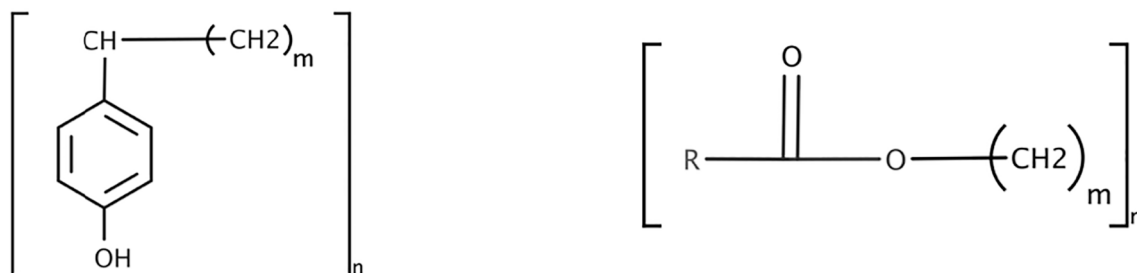


Fig. 1. Molecular structure of the two chemical additives used for WDM assessment: (a) dispersant D, and (b) crystal modifier CM. R is a functional group.

summarized in Table 2.

A schematic of the experimental set up is shown in Fig. 2. The chemical additives (D and CM) are both oil-soluble. They are mixed with the oil and loaded into a 60 mL syringe and kept at 55 °C (in convection oven) before injection. A syringe pump (KD Scientific Inc.) is used to inject the oil mixture into a stainless-steel capillary tube ($L = 1$ ft, $OD = 1/8$ in., $ID = 0.033$ in., and $PV = 0.167$ mL) at a constant rate. A 2-ft long tube ($PV = 0.334$ mL) is also used with the same inner and outer diameters to investigate the length effect.

The inlet pressure is measured by a pressure transducer, using two different diaphragms with spans of 5 and 30 psig (OMEGA® Eng. Inc.). The inlet pressure is equal to total pressure drop in the tube because the tube outlet is at atmospheric pressure. The syringe pump is manually stopped after the inlet tube pressure (threshold) exceeds 15 psig. The pump and pressure transducer are placed in an air bath of 55 °C. The capillary tube is placed horizontally outside the air bath at room temperature (25 °C). In tests with brine, a second syringe is filled with 5 wt% NaCl solution and is connected to the syringe pump. Equilibrium establishment is allowed at 55 °C before co-injecting with the oil sample. The brine injection rate is fixed at 2% and 4% of that of the oil (by volume). In flow tests with brine, the fluid streams are mixed in a union-te fitting located before the pressure transducer.

After each test, the capillary tube is heated to 80 °C and is blown with compressed air to displace the deposited wax. Then it is successively flushed with cycles of heptane, toluene and IPA, and is dried by flowing compressed air. The cleaning procedure is followed consistently in all tests to remove the deposited wax, and to restore the tube pristine wettability.

2. Results and discussions

In the following, the results of wax deposition flow tests are presented with and without the chemical additives. The effect of brine on wax deposition and interactions with the crystal modifier and dispersant are also discussed based on the inlet pressure and total pore volume passage (before blockage). Low injection rates in laminar flow are used in relation to blockage in producing wells in shale formations after the early period of high production rate. Only in the wax deposition tests to study the effect of CM concentration, a pressure drop threshold of 5 psi is used. For all other cases, a threshold of 15 psi is used to identify the blockage time. This pressure drop threshold is about two orders of magnitudes higher than the pressure drop before wax deposition build up in the tube. At this threshold, the tube may not be blocked

Table 2

A summary of experimental variables and values in the flow tests.

Experimental variables	Values
Flow rate (mL/h)	0.75, 1.5, 3 and 6
Water-to-oil ratio, WOR (vol%)	0, 2 and 4
Chemical additive	dispersant (D) and crystal modifier (CM)
Additive concentration (ppm)	0, 100, 200, 300, 500, 600, 800
Capillary tube length (ft)	1 (short), and 2 (long)

unambiguously, but it can be considered as practically blocked.

2.1. Wax deposition analysis in flow tests without additives

The effect of flow rate on the inlet pressure is shown in Fig. 3 without additives or brine. The tests are conducted in the shorter tube (1 ft) at three different flow rates of 1.5, 3 and 6 mL/h.

As seen in Fig. 3, the inlet pressure at different flow rates has the same features in the early period; there is no appreciable fluctuations. The pressure data in Fig. 3 show that there are two different trends of pressure increase upon flow: 1) gradual pressure increase, and 2) intense pressure spikes. The gradual increase in the injection pressure is due to continuous wax deposition onto the tube inner wall, reducing the area available for flow; at this stage, the flow is not yet blocked. The intense pressure spikes indicate major tube constrictions by the wax particle(s). At the choking location, fluid velocity increases which increases the shear force. The increased shear may dislodge at least a part of the wax deposit at the choking point, re-entraining it to the oil stream, resulting in a sudden decrease in pressure drop. The dislodged wax particle(s) may block a down-stream location. Numerical simulations of wax deposition show a specific choking point in the wax deposition process in tubes [45]. Due to stochastic nature of the shear removal process, the shape and size of the re-entrained wax particle(s), and down-stream constrictions will make it difficult to identify the actual constricting location in the tube. This is especially true at late stage deposition when the area available for flow is considerably reduced. Multiple pressure-drop spikes (in Fig. 3) that occur within varying distances (in terms of PV) from each other provide an indication of stochastic nature of blockage and shear removal. Similar intense pressure fluctuations are observed by asphaltene deposition in flow [50] and by water-in-oil emulsions flow [51].

From Fig. 3, it follows that major blockages occur at a later stage of deposition. At the three flow rates, several temporary occasions of minor blockage occur (identified with intense pressure rise < 15 psi). For these minor blockages, the shear force dislodges part of the deposited wax, resulting in a decrease in pressure drop to a value before flow restriction. At flow rates of 1.5, 3 and 6 mL/h, the blockage occurs after 102, 153 and 340 PV injection, respectively. At a higher injection rate, higher volume of oil pass before the capillary tube becomes practically blocked by wax deposits. Fig. 3 shows that the pressure spikes are more intense at higher flow rates.

The fluctuations in pressure drop are attributed to precipitation, deposition, and dislodging of the deposited wax. The flow tests are duplicated. The pressure drop replication results are presented in the Supplementary Material, showing that the pressure drop results are reproducible.

The reduced inner diameter of the tube (as results of wax deposition) can be calculated from the pressure drop method of Weingarten and Euchner [52], which simplifies to the Hagen-Poiseuille equation in laminar flow. This method is based on assumptions of a Newtonian fluid and uniform surface roughness – that is, similar to the clean tube. Fig. 4 shows the computed ratio of wax deposition thickness to the clean tube inner radius from the Weingarten and Euchner method [52]. In the

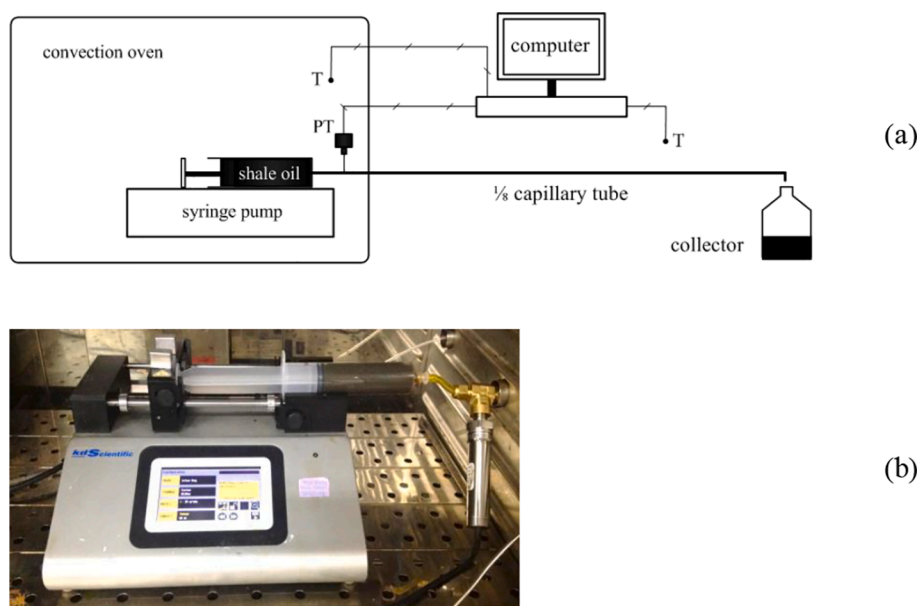


Fig. 2. Wax deposition flow test set-up: (a) process flow diagram, and (b) image (inside oven).

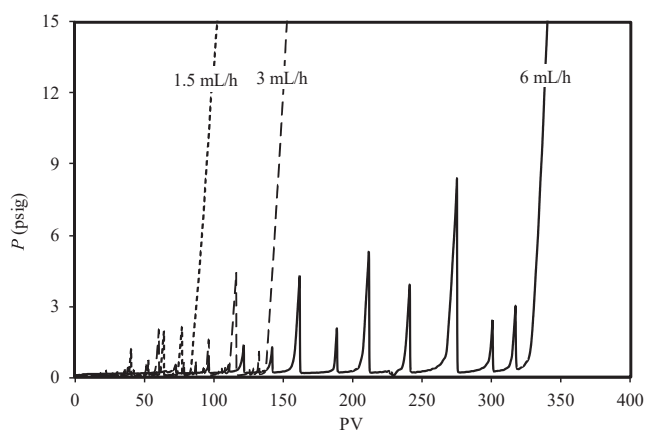


Fig. 3. Effect of flow rate on inlet pressure in wax deposition tests for shale oil without additives: 1-ft tube.

figure, the inlet pressure is plotted vs. PV and time for flow rates of 1.5 and 6 mL/h. The results for the intermediate flow rate of 3 mL/h (see Fig. 3) are not shown for clarity. From Fig. 4, it appears that the computed wax deposition thickness is higher at a lower injection rate, which can be explained based on: 1) longer contact time between the cold tube and warm oil, and 2) higher shear at the higher injection rate. Fig. 4 shows that the calculated deposit thickness at the constriction point controls the pressure drop in the tube. Calculation of wax thickness of the controlling constriction is challenging when several flow obstructions contribute to the pressure drop fluctuations simultaneously. In the simulation studies, the dynamics of pipeline blockage by wax deposits are usually inferred from average deposition thickness. Fluctuations are not considered and as a result, a monotonic thickness increase is calculated with time [5,53–58].

Fig. 4 shows that the ratio of wax thickness-to-radius returns to a base value of about 0.30 at 1.5 mL/h, following a fluctuation. At 6 mL/h, this ratio is about 0.2 and increases slightly with time. Similar to the simulation studies of wax deposition [5,53–58], the thickness of wax deposition in Fig. 4 approaches an asymptote near the blockage with the ultimate value changing with injection rate. Over 80% of the inner

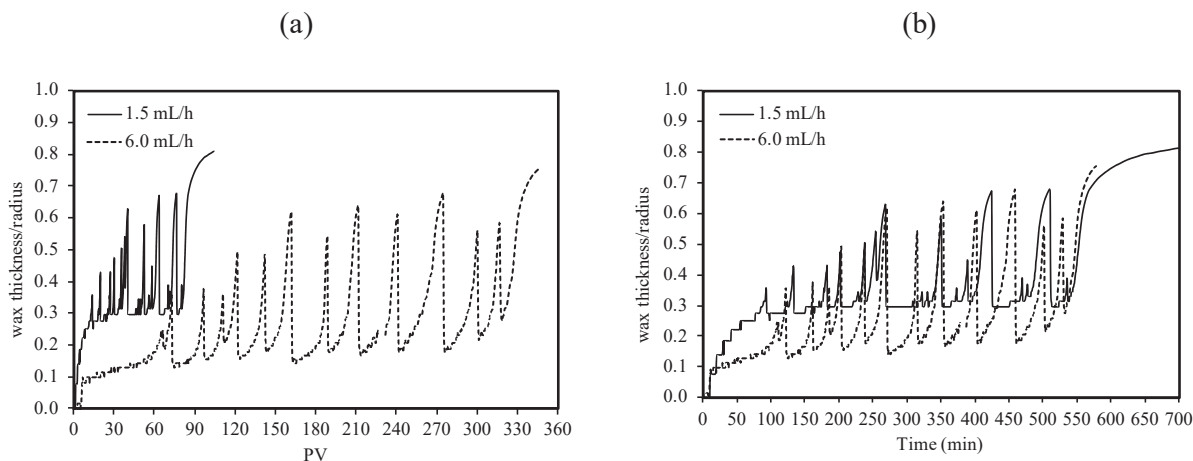


Fig. 4. Computed wax deposition thickness at flow rates of 1.5 and 5 mL/h in terms of ratio of thickness-to-radius vs. (a) PV, and (b) time: without additives, tube length = 1 ft.

diameter is blocked by wax deposition at the choking location after about 100 PV at flow rate of 1.5 mL/h. The blockage occurs at about 330 PV at 6 mL/h. The blockage at the higher flow rate occurs at significantly more fluid passage (Fig. 4(a)). But it is at about the same time for low and high flow rates according to Fig. 4(b). When comparing the deposition thickness at high and low flow rates, similar characteristics are observed, showing a monotonic increase in the wax thickness initially and at near blockage, along with spikes during flow. At 1.5 and 6 mL/h, the peaks in the wax thickness are close.

2.2. Effect of dispersant and crystal modifier on wax deposition mitigation

The effect of chemical additives and brine on deposition is shown in Fig. 5(a) at 500 ppm dispersant (D_{500}), and in Fig. 5(b) at 500 ppm crystal modifier (CM_{500}). The results are also compared to the baseline (without the additives) at 1.5 mL/h in the 1-ft capillary tube.

According to Fig. 5(a), without brine, the dispersant (D_{500}) does not significantly delay the blockage. It can be effective when brine is present. This figure shows that the blockage is significantly delayed by D_{500} and 4% brine, and the dispersant intensifies pressure fluctuations with or without brine. Fig. 5(b) shows that there is improvement in delaying wax deposition blockage by CM_{500} (compared to the baseline test without the additives). The brine does not significantly change the effectiveness of the crystal modifier. There are relatively mild pressure fluctuations before blockage. One can clearly conclude that the dispersant adheres to the pipe surface.

At molecular level, water molecules may interact with the hydroxyl functional groups of dispersant molecules through hydrogen bonding. From pressure fluctuations with dispersants (and unlike crystal modifiers showing much less pressure fluctuations) an argument is offered on the mechanisms. The formation of hydrogen bonding between the water molecule and phenol's hydroxyl group (in dispersant) is shown in Fig. 6. The interactions between water and dispersant molecules mitigate the growth of wax crystals. The mechanism is discussed in [49]. The hydrocarbon backbone in dispersant molecules co-crystalizes with wax, exposing the phenol functional groups to interact with water molecule to mitigate the wax growth. Therefore, dispersant and brine hinder the blockage through two simultaneous mechanisms: 1) mitigating the growth of wax particles in the bulk oil phase as observed by smaller wax particles in the vial tests [49]; and 2) mitigating the growth of wax deposition onto the tube surface, after a thin layer of wax co-crystalizes with the dispersant molecules.

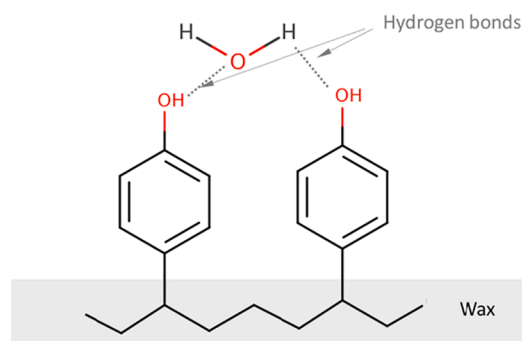


Fig. 6. Schematic of hydrogen bonding between water molecules and hydroxyl functional groups in dispersant molecules.

From Fig. 5(a), we suggest that the dispersant may adhere/adsorb to the capillary tube surface without water and with water. Without water the pressure fluctuations are more severe. Pressure fluctuations relate to adhesion and from dislodging. It is also likely that when wax and dispersants adsorb/adhere to the wall, water molecules may form association with the phenol OH and as a result there will be further reduction of adsorption/adhesion of waxes. The adsorption may change wettability of stainless steel to water-wetting. The contact angle of brine-air on the clean stainless-steel surface is around 103° . In the stainless steel coated with CM_{500} (in toluene), the brine-air contact angle is about 101° . The contact angle is 67° for the stainless steel coated with D_{500} (in toluene) [49]. The dispersant changes the wettability of stainless steel from (weakly) oil-wetting to (moderately) water-wetting in the air-brine-dispersant-steel system. Contact angle data with the oil phase may provide a more definitive reasoning. With water and dispersants, wax particles are smaller in the bulk oil as mentioned above [49]. Based on the above, the sketch in Fig. 6 applies to both bulk phase and the surface.

As seen in Fig. 3, there is flow enhancement from flow rate. The combined effects of water (WOR = 0, 2% and 4%) and dispersant at flow rate of 3 mL/h are compared in Fig. 7. The figure shows that brine and dispersant can be very effective in high fluid passage before blockage. Moreover, the effectiveness of the dispersant increases when the WOR is increased from 2% to 4%.

From Fig. 7, one obtains the pore volume passage at blockage (PV_b), showing that at 0, 2% and 4% WOR, $PV_b = 137, 189$ and 293 PV,

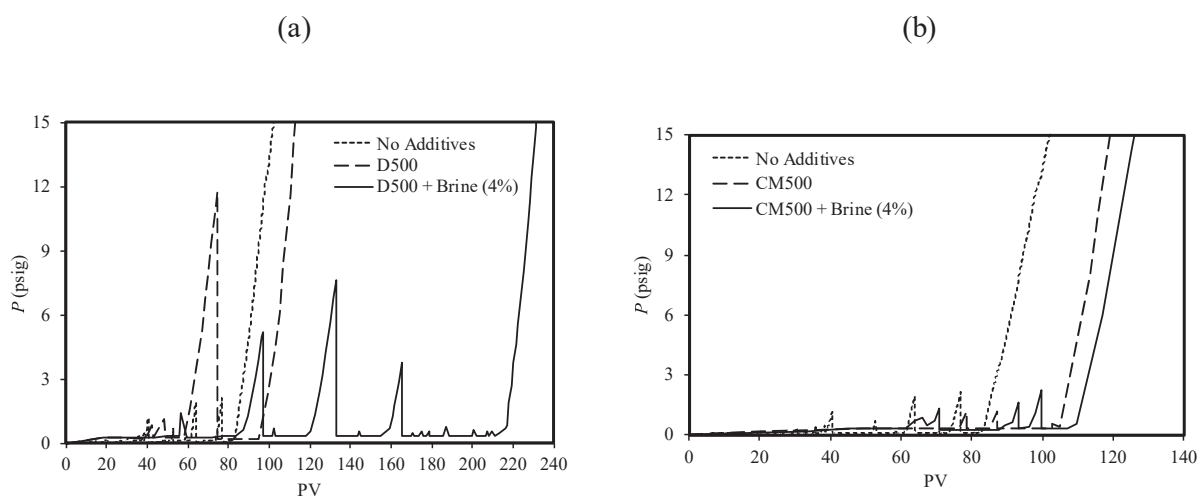


Fig. 5. Effect of brine on performances of 500 ppm additives: (a) dispersant D_{500} , and (b) crystal modifier CM_{500} : flow rate = 1.5 mL/h, tube length = 1 ft, water-to-oil ratio (WOR) = 4%.

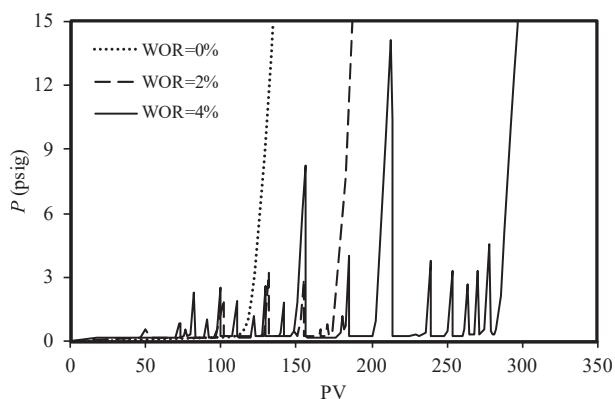


Fig. 7. Effect of water-to-oil ratio (WOR) on performance of dispersant (D_{500}): flow rate = 3 mL/h, tube length = 1 ft.

respectively. When the WOR increases from 0 to 2%, the PV_b increases from 137 to 189. There is about 38% enhancement in total fluid volume passage before blockage. The total PV of brine co-injected with oil is included in the total fluid passage (189 PV). WOR is defined as the ratio of water to oil volume. From the total of 189 pore volume passage, about 4 PV is brine and 185 PV is crude oil. Flow enhancement for total hydrocarbon pore volume passage at 2% WOR (using D_{500}) is about 35%. Similarly, with dispersant and 4% WOR, one observes 114% flow enhancement for total fluid and 106% for hydrocarbon passage compared to the dispersant alone.

The effect of crystal modifier concentration on WDM in the 1-ft capillary tube is shown in Fig. 8. A flow rate of 0.75 mL/h (4.5 PV/h) is used for comparison and a cut-off threshold of 5 psi as the blockage criterion in these runs. The results show that increasing the concentration of crystal modifier from 100 to 500 ppm enhances the total volume passage in the tube before blockage. A reverse trend is observed by increasing the concentration from 500 to 800 ppm, implying that the efficiency decreases at concentration beyond 500 ppm. The observation is in agreement with our vial cooling tests for which an optimal concentration of chemical additives can be found [49]. Self-association and association of crystal particles may be the reason for the reversal [49].

To the best of our knowledge, there is no reported work in the literature on a decrease in the effectiveness of dispersants and/or crystal modifiers with concentration in WDM. Previous reports on the optimal inhibitor concentration are related to the economic criterion where the addition of the inhibitors (beyond the optimal point) still improve the wax deposition mitigation; however, this improvements is not justified by the additional cost of the inhibitor [39,41].

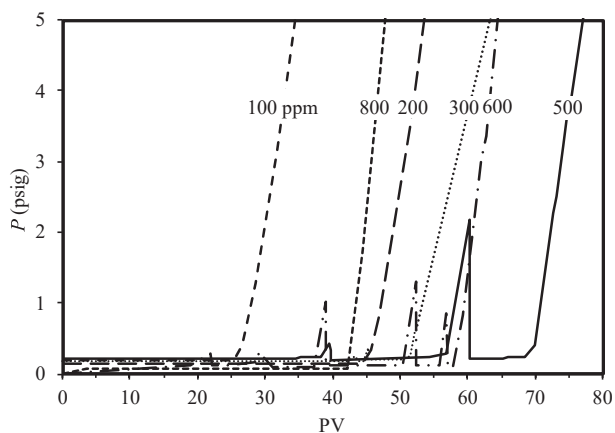


Fig. 8. Effect of concentration of the crystal modifier on wax mitigation performance: flow rate = 0.75 mL/h, tube length = 1 ft.

2.3. Total volume passage before blockage

From the inlet pressure data, total volume passage of oil before blockage (V_b , or alternatively PV_b) can be estimated using a threshold value for the pressure drop in the tube. The effectiveness of the two chemical additives can be expressed in percent increase in the PV_b (oil + additive + brine) before blockage compared to the baseline. In tests without brine, the baseline test is conducted using oil only (without an additive). For tests with varying levels of WOR and additives (oil + additive + brine), the baseline tests are conducted using (oil + brine) at the same WOR. One can compare the effectiveness of the chemicals in the same tube length based on flow rate, inlet oil temperature, and controlled environment temperature.

In all cases, two baseline runs are conducted for which an average PV_b is found by injecting warm oil (with or without brine) into the capillary tube held in a controlled environment at room temperature. Then, the effect of wax additive (either CM or D) on total volume passage is investigated.

In Fig. 9, the effectiveness of D_{500} and CM_{500} is shown in PV_b enhancement with and without brine. The “enhancement” is defined by the increase in PV_b for a given additive compared to the baseline. A high flow enhancement (%) is a measure of additive performance. Replicated runs are conducted for the effect of flow rate on enhancement; the data in Fig. 9 are based on the average values of the duplicates. The error bar indicates good agreement among replications; the variability is small except for the two runs conducted at the highest flow rate of 6 mL/h. As the Supplementary Material reveal, our inlet pressure data are reproducible at different flow rates and at different brine and additive concentrations. The variability observed in Fig. 9 is because of stochastic nature of blockage and shear removal.

There are several observations from Fig. 9 at flow rates of 1.5, 3 and 6 mL/h. At 500 ppm additive concentration, both the dispersant and the crystal modifier are effective with or without brine. The plots imply that more fluid can pass before blockage compared to the baseline test without the chemical additive at all three flow rates. In brine, flow enhancement is defined in comparison to a baseline using the oil at the same WOR (without additives). The minimum enhancement is about 14% using D_{500} and CM_{500} conducted at 1.5 mL/h without brine. Fig. 9 shows that the performance of CM_{500} is a strong function of flow rate, both with and without brine. The efficiency of D_{500} is only a relatively mild function of flow rate, but is strongly affected by brine. CM_{500} performance is not sensitive to brine. At a higher flow rate, the PV_b also increases as seen in Fig. 3. The effect of flow rate on effectiveness of the chemicals is more pronounced by CM_{500} . In tests with the oil alone, total PV_b increases from 97 PV at 1.5 mL/h to 337.5 PV at 6 mL/h. This corresponds to a 248% increase in total volume passage from flow rate effect. Using CM_{500} and without brine, PV_b increases from 110.5 PV at 1.5 mL/h to 773 PV at 6 mL/h, which is about 600% increase. Therefore, the enhancement in flow for CM_{500} is about 14% at 1.5 mL/h and 129% at 6 mL/h. There is a drastic difference in the performance of CM_{500} by increasing the flow rate in the range 1.5 mL/h to 6 mL/h as seen in Fig. 9.

Without brine, CM_{500} is more effective than D_{500} as observed in Fig. 9 (a). The superiority of the crystal modifier to dispersant without brine becomes more pronounced at higher flow rates. With brine, the dispersant becomes more effective as seen in Fig. 9 (b) and the superiority of dispersant compared to crystal modifier is more pronounced at a lower flow rate. There are residence time effects at a lower flow rate that allow the precipitated wax particle to grow in the tube as explained in relation to Fig. 4. The observations of effectiveness of D_{500} and CM_{500} and the effect of water on dispersant effectiveness are supported by the vial results [49].

A higher rate of thermal energy enters the capillary tube by increasing the oil flow rate. Because the capillary tube is placed in stagnant air, the rate of heat transfer from capillary outer wall to air controls the heat removal from the oil stream. Therefore, increasing the

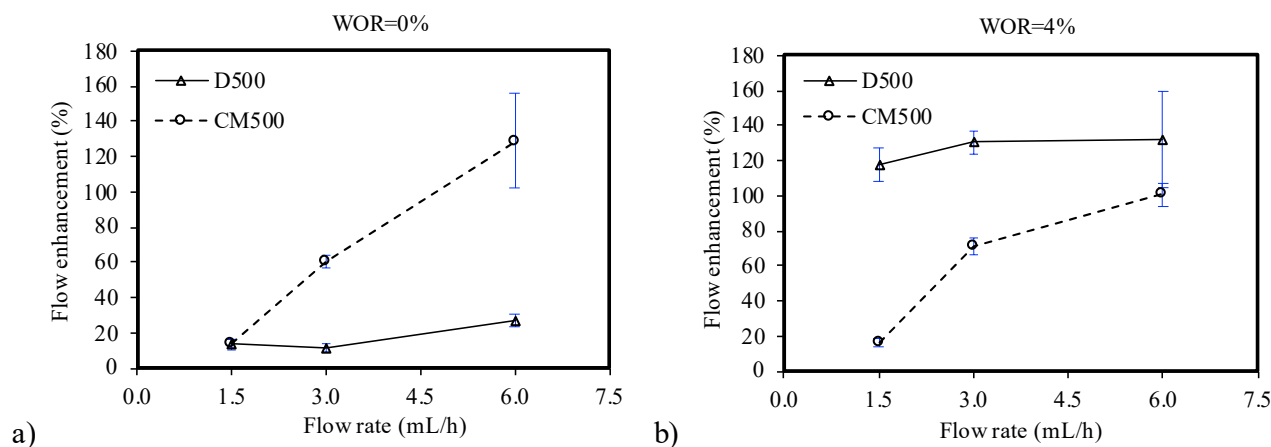


Fig. 9. Effect of flow rate and water-to-oil ratio on performance of dispersant (D) and crystal modifier (CM), (a) without brine, and (b) with 4% water-to-oil ratio (WOR): tube length = 1 ft.

oil flow rate will increase the temperature of stainless-steel capillary, especially near the entrance, resulting in less wax deposition because it is more soluble in the oil at a higher temperature near the tube inner wall.

With D₅₀₀, the maximum enhancement of 132% is achieved at 4% WOR at the highest flow rate of 6 mL/h. At this flow rate, the average flow enhancement without water is only 27% (Fig. 9(a)). At 4% WOR, the maximum flow enhancement by CM₅₀₀ is 101% at the highest flow rate of 6 mL/h (Fig. 9(b)), which is comparable to enhancement from crystal modifier without brine. Flow enhancement by D₅₀₀ without brine is about the same (14% flow enhancement) as by CM₅₀₀ at the lowest flow rate of 1.5 mL/h. The difference between the performance of dispersant and crystal modifier increases drastically with an increase in flow rate; at higher flow rates, CM₅₀₀ is much more effective than D₅₀₀ without the brine.

The effect of WOR on performance of dispersant is shown in Fig. 10 at the flow rate of 3 mL/h. The brine cannot appreciably change wax deposition without the dispersant. At a WOR of 4%, there is about 4% enhancement in the PV_b compared to the oil alone. Given that the total pore volume includes brine, there is no significant enhancement in the oil PV_b from brine. However, when dispersant is added, there is significant enhancement to the PV_b, and the dispersant becomes more effective as the WOR increases from 2% to 4% as seen in Fig. 10. There is 13% enhancement in total pore volume passage by dispersant without brine,

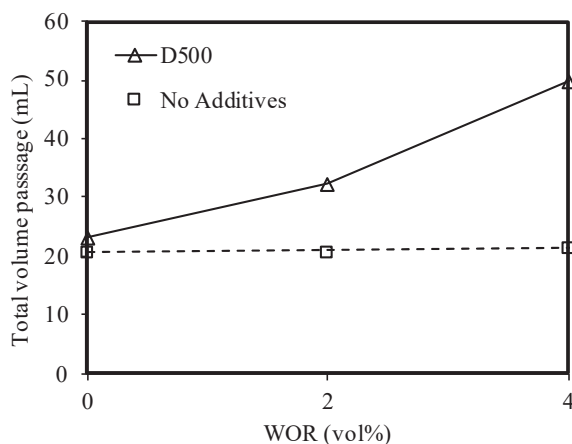


Fig. 10. Effect of water-to-oil ratio (WOR) on performance of dispersant (D₅₀₀): flow rate = 3 mL/h, tube length = 1 ft.

which increases to 58% at 2% WOR, and to 139% at 4% WOR.

A mixture of additives (D₅₀₀ and CM₅₀₀) is also investigated; no synergistic effect between the dispersant and crystal modifier is observed.

A summary of the results of the effect of flow rate, WOR and additive on PV_b is listed in Table 3. The PV_b shown in this table is the average of two duplicate runs at each flow rate. These results show a general behavior that both additives (D₅₀₀ and CM₅₀₀) improve total fluid passage, and the effectiveness of both additives increases with flow rate. Brine does not significantly change the performance of crystal modifier, while it substantially enhances the effectiveness of the dispersant. The results at the lowest flow rate, 0.75 mL/h, show that the dispersant at 500 ppm does not improve WDM, and it results in a decrease. Without brine at a flow rate of 0.75 mL/h, total fluid passage before blockage is 59 PV without dispersant, which decreases to about 39 PV with D₅₀₀. For all the other cases, the dispersant and crystal modifier are considered effective at 500 ppm concentration.

Flow tests are also conducted in the 2-ft long capillary tube with the same inner diameter and material as the 1-ft capillary tube to examine the length effect. A comparison between the deposition performance in the short (1 ft) and long (2 ft) capillary tubes is shown in Table 4. The flow rate is 1.5 mL/h in both tubes. Because the pore volumes of the short and long tubes are different, the total volume injected is used before blockage (V_b) in mL instead of PV. The PV of the clean empty tubes are 167 μL in the short capillary and 334 μL in the long capillary. Less fluid can pass through the longer tube before blockage, as shown in Table 4. Similar to the shorter tube, brine does not have a significant effect on the performance of CM₅₀₀ in the longer tube. However, brine

Table 3

A summary of combined effects of flow rate, wax additive, and water-to-oil ratio on the total pore volume passage. Results are the average of two runs.

Inhibitor	WOR (vol %)	PV _b at different flow rates (mL/h)				
		0.75	1.5	3	6	
-	0	59.0 ± 2.0	97.0 ± 8.0	123 ± 3.9	337.5 ± 8.8	
	4	57.5 ± 2.9	103.0 ± 2.0	127 ± 5.9	368.0 ± 17.6	
	D ₅₀₀	0	38.5 ± 1.0	110.0 ± 4.0	137 ± 3.9	429.5 ± 16.7
		4	71.0 ± 2.0	224.0 ± 13.7	292.5 ± 10.8	855.0 ± 141.2
CM ₅₀₀	0	84.0 ± 2.0	110.5 ± 2.9	197.5 ± 6.9	773.0 ± 125.4	
	4	86.0 ± 2.0	119.5 ± 5.9	217.5 ± 8.8	738.5 ± 34.3	

Table 4

The effect of tube length on total volume of fluid passage at 1.5 mL/h by the two wax additives and water-to-oil ratios. Results are based on average of two duplicates.

Inhibitor	WOR (vol %)	V_b (mL)		V_b , long/ V_b , short (mL/mL)	% FE (flow enhancement)		FE $\frac{\%_{long}}{\%_{short}}$ (% / %)
		short tube	long tube		short tube	long tube	
None	0	16.21 \pm 0.33	9.69 \pm 0.65	0.60 \pm 0.05	–	–	–
	4	17.21 \pm 0.33	10.53 \pm 0.33	0.61 \pm 0.02	6.2	8.6	0.60
D ₅₀₀	0	18.38 \pm 0.65	5.85 \pm 0.33	0.32 \pm 0.02	13.4	–39.6	–2.02
	4	37.43 \pm 2.29	14.37 \pm 1.96	0.38 \pm 0.06	117.5	36.5	0.31
CM ₅₀₀	0	18.46 \pm 0.49	11.53 \pm 0.98	0.62 \pm 0.05	13.9	19.0	1.37
	4	19.97 \pm 0.49	11.86 \pm 0.98	0.59 \pm 0.05	16.0	12.7	0.79

* FE is shown for flow enhancement (%), compared to the baseline tests without additive and at the same WOR.

significantly increases the performance of D₅₀₀ in the longer tube, similar to the shorter tube.

As seen in Table 4, D₅₀₀ at 4% WOR has the maximum enhancement in the long tube, for which a flow enhancement of 36.5% is observed compared to the baseline test (oil + 4% WOR). The efficiency of D₅₀₀ in WDM decreases more than the scaling factor (2:1) between the long and short tubes. This is not the case with CM₅₀₀, as can be inferred from the ratio of V_b in the long and short capillary tubes. This ratio is about 0.32 without brine and 0.38 with brine by D₅₀₀. The last column in the table shows the ratio of enhancement in flow in the long tube to that in the short tube. At 4% WOR, the enhancement in the long tube with CM₅₀₀, is about 80% of that in the short tube; this value is about 30% with D₅₀₀, which indicates the fast decline in the performance of dispersant and brine upon scale up. An interesting result is that at flow rate of 1.5 mL/h, the dispersant alone (without brine) is effective in WDM in the short tube for which about 14% improvement in total volume passage occurs before blockage. However, it is not effective in the longer tube. Table 3 shows that at a lower flow rate of 0.75 mL/h, the dispersant alone is not effective, even in the shorter tube (1 ft). From these observations, it appears that at a longer residence time, the dispersant alone without brine may even promote the blockage due to adsorption to the metal surface. In the vial testing [49], dispersant without brine gives a decrease in the average size of wax particles from 1.64 μ m in oil alone to 0.67 μ m with D₅₀₀ after 1 h and made the size distribution of the wax particle wider (higher poly dispersity) representing a shift in size distribution to larger values over time [49].

3. Conclusions

In this work, a fixed wax content in the inlet of a capillary tube is selected with the outlet open to atmospheric pressure to investigate effectiveness of dispersants and crystal modifiers in wax mitigation. The system may have merits over a flow loop system. The following conclusions are drawn from the work.

1. Significant pressure drop fluctuations are observed in the wax deposition flow tests. The pressure drop fluctuation are related to wax deposition and shear removal mechanisms at blockage state.

2. Pressure fluctuations are pronounced, for the dispersant due to adsorption to the wall surface. Adsorption to the surface by dispersants may decrease with water due to hydrogen bonding with dispersant phenol group.
3. The thickness of the deposited wax is higher at a lower flow rate.
4. There is an optimum concentration for the chemical additives, beyond which their effectiveness decreases. This optimum concentration in flow tests in our work is about 500 ppm. The optimum concentration has not been reported in the literature in the past to the best of our knowledge.
5. The crystal modifier (CM₅₀₀) used in our work is more effective than the dispersant (D₅₀₀) in wax mitigation without brine.
6. Brine/water has a substantial effect in improving the dispersant effectiveness.
7. Both additives are more effective at higher flow rates; the influence of flow rate is more pronounced on the crystal modifier than the dispersant.

CRediT authorship contribution statement

Minwei Sun: Conceptualization. **Nima Rezaei:** Conceptualization. **Abbas Firoozabadi:** Conceptualization, Supervision, Writing – review & editing, Funding acquisition.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2022.124687>.

References

- [1] Becker JR. Oilfield Paraffin Treatments: Hot Oil and Hot Water Compared to Crystal Modifiers. Society of Petroleum Engineers 2000. <https://doi.org/10.2118/63123-MS>.
- [2] Radulescu A, Fetters LJ, Richter D. Polymer-Driven Wax Crystal Control Using Partially Crystalline Polymeric Materials. Wax Crystal Control · Nanocomposites · Stimuli-Responsive Polymers, vol. 210, Berlin, Heidelberg: Springer Berlin Heidelberg; 2007, pp. 1–100. doi:10.1007/12_2007_124.
- [3] Aiyejina A, Chakrabarti DP, Pilgrim A, Sastry MKS. Wax formation in oil pipelines: A critical review. Int J Multiph Flow 2011;37:671–94. <https://doi.org/10.1016/j.ijmultiphaseflow.2011.02.007>.
- [4] Sarica C, Panacharoensawad E. Review of Paraffin Deposition Research under Multiphase Flow Conditions. Energy Fuels 2012;26:3968–78. <https://doi.org/10.1021/ef300164q>.
- [5] Huang Z, Lee HS, Senra M, Scott FH. A fundamental model of wax deposition in subsea oil pipelines. AIChE J 2011;57:2955–64. <https://doi.org/10.1002/aic.12517>.
- [6] Bern PA, Withers VR, Cairns RJR. Wax Deposition in Crude Oil Pipelines. Society of Petroleum Engineers 1980. <https://doi.org/10.2118/206-1980-MS>.
- [7] Holder GA, Winkler J. Wax crystallization from distillate fuels. Institute of Petroleum 1965;51:228–52. <https://doi.org/10.1002/cjce.22873/full>.
- [8] Paso KG. Paraffin gelation kinetics. University of Michigan; 2005. Ph.D. Thesis.
- [9] Yi S, Zhang J. Relationship between Waxy Crude Oil Composition and Change in the Morphology and Structure of Wax Crystals Induced by Pour-Point-Depressant Beneficiation. Energy Fuels 2011;25(4):1686–96.
- [10] Advances AOCEJ, 2021. Review of wax deposition in subsea oil pipeline systems and mitigation technologies in the petroleum industry. Elsevier n.d.
- [11] Bai J, Jin Xu, Wu J-T. Multifunctional anti-wax coatings for paraffin control in oil pipelines. Springer 2019;16(3):619–31.

- [12] Ragunathan T, Husin H, Wood CD. Wax Formation Mechanisms, Wax Chemical Inhibitors and Factors Affecting Chemical Inhibition. *Applied Sciences* 2020, Vol 10, Page 479 2020;10:479. doi:10.3390/app10020479.
- [13] Elganidi I, Elarbe B, Ridzuan N, Abdullah N. A review on wax deposition issue and its impact on the operational factors in the crude oil pipeline. *ScholarArchiveorg* 2021;17(1):44–9.
- [14] Afdhol MK, Abdurrahman M, Hidayat F, Chong FK, Zaid HFM. Review of Solvents Based on Biomass for Mitigation of Wax Paraffin in Indonesian Oilfield. *Applied Sciences* 2020, Vol 10, Page 479 2019;9:5499. doi:10.3390/app9245499.
- [15] Ashbaugh HS, Radulescu A, Prud'homme RK, Schwahn D, Dieter Richter A, Fetters LJ. Interaction of Paraffin Wax Gels with Random Crystalline/Amorphous Hydrocarbon Copolymers. *Macromolecules* 2002;35:7044–53. <https://doi.org/10.1021/ma0204047>.
- [16] Radulescu A, Schwahn D, Richter D, Fetters LJ. Co-crystallization of poly (ethylene–butene) copolymers and paraffin molecules in decane studied with small-angle neutron scattering. *J Appl Crystallogr* 2003;36:995–9. <https://doi.org/10.1107/S0021889803008525>.
- [17] Radulescu A, J. L, Richter D. Tailored Polymer Additives for Wax (Paraffin) Crystal Control. *Crude Oil Emulsions- Composition Stability and Characterization*. In: Abdul-Raouf M-S, editor. *Crude Oil Emulsions- Composition Stability and Characterization*. InTech; 2012.
- [18] Wei B. Recent advances on mitigating wax problem using polymeric wax crystal modifier. *J Petrol Explor Prod Technol* 2015;5:391–401. <https://doi.org/10.1007/s13202-014-0146-6>.
- [19] Ansaroudi HRJ, Vafaie-Sefti M, Masoudi S, Behbahani TJ, Jafari H. Study of the Morphology of Wax Crystals in the Presence of Ethylene-co-vinyl Acetate Copolymer. *Pet Sci Technol* 2013;31:643–51. <https://doi.org/10.1080/10916466.2011.632800>.
- [20] Dobbs JB. A unique method of paraffin control in production operations. *SPE Rocky Mountain Regional Meeting* 1999.
- [21] Manka JS, Ziegler KL. Factors Affecting the Performance of Crude Oil Wax-Control Additives. *Society of Petroleum Engineers* 2001. <https://doi.org/10.2118/67326-MS>.
- [22] Garcia MDC, Urbina A. Effect of Crude Oil Composition and Blending on Flowing Properties. *Pet Sci Technol* 2003;21:863–78. <https://doi.org/10.1081/LFT-120017454>.
- [23] Kriz P, Andersen SI. Effect of Asphaltenes on Crude Oil Wax Crystallization. *Energy Fuels* 2005;19:948–53. <https://doi.org/10.1021/ef049819e>.
- [24] Kelland MA. *Production Chemicals for the Oil and Gas Industry*. CRC Press 2014. <https://doi.org/10.1365/s10337-010-1557-2>.
- [25] Venkatesan R, Östlund J-A, Chawla H, Wattana P, Nydén M, Fogler HS. The Effect of Asphaltenes on the Gelation of Waxy Oils. *Energy Fuels* 2003;17(6):1630–40.
- [26] Roehner RM, Fletcher JV, Hanson FV, Dahdah NF. Comparative Compositional Study of Crude Oil Solids from the Trans Alaska Pipeline System Using High-Temperature Gas Chromatography. *Energy Fuels* 2002;16(1):211–7.
- [27] Edmonds B, Moorwood T, Szczepanski R, Zhang X. Simulating Wax Deposition in Pipelines for Flow Assurance †. *Energy Fuels* 2008;22:729–41. <https://doi.org/10.1021/ef700434h>.
- [28] Akbarzadeh K, Zougari M. Introduction to a Novel Approach for Modeling Wax Deposition in Fluid Flows. 1. Taylor–Couette System. *Ind Eng Chem Res* 2008;47: 953–63. <https://doi.org/10.1021/ie0711325>.
- [29] Ismail L, Westacott RE, Ni X. On the effect of wax content on paraffin wax deposition in a batch oscillatory baffled tube apparatus. *Chem Eng J* 2008;137(2): 205–13.
- [30] Merino-Garcia D, Corraera S. Cold Flow: A Review of a Technology to Avoid Wax Deposition. *Pet Sci Technol* 2008;26:446–59. <https://doi.org/10.1080/10916460600809741>.
- [31] Huang Z, Zheng S, Wax FHS. *Deposition* CRC Press 2016. <https://doi.org/10.1201/b18482>.
- [32] Gao C. Investigation of long term paraffin deposition behavior for South Pelto oil. University of Tulsa; 2003. Ph.D. Thesis.
- [33] Couto GH. Investigation of Two-Phase Oil-Water Paraffin Deposition. University of Tulsa; 2004. Ph.D. Thesis.
- [34] Bruno A. Paraffin deposition of crude oil and water dispersions under flowing conditions. University of Tulsa; 2006. M.Sc. Thesis.
- [35] Anosike CF. Effect of Flow Patterns on Oil-Water Flow Paraffin Deposition in Horizontal Pipes. University of Tulsa; 2007. Ph.D. Thesis.
- [36] Zhang Y, Gong J, Wu H. An Experimental Study on Wax Deposition of Water in Waxy Crude Oil Emulsions. *Pet Sci Technol* 2010;28:1653–64. <https://doi.org/10.1080/10916460903096822>.
- [37] Mendell JL, Jessen FW. Mechanism Of Inhibition Of Paraffin Deposition In Crude Oil Systems. *Society of Petroleum Engineers* 1970. <https://doi.org/10.2118/2868-MS>.
- [38] Hsu JJC, Santamaria MM, Brubaker JP. Wax Deposition of Waxy Live Crudes Under Turbulent Flow Conditions. *Society of Petroleum Engineers* 1994. <https://doi.org/10.2118/28480-MS>.
- [39] Bello OO, Fasesan SO, Teodoriu C, Reinicke KM. An Evaluation of the Performance of Selected Wax Inhibitors on Paraffin Deposition of Nigerian Crude Oils. *Pet Sci Technol* 2006;24:195–206. <https://doi.org/10.1080/1pet20.v024.i02;subPage:string:Abstract;journal:journal:1pet20;wgroup:string:Publication>.
- [40] Lashkarbolooki M, Esmailzadeh F, Mowla D. Mitigation of Wax Deposition by Wax-Crystal Modifier for Kermanshah Crude Oil. *J Dispersion Sci Technol* 2011;32: 975–85. <https://doi.org/10.1080/01932691.2010.488514>.
- [41] Hoffmann R, Amundsen L. Influence of wax inhibitor on fluid and deposit properties. *J Petrol Sci Eng* 2013;107:12–7. <https://doi.org/10.1016/j.petrol.2013.04.009>.
- [42] Venkatesan R, Sampath V, Washington LA. Study of Wax Inhibition in Different Geometries. *Offshore Technology Conference* 2012. <https://doi.org/10.4043/23624-MS>.
- [43] Adeyanju OA, Oyekunle LO. Influence of Long Chain Acrylate Ester Polymers as Wax Inhibitors in Crude Oil Pipelines. *Society of Petroleum Engineers* 2014. <https://doi.org/10.2118/172844-MS>.
- [44] Theyab M, Diaz PA. Experimental Study on the Effect of Polyacrylate Polymer (C16-C22) on Wax Deposition 2016.
- [45] Freund M, Csikos R, Keszthelyi E, Mózes G. *Paraffin Products*. 1983.
- [46] Chi Y, Daraboina N, Sarica C. Investigation of inhibitors efficacy in wax deposition mitigation using a laboratory scale flow loop. *AIChE J* 2016;62:4131–9. <https://doi.org/10.1002/aic.15307>.
- [47] Lashkarbolooki M, Seyfaee A, Esmailzadeh F, Mowla D. Experimental Investigation of Wax Deposition in Kermanshah Crude Oil through a Monitored Flow Loop Apparatus. *Energy Fuels* 2010;24:1234–41. <https://doi.org/10.1021/ef9010687>.
- [48] Hoffmann R, Amundsen L. Single-Phase Wax Deposition Experiments. *Energy Fuels* 2010;24(2):1069–80.
- [49] Sun M, Naderi K, Firoozabadi A. Effect of Crystal Modifiers and Dispersants on Wax Particles in Petroleum Fluids. *SPE J* 2019;24:32–43.
- [50] Hashmi SM, Loewenberg M, Firoozabadi A. Colloidal asphaltene deposition in laminar pipe flow: Flow rate and parametric effects. *Physics of Fluids* (1994-Present) 2015;27:1–15. doi:10.1063/1.4927221.
- [51] Rezaei N, Firoozabadi A. Pressure Evolution and Production Performance of Waterflooding in n-Heptane-Saturated Fired Berea Cores. *SPE J* 2014;19:674–86. <https://doi.org/10.2118/167264-PA>.
- [52] Weingarten JS, Euchner JA. Methods for Predicting Wax Precipitation and Deposition. *SPE Prod Eng* 2013;3:121–6. <https://doi.org/10.2118/15654-PA>.
- [53] Singh P, Venkatesan R, Fogler HS, Nagarajan N. Formation and aging of incipient thin film wax-oil gels. *AIChE J* 2000;46:1059–74. <https://doi.org/10.1002/aic.690460517>.
- [54] Ramirez-Jaramillo E, Lira-Galeana C, Manero O. Modeling Wax Deposition in Pipelines. *Pet Sci Technol* 2007;22:821–61. <https://doi.org/10.1081/LFT-120038726>.
- [55] Banki R, Hoteit H, Firoozabadi A. Mathematical formulation and numerical modeling of wax deposition in pipelines from enthalpy–porosity approach and irreversible thermodynamics. *Int J Heat Mass Transf* 2008;51:3387–98. <https://doi.org/10.1016/j.jheatmasstransfer.2007.11.012>.
- [56] Hoteit H, Banki R, Firoozabadi A. Wax deposition and aging in flowlines from irreversible thermodynamics. *Energy Fuels* 2008;22(4):2693–706.
- [57] Huang Z, Lu Y, Hoffmann R, Amundsen L, Fogler HS. The effect of operating temperatures on wax deposition. *Energy* 2011;25(11):5180–8.
- [58] Eskin D, Ratulowski J, Akbarzadeh K. Modelling wax deposition in oil transport pipelines. *The Canadian Journal of Chemical Engineering* 2014;92:973–88. <https://doi.org/10.1002/cjce.21991>.