Novel Approach for Improving the Flow of Waxy Crude Oil Using Thermochemical Fluids: Experimental and Simulation Study

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ABSTRACT: This article focuses on the flow assurance of waxy crude oil using an environmentally benign and cost-effective approach involving thermochemical reaction. The study incorporates experimental and simulation works to evaluate heat and pressure generation potentials and heat transfer efficiency of the thermochemical fluids. Experimental results reveal that at the concentration (1 M) of thermochemical fluid (TCF) ranging between 14 and 33% v/wt of the waxy oil, sufficient heat could be generated to raise the temperature of the oil significantly above the pour point (48 °C). In addition, from the bench-top treatment of a damaged tubing, it was observed that more than 95% of the deposited wax could be removed using the thermochemical solutions. Subsequently, a large-scale application of the technology in a long-distance flow assurance of waxy crude oil was confirmed through process simulation. Ultimately, the simulation results revealed the capacity of the method to improve the temperature and pressure profiles of the pipe flow system, and most significantly, to remove wax deposition up to 98%.

1. INTRODUCTION

Crude oil, a complex mixture of hydrocarbons, contains several components such as paraffins, aromatics, resins, and asphaltenes. Some of these substances, most especially the heavy molecules, paraffin wax, and asphaltene, cause serious flow assurance problems due to their thermodynamic instability. In fact, crude oils may contain up to 33% wax, which can crystallize during various hydrocarbon operations such as production, transportation, and storage.1–3

Generally, due to changes in thermodynamic intensive properties, viz., pressure, temperature, and composition of hydrocarbon, precipitation of organic flow assurance solids including gas hydrates, asphaltene, and paraffin wax often occurs.4 Thus, there are several complexities at different phases of operations in the oil and gas industries.5,6 Compared to other solids, wax precipitation is a major problem in oil production and transportation facilities.7–9 The high-molecular-weight paraffin wax (C_{20+}) at reservoir conditions is dissolved in the petroleum fluid. However, as the crude oil flows toward the processing facilities and gradually becomes colder, the solubility of the paraffin molecules reduces and, subsequently, wax deposition and accumulation may occur inside the good completion facilities, surface facilities, and transportation pipelines. Worse still, wax build-up in the pipeline could lead to significant pressure drop, which may result in a production shutdown.

Furthermore, wax precipitation is a function of temperature rather than pressure. Thus, it can deposit when the temperature falls below what is identified as the wax appearance temperature (WAT).10 At such a condition, the flow behavior becomes non-Newtonian and the effective viscosity increases significantly.11–14 The increase in viscosity leads to high resistance to flow and, invariably, increases the pressure drop along the production system.15 This eventually results in the loss of hydrocarbons, pipe plugging, and consequently high operational cost.2,3 Thus, transportation of waxy crude oil is normally performed above the WAT to avoid the stated problems.
Several preventive and remediation treatment strategies including thermal, mechanical, chemical, and biological methods have been applied to mitigate the wax deposition problem. Generally, in chemical treatment, polymeric chemical additives are used to decrease the pour point, viscosity, and yield stress of waxy crude oil. The polymers prevent aggregation or precipitation of wax-forming particles by forming the interparticle barriers (i.e., modify the crystallinity of the waxes), which ensures continuous flow of the paraffinic oil. However, such chemicals are often limited by compatibility issues, cost, and environmental or health implications. In the case of extreme fall in temperature, a large dosage of these chemicals might be required. On the other hand, due to the sensitivity of wax precipitation to temperature, a thermal method such as steam conditioning and thermal coating, injection of hot oil, thermal insulation, etc. have been considered as the most effective method to mitigate wax deposition problem. However, surface generation of steam and hot fluids can become less effective due to heat loss. In addition, other challenges such as environmental pollution from emission of greenhouse gas (GHG), and high operational cost are associated with steam generation through the conventional method.

These challenges have necessitated the search for alternative technologies to tackle the wax deposition problem. Recently, advancements in thermal stimulation technology, heat energy, and pressure generated from the exothermic reactions of certain chemical reactants have been assessed for their prospective applications in several areas of petroleum production, enhanced oil recovery, fracturing, and formation damage control. Thermochemical treatment is one of the promising methods that could be used for the thermal stimulation of the production wells to alleviate formation damage and improve hydrocarbon production. Using specific thermochemical fluids (TCFs), high temperature (up to 260 °C) and pressure (up to 2000 psi) can be generated downhole. The use of thermochemical fluids such as magnesium sulfate, ammonium chloride, and sodium nitrate solutions to generate heat and pressure at downhole conditions has been reported in the literature. Moreover, the heat and pressure generated during the typical thermochemical reaction can be controlled by adjusting the fluids’ concentration and pH. For example, lower pressure and temperature can be generated using low chemical concentrations or high solution pH. In addition, these chemicals may be injected using a pump in continuous, batch, or semibatch mode to ensure efficient performance and, ultimately, for safety purposes. Furthermore, depending on the specific technical requirement during typical field applications, such as internal corrosion control during transportation, the pH of the solution can be adjusted to a neutral level to avoid corrosion. Thus, the chemical formulation with a pH between 6.8 and 7 before and after the chemical reaction was used in this study.

However, despite the efficiency of the thermochemical treatment, it has not received much attention in the mitigation of flow assurance problem. In addition, prior to this article, similar scientific publications on wax mitigation using thermochemical treatment have rarely been reported. Moreover, the successful application of the technology required information, which can predict its performance on a large scale. Therefore, the focus of this work is to harness the potentials of the thermochemical technology in mitigating wax deposition problems and simulate the feasibility of the method for long-distance pipeline applications. Experimental studies were carried out to assess the heat and pressure released from a thermochemical reaction, as well as heat transfer efficiency in the presence of waxy crude oil. Subsequently, the information obtained from the experimental studies was used in the process simulation of the pipeline transportation of a typical waxy crude oil.

2. RESULTS AND DISCUSSION

2.1. Assessment of Thermochemical Heat Source. The thermochemical heat source involves exothermic reaction, with sufficient potential to release heat energy to the surrounding system. Essentially, this concept relies on dissolution or liquefaction of the deposited wax through heat transfer from the chemical reaction in the pipeline. Previous studies have shown that thermochemical fluids showed very effective performance in generating heat under certain conditions. As observed from the experimental studies, Figure 1 presents a typical temperature–pressure profile obtained from the reaction. The figure shows that the temperature change (ΔT) of 67 °C and the pressure change (ΔP) of 1610 psi, simultaneously, could be obtained from the reaction. Accordingly, the enthalpy change of the system, ΔH, due to heat released from the chemical reaction is 370 kJ/mol, regardless of the reactor operating temperatures ranging from 20 to ≈100 °C. Given the molarity of the reagents used in this study, the reaction was of first order (n = 1) with the activation energy Ea ≈ 35.5 kJ/mol.

Furthermore, Figure 2 is the temperature change obtained from the reaction of the thermochemical fluids in the presence of wax. From these results, it can be observed that the temperature of the system (a mixture of waxy crude oil and thermochemical fluid) increases due to heat transfer from the thermochemical reaction to the waxy crude oil. However, as expected, the temperature change varies with respect to the volume of thermochemical fluid added to the wax. The temperature change (ΔT) varies as 40, 44, 54, and 71 °C with 14, 22, 28, and 33% v/wt of the waxy crude oil, respectively.

2.2. Effect of Temperature on the Physical Properties of Wax. As stated earlier, temperature plays a major role in the phase behavior of hydrocarbon fluids. The discussion in this section is primarily informed by the intention to understand,
specifically, the effect of temperature on certain properties of interest, viz., the viscosity, density, and surface tension. This can also provide further clues on the prospects of the proposed cleaning method. In Figure 3, as expected, the results show that the viscosity of the waxy crude oil decreases from 76.4 cP at room temperature to 5.1 cP at 90 °C (and a constant shear rate of 5.1 s\(^{-1}\)). In addition, as presented in Figure 4, the rheological data indicate that the waxy fluid exhibit a non-Newtonian behavior at room temperature (23 °C) and low shear rates (0–200 s\(^{-1}\)). This observation might be connected with low fluidity at low shear rates and low temperatures. In comparison, at higher temperatures (38–90 °C), the fluid shows a negligible response to the shear rates (i.e., Newtonian behavior). Furthermore, the change in density and surface tension of the waxy crude oil due to temperature change is presented in Figure 5. It shows that the density reduces from 0.85 to 0.79 between room temperature (23 °C) and 90 °C, respectively. Similarly, the surface tension follows the same trend by decreasing from 69.8 to 59.5 mN/m between 23 and 90 °C, respectively. Thus, regarding the performance of the thermochemical reaction reported earlier, it could be concluded that the system can generate sufficient temperature to improve the flow behavior of typical waxy oil since the density and surface tension decreased significantly at similar temperatures generated by the reaction.

2.3. Performance of Thermochemical Treatment.

2.3.1. Wax Removal. Wax precipitation and deposition due to a decrease in the pipeline wall temperature below the WAT is a well-understood phenomenon. As earlier reported, when the temperature of the wall of the pipeline falls below the WAT, the wax layer is formed and grows with time. The deposited wax can reduce the inner diameter of the production pipes, which subsequently increases the required pressure to displace the hydrocarbon along the pipelines. In addition, the accumulated wax can increase the pipe roughness and then increase the pressure drop. Overall, the deposited wax on the pipe wall leads to a reduction in pipe durability and an increase in production cost.

Figure 6 shows the treated pipe before and after wax removal treatment. It was observed that 84.24% of the wax was...
removed during the first cycle of thermochemical injection (using thermochemical–wax crude oil ratio of 14% v/wt) and 15.16% of the wax was removed during the second cycle at the same ratio. As demonstrated in Section 2.2, the primary mechanism for removing the deposited wax is heat transfer from the thermochemical reaction. Furthermore, using 33% v/wt thermochemical to wax crude oil ratio, it was observed that 95% of wax was removed after a single treatment.

2.3.2. Integrity of the Production System. It is expected that wax removal methods may affect the integrity of the production system. Specifically, certain chemical treatments may cause corrosion of the pipe. Likewise, mechanical treatment could induce pipe enlargement, which could lead not only to significant pressure drop but also cause a reduction in strength and/or durability of the treated pipe.

As shown in Figure 7, by visual observation, no precipitation or debris was observed on the steel. This confirms that the thermochemical fluids did not react with the steel under the present experimental conditions. Moreover, as presented in Table 1, there was no change in the weight of the material after exposure to the thermochemical treatment.

| Table 1. Properties of the Treated Pipes before and after the Wax Removal Treatment |
|----------------------------------|----------------------------------|------------------|------------------|------------------|
| damage type | before treatment | after treatment | before treatment | after treatment |
| wax deposition | 1.59 | 1.59 | 7.93 | 7.93 |

Elsewhere in the literature, it was reported that typical thermochemical fluids could generate high temperature and pressure up to 260 °C and 5000 psi, respectively, based on the volume and concentrations. Therefore, the injected chemicals to remove the deposited wax should be precisely selected to avoid any damage to the production equipment.

2.4. Simulation Results: Improvement of Pipeline Flow Profiles. Heat and mass transfer occur during the flow of petroleum fluid through the pipeline. At a particular flow rate, the heat loss to the surroundings of the pipeline inadvertently causes the axial temperature profile along the pipeline. The temperature profiles along the pipeline of the waxy oil with different contents of thermochemical additives are presented in Figure 8. The figure shows that the temperature generally decreases along the length of the pipeline. However, the results clearly reveal the efficiency of the thermochemical additive in raising the temperature of the fluid. Specifically, compared to the reference case (without thermochemical additive), the fluid temperatures, by adding

Figure 6. Images for the production tubing before (a) and after (b) thermochemical treatment for removing the partial wax deposition.

Figure 7. Images of the treated tubing before wax deposition (top) and after thermochemical treatment (bottom).

Figure 8. Temperature profile along the pipeline at different quantities of TCF injected.
14–33% v/wt additive, show a significant increase above the pour point (48.8) of the crude oil considered in the simulation study.

Similarly, during the flow, mass transfer and/or molecular diffusion due to concentration gradient induces precipitation of wax and subsequent deposition on the wall of the pipeline. At the same time, the concentration gradient is influenced by the radial temperature gradient. The deposition thickness along the length of the pipeline at different concentrations of thermochemical additives is presented in Figure 9. This figure also shows that deposition thickness is higher at the inlet of the pipeline and decreases toward the outlet of the pipeline. Moreover, the addition of thermochemical also confirms that the thickness decreases as the concentration of the thermochemical additive increases. With reference to the onset deposition thickness (see Figure 10), the results show that wax deposition could be liquefied by 62, 84, 94, and 98% of the original wax due to the addition of 14, 22, 28, and 32% v/wt of the thermochemical fluid, respectively. These data are fairly comparable to the experimental data for wax removal from the contaminated pipe discussed earlier.

Finally, the pressure drop profile and total pressure drop along the pipeline are presented in Figures 11 and 12, respectively. The results indicate that the pressure decreases as the fluid flows toward the outlet of the pipeline. Most interestingly, it also confirms the ability of the proposed method to raise the flow pressure as well as the temperature. Therefore, in addition to mitigating wax deposition, the results show improved flow conditions due to enhancement of the flowing pressure, which is an advantage over the traditional hot fluid injection or thermal insulation techniques. Similar observations have been reported from our previous works focusing on heavy oil recovery using the thermochemical injection concept.

3. CONCLUSIONS

This investigation presents a novel and cost-effective technique for mitigating wax deposition and sustaining the flow of hydrocarbon in the pipeline. Therein, exothermic chemical reaction, which generates both heat and pressure at certain conditions, was performed. The study incorporates both experimental and process simulation approaches. Experimental results confirm that the chemical can sufficiently raise the temperature of the highly waxy oil above the pour point. It was also observed that more than 95% of the deposited wax could be removed from a contaminated tubing with no visible damage to the tubing material. Moreover, using the ratio of thermochemical fluid with waxy crude oil ranging between 14 and 33% v/wt, the simulation results show significant improvement in the flow conditions in terms of flow temperature, flow pressure, overall pressure drop, and, most significantly, reduction in wax deposition of up to 98%. Ultimately, the prospects of field-scale application for long-distance pipeline transportation of waxy crude oil has been confirmed.

4. EXPERIMENTAL SECTION

4.1. Experimental Materials. Original wax and waxy crude oil from an Arabian oil field were used in this study. The
stock solutions of thermochemical reagents were obtained from an Arabian Oil Company.

4.2. Experimental Methodology. 4.2.1. Assessment of Thermochemical Heat Source. To obtain quantitative energetic information, the thermochemical reaction was monitored in a close insulated system to study the heat and pressure generation. The schematic of the setup is shown in Figure 13. The setup consists of a high temperature and high pressure (HTHP) microreactor, nitrogen gas cylinder for pressure control, heater, and temperature and pressure sensors interfaced with a computer. Certain volumes of equimolar concentrations of the reactants (1 M) were fed into the reactor. The progress of the reaction was observed by collecting the data for an increase in temperature and pressure at equal time intervals through the data logging system. To ensure reliable temperature recording, a temperature meter (BST-DL102 Thermocouple Thermometer) was also used in

Table 2. Physical Properties of Crude Oil and Pipeline Conditions

| properties of crude oil |   |
|------------------------|---|
| viscosity (at 20 °C) cP | 97 |
| density (at 20 °C) kg/m³ | 983 |
| API                    | 13 |
| pour point (°C)        | 48.8 |

| pipeline and flow conditions |   |
|-----------------------------|---|
| material                    | mild steel |
| pipe inner diameter (in.)   | 101.6 |
| pipe outer diameter (in.)   | 127  |
| thickness (m)               | 0.0762 |
| thermal conductivity (W/mK) | 0.035 |
| ambient environment         | water |
| velocity of water           | 0.1 m/s |

**Figure 13. Setup for monitoring the progress of the thermochemical reaction.**

**Figure 14.** Description of reaction between thermochemical fluids and typical n-paraffin petroleum wax.

**Figure 15.** Illustration of the proposed thermochemical treatment method.

**Figure 16.** Fractional composition of the waxy crude oil.
conjunction with the temperature sensor. The stoichiometry equation of the thermochemical reaction is presented in eq 1

\[
\begin{align*}
\text{NH}_4\text{Cl} + \text{NaNO}_2 & \rightarrow \left[\text{NH}_4\text{NO}_2 + \text{NaCl} + \text{NH}_2\text{NO}_2\right] \\
& \rightarrow \text{NaCl} + 2\text{H}_2\text{O} + \text{N}_2 + \Delta\text{H}(\text{heat})
\end{align*}
\]

(1)

\[4.2.2.\text{ Measurement of Physical Properties of Wax.}\] Effects of temperature on some pertinent physical properties of waxy crude oil including surface tension, density, and viscosity were measured to gain a deeper understanding of this concept. The surface tension was tested at different temperatures (and atmospheric pressure) using the KRUSI Tensiometer (Model KI11, Germany) equipped with a Brookfield programmable temperature regulator. Likewise, the specific gravity was determined at different temperatures using the hydrometer and temperature-controlled environment (constant temperature hydrometer bath). The viscosity of the wax crude oil was measured using the Ofite Viscometer (Model 900, OFI Testing Equipment Inc., Houston Texas), which is a type of Couette coaxial cylindrical and rotational viscometer. About 160 mL of dispersion sample was used for each test run. The viscometer was set to precondition the sample by homogenizing it at the speed of 300 rpm and 30 °C for 5 min. The viscometer was operated at a low shear rate of 5.1 s\(^{-1}\) to a high shear rate of 1021.4 s\(^{-1}\) at a temperature between 23 and 90 °C. The instruments were regularly calibrated during the entire experiment.

\[4.2.3.\text{ Wax Dissolution Study: Bench-top Experiments.}\]

\[4.2.3.1.\text{ Thermochemical Reaction in the Presence of Wax.}\] The heat generation potential of the thermochemical reactants in the presence of wax crude oil was investigated. The temperature profile due to heat generation from the reaction was also recorded. This was done to study heat transfer efficiency and compatibility (possibility of forming precipitates) between the thermochemical reactants and wax. Thus, waxy crude oil and the thermochemical fluids at different concentrations (14, 22, 28, and 33% v/wt of waxy crude oil) were held in the microreactor. The reaction between the thermochemical fluid and typical wax (n-paraffin) is simplified in Figure 14.

\[4.2.3.2.\text{ Wax Removal from Production Facility.}\] Furthermore, with the aim of validating the efficiency of the proposed system, a sample of steel tubing containing accumulated wax was cleaned using thermochemical fluids. This was done by injecting the fluids into the material. Two cycles of injection were performed. The performance of thermochemical treatment was evaluated by measuring the weight of the wax removed after each cycle. The weight of the steel tubing was also measured before and after exposure to the thermochemical reactants for up to 1 h. The percentage of wax removal was calculated using eq 2.

\[
\text{wax removal (\%) } = \left(\frac{W_2 - W_3}{W_1 - W_2}\right) \times 100
\]

(2)

where \(W_1\) is the initial pipe weight before wax deposition (g), \(W_2\) is the pipe weight after wax deposition (g), and \(W_3\) is the pipe weight after thermochemical treatment (g).
4.3. Simulation of Single-Phase Flow Assurance of Waxy Crude Oil with Thermochemical Additive. The conceptual design of mitigation of wax deposition using thermochemical treatment is shown in Figure 15. The system refers to a similar case, which was designed for wax removal using fused chemical means.26 Essentially, the figure simplifies the proposed thermochemical injection method. It presents the potential offered by thermochemical reactants to raise the effective temperature within the flow line to the desired temperature above the WAT.

4.3.1. Process Modeling. Long-distance transportation scenario was simulated using AspenTech HYSYS process simulation package. The model considers the single-phase flow of incompressible fluid in the pipeline. The background mathematical functions presented in eqs 3–7 compute the temperature profile, wax deposition, pipeline wall heat transfer, pressure profile, and the total pressure drop, respectively.4,27 The bulk wall temperature profile along the pipeline due to the steady-state flow can be calculated using eq 3

\[ T_w(L) = T_i + \left( T_c - T_w \right) \exp\left( \frac{-U_{fl}D\delta}{mC_p} \right) \]  

where \( T_w \) is the temperature at distance \( L \) downstream the pipeline; \( T_i \) and \( T_c \) are the inlet and the constant ambient temperatures, respectively; \( m \) is the mass transfer of the fluid in the pipeline; \( D \) is the internal diameter of the pipe; \( C_p \) is the specific heat capacity of the fluid; and \( U \) is the overall heat transfer coefficient.

During the flow of the waxy crude oil, the wax is precipitated at the temperature below the WAT. With an assumption of instantaneous boundary layer precipitation rates, the wax deposition can be calculated using the molecular diffusion model, which is expressed as follows

\[ \frac{dm_i}{dt} = \rho_i A \delta_i \left( \frac{dT}{dr} \right) \]  

where \( m_i \) is the mass of wax-forming component, \( t \) is the time, \( \rho_i \) is the density of the waxy crude oil, \( \delta_i \) is the effective diffusion coefficient for the wax-forming component, \( A \) is the deposition area, \( \nu_i \) is the weight fraction of the wax-forming component, and \( r \) is the radial distance. \( dT/dr \) is the radial temperature gradient, while \( dw_i/dT \) is the solubility coefficient of the wax crystal in the oil phase.

The pressure gradient profile is calculated by solving the momentum equation describing the steady-state incompressible single-phase flow through a horizontal pipeline (eq 5).

\[ \rho u \frac{du}{dx} = -\frac{dp}{dx} - \frac{f\rho u^2}{2d} - \rho g \sin \alpha \]  

The total pressure over the entire pipeline (comprising the gravitation (g), acceleration (\( \alpha \)), and the friction (f) terms) is defined by eq 6.

\[ \Delta p_{li} = \Delta p_g + \Delta p_a + \Delta p_f \]  

Equation 5 reduces to the Darcy–Weisbach equation (eq 7) for a perfectly horizontal pipe with a uniform cross-sectional area.

\[ \Delta p_f = \frac{f}{2} \frac{1}{d} \rho u^2 \Delta L \]  

Moreover, a typical highly waxy crude oil having 35% wax content was selected from the simulator library. The physical properties of the oil and the pipeline conditions are detailed in Table 2. In addition, Figures 16 and 17 give the fractional composition and the wax distribution by composition of the oil, respectively.

The pipeline transportation model considers transportation over a distance of 3000 m (at the flow rate of 10 000 kg/h) with the elevation shown in Figure 18. The thermochemical additive to remove wax deposition was varied between 0 and 33% v/vt according to the information obtained from the experimental works. Figure 19 represents the thermochemical injection system and pipeline model used in the process simulation.

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Notes

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