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Experimental and Numerical Investigation of the Degelation Behavior and Non-Isothermal Flow Restart of a Waxy Oil Pipeline

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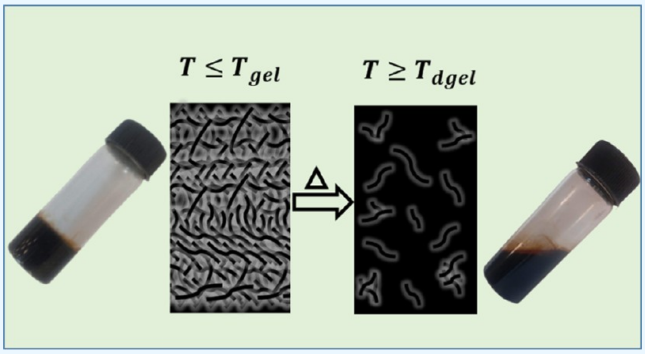
ABSTRACT: Flow assurance challenges associated with waxy crude oil precipitation at low ambient conditions are significant concerns for oil industries during production, transportation, and storage. Numerous methods have been employed to mitigate wax deposition and gelation issues. Since wax precipitation is temperature-sensitive, heating has emerged as a promising method to enhance oil flowability. The present work intends to examine the degelation behavior of waxy oil using rheometry, differential scanning calorimetry, and microscopy techniques. In addition, a non-isothermal flow restart simulation is performed using an in-house numerical simulator consisting of a rheological model of sol−gel transition developed in the current work. A numerical simulation of a preheated gelled pipeline demonstrates the significance of the degelation temperature. The effects of the wax concentration, initial gel temperature, and aging period on the degelation temperature are examined. The observed degelation temperature is higher than the gelation temperature, leading to thermal hysteresis. The extent of thermal hysteresis reduces with a decrease in the heating rate. The numerical simulation uses the finite volume method with variables placed on a staggered grid. The gel heated above and below the degelation temperature shows a significant variation in axial velocity profiles. However, further heating does not affect the velocity profiles. A shear banding type of effect is observed in the axial velocity profile above the degelation temperature. Heating the gelled oil to the degelation temperature instead of the wax disappearance temperature saves excessive heating energy during storage and transport operations.



1. INTRODUCTION

Several industrial fluids exhibit a temperature-dependent transition from solid-like to liquid-like upon heating or vice versa. This fluid class is termed “thermo-reversible gel”, notably due to significant changes in the viscous and elastic properties of fluids on successive heating and cooling.[1] Some commonly used thermoreversible materials are polymer gel, petroleum products, pharmaceutical products, waxes, and phase change materials. The thermo-reversible changes, leading to a significant rheological change in the fluids, create significant challenges during the transportation of these fluids. Hence, it is imperative to determine the transition temperature (i.e., gelation and degelation temperatures) at which rheological properties change significantly.

Waxy crude oil is an example of a thermoreversible gel comprising paraffin, asphaltene, aromatic, naphthene, and other hydrocarbons.[2−5] Proper handling of precipitating components such as paraffin and asphaltene is essential to efficiently transport crude oil from offshore reservoirs to onshore refineries. However, significant flow assurance risk arises from paraffin wax precipitation, especially during maintenance or emergency shutdown when extensive heat loss may result in gel formation, causing loss of flowability.[6] To mitigate this issue, pipeline heating is the most often utilized remedy. The minimum temperature at which the waxy crude oil starts to flow during the heating process is referred to as the degelation temperature. The gel network begins to destructure, and a substantial decrease in viscosity is observed at the degelation temperature. The present work utilizes an imposed shear stress method to evaluate the degelation temperature of waxy gelled oil. Understanding degelation characteristics is beneficial for ensuring flow during transportation, storage, and flow restart operation of gelled waxy crude oil. In addition, understanding the degelation behavior is also desirable for using waxes as phase change materials (waxes) for the thermal management of batteries[7] and electronic systems.[8] Moreover, the thermal degradation of gel during the degelation process is also an important topic of research in pharmaceutical, biological, medical, and polymer science fields.[9−11]

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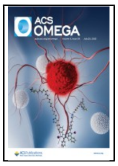

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The flow restart of waxy crude gelled pipeline has remained the major challenge for several decades, and a comprehensive understanding of gelation and degelation behaviors is sought.[12−19] Several techniques have been considered for performing flow assurance of a gelled pipeline.[20−24] These may be categorized into thermal, chemical, and mechanical treatment techniques, utilizing active or passive methods.[25−31] Pour point depressants are used as a chemical method to inhibit wax crystal agglomeration and gelation. Generally, polymers, comb-polymers, polymer nanocomposites, nanoparticles, and nanohybrids are utilized as pour point depressants, lowering the crude oil's viscosity and pour point.[27,32] Thermal methods consisting of insulating pipelines are considered one of the effective ways to reduce heat losses. However, their effectiveness is limited, especially during a prolonged shutdown.[33] Occasional maintenance or emergency shutdown may result in gel formation in the pipeline.[34] In such a case, thermal heating is a suitable option.[35] Electrical and thermochemical heat sources have been exploited to generate heat in pipelines.[24] Nevertheless, heating long pipelines involves a considerable cost.[36] Various studies on waxy crude oil have examined the temperature-dependent gelation and deposition behavior for comprehending the risk associated with wax precipitation and its remediation.[37−40] However, a comprehensive investigation of the degelation behavior and its dependency on critical parameters has not been detailed in earlier works. In the present work, the imposed shear stress approach is proposed to measure the degelation temperature of waxy oil. The temperature corresponding to the onset of a shear rate rise is referred to as the degelation temperature, while the sample remains under a small magnitude of an applied shear stress. The imposed shear stress is small enough to ensure that no crystal ruptures due to shear degradation during the thermal degradation. The degelation temperature gives an idea about the flowability of waxy oil during the heating process. Accordingly, it is essential to supply sufficient energy in the form of heat along the pipeline to allow a smooth flow restart of a plugged pipeline.

Recently, a few researchers have numerically examined the effect of preheating on the flow restart of a gelled pipeline.[13,41−43] The preheating process results in faster gel degradation and an effective reduction in viscosity, facilitating improvement in the flow restart operation. The heating of the waxy gel pipeline results in the de-crystallization of existing wax crystals in the vicinity of the pipeline wall. Subsequently, melted wax crystals (liquid oil) act as a lubricant for sweeping the remaining gel in the pipeline. Hence, it is essential to understand the minimum temperature requirement for gel degradation, eliminating extra heating (heating beyond the gel degradation temperature). A flow assurance engineer should have a detailed understanding of the temperature up to which the gel needs to be heated to optimize energy utilization. In this work, we have utilized the degelation temperature in our in-house numerical simulator to demonstrate its importance in the startup operation of a gelled pipeline.

In this work, we performed experimental studies to investigate the degelation characteristics of model waxy oil and real crude oil using rheometry, differential scanning calorimetry (DSC), and microscopy techniques. The imposed shear stress method was utilized to measure the degelation temperature and its variation for oils with different wax percentages. In addition, the effect of the heating rate on the thermal hysteresis during gelation and degelation processes was also explained. Finally, a thermal-cycle-based rheological model was developed for preheated gelled pipeline restart numerical simulation. The disparity between the flow restart behaviors of differentially preheated (i.e., heated for different durations) gelled pipelines was revealed by the numerical analysis results. The numerical simulation showed a shear-banding-like effect near the heated surface, illustrating the impact of the degelation temperature on the flow. Our results will assist a flow assurance engineer in utilizing degelation temperature conditions that are just enough for gel degradation and flow restart. Correct prediction of the degelation temperature helps avoid excessive heating during the preheating process.

2. EXPERIMENTAL SECTION

2.1. Materials. In the present experimental study, samples of a real crude oil and model oils were utilized to investigate the degelation characteristics. The crude oil was acquired from an undisclosed Western Indian oil field, and model oil samples were prepared by adding macrocrystalline wax, i.e., Sasolwax 5054, to dodecane with 99% mass fraction purity. The macrocrystalline wax was obtained from Sasol Wax Co. (Germany), whereas dodecane was obtained from Sigma-Aldrich (United States). The model oil samples were prepared by dissolving Sasolwax 5054 with concentrations ranging from 5 to 40 wt % in dodecane. The macrocrystalline wax (hereafter wax) has 78% w/w linear alkanes with carbon numbers ranging from C20 to C44 and 22% w/w cyclic and branched alkanes with carbon numbers ranging from C20 to C41. Additional information regarding composition analysis and properties of Sasol wax 5404 is reported in previous literature studies.[44−46]

2.2. Preconditioning. Before the rheometric experiments, the waxy oil sample is heated to at least 10−20 °C above the wax appearance temperature (WAT) for 30 min. The homogeneity of the sample is ensured by waxy oil pretreatment. The light hydrocarbons evaporate from the waxy oil sample during the thermal pre-treatment process, which helps in maintaining the composition of the sample during high-temperature rheological experiments. Pre-treatment of the waxy oil sample confirms the repeatability and reproducibility of experimental results.[47]

2.3. Rheological Experimentation. Rheological experiments were performed to examine the gelation and degelation behaviors of waxy crude oil on an Anton Paar (MCR 302) stress control rheometer. The rheometer is equipped with a computer feedback control system to regulate the shear rate. Therefore, the rheometer can also be utilized in strain-controlled mode. A Peltier system was used to regulate the temperature during rheological experiments. A cone-and-plate geometry with a 50 mm peripheral diameter and a 2° angle (CP2 50) was used for all of the rheological experiments.

2.3.1. Degelation Temperature Measurement with the Constant Imposed Stress Method. The sample of waxy oil is poured between the preheated (above WAT) CP2 50 geometry. The sample is maintained at a constant temperature for 10 min to ensure the solubility of wax crystals in the liquid oil. The model oil and real crude oil samples are cooled from 45 and 60 °C to below the gelation temperature, respectively, at a cooling rate of 1 °C/min under quiescent conditions. Subsequently, the gelled waxy oil samples are heated to above the degelation temperature at a heating rate of 1 °C/min. A small magnitude of shear stress, 0.1 Pa, is imposed during heating to track the viscosity and shear rate variation of the gelled sample. A shear stress of 0.1 Pa is small enough to ensure no shear-induced crystal rupture during the degelation process. The temperature corresponding to the onset of an abrupt rise in the shear rate observed during the heating process is referred to as the degelation temperature of waxy oil. Figure 1 gives additional information on the degelation temperature measurement protocol. The experimental parameters used to examine the degelling characteristics of waxy oil under various conditions are shown in Table 1.

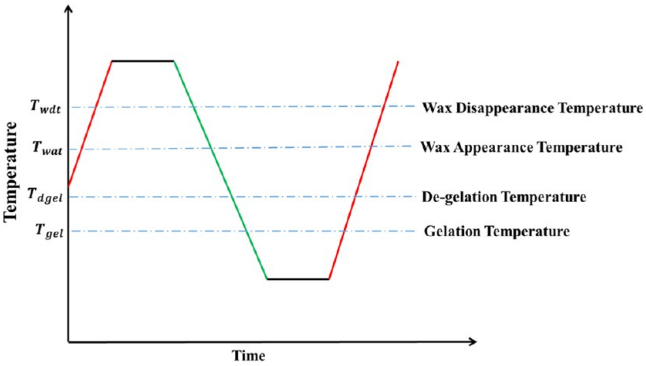

Figure 1. Schematic representation of the protocol of degelation temperature measurement.

Table 1. Experimental Conditions for Measuring the Degelling Characteristics of Waxy Oil

sr no.	test parameters		samples
1	wax content	5−40 wt %	model oil
2	aging period	0, 10, and 30 min	crude oil
3	starting cooling temperature (T_i)	40−70 °C	crude oil
4	heating rate	1, 2, and 5 °C/min	model oil and crude oil

2.4. Microscopy.

A pre-calibrated Linkam THMSG 600 stage attached to a Leica DM 2700P microscope is used to examine the changes in the wax crystal network during the heating and cooling cycle. The 15% model oil sample is heated at 45 °C, and then one drop of the sample is transferred to the slide and covered with a coverslip. The sample model oil is cooled at a rate of 1 °C/min from 45 to 15 °C, and subsequently, a gelled sample is heated at a heating rate of 1 °C/min. Finally, microscopic images of the complex crystal network are recorded through a 20× magnification objective with a digital camera to study the waxy gel degelation process during the heating cycle. The ImageJ software is utilized to examine the micrographs captured at various temperatures.

2.5. Differential Scanning Calorimetry.

A differential scanning calorimeter (DSC 250, TA Instruments) was used to study the crystallization behavior during cooling and the decrystallization behavior during heating of the waxy oil. A sample of the model oil with 15% wax was cooled to 15 °C at a cooling rate of 1 °C/min, and subsequently, it was heated at two different heating rates of 1 and 5 °C/min to investigate the effect of the heating rate on thermal hysteresis. Moreover, DSC results were also utilized to measure the WAT of waxy oil. The measured WATs for the 15% model waxy oil sample and real crude oil were found to be 27.5 and 37.5 °C, respectively. The details about the measurement of WAT using a heat flow diagram are provided in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Degelation Temperature Measurement.

We first performed three repeated rheometric experiments on a 15% model oil sample (15 wt % macrocrystalline wax in dodecane) to measure the degelation temperature using the imposed shear stress method. The test on the model oil sample was conducted by first static cooling below the gelation temperature followed by a temperature ramp to observe the phase transition with temperature. During static cooling, the loaded model oil sample was cooled from 45 to 15 °C (i.e., below T_{gel} = 27 °C) at a cooling rate of 1 °C/min and holding the temperature at 15 °C for 10 min. Subsequently, the resulting model oil gel was subjected to an increasing temperature ramp of 1 °C/min to 45 °C while applying a shear stress of 0.1 Pa. The applied shear stress was low enough to prevent gel network breakage by shear rejuvenation. Figure 2 shows the changes in viscosity and shear strain with the temperature rise. At low temperatures, ranging from 15 to 30 °C, the viscosity of the gel sample is very high and decreases gradually with the temperature rise. An instability in viscosity data is detected at low temperatures, which is an artifact of measurement. At a low temperature of 15 °C, due to intermolecular forces, the wax crystals are strongly interconnected. As the temperature increases, the volumetric-specific interfacial free energy of the interconnected crystal network (gel) decreases. This is because wax molecules have a higher kinetic energy at higher temperatures and are more likely to move and rearrange themselves to minimize the interfacial energy. A further increase in temperature results in the gradual dissociation of the wax molecules from the interconnected gel network, and they diffuse into the bulk of the solution. The heating starts disintegrating the wax crystal network, due to which a slight decrement in viscosity is noted. These observations are also confirmed with microscopy, which is discussed in detail in Section 3.2. The heating process may weaken the waxy gel network with the increasing temperature, but a three-dimensional volume-spanning gel network persists. The high

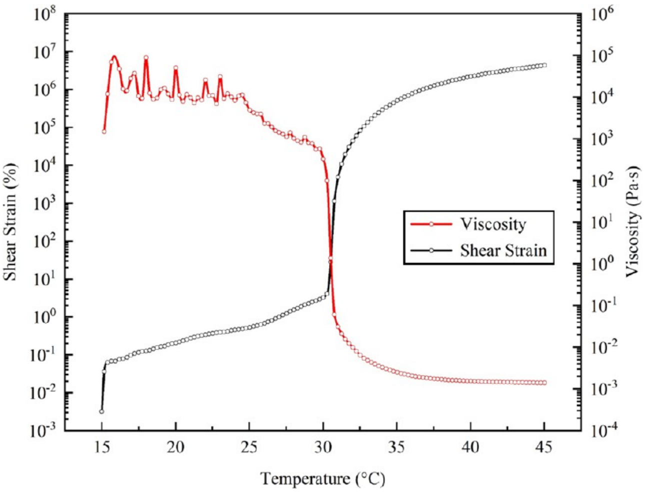

Figure 2. Variations of the viscosity and shear strain of the 15% model waxy oil sample with temperature while the sample was heated from 15 to 45 °C under an imposed shear stress of 0.1 Pa at a heating rate of 1 °C/min.

viscosity and low shear strain rate of the waxy gelled sample confirm this. A further increase in the waxy gel sample temperature results in the de-crystallization of wax crystals, and the gel network breaks significantly. The strength of the gel network strongly depends on the morphology of waxy crystals. This results in an abrupt drop in the viscosity of the gel sample. The temperature corresponding to an abrupt viscosity drop is referred to as the degelation temperature of the waxy oil sample. The degelation temperature is the lowest temperature at which the gel network does not exist during heating. It can also be observed that there is a sudden rise in the shear strain at the same temperature due to the complete degradation of three-dimensional gel networks. The abrupt change in the viscosity (shear strain) also follows the Arrhenius behavior above 40 °C (wax dissolution temperature), which is attributed to the complete dissolution of wax crystals.

Similarly, Figure 3 displays the variation of the shear rate with an increase in temperature. At lower temperatures, a small constant value (almost zero) of the shear rate is observed, which manifests the creeping flow behavior of the gel sample. As the gel sample temperature increases, a sharp increase in the shear rate is observed due to the transition of the sample behavior from a gel-like (soft solid) to a liquid-like behavior. The onset of temperature at which an abrupt increase in the shear rate is observed during the heating process is marked as the degelation temperature of waxy oil.

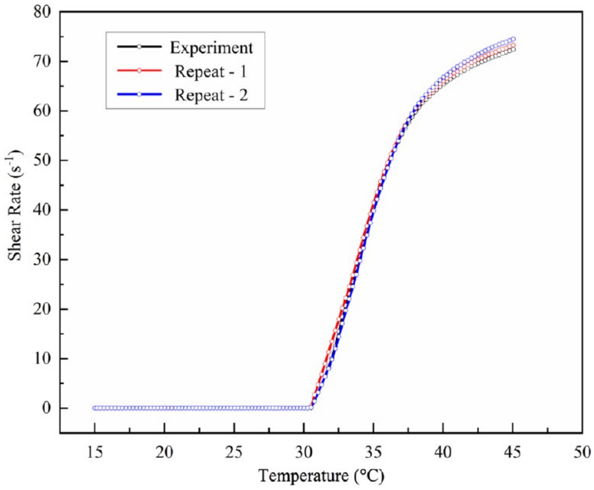

Figure 3. Repeatability of the shear rate measurement for the 15% model waxy oil sample with the temperature rise during degelation while the sample was heated from 15 to 45 °C under an imposed shear stress of 0.1 Pa at a heating rate of 1 °C/min.

Overall, during the heating of the waxy gelled sample, sudden increases in the shear strain and shear rate and a concomitant decrease in the viscosity are observed at the degelation temperature. For the 15% model oil sample, a sudden increase in the shear rate is observed at ∼31 °C. The degelation temperature is measured three times using the constant imposed shear stress method to ensure reliability. Figure 3 shows that the variation of the shear rate as a function of temperature matches very well in all of the repeated experiments, substantiating the repeatability of the measurements. To ascertain the validity of the proposed approach, the degelation temperature of the 15% model oil is also measured using the oscillatory method (further discussed in the Supporting Information). The results of degelation temperature measurement show good agreement. This signifies that the proposed approach is suitable for measuring the degelation temperature of waxy oil. In addition, the experiments are repeated for different wax contents using the imposed shear stress method. The results demonstrate adequate repeatability of the degelation temperature measurement.

3.2. Microscopic Image Analysis at Varying Temperatures.

The degelation characteristics of the model oil sample are explored using the microscopic experimental technique under non-isothermal conditions. In this study, a 15% model oil sample is cooled from 45 to 15 °C at a cooling rate of 1 °C/min. The gelled sample formed during cooling is subsequently heated from 15 °C to temperature until the complete dissolution of wax crystals at a heating rate of 1 °C/min. The micrographs of the gelled sample are captured during heating to probe the mechanisms of the degelation process. Figure 4 shows the micrographs of the model oil sample during the heating process at various temperatures. The morphology of wax crystals at 15 °C before starting the heating process is shown in Figure 4a. The crystal structure formed well below the gelation temperature (i.e., T_{gel} = 27 °C) shows stronger flocculation of wax crystals. Due to the interconnection of needle-like crystals, complex wax crystal networks are formed at a temperature lower than the gelation temperature. The cooling below the gelation temperature causes growth in the number and sizes of wax crystals, which is consistent with the observation of Haj-Shafiei et al.[48] Consequently, the formation of complex inter-connected crystal morphology collectively leads to an increase in gel strength.

During the heating of waxy gel, de-crystallization results in the dissolution of a portion of larger wax crystals. The wax crystals are smaller at higher temperatures compared to those at lower temperatures. Figure 4b−d shows the micrographs at different temperatures during the heating process. The microscopic observation reveals the reduction of the wax crystal's size as well as the number density with an increase in temperature. Moreover, the visualization shows the reduction of the interconnection between needle-like wax crystals. The gel network formed by smaller waxy crystals is less entangled, resulting in a weaker network. Further heating of the gel results in the dissolution of more wax crystals. Crystal−crystal interactions are also reduced due to a reduced wax crystal size, forming a weak gel network. Figure 4d−f shows that a further rise in temperature due to heating results in the disappearance of the portion of wax crystals by dissolution. A decrease in the crystal size and distribution is observed during heating, resulting in a sharp reduction in viscosity near the degelation temperature. A complex three-dimension network does not exist (Figure 4f) above the degelation temperature. The microscopic findings indicate that increasing the temperature causes a change in morphology and network structure due to a decrease in the size and number density of wax crystals. Hence, gel heating is chiefly responsible for the changes in the structural behavior of the waxy gel. A further increase in temperature, i.e., above ∼40 °C, results in the complete dissolution of the wax crystals, which is revealed in Figure 4h. The corresponding temperature is referred to as the WDT, above which wax crystals do not exist. It is the minimum temperature above which all precipitated wax molecules dissolve during the heating process.

3.3. The Gelation and Degelation Characteristics of Waxy Oil.

During the cooling of the waxy oil, a three-dimensional gel network forms (also known as a gel state) as

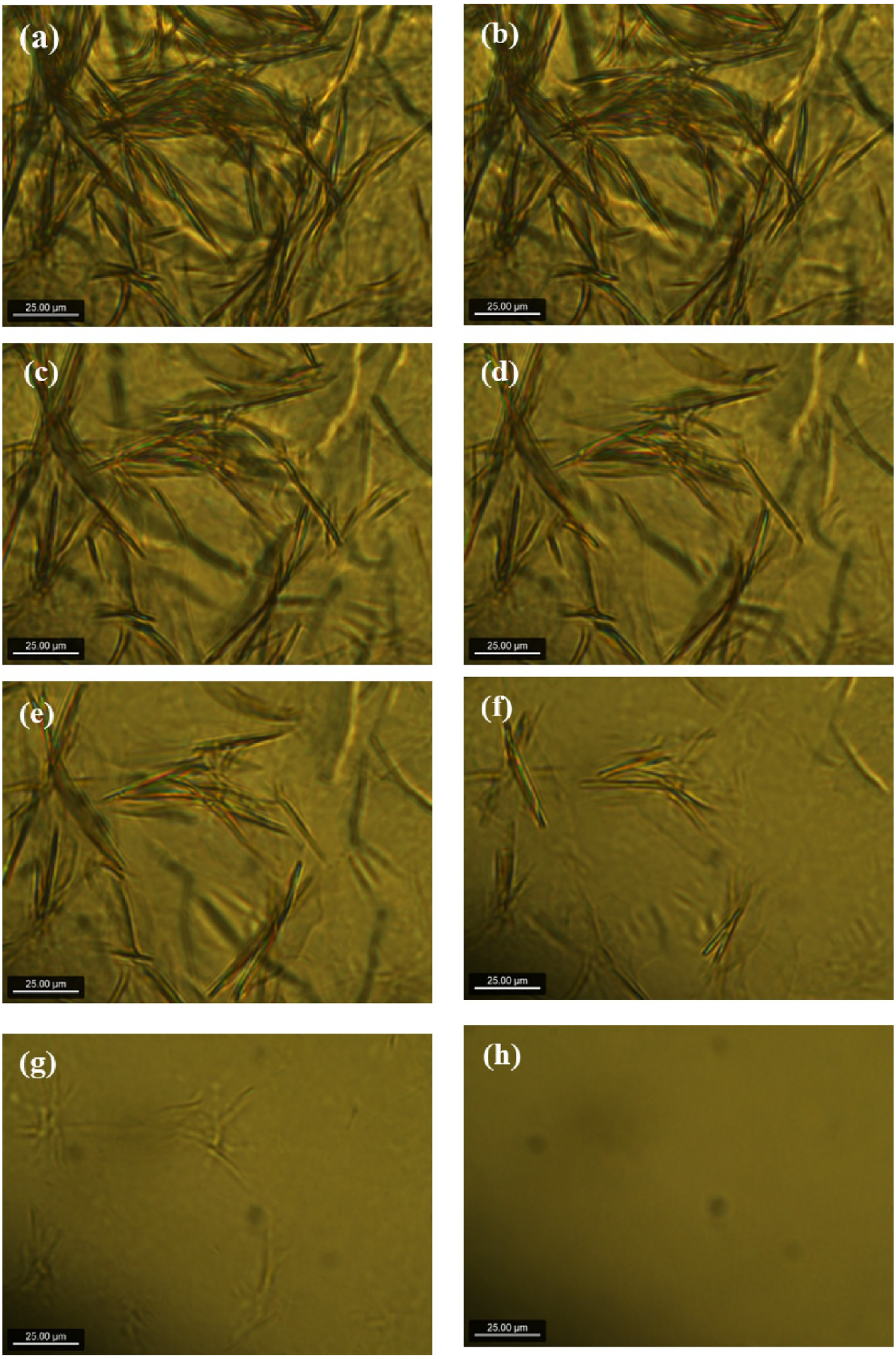

Figure 4. Microscopic images of the 15% model waxy oil sample at different temperatures, (a) 15, (b) 20, (c) 26, (d) 27.5, (e) 29, (f) 31, (g) 32.5, and (h) 40.2 °C, while the sample is heated from 15 to 45 °C at a heating rate of 1 °C/min.

the temperature reaches the gelation temperature. This must be heated to a temperature higher than the gelation temperature to dissolve the formed gel network in the remaining liquid phase. Waxy oils typically exhibit a gelation temperature lower than their corresponding degelation temperature. However, to the best of our knowledge, no previous research has studied the difference between degelation and gelation temperatures. These findings are similar to the observation that the WDT is higher than the WAT.[49] The gelation and degelation temperature difference is due to complex thermal hysteresis effects. It is usually driven by supercooling phenomena resulting from the complex nucleation and crystal growth mechanisms.[48]

The results of the DSC measurement shown in Figure 5 depict the thermal hysteresis during the wax crystal appearance and its dissolution. In addition, it has been observed that the dissolution endotherm was shifted higher than the crystallization exotherm for the waxy oil sample. A similar observation was also reported by Paunovic and Mehrotra.[50] Our findings regarding the degelation temperatures are consistent with the results of the WDT; i.e., the degelation temperature is higher than the gelation temperature. It is also observed from Figure 6 that the thermal hysteresis effect increases with an increase in the heating rate. Additionally, as the heating rate is increased, the endothermic peak shifts towards higher temperatures, indicating a prominent superheating effect compared to cases with lower heating rates.

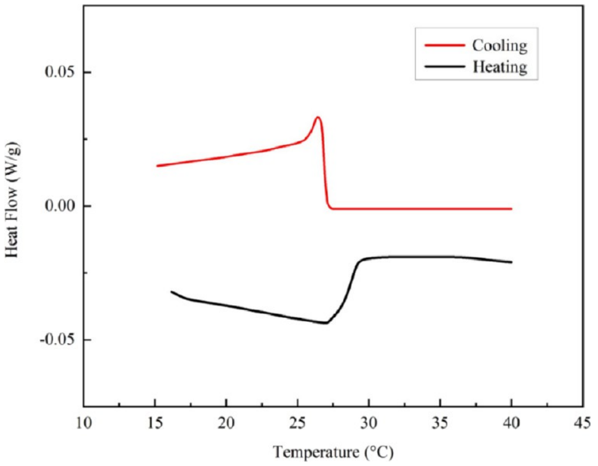

Figure 5. Heat flow curve during the cooling and heating process for the 15% model waxy oil sample with a heating and cooling rate of 1 °C/min.

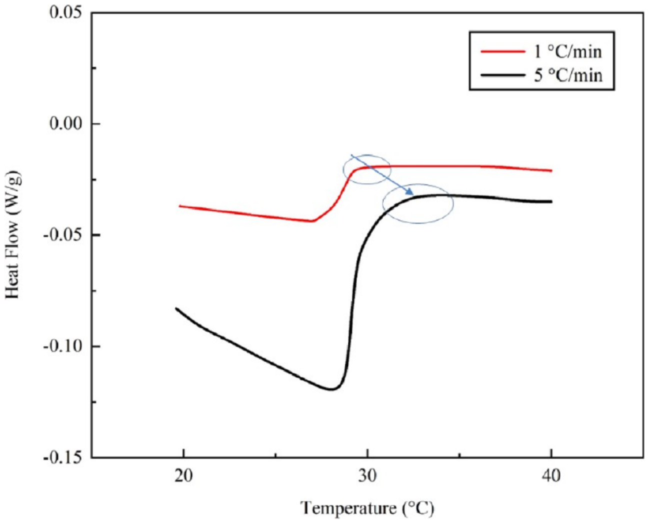

Figure 6. Heat flow diagram for the 15% model waxy oil sample for two different heating rates of 1 and 5 °C/min.

Figure 7 shows the shear rate and viscosity variations under an imposed shear stress of 0.1 Pa during the cooling and heating of the 5% model oil sample. During cooling, the gelation temperature is determined as the onset of the sudden shear rate drop under an imposed shear stress. It also corresponds to the liquid−solid transition. Likewise, the degelation temperature is measured during heating as the onset of the shear rate rise under a constant magnitude of shear stress. It also signifies the transition from solid to liquid. At the same temperature, during the cooling process, the viscosity value is observed to be lower than the viscosity value during the heating process. The dissimilarities between the cooling and heating curves are known as thermal hysteresis, resulting from discrepancies in the amount of wax crystals precipitated at a given temperature during the cooling and heating process. This discrepancy is primarily due to the supercooling effect.[51] During the degelation process, the sample changes from a gel state to a liquid state (i.e., from a molecular order state with a lower entropy to a molecular disorder state with a higher entropy). Hence, the sample does not necessarily reach equilibrium during the degelation process. Therefore, for the same heating and cooling rate, the effect of superheating during the degelation process is considerably less severe than that of supercooling during the gelation process. As a result, the precipitated wax content at any specific temperature below the WAT during cooling is always higher than that during heating.[52] Furthermore, wax crystals precipitate during cooling and form a gel network. Energy is released to the surrounding in the form of heat during the gel network formation process. The energy release is a result of the nucleation and crystallization of wax molecules. Thus, wax crystal precipitation leading to the formation of a volume-spanning gel network is regarded as an exothermic process. Meanwhile, during the heating of gelled waxy oil, energy has been absorbed to break the wax crystal network; hence, gel dissolution is regarded as

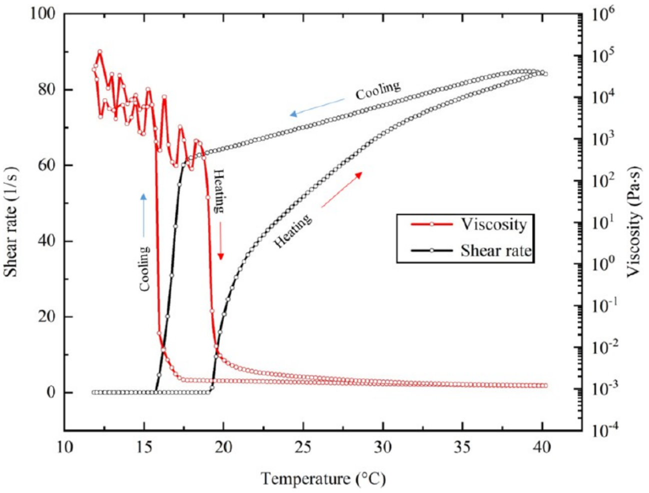

Figure 7. Shear rate and viscosity variations of the 5% model oil sample during cooling from 40 to 12 °C at a cooling rate of 1 °C/min; subsequently, the sample was heated to 40 °C at a heating rate of 1 °C/min under an imposed shear stress of 0.1 Pa (during cooling and heating).

an endothermic process. The oscillatory shear test experiment further investigates the gelation and degelation process. Figure 8 shows the variation of the storage modulus of the 5% model oil sample during cooling and heating. The results show different values of storage modulus during cooling and heating. The observations align with the observations using the imposed shear stress method.

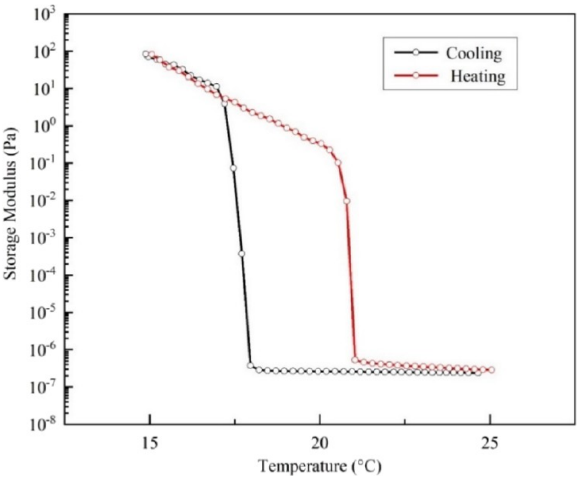

Figure 8. Variation of the storage modulus of the 5% model waxy oil sample during cooling from 25 °C at a cooling rate of 1 °C/min and subsequent heating from 15 °C at a heating rate of 1 °C/min while the sample is under an oscillatory stress of 0.1 Pa and a frequency of 0.5 Hz.

Furthermore, to examine the effect of the heating rate on thermal hysteresis, the gelled sample of 5% model oil is heated at three heating rates of 1, 2, and 5 °C/min. The temperature sweep curves during the cooling and heating process for the model oil samples (Figure 9) reveal the thermoreversible phase transition behavior of the waxy oil samples. The degelation temperature of the 5% model oil sample increases with the heating rate. At a higher heating rate, the dissociated wax crystals do not get sufficient time to migrate from the wax crystal network to the bulk of the oil. Hence, this prevents further dissolution of wax molecules, as in the absence of sufficient diffusion of dissociated wax molecules, local equilibrium is maintained (i.e., diffusion is the limiting step for the wax molecules' dissociation from the wax crystals). In addition, if the applied heating rate is too high, the wax crystals melt due to high local solubility, regardless of whether the solvent penetrated or not. This indicates that at very rapid heating rates, the energy input is sufficient to cause melting, even without significant solvent penetration. Conversely, if the heating rate is very low, wax molecules have sufficient time to reach thermodynamic equilibrium with the surrounding liquid oil, minimizing the superheating effect. Thus, the increase in the heating rate results in the superheating of the waxy gel sample. As a result of superheating, the thermal hysteresis effect will be stronger at higher heating rates.

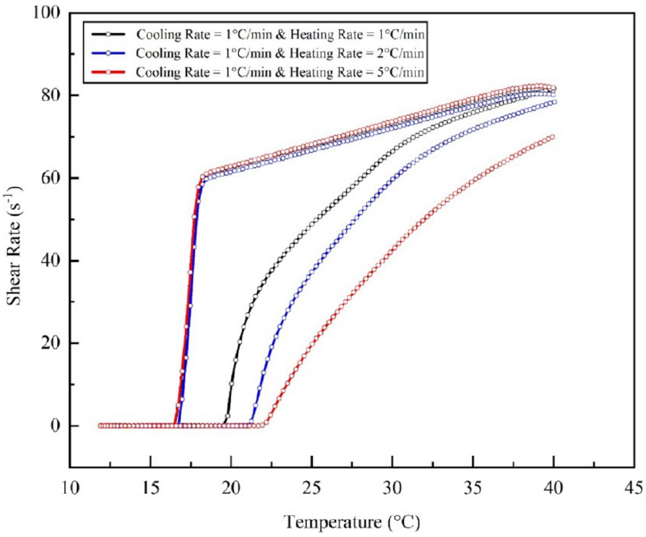

Figure 9. The effect of three different heating rates (1, 2, and 5 °C/min) on the thermal hysteresis of the 5% model oil gel sample under an imposed constant stress of 0.1 Pa. The oil sample is cooled at a prescribed cooling rate of 1 °C/min from 40 to 12 °C under the same stress conditions in all three cases.

Figure 10 shows that the degelation temperature is, on average, about 3–4 °C higher than the corresponding gelation temperature for various wax concentrations ranging from 5 to 40%. This shows that significant supercooling occurs in the waxy oil samples, which successively results in thermal hysteresis. In ideal equilibrium conditions, the wax crystallization during cooling and dissolution during heating should occur at the same temperature.[53] However, experimentally, it has been observed that wax dissolution occurs at higher temperatures compared to wax crystallization. Consequently, the degelation temperature is likely to be higher than the gelation temperature. This will result in thermal hysteresis. The nucleation process with a specific activation energy is involved in crystallization, resulting in supersaturation and supercooling. Both these effects are accountable for the dissimilarity in the gelation and degelation temperatures.

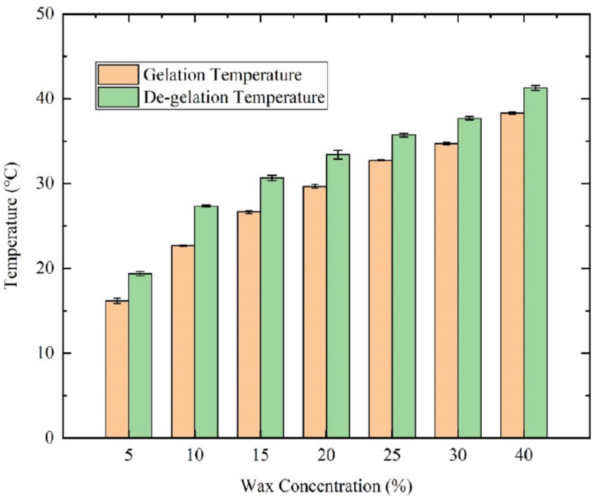

Figure 10. The gelation and degelation temperatures of various wax concentrations of model oil samples (ranging from 5 to 40%) were measured under the same cooling and heating rate of 1 °C/min and an imposed stress of 0.1 Pa.

3.4. Rheological Model for the Sol–Gel Transition of Waxy Gel. The rheological modeling of sol–gel transition is formulated on changes in physical properties with phase transition. It is interesting to see that waxy oil gel phase transition phenomena result in failure of the crystal network and are inadequate to retain the remaining liquid oil.

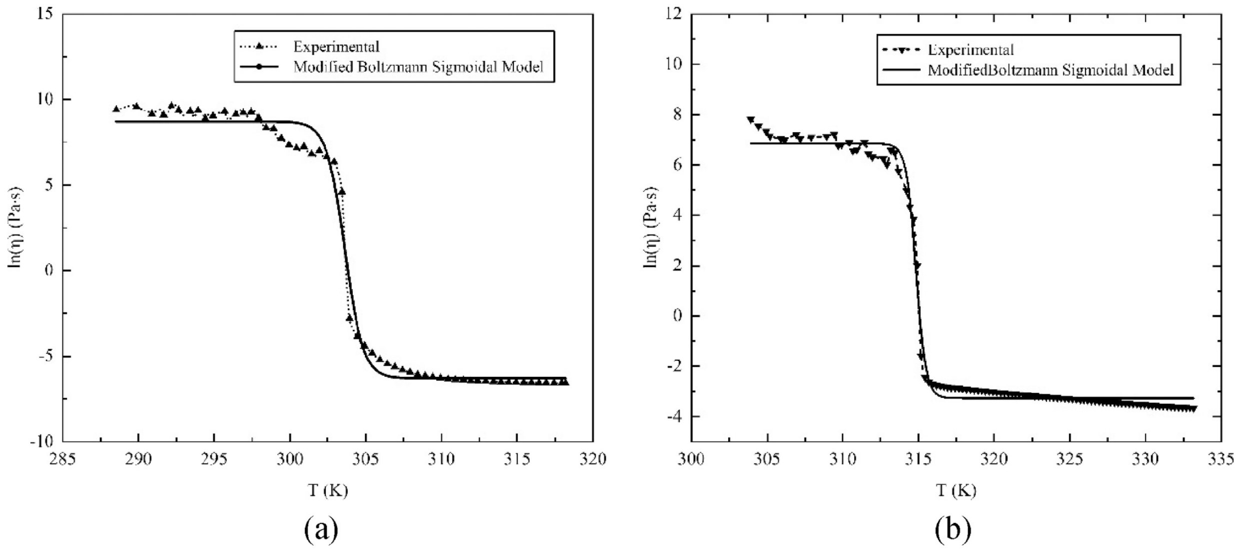

Figure 11. Modified Boltzmann sigmoidal model fitting for the (a) 15% model oil sample and (b) real crude oil sample.

Therefore, the high viscosity exhibited by waxy gel below the gelation temperature starts to change to low viscosity on phase transition. The increase in temperature above the degelation temperature results in development of fluid-like properties. Formulating a constitutive relation for the sol−gel transition is particularly useful for examining the flow restart behavior of the preheated gel pipeline. A modified sigmoidal curve generally represents the exponential growth curve across the critical sol−gel transition point. Thus, the proposed model accounts for the temperature-dependent viscosity changes in terms of a modified Boltzmann sigmoidal function. The low value of the imposed shear stress while heating the gel allows us to neglect the contribution of gel degradation due to shear rejuvenation while performing mathematical modeling of the sol−gel transition. Later, the mathematical modeling of temperature-dependent changes in viscosity is interlinked with the shear-strain-induced gel degradation rheological model.[54]

Navarro-Verdugo et al.[55] proposed the modified Boltzmann sigmoidal function in eq 1 to represent the phase transition phenomena, having details of the geometric location of the inflection point. However, the model is proposed to account for the volume changes at the phase transition. Here, the model is fitted to the exponential reduction in viscosity near the phase transition with temperature.

$$Y = A_2 + \frac{A_1 - A_2}{1 + \exp\left[\frac{\theta - \theta_o}{\varphi}\right]} \tag{1}$$

Here, Y is the instantaneous value of a temperature-dependent variable. A_1 and A_2 are the equilibrium values before and after the phase transition zone, respectively. θ and θ_o are the instantaneous and transition or degelation point temperatures, respectively. φ is the fitting parameter termed as "temperature constant". The experimental results of temperature-dependent viscosity changes obtained from the imposed shear stress method were utilized to fit into eq 3. The comparison of experimental data with the rheological model is presented in Figure 11a,b for both the model and real crude oils. In this section, in order to fit the equation with experimental data, all of the temperature parameters are considered in the kelvin scale.

$$\ln(\mu) = \ln(\mu_{\mathrm{eql}}) + \frac{\ln(\mu_{\mathrm{gel}}) - \ln(\mu_{\mathrm{eql}})}{1 + \exp\left[\frac{\theta - \theta_o}{\varphi}\right]} \tag{2}$$

Here, $Y = \ln(\mu)$, $A_1 = \ln(\mu_{\mathrm{gel}})$, $A_2 = \ln(\mu_{\mathrm{eql}})$, and μ_{gel} and μ_{eql} are equilibrium viscosity values before and after the phase transition zone, respectively.

$$\mu = \mu_s \exp\left[\frac{\ln(\mu_{\mathrm{gel}}) - \ln(\mu_{\mathrm{eql}})}{1 + \exp\left[\frac{\theta - \theta_o}{\varphi}\right]}\right] \tag{3}$$

The best-fitted curve parameters for the sol−gel transition model are obtained and mentioned in Table 2 for both model and the real crude oil samples. The degelation temperature (θ_o) of the model oil obtained from curve fitting is 303.68 K, which closely matches the experimental values of the degelation temperature, i.e., 303.85 K. Table 3 depicts the comparison of the degelation temperatures obtained with the experimental and Boltzmann models for the real crude oil and 15% model oil.

Table 2. Parameter Obtained Boltzmann Model Fitting of Experimental Results for the 15% Model Oil and Real Crude Oil Samples

properties	15% model oil	real crude oil
$\ln(\mu_{\mathrm{gel}})$	8.7089	6.84
$\ln(\mu_{\mathrm{eql}})$	−6.2914	−3.27
θ_o	303.7 K	314.8 K
φ	0.6048	0.33

Numerical simulation of the preheated gelled pipeline, with different periods of heating time, was performed. The viscosity

Table 3. Comparison of the Degelation Temperatures Obtained with the Experimental and Boltzmann Models

sample	experimental	Boltzmann model
15% model oil	303.8 K	303.7 K
real crude oil	315.1 K	314.8 K

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changes following the sol−gel transition rheological model were considered for numerical simulation. The numerical simulation comprised two stages; first, the gelled pipeline at 277 K was preheated by submitting it to a constant wall temperature of 313 K. Preheating the pipeline for a short period resulted in changes in the viscosity of the gelled fluid depending on the temperature distribution in the pipeline. Such a temperature distribution at the end of different heating periods was used as the initial condition in the second stage of the flow restart simulation. A conduction-based mathematical model (Fourier's law) governed the short period of heating of the high-viscosity gelled pipeline, expressed for 2-D axisymmetric cylindrical geometry in eq 4.

$$\frac{\partial\theta}{\partial t} - \frac{1}{r}\frac{\partial}{\partial r}\left(r\alpha\frac{\partial\theta}{\partial r}\right) - \frac{\partial}{\partial z}\left(\alpha\frac{\partial\theta}{\partial z}\right) = 0 \tag{4}$$

The initial temperature condition of the gelled fluid at rest is $\theta = \theta_i = 277$ K at time $t = 0$. A constant temperature of $\theta = \theta_w = 313$ K was applied along the pipe wall. The non-dimensionalization of the above equation (i.e., eq 4) with the non-dimensional number $\overline{\theta} = \frac{\theta - \theta_i}{\theta_w - \theta_i}$, $\overline{t} = \frac{t\alpha}{L^2}$, $\overline{z} = \frac{z}{L}$, $\overline{r} = \frac{r}{R}$, and $\epsilon = \frac{R}{L}$ leads to the following equation:

$$\frac{\partial\overline{\theta}}{\partial\overline{t}} - \frac{1}{\overline{r}}\frac{\partial}{\partial\overline{r}}\left(\overline{r}\frac{\partial\overline{\theta}}{\partial\overline{r}}\right) - \frac{\partial}{\partial\overline{z}}\left(\frac{\partial\overline{\theta}}{\partial\overline{z}}\right) = 0 \tag{5}$$

where R and L are the pipeline radius and length, respectively. The thermal diffusivity is defined in terms of thermal conductivity (k), fluid density (ρ_i), and specific heat capacity (c_p) as $\alpha = \frac{k}{\rho_i c_p}$ in m^2/s. Furthermore, three different temperature distribution profiles obtained at different times ($\overline{t} = 1.3 \times 10^{-7}$, 2.4×10^{-7}, and 5.4×10^{-7}) were chosen to initialize the flow restart simulation. The selected temperature distribution profile was based on the temperature or viscosity conditions at the exterior radial location of the gelled oil (i.e., preheated gelled oil temperature at $\overline{r} = 1.0$ before approaching the degelation temperature (i.e., $\overline{\theta} = 0.52$), just after it approaches the degelation temperature (i.e., $\overline{\theta} = 0.64$) and higher than the degelation temperature (i.e., $\overline{\theta} = 0.76$)) in the pipeline (Figure 12). The flow restart mathematical model of weakly compressible fluid is governed by a conservative governing equation given below:

Continuity equation:

$$\frac{\partial\rho_i}{\partial t} + \nabla\cdot(\rho_i \boldsymbol{U}) = 0 \tag{6}$$

Momentum equation:

$$\rho_i\frac{D\boldsymbol{U}}{Dt} = \rho_i\boldsymbol{g} - \nabla p + \nabla\cdot\boldsymbol{\tau} \tag{7}$$

Energy equation:

$$\rho_i c_p\frac{D\theta}{Dt} = \nabla\cdot(k\nabla\theta) + \boldsymbol{\tau}:\boldsymbol{d} \tag{8}$$

The axial and radial velocities are scaled by the velocity scale W_s and ϵW_s. The time $t = \hat{t}\left(\frac{L\sqrt{\chi_\theta P}}{W_s}\right)$ is scaled in terms of gel compressibility and pressure to capture pressure propagation in gelled oil. The details of the scaling and numerical simulation scheme in a preheated gelled pipeline are discussed in the work of Kumar et al.[13] and Sanyal et al.[41] In addition, the sol−gel transition-based rheological model is combined with the shear-strain-based gel degradation model utilized in the literature.[13,41]

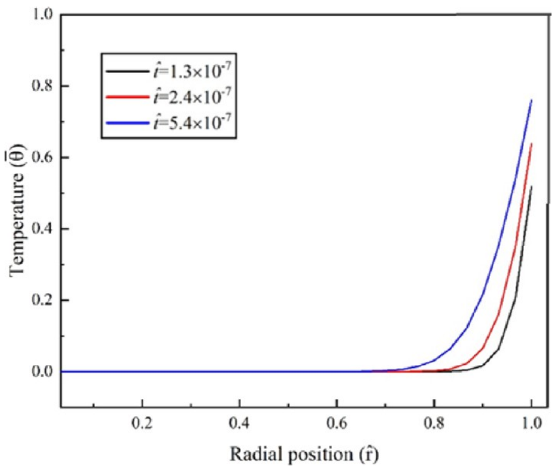

Figure 12. Radial temperature distribution for the gelled oil at an axial position $\overline{z} = 0.5$ for different durations of preheating.

$$\mu(\gamma) = \mu_s\left[1 + f\cdot\left\{\frac{1 - \exp(-m\gamma)}{\gamma}\right\}\right] \tag{9}$$

Combining the sol−gel transition-based rheological model in eq 3 with the shear-strain-based gel degradation model in eq 9 utilized in the literature,[13,41] we get

$$\mu = \mu_s\left[1 + f\cdot\exp\left(\frac{\ln(\mu_{\text{gel}}) - \ln(\mu_{\text{eql}})}{1 + \exp\left[\frac{\theta - \theta_o}{\varphi}\right]}\right)\left\{\frac{1 - \exp(-m\gamma)}{\gamma}\right\}\right] \tag{10}$$

In eq 10, μ_s is the slurry-state viscosity, f is a constant, m is the shear-induced degradation constant, and γ is the shear strain. It is important to note that the gel degradation parameter (m) is considered to have a very low value ($m = 10$) to emphasize the effect of preheating-based viscosity changes on restart simulation. Based on the above mathematical model, the numerical simulation of flow restart operation in a pipeline filled with gelled model oil for three different temperature profiles, as shown in Figure 12, is performed. The numerical simulation is performed in a pipeline with a radius $R = 0.1$ m and a length $L = 10$ m. The gelled oil density is a function of temperature and pressure and has a value of $\rho_i = 900$ kg/m^3 at 277 K. The viscosity of gelled oil at high shear rates is taken to be $\mu_s = 0.5$ Pa · s. In addition, the relative viscosity $\mu_r = 2000$ defines the ratio of pristine gel viscosity at the minimum temperature to the slurry-state viscosity at a high shear rate. Preheating causes radial variation in temperature and viscosity. The extended preheating period results in a lower oil viscosity near the pipe wall, allowing the gel plug to experience a lower shear resistance. Three flow restart numerical simulations have been performed based on the temperature distribution profiles shown in Figure 12. The variation of axial velocity in the radial direction for the three cases is compared in Figure 13. This comparison demonstrates the effect of the extent of preheating on the axial velocity profiles. At time $\hat{t} = 7.5$, a considerable variation in the axial velocity profile is evident near the pipe wall. The axial velocity profile shows a radial variation similar

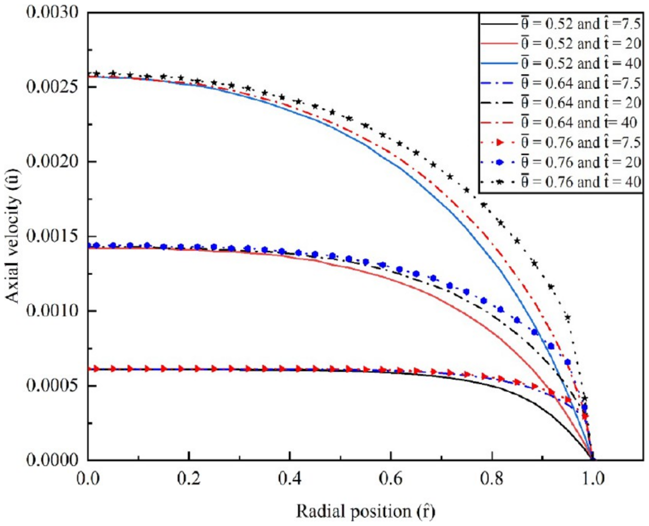

Figure 13. Comparison of axial velocities in the radial direction of the gelled pipeline ($\hat{z}$ = 0.2) that have been preheated differentially and subjected to the same restart pressure for the gelled oil having compressibility χ_θ = 10^{-9} Pa^{-1}, relative viscosity μ_r = 2000, steady-state Reynolds number Re_s = 360, and P = 4000 Pa, at time instants $\hat{t}$ = 7.5, $\hat{t}$ = 20, and $\hat{t}$ = 40.

to the shear banding effect causing plug-like flow in the pipeline. This is observed due to large variations in the viscosity of the gel near the wall and far away from the wall. The difference is predominantly due to a significant variation in viscosity across the degelation point. Interestingly, preheating the gel oil above the degelation temperature does not show a difference in the velocity profile, emphasizing that heating the oil to the degelation temperature optimizes the heating energy requirement. The extended period of heating results in the diffusion of heat radially inward, resulting in a difference in the velocity profile at a long period of flow restart. Such extended heating periods of $\overline{\theta}$ = 0.76 and $\hat{t}$ = 40 only increase the axial velocity profile and improves the intensity of the restarted flow.[42]

3.5. Degelation Behavior of Real Crude Oil Using the Small Imposed Shear Stress Method.

A series of experiments is performed to measure the degelation temperature of real crude oil samples using the imposed shear stress method. The sample preparation and measurement protocol details are discussed in the Experimental Section. Figure 14 depicts the temperature dependency of the shear rate for three repeated runs. A similar observation of an abrupt increase in the shear rate (analogues to model waxy oil) due to solid—liquid transition is also observed in the case of a real crude oil sample. The experiments to measure the degelation temperature are repeated thrice. Despite the presence of polar components in the crude oil, the result shown in Figure 14 has good repeatability.

Figure 15 shows the variation of viscosity and shear strain as a function of temperature. The waxy oil degelation process is composed of three regions. In the first region, the temperature ranges from 25 to ∼40 °C. In this region, the viscosity of the gel sample is very high, and it decreases gradually with increasing temperature (shown in Figure 15). In addition, an increase in the magnitude of the shear strain rate is observed with increases in temperature. This demonstrates that the waxy gel network (a three-dimensional volume-spanning gel network) becomes weak at high temperatures. Strong interfacial interactions exist between the wax crystals at lower temperatures, resulting in a network-like structure (gel) that entraps the wax molecules and reduces their mobility. Furthermore, the lower kinetic energy of wax molecules may lead to the entrapment of molecules into the wax crystals, especially when the attractive energy between wax molecules and neighboring crystals (e.g., van der Waals attraction) is higher than the kinetic energy of wax molecules. In the second region, a further increase in temperature results in an increase in the kinetic energy of wax molecules, which may overcome the intermolecular attraction, and the wax molecules gradually dissociate from wax crystals due to a temperature rise (increase in kinetic energy) and diffuse to the bulk of the solution. A sudden drop in viscosity is observed as the dissociation of wax molecules causes the disentanglement of wax crystals in the crystal network. Moreover, an abrupt rise in the shear strain is also observed at the same temperature. The corresponding temperature is referred to as the degelation temperature of the crude oil sample. This can also be considered the thermal yielding of material where a sudden increase in the shear rate

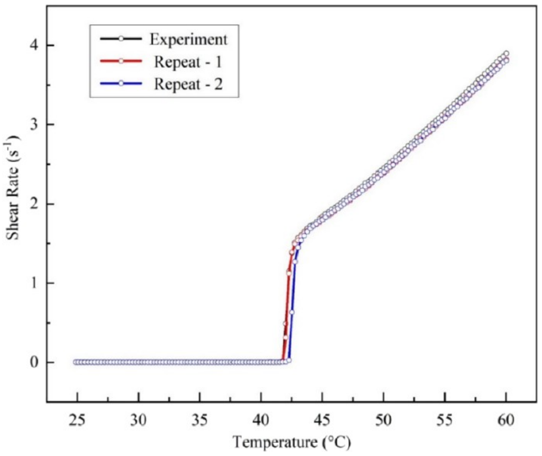

Figure 14. Repeatability of the degelation temperature measurement of a real crude oil sample using the imposed shear stress method while the gelled sample is heated from 25 to 60 °C under an imposed shear stress of 0.1 Pa at a heating rate of 1 °C/min.

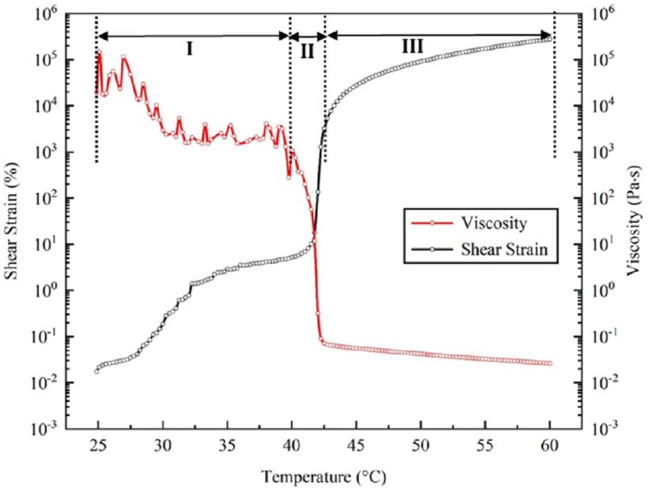

Figure 15. Variation of the viscosity and shear strain of the real crude oil sample with temperature while the sample is heated from 25 to 60 °C under an imposed shear stress of 0.1 Pa at a heating rate of 1 °C/min.

and a concomitant decrease in the viscosity are observed due to the solid−liquid transition of the crude oil sample. Once the complete gel network is destroyed (above 50 °C), an Arrhenius decrement in viscosity is observed, i.e., the third region.

3.6. Effect of Different Parameters on the Degelation Behavior of Waxy Oil.

In this section, the effect of various parameters like initial cooling temperature, aging period, and thermal treatment on the degelation behavior of waxy oil is investigated using the imposed shear stress method.

3.6.1. Effect of the Initial Cooling Temperature. The effect of four different initial temperatures, ranging from 40 to 70 °C, on the degelation temperature of real crude oil is experimentally investigated using the imposed shear stress protocol discussed in Section 2.3. Figure 16 presents the variation of shear rate with temperature for various initial cooling temperatures. A higher degelation temperature was reported for the sample having a higher initial temperature before cooling. This may be due to the fact that wax crystallization is a diffusion control process, as explained earlier. Hence, cooling from a higher temperature allows additional time for the diffusion and precipitation of wax molecules and the formation of stronger bonds with longer wax crystals.

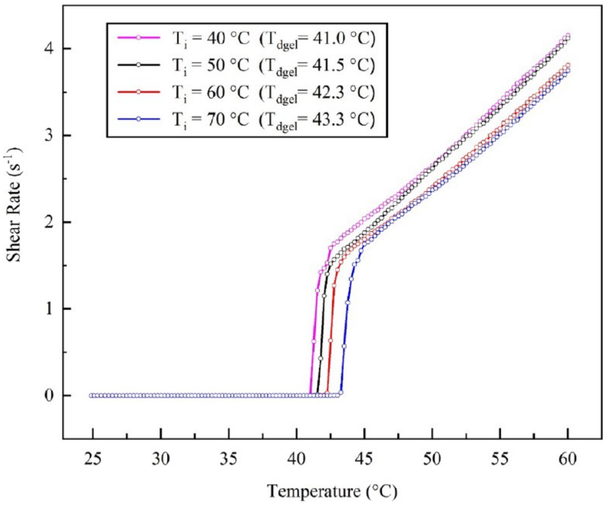

Figure 16. Effect of initial cooling temperatures on the measurement of the degelation temperature of the crude oil sample. Four different initial cooling temperatures are considered in the range of 40 to 70 °C while the sample was heated from 25 to 60 °C at a rate of 1 °C/min.

Furthermore, the microscopic images of precipitated wax molecules obtained for different initial cooling temperatures are presented in Figure 17. The dark brown color represents the precipitated wax crystals within which a light brown-colored liquid oil is entrapped. One may observe a formation of larger wax crystals with a lower crystal number density while cooling from a higher initial temperature, i.e., T_i = 70 °C in Figure 17a, whereas cooling from a lower initial cooling temperature, i.e., T_i = 40 °C, results in formation of smaller wax crystals with a larger number density, as shown in Figure 17b. Compared to smaller-sized wax crystals, larger-sized wax crystals result in the formation of stronger gel networks. Therefore, cooling the gelled oil from a higher initial temperature results in the formation of a stronger gel network as larger wax crystals are available for network formation. In the case of a stronger gel, a higher extent of heating is needed to dissolve it into viscous liquid form. As a result, a sample cooled from a higher initial temperature has a higher degelation temperature than a sample cooled from a lower initial temperature.

3.6.2. Effect of Aging. The effect of three different aging periods, ranging from 0 to 30 min, on the degelation temperature of real crude oil is experimentally examined using the imposed shear stress protocol discussed in Section 2.3. Figure 18 illustrates the increment of the degelation temperature with the aging period. A longer aging period allows wax molecules to diffuse to the existing crystals and precipitate, allowing wax crystals to grow. It results in the formation of an interconnected strong gel network. However, a shorter aging period hinders the growth of wax crystals due to insufficient time to attain a liquid−solid equilibrium. In the case of the aging of the gel for a shorter period, wax molecules located far from the wax crystals are unable to reach the already crystallized wax by diffusion. Hence, a weak gel network forms in a shorter aging period case. In the case of

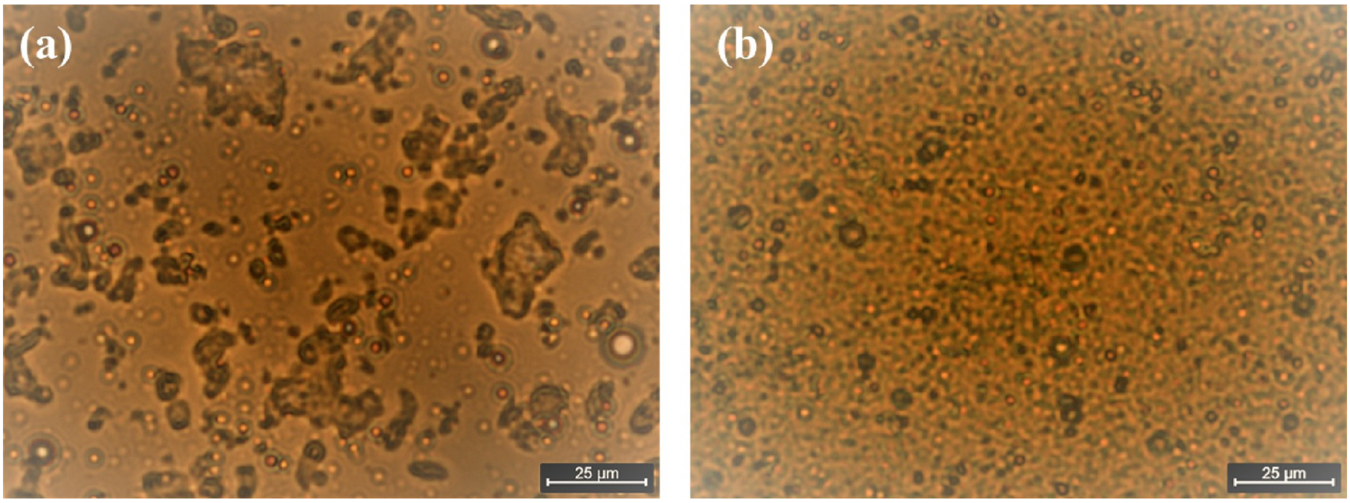

Figure 17. Microscopic images of the real crude oil sample at 25 °C while cooling the sample from different initial temperatures: (a) T_i = 70 °C and (b) T_i = 40 °C.

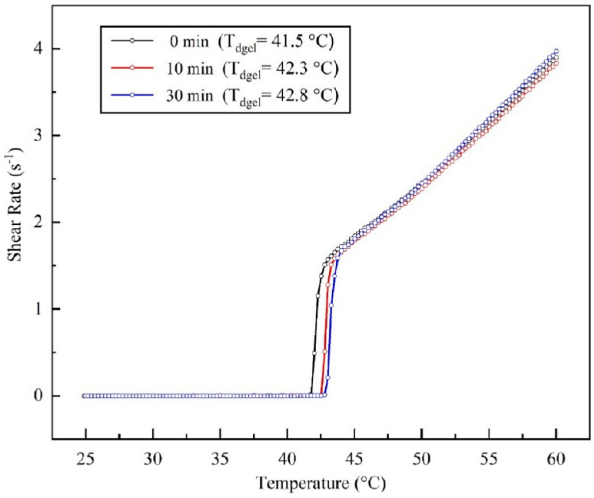

Figure 18. Effect of different aging periods ranging from 0 to 30 min on the degelation temperature of real crude oil. The gelled oil samples are heated from 25 to 60 °C at a 1 °C/min rate.

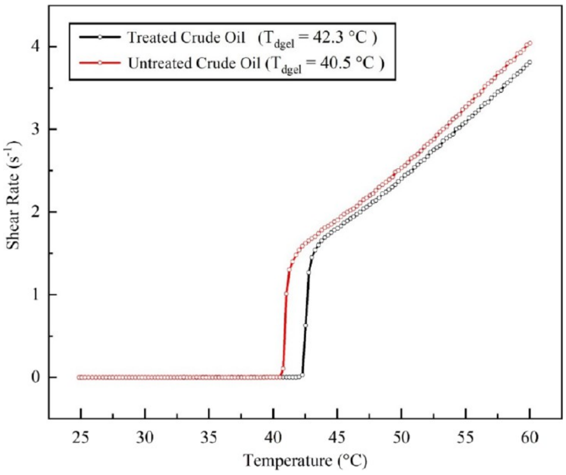

Figure 19. Effect of pretreatment on the degelation temperature of the crude oil samples. Both treated and untreated oil samples are heated from 25 to 60 °C under an imposed shear stress of 0.1 Pa at a heating rate of 1 °C/min.

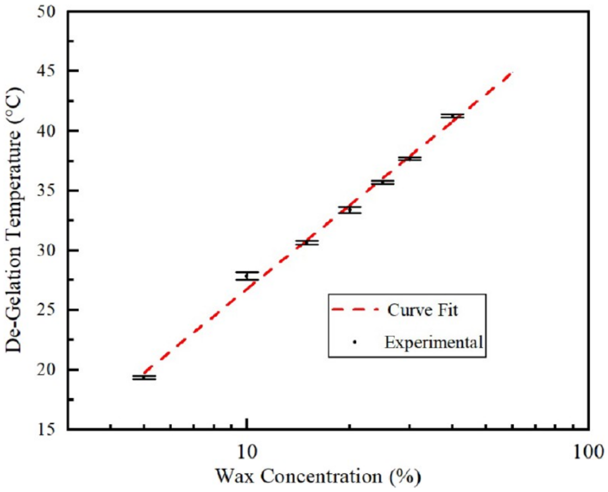

Figure 20. Dependence of the degelation temperature as a function of wax concentration ranging from 5 to 40%.

weak gel, a lower degree of heating is required to disentangle and dissolve the wax crystals into the bulk of the solvent. The low-viscosity liquid stage is attained once wax crystals are dissolved in the solvent. Therefore, the degelation of weak gel is observed during heating at a lower temperature instead of a strong gel. At equilibrium, there is a dynamic exchange of wax molecules from wax crystals to the bulk of the oil and from the bulk of the oil to wax crystals, without any net exchange of wax molecules. Hence, increasing the aging period beyond a limit when equilibrium is achieved will not affect the degelation temperature.

3.6.3. Effect of Thermal Treatment. The experimental investigation is conducted to study the effect of preheating on the degelation characteristics of real crude oil. The experimental protocol for measuring degelation temperature is similar to the protocol discussed in Section 2.3. The thermal pretreatment of the crude oil sample is carried out to improve composition stability, resulting in a more repeatable result. The experiments illustrated in the earlier section for the degelation temperature measurement are performed using the pretreated waxy oil sample. Figure 19 depicts the degelation temperature measurement for treated and untreated crude samples. An increase in the degelation temperature is observed for the samples that have undergone the thermal pretreatment process. The light paraffin evaporates due to the thermal pretreatment of the real crude oil sample. Therefore, a stronger gel network forms in the case of the pretreated sample. A higher degree of heating is needed for a stronger gel network to disentangle and dissolve than that for a weak gel network. Hence, a higher degelation temperature is observed with a strong gel network. Therefore, a pretreated sample has a higher degelation temperature compared to an untreated sample.

3.6.4. Effect of Wax Content. A set of experiments is performed to investigate the effect of seven different wax contents on the degelation temperature of model oil. The measurements are performed using the imposed shear stress protocol discussed in Section 2.3. Figure 20 elucidates the variation of the degelation temperature with wax concentration. The results reveal that the degelation temperature of the model oil samples increases with an increase in the wax content. A higher wax content results in more wax precipitation due to the local availability of wax molecules for crystallization, and a stronger interconnecting bond between the crystals will form. Consequently, it creates a stronger interconnected gel network at a higher wax content compared to the low wax content cases. Thus, a higher amount of kinetic energy is required for the wax molecules to diffuse in the bulk of liquid in the case of a stronger gel. Hence, a stronger gel network requires more heat to disintegrate the interlinked wax crystal network than a weak gel network. Therefore, to completely dissolve the wax crystal network in the waxy oil, high-wax-concentration samples are required to be heated at a higher temperature than low-wax-concentration samples. Our study reports the degelation temperature (∼34 °C) at a wax concentration of 20% and the degelation temperature (∼27 °C) at a wax concentration of 10%.

Figure 20 illustrates the degelation temperature increases in a logarithmic pattern with a wax concentration and is represented by eq 11.

$$T_{\mathrm{dgel}} = 10.133 \ln(X) + 3.4369 \tag{11}$$

T_{dgel} is the degelation temperature of the corresponding model oil formed with a wax content X. Figure 20 represents the best fit with an R^2 value of 0.9942 as a red dashed line.

3.7. Thermal Fluidity of Waxy Oil.

3.7. Thermal Fluidity of Waxy Oil. Thermal fluidity ($d\dot{\gamma}/dT$) is the rate of change of shear rate with temperature, describing temperature-dependent changes in the rate of shear deformation or structural degradation. It has been elucidated from Figure 21 that thermal fluidity is the highest near the degelation temperature. A further increase in temperature above the degelation temperature causes the thermal fluidity value to drop to a low and constant value, indicating that the maximum rate of gel degradation occurs near the degelation temperature.

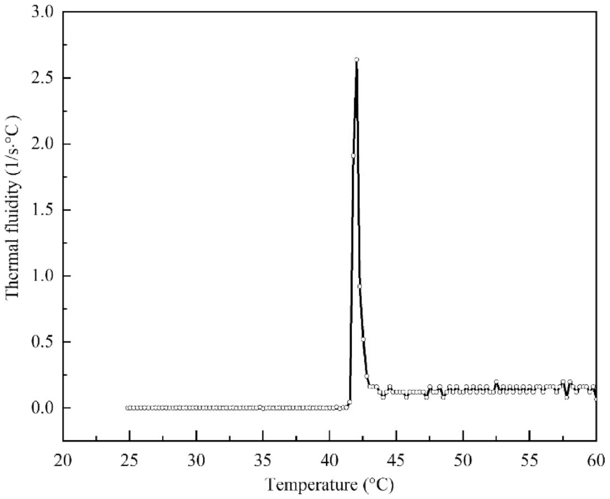

Figure 21. The variation in the thermal fluidity of waxy crude oil during the degelation process indicates the maximum gel degradation in the region of the degelation temperature while the sample was heated from 25 to 60 °C under an imposed shear stress of 0.1 Pa at a heating rate of 1 °C/min.

3.8. Calculation of the Time Saving in Flow Restart Operations. The time (t) required to raise the temperature of a unit mass (m_g) of crude oil from 25 °C, which is below the gelation temperature, to complete wax dissolution, i.e., WDT, at a heating rate ($\dot{T}_h$) of 1 °C/min is

$$t = \frac{(T_{wdt} - T_i)}{\dot{T}_h} = \frac{(56 - 25)}{1} = 31 \text{ min} \tag{12}$$

Similarly, the time (t) required to raise the temperature of a unit mass (m) of crude oil from 25 °C i.e., gelled state, to the degelation temperature, which is the minimum flow temperature, at a heating rate ($\dot{T}_h$) of 1 °C/min is given by

$$t = \frac{(T_{dg} - \text{T}_i)}{\dot{T}_h} = \frac{(42.5 - 25)}{1} = 17.5 \text{ min} \tag{13}$$

where T_{wdt}, T_{dg}, and T_i are the wax disappearance, degelation, and initial cooling temperatures, respectively.

Heating the crude oil near the degelation temperature can significantly reduce both time and energy requirements. The result demonstrates that approximately 43% of the time is reduced by just heating the gel up to the degelation temperature instead of heating the gel up to WDT during storage and transportation application. The finding shows that heating only to the degelation temperature is a more efficient and economical way of ensuring flow during crude oil storage, transportation, and flow restart operation. The equilibrium viscosity values of crude oil at the degelation temperature were found to be higher compared to the magnitude of viscosity at WDT. This observation is obvious because more precipitated wax crystals still exist at the bulk of crude oil near the degelation during heating. This may lead to a reduction in the flow rate. The rheometric result also shows that the steady-state shear rate at the degelation temperature of the real crude oil sample is found to be 1.16 s^{-1}, almost 31% of the shear rate magnitude at WDT. The finding of the rheometric study can conclude that at the degelation temperature, flow can be restarted in the actual field pipeline with a decreased discharged/flow rate compared to the flow at WDT. The above calculations give a basic understanding of the time saving during flow restart operations.

4. CONCLUSIONS

In the present work, the degelation characteristics of the model oil and real crude oil are experimentally analyzed using rheometry, DSC, and microscopy techniques. The degelation temperature is referred to as the minimum temperature during heating, at which the waxy gelled oil viscosity drops significantly. A reduction of viscosity is observed due to the dissolution of part of the wax crystal network, resulting in the crystal network being unable to retain the liquid oil. Understanding the sol−gel transition-based rheological characteristics of waxy gel plays a crucial role in a non-isothermal flow restart operation. The degelation temperature of waxy oil is experimentally measured using the imposed shear stress method. The degelation temperature is measured as an onset of a sudden increase in shear rate during the heating period. The results are repeatable and match with those of other methods. In addition, the effect of wax concentration, initial cooling temperature, heating rate, and aging period on the degelation temperature is also analyzed. The results exhibit an increase in the degelation temperature with the aging period, wax concentration, heating rate, and initial cooling temperature. The degelation temperature of various wax concentrations is found to be higher than the corresponding gelation temperature. The difference between gelation and degelation temperatures shows the complex thermal hysteresis effects that arise from the varying wax content available at a given temperature during the cooling and heating process. The supercooling effect is the primary cause of this disparity, as there is no requirement to surpass a critical nucleus during wax dissolution, unlike in the process of crystallization. The DSC analysis also indicates that the thermal hysteresis effect increases with an increase in the heating rate.

Furthermore, microscopic image analysis is carried out during the heating of the gelled oil to understand the mechanism of the complete degelation process. The microscopic observation shows the reduction of the wax crystal's size as well as the number density with an increase in temperature. The results also reveal that heating of the waxy gel results in the disappearance of the wax crystal aggregates due to the dissolution of wax molecules. At higher temperatures, the wax crystals are smaller compared to those at lower temperatures. The microscopic findings indicate that an increased temperature causes a change in morphology and network structure due to a decrease in the size and number density of the wax crystals.

Our results show a remarkable decrease in the viscosity near the degelation temperature, indicating that flow restarts at a temperature just higher than the degelation temperature can reduce the flow restart pressure requirement by several orders of magnitude. The numerical simulation of flow restart operation in a preheated gelled pipeline is performed to illustrate the influence of the degelation temperature on flow restart operation. The gels heated above and below the degelation temperatures show a significant variation in the axial velocity profiles. However, further heating above the degelation temperature does not affect the velocity profiles. A shear banding type of effect is observed in the velocity profile when preheating is done above the degelation temperature. The gel, preheated above the degelation temperature, has a significantly low viscosity (high fluidity), and the rest of the gel slips over the melted gel, causing a shear banding kind of effect. The existence of a shear band will help in cleaning the gelled pipeline. The variation in axial velocity profiles for different initial temperature conditions clearly elucidates the effect of the optimal heating temperature.

The measurements of the degelation temperature will assist in the optimal deployment of equipment during maintenance. Our result also demonstrates that both time and energy can be reduced by heating the gel to the degelation temperature during storage and transportation. Overall, this study will provide practical insights into reducing the economic losses in the heating process during storage and flow restart operations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c01963.

> Detailed measurement of the degelation behavior with different methods; effects of geometries, gaps, and other factors on the delegation temperature; a schematic representation of the degelation process (PDF)

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Notes

The authors declare no competing financial interest.

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■ NOMENCLATURE

Roman Symbols

C_p - specific heat capacity (kJ/kg·°C); k - thermal conductivity (W/m K); L - length of the pipeline (m); m - degradation rate constant; m_g - mass (kg); P - applied pressure difference (Pa); R - radius of the pipeline (m); Re_s - scaled Reynolds number; r - radial direction (m); T_i - starting cooling temperature (°C); T_{gel} - gelation temperature (°C); T_{dgel} - degelation temperature (°C); T_{wat} - wax appearance temperature (°C); T_{wdt} - wax disappearance temperature or wax dissolution temperature (°C); t - time (s); X - wax concentration (%); z - axial direction (m)

Greek Symbols

γ - shear strain; $\dot{\gamma}$ - shear rate (s^{-1}); θ_o - degelation temperature (K); θ_i - initial gel temperature (K); θ_w - pipeline wall temperature (K); ρ_i - gelled oil density (kg/m^3); α - thermal diffusivity (m^2/s); φ - temperature constant (K); τ - shear stress (Pa); μ - apparent viscosity (Pa·s); μ_s - slurry-state viscosity (Pa·s); μ_r - relative viscosity; μ_{gel} - equilibrium values of the viscosity before the phase transition zone (Pa·s); μ_{eql} - equilibrium values of the viscosity after the phase transition zone (Pa·s); χ_θ - gel compressibility (Pa^{-1})

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