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Liquid-Solid Equilibrium-Based Detection of Wax Precipitation in Hydrocarbon System Using the Wilson-SRK Coupled Model

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Abstract

Wax precipitation is one flow assurance problem in production from the oil and gas system. Its problems cause many production problems in reservoirs, near wellbores, production tubing, surface flow lines, and surface facilities that lead to more frequent shutdowns, operational problems, and high costs for cleaning. This study aims to proactively predict the temperature at which wax may precipitate and forecast the wax deposition envelope (WDE) and the probability that it will occur; this study attempts to build a thermodynamic model that provides an accurate indication of the temperature at which wax precipitation occurs. The study focuses on temperature because wax crystals depend significantly on temperature change rather than other factors. Solid-liquid equilibrium (Coutenho Framework) which are couple between SRK-EOS and Wilson equation, has been used to simulate the wax phase envelope and wax appearance temperature. which are coupled between SRK-EOS and Wilson equation. In this study, wax moves from a liquid to a solid state when it reaches 138.5°C, which represents the wax appearance temperature (WAT) at which the solid phase begins to develop. Continued temperature decrease below this threshold results in wax release as solid crystals and accompanying production issues. Testing the well's operating conditions on the phase diagram revealed a significant probability of wax production, especially at the wellhead and surface equipment. The primary conclusion is that the couple model may be utilized to predict wax with acceptable precision, which improves with the availability of accurate laboratory data.

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1. Introduction:

Wax deposition is a severe flow assurance concern that blocks the flow of crude oil through pipes that are clear in Figure .1, causes anomalous pressure, and, in extreme instances, may result in reduced production or facility shutdown [1]. Additionally, as solid wax precipitates, it causes formation damage close to the wellbore, decreased permeability, as well as variations in fluid characteristics including higher viscosity and gelation owing to phase separation. [2].

Figure 1: Wax Deposition in pipelines.

Crude oil's complicated structure causes wax to spontaneously develop in petroleum. Hydrocarbons, which can comprise a variety of substances including paraffin, naphthene, and aromatics, make up crude oil. Certain components of crude oil may solidify and separate from the liquid phase throughout production, transportation, and refining operations due to cooling and pressure changes, resulting in the formation of waxy deposits [3]. The long-chain hydrocarbons which make up these waxy deposits are mostly paraffinic in origin and have a tendency to harden at lower temperatures. The origin of the oil, its chemical constitution, and the processing environment can all affect the specific composition and properties of the wax produced from petroleum [3].

The characteristics of crude oil wax include composition, melting point, solubility, viscosity, density, molecular weight, and WAT (wax appearance temperature). The temperature at which the first wax crystals begin to form is known as the Wax Appearance Temperature (WAT). Wax molecules crystallize as a result of the saturation of long- chains of hydrocarbons, which mainly paraffin, in crude oil. Numerous methods, including optical microscopy, near-infrared scattering, rheology, visual PVT cell with a laser light transmitted solid detection system, and Differential Scanning Calorimetry (DSC), may be used to accurately measure the WAT. There are a number of commercial and non-commercial models that use different elements, such as WAT and wax precipitation curves (WPC), to predict the wax deposition possibility of crude oil, which is crucial for flow assurance management [4].

To predict the wax disappearance temperature (WDT), several models have been proposed by various researchers such as (J. Wen et al. 2025 , M. Milhet et al. 2005). severial of these models based on equation of state such as (SRK, PR, CPA, and PC-SAFT) [5, 6]. SRK EOS has been effectively used in a number of research to predict wax precipitation in conjunction with solid-phase models. For instance, earlier studies described the vapor and liquid phases using modified SRK EOS, while the solid wax phase was represented using models like UNIQUAC, which produced good agreement with experimental results. Additionally, because SRK EOS strikes a compromise between acceptable accuracy and computational efficiency, it has been frequently used to simulate complicated hydrocarbon systems and flow assurance problems, such as wax and asphaltene precipitation. W. Chen et al. (2007)

have suggested a novel thermodynamic model for forecasting crude oil phase equilibrium. The modified SRK EOS and UNIQUAC equations are utilized to characterize the vapor, liquid, and wax phases, respectively. Significant correlations have been developed for calculating the volume parameter, called c, in SRK-EOS and the heat of vaporization in the UNIQUAC equation or Wilson equation. The suggested improved model predicts wax precipitation in petroleum fluids for three different crude oil systems. The calculated findings were compared to experimental data and those obtained using standard solution models [7].

Chemical, mechanical, thermal, or a mix of these remediation techniques can minimize or eliminate wax deposition in crude oil production lines [8]. A wax gel layer rises quickly in thickness and obstructs the flow of oil because of the flow restriction if preventative steps for wax deposition are unsuccessful [9]. As the petroleum sector continues to extend deep water operations to higher depths and distance in cold settings, which presents a substantial challenge to the sector, those mitigating techniques become more and more important [10]. In order to save operational costs, it is crucial to be able to forecast the quantity and conditions of wax precipitation [11].

Thermodynamic models are developed and used for the purpose of proactively predicting the temperature at which wax may precipitate. In order to forecast the wax deposition envelope (WDE) and the probability that it will occur, this study attempts to build a thermodynamic model. This model provides an accurate indication of the temperature at which wax precipitation occurs.

2. Theory

2.1. Phase Behavior of Wax

Under typical reservoir conditions, paraffin waxes remain soluble components of crude oil in a state of equilibrium thermodynamically (**Figure. 2**). Paraffin can crystallize or precipitate when its thermodynamic equilibrium is upset by variables like pressure, temperature, or other changes. Additionally, paraffin may precipitate due to the loss of volatile light endings, which function as solvents in nature. Each component of the wax becomes less soluble as the fluid cools until the components with greater molecular weights harden. The cloud point, also known as the wax appearance temperature (WAT), is the temperature at which wax crystallization begins **[12]**.

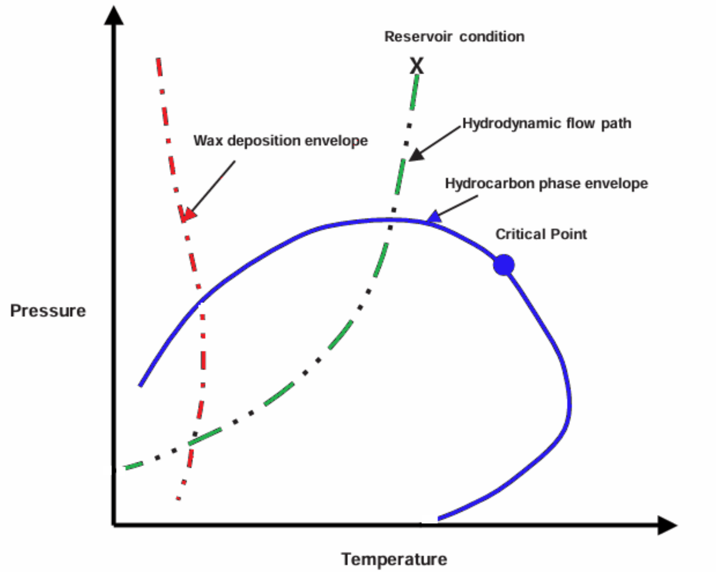

Figure 2: Phase Behavior of Wax.

2.2. Thermodynamic Modeling

The Coutinho framework created the wax precipitation model in Multiflash software, which combines the Soave-Redlich-Kwong equation of state (SRK-EOS), which simulates the behavior of the liquid and vapor phases, with the activity coefficient models by the Wilson equation or UNIQUAC model, which simulates the solubility behavior of the wax solid phase. The liquid-vapor-solid Coutinho framework accurately predicts wax behavior, including wax appearance temperature (WAT) and wax precipitation at various temperatures.

2.2.1. Soave-Redlich-Kwong Equation of State (SRK)

One popular thermodynamic model for determining the characteristics of fluids, especially gases and liquids, is the Soave-Redlich-Kwong equation of state. Based on changes to the original Redlich-Kwong (RK) equation put out by O. Redlich and J. N. S. Kwong in 1949, it was created by R. C. Reid, J. M. Prausnitz, and B. E. Poling in 1971 [13].

In order to properly account for molecular interactions with non-ideal behaviour, especially in systems with moderate to high pressures, the SRK equation contains adjustments to the RK equation [14]. The formula is written as follows:

$$p = \frac{RT}{v-b} - \frac{a}{v(v+b)} \qquad \ldots\ldots\ldots (1)$$

Where a and b are the EOS model parameters. The pure component parameters (a and b) can be calculated by:

$$a = \Omega_a \frac{R^2 T_c^2}{p_c} \alpha(T) \qquad \ldots\ldots\ldots (2)$$

$$b = \Omega_b \frac{RT_c}{p_c} \qquad \ldots\ldots\ldots (3)$$

$$\alpha(T) = \left[1 + m(\omega)\left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2 \qquad \ldots\ldots\ldots (4)$$

In equations 2, 3, and 4 the coefficients $\Omega_a = 0.42748$ and $\Omega_b = 0.08664$, and the value of $\alpha(T)$ can be calculated by:

$$m(\omega) = 0.480 + 1.574\omega - 0.176\omega^2 \ldots\ldots (5)$$

Where: P is the pressure, T is the temperature, V is the molar volume, R is the ideal gas constant, a and b are constants related to the molecular properties of the substance, the critical pressure (p_c), critical temperature (T_c), acentric factor (ω) and molecular weight (MW).

Solving these equations simultaneously for parameters a and b gives relationships identical. Which indicates that the SRK equation of state gives a universal critical gas compressibility factor, Zc , of 0.333, gives a co-volume value of 26% of the critical volume; that is ,

$$b = 0.26V \ \ldots\ldots (6)$$

Introducing the compressibility factor, Z, by replacing the molar volume, V, in the equation with (ZRT/P) and rearranging gives $P_cV_c = 1/3RT_c$

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \ \ldots\ldots (11)$$

With:

$$A = (\alpha\, a)\, p / (R\,T)^2 \ \ldots\ldots (12)$$

$$B = b\,p\,/\,R\,T \quad \text{.......} \; (13)$$

Where:
p = system pressure (psia) , T = system temperature (°R), and R = 10.730 (psia ft3/lb-mole °R).

2.2.2. Wilson Equation

The wax is approximated as a single solid solution using the Wilson model. This method is suggested for general engineering usage and flow assurance design since it is reasonably easy to implement and provides an accurate representation of the data **[15,16]**. The tendency of waxes to break into many distinct solid solution phases is modeled by the more intricate UNIQUAC variation **[17]**. In this study, the Wilson equation used is as follows:

$$\boldsymbol{Ln\,\gamma i = -Ln\left(1 - \textstyle\sum_j x_j A_{\frac{j}{i}}\right) + 1 - \textstyle\sum_j \left[x_j\left(1 - A_{\frac{j}{i}}\right) / \left(1 - \textstyle\sum_k x_k A_{\frac{k}{i}}\right)\right]} \quad \text{............} \; (14)$$

Where:
$\boldsymbol{x_j}$: Molar fraction,
$\boldsymbol{\gamma i}$: The activity coefficient**,**
T : Temperature, and
$\boldsymbol{A_{\frac{k}{i}}}$: Interaction energy.

2.2.3. Solid-Liquid Equilibrium Model Using Coutinho Framework

According to Coutinho's procedure, wax precipitation is viewed from a thermodynamic perspective as a liquid-solid equilibrium in which all other components of the oil are solvents and the n-paraffins are solutes. A non-ideal solid state of n-paraffins with different chain lengths is regarded as the wax phase. This model is represented by the following equation:

$$\boldsymbol{Ln\,Xi + Ln\gamma i} = \frac{\Delta H\,fus}{R}\left(\frac{1}{T} - \frac{1}{Tm}\right) \quad \text{...........} (15)$$

Where:

X_i : Mole fraction of component (i) in liquid (For Wax-Forming component, it represent the wax fraction for each N-Paraffin components).
γ_i : The activity coefficient of each component in solid phase.
ΔH_{fus} : Molar enthalpy change.
R : Universal gas constant.
T : system temperature.
T_m : Melting point for each component.

3. The Wax Precipitation Modelling Methodology

To ensure correct computation results, the wax model should be built using the following steps:

1. Collecting data, including experimental data on PVT parameters, compositional analysis of reservoir fluid, and basic information on the reservoir and well.

2. Input reservoir fluid composition (C_1 to C_n^+) and characteristics of the heavy component.

3. Identify the N-paraffin distribution using a statistical distribution function (exponential distribution) or directly from a gas chromatography experiment if known.

4. Based on carbon number (CN) and using the Won Correlation (1986) [18] and Pedersen Correlation (1991) [19], it is possible to measure or determine the wax characteristics (melting temperature, heat of fusion, and molecular weight) of heavy components.

5. Calculate the fugacity coefficient for each liquid phase component and compute the fluid parameters (oil formation volume factor, solution gas-oil ratio, fluid density, Z-factor, and relative volume) by solving the cubic SRK-EOS model to simulate liquid-vapor equilibrium. After comparing with experimental data and fine-tuning the equation parameters (acentric factor, critical pressure, critical temperature, and critical volume), this model becomes representative.

6. Estimate the mole fraction of component (X_i) in liquid (for the wax-forming component, it represents the wax fraction for each N-paraffin component). This calculation is a trial-and-error procedure, starting from assuming an equilibrium coefficient K value, then calculating X_i and y_i, then calculating the fugacity for each component, then stopping when there is coverage between the assumed and calculated values of K.

7. Use the Wilson equation (Eq. 14 in this study) to estimate the activity coefficient (γ_i) of each solid phase component in order to determine the solubility of the solid phase (wax).

8. The solubility limit (X_i^{sat}), which is the maximum quantity of wax that may be dissolved in the mixture, is determined using the Coutinho model. When this limit is surpassed, the solid (wax) is released and precipitates as a solid phase since the liquid mixture can no longer contain it.

9. When X_i^{sat} (Step -8) and X_i (Step -6) are compared, there is no wax precipitation where $X_i^{sat} > X_i$, the onset point at which the wax would precipitate (WAT) where $X_i^{sat} = X_i$, and a significant possibility of wax precipitation where $X_i^{sat} < X_i$.

10. Determine wax-phase envelope and WAT.

Figure .3 is the flowchart for this study, and each of the parts has been addressed comprehensively throughout this section.

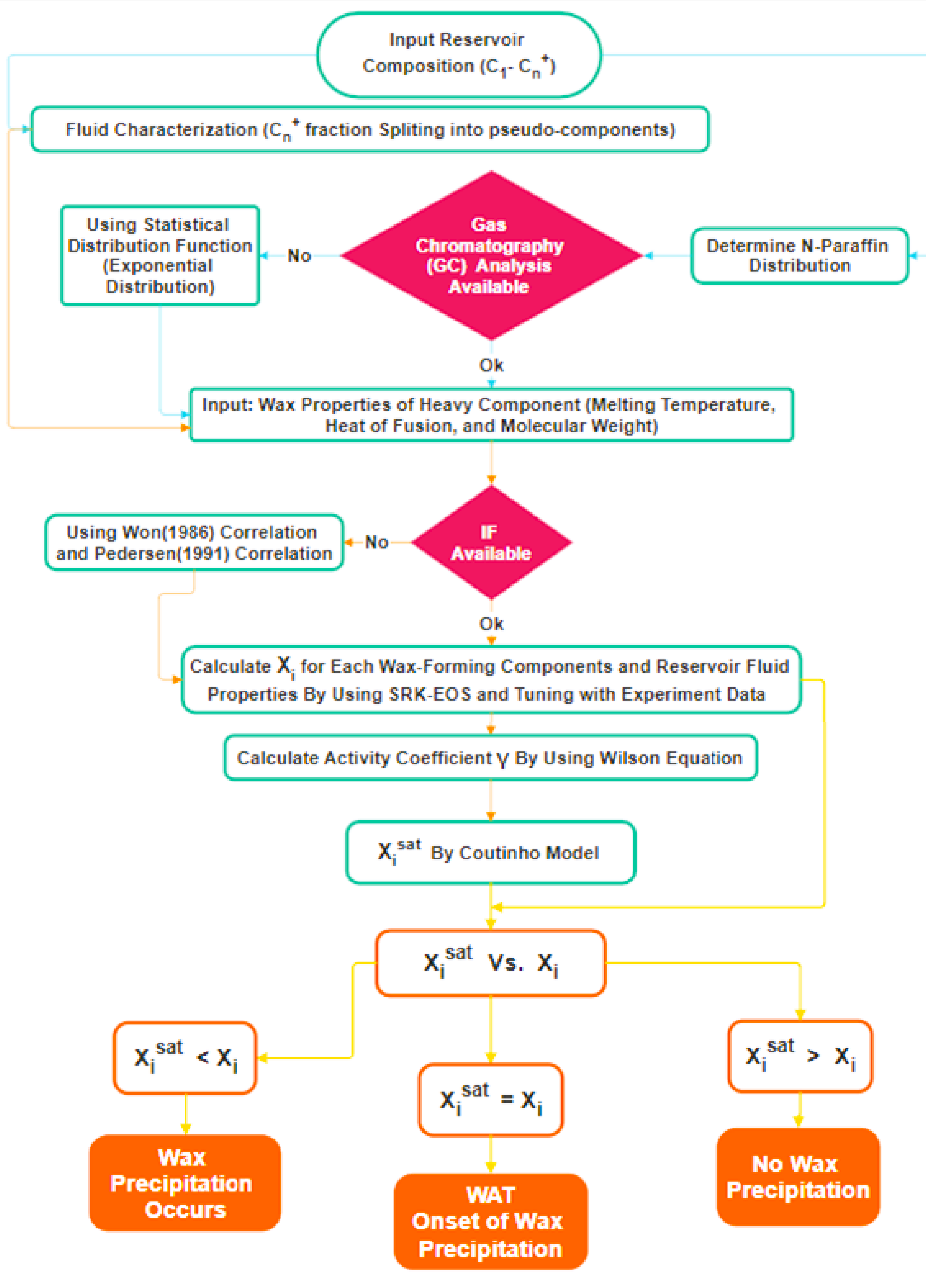

Figure 3: Wax Precipitation Modeling Flowchart. (This Study)

4. Results & Discussion

4.1.Reservoir Fluid Characterization:

Crude oil is a complex mixture made up of thousands of different compounds. It is not possible to study each reservoir fluid individually for modeling purposes. Instead, engineers describe the oil with a reasonable number of simplified components using a technique known as characterization.

The C_{20}^{+} fraction is divided into eight pseudo-components beginning with C_{20}. Because the gas chromatography analysis of n-paraffin is unknown, utilize the exponential distribution to determine its distribution. A distribution of single carbon numbers (SCN) may be used to represent oil, which is then corrected by laboratory testing and Pedersen correlation. In comparison to the lab report, this will offer a more detailed fraction distribution. Figure .4 depicts the n-paraffin distribution after fluid characterization.

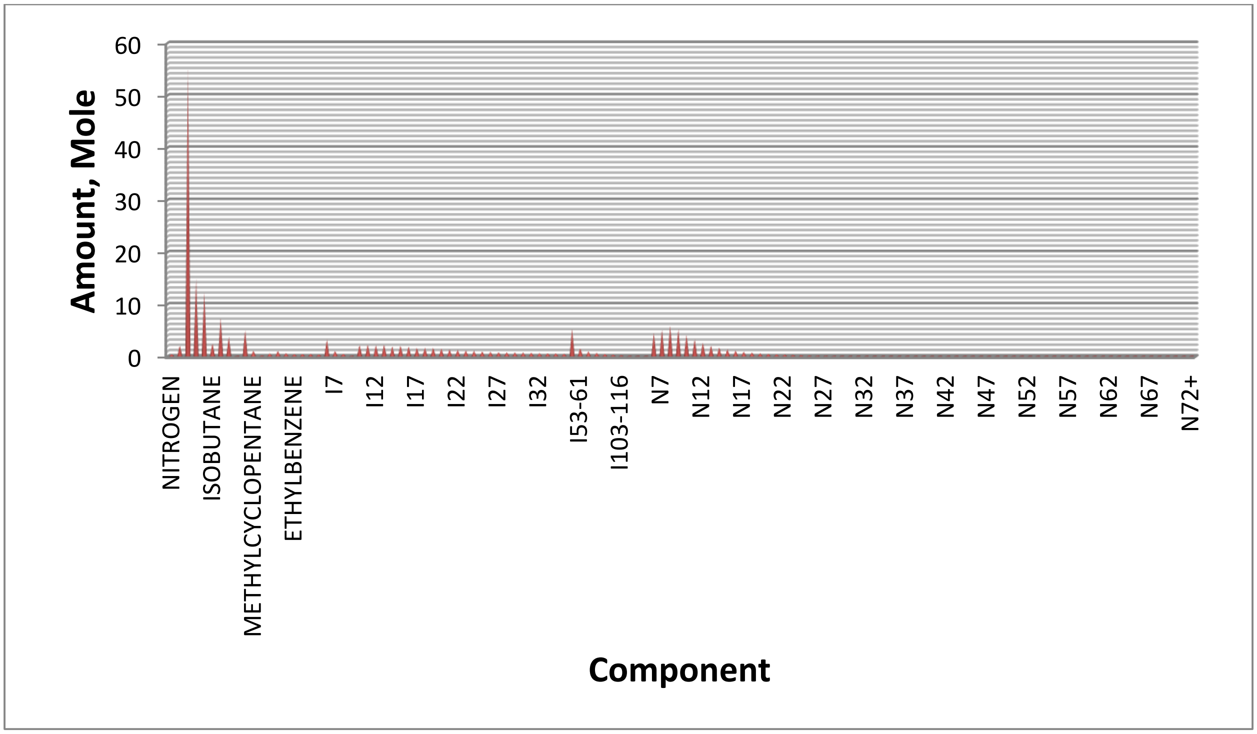

Figure 4: N-Paraffin Distribution After Reservoir Fluid Characterization

4.2.Tuning of SRK-EOS Model with PVT Experiments:

The matching results of each property as a result of applying the trial and error procedure that is described in the research methodology section. The tuning has been conducted due to a change in SRK-EOS parameters (critical pressure, critical temperature, and acentric factor) for undefined components. The results for each property are as seen below:

4.2.1. Bubble Point Pressure: Figure.5 illustrates how P_b matches at different temperatures. The experimental P_b levels and those determined by the SRK-EOS model correspond well, as can be seen from this figure.

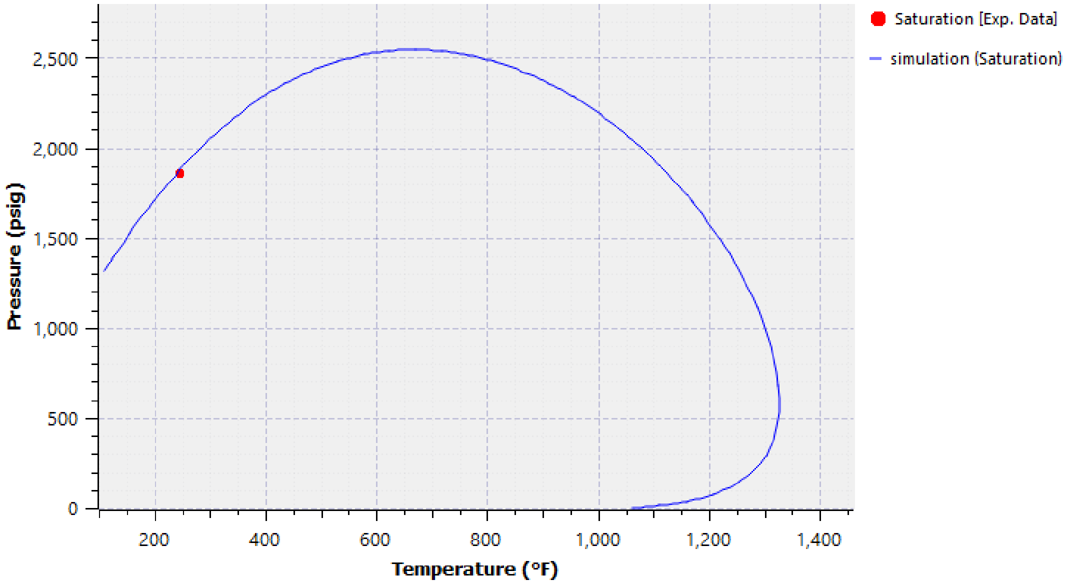

Figure 5: Bubble Point Matching

4.2.2. Differential Liberation Tests: Figures 6 and 7 show how Bo's and Rs' respective differential liberation tests correspond. It is evident that there are strong agreements between the experimental and simulated data.

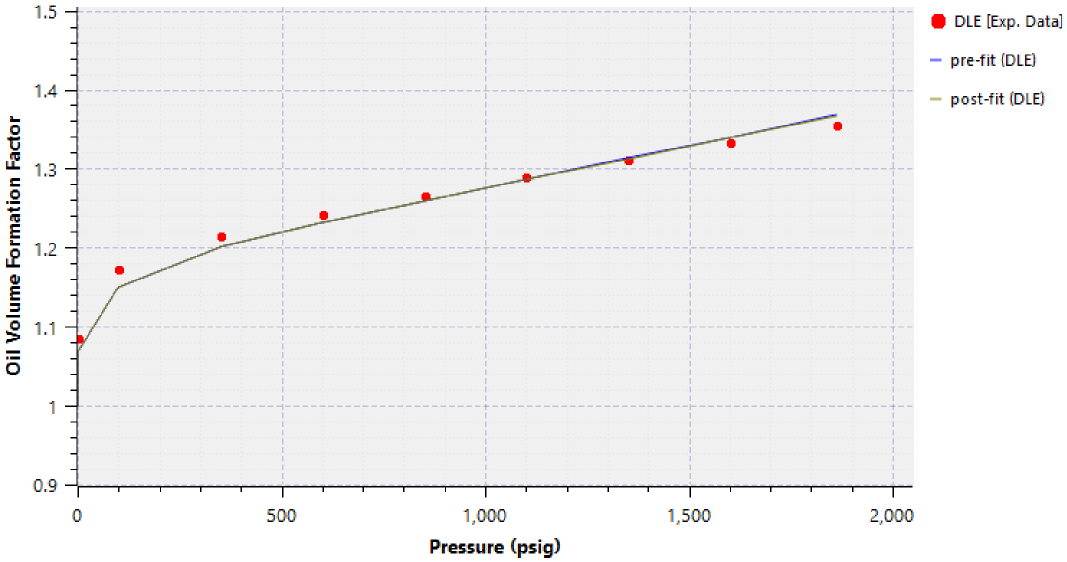

Figure 6: Oil Formation Volume Factor (Differential Liberation)

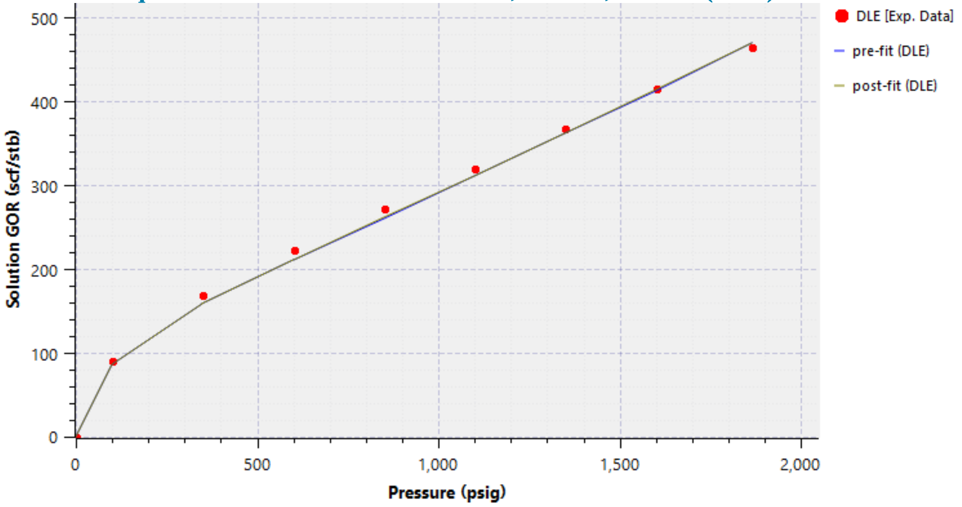

Figure 7: Solution Gas-Oil Ratio (Differential Liberation)

4.2.3. Flash Liberation Tests: Figures 8 and 9, respectively, display the matching of flash liberation tests (liquid density, relative volume). The simulated and experimental results correspond well, as can be shown.

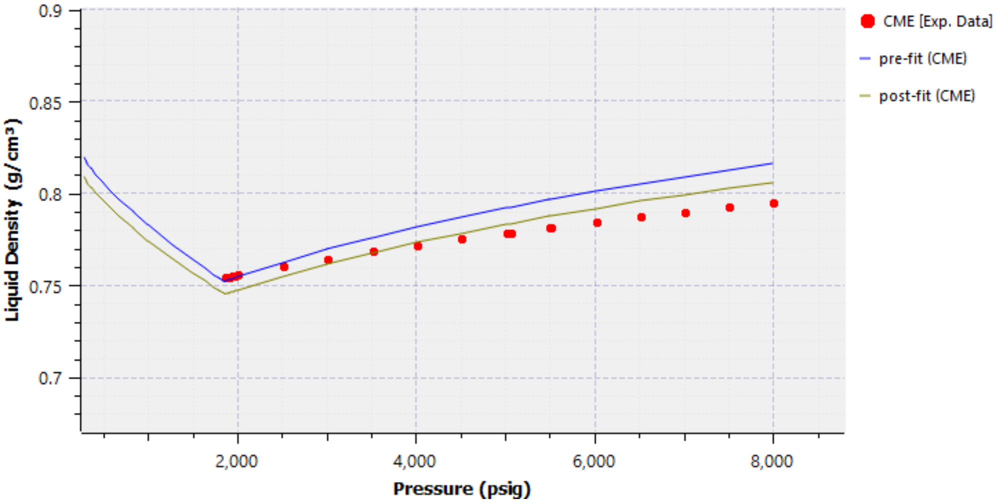

Figure 8: Liquid Density (Flash Liberation)

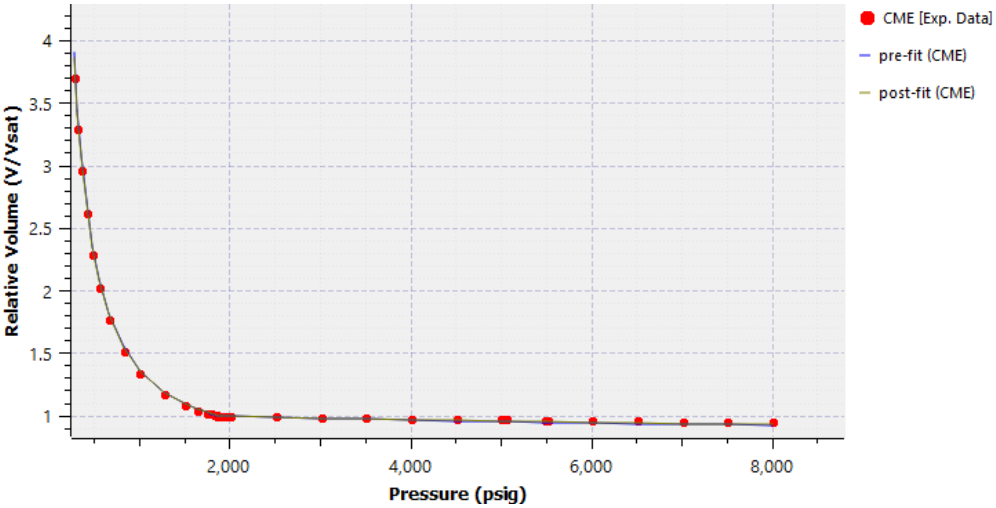

Figure 9: Relative Volume (Flash Liberation)

4.2.4. Viscosity Tests: As seen in Figures 10 and 11, respectively, the viscosity tuning at which the simulation model's viscosity calculations are defaulted based on the corresponding state concept in the form recommended by Pedersen et al.

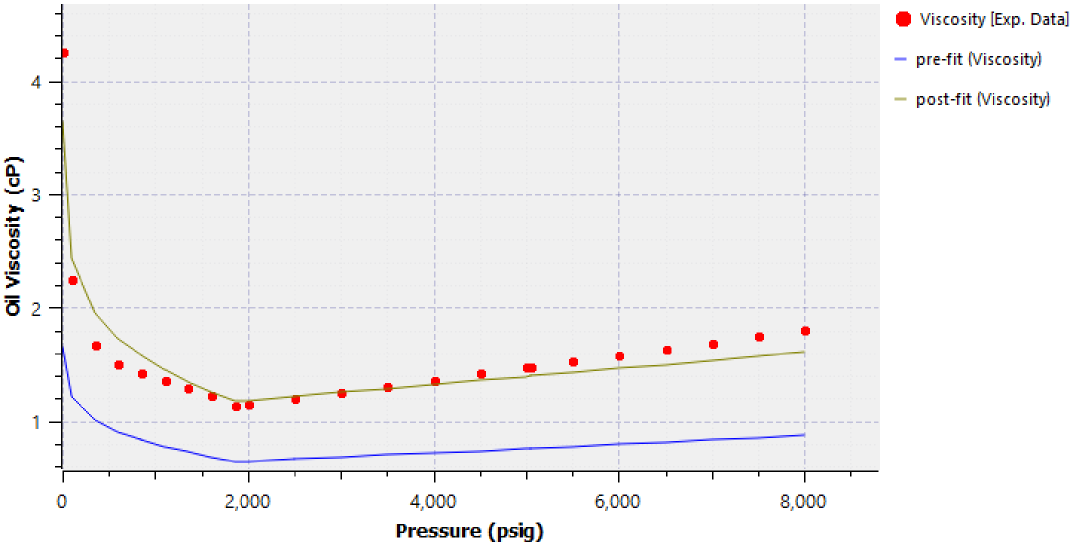

Figure 10: Oil Viscosity

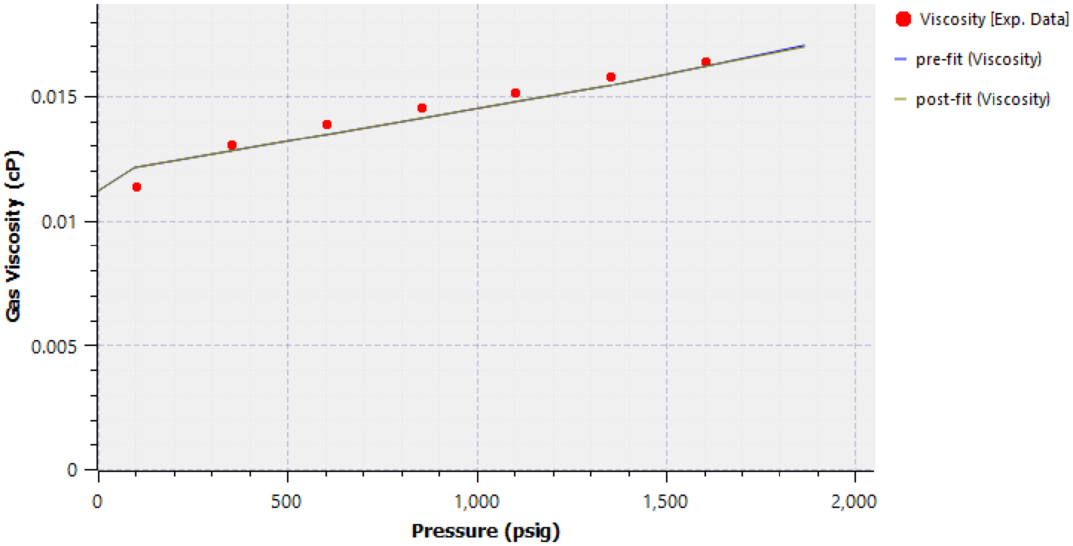

Figure 11: Gas Viscosity

4.3. Wax Precipitation Modeling Using Solid-Liquid Equilibrium (Coutenho framework)

The wax phase envelope is produced by the multiflash program using the Coutenho framework. The phase envelope between oil and gas is modelled by SRK-EOS, which is shown by the red line in Figure .12, where the region inside the line denotes a two-phase state and the area beyond the line represents a single phase. By using the Wilson equation to calculate the activity coefficient and coupling it with SRK in the Coutenho model, the solubility limit (X_i^{sat}), which is the maximum quantity of wax that may be dissolved in the mixture, is determined from the equation. 15, then comparing with the mole fraction of the component (i) in the liquid (for the wax-forming component, it represents the wax fraction for each N-paraffin component) was calculated from the flash calculation. At 138.5°F, X_i and X_i^{sat} values were identical, indicating the wax precipitation onset point at which the wax transitions from liquid to solid phase. When the temperature drops below 138.5°F, X_i exceeds X_i^{sat}, indicating that the liquid mixture can no longer hold all of the wax in a liquid state, allowing it to release and crystallize, resulting in precipitates. The wax phase envelope is represented by the blue vertical line, which sheds light on the temperature and pressure parameters that cause wax precipitation. The left side of the line denotes possible problems with wax precipitation, while the right side shows no concerns about wax precipitation.

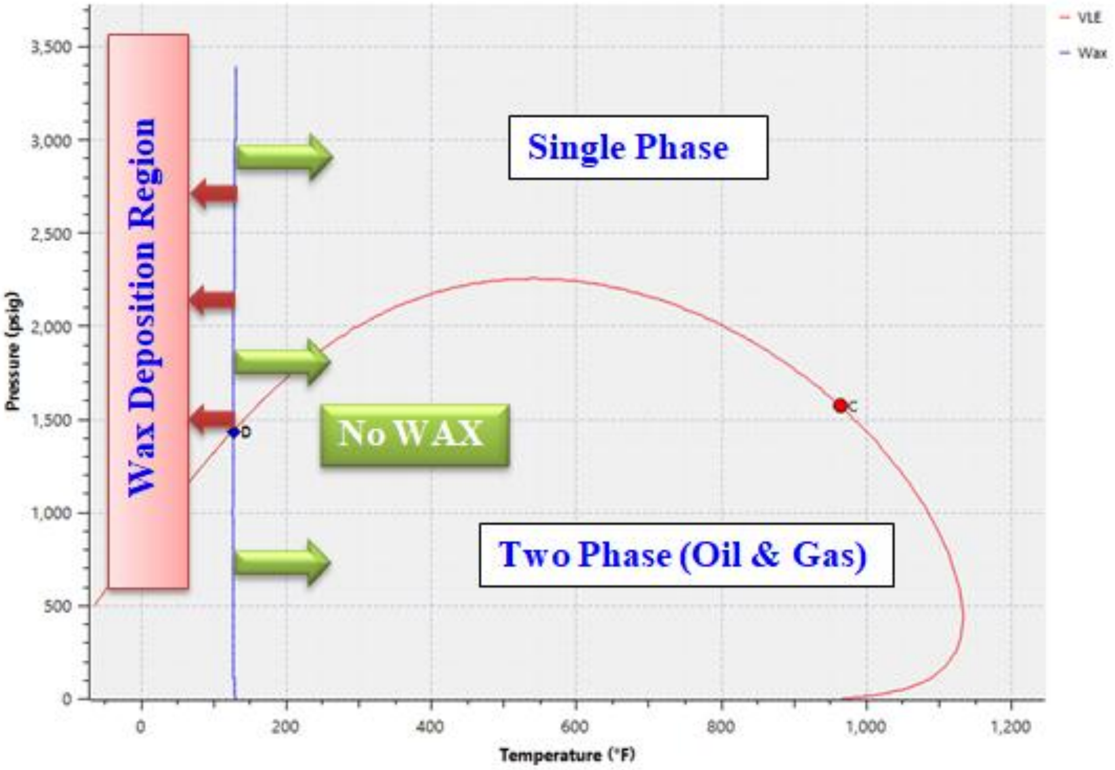

Figure 12: Wax P-T diagram

When the reservoir conditions of the X- formation are evaluated (As seen in Figure. 13), it is found that there is no risk of wax precipitation since the temperature and pressure values are in line with the non-wax side. On the other hand, the wellhead conditions—shown by the pink dot—fall on the left side of the wax line, indicating a possible issue with wax precipitation. The wax problem can become worse if production goes on in this manner. In this instance, the flow line and surface facilities will serve and may obstruct the pipes if the operation point is not changed for avoiding the wax issue.

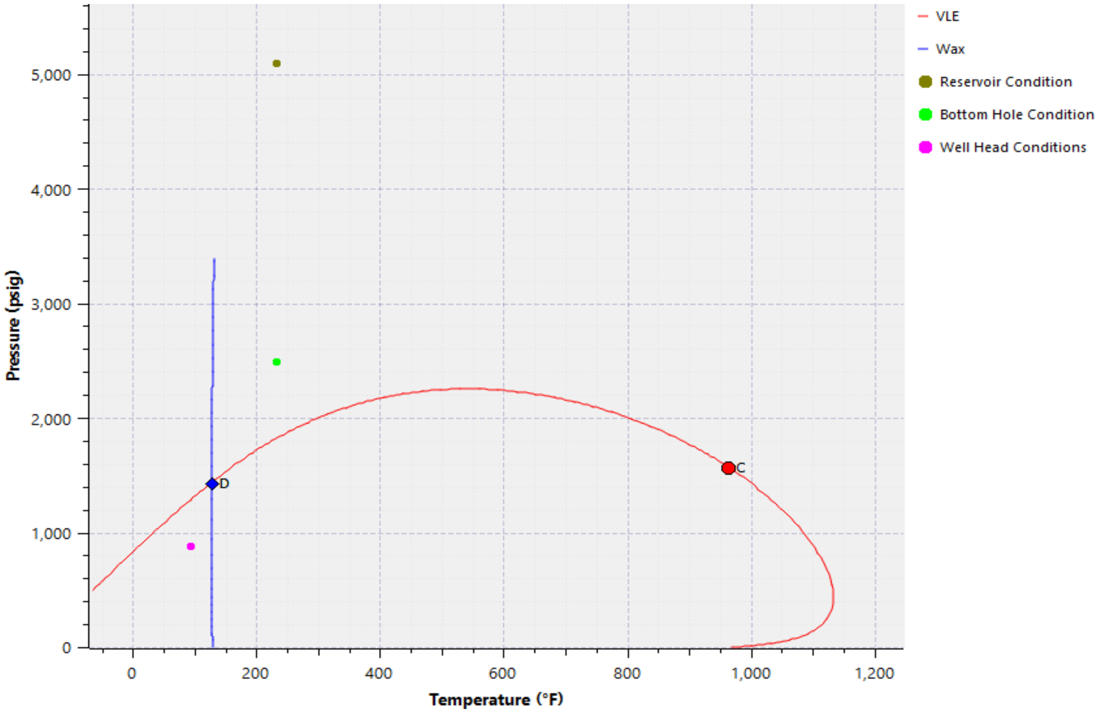

Figure 13: Wax P-T diagram with reservoir and well head conditions

5. Conclusions

1. In the present study, a thermodynamic framework integrating the SRK equation of state and the Wilson equation was employed. This dual model was used to simulate the phase change of wax from liquid to solid state. To some extent, this model is regarded as successful in simulating the phase behavior for the transition of heavy n-paraffin components from liquid to solid phase.
2. Wax deposition is an issue that arises when the temperature of the production system (wellbore, reservoir, and surface equipment) falls to less than 138.5°F, according to the current phase diagram.
3. This analysis revealed that if the temperature went below the one specified in the first conclusion, the existing well might have a partial or total blockage, as well as future production issues owing to wax deposition.
4. The model's correctness is determined by a number of criteria, including the availability of laboratory data defining the n-paraffin distribution in the mixture, rather than depending on correlations, which are vulnerable to mistakes.
5. By examining the phase diagram produced by this study, we infer that temperature change, especially a reduction in temperature, is the primary factor influencing wax deposition, as opposed to asphaltene deposition, which is predominantly reliant on pressure.
6. The model utilized is not the only one for simulating wax deposition. The SRK equation might be replaced by a more precise and sophisticated equation. However, the current model produced satisfactory findings, which are consistent with much earlier research that employed this equation.

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