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TÍTULO DO TRABALHO:

ANALYSIS OF PVT CHARACTERIZATION AND PHASE BEHAVIOR FOR A PARAFFINIC OIL USING THE MULTIFLASH

AUTORES:

Carlos F. Klug[1], Mariana D. Carvalho[1], Joana L. Augustin[1], Rafael M. D. Rosa[2], Gustavo G. Ribeiro[1], Antonio M. Barbosa Neto[1*]

INSTITUIÇÃO:

1 ThermoPhase – FCSRG, PPGEM, Santa Catarina State University
2 Department of Production Engineering, PetroRio.

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Abstract

Offshore oil production involves oil transporting from the reservoir to the topside facilities. This process is challenging due to low temperatures and substantial pressure drops during fluid flow in pipelines. These conditions induce the precipitation of solid phases such as paraffin, leading to the deposition of these components along the inner walls of the pipeline, causing a diameter reduction and resulting in production losses or even blockage. Studying the wax appearance temperature (WAT) is essential to prevent wax formation and minimize flow assurance issues caused by precipitation and deposition, which result in significant financial losses. This work aims to generate a comprehensive PVT characterization of paraffinic petroleum based on data from the literature. The chosen fluid for analysis is categorized as a waxy oil according to its composition and physical properties. This oil exhibits properties of dead oil, with its composition ranging from components C_2 to C_{20+}. Physical and critical properties were employed in Multiflash software to create the pseudo-components from the C_{20+} fraction, with a total wax content of 8.1% by mass, a molecular weight of 226.1 kg/kmol, and a specific gravity of 0.8487. The Multiflash wax module employs the Wilson model and CPA equation of state for calculating phase equilibria using a single solution approach. The simulation results were compared with experimental data available in the literature. The WAT temperature, calculated by Multiflash through CPM (Differential Power Calorimetry) and DSC (Differential Scanning Calorimetry) approaches, was found to be 49.18°C and 38.89°C, respectively. Comparing these results with the literature data revealed errors of 7.21% and 2.77%, respectively. The WAT curve varied from 60.90°C to 61.95°C, changing pressure from 1 bar to 55.75 bar. Considering the phase envelope for vapor-liquid equilibria (VLE), the critical point is at 36.22 bar and 536°C, the cricondenbar was found at 37.12 bar, and the cricondentherm at 574.43°C. Based on this, it is appropriate to predict that under these conditions, the fluid will present two phases at low pressures and high temperatures. Thus, the solid phase precipitation, according to the Wax precipitation curve, starts at 58.80°C with a maximum percentage of 4.36% of wax mass formed at 0°C. The software's effectiveness is perceptible when comparing these Multiflash data with experimental data for wax mass.

Keywords: Paraffinic fluid, PVT characterization, WAT, Multiflash.

Introduction

The petroleum is essential to various industries due to the variety of products derived from its complex composition of hydrocarbons (Krepcki, 2016). The hydrocarbons exhibit a range of volatility and melting point, and exist in solid, liquid, or gaseous states, depending on the pressure and temperature conditions (Lira-Galeana, Firoozabadi & Prausnitz, 1996). Deepwater reservoirs are submitted to low environmental temperatures that can reach $4\ °C$. These low temperatures, combined with pressure drop, can form solid phases, such as asphaltenes, paraffin, scale, and hydrates. The flow restrictions due to diameter reduction from the accumulation of these solids may happen throughout the entire system, such as well production tubing, in a jumper, in a flowline, in a riser, in an export pipeline, or in several locations simultaneously, causing production and mechanical integrity loss. (Coutinho & Daridon, 2001). When molecules of heavy hydrocarbons with straight chains of carbon atoms (normal paraffin) precipitate on cold surfaces and accumulate, paraffin wax deposit forms. The wax can be deposited from condensate during gas production as well as during oil production since condensates produced with free gas may contain heavier hydrocarbon molecules (Makogon, 2019).

In the analysis of wax precipitation, the wax appearance temperature (WAT), the wax dissolution temperature (WTD), the phase composition, and PVT properties such as GOR (gas/oil ratio) and bubble point are analyzed. The WAT is the temperature at which the first visible or detectable solid wax crystal precipitates and the WTD is the temperature at which the precipitated wax crystals completely redissolve in the volume of oil from which they crystallize (Makogon, 2019). The WAT is measured in laboratories with techniques such as visual observation, CPM, filter plugging, rheometry, DSC, and spectroscopic methods (Bagherinia, Assareh & Feyzi, 2016; Ji et al., 2004)Despite not being an equilibrium point and its value depending on the experimental procedures mentioned, it can be used in developing and validating wax models.(Ji *et al.*, 2004).

The information from reservoir modeling prediction of flow rates and thermodynamic PVT characterization of produced fluids underlies the analysis of multiphase fluid flow. Predicting and analyzing flow velocities and phase accumulation amounts in the production system through software that tracks and balances masses and velocities allows the design engineer to select sizes for well production tubing and gathering flowlines, as well as identify technologies needed to produce gas and oil. In this scenario, the aim of this work is to generate a fluid characterization in Multiflash to investigate wax deposition, study their behavior to generate results to optimize methodologies, spread knowledge, disseminate known techniques, and develop new ones.

Methodology

The methodology used to create a case study of wax deposition during the paraffinic oil flow consists of fluid characterization, using information such as temperature, pressure, composition, and properties as data input at Multiflash.

Thus, petroleum wax data from 17 North Sea Oils were analyzed in detail. Also, they are available in Rønningsen, Søemme & Pedersen (1997). In this context, Oil 3, a dead oil with a composition shown in Figure 1, was selected.

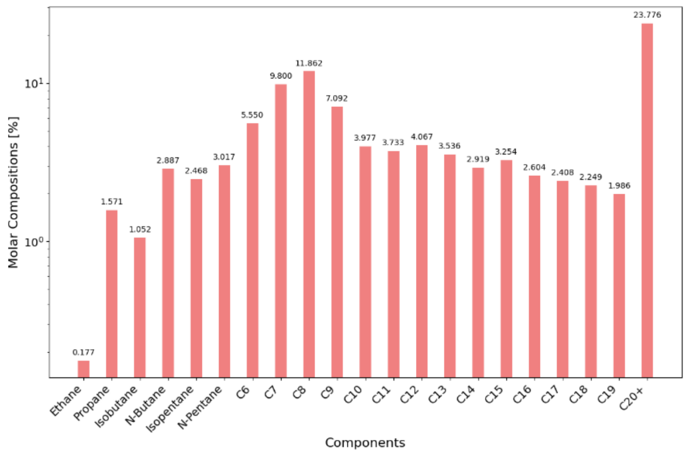

Figure 1 - Composition of Oil 3 applied to the fluid used in this work

Source: Adapted from Rønningsen, Søemme and Pedersen, (1997) apud Speranza and Zhang, (2014).

The characterization of a waxy or crude condensate fluid by Multiflash is determined by selecting the well-defined components and the number of pseudo-components for the n-paraffins and non-n-paraffins fraction (Speranza; Zhang, 2014). That way, the fluid data specified in Table 1, such as the molecular weight of the total fluid and specific gravity, were used to create these pseudo-components from C_{20+}.

Table 1 - Physical and critical properties of the fluid used to define the $C20^+$ fraction on Multiflash

Parameter	Value
Total wax content (% $mass$)	8.1
Molecular weight ($\frac{kg}{kmol}$)	226.1
Specific Gravity	0.8487

Source: Adapted from Rønningsen et al., (1991).

Thereat, to select the best-characterized fluid, four sensitivity analyses on this number of pseudo-components were made. From that, the final characterization has a distribution start of normal fraction from C_6 to C_{10} and of n-paraffins from N_6 to N_{80}, as shown in Figure 2.

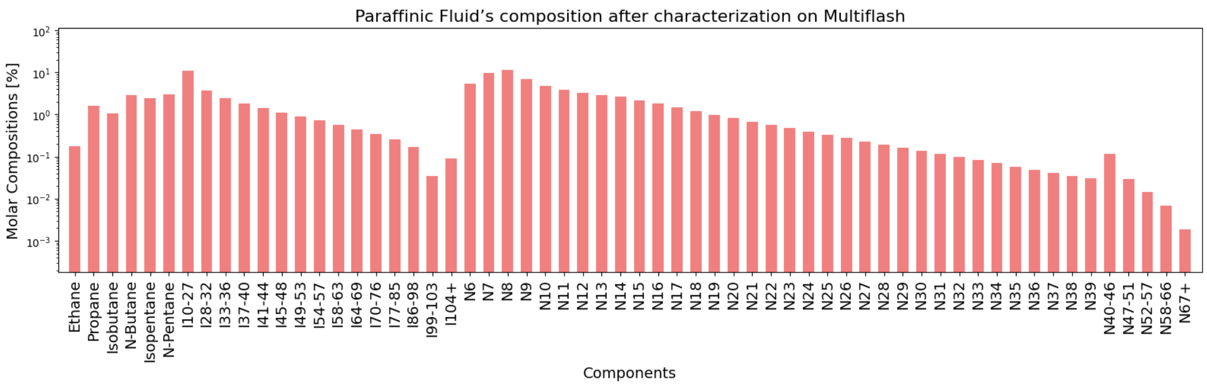

Figure 2 – Paraffinic Fluid’s composition after characterization on Multiflash

Source: Elaborated by the author, 2024

It is known that the wax precipitation modeling by Multiflash is structured on work by Coutinho et al. (2006) that represents wax as a solid solution since precipitated paraffins form a unique homogeneous solid phase in which its components are miscible with one another (Won, 1986). In this way, the behavior of this wax solution is approximated by the Wilson model as

$$\frac{G^E}{RT} = \sum n_i^w \ln\left(\sum x_j^w \exp\left(\lambda_{ji} - \lambda_{ii}\right)\right) \quad (1)$$

where its parameters and the Cross Terms between components are estimated, respectively, as:

$$\lambda_{ii} = -\frac{1}{3}\left(\Delta H_{sub,i} - RT\right) \quad (2)$$

$$\lambda_{ij} = \alpha_{ij} \min\left(\lambda_{ii}, \lambda_{jj}\right) \lambda_{ij} = \alpha_{ij} \min\left(\lambda_{ii}, \lambda_{jj}\right) \quad (3)$$

Therefore, the results for the WAT of Oil 3 obtained by CPM (Differential Power Calorimetry) and by DSC (Differential Scanning Calorimetry), according to Rønningsen et al. (1991), were compared with the results from Multiflash simulation. This comparison is made through the Mean Absolute Percentage Error (MAPE), presented in Equation 8.

$$MAPE = \frac{1}{n}\sum_{i=1}^{n} \frac{|yi - y\hat{} i|}{yi} \cdot 100\% \quad (8)$$

Furthermore, the Vapor-Liquid Equilibrium phase Envelope Properties with the Wax curve for Oil 3, obtained in Multiflash, were presented. Next, the experimental wax precipitation curve, using the Coutinho Wax Model, was compared to the simulated one. Finally, the influence of pressure on WAT variations will be analyzed.

Results and Discussions

This section exposes and discusses the results achieved with the simulations obtained through the detailed methodology.

Simulating the Oil 3 at $20\ °C$ and $1.101\ bar$ in Multiflash, the WAT calculated by CPM and DSC methods was $49.179\ °C$ and $38.891\ °C$, respectively. These values were compared with the values reported by Rønningsen et al. (1991) and presented the MAPE values shown in Table 3.

Table 2 - CPM and DSC WAT obtained at Multiflash

Method	Rønningsen et al., (1991) ($°C$)	**Multiflash** ($°C$)	**MAPE** (%)
CPM	53	49.179	7.209
DSC	40	38.891	2.772

Source: Elaborated by the author, 2022

With this simulation, the envelope of the vapor-liquid equilibrium phase and the wax curve for Oil 3, shown in Figure 3, can be demonstrated.

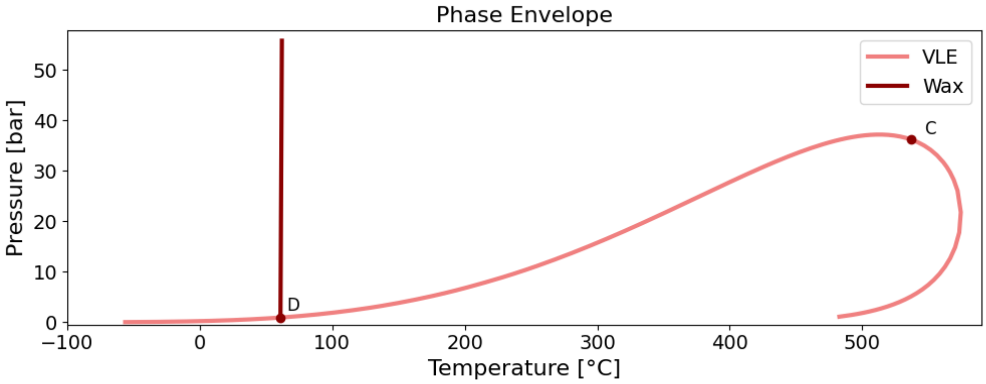

Figure 3 - Equilibrium Liquid – Vapor and Wax Curve for Oil 3
Source: Elaborated by the author, 2024

In this envelope, properties such as critical point, cricondenbar, and cricondentherm are evident. Its critical point is around $36.22\ bar$ and $536\ °C$. And is due to the low cricondenbar ($37.12\ bar$) and high cricondentherm ($574.43\ °C$), the fluid will show two phases at low pressure and high temperatures. Furthermore, the Wax curve varies between $60.896\ °C$ at $1\ bar$ and $61.949\ °C$ at $55.752\ bar$ showing a little pressure influence.

Figure 4 presents the wax precipitation curve obtained from Multiflash, and it specifies a WAT of $60.896\ °C$ at $1.0144\ bar$. Further, it also shows that the first portion of precipitated wax starts precisely at $58.7966\ °C$ achieving a maximum percentage of $4.36\ \%$ of wax mass at $0\ °C$. Lastly, the wax precipitation curve using the Coutinho Wax Model was compared with that generated in this work, under the same pressure and temperature conditions, as shown in Figure 4.

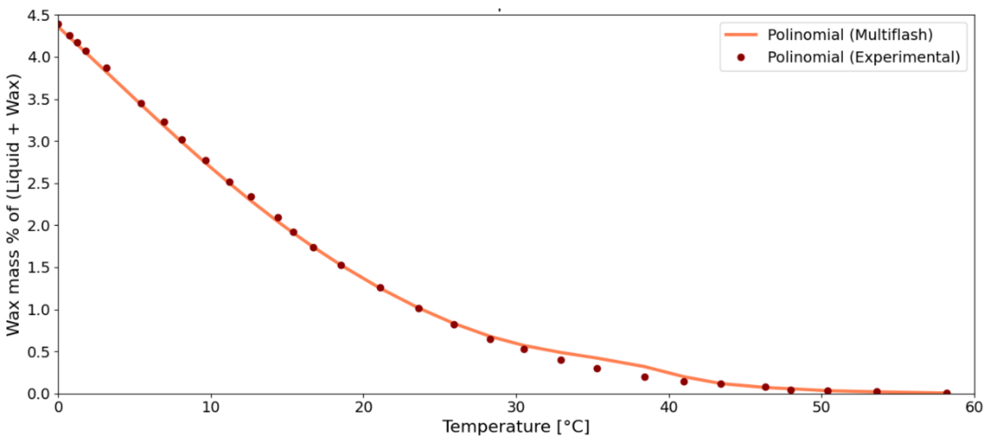

Figure 4 - Comparison between experimental and simulated Wax Precipitation Curve
Source: Elaborated by the author, 2024

The results presented a good data agreement between the results reported on Multiflash and the Experimental one. The software's effectiveness and functionality are evident. The most significant discrepancies occur between $30\ °C$ and $60\ °C$, with smaller average errors observed below this temperature, as presented in Table 3.

Table 3 - Average error between Experimental and Obtained Wax Mass %

Range of Temperature ($°C$)	**MAPE** (%)
$\mathbf{0-10}$	0.821
$\mathbf{10-20}$	1.010
$\mathbf{20-30}$	1.993
$\mathbf{30-40}$	32.654
$\mathbf{40-50}$	23.450
$\mathbf{50-60}$	22.906

Source: Elaborated by the author, 2022

The WAT typically varies with pressure. In this study, as shown in Figure 5, the pressure ranges from $1.01325\ bar$ to $250\ bar$, resulting in variations in WAT. As proof of this, at the lowest temperature of $42.3\ °C$, the wax percentage varies from 0.1502 at $1.01325\ bar$ to 0.3117 at $250\ bar$ demonstrating an increase of 207.52%.

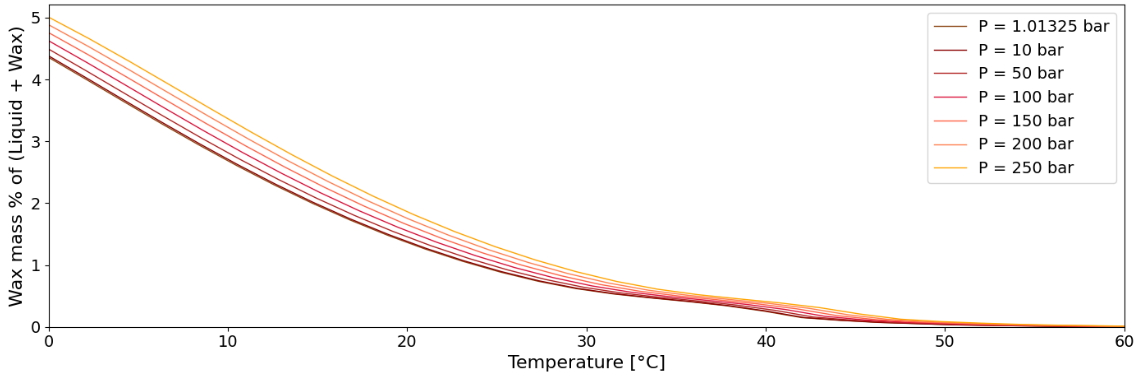

Figure 5 - Wax Precipitation Curve for different pressure

Source: Elaborated by the author, 2024

Conclusions

The case study, based on the data from Rønningsen et al. (1991), allowed us to model the fluid properties using Multiflash and perform the necessary sensitivity analysis of the composition of this fluid.

That way, the results obtained from Multiflash using both CPM and DSC methods demonstrated agreement with calculations performed by Rønningsen et al., (1991). Specifically, the average errors were 7.209% and 2.772% for CPM and DSC, respectively. The comparison of the wax precipitation curve with the data from Coutinho et al., (2006) for the same fluid showed agreement between most data points, with smaller average errors observed below $30\ °C$. In turn, due to the low cricondenbar and liquid-vapor curve displaced to the right at high temperatures, the fluid envelope phase showed a tendency of monophase equilibria. Finally, it is noticeable the pressure influences the WAT variations since at the lowest temperature, the wax percentage had an increase of 207.52% .

Therefore, this work demonstrates their collaboration regarding the PVT characterization of paraffinic fluids through the use of software that proved to be consistent with the experimental data and that represents wax as a solid solution based on the fact that precipitated paraffins form a unique homogeneous solid phase in which its components are miscible with one another.

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