



INFLUENCE OF NATURAL GAS COMPOSITION ON THE FORMATION AND DEPOSITION OF ELEMENTAL SULFUR IN PIPELINES

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ABSTRACT

The formation and deposition of elemental sulfur (S_8) in natural gas pipelines are a frequent problem. The formation of a yellow powder, which is known as S_8 , is influenced by operational condition changes, such as pressure and temperature drops, natural gas composition, and additives used in pipelines. S_8 may occur in pipelines due to the desublimation of sulfur dissolved in natural gas, where it changes into a solid state. This phenomenon may lead to serious consequences to gas production, processing, operation, and transportation. The objective of this study is to better understand the kinetics and operational variables that influence S_8 formation to find solutions for reducing or eliminating the occurrence of this compound during natural gas transportation in pipelines.

KEYWORDS

natural gas; elemental sulfur; desublimation; deposition; pipelines

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1. INTRODUCTION

Compared to other fossil fuels, natural gas is an energy source with innumerable environmental benefits, such as the reduction of sulfur dioxide, nitrogen oxides, particulate matter, and carbon dioxide emissions. For these reasons, the percentage of natural gas in the global energy matrix is increasing.

Different problems may occur during natural gas production and transport chains, including corrosion caused by the presence of water and contaminants, such as S_8 in its allotropic form.

The formation of a yellow powder, which is known as S_8 , in natural gas pipelines is explained by the Joule Thompson effect. It primarily occurs in the pilots of pressure-reducing valves and is influenced by changes in the system's operational conditions, such as pressure and temperature drops, variation in the gas composition, and the presence of additives used in the pipelines. The problem is not restricted to the transport stage, it can also be observed in gas processing equipment.

Santos et al. (2013) stated that the formation and deposition of sulfur in pipelines can cause serious consequences for the production, processing, operation, and transportation of gas. Pipe blockage and corrosion caused by sulfur deposition may damage equipment and affect gas production. It may also result in a plant shut down (**Zhou et al., 2013**).

Taylor et al. (2014) reported that when elemental sulfur deposits are in solid state, they can accumulate and may result in flow constriction. It can also block instrumented connections, causing a poor process control and requiring additional maintenance costs.

The deposition of S_8 in gas pipelines has been an object of study. For decades, it has been considered to be the cause of clogs in the top of the wells in oil reservoirs. The phenomenon was detected in 1990 in natural gas transport systems that operate at high pressures. It became more evident with the increase in natural gas consumption and has created significant operation and maintenance problems, with high costs for the industry (**Pack, 2005; Cézac et al., 2007; Pack et al., 2012; Cloarec et al., 2012**).

Pack et al. (2013) discovered that trace amounts of sulfur vapour in the gas stream could generate elemental sulfur deposits in the gas stream and, hence, cause an adverse impact in the accuracy of flow measurement during local depressurization, as observed in metering devices through the process of desublimation.

This study aims to improve the understanding of the influence of natural gas composition on the formation and deposition of S_8 in gas pipelines from a theoretical point of view. Alternatives to reduce or eliminate the formation of this undesired compound, which affects the operational safety of several systems and generates a significant increase in the transport cost of natural gas, were evaluated using the results of the study.

2. MATERIALS AND METHODS

Phase envelopes for different sets of operational conditions were obtained from simulations of natural gas flow in pipelines with the HYSYS® commercial computer package. The construction of equilibrium diagrams is essential to understand the factors that cause sulfur formation and deposition. Operational data on natural gas composition, amounts of S_8 and H_2S , temperature, pressure, and flow rate, were obtained from the Federal University of Bahia (UFBA) Field-School Project (FSP) and employed in the simulations. The influence of gas composition on the formation and deposition of S_8 was also evaluated using actual natural gas streams from other fields, as shown in Table 1.

The Peng-Robinson equation of state coupled with the HYSYS® version V7 was employed in the simulations of this study. This equation is frequently employed in studies about systems that contain different hydrocarbons. According to **Barbosa (2007)**, equations of state play an important role in the study of the phase equilibrium of fluid mixtures. They can be used in an extensive range of temperatures and pressures and can be applied to mixtures with different components, from light gases to heavy liquids. Once the Peng-Robinson equation is selected, the program uses the Envelope Utility tool to automatically generate equilibrium curves in a pressure vs. temperature diagram, without the need to input these variables.

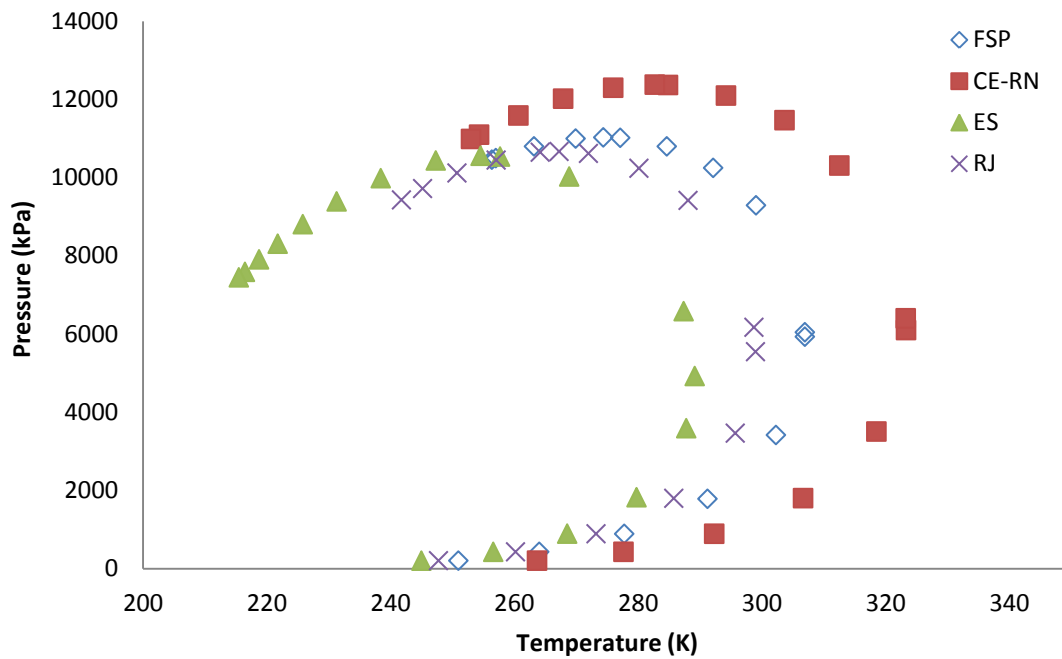


Figure 1. Comparison of the dew point curves of four natural gas compositions from Table 1.

The operational conditions for pressure and temperature in the natural gas transport process range from 500 to 8000 kPa and 250 K to 330 K, respectively. However, parts of the distribution networks may achieve maximum pressures of 12,000 kPa. Therefore, equilibrium diagrams were evaluated at a temperature of 300 K and a pressure of 4,000 kPa, which correspond to the average natural gas transport conditions. These conditions were applied to the gas from the UFBA Field-School Project and the gas streams from the remaining fields listed in Table 1.

The HYSYS® process simulator contains a help link where many of the necessary equations and parameters are provided. This help link enables the user to visualize the calculation methodology utilized by the simulator when the Peng-Robinson equation of state is applied in the Fluid Package.

The Peng-Robinson cubic equation of state is given by:

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b) + b(V - b)} \quad (1)$$

with

$$a = 0.45724(T_c R)^2 \times$$

$$\times \frac{\left[1 + (1.54226w + 0.3764 - 0.26992w^2) \sqrt{1 - \frac{T}{T_c}} \right]^2}{P_c} \quad (2)$$

and

$$b = \frac{0.0778RT_c}{P_c} \quad (3)$$

Where: P_c is the critical pressure; T_c is the critical temperature; V is the molar volume; R is the universal gas constant; w is the acentric factor; and a and b are mixture parameters that are dependent on the components' critical properties.

In the case of natural gas streams with different chemical compounds, a mixture rule must be applied to parameters a and b . In general, the Van der Waals mixture rule is applied, as shown in Equations (4) and (5). The methodology proposed by **Pack (2005)**, in which constant coefficients of binary interaction between the components were maintained, was adopted in the simulations.

$$a = \sum_i \sum_j y_i y_j \sqrt{a_i a_j} (1 - k_{i,j}) \quad (4)$$

and

$$b = \sum_i y_i b_i \quad (5)$$

Where: a_i is the mixture parameter of pure component i ; b_i is the mixture parameter of pure component i ; y_i is the vapor molar fraction of component i ; y_j is the vapor molar fraction of component j ; $k_{i,j}$ is the coefficient of the binary interaction between components i and j .

According to **Smith et al. (2005)**, these equations, which are known as Van der Waals prescriptions, enable the calculation of mixture parameters from the parameters of the pure components that comprise the mixture. Although they only yield satisfactory results for mixtures of simple and chemically similar molecules, they enable direct calculations and result in the solution of complex problems involving liquid/vapor equilibrium (LVE).

3. RESULTS AND DISCUSSIONS

Cézac et al. (2008) investigated the presence of some components in the process of sulfur deposition in pipelines. However, the authors focused on calculating the total percentage of desublimated sulfur and did not obtain comparative solubility curves for the different compositions of the gas streams. The results of natural gas streams with different compositions are relevant to verify whether variations in composition significantly modify equilibrium curves.

3.1 Influence of the natural gas composition

The gases streams listed in Table 1 were used to evaluate the effect of the natural gas composition. Constant values of the pseudo-critical properties of the gas mixture and the binary interaction parameters, which were previously calculated by the simulator, were maintained in all simulations.

Retrograde condensation is one of the factors that contributes to the formation and deposition of S_8 . The more likely this deposition is, the higher the amount of heavy hydrocarbons (C_3+ fractions) in natural gas. Thus, the influence of composition on condensation can be better understood and visualized in a $P \times T$ diagram. Figure 1 shows the

dew point curves of four of the compositions listed in Table 1.

Table 1 reveals that CE-RN natural gas contains the highest amount of heavy components. As shown in Figure 1, at the average simulated operating conditions ($T = 300$ K and $P = 4,000$ kPa), the operating point is in the two-phase region, where the condensation phenomenon may occur. Therefore, the ideal operating conditions should be in the high pressure and high temperature region because the cricondentherm, which is the maximum temperature above which liquid cannot form, is 323.3 K. This condition would prevent operation in the two-phase region, the occurrence of the retrograde condensation phenomenon and the formation of S_8 . The same behavior was observed for the natural gas from the Field-School Project due to a large amount of heavy components.

In the case of the gas from RJ, the cricondentherm in Figure 1 is 298.9 K. Although this point was not attained at the assumed operational conditions, it is significantly close to the two-phase region. Thus, operation at these operational conditions must be avoided because the condensation phenomenon may occur due to pressure and temperature drops. In the case of natural gas from ES, the solubility curve is displaced to the left due to a low amount of heavy components, which results in a lower cricondentherm (289.1 K). Therefore, the two-phase region is not close to the assumed operating conditions.

3.2 Influence of H_2S on the natural gas equilibrium diagrams

Depending on the region, the natural gas may have a significant amount of non-hydrocarbon components, for example, hydrogen sulfide, nitrogen, and carbon dioxide. Therefore, the effect of their presence in the gas stream should be evaluated.

The simulations to evaluate the influence of H_2S were obtained by adding the average amount of this component to each stream, per Table 1. The H_2S values added to the gas streams from the CE-RN, ES, RJ, and Field-School Project (FSP) were 7.2×10^{-7} , 5.0×10^{-6} , 4.3×10^{-6} and 5.0×10^{-6} , respectively, in molar fractions. In all cases, the samples were normalized prior to the simulations.

The impact of the presence of H_2S in the natural gas on the solubility curves, which would be a factor for the formation and consequent deposition of sulfur, was evaluated.

The results show that the presence of H_2S does not significantly change the natural gas equilibrium curves. These diagrams have a similar behavior with and without H_2S . As in the previous section, a more detailed comparison can be performed by joining all dew point curves (Figure 2) of the four compositions, with and without H_2S .

According to the analysis in Figure 2, the solubility curves do not change their behaviors in the phase-equilibrium region, even for high H_2S contents, such as in the gas streams from the ES and RJ fields and from the FSP. In each case, the points without H_2S (hollow symbols) match the points with H_2S (solid symbols). Thus, the influence of H_2S on the equilibrium curves of the gas streams is negligible.

3.3 Influence of N_2 on the natural gas

Although nitrogen does not interact with sulfur, as demonstrated by the null interaction coefficient

between nitrogen and sulfur (Pack, 2005), the presence of N_2 changes the properties of the gas mixture, which influences the estimate of S_8 equilibrium curves in the gas streams. This situation occurs because the binary interaction parameters between N_2 and the other components are not null (Pack, 2005). Thus, simulations with and without N_2 were performed using two compositions from Table 1. The first simulation was performed using the natural gas stream from the Field-School Project (low N_2 fraction), and the second simulation was performed using the natural gas from the Amazonas field (very high N_2 fraction), as shown in Figure 3.

As shown in Figure 3, both curves are similar in the case of the gas stream from the Field-School Project, where the nitrogen fraction is low (3.19% in volume). Because the N_2 content removed is small (condition without N_2), its effect on the new curve after normalization was minimal. The gas from the Amazonas field has a very high nitrogen percentage (11.12% in volume), which, after being removed from the composition, resulted in a significant change in the global composition after normalization. Thus, a modification in the position of the dew point curve at high pressures was

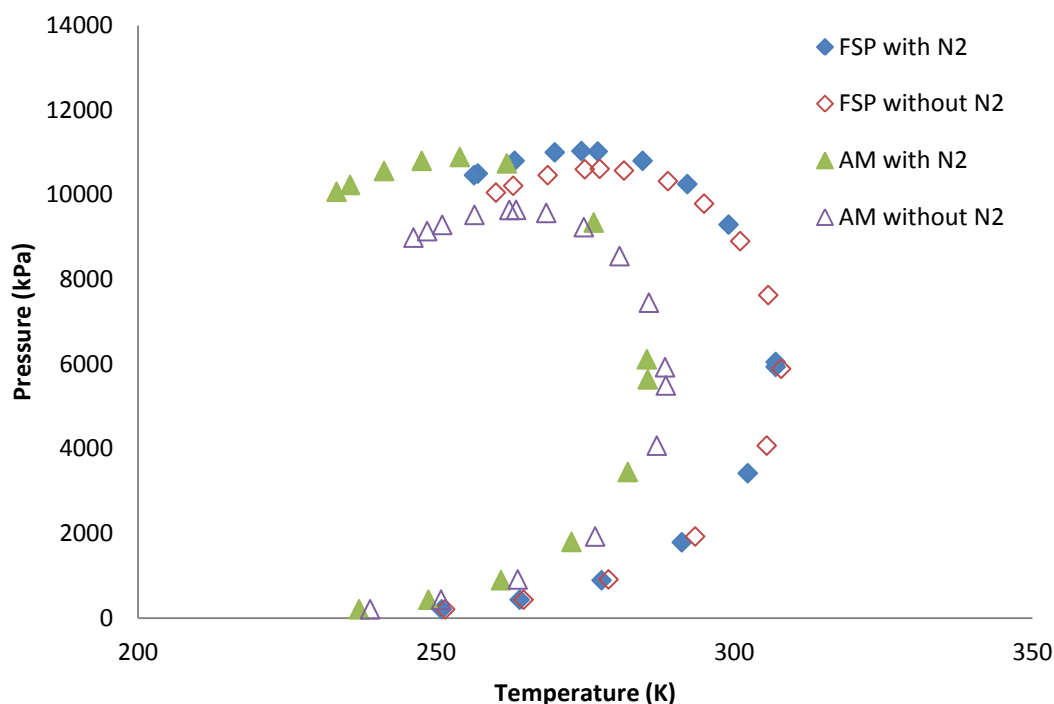


Figure 3. Comparison of the dew point curves of natural gas with and without N_2 .

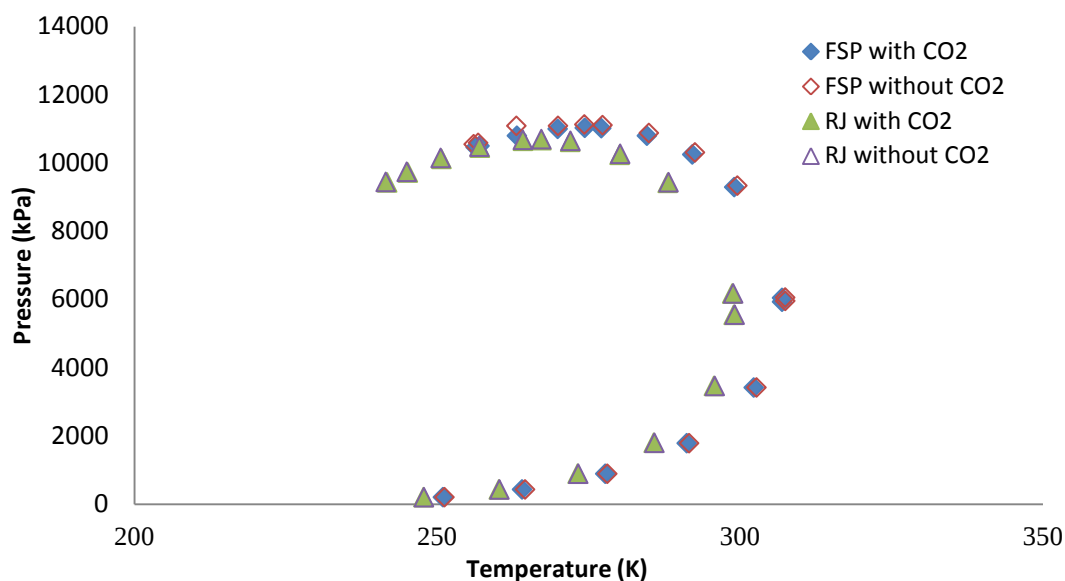


Figure 4. Comparison of the dew point curves with and without CO₂.

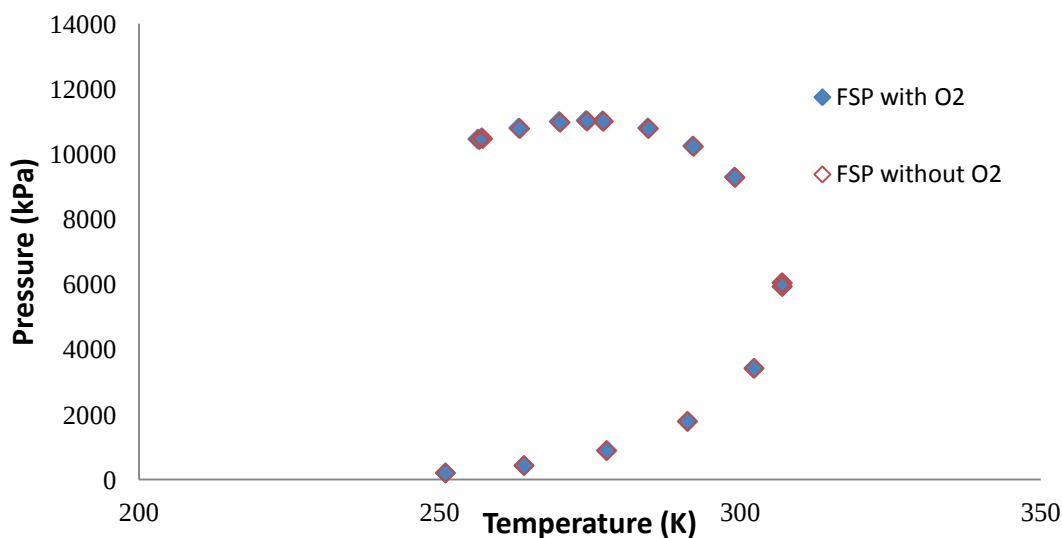


Figure 5. Comparison of the dew point curves of gas from the Field-School Project with and without O₂.

observed; however, the equilibrium region for the assumed gas transport conditions is not affected. Therefore, N₂ acts as an inert component, and the modification in the equilibrium regions may be caused by the change of properties of the gas mixture as a result of the removal of a very significant fraction of that component from the mixture.

3.4 Influence of CO₂ presence in natural gas

Carbon dioxide is also a component that is frequently detected in natural gas. For this reason,

the impact of its absence in the mixture may result in significant changes in the equilibrium regions of the gas stream. Thus, simulations with and without CO₂ were performed for the gas streams from the Field-School Project and the Rio de Janeiro field. The results are shown in Figure 4.

Figure 4 shows that CO₂ does not change the liquid-vapor equilibrium regions. Because the dew point curves are nearly identical in both compositions, the presence of CO₂ does not change the equilibrium.

3.5 Influence of O₂ on the natural gas

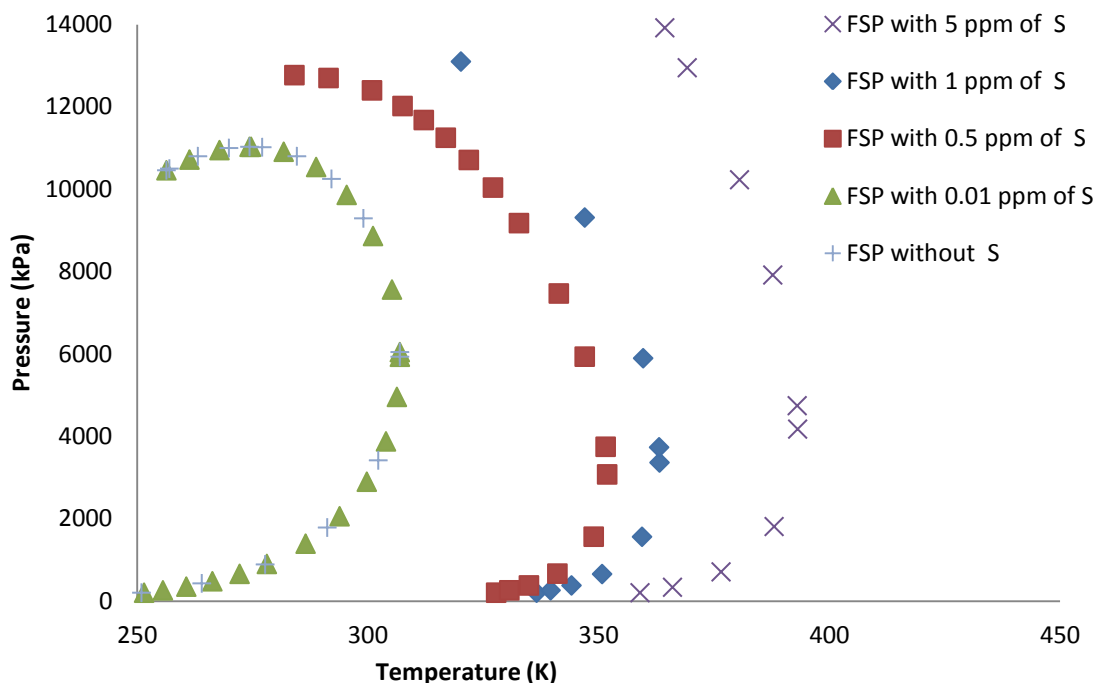


Figure 6. Comparison of the dew point curves of natural gas from the Field-School Project with different molar fractions of sulfur.

The change in the equilibrium diagrams caused by the presence of oxygen in natural gas is evaluated in this section. Because the gas stream from the Field-School Project is the only component that contains an O_2 fraction, it was evaluated with and without this component, as shown in Figure 5.

Similar to the other non-hydrocarbons evaluated in this study, Figure 5 shows that the presence of oxygen in the gas stream does not cause significant modifications in the liquid-vapor equilibrium region. Because the amount of oxygen removed from the gas stream was very small (0.33% in molar fraction), the curve did not suffer significant changes after being normalized; thus, both curves overlapped.

3.6 Influence of sulfur on the natural gas equilibrium curves

The amount of S_8 in natural gas is very low; therefore, its detection by chromatography is difficult. The concentration of S_8 in gas streams is estimated to be on the order of ppm (parts per million) or even ppb (parts per billion). To evaluate

the influence of this compound on the solubility of natural gas, different amounts of sulfur (on the order of ppm) were added to the natural gas from the FSP. Four simulations were performed with 0.01 ppm, 0.5 ppm, 1 ppm, and 5 ppm additions. For comparison, a simulation without sulfur was also performed, as shown in Figure 6.

Figure 6 shows that the presence of sulfur in natural gas, even for low concentrations, changes the gas equilibrium curves. A displacement occurs to the right due to an increase in sulfur percentages. This finding indicates that higher pressure and temperature conditions are necessary to prevent gas transport in the two-phase region. Because pressure and temperature may fall below the values shown in Figure 6 during gas flow, liquid droplets, which act as seeds for the formation and desublimation of supersaturated sulfur in the gas stream, are created.

4. CONCLUSIONS

Retrograde condensation has a higher

probability of occurrence when natural gas contains a high concentration of heavy components (C3+). Therefore, gas streams from the Espírito Santo field and from the Field-School Project are more likely to experience this phenomenon. These streams must be submitted to pressure and temperature conditions that are higher than the conditions in the simulations to prevent the formation of droplets, sulfur formation, and deposition.

Out of the non-hydrocarbon components evaluated in the study (H_2S , N_2 , CO_2 , O_2 , and S_8) that could exist in the gas stream, sulfur is the only component that may cause significant variations in the gas equilibrium region. Thus, the presence of this compound is very relevant, even at low proportions, considering that changes in the gas stream equilibrium may cause sulfur desublimation.

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