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Determination of elemental sulfur deposition rates for different natural gas compositions

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A B S T R A C T

Natural gas is increasing its share in the worldwide energy market. However, it poses several problems during transportation. The formation and deposition of elemental sulfur (S_8) in pipelines is the issue that has the greatest impact on both operational safety and maintenance costs. The formation of S_8 as a yellow powder may be influenced by changes in operational conditions, such as pressure and temperature drops, and by the composition of the natural gas stream. This study aims to examine the contribution of the nucleation phenomenon to the process of S_8 formation and deposition. Simulations were performed using the *HYSYS*® V7 process simulator, with the Peng-Robinson equation of state, and a MATLAB routine was devised to calculate the variables affecting the nucleation rate. The influence of natural gas composition on the nucleation rate was evaluated using thermophysical data of average gas streams from fields of the Brazilian states of Ceará/Rio Grande do Norte (CE/RN), Espírito Santo (ES), Rio de Janeiro (RJ) and Bahia (Fazenda Mamoeiro Field, FSP). The results show that gas composition and operational conditions may influence the amount of sulfur deposited in the pipelines, and the nucleation rate increases by reducing the temperature.

1. Introduction

Natural gas is increasing its share in the worldwide energy market because of industrial growth. Therefore, concerns about environmental risks and safety issues during its transportation and distribution must be taken into account. Several problems may occur during natural gas transportation, particularly the formation and deposition of elemental sulfur (S_8) in pipelines, which has high impact on both operational safety and maintenance costs.

Deposition of S_8 in pipelines is an increasingly observed and studied phenomenon. 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 caused by sulfur deposition and corrosion caused by perforated pipes and damaged equipment failure can seriously affect the normal operation of the field, resulting in low production or even shutdowns (Zhou et al., 2013).

Taylor and Kimtantas (2014) reported that solid elemental sulfur deposits can accumulate and cause flow constriction, thereby reducing the separation capacity of the equipment. They can plug instrumentation connections, cause poor process control, and require additional maintenance costs. Chesnoy and Pack (1997) have shown that elemental sulfur deposition onto measurement instruments may cause errors of up to 2%, or even higher in some cases, on the readings of transported gas volumes.

Pack et al. (2013) discovered that trace amounts of sulfur vapor in the gas stream could create elemental sulfur deposits in the gas stream during local depressurization, as occurs in metering devices, through the process of desublimation, and hence adversely impact the flow measurement accuracy.

According to Pack (2005) and Cézac et al. (2008), nucleation is the most probable mechanism to promote sulfur deposition in natural gas pipelines. According to these authors, the process of sulfur formation and deposition basically comprises three nucleation steps, namely particle formation, coagulation and/or condensation (particle growth), and deposition.

Zhu et al. (2011) concluded that temperature is the dominant

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parameter affecting condensate formation, whereas pressure is the dominant parameter for desublimation. In general, natural gas transportation systems operate with high flow rates, low temperature drops (due to thermal insulation) and high pressure drops (because of turbulent flow). Unless there is a sudden local temperature drop in the system, pressure variation seems to be an important parameter to describe the deposition mechanism. Thus, the mechanism of elemental sulfur deposition via nucleation and desublimation seems to be more probable.

Studies by Pack et al. (2012) validated by actual data on the deposition locations of elemental sulfur in pipelines show that flow dynamics in pipelines with “T” junctions may be an important parameter affecting preferential deposition in specific locations such as valves.

The problem has become more evident as natural gas consumption has increased, and has created significant operation and maintenance problems, resulting in high costs for the industry. Thus, the understanding of the problem and the consequent search for a solution are very important for the operation of natural gas transportation systems. Solving the problem can help to reduce maintenance costs and lessen the need for internal equipment inspections.

Nucleation has been mentioned as one of the factors that may contribute to sulfur formation and deposition (Pack, 2005; Cézac et al., 2008). However, studies on the nucleation process are still just beginning, and more research is needed. Therefore, investigating the mechanism of elemental sulfur formation is part of the objective of this work, and the aim is to better understand the contribution of the nucleation phenomenon to the process of S_8 formation and deposition.

2. Methodology

The simulations in this work were performed using the *HYSYS*® V7 process simulator, using the Peng-Robinson equation of state, and a MATLAB® program version R2010a was used to determine the nucleation rate. The methodology used for the simulations in the *HYSYS*® was the same used by Pack (2005). Information about the operational conditions of the Fazenda Mamoeiro Field, which belongs to the Field-School Project (FSP) of the Federal University of Bahia, allowed the simulations to be performed using actual parameters, such as natural gas composition, operating pressure and temperature conditions. The influence of natural gas composition on the homogenous nucleation rate was evaluated using thermmophysical data of average gas streams produced in the fields of the Brazilian states of Ceará/Rio Grande do Norte (CE/RN), Espírito Santo (ES), Rio de Janeiro (RJ) and Bahia (Fazenda Mamoeiro Field, FSP), as shown in Table 1.

Nucleation in natural gas transport is the process by which small nuclei grow and disperse, until they reach a certain size (critical nucleus) that enables the continuous growth of crystals. The nucleation process is a microscopic phenomenon that involves from tens to thousands of molecules, so it is difficult to observe it experimentally in pipelines.

Table 1
Composition of natural gas samples used in the simulations

Composition (% vol)	CE/RN	ES	RJ	FSP
Methane	74.53	88.16	79.69	69.79
Ethane	10.40	4.80	9.89	14.33
Propane	5.43	2.75	5.90	6.24
i-Butane	0	0	0	1.15
Butane	2.81	1.55	2.13	1.83
Pentane	1.30	0.44	0.77	1.14
C6+	1.40	0.44	0.44	0.49
Nitrogen	1.39	1.62	0.80	3.19
CO_2	2.74	0.24	0.50	1.51
O_2	0	0	0	0.33
H_2S (mg/m³)	1.50	7.50	6.70	7.60

Source: Vaz et al. (2008), modified.

Zhu et al. (2011) showed that the precipitation of elemental sulfur does not occur immediately at the point in the pipeline where the gas stream flows. At this point, the initial concentration of sulfur in the vapor phase reaches the maximum solubility in natural gas. A limit of this barrier, which is controlled by the Gibbs free energy, has to be overcome to form a critical nucleus, based on the Classical Nucleation Theory. The nucleation rate can be obtained from the combination of Eq. (1)–(5) according to Turk (2000):

$$J = Ke^{(\frac{-\Delta G}{k_B T})} \tag{1}$$

where J is the nucleation rate ($cm^{-3}\ s^{-1}$); K is the pre-exponential factor ($cm^{-3}\ s^{-1}$); ΔG is Gibbs free energy (J); k_B is the Boltzmann constant (J/K); and T is the temperature (K).

The Gibbs free energy is a state function which depends only on the initial and final states. Enthalpy and entropy values of the initial and final states can be obtained from *HYSYS*®, together with information on natural gas composition, pressure and temperature. Using these values calculated for the gas streams from the desired fields, the variation of the Gibbs energy can be obtained from Eq. (2):

$$\Delta G = \Delta H - T\Delta S \tag{2}$$

where ΔG is the change in Gibbs free energy (kJ/kg); ΔH is the change in enthalpy (kJ/kg); ΔS is the change in entropy (kJ/kg K).

The pre-exponential factor of Eq. (1) is given by:

$$K = \theta \alpha_c v_s N^2 [\frac{2\sigma}{k_B T}]^{\frac{1}{2}} \tag{3}$$

where Θ is the non-isothermal factor (=1 for diluted mixtures); α_c is the condensation factor (m/s); v_s is the solute's molecular volume (m³); N is the number of condensable molecules (cm^{-3}); and σ is the solute's interfacial tension (N/m).

The solute's molecular volume can be calculated for each point as a function of temperature, according to Eq. (4):

$$v_s = \frac{1}{[M(3 - 2(\frac{T}{T_b}))^{0.31} N_A]} \tag{4}$$

where M is the molar volume of sulfur (mol/m³); N_A is Avogadro's number (mol^{-1}); and T_b is the bubble point temperature (K).

The number of condensable molecules is calculated by Eq. (5):

$$N = \rho_M y_E N_A \tag{5}$$

where ρ_M is the density of the mixture (mol/cm³); and y_E is the solute's molar fraction under the extraction conditions.

The interfacial tension of sulfur can be expressed by Eq. (6) according to Zhu et al. (2011):

$$\sigma = P_c^{2/3} T_c^{1/3} [0.1207(1 + \frac{T_{br} \ln P_c}{1 - T_{br}}) - 0.281](1 - T_r)^{1.222} \tag{6}$$

where P_c is the critical pressure (MPa); T_c is the critical temperature (K); T_{br} is the reduced bubble point temperature; and T_r is the reduced temperature.

The mass of sulfur that can be deposited through the nucleation/desublimation process at a certain point, based on the rate of nuclei formation, can be obtained using Eq. (7) according to Pack (2005):

$$m = n.\ MM \tag{7}$$