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Comparison of different processes for preventing deposition of elemental sulfur in natural gas pipelines: A review



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1. Introduction

ABSTRACT

The presence of S_8 in natural gas streams has caused many problems at the delivery points and measuring equipment. There are many treatment processes, including absorption, adsorption, membranes and conversion processes. In this work, a literature review was carried out on the main methods available for removal of sulfur compounds from gas streams as well as an analysis of the feasibility of its application in pipelines. The results showed that, due to the complexity of the processes and to the costs involved in implementation and maintenance, the mechanisms of control by adsorption are the most attractive for use in pipelines.

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Natural gas is a fossil fuel that is gaining an increasingly significant portion of the global energy matrix. This change is due to the technical and economic benefits provided by the use of this energy source. Natural gas is cheaper than other sources of fossil fuels and reduces the costs associated with maintenance. As for the environmental aspects, the use of natural gas as a form of energy brings benefits such as reductions in sulfur dioxide (SO₂), nitrogen oxides (NO_x), particulate matter and carbon dioxide (CO₂).

Natural gas consists of a mixture of light hydrocarbons that, under normal pressure and temperature conditions, is in gaseous state. According to Lopes (2003) natural gas is composed predominantly of methane (CH₄), ethane (C_2H_6), propane (C_3H_8) and, in smaller proportions, other higher molecular weight

hydrocarbons. It may also have low levels of contaminants such as nitrogen (N₂), carbon dioxide (CO₂), water (H₂O) and sulfur compounds such as hydrogen sulfide (H₂S), mercaptans (RSH), carbonyl sulfide (COS), carbon disulfide (CS₂) and elemental sulfur (S₈).

In the production and transportation of natural gas, several problems may occur, among which the formation and deposition of elemental sulfur is one of the most widely observed. Santos et al. (2013) stated that the formation and deposition of S_8 in pipelines can lead to various problems that affect safe transport from the production in the wells to the processing of the natural gas. According to Zhou et al. (2013), the pipe blockage caused by sulfur deposition and the corrosion caused by perforated pipes and damaged equipment can seriously affect the normal operation in the field, resulting in low production or even shutdowns.

Pack et al. (2013) concluded that the presence of traces of sulfur vapor in the gas stream could lead to the formation of elemental sulfur deposits by desublimation in the metering devices during the depressurization process. Chesnoy and Pack (1997) and Pack et al. (2012) have shown that elemental sulfur deposition onto measurement instruments may cause errors of up to 2%, or even higher in some cases, in the readings of transported gas volumes.

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Menezes et al. (2014) showed in his research that an error of 2% in the measurement of the volume traded can cause losses of extremely significant revenues for the company when large volumes of natural gas are transported, and the company may suffer financial penalties from the regulatory agency, depending on the country where the gas transporter carries out its activities.

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.

Several studies have been conducted to investigate the mechanisms of formation and deposition of elemental sulfur in natural gas pipelines. According to Pack (2005) and Cézac et al. (2008), nucleation is the most probable mechanism promoting sulfur deposition in natural gas pipelines. According to these authors, the processes of sulfur formation and deposition essentially comprise three nucleation steps, namely particle formation, coagulation and/ or condensation (particle growth), and deposition.

Santos et al. (2013) reported that the formation of yellow powder, also known as elemental sulfur, can be influenced by changes in operating conditions such as pressure and temperature drops, as well as the gas composition and additives used during transport in pipelines. These authors constructed phase diagrams for various compositions of natural gas using the HYSYS[®] process simulator, and they showed that the phase equilibria is best represented by the state Peng-Robinson equation. Moreover, the results showed that nucleation and desublimation are the most likely mechanisms that lead to the formation and deposition of elemental sulfur.

Serin et al. (2005) studied the process of expansion of natural gas by means of a flash to study the sulfur desublimation process. The authors modeled the phenomenon and conducted an experimental procedure that allowed the determination of the mass of sulfur deposited depending on the gas flow rate. Thus, the results obtained by the modeling and the experimental values for the deposited sulfur helped confirm the hypothesis of desublimation.

Zhu et al. (2011) concluded that temperature is the dominant parameter affecting condensate formation, whereas pressure is the dominant parameter for desublimation. In general, natural gas transportation systems operate under conditions of 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 for describing the deposition mechanism. Thus, the mechanism of elemental sulfur deposition via nucleation and desublimation seems to be more probable. Cézac et al. (2008) stated that the desublimation occurs due to temperature reduction at pressure drop points where the final temperature is below the temperature of the triple point of sulfur (368.5 K). Therefore, the sulfur present in the gas stream is converted directly from the gaseous phase to the solid phase, and it deposited downstream of pressure reduction equipment.

The solubility of sulfur in the gas stream is directly influenced by temperature, pressure and gas composition. Sun and Chen (2003) evaluated the influence of pressure and temperature on the solubility of sulfur with different gas compositions, and they concluded that the temperature has greater influence on the solubility than the pressure. Cézac et al. (2008) found that, in the processed gas under the conditions of transport, the solubility of sulfur in the gas is very low, less than 0.005 mg/m³. This justifies the fact S₈ deposits occur even when the concentration of sulfur in the gas stream is very low.

Santos et al. (2015) studied the influence of the amount of sulfur present in the vapor phase in the gas stream using the gas

equilibrium diagrams. Four simulations were performed using the HYSYS[®] process simulator and the Peng-Robinson Equation of State. Simulations were performed with added sulfur contents of 0.01, 0.5, 1 and 5 ppm in the current natural gas of the Field-School Project of the Fazenda Mamoeiro field in the state of Bahia, Brazil. The results showed that, even at low concentrations, the presence of sulfur modifies the equilibrium diagrams, requiring higher temperatures for maintaining equilibrium when the concentration of S₈ in the gas stream increases.

In Brazil, for delivering natural gas to the customer, it is necessary that existing contaminants are within an acceptable level determined by the National Agency of Petroleum, Natural Gas and Biofuels (ANP). According to Santana and Machado (2014), the maximum level of sulfur compounds allowed by the ANP in the natural gas delivered to the customer is 70 mg/m³. In other countries, this maximum level is also stipulated in their legislation. According to Lopes (2003) in the United States, the H₂S content is often limited to 4 ppmv. There are levels specified as low as 1 ppmv in some European countries. The maximum total sulfur content, including carbonic sulfides, disulfides, etc., usually has contents ranging from 10 to 20 ppmv.

The aforementioned studies show that the mechanism of formation of elemental sulfur, as well as the problems caused due to deposition, are well documented in the literature. Thus, it is evident that studies are needed with the goal of searching for alternatives that can eliminate and/or reduce the presence of this compound. Worldwide, there are a number of studies and patents that have been developed for use in removing sulfur compounds in natural gas streams. The vast majority of these processes have been developed for use in Natural Gas Processing Units (NGPU's). The goals of this study are to carry out a literature review on the desulfurization processes of gaseous streams and to analyze the feasibility of their application in pipelines as an alternative to preventing the formation and deposition of S_8 in transmission lines, control equipment and measurement devices.

2. Materials and methods

The methodology used in this work was to conduct a literature review using the main portals and patent search banks on methods of gas stream desulfurization. The research portals used included Science Direct, Periodic Capes, Scopus and Google Scholar for scientific articles and the National Institute for Industrial Property (INPI) and World Intellectual Property Organization (WIPO) for the patent search. The keywords used in searches were as follows: desulfurization methods, removal of sulfur, natural gas, absorption, adsorption, membrane, and sulfur compounds conversion processes.

Silva Filho (2013) stated that the most important processes for removing H_2S from gas streams were proposed by Kohl and Nielsen (1997) and can be grouped into liquid absorption, adsorption on solids, permeation through membranes, and conversion. Szarblewski et al. (2012) grouped the sulfide removal processes of hydrogen into in three principle approaches: chemical, physical and biological.

3. Literature review

From the literature, the main processes that were found consist of technology to be employed in NGPUs, the so-called desulfurization units. These technologies most often are employed to remove H_2S and recover elemental sulfur from gas streams. According to Tagliabue et al. (2009), gas treating technologies can be roughly divided into two main categories: (i) separation, with contaminant concentrations of 10 wt% or higher in the feed; and (ii) purification, with contaminant concentrations less than approximately 3 wt% in the feed.

According to Santana and Machado (2014), methods for H₂S removal may be grouped into two categories: physical and chemical methods, such as dry chemical adsorption (iron oxides, activated carbon, etc.) or chemical absorption of oxidants, alkaline solutions and chelated metals; and biological methods such as biofiltration with microorganisms.

According to Silva Filho (2009), over thirty processes are currently available for removing H_2S from gas streams. The author states that, although the choice of the process is related to the concentration of this contaminant in the feed stream, one should take into account factors such as the operating conditions of pressure and temperature, the selectivity required for removal of H_2S , environmental regulations, and sales specification. According to Rahimi et al. (2015) process parameters, such as composition conditions or temperature and pressure at the inlet and outlet of the gas stream, will affect the choice of the method of removal of sulfur compounds. According to Martin (2008), though there are many technologies available for removal of hydrogen sulfide, it is hard to find a way that is inexpensive and exhibits good efficiency in the removal process.

Tennyson and Schaaf (1977) cataloged a number of processes that can be used in the removal of H_2S from natural gas. These authors prepared a guide that can be used for selecting the process to be used in the treatment, as shown in Fig. 1.

As seen, there are a variety of methods for removing H_2S from gas streams. Thus, the analysis of these methods as alternatives for use in pipelines will be conducted in accordance with the classification proposed by Kohl and Nielsen (1997).

3.1. Absorption processes in liquids

The absorption of H_2S across the liquid consists of a process that involves the transfer of a component present in the gas phase (absorbate) to the liquid phase (stripping) through a boundary phase.

Absorption of acid compounds in gaseous streams by the use of solutions has been studied. The use of processes through mixing solutions (mixtures of water and amine), such as Sulfinol, Ucarsol, Flexsorb, and Optisol, was proposed by Ballard (1986). Chen et al. (2001) studied the feasibility of removing H₂S from gas streams through experiments conducted in a pilot plant using aqueous solutions of NaOCl/NaOH packaged in a gas scrubber. The results showed an efficiency of 99.2% H₂S removal for a gas flow rate of 790 lb ft²-hr and a liquid-gas ratio of 5.06. Lopes (2003) and Silva Filho (2009) conducted studies using an absorption column filled with Raschig rings, with a microemulsion composed of dodecylamine chloride as the adsorbent material, for removal of H₂S from natural gas streams. The results showed that the microemulsion exhibited a significant absorption capacity compared with other H₂S removal processes. Maat et al. (2005) conducted experimental studies of desulfurization of gas streams using an aqueous solution composed of iron sulfate II (FeSO₄), zinc sulfate (ZnSO₄) and copper sulfate (CuSO₄) as a washing liquid. The experimental results showed that the proposed process can efficiently remove H₂S when the three solutions were used as an absorption medium. Maat et al. (2007) conducted experimental and theoretical studies of desulfurization processes in gas streams using aqueous solutions of copper sulfate (CuSO₄) as a wash liquid, and they used a model proposed by Al-Tarazi et al. (2004), which is a simplified model that takes into account an instantaneous irreversible reaction, to determine the rate of absorption of H₂S in the aqueous solution of CuSO₄. The comparison between predicted and experimental results showed that the simplified model was able to determine the absorption rate of H₂S in CuSO₄ for industrially relevant conditions, whereas the model proposed by Al-Tarazi et al. (2004) did not show good agreement. Vakili et al. (2012) studied the process of removal of hydrogen sulfide of gas streams using an aqueous solution of iron sulfate $(Fe_2(SO_4)_3)$ as the absorbent liquid. The results showed that, at high pressure and low temperature conditions, the process has a higher efficiency, and an optimal concentration (lower) of Fe₂(SO₄)₃ should be used in the process. Silva Filho (2013) performed experimental studies to measure and model the mass transfer and the kinetics of H₂S removal reactions from natural gas flows through packed column absorption. Aqueous solutions of sodium hydroxide, copper sulfate, ferric chloride, zinc chloride, potassium chromate, and manganese sulfate were used, with all solutions at low concentrations on the order of 10 ppm. The results showed that the rate of removal is greater for NaOH, although the use of CuSO₄ and FeCl₃ also yielded good removal efficiency.

Mixtures of amines are also seen as having potential for the



Fig. 1. Guide for selection of processes for removal of sulfur from gas streams. Modified from Tennyson and Schaaf (1977).

removal of H₂S from gas streams. Lu et al. (2006) conducted experimental studies of the H₂S removal process of gas streams using a mixture of methyldiethanolamine (MDEA) and 2tertiarybutylamino-2-ethoxyethanol (TBEE) and maintaining the conditions of atmospheric pressure and constant fluid flow. The results showed that the H₂S removal efficiency for the mixture was higher than that obtained using only the MDEA solution. Furthermore, regeneration of the mixture was easier than for the MDEA solution. Godini and Mowla (2008) investigated, in theoretical and experimental studies, the simultaneous absorption of H₂S and CO₂ using a packed column with a solution of monoethanolamine (MEA). A theoretical mathematical model, using the theory of two films to model mass transfer, was proposed to investigate the performance of H₂S and CO₂ absorption by MEA solution. The results showed that the absorption efficiency could reach approximately 20% when the liquid-gas ratio is appropriately manipulated. The experimental and calculated data were compared, and the model was able to predict the influence of different parameters on the absorption, with the following maximum errors: 7% for bed size, and 14% and 6% for the effects of pressure in terms of absolute and relative efficiency, respectively. Flare et al. (2009) conducted experiments to determine the reduction in the H₂S content in biogas streams using a process of absorption with chemical reaction with a solution of Fe/EDTA (iron/ethylene diamine tetra acetic acid). Experimental tests were performed at 25 °C while varying the solution flow rates in the range of 22-250 mL/min and using a gas flow rate of 265 mL/min. The results showed that the optimal ratio of L/G for the total removal of hydrogen sulfide must be equal to or greater than 0.46 for biogas concentrations and Fe/EDTA in the interval investigated. Koto (2014) developed simulations of the process of absorption by amines for removal of CO₂, H₂S and other sulfur compounds from a liquefied petroleum gas plant (LPG). The results of the properties of the sweetened gas stream show that virtually the entire contents of H₂S and CO₂ from the feed stream were removed, which shows that the process is really efficient. Zhang et al. (2010) developed a new solvent, called XDS, for removal of H₂S, organic sulfur and acidic compounds from natural gas streams without processing. The results showed that the new solvent has good selectivity for organic sulfur compared with the solvent MDEA (methyldiethanolamine), which is conventionally used in industry. The rate of removal of organic sulfur by the new solvent could reach up to 93.7%, whereas the value for MDEA was approximately 30%.

3.2. Adsorption processes in porous solids

The desulfurization of gas streams by adsorption is a process where molecules of sulfur compounds (adsorbate) are retained by physical or chemical forces existing on the surface of a porous solid (adsorbent). Accomplishing the removal of the sulfur compounds from the gas stream requires the construction of a filling column or sieve tray covered with the adsorbent material. The adsorbents are materials that must have a large surface area per unit weight because the degree of adsorption depends on temperature, pressure and the surface area of the material. When the medium adsorbent is saturated with the acid gases, it must be replaced or regenerated to maintain system efficiency.

Iron oxide and zinc have been used in the removal of sulfur compounds from gas streams. According to Lopes (2003), the Sulfatreat process uses impregnated iron oxide on a porous solid material, where the adsorption columns are filled with this material for selective removal of hydrogen sulfide (H₂S) and mercaptans (RSH) present in natural gas. Sekhavatjou et al. (2014) evaluated the performance of zinc oxide and iron nanoparticles on two particle sizes as the absorbent of sulfur compounds in natural gas (H₂S, COS,

methyl mercaptans, ethyl mercaptans, dimethyl sulfide and carbon disulfide) by a process of oxidation. The standard gas with sulfur components passed through a glass column filled with the adsorbent material (at 25 °C and 15 psia) and connected to a gas chromatograph. The results showed that the reduction in size of the iron oxide particles (from 0.140 μ m to 20 nm) resulted in increased sulfur removal rates of 37.9–63.1% for all gas components.

Silveira (2006) conducted an experimental procedure using the ion exchange resins MN-202 (basic polystyrene and divinylbenzene), A-850 (acrylic base and divinylbenzene functional group quaternary ammonium) and A-847 (acrylic base and divinylbenzene and tertiary ammonium functional group) for removal of H₂S from natural gas. The results showed that, for the A-847 resin compared with Sulfatreat under the same experimental conditions, the performances in terms of retention time and absorption capacity were similar.

Studies of the use of zeolites and compounds of mesoporous silica for the removal of sulfides from gas streams were conducted. Melo et al. (2006) conducted studies of the use of Zeolite 13X and Zinox 380 as H₂S adsorbents with natural gas in an adsorption column at 25 °C. The results revealed that both studied materials can be used as adsorbents for H₂S in natural gas, whereas the zeolite 13X showed better adsorption capacity than Zinox 380 at 25 °C. Ko et al. (2007) studied the removal of sulfur compounds such as tetrahydrothiophene (THT) and tert-butylmercaptane (TBM) from gas streams using silver nitrate impregnated on Beta zeolite (BEA), mesoporous silica MCM-41 and SBA-15 (AgNO₃/BEA, AgNO₃/MCM-41, AgNO₃/SBA-15) as adsorbents. The results showed that, although the BEA zeolite had a lower pore volume and a smaller surface area compared with MCM-41 and SBA-15, the sulfur adsorption capacity of AgNO₃/BEA was higher than those of AgNO₃/ MCM-41 and AgNO₃/SBA-15. Ryzhikov et al. (2011) studied the adsorption of methyl mercaptans and carbonyl sulfide present in natural gas using zeolite metal exchanges (NaX, CsNaX, CaX, MgNaX, Bax, ZnNaX, NiNaX, NaY, CSY and NiY) and double layered hydroxides (LDHs) comprising $NO_3 - M^{II}/AI$ LDHs ($M^{II} = Mg$, Zn or Ni) at atmospheric pressure and at a temperature of 25 °C. The results showed that the affinities of both sulfur compounds were higher for zeolites than for LDHs. Furthermore, it was concluded that the CH₃SH adsorption capacities of zeolites exchanged with metal decreased in the sequence NaX > CaX > MgNaX > ZnNaX > Bax > NiNaX > NaY > CSY > CsNaX > NiY. Ratnasamy et al. (2012) conducted studies of an adsorbent based on zeolite metal exchange (Ca-X and Na-X) and mixed metal oxides (Cu-Mn and Fe-Mn) supported on alumina and on the process conditions for removal of sulfur compounds (H₂S, dimethyl sulfide (DMS), carbonyl sulfide (COS), mercaptans ethyl (MS), and tertiary butyl mercaptan (TBM) of natural gas. The authors concluded that, when the process conditions were equal to 38 °C and 15 psig, with a space velocity of the gas of 6000 h⁻¹, a sequential bed system consisting of Ca-X followed by Fe-Mn oxides on alumina had a significant desulfurization capacity. Oliveira et al. (2014) conducted experimental studies of the adsorption of the mixture $CH_4 + CO_2 + H_2S$ in zeolite NaY at 30 °C and pressure conditions of 1, 20 and 50 bar. The results obtained by the Langmuir model showed maximum adsorption capacities of 3.77, 7.06 and 7.02 mol/kg for CH₄, CO₂ and H₂S, respectively. This showed that the zeolite NaY is seen as technically promising for the separation of methane from acid compounds.

Cui et al. (2009) investigated the use of an activated commercial carbon (Calgon XC plus 12X30) modified by oxidation and impregnation of materials as the adsorbent for the removal of hydrogen sulfide (H_2S), methyl mercaptans (MM) ethyl mercaptans (MS), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), tetrahydrothiophene (THT) and ethyl disulfide (EDS) chains of synthetic

natural gas. The results showed that carbon activated with Cu and Zn had a higher H_2S removal capability, whereas carbon impregnated with Fe was more efficient for the removal of DMS (the most difficult S compound to remove), and oxidized carbon with HNO₃ was the best for the removal of THT. Boulinguiez and Cloirec (2009) conducted studies of the removal of THT from natural gas streams in fuel cells using three types of activated carbon as adsorbents, namely two granular materials (GAC) and a cloth fiber material (ACFC). The results showed that ACFC exhibited a higher adsorption rate than the GAC. Furthermore, the Langmuir equation was applied, and the parameters obtained by the model showed that ACFC had the highest adsorption capacity for the magnitude of the THT concentration in natural gas.

Batista (2012) studied the synthesis of arrays of commercial white clay base composed of a large amount of kaolin clay and mixed with a percentage of iron oxide as the adsorbent for H_2S from natural gas. Based on gravimetric results, the array that had the highest adsorption capacity was replaced with Ni² ⁺ ions, obtaining a H_2S removal performance of 11.13 mg/g matrix, followed by the matrix coated with rhodamine B, which reached 10.13 H_2S mg/g matrix.

3.3. Permeation processes in membranes

The separation processes by membranes are based on gas diffusion. The membranes used consist of thin barriers formed by polymers that allow the passage of certain substances to the detriment of the others. The surface of the membrane consists of thousands of capillaries through which the gases diffuse. Regarding the removal of acid gases from the natural gas stream, CO₂ and H₂S will permeate the membrane at a higher speed than the hydrocarbons due to differences in solubility and the diffusion capacity of these gases through the membrane.

The use of hollow fiber membranes is a technology that has been studied for the removal of sulfur compounds from gas streams. Jefferson et al. (2005) investigated the use of a gas absorber, comprising a hollow fiber membrane of polypropylene and a dilute NaOH solution, for removing H₂S from a synthetic gas $(O_2 + N_2)$. The experiments showed that this technology can effectively remove H₂S with 96% efficiency at a pH of 13, a gas/liquid ratio of 50 and concentrations of contaminants of up to 2000 ppmv. Hedayat et al. (2011) investigated the simultaneous absorption of H₂S and CO₂ using a hollow fiber membrane with PVDF contact modules (vinylidene fluoride) and polisulfano (PSF) with MDEA solutions and mixtures of MDEA/DEA, and MDEA/MEA as liquid absorbents. The results showed that, when the objective of the system is to achieve high selectivity of H₂S, it is preferable to use a poor solution of MDEA. However, when a high removal efficiency is required, it is better to use a mixture of MDEA solution with DEA. Chenar et al. (2011) investigated the use of two hollow fiber membranes, polyimide (PI) and polyphenylene oxide (PPO), which are commercially available for the separation of mixtures of H₂S/ CH₄ in various concentrations of hydrogen sulfide in a series of experiments on a scale bench. The results showed that the separation factors for H₂S/CH₄ were 6 and 4 for the PI membranes and PPO, respectively. They also found that, despite the fact that the increased temperature increased the permeability of the components, the separation factor remained the same. Mahdavian et al. (2012) theoretically studied the use of methanol solvent for physical adsorption of H₂S and CO₂ from a mixture containing CO₂/H₂S/ CH₄ in a hollow fiber membrane of a gas-liquid absorber (HFMGA). The relative rate of absorption of H₂S using methanol as an absorbent was in the range of 2.9-3.75 compared with the case of water as the absorbent. This shows that the methanol solvent may be used successfully in the absorption of these components in the membrane gas absorber.

Lee et al. (2006) developed a new liquid membrane of poly vinylidene fluoride (PVDF) for removing CO₂ and H₂S from natural gas. The results showed that the new membrane showed excellent stability under severe operating conditions and exhibited extremely high permeability coefficients for CO₂ and H₂S and high selectivity for the systems H₂S/CH₄ and CO₂/CH₄. Park et al. (2009) developed a new method for the removal of acidic gases from crude natural gas with the use of room temperature ionic liquids (RTILs) and polymers, as well as new supported ionic liquid membranes (SILMs). PVDF and BMImBF₄ were used as polymer materials for the membrane and RTILs, respectively. The results showed that the permeability coefficient of gas increased substantially with increasing RTIL content in the membrane, especially for acid gases. Furthermore, they concluded that, as the temperature increased, the gas permeability coefficient increased, whereas selectivity decreased due to the increased mobility of the membrane.

Tao et al. (2007) performed a literature review regarding the desulfurization of gas streams by membranes processes. The authors concluded that the process combined with a catalytic membrane reactor and microwave irradiation can be integrated, becoming promising for desulfurization of natural gas on a large scale and with high efficiency. Rongwong et al. (2012) studied the simultaneous absorption of H₂S and CO₂ from biogas using a capillary membrane contactor. The absorbents used were water and MEA solution, and the composition of the synthetic biogas was 250-1000 ppm of H₂S and 20-40% of CO₂ and CH₄. The experimental results showed that removal of H₂S from the CH₄ stream using MEA solution was greater than when water was used as the absorbent. Furthermore, due to the large difference in the concentration of contaminants in biogas, the H₂S absorption is strongly influenced by the presence of CO₂. Costa (2014) tested the use of a bio-silicone membrane for the removal of hydrogen sulfide from the biogas. The biomembrane showed higher H₂S removal efficiency, reaching an overall removal efficiency of 55-70%. After 3 h, the experiment reached a final H₂S concentration in the biogas of 1.5-1.8 mg/L.

3.4. Conversion processes

According to Abedini et al. (2010), the Claus process is the most known and used in the industry for over 100 years (patented in 1883). According to Afonso and Pereira (2010) and Mokhatak and Poe (2014), elemental sulfur in the original Claus process was produced by the partial oxidation of H₂S in a single step over a preheated catalyst bed. After 1940, there was a very important change in the Claus process that allowed the best recovery of sulfur. In the modified Claus process, the sulfur recovery occurs in two steps: the first thermal and the second catalytic. In the thermal section, air is added in sufficient quantities to oxidize one third of the H₂S to SO₂. In the second step, the remaining H₂S reacts with the SO₂ to form elemental sulfur vapor, a non-aggressive substance from the environmental point of view.

Ball et al. (2007) evaluated the bacterial oxidation potential of the hydrogen sulfide as a method of purification of acid gas streams. The authors used a continuous culture of Chlorobium limicola, which made it possible to obtain high oxidation efficiencies of soluble and gaseous sulfides, with an oxidation efficiency for gaseous sulfides exceeding 95%.

Ma et al. (2008) studied the direct conversion of H_2S to S and H_2 using a photocatalytic reaction under visible radiation with ethanolamine as a solvent. Under room temperature conditions, the photocatalyst of Pt/CdS showed high activity in the production of hydrogen by all of the solvents using ethanolamine (MEA, DEA and TEA). The results demonstrated the possibility of direct conversion

of H₂S to H₂ and S by photocatalysis.

According to Gendel et al. (2009) the use of redox solutions mainly composed of Fe (III)/Fe (II) as a means of chemical adsorption of hydrogen sulfide is becoming an effective technique. In this system, a Fe oxidizing solution (III) is used that is capable of rapid oxidation of H_2S to elemental sulfur. After this, the sulfur may be removed by filtration or gravity.

Abedini et al. (2010) mathematically modeled and simulated, using MATLAB, the sulfur recovery process in a catalytic bed. The modeling process consisted of steps involving mass balance, energy and condensate formation. The operating conditions of the process, as well as the physical and chemical characteristics of the component, are considered in the simulations. The obtained model allows easy determination of the sulfur condensate quantity in each bed. Mahdipoor et al. (2014) investigated different methods for reheating of the Claus hydrolysis reactor in a sulfur recovery unit (SRU) using superheated steam at 260 °C and 41.5 bar. The results showed that the use of hot gas appears to be better than the other methods, especially when COS and CS₂ are the main problem in the SRU.

Sahu et al. (2011) conducted experimental studies of the use of red mud (RM), a byproduct of the alumina industry, in the removal of H_2S from gas streams. Hydrogen sulfide was removed under ambient conditions in the forms of FeS₂, FeS, calcium sulfate, sulfur, sodium bisulfite, and other minerals. The results showed that RM, a product of no commercial value, may be an alternative for removal of H_2S and hence reducing the industrial pollution in the air.

4. Evaluation of the desulfurization methods

The transport of natural gas can be achieved in liquefied or gaseous form. The most widely used form of transport is through high-pressure pipelines. The pipelines are made of successive segments of tubes connected to each other, and they can be hundreds of kilometers long, connecting the origin and destination of the natural gas. To adjust the gas delivery pressure to the customer, pressure drop points are installed along the pipelines. The elemental sulfur deposits are most commonly encountered immediately after the pressure reducing equipment as well as in places or in equipment where there is reduction in pressure and a consequent reduction in temperature, such as pressure control valves and nozzles. Thus, the evaluation of desulfurization methods of gaseous streams studied throughout this work was conducted by taking into account the feasibility of their application in pipelines as alternative solutions to the problem of deposition of elemental sulfur.

The choice of the deposition control method for S_8 must be made by taking various factors into account, such as the site of application, process complexity, technical-economic feasibility of the installation, and removal capability. As the vast majority of cases studied were designed with the purpose of application in refineries or NGPU's, many may become complex in terms of its application in pipelines. Table 1 shows a comparison of the methods studied, presenting their main advantages and disadvantages regarding their use in removing sulfur from gas streams.

From Table 1, it can be concluded that the methods for removal of sulfur compounds through absorption are not optimal for removal of elemental sulfur in pipelines. Although this process has interesting characteristics, such as high removal rates and low costs of installation and maintenance (which are extremely important parameters for choosing a desulfurization method), factors such as high L/G ratio, high consumption of energy for pumping and regeneration of the absorbent solution, as well as the complexity of the process, can impede their application.

The pipelines operate with high gas flow rates, which

sometimes can achieve flows of millions of cubic meters per day. Therefore, achieving higher L/G ratios would require very large amounts of absorbent solutions. Another problem is that the amine derivative processes can result in the appearance of insoluble precipitates, which can lead to clogging of the pipes and generation of wastes that are not environmentally friendly. This makes the operating process very complex, and the formulation costs, storage of large volumes and regenerating of the absorbent solution, as well as removing the precipitates, can make the process economically unviable.

Moreover, the removal processes of sulfur compounds of gas streams by absorption perform better when the concentration of the contaminant in the feed stream is high (Tennyson and Schaaf, 1977). In the elemental sulfur problem in pipelines, S_8 is solubilized in the gas stream transported at very low levels (ppmv or even less); thus, the absorption processes are not suitable for this scenario. However, for a scenario where gas streams have high concentrations of sulfur compounds in the feed stream and/or where gas pipelines have low transport rates, the use of absorbent solutions can be feasible.

According to the guide proposed by Tennyson and Schaaf (1977), it is clear that, in the case of elemental sulfur in gas pipelines, where the concentration of S₈ is too small, the processes of direct oxidation, molecular sieves and batch reactors are the most appropriate. Thus, from Table 1 together with the guide proposed by Tennyson and Schaaf (1977), it is clear that the adsorption processes can eliminate and/or mitigate the problem of elemental sulfur in the pipelines. These methods show good removal efficiency when the concentrations of sulfur compounds in the feed stream are low (i.e., the scenario presented by S₈ in natural gas transportation pipelines). Furthermore, adsorption processes show attractive features for pipelines such as ease of operation, continuous operation, moderate capital costs, ability to remove various sulfur species, and operating at room temperature. Although there are disadvantages such as high costs for regeneration and/or replacement of the adsorbent material, these problems can be circumvented. The choice of a material with a high capacity for adsorption of sulfur compounds on its surface area, a long time of use until inactivation, and the ability to be regenerated, makes the process viable. In this scenario, adsorbents such as zeolites, iron oxides, zinc oxides and activated carbon can be best studied for application under the working conditions of the pipelines.

The removal methods of acidic compounds from gas streams by membranes have interesting features such as simplicity, low capital and operating costs, low space requirement for operation, and low environmental impact. However, they are also not suitable for application in pipelines because, in most cases, they require the use of absorbent solutions to assist in the removal of acidic components from the gas stream by hollow fiber membranes or by the membrane itself when it is liquid. Thus, the process would become a combination of absorption solutions and membranes. As already discussed, the use of high flow rates of aqueous solutions, as well as the fact that absorption solutions show best efficiency when the concentrations of the sulfur compounds in the feed stream are high, can impair the application of the combined process in pipelines. Furthermore, the presence of sulfur compounds solubilized in the gas stream can contaminate the membrane, or the solvent may even degrade the membrane. This would result in the need to frequently replace membranes, which have high procurement costs.

The methods for converting other sulfur compounds to elemental sulfur are also not suitable for the pipeline scenario. The solution of the S_8 problem consists of removing elemental sulfur that is already present in the gas stream. In this case, the application of traditional processes such as Claus would only lead to the

Table 1

Comparison of methods of desulfurization of gas streams.

Process	Advantages	Disadvantages
Absorption	High removal capacity of pollutant gases (Kohl and Riesenfeld, 1985; Chen	High installation costs and energy costs for pumping (Kohl and Riesenfeld,
	et al., 2001; Zhang et al., 2010; Kulkarni and Shinde, 2014);	1985; Mahdavian et al., 2012);
	Possibility to regenerate the solution (Lopes, 2003; Horikawa et al., 2004;	High energy consumption for recovering the solvent (Rahimi et al., 2015);
	Gendel et al., 2009; Vakili et al., 2012; Koto, 2014);	Demand for high liquid-gas ratios (L/G) for high removal efficiencies (Chen
	Low to moderate costs for maintenance (Reijenga et al., 2008; Lasocki et al.,	et al., 2001; Godini and Mowla, 2008; Flare et al., 2009);
	2015);	Processes such as Sulfinol [®] and Flexsorb [®] require license, payment of fees and
	Easy operation of the system (Reijenga et al., 2008; Gendel et al., 2009);	royalties for operation (Lopes, 2003; Cachima et al., 2005);
	Operates at room temperature (Horikawa et al., 2004; Gendel et al., 2009).	The vast majority of processes have been developed for H_2S (Chen et al., 2001;
		Lee et al., 2006; Maat et al., 2007; Silva Filho, 2013).
Adsorption	Mechanically simple and occupies a small area (Szarblewski et al., 2012; Kohl	Very high operating costs with replacement/regeneration of the adsorbent
	and Riesenfeld, 1979);	(Fischer, 2010; Siefers, 2010);
	Efficient for low concentrations of contaminant (Boulinguiez and Cloirec,	Reduction of removal efficiency after regeneration (Abatzoglou and Boivin,
	2009; Chen, 2013);	2009; Siefers, 2010);
	Moderate capital costs (Fischer, 2010; Chen, 2013);	Some adsorbents cannot be regenerated (Lopes, 2003; Cachima et al., 2005;
	Removal capacity for different sulfur species (Ko et al., 2007; Cui et al., 2009;	Angelis, 2012);
	Ryzhikov et al., 2011; Ratnasamy et al., 2012);	Low adsorption capacity per unit area of the adsorbent (Cui et al., 2009);
	Can be used under ambient conditions (Melo et al., 2006; Ratnasamy et al.,	Requires high temperatures for regeneration of the solid adsorbent
	2012; Oliveira et al., 2014).	(Szarblewski et al., 2012).
Membranes	s Simplicity, versatility and low operating capital (Abedini and	The membranes have high cost (Reijenga et al., 2008; Amaral, 2009);
	Nezhadmoghadam, 2010; Chenar et al., 2011; Shimekit and Mukhtar, 2012);	Membranes can be easily contaminated by suspension present in the gas to be
	Demanding little space and flexibility in the process (Abedini and	treated (Reijenga et al., 2008; Amaral, 2009; Chenar et al., 2011)
	Nezhadmoghadam, 2010; Chenar et al., 2011);	Some solvents may degrade the membrane (Lee et al., 2006; Reijenga et al.,
	Low energy requirements (Amaral, 2009; Chenar et al., 2011);	2008; Amaral, 2009);
	Stability at high pressures (Shimekit and Mukhtar, 2012);	Moderate purity (Shimekit and Mukhtar, 2012);
	Less environmental impact (Shimekit and Mukhtar, 2012).	Increases the mass transfer resistance (Rongwong et al., 2012; Rahimi et al., 2015)
Conversion	Most commonly used technology for sulfur recovery (Abedini and	Process feasible only for sites with high amounts of daily removal (Li, 2008:
	Nezhadmoghadam, 2010: Mahdipoor et al., 2014: Mokhatak and Poe, 2014):	Rahimi et al., 2015):
	High removal efficiencies (Abedini and Nezhadmoghadam, 2010; Mokhatak	Traditional processes involve high temperatures (Abedini and
	and Poe, 2014; Rahimi et al., 2015);	Nezhadmoghadam, 2010; Mokhatak and Poe, 2014; Rahimi et al., 2015);
	Low chemical consumption (Li, 2008);	High cost of installation (Li, 2008; Rahimi et al., 2015);
	Small environmental impact (Ma et al., 2008; Li, 2008; Rahimi et al., 2015).	Need for an additional method for the removal of sulfur (Gendel et al., 2009).

formation of further elemental sulfur in the pipeline, which requires an additional method for removal. Furthermore, this process involves high temperatures, which would make the cost of heating the gas stream in a pipeline unfeasible. After conversion of sulfur compounds to elemental sulfur, it becomes necessary to employ an additional method for recovery of the produced sulfur. This would entail the need to build a sulfur recovery unit in the pressure reduction site (customer delivery stations), which would make the process technically and economically impossible due to high costs. Therefore, this process would only be suitable for a situation where the daily production of sulfur is large enough for it to be marketed.

5. Conclusions

In this study, a literature review was carried out on the desulfurization methods of gas streams as alternative solutions to the problem of elemental sulfur deposition at pressure drop points and in measuring equipment in pipelines. The results showed that adsorption methods are the most suitable for assisting in the removal of elemental sulfur, as they are capable of removing various sulfur species such as S_8 , even at low concentrations in the feed stream. Adsorbents such as zeolites, iron oxides, zinc and activated carbon show potential for solving the problem and should be better studied under operational scenarios associated with pipelines. The other methods evaluated (absorption, membrane separation and conversion of sulfur compounds to elemental sulfur) would not be viable when the technical and economic conditions for its application in pipelines are taken into account.

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