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Simulation and comparison of Sulfinol solvent performance with Amine solvents in removing sulfur compounds and acid gases from natural sour gas





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ABSTRACT

Natural gas issued from well production has to be treated to remove acid gases (CO₂ and H₂S) and sulfur compounds so that it meets transport requirements and sale gas specifications. Two great families of solvents are used for this kind of gas treatment: chemical and physical solvents. Ilam gas refinery (one of the main gas refineries in Iran) discharges high levels of mercaptans in the production of raw LPG and condensates, and also there are problems with sulfur compounds because of the lack of Merox unit. In this research, we carry out the simulation and study of removing acid gases (CO₂, H₂S) and sulfur compounds (methyl and ethyl mercaptans, dimethyl-sulfide, COS) with mixed solvent Sulfinol $(Sulfolane + MDEA + H_2O)$ and DGA, MDEA + AMP solvents and compare it with the present solvent MDEA. The purpose of this research is the feasibility study of utilizing Sulfinol-M solvent to replace the aqueous amine solvent in the gas sweetening unit of Ilam gas refinery. The results of the simulation show that more than 30-40% of mercaptans along with sour gas is absorbed with Sulfinol-M solvent of lower flow rate and a considerable 10–25% less energy is required for solvent regeneration; furthermore, very little waste of solvent is observed compared with amine solvents (MDEA + AMP, DGA, MDEA). Many of the process parameters are controlled more easily than amine solvents with the characteristic of the composition of Sulfinol-M compound and there will be energy and economic saving in different sections of mercaptan and acid gas absorption.

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1. Introduction

Coal, oil compounds, and natural gas contain sulfur compounds that are inappropriate in terms of environmental and processing issues. Some sulfur compounds such as COS, methyl-mercaptan, ethyl-mercaptan, and dimethyl-sulfide are unstable and toxic for industrial catalysts. Therefore, separation of gas impurities is important from different viewpoints of catalyst poisoning, safety and corrosion control, and reaching the acceptable environmental pollution limit (Mokhatab and Poe, 2012).

There are many methods for removing impurities from natural gas, of which removing impurities with chemical solvents has been used much more than other methods (more than 95%). In this method, solvents such as amines, carbonates, and special chemical

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solvents are used, among which amine solvents predominate in natural gas treating units (Mokhatab and Poe, 2012).

Acid gases (carbon dioxide and hydrogen sulphide) are removed from gas streams with absorption by a solvent. Two general classes of solvents are used: chemical and physical solvents. The former is usually an aqueous solution of an alkanol amine, which reacts chemically with the acid gases. The latter class is an organic compound, which has a strong affinity for the acid gases, without a chemical reaction taking place. Chemical solvents have the advantages of removing the acid gases to low levels at low partial pressures, losses are not serious because most of the solvent is water, and hydrocarbons are almost insoluble in the solution. On the other hand, physical solvents have the advantages of unlimited absorption out of stoichiometry, the regeneration of the solvent by the pressure reduction, and ability to remove sulfur compounds (COS and thiols) (Schäfer et al., 2002). Amine solutions are weak organic bases that can absorb gas impurities at room temperatures. Alkanolamines are nitrogenous organic materials that result from compounding special organic materials with ammonia (NH₃) and

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are classified according to the organic groups connected to nitrogen as follows:

- Primary amines such as mono ethanol amine (MEA) and diglycol amine (DGA).
- Secondary amines such as di-ethanol amine (DEA) and diisopropanol amine (DIPA).
- Tertiary amines such as tri-ethanol amine (TEA) and methyl diethanol amine (MDEA).

Amines of the first type are stronger bases compared to those of the second type and have higher tendencies to react with H_2S and CO_2 and form stronger bonds with acidic gases. Generally, alkalinity and reactivity of the first type of amines are more than the second type and those of the second type are more than the third (Mokhatab and Poe, 2012; Schäfer et al., 2002).

In addition to chemical solvents, we can use the mixture of physical and chemical solvents to remove the impurities. Acid gas and sulfur compound solubility is almost linear in physical solvents. Mixed solvents are an attempt to combine the advantages of both types of solvents. One of the first mixed solvents to be used was sulfinol, a mixture of di-isopropanol amine, sulfolane (tetramethylene sulfone (TMS)), and water (Jou et al., 1990). Later, diisopropanol amine was replaced with methyldiethanol amine (MDEA) and the solvent was called sulfinol-M (Jou et al., 1990). By using the mixture of physical and chemical solvents, we can benefit from its features in a wide range of pressures. Some of the problems with using amine solvents are as follows: impurity absorption limitation to chemical reactions' ratios, high energy requirement for regeneration, lower absorption of sulfur compounds, requirement of dimethyl-sulfide, ethyle-mercaptan, methyl-mercaptan, COS, and high wasting of such compounds. These problems can be solved to some extent with alternative physical-chemical solvents such as Sulfinol-M and Sulfinol-D (Jou et al., 1990; Badawi et al., 2008).

In Ilam gas refinery (one of the most important gas refineries in Iran), high levels of mercaptans and the lack of Merox unit in the process cause great amounts of mercaptan and sulfur compounds in raw LPG and condensates produced. In the present work, different variations on the process have been studied such as changing the solvent type from MDEA to MDEA + AMP, DGA and Sulfinol-M, evaluation of alternative energy, checking out the wasting level to remove dimethyl-sulfide, mercaptan, ethylmethyl-mercaptan, and COS. The simulation results showed that the Sulfinol-M replacement has better impacts on the process performances than the chemical solvents alone.

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The inlet gas compounds.

Industrial data	Sour gas feed to sweetening unit	
Parameter		
Gas flow rate (kgmol/hr)	6143.94	
Gas temperature (°C)	33.6	
Composition components		
CO ₂ (%mole)	3.75	
H ₂ S (%mole)	3.27	
CH ₄ (%mole)	82.67	
COS (%mole)	0.0024	
Methyl-Mercaptan (%mole)	0.1299	
Ethyl-Mercaptan (%mole)	0.0031	
Dimethyl-Sulfide (%mole)	0.0175	

2. Simulation

Amine system (MDEA 45%wt) is used in llam refinery and its gas treatment unit's feed contains high percentages of sulfur compounds and mercaptans, dimethyl-sulfide, COS, carbon dioxide (CO₂), and hydrogen sulfide (H₂S) (De Angelis, 2012). The inlet gas compounds are presented in Table 1. In this research, Aspen Plus software ver. 7.2 has been used with the thermodynamic model of ELECNRTL (Shahsavand and Garmroodi, 2010; Zong and Chen, 2011; Simoni et al., 2007). The outline of the simulation is shown in Fig. 1.

The simulation was carried out based on the removal of acidic gases from the natural gas and controlling the dew point of the water and hydrocarbons in the output gas. In the simulated process, firstly, sour gas enters the Knock Out Drum (K.O.D) to separate the suspended liquid particles, water, and heavy hydrocarbons as liquid. This flow is sent to the stabilizer unit so that hydrogen sulfide is absorbed to the sour water and its organic phase. The output gas from the top of the K.O.D enters the absorption tower to contact the acid gas with amine, which is most often divided between two towers. The gas sweetening unit of llam refinery uses MDEA with 45%wt in two parallel towers and the saturated solvent is regenerated in two other parallel towers (Shahsavand and Garmroodi, 2010).

The gas enters the contactor from the bottom of a 20 tray tower and amine enters from the top. The lean solvent enters from the top of the tower with a temperature of 50 °C higher than that of the input gas and after passing through the trays, it exits from the bottom of the tower. The output gas will be heated due to receiving amounts of the heat resulting from H₂S and CO₂ absorption. Therefore, it enters the treated gas cooler and its temperature decreases. The gas then enters the treated gas separator and the solvent is separated from the gas. To facilitate this process, treated gas water spray pump sprinkles water on to the sweet gas separator in the input line. After passing the treated gas separator, the gas enters the treated gas filter separator and all types of possible particles, solvent, and heavy hydrocarbons are separated; the gas is then ready to enter the dew point control system. The separated liquids in this filter and liquids from treated gas separator are sent to the flash drum and also the sweet gas is sent to the dehydration unit to control the dew point (Fig. 1) (Shahsavand and Garmroodi, 2010; Bolhàr-Nordenkampf et al., 2004).

3. The simulation results

The solvents and their flow rate and concentration specifications used in the simulation are given in Table 2. The specifications are chosen in a way that all mercaptans and sour gases are absorbed during the process and, indeed, energy consumption minimizes (Fahim et al., 2010). The simulation results are presented in Table 3. As can be observed, most compounds including dimethyl-sulfide, ethyl-mercaptan, COS, and methyl-mercaptan have been removed. A comparison between solvents used in the simulation is also provided. The Sulfinol-M with low flow rate shows higher performance to remove the above-mentioned compounds.

The water used to make solvents is demonstrated statistically in Fig. 2. The Sulfinol-M solvent consumes minimum water to prepare, a property which has been used in this research. By adding sulfolane to replace part of water, the amount of water to enter the gas treating unit together with the solvent decreases. Different compound absorption values by different solvents versus the number of trays in contact towers are illustrated in Figs. 3–9. As is seen, amines and the Sulfinol-M are absorbed, the performance of Sulfinol-M being more desirable.

H₂S reaction with amine needs no water; therefore, a decrease

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