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Retrofitting amine absorption process for natural gas sweetening via hybridization with membrane separation

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ABSTRACT

In chemical process industries, new external and internal conditions squeeze profit margin of conventional processes. In this challenging scenario, process retrofit is becoming a key issue for existing industrial chemical processes. Among various retrofitting designs, hybridization, which involves more than one technique by using their synergy, has good potential to overcome the limitations of the technologies involved, thus achieving cost-effective retrofit solutions. In this study, an amine absorption process, which removes acid components from natural gas, is retrofitted by adding a membrane unit(s) to sweeten a new feedstock with increased CO_2 mole fraction from 0.082 to 0.20. As the existing plant is unsuitable for this new feedstock, two retrofit options: one-stage and two-stage membrane-absorption hybrid retrofit designs are analyzed. Results suggest 27% saving for the former and 11% for the latter, in separation cost per unit feed ($/kmol) compared to building a new amine absorption plant, highlighting the attractiveness of retrofitting the existing process through hybridization. The two retrofit designs are also analyzed for processing feed with different CO_2 concentrations.

1. Introduction

An increasing demand for energy has been motivating the search for alternate energy sources across the world. Although solar panels, wind turbines and geothermal energy are developing, the major alternative energy source is natural gas (NG). According to IEA (2013), the total recoverable gas reserves currently stand at 800 trillion cubic meters (tcm), consisting of 400 tcm of recoverable conventional resource and another 400 tcm of recoverable unconventional resource. Altogether, it will last for around 250 years based on current rates of gas consumption (BP, 2013). NG needs to be transported to end users; one of the popular ways is through pipelines. However, acid gases (mainly, CO_2 and H_2S) contained in the crude NG cause corrosion to the pipelines, and so they need to be removed before transportation. Pipeline NG specifications in United States are: CO_2 < 2 mol% and H_2S < 4 ppm (Baker, 2001).

The most common technology used for acid gas removal is chemical absorption, which is based on reversible exothermic reaction of a suitable solvent with the gas stream to remove CO_2 and H_2S present. Unlike physical absorbents, water content in chemical absorbents minimizes heavy hydrocarbon absorption, making it more suitable for feed gas containing heavy (C_4^+) hydrocarbons. There are generally two categories of absorbents: potassium carbonate and amine based absorbents (e.g., mono-ethanolamine (MEA), di-ethanolamine (DEA) and methyl-di-ethanolamine (MDEA)). Potassium carbonate causes stress corrosion to the units, and also reacts with some corrosion inhibitors and causes erosion to the units. All these lead to higher capital investment than that for amine based absorbents. Hence, amine absorption process is the most commonly used acid gas removal technology. In this process, sour gas enters the absorption tower at the bottom, whilst lean amine from the stripper comes into the tower near the top. Sweet gas (with sour components meeting the pipeline specifications) leaves the absorption tower at the top, and saturated amine is sent to the stripper for regeneration.

There have been a number of studies discussing the amine absorption process. For example, Sohbi et al. (2007) explored the use of mixed amines in an industrial gas sweetening plant; their results suggest several optimal configurations for different feeds. Halim and Srinivasan (2009) proposed a simulation–optimization framework comprising HYSYS simulator and a jumping gene based multi-objective simulated annealing, to evaluate the efficacy of CO_2 removal using DEA. Plaza et al. (2010) studied several thermodynamic models in Aspen Plus for modeling amine absorption process. Loading and removal for the absorber were predicted within 6%, and average difference of 3.8% between measured and calculated values in the stripper was achieved. Abdulrahman and Albarzenji (2012) used 35 wt% DEA to treat NG containing

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5 mol% acid gas; they developed a 10-step methodology to calculate the most important design variables. Lee et al. (2013) simulated amine absorption process with different solvents. A multi-objective genetic algorithm was used to determine the best process design and operating conditions for each solvent.

In the above studies, partial pressure of acid gas was at low to moderate levels due to the inherent drawback of amine absorption process, namely, large amount of steam required for regenerating the absorbent. According to Øi (2007), energy consumption for reducing CO_2 in NG is 3.4 MJ per kg of CO_2. If the acid gas concentration is above 20 mol%, energy consumption in the amine absorption plant will be very high. Existing amine plants designed for low to moderate level of acid gas may need to be retrofitted to process feedstock with high mole fraction of acid gas. NG with high level of acid gas is regarded as low quality NG; reservoirs of such NG include South China Sea, Gulf of Thailand, Central European Pannonian basin and Australian Cooper–Eromanga basin (Grimalt and Dorronsoro, 1995). With rising energy cost, it is profitable to process such low quality NG. Further, when the gas reservoir depletes, partial pressure of acid gas can be two to three times as much as it used to be when the reservoir began operation.

Some researchers studied the membrane process to treat the low quality NG. For example, Hao et al. published two papers on removing acid gas from NG using polymer membrane. In Hao et al. (2002), no recycle stream was considered, and it was found that gas processing cost was dominated by the cost of CH_4 lost in the permeate stream; in the later paper (Hao et al., 2008), a recycle stream was considered, and four optimal configurations were identified for different feed conditions. Ahmad et al. (2012a,b) simulated the process with a membrane unit as a user defined unit operation in Aspen HYSYS, and validated the model using published experimental data from Pan (1986) and simulation results of Qi and Hensen (1998). Then, they simulated 6 configurations: (1) single stage, (2) single stage with permeate recycle, (3) two stage with permeate recycle, (4) two stage with retentate recycle, (5) three stage with retentate recycle, and (6) three stage with permeate and retentate recycle, and concluded that the two stage membrane system with permeate recycle has the minimal gas processing cost. Peters et al. (2011) compared the amine absorption process with the membrane process. Their results suggest that the latter process consumed less energy and had a smaller footprint compared to the amine absorption process; on the other hand, it yielded higher partial pressure of acid gas in sweet gas than the latter but still met the pipeline specifications. Note that these results were for NG feed without H_2S.

Besides scientific studies, acid gas removal via membrane is becoming popular in industries. For example, UOP has supplied 250 membrane units for acid gas removal, which include one plant in Pakistan with a capacity of 240 MMSCFD (Cnop and Braeuer, 2009). Moreover, on-going research and development in membrane technology are likely to result in more durable and reliable membranes with lower manufacturing cost. On the other hand, one common problem for gas permeate membrane is fouling caused by liquid depositing in the membrane surface. However, this is not a major concern for acid gas removal because the main liquid component in crude NG (namely, water) is removed by dehydration before the feed enters the acid gas removing process (Kidnay et al., 2011). Moreover, to cater for various problems, membrane replacement cost (assuming reasonable membrane life) can be considered in the analysis and evaluation of a design.

Although membrane is efficient in bulk removal of acid gas, it is very difficult to meet stringent specification of H_2S less than 4 ppm because partial pressure of acid gas in the retentate stream near the outlet is already low, which means driving force is small. To tackle this challenge, a few researchers attempted to use both amine absorption and membrane processes together, called membrane-absorption hybrid (MAH) process. Mckee et al. (1991) employed a single stage MAH process for acid gas removal from NG, with feed flow rate of 40 MMSCFD, inlet pressure of 1000 psia and 16 mol% CO_2; their results suggest that, for these feed conditions, MAH process has a lower processing cost over both membrane and amine absorption processes. Bhide et al. (1998) employed a three-stage MAH process to purify two feeds (one with H_2S and another without H_2S), and compared its performance with that of both membrane and absorption processes. For feed without H_2S, the best solution was membrane separation, whereas the optimal solution for feed with H_2S depends on acid gas partial pressure, feed flow rate and pressure. The best solution for feed with 25 mol% CO_2, 1 mol% H_2S and flow rate of 35 MMSCFD at 800 psia, was the hybrid process. However, there are two limitations in the study of Bhide et al. (1998); firstly, only three-stage membrane configuration was considered for hybridization with absorption process; secondly, it is not clear whether their processes were rigorously simulated using a commercial simulator. All the above studies on MAH process are from the perspective of grass-roots design.

Given that most of operating acid gas removal plants are based on amine absorption, it is necessary to analyze retrofitting them for treating feed with high acid gas concentration in the near future. To the best of our knowledge, there is no study on retrofitting NG sweetening process in the open literature. Hence, this study analyzes retrofitting an amine absorption process with membrane separation, for treating NG feed with significantly increased CO_2 concentration. First, the base case is simulated for moderate acid gas level in the feedstock (CO_2 = 8.2 mol% and H_2S = 0.5 mol%). Then, two retrofit designs, namely, one- and two-stage MAH processes for treating 25 mol% CO_2 in NG feed, are optimized for minimizing gas treatment cost. These results are analyzed and compared to a new amine absorption plant for 25 mol% CO_2 in NG feed. Note that the existing amine absorption process is unsuitable for sweetening the new NG feed. So, another retrofit design, namely, adding physical absorption system in the upper stream (as a pretreating unit) is compared with membrane based retrofit designs.

The rest of this paper is organized as follows. Section 2 analyzes the base case used for retrofitting. Sections 3.1 and 3.2 discuss respectively the one- and two-stage MAH retrofit designs for feedstock with higher content of CO_2. Section 3.3 compares OSMAHRD and TSMAHRD with other possible retrofit designs, and Section 3.4 compares the membrane based retrofit designs with building a new amine plant. Section 3.5 analyzes the performance of the developed retrofit designs for NG feed with other CO_2 concentrations. Section 3.6 considers using waste permeate stream from the membrane unit to generate steams for use in the reboiler of the regenerator. Section 4 briefly discusses waste acid gas treating. Conclusions of this study are presented in Section 5.

2. Base case simulation and analysis

2.1. Feedstock and process description

In this study, a moderate feed flow rate of 1743 kmol/h, inlet pressure of 5516 kPa and temperature of 30 °C are assumed. The feedstock is assumed to contain methane (CH_4), carbon dioxide (CO_2), hydrogen sulfide (H_2S), ethane (C_2H_6), propane (C_3H_8) and Butane (C_4H_{10}). This is realistic and similar to that used in Bhide et al. (1998) and Peters et al. (2011), compared to studies like Patil et al. (2006), which consider methane and acid components only. Feedstock composition is highly dependent on reservoir. In this study, data of a USA reservoir from Kidnay et al. (2011) is adopted (see Table 1).

Absorption of acid gas in amine involves chemical reactions between the gaseous components (being absorbed) and a