Journal of Natural Gas Science and Engineering 26 (2015) 758–769

Contents lists available at ScienceDirect

Journal of Natural Gas Science and Engineering

journal homepage: www.elsevier.com/locate/jngse

Mercaptan removal from natural gas by the efficient cyclic adsorption process; a simulation study

Zahra Tohidi, Shohreh Fatemi*, Omid Taheri Qazvini

School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran

ARTICLE INFO

Article history:
Received 26 May 2015
Received in revised form
7 July 2015
Accepted 8 July 2015
Available online 13 July 2015

Keywords:
Cyclic adsorption processes
Mercaptan removal unit
Natural gas
PVSA process
PTSA process
Economic study

ABSTRACT

A more efficient and economical cyclic adsorption process was proposed for mercaptan removal from natural gas (NG) to reduce mercaptan content to less than 10 ppm and meet the environmental rules. Continuous sulfur removal is studied for the NG feed stream, with pressure of 6.8 MPa, flow rate of 2850 Nm^3/hr and molar composition of 95.98% methane, 0.00182% water vapor, 1% carbon dioxide, 0.0134% mercaptan and 3% heavier hydrocarbons ($C3^+$). The proposed process of Pressure Vacuum Swing Adsorption (PVSA) was designed and simulated as a more efficient alternative process against the current Industrial Pressure-Temperature Swing Adsorption (PTSA). In this work, an improved PVSA process was simulated with sequences of bed pressurization, adsorption, equalization, blow down, bed regeneration by vacuum and purge by product, in each process cycle. Vacuum condition of 10 KPa with the molar purge/feed ratio of 0.06 and temperature of 350 K was required for appropriate bed regeneration from adsorbed mercaptan to approach to the continuous cyclic steady condition. Comparison between PVSA and PTSA, at the same feed characteristics, same packed columns and adsorption operating conditions, revealed that the PVSA process, with less cycle time than PTSA, could achieve the same product purity with 94.8% recovery and 3.90 [mol/kg day] productivity, whereas PTSA has the recovery of 74.04% and productivity of 2.79 [mol/kg day]. At the same time, operating with PVSA, instead of PTSA process, would reduce the operating cost from 88 to 70 [Thousand $/year].

1. Introduction

The progress of the international energy demand shows an average of 1.7% annual growth in the 2005 to 2020. This growth concerns all energy sources and natural gas demands which would be accounted for the highest growth rate in 2020 (Tagliabue et al., 2009). Increasing concerns of the harmful effects of natural gas contaminants on environment has led to the introduction of a number of natural gas treatments. Out coming NG from the well contains methane with impurities such as water vapor, carbon dioxide, nitrogen, hydrogen sulfide, light mercaptans, ethane and heavier hydrocarbons. Some part of the natural gas impurities must be removed before commercial use. Today, according to the recent environmental legislations, the sulfur emission in the atmosphere should be considerably reduced to less than 20 ppm (Bellat et al., 2008). Mercaptans, or more correctly thiols, are organic compounds in which the −SH groups are present in the molecular structure of the hydrocarbons. The mercaptans must be removed mainly for three reasons: (a) they have acidic property and can cause serious corrosion problems, (b) they have offensive odor and they are very inappropriate to be burnt, (c) most of them are highly toxic and affect the subsequent catalytic reactions (Tamai et al., 2006). In the conventional processes, the acid gases such as hydrogen sulfide and carbon dioxide are mostly removed in an amine-wash unit. Since light mercaptans are not as acidic as hydrogen sulfide, they cannot be removed properly by amine washing and an additional step is required to reduce the sulfur concentration to an appropriate level. Gas purification by the adsorption process could be as an alternative process in progress for sulfur removal from NG (Bellat et al., 2008). Modeling and simulation of the gas adsorption processes have been investigated previously by some researchers. Some limited works have been done for investigating mercaptan removal by adsorption using different adsorbents (Bellat et al., 2008; Weber et al., 2008; Cavenati et al., 2006; Dantasa et al., 2011; Mulgundmath et al., 2012; Clausse et al., 2004; Zhang et al., 2009, 2008; Campo et al., 2013). Shirani et al. (2010) also simulated mercaptan adsorption

* Corresponding author. School of Chemical Engineering, College of Engineering, University of Tehran, Enghelab Avenue, Iran.
E-mail address: shfatemi@ut.ac.ir (S. Fatemi).

http://dx.doi.org/10.1016/j.jngse.2015.07.010
1875-5100/

on 13X adsorbent in presence of water vapor at isothermal condition and presented the breakthrough curves from the packed bed. In another work, Qazvini and Fatemi (2014) simulated a PTSA (Pressure-temperature swing adsorption) unit for mercaptan removal in South Pars region. However, the high cycle time taking for cooling down and the high economic costs are the main disadvantages of the mentioned process. It believes that, by replacing the current PTSA process with PVSA (Pressure-vacuum swing adsorption), the efficiency of the process would be improved. In addition, in PTSA process, the temperature shock induced to the solid adsorbents by temperature variation in adsorption–desorption steps would reduce the life time of the adsorbents, whereas PVSA doesn't require energy induction to the adsorbents. It should be noted that, there is no evidence in the literature about mercaptan removal by PVSA from NG in presence of other impurities such as CO_2, water vapor and heavier hydrocarbons. In this work, a systematic simulation of mercaptan removal from NG in presence of other impurities is carried out by the PVSA process in face of the industrial PTSA process simulated by Qazvini and Fatemi (2014) with the same bed configurations and design. This comparison is carried out on the base of different regeneration conditions and the results are presented in terms of concentration and temperature profiles, and performance parameters such as purity, productivity and recovery as well as a brief economical study. In this research, industrial PTSA refers to the real mercaptan removal unit (MRU) in South Pars region of Iran that is already working, and the process design parameters and the real outlet data are taken from there (Qazvini and Fatemi, 2014).

2. Process description and design

2.1. Description of process

A systematic adsorption model has been presented and implemented to simulate the PVSA process proposed for purification of natural gas (NG) from light mercaptans in presence of other impurities such as water vapor, CO_2 and heavier hydrocarbons (C3+). The industrial mercaptan removal unit (MRU) is currently working in South Pars region of Iran and this process is designed in the mode of PTSA. This unit consists of six insulated two-layer packed bed columns in which the regeneration step is carried out by increasing temperature of the bed by the hot gas NG. The pressure of the upcoming feed is 6.8 MPa and the adsorption process has been initially designed to work at this high pressure. The properties of the inlet NG is specified at Table 1. In addition, the adsorption bed dimensions in industrial scale and the type and amount of the adsorbents are presented in this table.

Each column consists of two layers: 13X zeolite and activated alumina. The 13X zeolite is used for major adsorption of mercaptan, however because of high affinity of 13X to water vapor, water plays competitive role in mercaptan adsorption. Therefore, a pre-layer of Activated alumina is required to adsorb water vapor before entering the 13X layer. Adsorption of mercaptan and $C3^+$ is ignorable compared to H_2O and CO_2 adsorption by activated alumina. (Ferreira and Magalhães, 2011; Baumgarten et al., 1977). Physical properties of the adsorbents are reported in Appendix A1.

In this work, the process of PVSA is designed on the base of existing PTSA, but different according to the regeneration step and its operating conditions. A simple PVSA with no equalization and an improved PVSA with pressure equalization steps are planned to study the impact of pressure equalization step on purity, recovery and productivity of the process.

These results would be comparable with the established industrial PTSA that is currently working with no pressure equalization. The current PTSA process consists regeneration step including two heating stages; 1st stage working at 480 K and the 2nd one working at 590 K.

The proposed simple PVSA process is designed to include 10 steps as following:

I. Adsorption step; during 18 h, the NG feed is introduced from top of the bed with a flow rate of 2.2 kmol/s at pressure of 6.8 MPa and temperature of 302 K.
II. 1st depressurizing step; the bed pressure is decreased for 6.8 to 4 MPa during 10 min. The gas content of the bed is released to the atmosphere, from the top.
III. 2nd depressurizing step; the bed pressure is decreased from 4 to 1.5 MPa during 10 min by releasing from the top of the bed to atmosphere.
IV. Blow down step; the rest of the bed pressure is reduced down to the atmospheric pressure. 10 min time is considered for this step.
V. Evacuation step; the bed pressure is evacuated by a vacuum pump to reach to 0.01 MPa during 10 min.
VI. 1st purge step; the bed is purged counter-currently with 2% of the product stream at the vacuum pressure of 0.01 MPa during 10 min.
VII. 2nd purge step; the bed is purged counter-currently with 6% of the product stream in atmospheric pressure and temperature of 350 K during 15 h and 40 min.
VIII. 1st pressurizing step; the bed pressure is increased up to 1.5 MPa through feed introducing from top of the bed during 10 min.
IX. 2nd pressurizing step; the bed pressure is increased from 1.5 to 4 MPa during 10 min.
X. 3rd pressurizing step; the bed pressure is increased from 4 to 6.8 MPa during 10 min.
XI. Rest; the bed is put on the rest for one hour to be prepared for the next cycle.

The improved PVSA process was designed as the alternative of simple PVSA with the same conditions but considering pressure equalization steps between the columns. Pressure equalization step provides inter-connection between two columns in which one of the columns is working at depressurizing mode and the other one is at repressurizing mode. According to the above modes, step III is

Table 1
Feed specifications and the bed characteristics.

Parameter	Value	Bed	13X	AC
Flow rate (Nm^3/hr)	2850	Bed length (m)	4.65	0.75
Pressure (Mpa)	6.8	Bed diameter (m)	3.7	3.7
Temperature (k)	302	Bed void fraction	0.37	0.26
Water vapor fraction (ppmv)	18.2	Bulk density (kg/dm^3)	0.69	0.82
Mercaptan fraction (ppmv)	133.8	Adsorbent weight (ton)	21.723	4.89
CO_2 fraction (ppmv)	1.0×10^4			
Heavy hydrocarbons fraction (ppmv)	3.0×10^4			
Methane fraction (ppmv)	95.9848×10^4			