Separation and Purification Technology 139 (2015) 88–103

Contents lists available at ScienceDirect

Separation and Purification Technology

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

# Modeling and simulation pressure–temperature swing adsorption process to remove mercaptan from humid natural gas; a commercial case study

Omid Taheri Qazvini, Shohreh Fatemi *

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

ARTICLE INFO

*Article history:*
Received 26 May 2014
Received in revised form 31 August 2014
Accepted 30 September 2014
Available online 8 October 2014

*Keywords:*
Cyclic adsorption process
PTSA commercial process
Mercaptan removal
Natural gas purification
Simulation

ABSTRACT

Simulation of pressure–temperature swing adsorption (PTSA) process was performed in a commercial two-layer six-bed adsorption system during six sequential steps of cyclic operation to remove mercaptans from natural gas. The feed is a mixture of methane with water vapor, carbon dioxide, heavy hydrocarbons ($C_{3+}$) and mercaptan impurities. The process is working in the cyclic operational mode to continuously reduce the mercaptan content from 134 to less than 10 ppmv which is determined as the standard level in the environmental regulations. The bed consists of two layers of activated alumina to specifically remove water vapor and 13X zeolite to remove mercaptan, respectively, from natural gas. The cycle steps i.e. adsorption at high pressure, depressurization to the lower pressure, two steps heating with purging hot purified natural gas, cooling the column and pressurization by feed were simulated sequentially. The dynamic model equations were constructed from four mole balances; model molecule of mercaptans, model molecule of heavy hydrocarbons, carbon dioxide and water vapor in natural gas, a total mass balance, a pressure drop equation and two energy balances of solid and gas phases in the adiabatic column. It was observed that the cyclic adsorption was approached to the steady conditions after seven cycles running the program. The predicted molar fractions out of the process were compared with the real results and good agreement was observed between the real data and simulated results. The influential parameters of the process were investigated through a parametric analysis of the process efficiency. Pressure of adsorption stage, purge to feed ratio at regeneration step and temperature of the 1st and 2nd heating steps were found to be the most influential parameters affecting the natural gas purification efficiency. For the sake of energy saving some suggestions were proposed for upgrading the design conditions with no significant effect on the purification performance. The results revealed that reduction of adsorption pressure from 6.8 to 6.1 Mpa, changing purge/feed ratio from 0.06 to 0.045, and combination two heating stages to one stage with 510 K and 12 h operation could be replaced in the operational conditions without significant changes in purification of the product.



## 1. Introduction

Natural gas is a hydrocarbon gas mixture consisting primarily of methane including impurities of water vapor, carbon dioxide, sulfuric compounds such as hydrogen sulfide and light mercaptans (mostly ethyl and methyl mercaptan). Water and sulfur impurities cause several problems like corrosion, condensation, air pollution and lowering natural gas energy content. In the near future the environmental rule will force a reduction of sulfuric emission in the atmosphere (less than 20 M ppmv) [1–3]. In the typical industrial plants, natural gas is separated from hydrogen sulfide by soda washing followed by amine-wash to separate other sulfuric compounds, and finally it is dried in the glycol dehydration unit. However, these treatments are not sufficient to completely separate sulfuric compounds and the presence of some light mercaptans would cause violation from environmental regulations [3]. As a result it would be necessary to add a new downstream treatment process to reduce sulfur down to the environmental issue requirements. In this situation, adsorption process as a simple, high selective and modern method that is developing for purification of natural gas would be an alternative process for sulfur removal.

A large number of modeling and simulation of gas cyclic adsorption are available in the literature. Kim et al. [4] investigated a parametric study on a six-step pressure swing adsorption (PSA) purifier using carbon molecular sieve to produce $O_2$ with a high

* Corresponding author.
*E-mail address:* shfatemi@ut.ac.ir (S. Fatemi).

http://dx.doi.org/10.1016/j.seppur.2014.09.031
1383-5866/

**Nomenclature**

| | |
|---|---|
| $a$ | heat capacity equation parameter (J/mol/K) |
| $a_p$ | specific area of adsorbent (1/m) |
| $A$ | thermal conductivity equation parameter |
| $b$ | heat capacity equation parameter (J/mol/K) |
| $B_i$ | affinity constant (1/kpa) |
| $B_{0,i}$ | affinity constant at infinite temperature (1/kpa) |
| $c$ | heat capacity equation parameter (K) |
| $C_i$ | concentration of species $i$ in the gas (mol/m$^3$) |
| $C_{pg}$ | heat capacity of gas (J/mol/K) |
| $C_{ps}$ | heat capacity of adsorbent (J/kg/K) |
| $d$ | heat capacity equation parameter (J/mol/K) |
| $D$ | thermal conductivity equation parameter |
| $D_{ax,i}$ | effective axial dispersion coefficient of species $i$ (m$^2$/s) |
| $D_{m,i}$ | molecular diffusivity of species $i$ in mixture (m$^2$/s) |
| $D_{K,i}$ | Knudsen diffusivity of species $i$ (m$^2$/s) |
| $D_{i,j}$ | molecular diffusivity of species $j$ in $i$ (m$^2$/s) |
| $e$ | heat capacity equation parameter (K) |
| $E$ | characteristic energy of the adsorbent (J/mol) |
| $F$ | thermal conductivity equation parameter |
| $h_i$ | film heat transfer coefficient between gas and solid (W/m$^2$/K) |
| $\Delta H_i$ | heat of adsorption of species $i$ (J/mol) |
| $K_g$ | gas thermal conductivity (W/m/K) |
| $k_{f,i}$ | film mass transfer coefficient of species $i$ (m/s) |
| $k_{p,i}$ | pore diffusivity of species $i$ (m$^2$/s) |
| $k_i$ | overall mass transfer coefficient (s$^{-1}$) |
| $K_{ax}$ | effective axial thermal conductivity (W/m/K) |
| $k'_g$ | gas thermal conductivity at atmospheric pressure (W/m/K) |
| $L$ | length of the bed (m) |
| $m$ | Dubinin-Astakhov exponent |
| $M$ | molecular weight (g/mol) |
| $N$ | viscosity equation parameter |
| $Nu$ | Nusselt number |
| $n_c$ | number of the adsorbed components in the mixture |
| $n_{cycle}$ | number of cycle |
| $n$ | number of all component in gas mixture |
| $P$ | pressure (kpa) |
| Pr | Prandtl number |
| $p_i$ | partial pressure (kpa) |
| $p_0$ | saturation pressure (kpa) |
| $P_c$ | critical pressure (pa) |
| $q_i$ | adsorbed phase concentration of species $i$ (mol/kg) |
| $q_i^*$ | equilibrium adsorbed phase concentration (mol/kg) |
| $q_{m,i}$ | maximum adsorbed phase concentration (mol/kg) |
| $R$ | ideal gas law constant (J/mol/K) |
| $r_p$ | adsorbent radius (m) |
| $r_{pore}$ | pore radius (m) |
| $Re$ | Reynolds number |
| $Sc$ | Schmidt number |
| $Sh$ | Sherwood number |
| $t$ | time (s) |
| $T$ | gas temperature (K) |
| $T_s$ | adsorbent temperature (K) |
| $T_r$ | reduced temperature |
| $T_c$ | critical temperature (K) |
| $u$ | superficial gas velocity (m/s) |
| $V_c$ | critical molar volume (m$^3$/kmol) |
| $y_0$ | initial mole fraction |
| $y_i$ | mole fraction of species $i$ |
| $z$ | axial coordinate in the bed (m) |
| $Z_c$ | critical compressibility factor |

*Greek letters*

| | |
|---|---|
| $\varepsilon$ | bed porosity |
| $\varepsilon_p$ | adsorbent porosity |
| $\tau$ | tortuosity factor |
| $\rho_s$ | adsorbent density (kg/m$^3$) |
| $\rho$ | gas density (mol/m$^3$) |
| $\rho_r$ | reduced density |
| $\mu$ | gas viscosity (kg/m s) |
| $\mu_0$ | gas viscosity at low pressure (kg/m s) |
| $\varphi$ | shape factor |
| $\delta$ | convergence parameter |
| $\gamma$ | purge to feed ratio |

*Subscripts*

| | |
|---|---|
| F | feed |
| H | high pressure |
| L | low pressure |
| A | adsorption |
| R | regeneration |
| D | depressurization |
| P | pressurization |

purity. Knaebel et al. [5] simulated and optimized a pressure swing adsorption for recovering hydrogen from methane. Silva and Rodrigues [6] and Mendes et al. [7] studied the effect of operating parameters on separation of various mixtures after running a pressure swing adsorption process. Experimental studies on adsorption of various gases are countless but fundamental studies on the adsorption of mercaptans in the nanoporous materials are rarely found. Weber et al. [2] and Bellat et al. [3] measured adsorption equilibrium of binary ethyl mercaptan/hydrocarbon mixtures on a 13X zeolite. Bashkova et al. [8] also they presented adsorption equilibrium of methyl mercaptan on activated carbon adsorbent. In addition, there is much less reports about the cyclic adsorption processes for adsorption of mercaptan from natural gas. Shirani et al. [9] studied water vapor and mercaptan adsorption on 13X zeolite in natural gas purification process. Zhou et al. [10] studied removing of $H_2S$ from natural gas by applying a pressure swing adsorption to investigate the possibility of purification.

For the case of deep desulfurization of natural gas, two main technologies (temperature swing adsorption (TSA) and pressure swing adsorption (PSA)) should be combined together. Pressure is required for the adsorption step and increasing temperature is required for the efficient regeneration of adsorbents in desorption step. Although the process of PTSA for natural gas purification from sulfur compounds was not found in the literature survey, some studies are found for separation and purification by this process. Cho et al. [11] proposed PTSA cyclic process for removing greenhouse gas $SF_6$ from a mixture of $N_2$ and 1.3% of $SF_6$ by activated carbon. The maximum purity of 19.5% and recovery of 50.1% were obtained with adsorption pressure of 2.5 atm, desorption temperature of 200 °C and evacuation of 1 h. Mulgundmath and Tazel [12] optimized a PTSA cyclic adsorption process for capturing carbon dioxide released from post combusted natural gas. In the study, Pressure Swing Adsorption (PSA) process has been compared with Thermal Pressure Swing Adsorption (TPSA) process for $CO_2$ recovery from a flue gas composition of 10% $CO_2$ (by vol) in $N_2$using Ceca 13X adsorbent. In another work, Pugsley et al. [13] simulated a novel $CO_2$ separation process known as the circulating fluidized bed pressure–temperature swing adsorber