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Numerical simulation of a three-bed PSA cycle for the methane/nitrogen separation with silicalite

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ABSTRACT

In this work, a three-bed PSA cycle for recovering methane from methane/nitrogen mixtures using silicalite is analysed by numerical simulation, including two equalization steps and a rinse step. The model employed is derived from conservation equations, considering assumptions widely accepted for these systems. The experimental adsorption isotherms of methane and nitrogen required for the PSA model have been measured up to 10 bar, and the mass transfer coefficients of these gases on silicalite have also been estimated from experimental data. According to the simulated results, it is possible to recover methane with pipeline quality in one stage with high recovery (87–96%) from mixtures with nitrogen content as high as 50%. This process has the potential of significantly increasing the adsorbent productivity with respect to the reported values for the same separation by PSA, and the theoretical power consumption is lower than the one reported using membrane technology.

1. Introduction

The typical pipeline specification of natural gas is a total inert content (predominantly nitrogen) below 4%. Many gas reserves cannot be used because of their high nitrogen content [1,2]. Cryogenic distillation is employed nowadays to remove the excess nitrogen, but this process is most suited for large gas fields that can deliver 1.4–14 million SCMD of gas for 10–20 years [3]. In this case, the high capital cost of cryogenic distillation can be recovered during the process lifetime. Many small gas wells are closed because small-scale nitrogen separation technology is not as developed as distillation technology. Typically, the nitrogen content in low-quality gas is about 20% [1], although it depends on the gas source. New technologies have been proposed for the methane/nitrogen separation [1,7,8], including the commercial natural gas upgrading PSA process of Engelhard Corporation, based on an adsorbent which selectively excludes methane due to its larger molecular size, whereas it adsorbs nitrogen, and membrane systems using methane selective polymeric membranes [3]. However, it is difficult to get high methane recovery (above 90%) with single PSA cycles based on nitrogen-selective adsorbents [8], so two-stage PSA cycles are employed (the nitrogen-enriched product at low pressure of one cycle is compressed to be the feed stream for other cycle). The methane upgrading process with polymeric membranes is economical for nitrogen contents below ∼30%, due to low selectivity towards methane of the available membrane materials (about 3–3.5). In spite of this, this process has been developed commercially, and it claimed to be the lowest cost treatment option for many natural gas streams [3]. Methane adsorbs stronger than nitrogen on most adsorbents due to its higher polarizability. The recovery of the heavy (more adsorbable) component from gaseous mixtures by PSA has already been patented [4–6]. However, less attention has been devoted to the separation of nitrogen/methane mixtures using methane selective adsorbents. The separation of methane/nitrogen mixtures using 5 A zeolite was studied by Turnock and Kadlec [9], and by Baksh et al. [10], using activated carbon impregnated with MoO_2. In a previous work [11], we studied the methane/nitrogen separation by PSA using silicalite as adsorbent, which is also methane-selective. This adsorbent has several advantages: (i) it is hydrophobic, so its working capacity is not drastically reduced by the presence of water in the feed gas, and (ii) it has high thermal and chemical stability, so it is resistant to aging. The objective of this work is to design a three-bed PSA process for the methane/nitrogen separation using silicalite as adsorbent, which gives a higher productivity (producing 96% methane with a recovery above 95%) than other PSA processes proposed in the literature for obtaining methane from methane/nitrogen mixtures (as it is shown in Table 1). A recovery above 93% of the feed gas methane as useful product gas is an acceptable performance for most small producers [3]. It must be noted that the methane/nitrogen separation is quite difficult because of the low methane/nitrogen selectivity of most adsor-

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Nomenclature

b	adsorption affinity ($\mathrm{Pa^{-1}}$)
b_0	preexponential factor of b ($\mathrm{Pa^{-1}}$)
C	total gas concentration ($\mathrm{mol\,m^{-3}}$)
D	diffusivity ($\mathrm{m^2\,s^{-1}}$)
q^*	overall concentration in equilibrium with the gas phase ($\mathrm{mol\,kg^{-1}}$)
$\bar{q}$	average concentration in the particle ($\mathrm{mol\,kg^{-1}}$)
c_p	heat capacity at constant pressure ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
c_v	heat capacity at constant volume ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
D_L	axial dispersion coefficient ($\mathrm{m^2\,s^{-1}}$)
k	$c_{p,g}/c_{v,g}$
k_f	external mass transfer coefficient ($\mathrm{m\,s^{-1}}$)
k_s	lumped mass transfer coefficient ($\mathrm{s^{-1}}$)
L	bed length (m)
n	number of components
n_{ads}	adsorbed concentration ($\mathrm{mol\,kg^{-1}}$)
N_i	rate of adsorption ($\mathrm{mol}_i\,\mathrm{m_{bed}^{-3}\,s^{-1}}$)
P	pressure (Pa)
Q	volumetric flow rate ($\mathrm{m^3\,s^{-1}}$)
d_p	particle diameter (m)
R	gas constant, 8.31 $\mathrm{J\,mol^{-1}\,K^{-1}}$
r_p	particle radius (m)
R_{bed}	bed radius (m)
T	temperature (K)
t	time (s)
t_{step}	step duration (s)
u	superficial velocity ($\mathrm{m\,s^{-1}}$)
x	dimensionless axial coordinate
y	mole fraction in the gas phase
ΔH	adsorption enthalpy ($\mathrm{J\,mol^{-1}}$)

Greek symbols

ε	bed voidage fraction
λ	thermal axial dispersion coefficient ($\mathrm{W\,m^{-1}\,K^{-1}}$)
μ	gas viscosity (Pa s)
ρ	density ($\mathrm{kg\,m^{-3}}$)
η_C	compressor efficiency
τ	tortuosity

Subscripts

c	crystal
F	feed
g	gas
$macro$	macropore
max	maximum capacity
p	particle
s	solid
L	low pressure
H	high pressure
E	equalization
$pres$	pressurization (or pressure change)
0	initial

bents [2]. Although the cycle includes steps which are not new (pressurization, feed, rinse, equalization and blowdown), the new feature of the proposed cycle is the combination of a rinse step with two cocurrent equalization steps in a three-bed system, which has not been previously considered for the methane/nitrogen separation, resulting in high methane purity, recovery and productivity in one stage. The effect of increasing the number of equalization steps in the cycle from 0 to 2 on the performance has also been studied. The power requirement has been estimated either, which has not been done in previous works in the literature about the methane/nitrogen separation by PSA. The model employed is derived from conservation equations, considering assumptions widely accepted for these systems. The experimental adsorption isotherms of methane and nitrogen required for the PSA model have been measured up to 10 bar, and the mass transfer coefficients of these gases on silicalite have also been estimated from experimental data. The performance of the cycle for different nitrogen contents in the feed mixture (8–50%) is analysed by numerical simulation.

2. Experimental

All the gases used in this work had purity higher than 99.5%, supplied by Praxair. The adsorbent used was commercial agglomerated silicalite (30% binder) in the form of cylindrical pellets, supplied by CECA. Adsorbent properties are shown in Table 2. Adsorption equilibrium data at high pressure (100–1000 kPa) at different temperatures (279, 293 and 308 K) were obtained in a volumetric installation following established procedures described elsewhere [12]. The adsorption equilibrium data at 298 K in pressure range between 10 and 100 kPa were obtained in a fixed-bed installation, and they were reported previously [11]. The diffusion rates of methane and nitrogen could not be measured in that work because the response speed of the analytical technique employed (gas chromatography) was not fast enough for the bed contact times employed. In this work, the adsorption kinetics were analysed in other fixed-bed installation with a shorter bed (Table 2) and using higher gas flowrates (Table 3). A mass spectrometer connected to the bed outlet was used as detector, which allowed to measure the fast diffusion rates of methane and nitrogen in silicalite. This experimental set-up and the methodology employed have also been described elsewhere [13]. A tracer experiment with helium as non-adsorbing gas was carried out to model the effect of the void volume on the detector signal, purging the bed with nitrogen after equilibrating it with an helium/nitrogen mixture (5/95%, v/v), and recording the signal of helium.

2.1. PSA cycle

The PSA cycle proposed consists of three beds passing through twelve consecutive steps. A scheme of the cycle is shown in Fig. 1(a), and the sequence table is shown in Fig. 1(b). Feed (low-quality natural gas) at high pressure (P_H) is introduced in the first bed in Step I, and waste gas is obtained as product. In Step II, a portion of the extract (methane-rich product) is introduced as feed (rinse step), in order to increase the proportion of methane in the bed, displacing nitrogen from the adsorbent and from the gas in the voids. This portion must be pressurized from 1 bar to the high pressure, which is considered in the calculation of cycle power consumption (Eq. (12)). In Step III, the first bed is connected with a bed with low intermediate pressure (co-current equalization). Using adequate values of the operational variables, the exchanged gas in this step has a high nitrogen concentration, which leads to a further increase of the methane concentration in the depressurizing bed (the proportion of methane in the bed increases). At the same time, the other bed with low intermediate pressure is depressurized countercurrently down to the low pressure (P_L) where the methane rich product is obtained at 1 bar (blowdown or extraction step). In Step IV, the first bed is connected to the bed previously evacuated (a second co-current equalization step), resulting in the same effect previously commented, and the other bed is pressurized with feed up to the high pressure. The rest of the steps are the same for the other two beds.

The key feature of the proposed cycle to get high methane purity and recovery is the combination of the rinse and the two cocurrent