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Two-stage PSA/VSA to produce H_2 with CO_2 capture via steam methane reforming (SMR)

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ABSTRACT

A two-stage pressure/vacuum swing adsorption (PSA/VSA) process was proposed to produce high purity H_2 from steam methane reforming (SMR) gas and capture CO_2 from the tail gas of the SMR-H_2-PSA unit. Notably, a ten-bed PSA process with activated carbon and 5A zeolite was designed to produce 99.99+% H_2 with over 85% recovery from the SMR gas ($CH_4/CO/CO_2/H_2$ = 3.5/0.5/20/76 vol%). Moreover, a three-bed VSA system was constructed to recover CO_2 from the tail gas using silica gel as the adsorbent. CO_2 product with 95% purity and over 90% recovery could be attained. Additionally, the effects of various operating parameters on the process performances were investigated in detail.

Introduction

Pressure swing adsorption (PSA) is a highly versatile separation and purification technology employed in the industry [1,2]. Recently, extensive researches and developments of various PSA processes, particularly in relation to H_2 purification, have been reported [3–6].

H_2, considered as one of the most promising ecologically clean and sustainable energy sources, is predicted to be a key contributor towards the reduction of the greenhouse effect, climatic changes, and energy crisis [7–9]. Currently, H_2 is mainly produced from fossil fuels, notably natural gas, with steam methane reforming (SMR) being the dominant industrial process for H_2 production [10,11]. The process is generally followed by a water gas shift (WGS) conversion stage and final H_2 purification by PSA [12]. The typical gas mixture composition drawn from SMR to the PSA unit comprises 75–80% H_2, 15–25% CO_2, 1–5% CH_4, 0.1–1% CO, and trace N_2 at a pressure over 22 bar [13,14]. To attain a good performance, an industrial PSA process typically comprises 4–12 parallel beds with hybrid adsorbents such as activated carbon (AC) and zeolite to remove contaminants [15]. However, the achievement of both a high recovery and purity (98%–99.999%) of H_2 is challenging. Thus, the effects of different parameters on the process performances have been reported in the literature.

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Nomenclature

English Symbols

c_i	gas phase concentration of component i ($mol \cdot m^{-3}$)
$C_{pa,i}$	specific heat capacity of adsorbed phase of component i ($J \cdot mol^{-1} \cdot K^{-1}$)
C_{ps}	specific heat capacity of adsorbent ($J \cdot kg^{-1} \cdot K^{-1}$)
C_{pw}	specific heat capacity of bed wall ($J \cdot kg^{-1} \cdot K^{-1}$)
C_{vg}	specific gas phase heat capacity at constant volume ($J \cdot mol^{-1} \cdot K^{-1}$)
$D_{ax,i}$	axial dispersion coefficient of component i ($m^2 \cdot s^{-1}$)
D_b	bed diameter (m)
$D_{e,i}$	effective diffusion coefficient of component i ($m^2 \cdot s^{-1}$)
$D_{k,i}$	knudsen diffusion coefficient of component i ($m^2 \cdot s^{-1}$)
$D_{m,i}$	molecular diffusion coefficient of component i ($m^2 \cdot s^{-1}$)
F	molar flow rate (SLPM)
h_{amb}	wall-ambient heat transfer coefficient ($W \cdot m^{-2} \cdot K^{-1}$)
h_f	gas-solid heat transfer coefficient ($W \cdot m^{-2} \cdot K^{-1}$)
h_w	gas-wall heat transfer coefficient ($W \cdot m^{-2} \cdot K^{-1}$)
H_b	height of adsorbent layer (m)
$IP_{1\text{-}4i}$	isotherm parameters of 1–4 for component i
k_g	gas phase thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)
k_{LDFi}	mass transfer coefficient for component i
k_s	solid thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)
k_w	thermal conductivity of bed wall ($W \cdot m^{-1} \cdot K^{-1}$)
M	molar weight ($kg \cdot mol^{-1}$)
P	pressure (Pa)
q_i	adsorbed phase concentration of component i ($mol \cdot kg^{-1}$)
q_i^*	adsorbed phase concentration in equilibrium with bulk component i ($mol \cdot kg^{-1}$)
$q_{m,i}$	specific saturation adsorption capacity of component i ($mol \cdot kg^{-1}$)
T_w	bed wall temperature (K)
r_p	adsorbent particle radius (m)
R_g	ideal gas constant ($J \cdot mol^{-1} \cdot K^{-1}$)
t	time (s)
T	temperature (K)
T_0	inner temperature of the bed wall (K)
T_{amb}	ambient temperature (K)
T_g	gas phase temperature (K)
T_s	solid temperature (K)
v_g	gas phase superficial velocity ($m \cdot s^{-1}$)
V	standard volume flow rate ($m^3 \cdot h^{-1}$)
W_t	thickness of bed wall (m)
Z	axial direction (m)

Greek symbols

α_p	specific particle surface area per unit volume of bed (m^2/m^3)
ρ_b	bulk density of adsorption bed ($kg \cdot m^{-3}$)
ρ_g	gas phase molar density ($mol \cdot m^{-3}$)
ρ_p	adsorbent particle density ($kg \cdot m^{-3}$)
ρ_w	density of bed wall ($kg \cdot m^{-3}$)
ΔH_i	isostatic heat of adsorption of component i ($kJ \cdot mol^{-1}$)
μ	bulk gas phase mixture viscosity ($kg \cdot m^{-1} \cdot s^{-1}$)
Ψ	shape factor of adsorbent particle (dimensionless)
γ	ratio of specific heats (C_p/C_v) (dimensionless)
η	compressor efficiency (dimensionless)
ε_b	bed porosity (dimensionless)
ε_p	particle porosity (dimensionless)
τ	pore tortuosity (dimensionless)

Sircar et al. [16,17] reviewed recent ideas that further improve H_2 recovery from H_2-PSA processes. They reported that H_2 recovery could be significantly improved by using an additional unit from the SMR-off gas (SMROG). Several PSA simulations for H_2 purification, with different cycles under various operation conditions, were performed by Lopes et al. [18]. The results revealed that H_2 recovery could be significantly improved with an increase in the pressure equalization steps; this was also verified by Milad [19].

As a corollary, two aspects can be considered to improve H_2 recovery: 1) the current H_2-PSA process can be upgraded or a new H_2-PSA process can be designed to reduce the release loss of H_2. 2) Another unit can be constructed to recover the H_2 lost in the tail gas. Accordingly, a typical H_2-PSA tail gas comprises 50–55 vol% CO_2, 24–26 vol% H_2, 15–20 vol% CH_4, 0–2 vol% CO, and 0–5 vol% H_2O, depending on the operating parameters [20]. In addition, the unit used to recover H_2 should simultaneously capture CO_2 from the tail gas.

In conclusion, a two-stage PSA/VSA process can add significant value to the separation process by recycling CO_2 as a product. Thus, the fuel value of the waste gas increases, which has a high Btu value with only 8–10% CO_2. Subsequently, the remaining gases can be reintroduced into the SMR unit as a fuel gas.

The main objective of this paper is to upgrade the performance of the H_2-PSA process:

(1) A ten-bed PSA process with four pressure equalizations was designed to produce high purity H_2 from the SMR stream.
(2) The adsorption equilibria of pure CH_4, CO, CO_2, and H_2 were measured on AC, 5A zeolite, and silica gel.
(3) The effects of different operating parameters, including the feed flow rate, the purge-to-feed ratio and carbon-to-zeolite ratio, on the system performance were assessed.
(4) The use of a three-bed VSA process with silica gel as the adsorbent to recover H_2 and simultaneously capture CO_2 from the tail gas was investigated by simulations.