



Two-train elevated-temperature pressure swing adsorption for high-purity hydrogen production

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HIGHLIGHTS

- Two-train elevated temperature pressure swing adsorption for H₂ purification.
- Optimal process achieves 99.9994% hydrogen purity and 97.51% hydrogen recovery ratio.
- Total steam consumption is significantly reduced with reflux structures.

ARTICLE INFO

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ABSTRACT

The trade-off between hydrogen recovery ratio (HRR) and hydrogen purity (HP) is one of the main drawbacks in normal temperature pressure swing adsorption (NT-PSA) for producing high-purity hydrogen from shifted gas. In this paper, a two-train elevated-temperature pressure swing adsorption (ET-PSA) process that achieved 99.9994% HP and over 95% HRR is proposed, which has wide application potentials in fuel cells and chemical industries. Potassium-promoted layered double oxide (K-LDO), which shows reasonable working capacity and fast adsorption/desorption kinetics at elevated temperatures (200–450 °C), is adopted as the CO₂ adsorbent. CO in the shifted gas is co-purified by high-temperature water gas shift (WGS) catalysts added to the columns. The first-train ET-PSA adopted an eight-column thirteen-step configuration with shorter step time to remove most of the CO/CO₂ in the shifted gas, and the second-train ET-PSA adopted a double-column seven-step configuration with longer step time to purify the residual gas impurities. The introduction of co-current high-pressure steam rinse and counter-current low-pressure steam purge is the key to achieve both high HRR and HP. The high-temperature steam is the main energy consumption of ET-PSA rather than low HRR in NT-PSA, and the total steam consumption is reduced by adopting the tail gas from second-train ET-PSA as the purge gas for first-train ET-PSA. The optimal results achieved 97.51% HRR and 99.9994% HP with only 0.188 rinse-to-feed ratio and 0.263 purge-to-feed ratio, which are the highest values reported for PSAs producing high-purity hydrogen from carbon-based fuels.

1. Introduction

With the growing demand for energy and increasing environmental pressure around the world, it has become necessary to replace the current main energy source (combustion of fossil fuels) with cleaner and more efficient energy systems. Hydrogen is expected to be a fuel of the future and has the potential to contribute to 90% energy generation in 2080 [1]. Emerging technology is expected to break the present energy systems by combining hydrogen as an energy carrier with fuel cells as an electricity generator [2]. Hydrogen is also an important raw material that is widely used in chemical industries (for instance,

ammonia synthesis) [3]. Hydrogen is conventionally produced by hydrocarbon reforming [4], biomass processes [5], and water splitting (including photocatalytic processes [6], electrolytic processes [7], and thermal processes [8]). Despite renewable sources attracting attention, steam methane reforming (SMR) and coal gasification (CG) are the most cost-effective processes for producing hydrogen, at present and for the near future [9].

In hydrogen production processes from SMR or CG, a two-stage water gas shift (WGS) reactor is adopted to remove carbon gases from reformed gas, followed by CO₂ absorption and methanation for CO purification, or alternatively, a pressure swing adsorption (PSA) unit

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Nomenclature

A_i	pre-exponential factor for reaction rate, s^{-1} or $kg/mol\ s$	P_{dep}	given pressure for blowdown, Pa
c	fitting parameter for pressure effect, –	P_{purge}	purge pressure, Pa
C_i	gas molar concentration, mol/m^3	q_i	site concentration, mol/kg
$C_{feed,i}$	feed gas molar concentration, mol/m^3	$q_{i,0}$	initial site concentration, mol/kg
$C_{rinse,i}$	rinse gas molar concentration, mol/m^3	q_{total}	total CO_2 adsorption capacity, mol/kg
$C_{purge,i}$	purge gas molar concentration, mol/m^3	q_{AS}	sum of q_A and $q_{O(s)}$, mol/kg
$C_{pep,i}$	given gas molar concentration for pressure-equalization pressurization, mol/m^3	$Q_{product,out}$	outlet flow rate of the product column, m^3/s
$C_{pp,i}$	given gas molar concentration for product pressurization, mol/m^3	Q_{feed}	feed flow rate of the product column, m^3/s
C_T	total gas molar concentration, mol/m^3	$rate_a$	CO_2 adsorption rate, $mol/kg\ s$
$\dot{C}_{transfer,i}$	mass transfer between bulk gas and particles, $mol/m^3\ s$	$rate_c$	catalytic reaction rate, $mol/kg\ s$
$D_{ax,i}$	axial dispersion coefficient, m^2/s	R	ideal gas constant, $J/mol\ K$
D_p	diameter of adsorbent/catalyst particles, m	SA	specific surface area, m^2/kg
E_i	activation energy, J/mol	t	time, s
E_i^0	initial activation energy, J/mol	t_{total}	total operating time, s
k_i	reaction rate, s^{-1} or $kg/mol\ s$	T	temperature, K
k_{ped}	valve rate for pressure, –equalization depressurization, s^{-1}	v	gas velocity, m/s
k_{dep}	valve rate for blowdown, s^{-1}	v_{feed}	feed velocity, m/s
K_{eq}	equilibrium constant for WGS reaction, –	v_{rinse}	rinse velocity, m/s
L_b	column length, m	v_{purge}	purge velocity, m/s
$m_{adsorbents,total}$	total adsorbents mass, kg	v_{pep}	given velocity for pressure, –equalization pressurization, m/s
M_{CO_2}	CO_2 molar mass, kg/mol	v_{pp}	given velocity for product pressurization, m/s
M_g	mixed gas molar mass, kg/mol	$vol_ratio_{a/c}$	packing volume ratio of adsorbent and catalyst, –
p	pressure, Pa	x_i	molar fraction of component i , –
p_0	standard atmospheric pressure, Pa	$x_{product,i}$	molar fraction of component i in the product column, –
p_i	partial pressure of component i , Pa	x_K	ratio of K-related sites to non-related sites, –
p_{feed}	feed pressure, Pa	α	fitting parameter for E_{if} , J/mol
p_{rinse}	rinse pressure, Pa	β	fitting parameter for E_{1b} , J/mol
p_{ped}	given pressure for pressure, –equalization depressurization, Pa	ε_b	void ratio of fixed bed, –
		ρ_a	adsorbent density, kg/m^3
		ρ_c	catalyst density, kg/m^3
		ρ_g	gas density, kg/m^3
		μ	gas viscosity, $Pa\ s$

[4]. From the perspective of exergetic evaluation, PSA is a desirable hydrogen purification technology achieving above 99.9% hydrogen purity (HP) [5]. Common PSA systems work at normal temperature ranges (NT-PSA) by adopting physical adsorbents such as activated carbon, zeolite, and silica gel [10]. NT-PSA is a cyclic process where the gas impurities are first adsorbed on the surfaces of adsorbents and then desorbed by reducing the pressure [11]. Thermal energy duty for regeneration is avoided during NT-PSA operation. However, for achieving high HP, NT-PSA faces limitations such as low hydrogen recovery ratio (HRR) and high system complexity [12]. For hydrogen production from typical steam methane reformed gas (70–80% H_2 , 15–25% CO_2 , 3–6% CH_4 , 1–3% CO , and trace N_2), a typical NT-PSA achieves 98–99.999% HP and 70–90% HRR [10].

When fixing the column number of NT-PSA, there is a trade-off between HRR and HP. Ribeiro et al. [13] demonstrated that shortening the adsorption time from 160 s to 120 s increased HP of a four-column eight-step NT-PSA from 99.8193% to 99.9992% while decreasing HRR from 71.8% to 62.7%. A similar phenomenon was found when counter-current purge rate was increased when hydrogen was commonly adopted as purge gas [14]. When the column number was increased, both HRR and HP increased due to increase in pressure-equalization steps. Moon et al. [15] indicated that a two-column NT-PSA achieved 99.77–99.95% HP with 73.30–77.64% HRR, and a four-column NT-PSA could achieve above 99.97% HP with 79% HRR. Lopes et al. [16] proposed a ten-step NT-PSA with three pressure-equalizations, which achieved 99.981% HP and 81.6% HRR from a five-component gas (79% H_2 , 17% CO_2 , 1.2% CO , 2.1% CH_4 , and 0.7% N_2). HRR could be further increased to 92.7% with 99.993% HP for a twelve-column thirteen-step NT-PSA to purify raw hydrogen fuel gas in IGCC power plants [17].

However, the large column number decreased productivity and increased the operating complexity and capital cost (CAPEX) [18].

Alternatively, the concept of elevated-temperature pressure swing adsorption (ET-PSA) has been proposed for producing hydrogen from shifted gas [19]. ET-PSA works at elevated temperatures (200–450 °C), thus allowing the shifted gas to directly enter the purification unit without pre-cooling. Chemisorbents like potassium-promoted layered double oxides (K-LDOs) [20] and molten salt-promoted MgO [21], which show high CO_2 working capacity and fast adsorption/desorption kinetics at elevated temperatures, are adopted as CO_2 adsorbents in ET-PSA system. ET-PSA allows the use of steam as rinse and purge gas, where the co-current steam rinse squeezes residual hydrogen out of the column after the adsorption step and counter-current steam purge is adopted to replace hydrogen purge in the NT-PSA process [22]. The high temperature steam, which could be produced in a heat recovery boiler with waste heats from the gasifier, the exhaust gas from gas turbine or other subsystems, was the main energy consumption of ET-PSA [23]. The ET-PSA process can be applied in sorption-enhanced water gas shift (SEWGS), where WGS catalysts are mixed into CO_2 adsorption columns to transform the residual CO in the shifted gas to produce extra H_2 [24].

A series of ET-PSA processes including four-column eight-step cycle [25], six-column eight-step cycle [26], seven-column ten-step cycle [27], eight-column eleven-step cycle [28], and nine-column eleven-step cycle [29] has been proposed. One of the optimization objectives for ET-PSA is to reduce the steam amount for rinse and purge, as it is the main energy consumer in ET-PSA [23]. For SEWGS process, Reijer et al. [26] showed that the rinse mainly affected CO_2 purity and the purge mainly affected CO_2 capture ratio. The rinse-to-carbon and purge-to-

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