Simulation and optimization of pressure swing adsorption process for high-temperature air separation by perovskite sorbents

Mai Xu, Han-Chun Wu, Y.S. Lin, Shuguang Deng*
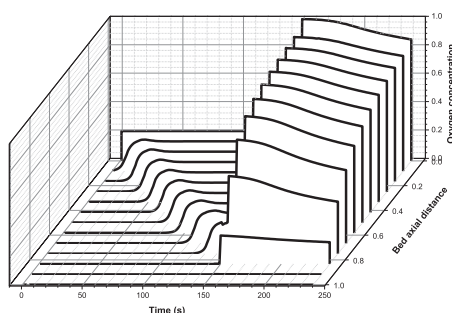
School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ 85287, United States

HIGHLIGHTS

- Combined experimental and simulation study on PSA for O_2 separation at high temperature.
- $La_{0.1}Sr_{0.9}Co_{0.9}Fe_{0.1}O_{3-\delta}$ (LSCF1991) sorbent with infinite O_2/N_2 separation selectivity.
- LSCF1991 pellets have good mechanical properties.
- Oxygen purity of 98.21% and recovery of 74.05% achieved in optimized PSA cycles.

GRAPHICAL ABSTRACT

The oxygen mole fraction profile in the adsorption bed at the last cycle under the optimum condition.

ABSTRACT

This work presents an experimental and simulation study on a low-cost and efficient high-temperature air separation technique using perovskite oxide sorbents by pressure swing adsorption (PSA). The sorbent material, $La_{0.1}Sr_{0.9}Co_{0.9}Fe_{0.1}O_{3-\delta}$ (LSCF1991), have a large oxygen adsorption capacity, a relatively high adsorption and desorption rate, and an infinitely large oxygen selectivity over nitrogen or other non-oxygen species due its unique oxygen storage property. The oxygen nonstoichiometry of LSCF1991 at different temperatures and oxygen partial pressures was measured by thermogravimetric analysis (TGA). The adsorption dynamic behavior of the LSCF1991 pellets was investigated by fixed-bed breakthrough experiments. A numerical process simulation model of the PSA process for the high-temperature air separation using LSCF1991 was developed in Matlab. The model was validated by comparing the simulation results with the experimental results from fixed-bed experiments. A parametric study was performed to design and optimize the operating parameters of the PSA process by investigating their effects on the oxygen purity, recovery and productivity. Under the optimum conditions, oxygen purity of 98.21%, recovery of 74.05% and productivity of 1.22 mmol/s/kg were achieved. The obtained values are much higher than the reported values form previous studies. Additionally, the energy assessment results showed that the energy consumption of the new process is lower than both the cryogenic distillation method and the conventional PSA process.

1. Introduction

The production of oxygen by air separation is an important chemical engineering process. So far, cryogenic distillation method has been widely used as a commercial production process of high-purity nitrogen and oxygen. But this method is more suitable for a large production

Nomenclature

A	initial sample weight for attrition test (g)
B	sample weight after attrition test (g)
d_p	diameter of adsorbent particle (cm)
D_L	axial dispersion coefficient (cm^2/s)
D_m	molecular dispersion coefficient (cm^2/s)
i.d.	bed internal diameter (cm)
K	constant of oxygen nonstoichiometry correlation (atm^{-n})
$K_{p,i}$	effective mass transfer coefficient of i compound (1/s)
Ko	Kozeny constant
L	bed length (cm)
M_g	molecular weight of gas (g/mmol)
M_i	atomic/molecular weight of element/molecule i (g/mmol)
M_w	molecular weight of LSCF1991 (g/mmol)
n	constant of oxygen nonstoichiometry correlation
P	pressure (atm)
P_0	initial pressure of the bed (atm)
P_a	adsorption pressure (atm)
P_d	desorption pressure (atm)
P_i	partial pressure of i compound (atm)
q_i	partial concentration of i compound in the adsorbed phase (mmol/g)
q_i^*	partial concentration at the solid interface of i compound (mmol/g)
Q	mass flux of gas ($mmol/cm^2/s$)
Q_f	flow rate of feed gas (mmol/s)
Q_p	flow rate of purge gas (mmol/s)

$Q_{feed,ads}$	feeding gas mass flux ($mmol/cm^2/s$)
$Q_{exit,des}$	exit gas mass flux ($mmol/cm^2/s$)
t	time (s)
t_{pre}	duration of pressurization step (s)
t_{ads}	duration of adsorption step (s)
t_{dep}	duration of depressurization step (s)
t_{des}	duration of desorption step (s)
t_{cycle}	duration of a PSA cycle (s)
T	temperature (K)
$\sum V_i$	molecular diffusion volumes of component i (cm^3/mol)
x	weight loss percentage of LSCF sample after reduction (%)
y_i	mole fraction of component i
$y_{O_2,feed,ads}$	feeding oxygen molar fraction during adsorption step
$y_{O_2,exit,des}$	exit oxygen molar fraction during desorption step
z	bed axial distance (cm)

Greek letters

δ	oxygen vacancy (oxygen nonstoichiometry)
δ_0	oxygen vacancy at the reference state
ρ_p	density of the adsorbent particle (g/cm^3)
ρ_g	gas density ($mmol/cm^3$)
ε	porosity of the adsorbent bed
μ	dynamic viscosity of gas (g/cm/s)
κ	bed permeability (cm^2)
γ	adiabatic index
η_b, η_v	efficiency of blower and vacuum pump

scale due to its high energy cost [1,2]. Zeolites adsorbents, with their merits of low energy consumption and low investment, have been recently used in commercial pressure swing adsorption (PSA) [3–5]. However, most zeolite adsorbents separate air by adsorbing nitrogen not oxygen. Larger quantities of adsorbents will be required because the amount of nitrogen in air is nearly four times that of oxygen [6]. In addition, oxygen can be hardly separated from argon in the air under normal conditions by most zeolite adsorbents due to their weak or nonpolar nature and comparable polarizabilities [3]. The final product is a mixture of oxygen and argon, and the purity is limited to ~95% [7,8]. Thus, new adsorbent materials with advanced adsorption properties and higher efficiency are desired to meet the industrial demand.

A novel high-temperature sorbent-based air separation process has drawn intense attention owing to the unique oxygen storage property of the perovskite oxide sorbents. As reported by Lin's group [9,10], perovskite oxides exhibits some important characteristics that might overcome the drawbacks of zeolite adsorbents. These characteristics include a large oxygen adsorption capacity, a high oxygen adsorption rate and an infinite selectivity of oxygen over nitrogen or other gas species. Moreover, the high-temperature air separation process will be more suitable for some high-temperature applications than previous air separation processes like cryogenic distillation or conventional PSA process based on zeolites [11]. Oxy-combustion is one example, where fuel is combusted with oxygen or oxygen enriched gas instead of air to produce exhaust consisting primarily of CO_2 and water vapor. The process substantially reduces NO_x emissions and makes it easier for CO_2 capture and sequestration [12]. At present, cryogenic air separation is the default technology for oxy-fuel power plants. However, its high energy consumption reduces the total plant efficiency by 8–12% [13]. The novel high-temperature air separation process based on perovskite oxide sorbents are perceived as the best alternative to cryogenic air separation as the high temperature oxygen enriched gas product can be combined with a combustion process very efficiently [14].

Perovskite oxides are a group of metal oxides having the general formula ABO_3 [15]. Oxygen nonstoichiometry occurs in perovskite

oxides with A- and B-site cations partially substituted by another cation with a lower oxidation state. The oxygen content in perovskite oxides varies continuously as a function of oxygen partial pressure and temperature, through the creation and destruction of oxygen non-stoichiometry in the crystal lattice. The transition of oxygen non-stoichiometry, represented as δ, between the fully oxidized state and reduced state in perovskite oxides is shown in Eq. (1). Oxygen is stored in the oxide lattice during the sorption step and releases to form oxygen nonstoichiometry during the desorption step.

$$ABO_3 \leftrightarrow ABO_{3-\delta} + \frac{\delta}{2}O_2 \tag{1}$$

Among the group of perovskite oxide materials, $La_{0.1}Sr_{0.9}Co_{0.9}Fe_{0.1}O_{3-\delta}$ (LSCF1991) has been reported [15–17] to exhibit large oxygen sorption capacity and relatively high oxygen adsorption and desorption rate. Moreover, Yin et al. proved [18] the presence of an endothermic disorder-order phase transition of oxygen nonstoichiometry during the exothermic adsorption step for LSCF1991. By taking advantage of the synergic effects of these two, the heat effects of the oxygen adsorption process can be lowered to further reduce the operational cost of high-temperature air separation. LSCF1991 was therefore selected as the representative adsorbent for high-temperature air separation in this work.

Recent work [15,19–21] has shown the potential for applying the PSA technique in the high-temperature air separation process by conducting thermogravimetric analysis (TGA) and fixed-bed breakthrough experiment with perovskite oxide sorbents. The PSA process is an industrial unit operation for separating gas mixtures by repeatedly changing the ambient pressure. The pressure of the system swings between high pressure in adsorption and low pressure in desorption in a cyclic manner. Despite there being many investigations which were performed on the dynamics of oxygen adsorption and desorption of different kinds of perovskite oxide adsorbents, the performance of PSA operations on high-temperature air separation has been rarely studied as yet. In addition, the operating conditions of this high-temperature