



# A Comparison between the Product-Refill and the Equalization Oxygen Pressure Swing Adsorption Processes

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## Abstract

This work presents a design for a pressure swing adsorption process (PSA) to separate oxygen from air with approximately 95% purity, suitable for different numbers of columns and arrangements. The product refill PSA process was found to perform 33% better (weight of zeolite required or productivity) than the pressure equalization process. The design is based on the adsorption equilibrium of a binary mixture of O<sub>2</sub> and N<sub>2</sub> for two of the most commonly used adsorbents, 5A & 13X, and extension from a single column approach. Zeolite 13X was found to perform 6% better than zeolite 5A. The most effective variables were determined to be the adsorption step time and the operational pressure. Increasing the adsorption step time from 1 to 5 minutes decreased the performance by approximately 5 times. Increasing the pressure from 2 to 6 bars increased the performance by approximately 3 times.

*Keywords: Oxygen production, PSA, process design, product refill, equalization*

## 1- Introduction

The pressure swing adsorption (PSA) process for oxygen separation from air is an important alternative unit operation in the chemical industry. It has advantages in energy consumption and cost over other methods, but is only used in approximately 20% of oxygen production especially on the small-to-moderate scale. However, the cryogenic process is currently used in approximately 80% of all oxygen production on the moderate-to-large scale.

The analysis of previous works over the last three decades regarding the PSA process for oxygen separation from air using one-, two-, three-, and four-columns with different steps and arrangements allowed for the design of a process that produces high-purity oxygen with reasonable recovery and productivity. Two main arrangements of the PSA process were found: the product refill process and the pressure equalization process. The commercial zeolites 5A and 13X were the primary adsorbents used in these works. The end product is limited to 95% oxygen because of the presence of argon in air and because the zeolite adsorbents present have similar adsorption capacities for oxygen and argon [1-23].

The design of the PSA process was based on two principles. The first is the equilibrium between solutes in the fluid phase and the solute-enriched phase of the solid adsorbent.

The understanding of the adsorbent material equilibrium properties, especially capacity as a function of pressure, is of primary importance. The second is that the fixed-bed process operates as a periodic or cyclic steady state, with several different steps constituting a cycle.

Thus, knowledge of the transitional behavior of a single bed is necessary for the system design. Both time and space were used in the analysis, which is in contrast to many chemical engineering operations that can be analyzed at the steady state that only have a spatial dependence.

For an optimal design, it is crucial to understand fixed-bed performance in relation to the adsorption equilibrium and rate behavior.

An empirical approach is frequently used to design the PSA process, using the adsorption equilibrium capacity of the adsorbents, breakthrough time of a single column, and mass transfer zone (MTZ) approach [24-27].

The PSA process performance is represented by the oxygen purity of the product, recovery (oxygen in product to oxygen in feed) and productivity (continuous oxygen product flowrate to zeolite weight).

The performance is affected by the following variables: pressure, cycle time or adsorption step time, purge flow ratio, feed flowrate, and product flowrate.

No comparison study between the two PSA process arrangements, the product refill and the equalization process has been performed.

The objectives of this study are to develop a simple empirical design model of the PSA process for the separation of oxygen from air that is suitable for different numbers of columns, to compare the two PSA process arrangements (product refill process and pressure equalization process), and to study the effect of system variables on the zeolite weight required and/or the process productivity for a specified function.

## 2- Process Design Approach

In this work, the adsorption equilibrium, the single column breakthrough approach, stoichiometry and the experience of the different process steps times were used as a basis for the design of the PSA process for oxygen separation from air.

### 2.1. Equilibrium Isotherm

The nitrogen adsorption equilibrium capacity for the adsorbents can be approximated by the following linear Henry like equation as follows:

$$q = K_z P \quad (1)$$

The value of  $K_z$  equals 0.17 and 0.18 mole  $N_2$ /kg zeolite.bar for 5A and 13X zeolites, respectively. The values were obtained by the analysis of the literature data [10-11, 23].

### 2.2. Breakthrough of Single Column

The single column breakthrough approach was used as a basis for the design using a factor,  $K_B$ , representing the fraction of bed that was used, as shown in Fig. 1.

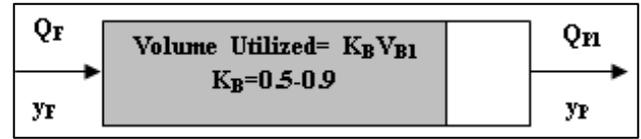


Fig. 1. Single column breakthrough

Breakthrough time was used as a guide for cycle time selection, which is approximately given by the following simple mass balance equations;

$$m_{B1} = V_{B1} \rho_B = Q_{P1} \rho_G \tau_B / 21 K_B q / 79 \quad (2)$$

$$Q_{P1} = Q_F y_F / y_P \quad (3)$$

### 2.3. PSA System

Fig. 2 shows the five PSA process cases used in present study.

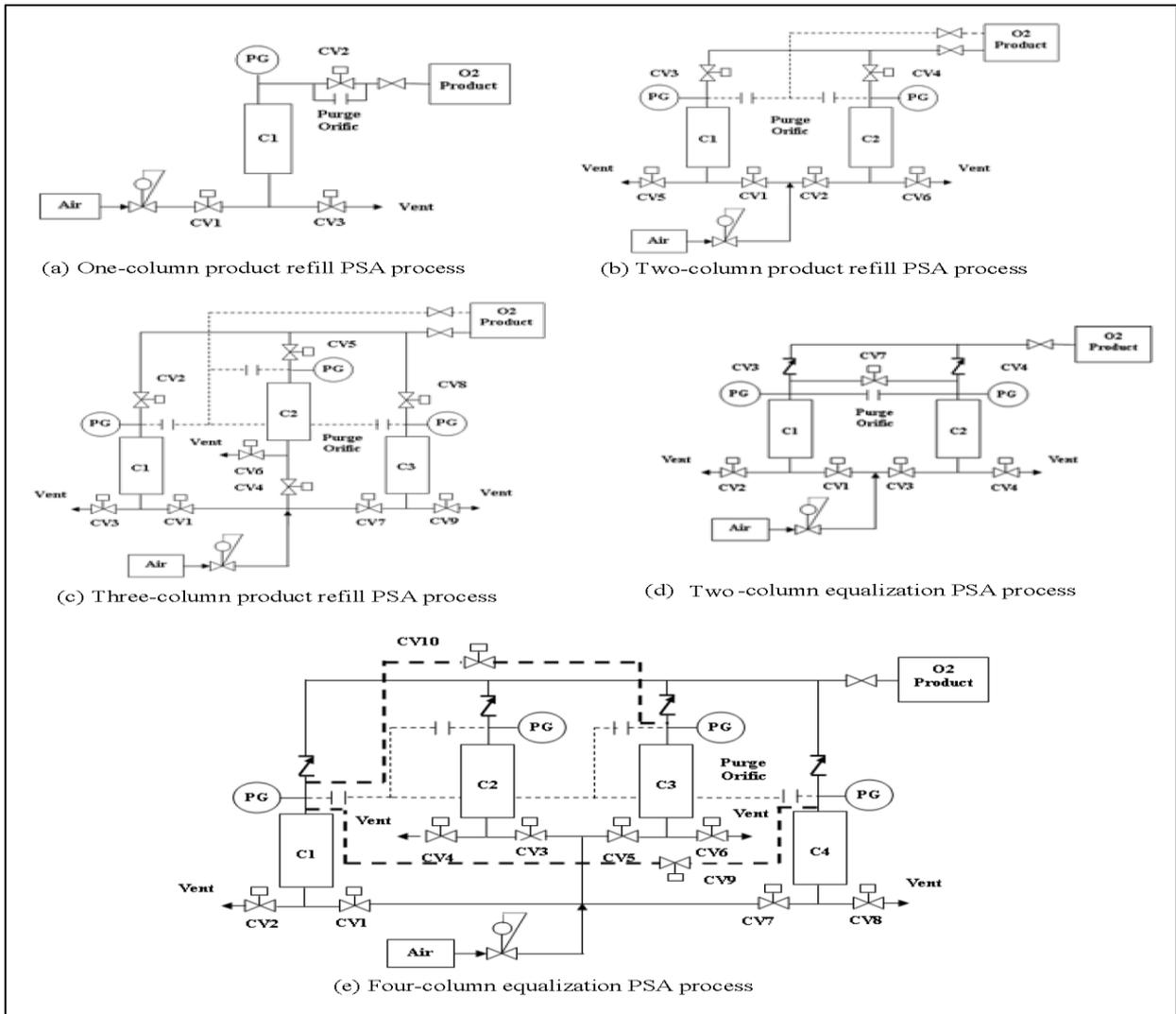


Fig. 2: The five PSA process cases used in present study

The five PSA process cases of the two main process arrangements were considered in this work as follows;

- a. Product refill or pressurizing arrangement PSA processes, 4-steps (AD-DP-PG-PP) system, were used for one-column with a product flow utilized time fraction  $K_C=1/3$ , two-columns with  $K_C=2/3$  and three-columns with  $K_C=1$ , as shown in Table 1.

Table 1. Product refill process steps

Columns	Steps						$K_C$
One-Columns							
One-Column	AD	AD	DP	PG	PG	PP	1/3
Two-Columns							
1 <sup>st</sup> column	AD	AD	DP	PG	PG	PP	2/3
2 <sup>nd</sup> column	DP	PG	PG	PP	AD	AD	
Three-Columns							
1 <sup>st</sup> column	AD	AD	DP	PG	PG	PP	1
2 <sup>nd</sup> column	PG	PP	AD	AD	DP	PG	
3 <sup>rd</sup> column	DP	PG	PG	PP	AD	AD	

- b. Equalization arrangement PSA processes, 6-steps (AD-ED-DP-PG-EP-FP) system, were used for two-columns with a product flow utilized time fraction  $K_C=1/2$  and four-columns with  $K_C=1$ , as shown in Table 2.

Table 2. Pressure equalization process steps

Columns	Steps								$K_C$	
Two-Columns										
1 <sup>st</sup> column	A	A	E	D	P	P	E	F		1/2
	D	D	D	P	G	G	P	P		
2 <sup>nd</sup> column	P	P	E	F	A	A	E	D		
	G	G	P	P	D	D	D	P		
Four-Columns										
1 <sup>st</sup> column	A	A	E	D	P	P	E	F		1
	D	D	D	P	G	G	P	P		
2 <sup>nd</sup> column	E	F	A	A	E	D	P	P		
	P	P	D	D	D	P	G	G		
3 <sup>rd</sup> column	P	P	E	F	A	A	E	D		
	G	G	P	P	D	D	D	P		
4 <sup>th</sup> column	E	D	P	P	E	F	A	A		
	D	P	G	G	P	P	D	D		

The total cycle time is the summation of the process steps times;

$$\tau = \sum_{i=1}^n \tau_i \quad (4)$$

The 4-steps for the product refill PSA process cycle ( $\tau=3\tau_{AD}$ ) is as follows:

- 1- The adsorption (AD) step was taken time  $\tau_{AD}=1-5$  minutes.
- 2- The depressurizing (DP) step was taken time  $\tau_{DP}=0.5 * \tau_{AD}$ .
- 3- The purging (PG) step was taken time  $\tau_{PG} = \tau_{AD}$ .
- 4- The product pressurizing (PP) step was taken time  $\tau_{PP}=0.5 * \tau_{AD}$ .

The 6- steps PSA equalization process cycle ( $\tau=4\tau_{AD}$ ) is as follows:

- 1- The adsorption (AD) step was taken time  $\tau_{AD}=1-5$  minutes.
- 2- The equalization depressurizing (ED) step was taken time  $\tau_{ED}=0.5 * \tau_{AD}$ .
- 3- The depressurizing (DP) step was taken time  $\tau_{DP}=0.5 * \tau_{AD}$ .
- 4- The purging (PG) step was taken time  $\tau_{PG} = \tau_{AD}$ .
- 5- The equalization pressurizing (EP) step was taken time  $\tau_{EP}=0.5 * \tau_{AD}$ .
- 6- The feed pressurizing (FP) step was taken time  $\tau_{FP}=0.5 * \tau_{AD}$ .

In the PSA process, the product flowrate is not actually continuous, but was assumed to be continuous to simplify the design. As a result a factor,  $K_C$ , the utilized time fraction for the product flow, was introduced and calculated from the following equation;

$$K_C = N \tau_{AD} / \tau \quad (5)$$

The PSA system approach introduced the product flow utilizes time fraction  $K_C$  for different system arrangements, and the purge flow factor  $K_P$  (fraction of product flow in a single column), as shown in Fig. 3.

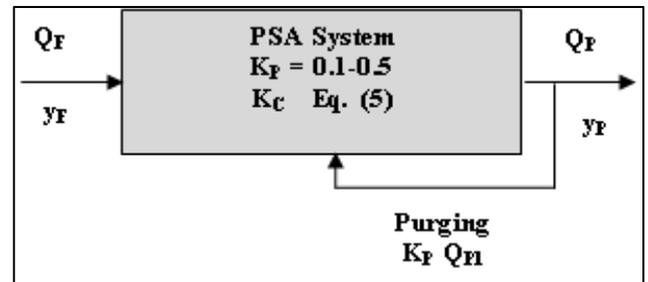


Fig. 3. PSA system

For the PSA system, the product flowrate and productivity were calculated from the following equations;

$$Q_P = K_C(1 - K_P)Q_{P1} \quad (6)$$

$$m_B = Nm_{B1} \quad (7)$$

$$Productivity = Q_P y_P / m_B \quad (8)$$

The recovery was difficult to calculate accurately because of intermediate steps and because the feed is not actually continuous.

A case study of a PSA process of 1 kg/h production of approximately 95% oxygen purity was used in the present study. Four process variables were studied, the adsorption step time  $\tau_{AD}$  (1-5 minutes), pressure P (2-6 bar), utilized bed factor  $K_B$  (0.5-0.9), and purge factor  $K_P$  (0.1-0.5).

### 3- Results And Discussion

Figures (4) and (5) show the effect of the adsorption step time, zeolite type and PSA system arrangement on the process performance (weight of zeolite required or productivity), at constant values for P,  $K_B$  &  $K_P$  of 6 bar, 0.9, and 0.1, respectively.

Zeolite 13X only had an approximately 6% better performance than 5A zeolite.

This is in agreement with data obtained by Mofarahi & Shokroo [23].

The product refill 4-steps PSA process had an approximate 33% better performance than the pressure equalization 6-steps process. This is a novel point found by this work that has not been mentioned in the literature.

Increasing the adsorption step time ( $\tau_{AD}$ ) from 1 to 5 minutes decreased the performance by an approximate factor of 5. The adsorption time was the most effective variable.

The present work productivity range results (5-35 liter oxygen/kg zeolite h) are in agreement with most of the current literature.

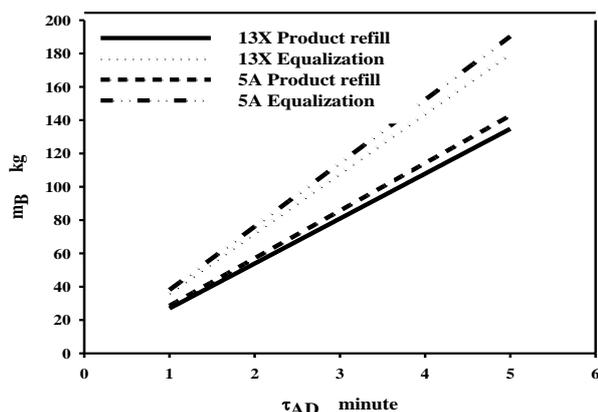


Fig. 4. Effect of the adsorption step time, zeolite type and PSA system on zeolite weight at P=6 bar,  $K_B=0.9$  &  $K_P=0.1$ .

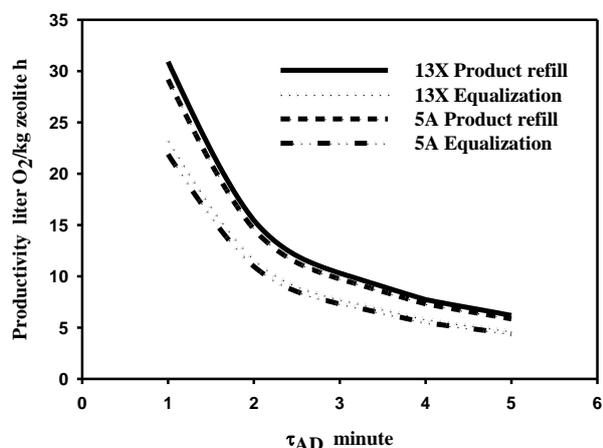


Fig. 5. Effect of the adsorption step time, zeolite type and PSA system on productivity at P=6 bar,  $K_B=0.9$  &  $K_P=0.1$ .

Figure (6) shows the effect of the operating pressure (P) on the process productivity, at constant values for  $\tau_{AD}$ ,  $K_B$  and  $K_P$  of 1 minute, 0.9, and 0.1, respectively. Increasing pressure from 2 to 6 bars increased the performance by an approximate factor of 3. The operating pressure was the most effective variable after the adsorption step time variable ( $\tau_{AD}$ ). This result is in agreement with several published works [19-22], whereas other works noted negative results for the effect of increasing pressure [1,9-11,23]. This contradiction may be due to the variables being highly interacted.

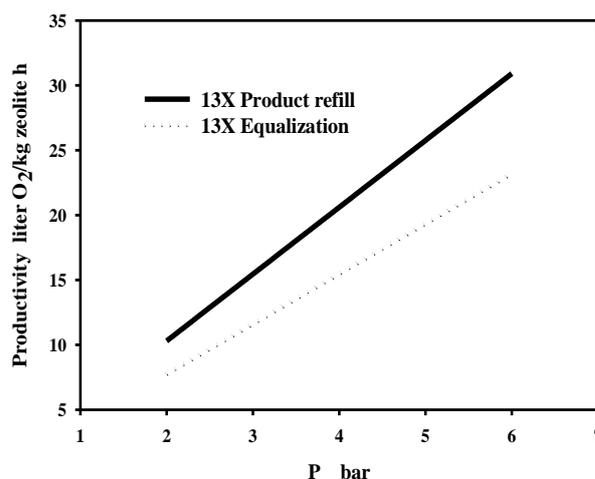


Fig. 6. Effect of the operating pressure on productivity at  $\tau_{AD}=1$  minute,  $K_B=0.9$  &  $K_P=0.1$ .

Figure (7) shows the effect of the utilized bed factor ( $K_B$ ) on the process productivity at constant values for  $\tau_{AD}$ , P and  $K_P$  of 1 minute, 6 bars, and 0.1, respectively. Increasing the utilized bed factor from 0.5 to 0.9 approximately doubled the performance.

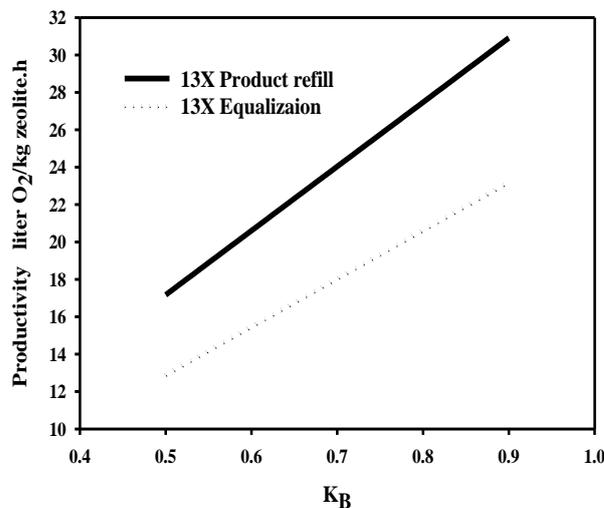


Fig. 7. Effect of the bed volume utilized factor on productivity at  $\tau_{AD}=1$  minute, P=6 bar, &  $K_P=0.1$ .

Figure (8) shows the effect of the purge factor ( $K_P$ ) on the process productivity at constant values for  $\tau_{AD}$ ,  $P$  and  $K_B$  of 1 minute, 6 bars, and 0.9 respectively. Increasing the purge factor from 0.5 to 0.9 decreased the performance by approximately half.

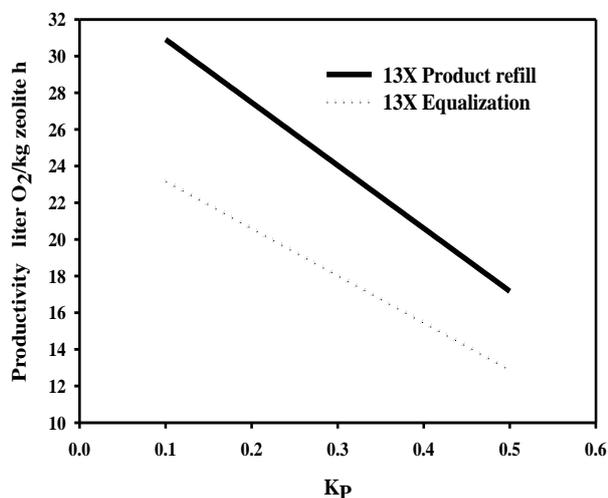


Fig. 8: Effect of the purge factor on productivity at  $\tau_{AD}=1$  minute,  $P=6$  bars, &  $K_B=0.9$

#### 4- Conclusions

- 1- The product refill 4-steps PSA process had a 33% improved performance (weight of zeolite required or productivity) compared with the pressure equalization 6-steps process. This is a novel point found by the present study and has not reported in previous published works.
- 2- Zeolite 13X only had a 6% higher performance than 5A zeolite.
- 3- The most effective variables were the adsorption step time and pressure. Increasing the adsorption step time from 1 to 5 minutes decreased the performance by a factor of 5, and increasing the pressure from 2 to 6 bars increased the performance by a factor of 3.

#### Nomenclatures

##### Symbols

$K_B$	Bed volume utilized fraction
$K_C$	PSA system product flow utilized time fraction
$K_P$	Purge flow fraction
$K_Z$	Adsorption constant, mole $N_2$ /kg zeolite. Bar
$m_B$	Total zeolite weight, kg
$m_{B1}$	Single column zeolite weight, kg
$n$	Number of steps
$N$	Number of columns
$P$	Pressure, bar

$q$	Equilibrium capacity, mole $N_2$ /kg zeolite
$Q_F$	Feed flowrate, $m^3/h$
$Q_P$	Product flowrate, $m^3/h$
$Q_{P1}$	Single column product flowrate, $m^3/h$
$V_B$	Total zeolite bed volume, $m^3$
$V_{B1}$	Single column zeolite bed volume, $m^3$
$y_F$	Feed oxygen fraction
$y_P$	Product oxygen fraction

##### Greek Symbols

$\rho_B$	Zeolite bed bulk density, $kg/m^3$
$\rho_G$	Gas density, $kg/m^3$
$\tau$	Total cycle time, minute
$\tau_{AD}$	Adsorption step time, minute
$\tau_B$	Breakthrough time, minute
$\tau_{DP}$	Depressurizing step time, minute
$\tau_{ED}$	Equalization depressurizing step time, minute
$\tau_{EP}$	Equalization pressurizing step time, minute
$\tau_{FP}$	Feed pressurizing step time, minute
$\tau_i$	General step time, minute
$\tau_{PG}$	Purging step time, minute
$\tau_{PP}$	Product pressurizing step time, minute

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