An experimental and statistical model of a cyclic pressure swing adsorption column for hydrogen purification

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Abstract−An experimental and statistical study was performed for the purification of hydrogen in an H_2/CO_2 mixture using the PSA process with activated carbon. This process has been extensively used for the high purification of gas mixtures. Central composite design (CCD) was used for the modeling and optimization of the process, regardless of complex and time-consuming equations generally employed in the literature. The statistical analysis of models, as obtained from the CCD method, revealed that distinct second-order polynomial equations, with F-value more than 200, p-value less than 0.0001, and R-squared more than 0.9900, could predict the experimental data for purity, recovery and productivity of hydrogen. Based on the established models, as the purge-to-feed (P/F) ratio increased, the purity increased, while the recovery and productivity decreased. The recovery and productivity first increased and then decreased as adsorption time increased. Thus, the optimal condition of the PSA process was obtained using the CCD models.

Keywords: Hydrogen Purification, PSA, CCD Method, P/F Ratio, Adsorption Time

INTRODUCTION

Hydrogen is a noteworthy fuel due to its high energy content, environmental friendliness, and numerous applications in petroleum and chemical processing industries [1]. Therefore, considerable attention has been paid to the purification of hydrogen [2-4]. The pressure swing adsorption (PSA) process is extensively applied to obtain high purity hydrogen, such that more than 85 percent of global hydrogen production units utilize the PSA process for hydrogen purification [2]. The potential of the PSA process for hydrogen or other gases purification has been reviewed thoroughly in the literature [5,6].

Typically, each cycle of the PSA process contains five steps [1,7]:
I) Pressurization
II) Adsorption
III) Cocurrent depressurization
IV) Countercurrent blowdown
V) Purge

In step I, the adsorption bed is pressurized to the desired value by the feed stream. In step II, feed flows through the bed, pure hydrogen is produced, and impurities are adsorbed. Adsorption time (Ad.t) in step II is a key parameter influencing the PSA performance. Cocurrent blowdown in step III is used to recover the hydrogen remaining in the bed. By depressurization in this step, desorption of the adsorbates is initiated. In step IV, the maximum desorption of impurities is performed countercurrently to the feed direction. In step V, the adsorption bed is cleaned from impurities by using a purge gas. Another key parameter in the PSA process is

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purge-to-feed ratio (P/F), which is defined as the amount of hydrogen used in step V divided by hydrogen entering into the bed in step II. The performance of a PSA process is measured by purity, recovery, and productivity of hydrogen. Hydrogen purity is defined as the volume percent of pure hydrogen on product stream. The recovery and productivity of hydrogen are defined as shown in the following equations [8]:

$$
\begin{aligned}
&H_2 \text{ Recovery (\%)} \\
&= \frac{H_2 \text{ from step II (lit)} - H_2 \text{ used in step V (lit)}}{H_2 \text{ in step I and II (lit)}} \times 100
\end{aligned}
\tag{1}
$$

$$
\begin{aligned}
&\text{Productivity} \left(\frac{\text{lit}}{\text{gr} \cdot \text{s}}\right) \\
&= \frac{H_2 \text{ from step II (lit)} - H_2 \text{ used in step V (lit)}}{\text{total cycle time (s)} \times \text{adsorbent used (gr)}}
\end{aligned}
\tag{2}
$$

Numerous applications in chemical engineering, especially fuel cells, require high purity hydrogen. Based on the production method, some impurities exist in hydrogen. For instance, the product stream of steam methane reforming consists of hydrogen, carbon dioxide, carbon monoxide, water vapor, methane, etc. [1]. Carbon dioxide is also produced by other reforming methods; thus great attention has been paid to removing this gas in the H_2/CO_2 mixture using activated carbon in the PSA process [9,10].

Based on the literature, great effort has been devoted to providing a reliable model and optimizing the variables for the PSA process. Kim and Suh [11] developed a model describing mass transfer rates in a spherical particle by adsorption and desorption steps. Choi et al. [12] suggested a model of the PSA process for CO_2 separation in three adsorption beds; based on their model, they optimized the variables of reflux and adsorption time. Yang and Doong [7] showed a pore diffusion model can predict all PSA process char-

acteristics successfully. Yang et al. [13] studied the bulk separation of two binary systems (H_2/CO_2 and H_2/CO) with zeolite 5A by the one-column PSA, and their results showed that the performance of all steps of the PSA process could be predicted by a linear driving force (LDF) model accompanied with equilibrium relationships and the energy balance. Mivechian and Pakizeh [14] simulated a PSA, membrane and gas absorption process for hydrogen recovery from Tehran refinery off-gas, and reported the effects of variables. Based on their calculations, the total cost of the PSA process was lower than that of the other processes.

Generally, modeling and optimization of the PSA process involves the complex PDEs system and a time-consuming procedure. Therefore, it is very important to present a method to obtain a reliable and simple model of the PSA process without common complications. Recently, application of the CCD method has been of interest in other adsorption processes due to fewer experimental tests, consideration of the interaction between variables, reliable modeling, etc. For instance, the CCD method has been used in the adsorption of safaranin O by tin sulfide nanoparticles loaded on the activated carbon [15], Fe(III) adsorption from water using Bentonite clay [16], adsorption of brilliant green and eosin B onto ZnS nanoparticles loaded activated carbon [17], etc. Statistical model using central composite design for the PSA process has received much less attention, as compared to other applications. Therefore, the potential of CCD method for modeling as well as optimization of the one-column PSA process has been investigated in this research.

The main purpose of this study was to develop a statistical model for the PSA process to optimize effective parameters contributing to the purification of hydrogen in an H_2/CO_2 mixture. In the present study, the effects of P/F ratio and adsorption time (as variable factors) on hydrogen purity, productivity, and recovery were simultaneously investigated by employing the CCD method. The interaction between variables was also considered, something which has received much less attention in the literature. Based on the impor-

Table 1. Characteristics of the adsorption column

Bed length	75 cm
Bed inside diameter	0.87
Bed outside diameter	1.27 cm
Particle density	440 kg/m^3
Mesh size	10-20
Total void fraction	0.75

tance of each response, optimizations were also performed by the desirability function. The details are described in the following discussion.

MATERIALS AND METHODS

1. Materials

A single-bed column was filled with approximately 12 g of the commercial activated carbon (Jahan Shimi Company). The adsorption column was 75 cm in height and 1.27 cm in diameter. A stainless-steel pipe was chosen to carry out the experiments. The characterization of the adsorption column is shown in Table 1. The feed consisted of equal volumetric fractions of H_2 and CO_2 (50 : 50%) with 99.9% purity. The gases were analyzed by an online gas chromatography (TGF, 2552) equipped with Propack Q column, FID detector, and a methanizer.

2. Process Description

A schematic diagram of the PSA unit is shown in Fig. 1. To analyze the feed composition before each run, valve 06 (V-06) was opened, others were closed, and then the feed was directly sent to the GC. As mentioned earlier, five steps could be considered for the PSA column. Therefore, to satisfy these steps, the experiments were carried out at the pressure of 6 bar in the following steps:

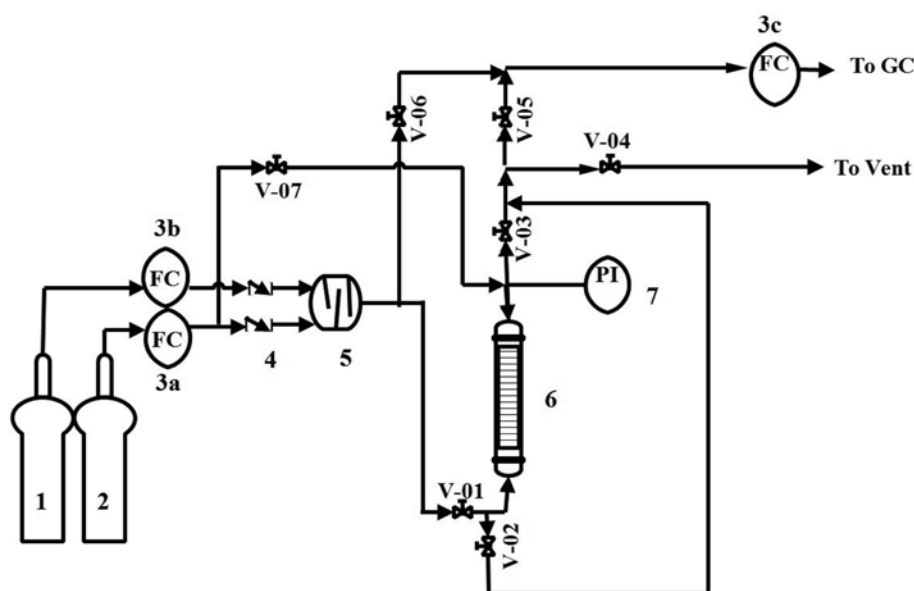1) First, valves 2, 4, 6, and 7 were closed and valves 1, 3, and 5 were opened.

Fig. 1. A schematic diagram of the PSA experiments.
    1. CO$_2$ cylinder   2. H$_2$ cylinder   3. Mass flow meter   4. Check valve   5. Gas mixer   6. Adsorption column   7. Pressure gage

2) MFCs (Alicat Scientific, M-1000SCCM-D) 3a and 3b were adjusted at the designed value and MFC 3c was adjusted at the value of zero (step I).

3) When the pressure reached to 6 bar, MFC 3c was adjusted at the desired value and time was measured by chronometer (step II).

4) The outlet gas was analyzed by GC a few times before step II.

5) After step II, MFCs 3a and 3b were set at zero. The needle valve 4 (V-04) was slightly opened to drop the pressure to 3 bar in 2.5 minutes (step III).

6) Valve 3 was closed, and valves 2, 4, and 7 were completely opened. Then MFC 3a was adjusted in the designed value to purge the adsorption bed by pure hydrogen (steps IV and V).

The desorption of CO_2 was completely performed using pure hydrogen before the beginning of each PSA experiment. These six steps were continued till a steady state condition was reached. For each run, 10-15 cycles were carried out to achieve the steady state condition.

3. Experiment Design

The CCD method was used for experiment design and the optimization of the factors. The CCD technique was introduced by Box and Wilson [18]. This design consists of the following parts: fractional factorial design points (+1 and −1), axial points (+α and −α), and center points. +1 and −1 levels are the boundary of modeling space. The maximum and minimum of each variable are indicated by +α and −α levels, respectively. The α value, which depends on the number of variables (k), can be determined by $\alpha=2^{k/4}$. The total number of required tests (N) can be calculated by Eq. (3) [18]:

$$N=2^k+2k+N_0 \tag{3}$$

where 2^k, 2k, and N_0 refer to factorial, axial, and the central points of runs, respectively. For instance, if the number of variables is equal to 2, the experiment tests include (−1, −1), (+1, −1), (−1, +1), and (+1, +1) as the factorial points, (−α, 0), (+α, 0), (0, −α) and (0, +α) as the axial points, and (0, 0) as the center point. These nine points were specified with the range of variables. The center point is usually repeated four to six times to get a good estimate of the experimental error [18]. With respect to the experimental data as well as the statistical parameters, the CCD method can develop an appropriate second order polynomial equation as shown below [19].

$$y=\beta_0+\beta_1x_1+\beta_2x_2+\beta_3x_3+\beta_{11}x_1^2+\beta_{22}x_2^2+\beta_{33}x_3^2+\beta_{12}x_1x_2+\beta_{13}x_1x_3+\beta_{23}x_2x_3 \tag{4}$$

where y is the predicted response, and (β_0), (β_1, β_2, β_3), (β_{12}, β_{13}, β_{23}), and (β_{11}, β_{22}, β_{33}) represent intercept, linear, interaction, and quadratic coefficient, respectively. According to Eq. (4), optimization of the response (y) can be applied.

In this study, the P/F ratio and adsorption time were chosen as the independent factors, so there were four factorial points, with four axial points and N_0 was equal to 5. The responses which should be modeled and optimized were purity, recovery, and productivity of hydrogen.

RESULTS

1. Preliminary Experiments

To recognize the experimental region of the variable factors, some preliminary experiments were carried out. Fig. 2 represents the
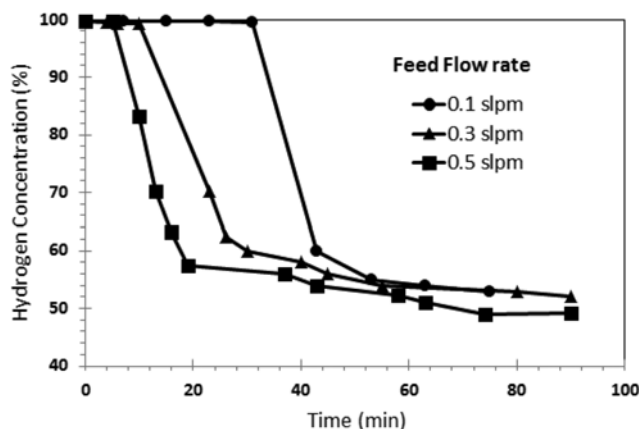
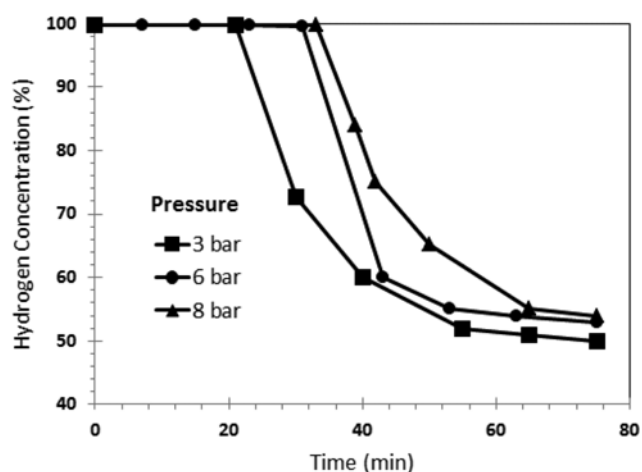Fig. 2. The effect of feed flow rate on breakthrough curves at 6 bar and $H_2/CO_2=1$ in the one-column PSA process.

Fig. 3. The effect of pressure on breakthrough curves at the constant feed flow rate (0.1 slpm) and $H_2/CO_2=1$ in the one-column PSA process.

effect of feed flow on breakthrough curves at the constant pressure (6 bar). As can be seen, the slower the feed flow rate, the longer the breakthrough time. In addition, the breakthrough time had a non-linear trend in the feed flow rate. This non-linear trend could be attributed to the mass transfer resistance, which decreases non-linearly with increasing the feed flow rate. It seemed that at 0.1 slpm (standard liter per minute), there was enough time for step II in the experiments. Fig. 3 shows the effect of feed pressure on breakthrough curves at the constant feed flow (0.1 slpm). The breakthrough time increased as the pressure was raised. However, pressure did not make much difference in the breakthrough time at 8 bar, as compared to that at 6 bar. This trend could be attributed to the adsorption capacity of the activated carbon. As pressure increased, more sites in the adsorbent were accessible, so greater amounts of CO_2 were adsorbed till the capacity of adsorbent reached to the maximum value. According to the results of these preliminary experiments, the one-column PSA process was carried out at feed velocity of 0.1 slpm and the pressure of 6 bar.

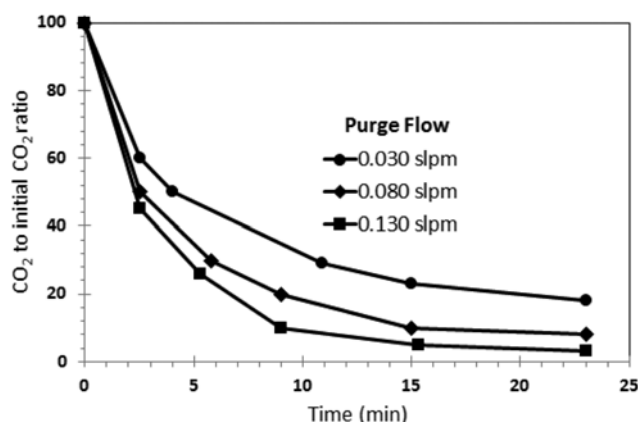To study the capability of desorption, pure hydrogen at various

Fig. 4. Desorption of CO_2 with H_2 at different purge flows in the one-column PSA process.

Table 2. The range and levels of the independent factors

Factors	Range and level				
	$-\alpha$	-1	0	$+1$	$+\alpha$
P/F	0.10	0.13	0.2	0.27	0.30
Ad.t (min)	5	6.46	10	13.54	15

flow rates was used to regenerate the adsorption bed which had been fully saturated with CO_2. As can be seen in Fig. 4, the desorption time was increased as purge flow rate was decreased, although, after 2.5 min, more than 40% of CO_2 was removed from bed in each purge flow rate. During the adsorption time (step II), the bed was not saturated and at 2.5 min, the slope of Fig. 4 was very sharp, so it seemed that 2.5 min was suitable for purge step (step V).

2. Experimental Design and Statistical Model

The P/F ratio and adsorption time were considered as two independent factors. Based on the CCD methodology, each numeric factor was varied over three groups of design points: $+\alpha$ and $-\alpha$

Table 4. Analysis of variance for the established models of purity, recovery, and productivity

Parameter	Model		
	Purity	Recovery	Productivity
F value	204.81	367.00	483.92
P value	<0.0001	<0.0001	<0.0001
R-squared	0.9903	0.9946	0.9959
Adeq precision	41.405	49.374	61.653

as axial points, and $+1$ and -1 as the factorial points, and the central points. According to some preliminary experiments as well as the literature review, the ranges of the factors and their levels are shown in Table 2. Thirteen runs based on CCD methodology were designed, as given in Table 3. According to each response run and regression analysis, the experimental values could be modeled by a second-order polynomial equation, as represented in Eqs. (5)-(7) for purity, recovery, and productivity, respectively.

$$\text{Purity} = 62.84 + 231.76\,(\text{P/F}) + 2.38\,(\text{Ad.t}) - 447.35\,(\text{P/F})^2 - 0.18\,(\text{Ad.t})^2 \quad (5)$$

$$\text{Recovery} = 12.01 + 90.34\,(\text{P/F}) + 6.37\,(\text{Ad.t}) - 306.00\,(\text{P/F})^2 - 0.28\,(\text{Ad.t})^2 \quad (6)$$

$$\text{Productivity} = 3.85 \times 10^{-6} + 5.66 \times 10^{-5}\,(\text{P/F}) + 4.41 \times 10^{-6}\,(\text{Ad.t}) \\ - 1.91 \times 10^{-4}\,(\text{P/F})^2 - 1.82 \times 10^{-7}\,(\text{Ad.t})^2 \quad (7)$$

In the present study, p-value for terms P/F, Ad.t, $(\text{P/F})^2$, and $(\text{Ad.t})^2$ was less than 0.0001, showing that these terms were significant in all the models. The interaction between variables (P/F× Ad.t) was not significant (p-value>0.10), so it was neglected. Note that if the "p-value" is less than 0.05, the model terms are significant, and if it is greater than 0.10, they are not [19]. The statistical parameters for the established models are presented in Table 4. The F-value for purity, recovery, and productivity was 204.81, 376.00, and 483.92, respectively. Regarding p-value and F-value of the responses, it could be concluded that models were significant, and there was only a 0.01% chance that a Model F-value could occur due to noise

Table 3. The designed experiment by CCD method and the corresponding responses for the PSA process

Run	Type of points	The factors		The responses		
		P/F	Ad.t (min)	Purity (%)	Recovery (%)	Productivity (lit/gr·s)
1		0.30	10	98.53	48.01	2.97E-05
2	Axial points	0.10	10	86.53	53.62	3.32E-05
3		0.20	5	98.99	42.59	2.49E-05
4		0.20	15	85.96	51.34	3.27E-05
5		0.27	13.55	91.75	49.22	3.12E-05
6	Factorial points	0.27	6.45	99.64	43.72	2.62E-05
7		0.13	6.45	93.65	48.54	2.90E-05
8		0.13	13.55	84.83	54.60	3.46E-05
9		0.20	10	96.96	53.92	3.34E-05
10		0.20	10	97.57	54.35	3.37E-05
11	Center points	0.20	10	96.97	53.93	3.34E-05
12		0.20	10	96.53	53.62	3.32E-05
13		0.20	10	96.90	53.88	3.34E-05

for all models [19].

R-Squared was more than 0.9900 for all models, indicating that the regression line approximated the real data points properly. Adeq Precision measures the signal to noise ratio and a ratio greater than 4 is desirable. For all models, Adeq Precision was greater than 4. Therefore, the proposed models, as obtained from the CCD method, could be used to navigate the design space, regardless of complex and time-consuming equations which generally were employed in the literature. Thus, the models are more reliable and accurate than
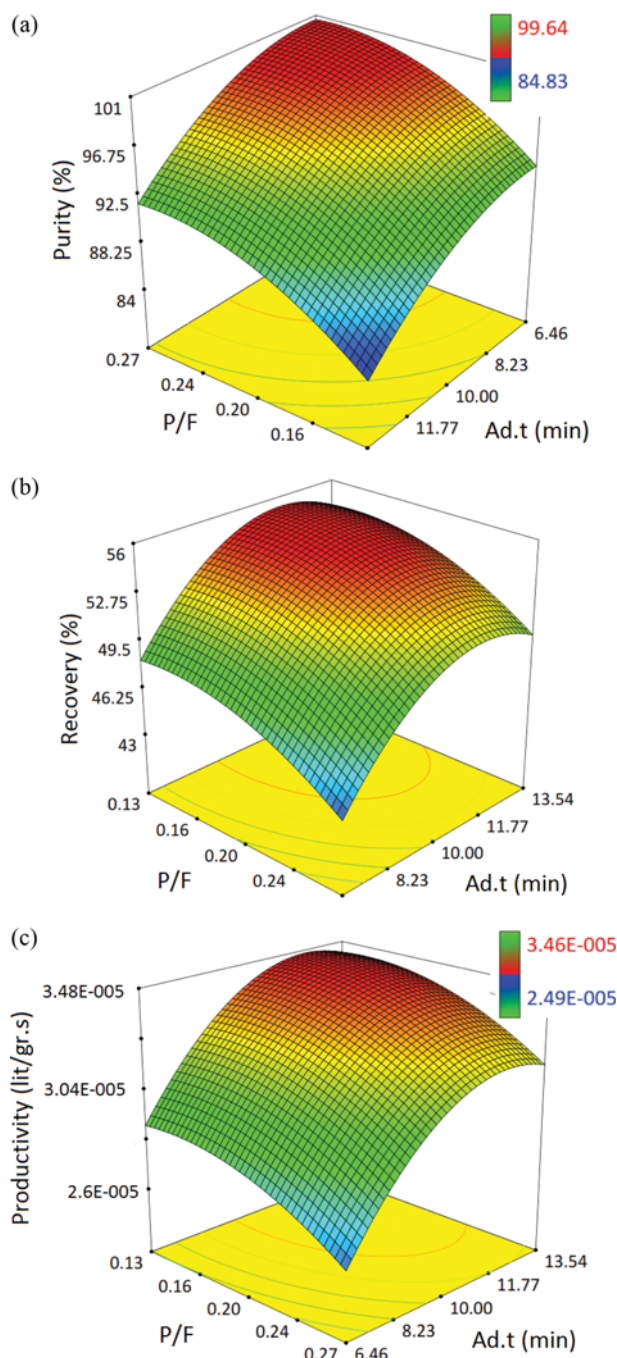

Fig. 5. Response surface plot of (a) purity, (b) recovery, and (c) productivity vs. the P/F ratio and Ad.t in the one-column PSA process.

the pre-existing models in a wider range of process conditions. The modeling of the PSA process with CCD method by considering the large number and wide range of factors can be studied in the future research.

3. The Effect of Independent Factors on Responses

To measure the performance of the PSA process, we studied three vital parameters of purity, recovery, and productivity. Fig. 5 shows the effect of independent factors on the mentioned parameters. As can be seen, an increase in P/F ratio caused purity increased (Fig. 5(a)), recovery (Fig. 5(b)) and productivity (Fig. 5(c)) decreased. When the P/F ratio increased, the high length of adsorption bed was cleaned and more fresh adsorbent could be used in each cycle, so purity reached the maximum value. In contrast to the purity, the recovery of hydrogen and productivity dropped, as P/F ratio increased, due to the higher amount of hydrogen used in the purge step. As adsorption time increased, purity had an approximately constant value up to 10 min and then it declined due to the less amount of the available fresh adsorbent at a higher adsorption time. The recovery and productivity first increased and then slightly decreased as the adsorption time enhanced. When the adsorption time varied from 6.46 min to 10 min, the purity had an almost constant value and more hydrogen was produced; thus, recovery and productivity increased. As adsorption time exceeded 10 min, the purity sharply decreased, so less hydrogen was produced, which led to lower recovery and productivity. The results were confirmed by the experimental data, as well as the statistical parameters in Table 4. Furthermore, these trends were in a good agreement with other studies [7,13] using different approaches.

4. Process Optimization

The one-column PSA process could be optimized for specific purposes by using the selected models. The P/F ratio and adsorption time could make a different trend on the mentioned models. Therefore, the variables were optimized to maximize the responses within the experimental region. Depending on the response which was "in range" or "maximize," seven cases could be found in Table 5. Note that the goal of all operating factors was set "in range." It could be seen that the predicted values were very close to the practical values in each case. Therefore, the models could predict the optimum values. Based on the importance of each response, one case could be considered. For instance, if purity and productivity are the major responses, case 2 can be used, because these responses are "maximize" and recovery is "in range." If only purity is the major response (seventh case), P/F of 0.27 and Ad.t of 8.91 min are the optimum values. In this case, maximum purity can be achieved at the expense of low recovery and productivity.

In some cases, as shown in Table 5, more than one prediction has been produced, but one of them is reported. The overall desirability (D) is a key parameter to select the best point of prediction values. The overall desirability is an objective function whose value varies from 0 to 1. The numerical optimization finds a point that maximizes the desirability function. When maximization of responses is required, the overall desirability and desirability for each response are defined by Eqs. (8) and (9), respectively [20].

$$D = (d_1^{r_1} \times d_2^{r_2} \times \ldots \times d_m^{r_m})^{\frac{1}{r_1+r_2+\cdots+r_m}} \tag{8}$$

Table 5. Various conditions for the maximization of responses

No.	Productivity (lit/gr·s)			Purity (%)			Recovery (%)			P/F	Ad.t	D
	Goal	Pre $\times 10^5$	Prac $\times 10^5$	Goal	Pre	Prac	Goal	Pre	Prac			
1	M	3.45	3.40	In	87.31	86.23	In	54.59	53.86	0.15	13.26	0.988
2	M	3.31	3.27	M	97.71	96.54	In	53.37	52.86	0.21	9.96	0.855
3	M	3.37	3.30	M	96.31	95.09	M	54.31	53.25	0.2	10.42	0.884
4	M	3.47	3.37	In	89.87	88.03	M	55.19	53.55	0.16	12.39	1
5	In	3.30	3.32	M	97.71	98.14	M	53.41	53.67	0.21	9.77	0.885
6	In	3.42	3.36	In	94.71	93.25	M	54.93	53.99	0.18	10.85	1
7	In	3.02	3.01	M	99.66	99.60	In	49.21	49.06	0.27	8.91	1

M: Maximize, In: In range, Pre: Predicted, Prac: Practical, D: Overall desirability

$$d_i = \left(\frac{y_i - L}{T - L} \right)^w \tag{9}$$

When a response is in range, the desirability is defined as shown in the following procedure:

$d_i = 0$ if response<low value
$d_i = 1$ as response varies from low to high
$d_i = 0$ if response>high value

where D is the overall desirability, d_i is desirability for each response, r_i represents the importance of each response, which varies from 2 to 5, and w is the weight of each response. T and L represent the maximum and minimum possible value for the responses, respectively; y_i is the optimum value. Moreover, d_i for "in range" is included in the overall desirability equation (Eq. (8)), but it is not counted in determining "r_i". The value of overall desirability is completely dependent on how closely the lower and upper limits are set relative to the actual optimum [20].

Fig. 6 represents the overall desirability versus P/F and Ad.t, when purity was maximum, and recovery and productivity were in range. As can be seen, there was a surface for the desirability of 1, with the purity having the maximum possible value. This surface was close to the maximum value of P/F and the minimum value of Ad.t. Based on the operating conditions and other limitations, a point on this surface could be selected. For instance, in this surface maximum Ad.t and minimum P/F were considered to achieve the maximum recovery and productivity. In this case, P/F of 0.24 and Ad.t of 8.21 min led to the productivity and recovery of 3.04×10^{-5}, 49.82, respectively. This case was a little better than the seventh case in Table 5, which had the same purity, but greater amount of productivity and recovery could be obtained. Therefore, the surface with a desirability of 1 provided a flexible PSA process at the maximum purity. Other cases can also be analyzed with this method. A practical test in this case was carried out and no significant difference with the prediction values was observed. Therefore, the PSA process was accurately optimized by this noble approach. There was a surface with the overall desirability of 0 near the high adsorption time and low P/F ratio, indicating that recovery (or productivity) was obtained out of the experimental values; thus, the purity could not be maximized in this surface. Other independent factors and operating conditions in the PSA process by CCD method can be studied in the future research.

CONCLUSION

We used a one-column PSA process to separate hydrogen from a H_2/CO_2 (50/50 volume percent) mixture. Based on the preliminary tests and CCD methodology, some experiments were designed and performed. In accordance with statistical analysis, the experimental data were modeled, and for each response a distinct second-order polynomial equation was obtained. The interaction between factors did not take place for all the responses. With respect to statistical parameters, the PSA process could be modeled appropriately by employing the CCD methodology. As the P/F ratio increased, purity increased, but recovery and productivity decreased. As adsorption time increased, purity had an almost constant value till 10 min and then declined, which could be attributed to the lesser amount of the available fresh adsorbent at the higher adsorption time. Depending on the response which was "in range" or "maximize," optimization of process was performed. When the goal of all responses was "maximize," P/F=0.2, Ad.t=10.42 min, Purity=96.31, Recovery=54.31, and productivity=3.37×10^{-5} were obtained with the desirability of 0.884. For various optimization conditions,
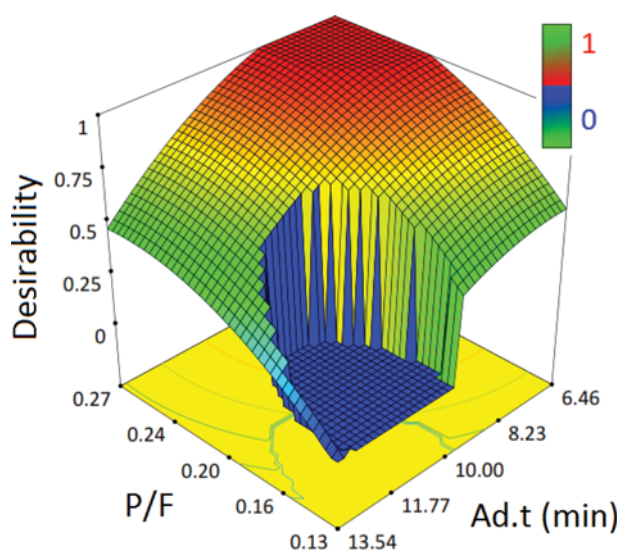

Fig. 6. Response surface plot of desirability vs. the P/F ratio and Ad.t in the one-column PSA process.

the predicted values were very close to the practical values obtained from the experiments, due to the high precision of the models. The purity in the maximum possible value is often the most desirable case, which models predicted a surface with the desirability of 1 for this case. Maximization of the recovery and productivity in this surface resulted in P/F=0.24, Ad.t=8.21 min, Purity=99.73, Recovery=49.82, and productivity=3.04×10^{-5}.

NOMENCLATURE

Ad.t : adsorption time [min]
P/F : purge to feed ratio
N : number of required tests
k : number of factors
N_0 : number of same tests
D : overall desirability
d : desirability
r_i : degree of the importance of responses
w : weight of responses
y_i : optimum value
l : maximum possible value
T : minimum possible value

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