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Purification of Hydrogen from a Thermo-chemical Process using a Single-Column Pressure Swing Adsorption System with Compound Adsorbent.

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Abstract

The thermo-chemical conversion of industrial sludge at atmospheric pressure and temperatures as a high as 750 degrees Celsius generates synthesis gas with the approximate per cent composition (volume basis): hydrogen, 45; carbon monoxide, 35; methane, 20. With these three gases as adsorbates, a single-bed pressure swing adsorption (PSA) system with activated carbon and molecular sieve 5Å as adsorbents has been used to purify hydrogen to a per cent purity of 99.9999 %. This purity was the same for feed rates of 7 and 10 liters per minute at operating pressures of 45, 90 and 103 psi. The per cent recovery (productivity) varied from 22.7±0.6 at a pressure of 45 psi and a feed flow rate of 10 L/minute to 85.4±0.3 at a pressure of 103 psi for a feed flow rate of 10 L/minute. The maximum throughput (rate of hydrogen produced) was 3.84±0.01 when the pressure was 103 psi at a federate of 10 L/min. This work shows that with effective regeneration an alternation between two adsorbent beds can be used to separate methane and carbon monoxide from a mixture containing hydrogen with a volumetric concentration as low as 45 versus 60 volume per cent using PSA units with multiple beds.

Key words: thermo-chemical, single-bed, adsorbent, adsorbates, PSA, purity, recovery, throughput.

Introduction

Hydrogen is a clean fuel which burns to produce water and thermal energy only. With its high energy density it is a viable energy carrier that is used in many applications such as fuel cells development, semiconductor processing and in refineries and petrochemical industries, Yang et al 2008. For example in refineries, the catalytic cracking process produces hydrogen as a by-product which upon purification is fed into the hydrogen consuming hydro-cracking unit to produce high – octane gasoline.

Different gases (impurities) have different adsorption affinities onto adsorbents at high pressures. This affinity is lost at low pressures and is the basic property differential that permits the separation of a mixture of gases by the PSA technique. Increasing the pressure (at pressurization) causes the adsorption of gas species with high adsorption affinities. Decreasing the pressure (at depressurization) leads to the desorption of the adsorbed species (impurities). At pressurization, the difference between the column pressure and that of the off-gas delivery line are maintained at between 0- 0.5 atmosphere for optimum performance. A typical PSA system involves a cyclic process where a number of connected vessels containing adsorbent materials undergo successive pressurization and depressurization steps in order to produce a continuous stream of purified gas. Because the separation takes place at ambient conditions, the energy consumption is reduced versus other separation techniques. The same purified product gas from one column or vessel can be used to build pressure in the next vessel.

The development of polybed system for impurities removal has led to improvements in hydrogen recovery, unlimited capacity and increased unit utilization. With the development of polybed adsorption it now has become possible to operate PSA units with only one adsorption column with high per cent purity and recovery. Hence different combinations of adsorbents are used in the same column to improve overall system performance (Stöcker et 1998, Fatehi et al 1995). Molecular sieves and activated carbon have been used extensively in PSA separation systems because of their selectivity, adsorption capacity and stability for gas separation and purification. When molecular sieve 5Å and activated carbon are used in the purification of a mixture containing hydrogen, carbon monoxide and methane, the adsorption of carbon monoxide and methane is split between the two adsorbents for the recovery of high purity hydrogen (Nam et al 2005, Yang et al 2009; Jeong et al 2007).

The PSA system is highly recommended for purification of a mixture containing at least 50 volume per cent of hydrogen in the feed gas. This is because the high concentration is necessary to deliver the required amount of hydrogen in the next vessel during depressurization and pressure equalization steps in a multiple column operation. When only a single column or vessel is used, the cycle steps become much simplified to pressurization and depressurization of the same column. Pressurization with feed gas leads to the production of pure hydrogen and depressurization (counter-current) leads to removal and wasting of the impurity gases. With efficient regeneration of the previously pressurized column, two vessels can be alternately connected to the feed gas line for continuous pure hydrogen gas production, Sunny et al 2000.

In this paper we report the use of a dual-bed one-column PSA system to purify a gas mixture whose per cent composition simulates that of the syngas produced in our pyrolysis unit. A 99.9999 % purity was reported for pressures as low as 45 psi and as high as 103 psi for feed rates of 7 and 10 liters per minute.

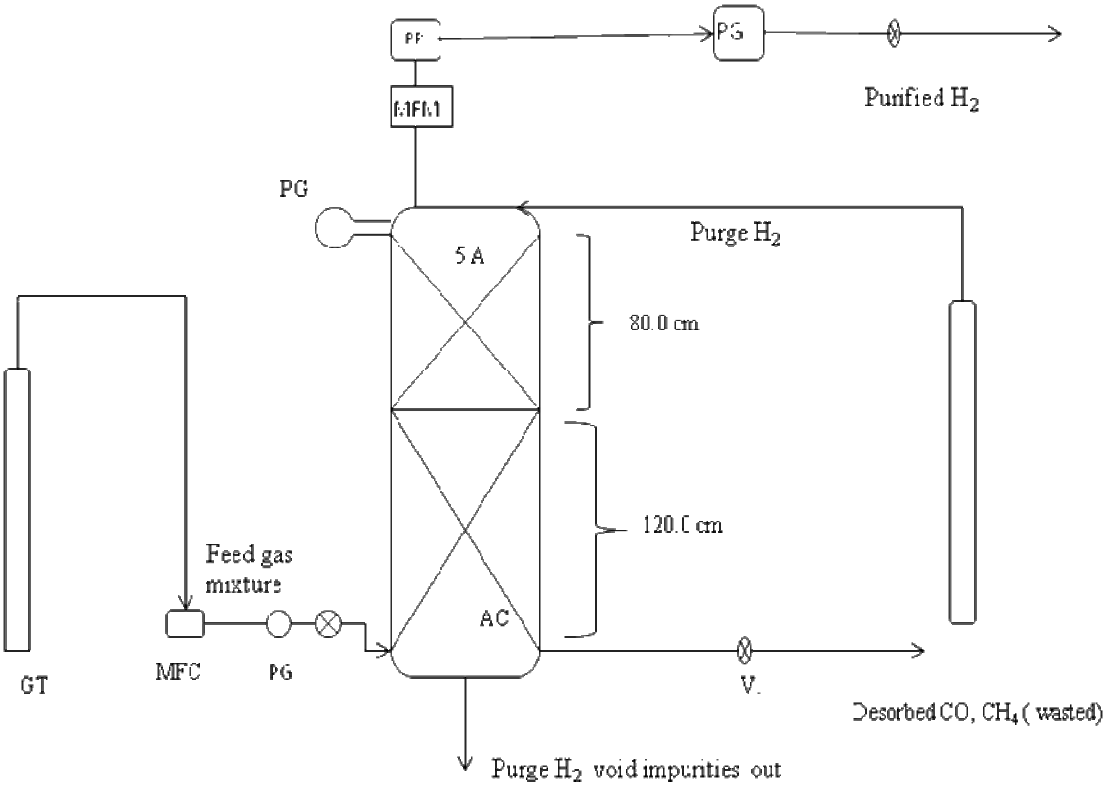
1 Experimental.

We describe here the steps involved in the separation of hydrogen from a mixture with 45 volume % hydrogen, 35 volume % methane and 20 volume % carbon monoxide at feeds rates of 7 and 10 liters per minute for the different pressures 45, 90 and 103 psi. The adsorbents used were molecular sieve 5Å 1/16 pellets supplied by UOP and coca 60,4*8 activated carbon supplied by Activated Carbon Corporation. The column (a 2.0 m tall steel pipe) was first filled to 120 cm with 1585 g of activated carbon and then topped with 1307 g of molecular sieve 5Å. Properties and characteristics of the column and adsorbents are shown in Table 1.

Table 1 Typical Physical Properties/Specifications for Adsorbents.

	Activated Carbon (AC)	
total mass used	1585	g
iodine number (ASTM D-3467)	60	Mg/g
apparent density (ASTM D-2854)	0.45-0.48	g/cc
US standard sieve size	4×8	
BET surface area	1150-1250	m^2/g
	Molecular sieve 5Å	
total mass used	1307	g
nominal pore diameter	5	Å
bulk density	32	lb/ft^3
particle size	<10	microns
equilibrium water capacity	26	Wt %

A digital pressure gauge supplied by Cole Parmer(and measuring up to 200 psi) was attached at the end of the column and on the off-gas line a digital hydrogen flow meter supplied by Mcmaster Carr (capable of measuring up to 10 L/minute total hydrogen) was connected. Upstream the column at the feed end, mass flow meters and programmable flow controllers were installed. Downstream the flow meter a pressure regular supplied by Mc master Carr was used to maintain off-gas pressure to the pressure of the pressurized column. At the end of pressurization, a sample was collected using teddlar bags and injected into a SRI 8610 multi-gas analyzer GC. A schematic of the manual PSA setup is diagrammed in Figure 1.



Process Legend : GT = gas tank, MFC = mass flow controller, PG= pressure gauge, AC= activated carbon, MFM= hydrogen mass flow meter, PR= pressure regulator, V = needle valve.

Figure 1 Process schematic.

The key steps involved can be summarized as follows:

1 Pressurization: The feed flow rate was selected and column was pressurized at this rate until the set pressure 45, 90 and 103 psi was achieved. A sample was instantaneously collected.

2 Depressurization: The column was counter currently depressurized at atmospheric pressure in order to desorb impurity CO and CH_4 gases. The depressurization was continued until the column pressure reached 0.3 psi. The desorbed gases were simply wasted

3 Purge: The column was again repressurized counter-currently to 35 psi (counter current to the feed gas) with pure hydrogen fed from an industrial grade hydrogen gas tank and counter currently depressurized to clear void spaces filled with undesorbed CO and CH_4. The residual gases were again wasted.

4 Regeneration: The column was heated with a band heater to 125 degrees Celsius and cooled to room temperature.

5 Vacuum cleaning: The entire system and connecting lines was connected to a 22.4 mmHg vacuum pump and vacuum cleaned to -21.1 inchHg.

We defined the assessment metrics % purity, % recovery (productivity) and system throughput (L/minute) for purified hydrogen as follows:

$$Purity\ (\%) = \frac{Composition\ of\ Hydrogen\ (v\ \%) in\ Effluent\ Stream}{Total\ Composition\ (v\ \%) of\ Individual\ Gas\ Species\ in\ Effluent\ Stream} \times 100\ \% \ldots\ldots 1$$

$$Recovery\ (\%) = \frac{Rate\ of\ Hydrogen\ Flow\ Out}{Rate\ of\ Hydrogen\ Flow\ in\ the\ Feed\ Stream} \times 100$$

%...2

Throughput was taken to be the rate of pure hydrogen out as read from the hydrogen flow meter – the numerator of Equation 2. Different combinations of column pressure and feed rate were studied in triplicate for pressures of 45, 90 and 103 psi and feed gas flow rates of 7 and 10 L/minute for a total of 15 runs. Data for the parameters were analyzed using Design Expert® and regression models were generated.

2 Results and Discussion.

2.1 hydrogen purity

The per cent purity of hydrogen obtained was the same for all pressures and feed flow rates and the predictive model for this parameter turned out to be significant at a 95 % confidence level as shown in Table 2.

Table 2 Anova Data : % Purity

Response 1 Purity
ANOVA for Response Surface 2FI Model
Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	0.000	3	0.000			significant
A-Pressure	*2.553E-028*	*1*	*2.553E-028*	*6.366E+007*	*< 0.0001*	
B-Feedflow	*1.434E-028*	*1*	*1.434E-028*	*6.366E+007*	*< 0.0001*	
AB	*3.265E-028*	*1*	*3.265E-028*	*6.366E+007*	*< 0.0001*	
Residual	0.000	11	0.000			
Lack of Fit	*0.000*	*1*	*0.000*			
Pure Error	*0.000*	*10*	*0.000*			
Cor Total	3.029E-027	14				

The interaction between the two main factors (effects) was significant with a p-value of <0.0001. The generated predictive was not used to analyze the results because the per cent purity remained constant for all feed flow rates and pressures as shown in Figure 2.

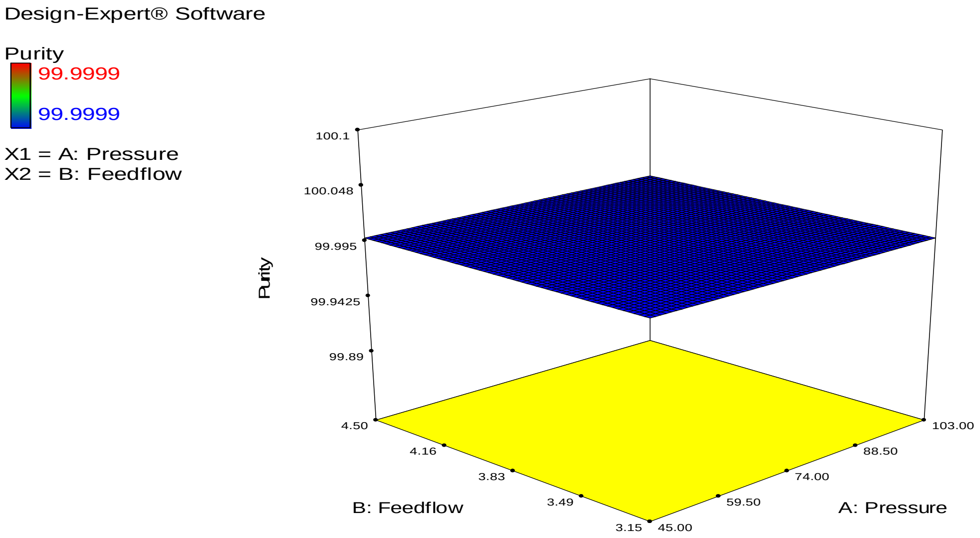


Figure 2 Response Surface Model for % Purity

2.2 hydrogen % recovery (productivity)

The per cent recovery (data not shown) varied from 22.7± 0.6 for a pressure of 45 psi and a feed flow rate of 10 L/minute to 85.4±0.3 for a pressure of 103 psi and 10 L/minute feed flow rate. Table 3 summarizes the results. In order to have a better fit of the data an inverse square root transformation was used. The Model F-value of 2429.07 implies the model is significant at the 95 % confidence level. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Table 3 Anova Data: % Recovery (Productivity)

Response 2 Productivity/recovery
Transform: Inverse sqrt Constant: 0
ANOVA for Response Surface 2FI Model
Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	0.021	3	7.157E-003	2429.07	< 0.0001	significant
A-Pressure	*1.594E-003*	*1*	*1.594E-003*	*541.16*	*< 0.0001*	
B-Feedflow	*1.320E-003*	*1*	*1.320E-003*	*448.14*	*< 0.0001*	
AB	*3.771E-004*	*1*	*3.771E-004*	*127.97*	*< 0.0001*	
Residual	3.241E-005	11	2.946E-006			
Lack of Fit	*3.315E-006*	*1*	*3.315E-006*	*1.14*	*0.3109*	*not significant*
Pure Error	*2.910E-005*	*10*	*2.910 E-006*			
Cor Total	0.022	14				

Both factors and the interaction term turned out to be significant study parameters in determining % recovery. The empirical model was robust enough to be used to predict % recovery within range of experimental conditions because the lack fit was not significant. The regression model approximated a power function but it is expected to taper at higher pressures when the rate of hydrogen fed into the column almost balances the rate at the exit at equilibrium. This means that a dual bed single column PSA system can be used to increase the % recovery to near 90 % at higher pressures (such as 150 psi or 10 atmosphere). Figure 3 shows the variation of the recovery with changes in both main effect parameters.

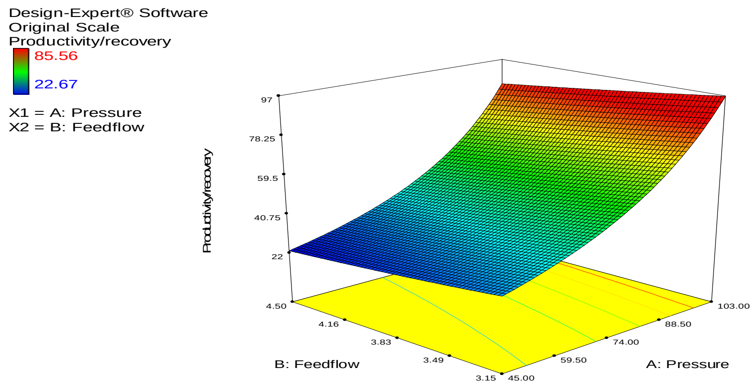


Figure 3 Response Surface Model for % Recovery or Productivity.

2.3 hydrogen production throughput.

Measuring the amount of pure hydrogen (L/minute) that can be delivered by PSA column of given capacity can be used to gauge the capacity of the system. Our study showed that this rate if impacted by the column pressure, feed gas rate and a combination of both acting together. The results are shown in Table 4. The Model F-value of 2762.50 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Table 4 Anova Data: Throughput (L/min)

Response 3 Throughput
Transform: Inverse sqrt Constant: 0
ANOVA for Response Surface 2FI Model
Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	0.58	3	0.19	2762.50	< 0.0001	significant
A-Pressure	*0.021*	*1*	*0.021*	*296.58*	*< 0.0001*	
B-Feedflow	*3.905E-003*	*1*	*3.905E-003*	*55.94*	*< 0.0001*	
AB	*1.705E-003*	*1*	*1.705E-003*	*24.42*	*0.0004*	
Residual	7.678E-004	11	6.980E-005			
Lack of Fit	*9.540E-005*	*1*	*9.540E-005*	*1.42*	*0.2611*	*not significant*
Pure Error	*6.724E-004*	*10*	*6.724E-005*			
Cor Total	0.58	14				

Since the lack of fit of the model was not significant, within the range of pressure and feed rate the model could be accurately used to predict the throughput of the system. Our study showed that the throughput ranged from 1.02±0.01 (45 psi, 7 L/min) to 3.841.02±0.01 (103 psi, 10 L/min). The 3.84 L/minute hydrogen production throughput corresponded to a recovery (%) of 84.6 % for pure hydrogen feed rate of 4.15 L/min. Figure 4 shows the variation of throughput with feed rate and pressure. When combined with experimental or predictive breakthrough curve, PSA system throughput can be useful in estimating the volume of hydrogen in each time cycle, Zheng et al 1988.

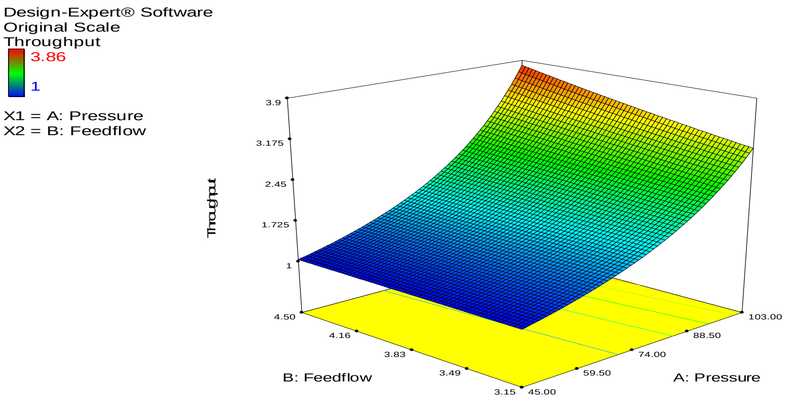


Figure 4 Response Surface Model for Throughput (L/minute)

3 Conclusions

A dual bed single column manual PSA unit has been used to purify the mixuture from a pilot scale pyrolysis unit. The per cent purity was 99.999 for pressures and feed rates within the range 45-103 psi and 7 -10 L/min. Throughput was in the range of 1.02 L/min (45 psi, 7 L/min) and 3.84 L/min (103 psi, 10 L/min). A recovery as high as 84.6 % was achieved at the pressure of 103 psi and a flow rate 10 L/min.

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