Hydrogen Purification By Pressure Swing Adsorption

Dragan Nikolic[1], Apostolos Giovanoglou[2], Michael C. Georgiadis[3], Eustathios S. Kikkinides[1,*]

[1] University of Western Macedonia, Department of Engineering and Management of Energy Resources, Sialvera & Bakola Str., 50100 Kozani, Greece

[2] Process Systems Enterprise Ltd, Thermi Business Incubator, 9th Km Thessaloniki-Thermi, 57001 Thessaloniki-Thermi, Greece

[3] Imperial College London, Centre for Process Systems Engineering, Department of Chemical Engineering, London SW7 2AZ, UK Address

Production of pure hydrogen from various gas mixtures by using Pressure Swing Adsorption (PSA) has become the state-of-the-art industrial technology. Recent ideas to increase a separation quality (product purity/recovery) and to decrease power requirements, such as the specially designed PSA processes for simultaneous production of pure H_2 and CO_2 from steam methane reforming off-gas (SMROG), have attracted an increasing interest. In this work, the PSA modelling framework developed in the previous work has been employed in a design and modelling of several PSA configurations for production of H_2 and CO_2 from SMROG. Based on the existing industrial system, new and modified PSA cycle configurations consisting of two groups of adsorption columns undergoing different cycle steps have been designed and simulated by using the modelling framework. The simulation results have been compared to the results of the existing commercial process.

1. Introduction

From an operational point of view PSA is an intrinsic dynamic process operating in a cyclic manner with each bed undergoing the same sequence of steps. One of the major industrial applications of PSA is hydrogen production from various gas sources. The typical industrial systems (Sircar and Golden, 2000) can produce 99.99^{+}% pure H_2 product with a recovery of 86%. Several ways to improve the separation quality (product purity/recovery) and power requirements of the process exists and have been reported in the literature such as the use of multibed PSA configurations, multilayered adsorbents, or development of hybrid systems (such as hybrid PSA and membrane units). Further, a specially designed multibed PSA process for the simultaneous production of pure H_2 and CO_2 from SMROG (Sircar and Golden, 2000) has been designed. Such process can produce a primary H_2 product at a purity of 99.999% and recovery of 87.1%

* Corresponding author. E-mail: kikki@cperi.certh.gr

while simultaneously producing secondary CO_2 product at a purity of 99.4% with a recovery of 94%. Another advantage of the process is absence of large amounts of CO_2 in the waste gas (during blowdown and purge steps) making it a fuel gas of high calorific value.

2. Modelling framework

The mathematical modelling framework (Nikolic et al, 2006) has been employed in the simulation of underlying problem. The developed framework is general enough to support an arbitrary number of beds, a customized complexity of the adsorbent bed model, one or more adsorbent layers, automatic generation of operating procedures, all feasible PSA cycle step configurations and inter-bed connectivities. The modified auxiliary application for generation of operating procedures for the whole network of beds (Nikolic et al, 2006) according to the given number of beds and sequence of operating steps in the A and B group of beds has been used to design modified PSA cycle configurations.

3. Process description

The process for the simultaneous production of pure H_2 and CO_2 consists of two groups of beds (called A and B group of beds). The A beds are connected to the B beds in series. Each group of beds contains different adsorbent and undergoes different cycle steps. The most distinguishing features of this process (Sircar and Golden, 2000) are: (a) co-current CO_2 rinse at feed pressure; (b) use of different regeneration methods for A (depressurization and evacuation) and B (depressurization and purge) beds; and (c) pressure equalization between A and B and B and B beds to conserve the void gases.

The general sequence of steps is adopted from the work of Sircar and Golden, 2000 and the sequence in the A group of beds is following: (a1) Adsorption (the feed gas is passed through a train of A and B beds and pure H_2 at feed pressure is produced); (a2) Co-current CO_2 rinse (a stream of pure CO_2 at feed gas pressure is co-currently passed through the A bed. The effluent gas from the A bed is recycled as feed gas. The A bed is saturated with CO_2 at the end of this step); (a3) Counter-current blowdown (the A bed is depressurized to an ambient pressure level and the secondary CO_2 is produced); (a4) Counter-current evacuation (the A bed is then evacuated to the sub-atmospheric pressure. The effluent is again pure CO_2 which is withdrawn as the secondary product); (a5) Pressurization equalization – repressurization (optional step; the column is pressure equalized with a B bed which has just finished adsorption step); (a6) Counter-current pressurization (the A bed is finally repressurized with a pure H_2 gas. The general sequence of steps in the B group of beds is: (b1) Adsorption (the B bed is connected with an A bed in series undergoing adsorption step); (b2) Pressurization equalization I – depressurization (optional; the B bed is connected with an A in order to pressure equalize the two beds); (b3) Pressurization equalization II – depressurization (optional; the B bed is connected with another B bed in order to pressure equalize those beds); (b4) Counter-current blowdown (the B bed is depressurized to ambient pressure level and the effluent gas is wasted); (b5) Counter-current purge (the B bed is purged with pure H_2

and the effluent is wasted); (b6) Pressure equalization I – repressurization (optional; B bed is then connected with another B in order to pressure equalize the two beds); (b7) Counter-current pressurization (the B bed is finally repressurized by the pure H_2 gas).

The most important design and operating characteristics of the process are: the A beds are packed with activated carbon which selectively remove CO_2 from the SMROG while the B beds are packed with zeolite for selective removal of the remaining impurities; the process is designed in such a fashion that very little CO_2 breaks through the A beds during the adsorption step; during the co-current CO_2 rinse step all effluent is recycled as a feed stream; after the co-current CO_2 rinse step bed is completely saturated with CO_2; effluent gas from A beds during the blowdown and the evacuation steps are collected as the secondary product (pure CO_2); effluent stream from the blowdown and purge steps in B beds are collected as a high caloric fuel gas (containing low concentration of CO_2).

4. Simulation results

In this work three new PSA cycle configurations have been designed and simulated by using the developed framework. The only difference to the existing process is the number of beds and number and type of pressure equalization steps. Configuration (2+1) contains three beds and no pressure equalization steps, configuration $(4+2)^a$ contains four beds and pressure equalization between A and B group of beds, and finally configuration $(4+2)^b$ six beds with pressure equalization between beds in B group only. The new cycle configurations are presented in Table 1 while nine-bed one can be found elsewhere (Sircar and Golden, 2000). In the Table 1 mark A represents *Adsorption* step, B is *Counter-current blowdown*, P is *Counter-current purge*, R is *Co-current rinse* with CO_2, E is *Counter-current evacuation*, ER1 is *Pressure equalization* (repressurization), ED1 is *Pressure equalization* (depressurization), and P+ is *Counter-current pressurization.*

The geometrical data of a column, adsorbent and adsorption isotherm parameters for activated carbon have been adopted from the work of Nikolic et al, 2006. Gas stream flowrates and duration of the feed, rinse and purge steps were kept constant in all simulations. The duration of all steps are shown in Table 1. The Simulation results are presented in Table 2.

Configuration (2+1)

Simulation results show that in comparison to the existing nine-bed industrial process the hydrogen and carbon-dioxide purities are the same while the hydrogen recovery is lower which can be attributed to the absence of pressure equalization steps.

Configuration $(4+2)^a$

Simulation results show that compared to the existing process the hydrogen and carbon-dioxide purities are essentially the same. In this case hydrogen and carbon-dioxide

recoveries are comparable to the nine-bed results due to the pressure equalization step between B and A group of beds.

Configuration (4+2)[b]

Similar to the previous two cases, hydrogen and carbon-dioxide purities are the same as in the nine-bed configuration. Hydrogen recovery is slightly higher than in the case (4+2)[a] due to the pressure equalization between only B group of beds (since almost all hydrogen losses occur in the B group of beds). However, power requirements of this configuration are somewhat higher since the final equalization pressure is higher than in the (4+2)[a] case.

Table 1 PSA cycle configurations

(2+1) configuration

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
B-1	A	A	R	R	B	B	B	E	E	P+
B-2	B	B	E	E	P+	A	A	R	R	B
B-3	A	A	B	P	P+	A	A	B	P	P+

(4+2)[a] configuration

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
B-1	A	A	R	R	B	B	B	B	B	B	E	E	E	E	ER1	P+
B-2	E	E	E	P+	A	A	R	R	B	B	B	B	B	B	E	E
B-3	B	B	E	E	E	E	ER1	P+	A	A	R	R	B	B	B	B
B-4	B	B	B	B	B	B	E	E	E	E	ER1	P+	A	A	R	R
B-5	A	A	E	B	B	B	P	P	A	A	ED1	B	B	P	P	P+
B-6	B	P	P	P+	A	A	ED1	B	B	P	P	P+	A	A	ED1	B

(4+2)[b] configuration

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
B-1	A	A	R	R	B	B	B	B	B	B	E	E	E	E	P+	P+
B-2	E	E	P+	P+	A	A	R	R	B	B	B	B	B	B	E	E
B-3	B	B	E	E	E	E	P+	P+	A	A	R	R	B	B	B	B
B-4	B	B	B	B	B	B	E	E	E	E	P+	P+	A	A	R	R
B-5	A	A	ER1	B	P	P	ER1	P+	A	A	ED1	B	P	P	ER1	P+
B-6	P	P	ER1	P+	A	A	ED1	B	P	P	ER1	P+	A	A	ED1	B

Table 2 Operating characteristics of the process

	Duration, min						
	Feed	**Rinse (by CO_2)**	**Purge (by H_2)**	**Blowdown (A, B bed)**	**Evacuation**	**Pressure Equal. (A-B)**	**Pressure Equal. (B-B)**
(2+1)	4	4	2	6, 2	4	-	-
(4+2)[a]	4	4	4	12, 4	8	2	-
(4+2)[b]	4	4	4	12, 4	8	-	2
(6+3)	4	4	2	8, 2	4	1	1

Table 3 Comparison of the simulation results

		Products	
Configuration		**H_2**	**CO_2**
(2+1)	Purity, %	99.992	99.948
	Recovery, %	82.289	85.664
(4+2)[a]	Purity, %	99.997	99.940
	Recovery, %	85.560	85.731
(4+2)[b]	Purity, %	99.991	99.938
	Recovery, %	86.038	86.209
(6+3)	Purity, %	99.99^{+}	99.40
	Recovery, %	87.10	94.00

5. Discussion

The simulation results show the advantages and disadvantages of the modified configurations. As the original process, new ones offer high hydrogen and carbon-dioxide purity and recovery and a good quality tertiary product stream (suitable for a fuel gas). In addition, the capital costs are much lower compared to the nine-bed process. However, some aspects of the original system are not present, such as continuous production of primary and secondary products and continuous operation of the compressors and pumps. Also, the power requirements are somewhat higher due to the less efficient utilization of the available feed pressure energy.

6. Conclusions

The previously developed generic PSA modelling framework and the auxiliary application for PSA flowsheet generation have been successfully employed in the process of the simultaneous production of H_2 and CO_2 from SMROG under high product purity and recovery requirements. In order to improve the separation quality new complex PSA cycle configurations have been designed and simulated. New processes offer essentially the same primary and secondary product purities as the original one, while the product recoveries are slightly decreased. At the same time capital costs are lower due to the lower number of beds involved in the process, but on the other hand power requirements are gradually higher. In conclusion, the newly designed configurations offer the comparable separation quality to the existing industrial systems and provide the useful alternative.

7. Acknowledgements

Financial support from PRISM EC-funded RTN (Contract number MRTN-CT-2004-512233) is gratefully acknowledged.

8. List of references

Sircar, S., Kratz, W.C., 1988, Simultaneous production of hydrogen and carbon dioxide from steam methane reformer off-gas by pressure swing adsorption, Separation Science and Technology, 23, 2397.

Kikkinides, E.S., Yang, R.T., 1993, Concentration and recovery of CO_2 from flue gas by pressure swing adsorption, Industrial and Engineering Chemistry Research, 32, 2714.

Sircar, S., Golden, T.C. 2000, Purification of hydrogen by pressure swing adsorption, Separation Science and Technology, 35(5), 667.

Nikolic, D., Giovanoglou A., Georgiadis M.C., Kikkinides, E.S., 2006, Modelling and optimization of multibed pressure swing adsorption flowsheets, PRES06, Prague.