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Application of Pressure Swing Adsorption Cycle in the quest of production of Oxygen and Nitrogen

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Abstract*— Cryogenic Engineering is often faced with the problem of separating a gas mixture or removing undesirable components from a gas stream to be used in a liquefier or in a refrigerator. Pressure Swing Adsorption (PSA) has revolutionized the gas purification and separation system. PSA is a technology used to separate some gas species from a mixture of gases under pressure according to the species molecular characteristics and affinity for an adsorbent material. Research and developmental work on various PSA systems are going on around the globe. The present paper is a state of art report on the various aspects of PSA system towards production of pure oxygen and nitrogen for their eventual liquefaction towards the various cryogenic applications. The paper also highlights advantages and disadvantages of PSA method over membrane and cryogenic separation.

***Key Words*— Carbon Molecular Sieve (CMS), Gas purification, Pressure Swing Adsorption, Separation Technology.**

I. INTRODUCTION

Cryogenic distillation of air has been widely used for air separation over the last 80 years. Since the advent of synthetic zeolites in 1950s and pressure swing Adsorption (PSA) processes in 1970s the small and medium scale air separations are being increasingly accomplished by adsorption. Pressure Swing Adsorption is a gas separation process in which the adsorbent is regenerated by reducing the partial pressure of the adsorbent either by lowering the total pressure or using a purge gas. PSA process has revolutionized the gas purification and separation industries. It has seen tremendous growth during the last decades mainly due to its simplicity and low operating costs and air separation becomes more economical for production rate up to 10,000 standard cubic meters per hour compared to cryogenic distillation [**1**]. Presently, one-fifth of air separation is carried out using adsorption technologies, i.e., PSA and vacuum swing adsorption (VSA) [**2**]. In pressure swing adsorption (PSA) and vacuum pressure swing adsorption (VPSA), the adsorbent is regenerated by decreasing the total or partial pressure. Thermal (or temperature) swing adsorption (TSA) regenerates the sorbent by increasing temperature. PSA processes may be suggested as an energy-saving process and as an alternative to traditional separations [**3**] for bulk gas separations. PSA operation has initially adopted the steps of the classical Skarstrom cycle: pressurization with feed, adsorption with high pressure, depressurization, and purge. A pressure equalization step was suggested to save repressurization energy after the purge step **[4]-[7]**. Grande and Rodrigues [**8**] analyzed vacuum pressure swing adsorption (VPSA), in which the recovery step is carried out at sub atmospheric pressure.

The present paper highlights the various development of PSA system towards production of pure oxygen and nitrogen for their eventual liquefaction towards the various cryogenic applications. The paper also presents advantages and disadvantages of the method over membrane and cryogenic separation.

II. PSA PROCESS

Impurities from the compressed air is first removed in a pretreatment unit and subsequently collected in an air receiver from where it is made to pass through a double column PSA unit with CMS for oxygen removal. The process is made automated and continuous by number of solenoid valves, operating in definite combination for the production of nitrogen gas having purity up to 99.5% to 99.9%.Pure nitrogen may be collected in a buffer vessel from where it is supplied at a reduce pressure to the cryogenerator for production of liquid nitrogen as shown in Fig. 1.

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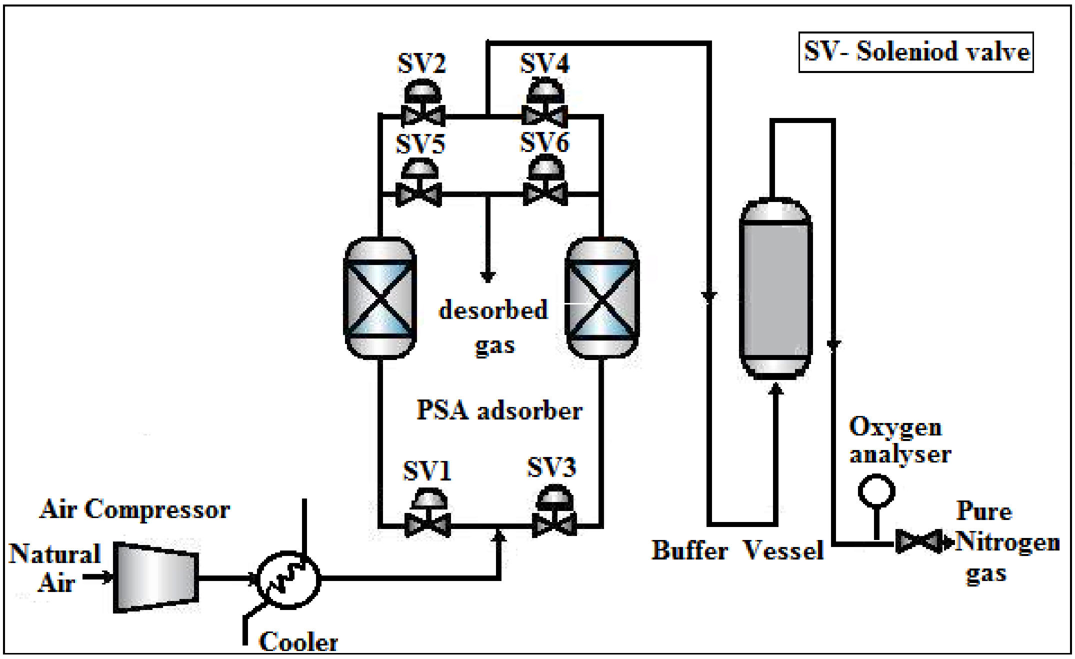

Fig. 1 PSA process

III. TECHNICAL ADVANCEMENT

Zeolite shows preferential adsorption of nitrogen over oxygen under equilibrium conditions and hence is used for the production of oxygen whereas separation of air for the production of nitrogen is normally carried out by pressure swing adsorption over a carbon molecular sieve. Carbon molecular sieves (CMS) are kinetically oxygen selective and are used in kinetic separation of air in a PSA system. Commercial nitrogen generators using carbon molecular sieves capable of producing 99.5% N_2 are currently available in market. The fixed bed processes essentially consist of two steps: the adsorption step and the desorption step. The desorption operation is usually performed either by raising the temperature or by reducing the total pressure. A detailed study of these processes can be found in the literature **[9]-[13]**.

Oxygen is reported to be produced by adsorbing the nitrogen gas in PSA system using zeolite as adsorbent at a pressure of 150 KPa and is desorbed at atmospheric pressure. Adsorption of N_2, CO, CO_2 and NO has been studied on various molecular sieves using the gas chromatographic method to determine the potential for separation of these common atmospheric contaminants from air. The molecular sieves studied include H-Mordenite, 4A and 5A zeolite, a natural clinoptilolite and an activated carbon. Henry's law constants have been determined over a variety of temperature ranges from 243 to 473 K. Van't Hoff plots are presented for CO on all materials and for NO on all but 4A zeolite. Adsorption of CO2 on the clinoptilolite was too strong to produce an interpretable response peak. Results of CO adsorption on 4A and 5A zeolites have been compared to and are supported by data available in the literature. Heats of adsorption for CO, NO and N_2 were determined. For CO the heats of adsorption decrease in the order of clinoptilolite> 5A zeolites > 4A zeolites > H Mordenite > activated carbon. For adsorption of NO the heats of adsorption decrease in the order of clinoptilolite > 5A zeolite > activated carbon. Separation factors are also presented for the CO/N_2 and NO/N_2 systems. The natural clinoptilolite shows most promise for the separation of CO and NO from N_2 at the temperature range 273-398 K. Diffusion coefficients for CO and Na on clinoptilolite between 348 and 423 K were also determined. Micro pore diffusion proved to be the dominant mass transfer mechanism for both CO and N_2 in clinoptilolite under the conditions examined as per **[14]**.CMS-HP type molecular sieve is used to produce nitrogen from air using single adsorption column (700 mm length, 50 mm i.d.).The gas analysis was done using gas chromatography at each step. Operating conditions of experimental plant was selected as 4 bar adsorption pressure; ambient temperature; 10 to100 L/h gas exit flow rate; 1 min adsorption time; 6 to $8*10^{-2}$ bar desorption pressure**[15]**. Oxygen gas was generated from air by using different cryogenic and non-cryogenic application such as adsorption, polymeric membrane, chemical process, ion transport membrane process. Among these process PSA process was performed using zeolite for producing pure oxygen and the system was optimized on the basis of flow, purity and pressure, energy cost and expected operating life and got oxygen purity is typically 93–95 volume % **[3**]. Pressure Swing Adsorption as a process for separating multicomponent gas mixtures was studied [**16**]. The applications of a new generation of adsorbents, such as zeolite, carbon molecular sieves, and, more recently, pore engineered molecular sieves, are highlighted. A higher degree of O_2 separation from air is obtained with the combined pressure swing adsorption —continuous membrane column (CMC) process. Based on the separation performances and materials that are already available, PSA-CMC process was developed for the small-scale continuous production of oxygen [**17**]. Exploiting differences in intra-particle rates of diffusion, rather than differences in adsorption isotherms, several critical PSA operating conditions, including step times, velocities, and pressures are studied in the context of separation of nitrogen from air with zeolite 4A. A novel 2-bed 4-step enriching pressure vacuum swing adsorption (PVSA) cycle was developed for the production of N2 from air, using an X-type zeolite, with the separation being equilibrium-driven **[18]**. The four steps were low-pressure feed, countercurrent heavy product pressurization, countercurrent high-pressure heavy reflux and cocurrent depressurization. The enriched heavy and light products (N_2 and O_2, respectively) were withdrawn from the system during the feed and heavy reflux steps, with both products being produced at the high pressure. The experimental studies were carried out in two conventional bench scale PSA units for producing N_2 from air in ambient temperature. Both the unit have same bed diameter of 4.1 cm but bed length are 75 cm and 225 cm respectively for the first and second unit **[19].**A relatively simple twin-bed PSA process can be used to highly concentrate a heavy component from a dilute feed stream, based on an ER (Enriching reflux) PSA cycle **[20]**. A secondary objective is to show that the performance can be improved even further by employing a novel mode of pressure equalization, namely parallel equalization. In this first of its kind experimental study, Xe as a valuable component in one set of experiments and CO_2 as a model component in another set of experiments are extracted from air and highly concentrated using a 13X molecular sieve zeolite and the proposed ER PSA process. The performance of this new PSA process is judged against a conventional SR PSA process under identical conditions. The effects of various parallel equalization modes are also examined, and a detailed parametric study is carried out to determine the effects of some of the most important process parameters on the enrichment of these two gases in air. Four PSA cycles of two bed PSA unit, using CMS to purify oxygen to a level of over 99% was examined. The cyclic performances such as purity, recovery, and productivity of these PSA cycles were compared experimentally and theoretically under non-isothermal conditions. The adsorption beds were made of stainless steel columns with a length of 100 cm, ID of 2.2 cm, and thickness of 0.175 cm **[21]**. Brief reviews of the theoretical developments are also reported in the literature [**22]-[24**]. Linear adsorption isotherms are used in most of the published PSA models, thus limiting the models to adsorption of dilute species. The only exceptions are the model by Chihara and Suzuki [**25**] and that by Carter and Wyszynski [**26**] where the linear driving force approach for mass transfer rates is used. The method of characteristics is used in these models to derive simple algebraic equations in order to estimate the steady-state performance for simplified PSA cycles. The equilibrium models include those of Shendalman and Mitchell [**27**], Weaver and Hamrin [**28**], Fernandez and Kenney [**29**], and Hill et al. [**30**], for one adsorbate and Chan et al. [**31**], Nataraj and Wankat [**32**], and Knaebel and Hill [**33**], for two or more adsorbents. In addition, the mass-transfer limitation in PSA is approximated by the linear driving force approach.

IV. PERFORMANCE OF PSA WITH RESPECT TO CRYOGENIC AND MEMBRANE SEPARATION

The different techniques for gas separation and purification were developed in order to make the process or work easier, less time consuming and cost effective. Nitrogen and oxygen gas can be produced by (i) Cryogenic distillation, (ii) PSA, (iii) Membrane separation. Each process has its own merits and demerits in terms of efficiencies, costs, operating range and economic point of view. Pressure swing adsorption (PSA) and membrane separation technologies are well-suited for small scale oxygen production (< 200 t/d); whereas cryogenic plants can be designed for large-scale oxygen production. Cryogenic separation requires a combination of low temperature and high pressure to liquefy air to be separated by distillation. The process is energy intensive and requires high capital investment. Membrane permeation is based on fact that when the pressure differential exists across a special membrane, one gas will pass through the membrane than other. As compared to other method, a lower pressure or vacuum is used to desorb the adsorbent bed and PSA cycle can be operating close to isothermal condition without heating and cooling steps, for these reason PSA cycle is attractive to bulk separation operations. One advantage of this process is to use gas compression as the main source of energy. The PSA processes are normally associated to low energy and capital when compared to other technologies [**34]-[37**] for which gas are separated easily. The principal disadvantage of the PSA cycle is high gas loss resulting from the pressure release during desorption. PSA requires low power to operate. Cryogenics process is suitable for large scale product with high purity. Scaling up does not need new equipments in the process. The process makes no use of chemicals. Cryogenic processes require the use of numerous equipments and devices, like compressors, turbines, heat exchangers, insulators, and distillation columns and maintenance of these equipments makes it capital intensive. Compactness, light in weight, low labor intensity, modular design permitting easy expansion or operation at partial capacity, low maintenance, Low energy requirements and low cost especially for small sizes certainly makes a membrane process advantageous, but Membranes are expensive, certain solvents can quickly and permanently destroy the membrane, The energy costs and capital cost are also higher. Maximum inlet air pressure for PSA is 10.3 bars as compared to membrane inlet pressure of 15.5 bars. Life cycle of adsorbent is more than 10 years which is comparable to that of membrane.

V. CONCLUSION

From the fore going discussion, it is revealed that the control of flow rate or step time of each step is a key factor in producing high-purity oxygen or nitrogen gas with a high productivity rate because, in the PSA cycle two stage occurs, one stage is used for purge gas and the other for pure gas production. With the increase in temperature, fast diffusion rate of gases occurs. Increasing or decreasing of feed throughput is also the factor through which purity and high production of gases occurs. It can be seen that both the specific product and yield go through a maximum as the pressurization varies. The longer contact time during the pressurization of the adsorbent bed allows removal of more gases and a higher purity can be achieved. Slow pressurization reduces the adsorption. Production and purity of gases depends on the bed height. For bed lengths greater than 1.3 m, constant specific product and yield are expected. However, for shorter beds a significant decrease in the performance is observed. PSA technology can be considered a most preferred technology in air separation, but there is scope of plenty of work to establish this technique in other fields also [**38**]. Since pressure swing can be achieved much rapidly as compared to temperature swing, the PSA process is more suitable for rapid cycling and PSA can be recommended for product of both pure oxygen and nitrogen in small and medium scale.

A cryogenerator is being developed to feed the system, a PSA system is designed which will be incorporated with the cryogenerator in collaboration with the help of industrial concern for producing nitrogen to be liquefied in the cryogenerator.

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REFERENCES

[1] R. Agarwal, “Separations: perspective of a process developer/ designer,” A.I.Ch.E. J. vol. 47, pp 967, 2001

[2] S.U. Rege, and R.T. Yang, “Limits of air separation by adsorption with LiX zeolite,” Ind. Eng. Chem. Res. vol. 36, pp.5358– 5365, 1997

[3] A.R. Smith, and J. Klosek, “A review of air separation technologies and their integration with energy conversion processes,” Fuel Processing Technol. vol.70, pp.115–134, 2001.

[4] C. W. Skarstrom, “Method and apparatus for fractionating gaseous mixtures by adsorption,” U.S. Patent No. 2944627, 1960.

[5] W. D. Marsh, F. S. Pramuk, and R. C. Hoke, “Skarstrom, C.W. Pressure equalization depressurizing in heatless adsorption,” U.S. Patent No. 3, 142, pp. 547, 1964.

[6] N. H. Berlin, “Method for providing an oxygen-enriched environment,” U.S. Patent No. 3,280, pp. 536, 1966.

[7] J. L.Wagner, “Selective adsorption process,” U.S. Patent No. 3, 430, pp. 418, 1984.

[8] C. Grande, and A. Rodrigues, “Biogas to fuel by vacuum pressure swing adsorption I. Behavior of equilibrium and kinetic-based adsorbents,” Ind. Eng. Chem. Res, vol. 46, pp. 4595−4605, 2007.

[9] Y.D. Chen, R.T. Yang, and P. Uawithya, “Diffusion of oxygen, nitrogen and their mixtures in carbon molecular sieve,” A.I.Ch.E. J., vol.40, pp. 577–585, 1994.

[10] H. Juntgen, K. Knoblauch, and K. Harder, “Carbon molecular-sieves production from coal and application in gas

separation," Fuel, vol.60, pp. 817–822, 1981.

[11] D. M. Ruthven, "Principles of adsorption and adsorption processes," New York: Wiley, 1984.

[12] R. T. Yang, "Gas separation by adsorption processes," Boston: Butterworth. 1987.

[13] D. M. Ruthven, S. Farooq, and K. S. Knabel, "Pressure swing adsorption," New York: VCH. 1994.

[14] R.W. Triebe, and F.H. Tezel, "Adsorption of nitrogen, carbon monoxide, carbon dioxide and nitric oxide on molecular sieves," Gas. Sep. Purif., vol. 9, No. 4, pp. 223-230, 1995.

[15] M. Vaduva, and V. Stanciu, "Separation of nitrogen from air," Revue Roumaine de Chimie, vol. 53, Issue 3, pp. 223–228, 2008.

[16] R. V. Jasra , N. V. Choudary, and S. G. T. Bhatt, "Separation of Gases by Pressure Swing adsorption," sep. sci. and technol., vol 26, issue 7, 1991.

[17] P.V. Mercea, and S.T. Hwang, "Oxygen separation from air by combine pressure swing adsorption and continuous membrane column process," Journal of Membrane Science, vol. 88, Issues 2–3, pp. 131-144, 16 March 1994.

[18] S. P. Reynolds, A. D. Ebner, and J. A. Ritter, "Enriching PSA Cycle for the Production of Nitrogen from Air," Ind. Eng. Chem. Res., vol. 45, pp. 3256-3264, 2006.

[19] A.I. LaCava and N.O. Lemcoff, "Single bed pressure swing adsorption process to generate high purity nitrogen," Gas. Sep. purif., vol. 10, No. 2, pp. 113-115, 1996.

[20] M. Yoshida, J. A. Ritter, A. Kodama, M. Goto, and T. Hirose, "Enriching Reflux and Parallel Equalization PSA Process for Concentrating Trace Components in Air," Ind. Eng. Chem. Res., vol. 42, pp. 1795-1803, 2003.

[21] J.G. Jee, M.B. Kim, and C.H. Lee, "Pressure swing adsorption processes to purify oxygen using a carbon molecular sieve," Chem. Eng. Sci., vol.60, pp. 869 – 882, 2005.

[22] H. C. Cheng, and F. B. Hill, "In Industrial Gas Separations," Whyte, T. E., Yon, C. M., Wagener, E. H., Eds.; American Chemical Society: Washington, DC, ACS Symp. Ser., vol. 223, pp. 195, 1983.

[23] P. C. Wankat, A. E. Rodrigues, and D. Tondeur, "In Percolation Processes," Eds.: Sijthoff and Noordhoff: The Netherlands, pp. 443, 1981

[24] W. N. Chen. and R. T. Yang, "In Recent Developments in Separation Science,": Li, N. N., Calo, J. M., Eds.; CRC: Cleveland. OH, vol. IX, 1985.

[25] K. Chihara, and M. Suzuki, "Adsorption Engineering," J. Chem. Eng. Jpn., vol. 76, pp. 53, 1983.

[26] J. W. Carter, and M. L.Wyszynski, "The pressure swing adsorption drying of compressed air," Chem. Eng. Sci., vol. 38, pp. 1093, 1983.

[27] L. H. Shendalman, and J.E. Mitchell, "A study of heatless adsorption in the model system CO_2 in He," Chem. Eng. Sci., vol. 27, pp. 1449, 1972.

[28] K. Weaver, and C. E. Hamrin, "Separation of Hydrogen Isotopes by. Heatless Adsorption," Jr. Chem. Eng. Sci., vol. 29, pp. 1873, 1974.

[29] G. F. Fernandez, and C. N. Kenney, "Modelling of the pressure swing air separate process," Chem. Eng. Sci., vol. 38, No. 6, pp. 827, 1983.

[30] F. B. Hill, Y. W. Wong, and Y. N. I. Chan, "A temperature swing process for hydrogen isotope separation," AIChE J., vol. 28, pp. 1-6, 1982.

[31] Y. N. Chan, F. B. Hill, and Y. H. Wong, "Equilibrium theory of a pressure swing adsorption process," Chem. Eng. Sci., vol. 36, pp. 243, 1981.

[32] S. Nataraj, P. C. Wankat, Y. H., Ma, J. P. Ausikaitis, M. D. Le Van, N.H. Sweed, "In Recent Advances in Adsorption and Ion Exchange," Eds. AIChE, New York, 1982.

[33] K. S. Knaebel, and F. B. Hill, "Pressure Swing Adsorption: Development of an Equilibrium Theory," Chem. Eng. Sci., 40, 2350-2351, 1985.

[34] J.L. Humphrey, G.E. Keller, "II. Separation Process Technology, McGraw-Hill," New York, 1997.

[35] A. Mersmann, B. Fill, R. Hartmann, and S. Maurer, "The Potential of Energy Saving by Gas Phase Adsorption Processes," Chem. Eng. Technol., vol.23, pp. 937-944, 2000.

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[36] S. Sircar, "Pressure swing adsorption," Ind. Eng. Chem. Res., vol. 41, pp. 1389-1392, 2002.

[37] C. Voss, "Applications of Pressure swing adsorption Technology," adsorption, vol. 11, pp. 527-529, 2005.

[38] D. M. Ruthven, "Past Progress and Future Challenges in Adsorption Research," Ind. Eng. Chem. Res., vol. 39, pp. 2127-2131, 2000.

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