Separation of High Purity Nitrogen from Air by Pressure Swing Adsorption on Carbon Molecular Sieves

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Abstract— Nitrogen is produced mainly from its most abundant source, the air, using three processes: membrane, pressure swing adsorption (PSA) and cryogenic distillation. By considering the operating conditions, flow rate and purity of Nitrogen, the most economic technology for separation of Nitrogen from the air can be chosen. Of course for some values of purity and flow rate, more than one technology can be selected. In these ranges, other parameters such as economic value of by-products phase of delivered product fluid (liquid or gaseous) and the product applications should be taken into account. Onsite nitrogen generators, such as pressure swing adsorption (PSA) or membrane systems, can be more cost effective than traditional cryogenic distillation or stored liquid nitrogen, particularly if an extremely high purity (e.g., 99.9999%) is not required. The theory accurately portrays the overall behavior of the process, why pressure swing adsorption (PSA) can be a cost effective method of onsite nitrogen generation for a wide range of purity and flow requirements and also why carbon molecular sieves (CMS) adsorbent is best suited for the production of high pure (99.9995 %) nitrogen from air.

Keywords— Air separation, Nitrogen, Adsorption, Adsorbent, Pressure swing adsorption (PSA), Membrane, Carbon molecular sieves (CMS).

I. INTRODUCTION

Air is composed essentially by nitrogen, oxygen, and argon, with traces of other components, such as carbon dioxide and water vapor. It is used as raw material in the production of nitrogen and oxygen up to various purities [4]. This work focuses on the recovery of nitrogen from air. Nitrogen (N2) is an industrial gas with numerous applications: ammonia production, safety blanket gas for inflammable material storage tanks, replacing air for storage, packaging and freezing of food products and as refrigerant in cryogenic cycles. In the chemical process industry, N2 is applied as an inert material in chemical reactors and also as corrosion preventer in pipe lines. N2 is injected into oil and gas reservoirs for pressure buildup in Enhanced Oil Recovery (EOR) operation [2].

The main criteria for choosing suitable process of air separation are: selection between O2 or N2 as the main product, process operating conditions (flow rate, high or low pressure, desired phase of product (gas or liquid)), purity of product, and energy cost. For several years, nitrogen was produced from air by cryogenic distillation, and more recently by pressure swing adsorption (PSA). Often, the latter technology involves the use of carbon molecular sieve (CMS) adsorbents packed in two beds [5].

The original idea of using pressure swing to separate air was disclosed in a patent by Skarstrom and independently, in a different version, by Guerin de Montgareuil and Domine [9], both filed in 1958. The basic difference between the two is that in the Skarstrom cycle the saturated bed is purged at a low pressure by a fraction of the light product, whereas in the Guerin Domain cycle, vacuum desorption is used. Many process improvements have subsequently been developed based on the Skarstrom cycle, which enable the rapidly growing commercial use of PSA for air separation, hydrogen production, hydrogen purification, and an increasing number of other applications [3].

II. PRESSURE SWING ADSORPTION (PSA) PROCESS

Pressure swing adsorption (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.

A. Working of PSA

In this process air is flown alternately on two beds of adsorbent material. Each bed acts alternately and sequentially as an adsorber and a regenerator to complete one cycle of events. The plant layout and pipe work connections between the two columns is illustrated in Figure 1 and the cycle is described by Figure 2 which shows how each column is utilized during a single cycle.
To illustrate the operation, we suppose that each bed in Figure 1 contains a molecular sieve carbon adsorbent whose capacity for adsorbing oxygen from air is greater than its capacity for adsorbing the nitrogen component of air. For the first step column 1 is pressurized to several atmospheres with air while isolated from column 2. During the second step of the cycle columns 1 and 2 are connected and nitrogen (which is the least strongly adsorbed component of air) together with some oxygen remaining unadsorbed issues from both columns; meanwhile the majority of the oxygen is adsorbed and retained in column 1. The third step occurs when the columns are again isolated and column 1 is depressurized to atmospheric pressure (commonly known as blow down) causing oxygen to be desorbed and flow from the bed (countercurrent to the direction of feed in the second step).

The last step is for the beds to be reconnected and some nitrogen (produced from the second step in the cycle) is passed through both columns countercurrent to the direction of the air feed. This latter step of the cycle ensures that any adsorbed oxygen in the bed is flushed towards the column entrance thus allowing the major portion of the bed to be free of adsorbed oxygen and ready for the whole cycle to be repeated. Column 2 goes through a similar cycle of events to column 1 during a cycle. This process for air separation was developed by Skarstrom (1960 and 1975) and is used for small-scale separation units [8].

### III. ADSORPTION PROCESS

Innumerable physical, chemical and biological processes take place at the boundary between two phases, while others are initiated at that interface. The change in concentration of a given substance at the interface as compared with the neighboring phases is referred to as adsorption. Depending on the type of phases in contact, we can consider this process in the following systems: liquid-gas, liquid-liquid, solid-liquid and solid-gas. The term ‘adsorption’ deals with process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Similar to surface tension, adsorption is a consequence of surface energy. Let us consider this concept in terms of the solid gas interface. If there is a very strong reaction between the solid and the gas, the adsorption process is called the chemical adsorption. If only weak intermolecular forces, called van der walls forces are brought into play, the process is called physical adsorption. The substance attached to the surface is called adsorbate, and the substance to which it is attached is known as adsorbent [1, 7, 8, 13].

#### A. Adsorbent

To be technically effective in commercial separation process, whether this be a bulk separation or purification, an
adsorbtion material must have a high internal volume which is accessible to the components being removed from the fluid. Such a highly porous solid may be carbonaceous or inorganic in nature, synthetic or naturally occurring, and in certain circumstances may have true molecular sieving properties. The adsorbent must also have good mechanical properties such as strength and resistance to attrition and it must have good kinetic properties, that is, it must be capable of transferring adsorbing molecules rapidly to the adsorption sites. The high internal surface area of an adsorbent creates the high capacity needed for a successful separation or purification process. Adsorbents can be made with internal surface areas which range from 100m2/g to over 3000m2/g. For practical applications, however the range has been restricted to about 300-1200m2/g. For most adsorbents the internal surface area is created from pores of various sizes. The structure of an adsorbent is shown in idealized form in fig.3. [7, 8]  

Figure 3. General structure of an adsorbent particle and associated resistances to the uptake of fluid molecules[7].

- Carbon molecular sieves (CMS)

Special manufacturing procedures can be used to make amorphous carbons which have a very narrow distribution of pore sizes with effective diameters ranging from 0.4-0.9 nm. Raw materials can be chemicals such as polyvinylidenedichloride and phenolic resin, or naturally occurring materials such as anthracite or hard coals.

Figure 4. Molecular sieve carbons made by Bergbau-Forschung: (a) Type CMSN2 with bottlenecks near 0.5 nm formed by coke deposition at the pore mouth; (b) Type CMSH2 formed by steam activation (redrawn from JEintgen et al. 1981).[8]

As shown in Figure 4 the pore structure of activated carbons can be modified to produce a molecular sieve carbon by coating the pore mouths with a carbonized or coked thermosetting polymer. In this way, good kinetic properties may be obtained which create the desired selectivity, although the adsorptive capacity is somewhat lower than for activated carbons. The surface is essentially non-polar and the main process application is the production of high purity nitrogen from air by pressure swing adsorption [7, 8, 13].

Despite the fact that much of the early work was based on polymeric precursors, the first industrial manifestation of pressure swing adsorption technology with carbon molecular sieves in the 1970s was based on Bergbau Forschung’s coal-derived material which was manufactured by modifying the underlying carbon pore structure by depositing carbon in the pore mouths through the cracking of an organic material (JEintgen et al. 1981). This development was followed by a competitive CMS from Japan, which was again based on pore structure modification by carbon deposition but this time using a coconut shell char precursor (Ohsaki and Abe 1984). More recently there has been a resurgence of interest in the production of new CMS materials with the emphasis being placed on higher pore volume precursors combined with the use of chemical vapor deposition using organics such as isobutylene for improving the oxygen to nitrogen selectivity (Cabrera et al. 1993)[8].

IV. WHY CMS IS USED IN THE SEPARATION OF NITROGEN FROM AIR?

Gaseous mixtures can get split employing adsorptive separation based on one or a combination of the three distinct mechanisms,
1. Steric Separation
2. Equilibrium Separation

(1) Air separation using carbon molecular sieves is carried out using pressure swing adsorption (PSA) techniques, which utilize differences in the kinetics of adsorption of oxygen and nitrogen. Oxygen has a kinetic diameter of 0.346 nm, whereas that of nitrogen is 0.364 nm. So oxygen diffuses much faster than nitrogen. [12]

(2) Micro pore size distributions of different adsorbents are shown in figure,
The only class of molecular sieves which operate through the kinetic separation is carbon molecular sieves (CMS) because they have a distribution of pore sizes as shown in Figure 5. This means that having such distribution of pores not only allows diffusion of different gases at different rate, but also avoids exclusion of any gases in the mixture. Therefore, although CMS has a smaller capacity compared to most of the other zeolites, it is more efficient to use CMS for nitrogen generation from air [8, 16].
(3) The most important requirement of any economic adsorption process is finding an adsorbent with sufficient selectivity, capacity, kinetics, and regenerability. High selectivity and capacity (which is measured using adsorption isotherms) result in high productivity [11].

The equilibrium isotherms for oxygen and nitrogen on a carbon molecular sieve are shown in Figure 6. For this adsorbent it is clear that the differences in the isotherms might not be large enough to create a commercially attractive separation of oxygen and nitrogen if the equilibrium effect were to be used.

Figure 7 however shows that the rate of uptake of oxygen by the carbon molecular sieve is 40-50 times that of nitrogen, particularly in the first few minutes. The reason for this, while not completely understood, is associated with the greater effective diffusivity of oxygen than nitrogen in the carbon molecular sieve. It is clear therefore that to produce high purity nitrogen from air using a carbon molecular sieve the adsorption time needs to be relatively short to exploit the kinetic effect and not allow the equilibrium effect to become significant [7,8,16].

(4) Carbon molecular sieves (CMS) are less hydrophilic and still have the molecular sieving properties so, corrosion of the sieve due to the oxidation is not a significant problem in the case of CMS [9].

V. WHY PRESSURE SWING ADSORPTION (PSA) IS USED IN THE SEPARATION OF NITROGEN FROM AIR?

PSA system operation is based on physical adsorption of O2 over adsorbent materials which are usually active carbon, alumina and zeolite. For N2 production, only active carbon and zeolite (4A) are used [5]. In this system, air initially passes through the first adsorbing bed where O2 is adsorbed and N2 pass through as product.

PSA process advantages are as follows:

(1) If the amount of N2 needed is less than 560 m³/hr (20,000 SCFH), selecting a PSA process is more economical than a cryogenic process.
(2) During the shutdown period, the loss of profit is less than cryogenic processes.
(3) PSA units are readily available and can be purchased and delivered quickly [2].
(4) PSA process is good for weakly adsorbed species required in high purity [7].
(5) Changes of pressure can be effected very much more quickly than changes of temperature and thus cycle times of pressure swing adsorption (PSA) processes are typically of the order of minutes, and for rapid cycle systems of the order of seconds. The faster the cycle time the lower is the size of the equipment and the inventory of adsorbent. Thus PSA processes are attractive for bulk gas separations and purifications for those situations in which the adsorptive forces are relatively weak.
(6) It is desirable to operate PSA processes close to ambient temperature to take advantage of the fact that for a given partial pressure the loading is increased as the temperature is decreased. It is not usually worth attempting to reduce the temperature to below ambient [5].
(7) Other advantages of PSA are,
• Complete automation and simplicity of operation
• No manned attendance required during operation
• Enhanced failure safety and reliability
• Quick start and stop
• Moderate dimensions and light weight
• Low noise level
• Extended operation life
• Low operating costs
• No special workshop requirements
• Easy installation and integration into an existing air system [2].

VI. CONCLUSION

The present work deals with the separation of gases using adsorption process. The described work reveals that since CMS has high adsorption capacity for oxygen, the oxygen is adsorbed and nitrogen is obtained with desired purity. The PSA is used since it is quite fast/accurate in operation as compared to TSA. The adsorbent used is activated charcoal-CMS because it has the highest surface area available for adsorption.

ACKNOWLEDGMENT

The authors would like to thank H.O.D and teaching staff of mechanical and cryogenics engineering department for providing their valuable guidance and overwhelming support to carrying out this work.

REFERENCES