Chemistry Project

Class 12

Oxygen Concentration

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Abstract

The Covid-19 pandemic caused a short supply of oxygen to various parts of the world, and especially India. This project aims to illustrate two methods of production of oxygen – Fractional distillation and Pressure Swing Adsorption (PSA). The setup, working, uses, drawbacks and limitations have been described.

Introduction

Air is approximately comprised of 78% nitrogen (N_2), 21% oxygen and the remaining 1% of other gases like Argon (Ar), Neon (Ne), Helium (He), Carbon Dioxide (CO_2), Water vapour etc. This can be seen in figure 1.

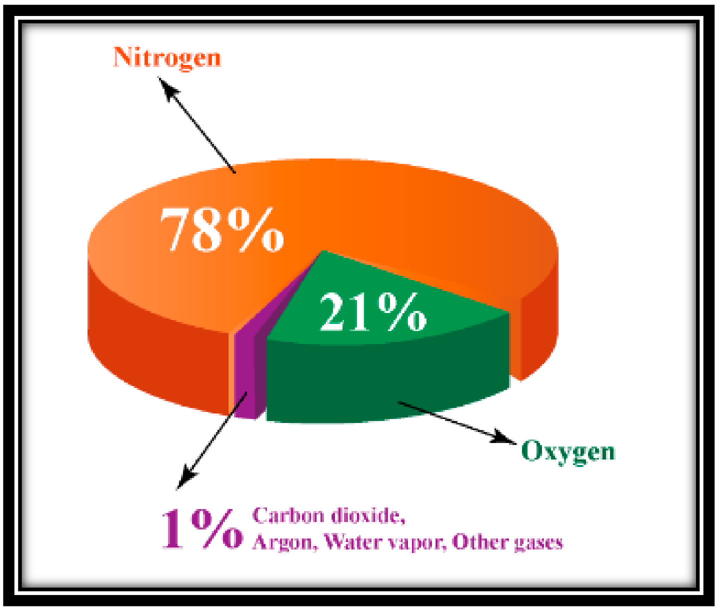


Figure 1

The oxygen present in the atmosphere may not be enough for some purposes. Some applications require a higher concentration of oxygen. For example, in medical applications, the purity of oxygen supplied by a Pressure Swing Adsorption unit must be between 90% (v/v) to 96% (v/v) as prescribed by the World Health Organisation (WHO).

This project describes two methods of concentration of oxygen from the atmosphere. Both purposes are widely used and have their own specific advantages and limitations. Fractional distillation and Pressure Swing Adsorption have been described below, in detail.

Fractional Distillation

Overview

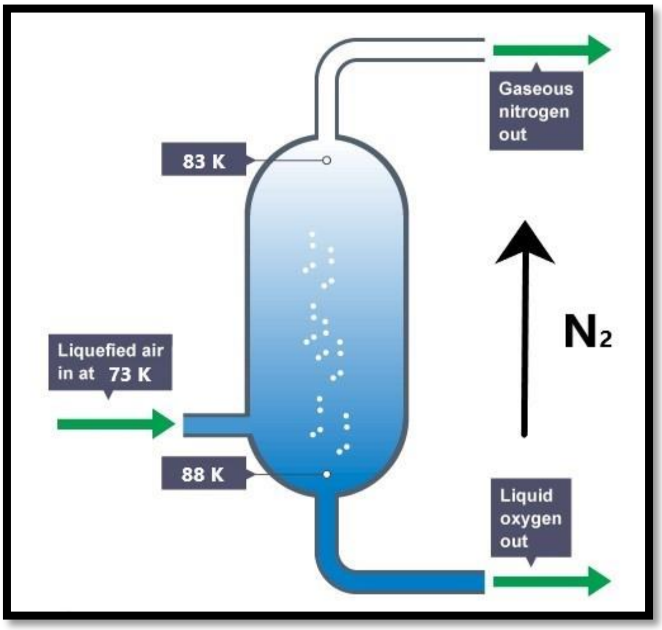
Fractional distillation is a process that separates a mixture into its component parts. It is used for those mixtures whose components have a difference in boiling point of less than 25 K, where simple distillation is not possible.

It is based on the principle of difference in boiling points (or difference in volatility) of the components of a mixture. The various components are separated by heating (or cooling) the mixture to a temperature between the boiling point of the two components, thus letting one vaporize and the other remain liquid.

In the separation of oxygen from air, fractional distillation may be used since oxygen has a boiling point of 90 K (-183 °C) and nitrogen (largest constituent of air) has a boiling point of 77 K (-196 °C).

Setup

The general setup of fractional distillation for oxygen is given below. Some



parts of the setup are not included in the picture. However, they shall be explained.

Working

Air is taken from the atmosphere and purified to remove any water vapour, dust and carbon dioxide. When cooled to low temperatures (<200 K), carbon dioxide sublimes to the solid state (it does not exist in the liquid state at ordinary atmospheric pressure).Therefore, these particles of carbon dioxide might hinder the distillation process.

The dried and purified gas mixture is now compressed. Due to increase in pressure, the temperature of the mixture increases. The compressed gas is made to spin a turbine (for secondary uses), the energy of which can be used for fractional distillation. The temperature of the mixture then reduces a little due to the work done by it. This step can be skipped as it is not vital to the entire process.

The compressed gas mixture is then made to go to a region of extremely low pressure. Due to the change from high pressure to low pressure, the mixture experiences Joule-Thomson effect (*"when a highly compressed gas, at a temperature below its inversion temperature, is passed through a porous plug from a region of high pressure to low pressure under adiabatic conditions, it suffers a fall in temperature."* The inversion temperatures for O_2 and N_2 are over 600K, much higher than the temperatures at which fractional distillation is executed), and its temperature reduces. This temperature reduction is carried out in a manner such that the gaseous mixture reaches a temperature of about 73 K (-200 °C). This is then transferred to the fractionating column (the main tank-like object shown in the figure). The mixture warms a little, and the light, gaseous nitrogen (boiling point = 77K) rises to the top of the column. Meanwhile, the heavy, liquid oxygen (boiling point = 90 K) settles at the bottom. This can be collected, and be used, or distilled again using the same process for a higher percentage purity.

Uses

- Manufacture of Medical oxygen (purity > 99%).
- Production of various hydrocarbons from Crude Oil.
- Separation of immiscible liquids (E.g. Water and Ethanol).
- Purification of water
- Manufacture of Distilled water.
- Manufacture of oxygen for large scale industrial purposes.

Advantages

- Ideal for Large scale production.
- Very high purity (>99%).
- Easy to implement.

Limitations

- The boiling points of the components need to be known.
- High energy requirements.
- Slow process.
- Can be dangerous and hazardous.

Pressure Swing Adsorption (PSA)

Overview

Pressure Swing Adsorption (PSA) is a technique used for the separation of gases, drying gases and hydrogen purification. It is based on the principle that different gases have different affinities for the adsorbent material and on the principle of preferential adsorption.

Adsorption is defined as the change in concentration of the adsorbate (the substance that gets adsorbed) at the surface of the adsorbent (the substance which invites the adsorbate). It is a surface phenomenon and is of two types:

1) Physical Adsorption or Physisorption – when the forces responsible for adsorption are *weak* van der Waals' forces. No chemical bond is formed in such adsorption. The adsorbent can be desorbed (removal of adsorbate from the surface of the adsorbent, opposite or reverse of adsorption) by heating the adsorbent (thus weakening the van der Waals' forces) or by reducing the concentration of the adsorbate. When gaseous, the adsorbate can also be desorbed by reducing the pressure (at constant volume and temperature). This can be understood by the Ideal Gas Law:

$$PV = nRT$$

$$P = n\frac{RT}{V}$$

$$P = \frac{n}{V}K \text{ , K = RT = Constant}$$

$$\text{P} \propto \text{c, c = n/V = concentration.}$$

2) Chemical Adsorption or Chemisorption – forces responsible are *strong* valence bond forces, which cannot be broken by simple methods like heating due to the presence of chemical bonds.

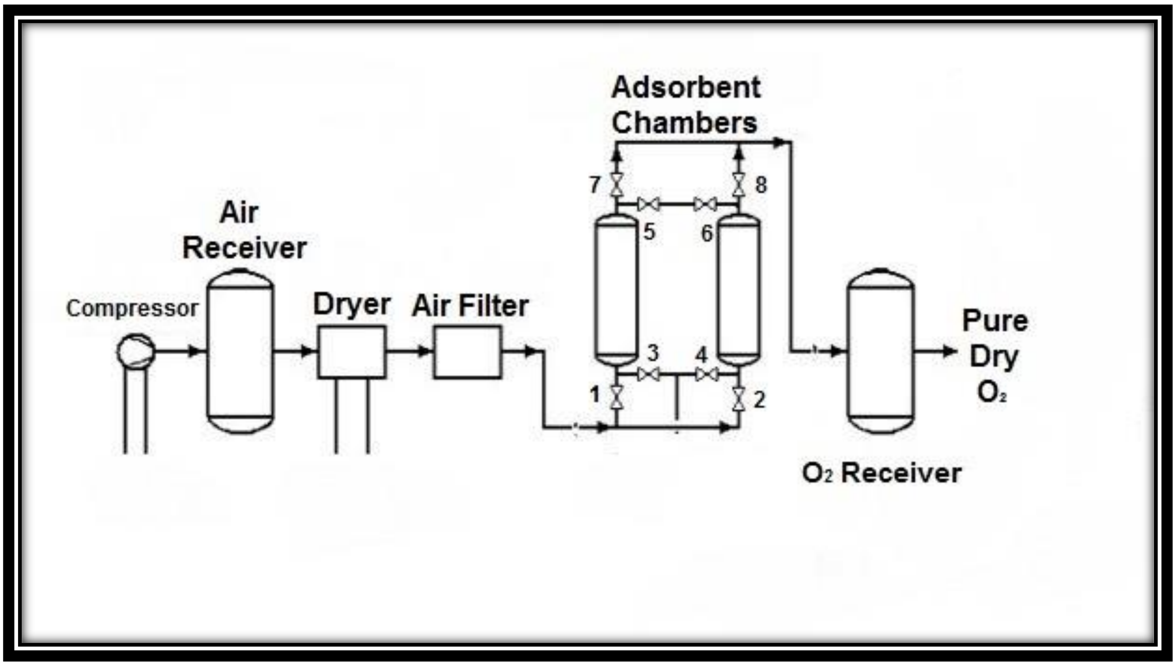
In Pressure Swing Adsorption, Physisorption is employed so that the adsorbent may be easily desorbed (or *regenerated*) and used multiple times. This is achieved by lowering the pressure of the incoming (input) gas. It can also be achieved by increasing the temperature. However, this is done in a different process called Thermal Swing Adsorption (TSA). TSA is out of the scope of this project. The forthcoming sections will discuss the various aspects of PSA.

The procedure of PSA is briefly summarised below.

First, atmospheric air is compressed and supplied to the PSA unit. Next, it is dried, usually by passing it through Silica Gel (SiO_2). The dried air is now passed to the adsorbent, usually a compound of zeolite, where the nitrogen (N_2) is preferentially adsorbed. The resulting air is mainly composed of oxygen (O_2) which is then either compressed or directly used.

Pressure Swing Adsorption Unit

A representative diagram of the Pressure Swing Adsorption Unit is shown below in Figure 3.



A brief description of the various parts of the PSA unit is given below.

Figure 3

1. **Compressor** – This is responsible for taking in atmospheric air, rich in nitrogen, and compressing it. It then feeds the compressed air to the air receiver.

2. **Air receiver** – This subunit supplies the air to the refrigerated dryer. In some modified PSA units, it can also take in the output gas of the "purge

process” (discussed later) from the adsorbent chamber. It is a temporary storage unit for the transitioning gas.

3. **Dryer** – This unit is vital to the increased efficiency of the PSA unit. It is composed of a chamber in which Silica Gel (drying agent) is present. The compressed gas is passed, and any moisture present is adsorbed. Moisture present may contaminate the adsorbent material and hence reduce the efficiency of the process.

   When dry, Silica Gel is blue (because of added Cobalt Chloride, $CoCl_2$). After adsorbing atmospheric moisture, it turns pink due to the formation of the Cobalt Chloride hydrate:

   $$CoCl_2 + nH_2O \rightarrow CoCl_2.n(H_2O)$$

   This indicates that the silica gel may either be replaced or regenerated by heating (to approximately 393 K) for 1-2 Hours.

4. **Air filter** – These are conventional filters used for the removal of any pollutants like dust, pollen etc.

5. **Adsorbent Chambers** – This is the most important subpart of the PSA unit. It comprises of a system of 2 or more chambers [where a compound of zeolite is kept. e.g. LiAgX, where X represents zeolite- $Na_2Al_2Si_2O_8$ (This is found to be the most effective form of zeolite for N_2 adsorption)] and valves (numbered 1-8) that connect the chambers. The valves can be opened or closed as per the functioning of the PSA unit.

   There are various types of zeolites – Silver zeolite, Lithium zeolite, Sodium zeolite etc.

   Silver zeolites adsorb argon in addition to nitrogen, making them very efficient. However, they are expensive and it is not practical to get oxygen purity where the argon content will make a difference (>99% of oxygen).

   Sodium Zeolites adsorb nitrogen fairly well, but Lithium zeolites adsorb better as Lithium ions (Li^+) are smaller than Sodium ions (Na^+). Therefore, surface area increases and hence adsorption increases. However, Lithium Zeolite is more expensive.

6. **O_2 Receiver** – It is a temporary storage container for the collection of oxygen. It can also be modified to produce compressed oxygen by attaching a compressor. This is the last part in sequence of the PSA unit.

Working

Note: While describing the working of PSA, figure 2 will be used.

The detailed working of the process involving each subpart of the PSA unit is given below:

1. **Compression** – Air is taken from the atmosphere and compressed with the help of the compressor. This is achieved by forcing the air into a container and increasing its pressure. Next, the compressed air is given to the air receiver, which temporarily stores it.
2. **Drying** – The compressed air is taken from the air receiver and dried with Silica Gel. It adsorbs the moisture, which could contaminate the zeolite, from the air.
3. **Filtering** – Air is taken from the dryer and filtered in the particulate air filter to remove any contaminants such as pollen, dust, mold or bacteria.
4. **Pressure Swing Adsorption** – For simplicity, this article will consider only 2 adsorbent chambers as shown in the figure.

   This step is the crux of the complete PSA process. It can be subdivided into the following steps.

   a) **Adsorption** – During this phase, valves 1, 3 and 7 are open, while the other valves are closed. The compressed, dried, filtered gas is passed through the left adsorbent chamber at a relatively high pressure, through valve 1. The adsorbent material adsorbs the nitrogen and the air coming out of the chamber, through valve 7, is rich in oxygen.

   b) **Depressurization or "Pressure Swing" or Purge** – After the first step of adsorption, valves 1 and 7 are closed, while valves 2 and 8 are opened. The left adsorbent chamber is now depressurized, i.e., experiences pressure swing.

   Meanwhile, the right adsorbent chamber undergoes the previous process, i.e., Adsorption. Air from the Air filter enters the right adsorbent chamber through valve 2, and the oxygen-rich air (nitrogen adsorbed) exits through valve 8 after adsorption.

   c) **Regeneration -** Due to the sudden drop in pressure (Pressure Swing) in the left adsorbent chamber, the adsorbed nitrogen is desorbed. The desorbed nitrogen exits via valves 3 and 5. This is called the "residual air" or the "adsorbed air". This air can either be used for the concentration of nitrogen or just released again into the atmosphere.

Now, valves 2 and 8 are closed. The right adsorbent chamber undergoes Pressure Swing.

d) **Re-pressurization or "Second Adsorption"** – Valves 1 and 7 are reopened and the Adsorption process is repeated thus completing a cycle.

Valves 4 and 6 are opened and the right adsorbent chamber undergoes regeneration. The adsorbed nitrogen is now desorbed due to the sudden drop in pressure. This nitrogen exits via valves 4 and 6.

The right adsorbent chamber then undergoes Re-pressurization while the left adsorbent chamber undergoes the "Second Pressure Swing".

As there is more than 1 adsorbent chamber, there is a continuous output of oxygen, whose purity varies upon the efficiency of the PSA system (usually 90 ~ 97%).

If there was only 1 adsorbent chamber, during the Pressure Swing and Regeneration processes, unit will not be able to supply any output. Hence, the efficiency of a PSA unit with 1 adsorbent chamber is quite low. In general, with an increase in the number of adsorbent chambers, the efficiency increases.

Possible Modifications to PSA

Vacuum Pressure Swing Adsorption (VPSA)

In this technique, during the de-pressurization (Pressure Swing) process, in addition to suddenly lowering the pressure, the adsorbent chamber is subjected to vacuum. This facilitates better desorption, which in turn dramatically increases the efficiency of the process. One drawback, however, is that the energy consumption is increased.

Addition of more Adsorbent Chambers

As described before, the addition of more adsorbent chambers increases efficiency. It also increases the life of each adsorbent zeolite.

Combination of TSA and PSA

In some large-scale applications (E.g. >80 Metric Tonnes of Liquid Oxygen per Day), a combination of Thermal Swing Adsorption and Pressure Swing Adsorption is employed. However, this is not suitable for small factories or ventilators because the "Thermal Swing" takes time and is not feasible.

Oxygen-Nitrogen Concentrator

In addition to concentration of air to obtain oxygen, the adsorbed air that is eventually released back into the atmosphere can be used in the concentration of nitrogen. This adsorbed gas is already very rich in nitrogen due to the removal of oxygen.

Uses

The unique process of Pressure Swing Adsorption gives it unique uses in life. Some of them are listed below.

- **Personal Oxygen supply** for both humans and animals that need a continuous supply to live. In such cases, a PSA unit might be modified to supply the oxygen to a ventilator.
- **Medical Uses –** stored for later use in hospitals, medical clinics etc.
- **Commercial Uses –** factories that require oxygen for various purposes. E.g. Glass factories (for blowing glass), in precision welding (for use with an acetylene torch) etc.
- **Industrial Uses –** Although PSA is not widely used for Industrial purposes, some people still employ it. It is used in the manufacture of other chemicals or substances that need oxygen as a raw material. E.g. Petroleum recovery and refining, metal production and steel manufacture, making oxides of metals etc.

Merits

Pressure Swing Adsorption is a versatile and flexible process as new elements can be added to the basic process to tailor to one's needs. This gives it some advantages (over other processes) which are listed below.

- **Quick** – PSA is a quick process compared to TSA or fractional distillation.
- **Inexpensive** – PSA units are both inexpensive to procure and use. Their cost to produce smaller quantities of oxygen is much lower than that of fractional distillation.

- **Continuous Supply of Oxygen**
- **Efficient** – PSA units can have efficiencies of up to 99%. Hence, there is minimal wastage.

Drawbacks

Although PSA is such a user-friendly process, it suffers from the following limitations.

- It is only suitable for small scale production of oxygen.
- The adsorbent zeolite and silica gel have to be periodically replaced, due to degeneration, for optimum working.
- Due to short cycle times, PSA suffers from “High Switch” losses, i.e., losses in the input gas after releasing the purge gas back into the atmosphere.
- At low pressures, PSA adds impurities that can affect the final purity of oxygen or interfere with the optimal working of the PSA unit.

Implementation of the PSA unit

In implementing the PSA unit the following were used:

- An existing 10 HP compressor capable of producing compressed air up to 10 bar
- A heat exchanger in the form of a copper coil – compressed air is hot, and the heat exchanger reduces its temperature to less than 300 K (27 °C)
- An extra air filter cum dehumidifier
- Pressure Regulators (2-10 bar) and Pressure Gauges
- An air filtering chamber, which houses cotton-wool to remove pollutants and particulate matter
- 2 chambers of Silica Gel (dehumidifier) with 1 kg each of Silica gel
- 3/2 solenoid valves (2 Nos.) at the input of the zeolite chambers
- Arduino Uno Board with 4 relays to open, close and coordinate the various valves
- 2 Sodium zeolite chambers with 2 kg each of zeolite
- 2/2 solenoid valve for pressure equalization

- Orifice and non-return valve at the outputs of the zeolite chambers
- A surge tank for oxygen to ensure continuous output
- 0-30 LPM (Litres per Minute) flow meter
- Electrochemical oxygen sensor

Notes and Highlights

- Leakage issues – the silica gel canisters and the zeolite chambers needed to be made air tight to deal with high pressures. Leakages result in inefficiencies.
- The temperature in Chennai can become quite high. High temperatures impede the functioning of the zeolite sieves. Therefore, an extra copper coil was added.
- The relative humidity in Chennai is almost always higher than 70%, which obstructs the proper functioning of the zeolite sieves. To address this, an extra chamber of Silica gel was added.
- Pressure plays a crucial role in the PSA process. With an increase in pressure, rate of adsorption increases. At the same time, with a decrease in pressure rate of desorption increases. Therefore, greater the magnitude of pressure swing better will be the purity of oxygen.
- According to ambient conditions, the valve timing must be calculated through trial and error. The timings for the opening and closing of valves that give highest purity of oxygen should be implemented into the Arduino Uno board.
- One concept not addressed in the theoretical discussion of the PSA unit and process is the equalization and the equalization valve. When one zeolite chamber experiences a swing from pressurisation to depressurisation and the other chamber experiences the opposite, to save energy in pressurizing the second chamber, the equalization valve allows compressed air of the first into the second. This not only depressurizes the first chamber but also pressurizes the second chamber.
- The oxygen concentrator built gave an output oxygen purity of 80% at a maximum flow rate of 25 Litres Per Minute (LPM)

Figure 4

Figure 5

Further Course of Action

- Using Aluminium extruded canisters for the silica gel and the zeolite chambers instead of PVC.
- Implementing Vacuum Pressure Swing Adsorption (VPSA) to increase purity of oxygen obtained.
- Using Lithium Zeolite to enhance oxygen purity.

Conclusion

While fractional distillation might be preferred for large scale application, individuals requiring oxygen for personal consumption or small scale factories might prefer PSA, for its cheap, quick and continuous oxygen supply. As mentioned before, both of these processes have their own advantages and limitations. One must thoroughly evaluate his or her requirements and constraints before opting for one of these processes.

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