Oxygen and Nitrogen Separation from Air Using Zeolite Type 5A.

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ABSTRACT

An adsorption (PSA) unit consist of two – tubes columns pressure swing, (6cm diameter and 70cm bed length) and a dryer part (12cm diameter and 27cm) filling with activated alumina (Al_2O_3) have been constructed to study the separation of oxygen and nitrogen from air using commercial 5A zeolite under the effect of adsorption pressure (1 to 6 bar), adsorption time (20s), product flow rate (1 liter/min) on the product oxygen purity. For the case of 2-column, 4-step operation, the results show that an optimum concentration product of oxygen was 76.9%purity,at the adsorption pressure 4bar, Temp 17.4^{o}C.Nitrogen optimum production was78.8% purity, at 1 bar.

KEY WORDS: Pressure swing adsorption (PSA), Oxygen production using Zeolite 5A, Air separation, Equilibrium adsorption, Oxygen concentrator unit.

فصل الاوكسجين والنتروجين من الهواء باستخدام زيولايت نوع A5.

د.حسين حبيب حميد

الكلية التقنية – كركوك – قسم هندسة تقنيات الوقود والطاقة

الخلاصة :

تم تصنيع منظومة للامتزاز بتغيير الضغط (PSA) بعمودين اسطوانيين، قطرالعمود الواحد (6 سم وطوله 70سم) وجزء مجفف بقطر(12 سم وطول 27 سم) مملوء بمادة اوكسيد الالمنيوم المنشط(Al_2O_3) لدراسة فصل الاوكسجين والنتروجين من الهواء باستعمال الزيولايت 5A. استعملت طريقة التشغيل ذات الاربعة خطوات (بوجود خطوة تعادل الضغط) ، تمت دراسة تاثير الضغط التشغيلي للمنظومة على نقاوة الاوكسجين والنتروجين المنتج بزمن امتزاز (20 ثانية) ومعدل جريان (1 لتر/دقيقة) ولحالة عمودين واربعة خطوات تشغيلية كانت النتائج تشير الى ان تركيز الاوكسجين المنتج (76.9%) لضغط تشغيلي 4 بار ودرجة حرارة 17.4 سيليزية.وبالنسبة للنتروجين وصلت النقاوة الى(78.8%)عند ضغط 1 بار ودرجة حرارة 17.4 سيليزية.

INTRODUCTION:

Adsorption processes are often identified by their method of regeneration. Temperature-swing adsorption (TSA) and pressure swing adsorption (PSA) are the most frequently applied process cycles for gas separation. The basic difference between the two processes is shown schematically in **Figure (1)**. Because changes in pressure can be brought about more rapidly than changes in temperature, pressure-swing regeneration can be used with shorter cycle-times than was possible with temperature-swing. This, in turn, allows smaller beds to be used and consequently a smaller inventory of adsorbent is needed in the system**.[Moghadazadeh,et.al,2008,.Masoud,2013,Kirk-Othmer,1998]**.

Atypical total cycle time for the PSA process is between one to several minutes [Sircar, 1988], compared to the TSA process cycle time of hours.

Pressure swing adsorption (PSA) processes, first suggested by Skarstrom in the form of a 'heatless drier' have found widespread application in hydrogen purification and air separation, as well as in air drying**[Skarstrom, C. W.,1959,Skarstrom, C. W.,1960,Skarstrom, C. W.,1972]**. The PSA process could be described briefly as follows:

Two columns operate semi-continuously in four stages to supply the desired purity and flow rate of oxygen. Adsorbents are selectively chosen to provide for the most beneficial design. The PSA stage operation is described in **Figures 2-5[Ruthven, et.al ,1994,Oxygen Generating System Intl. Web site,2007]** as following;

-**Stage 1**: Compressed air is fed into the first bed. Nitrogen molecules are trapped, while oxygen is allowed to flow through **Fig(2**).

-**Stage 2**: When the adsorbent in the first bed becomes saturated with nitrogen , the air flow feed is directed into the second bed **Fig(3).**

-**Stage 3**: The adsorbent adsorbs nitrogen in the second bed. The first bed is depressurized allowing nitrogen to be purged out of the system and released to the atmosphere **Fig(4).**

-**Stage 4**: The process starts over. Compressed air is once again fed into the first bed. The second bed is depressurized releasing argon and nitrogen molecules to the atmosphere. The process is repeated continuously producing a constant flow of purified oxygen **Fig(5).**

A very important improvement was the introduction of the pressure equalization step. **[Pramuk, et.al,1964,Berlin, 1966,Wagner, 1969]**.The pressure equalization, using a product-enriched current, leads to a significant economy in energy consumption, since less mechanical energy is required to re-pressurize the column at low pressure, after the purge stage. The product recovery is, in this way, also increased because less feed gas is necessary to re-pressurize the column**.[Cruz, et.al,2003]**.

Oxygen production (purity below 95%) from air, using nitrogen selective zeolites of type A (5A) or X (13X-NaX, LiX, or LiLSX), by means of pressure swing adsorption (PSA) processes has noticeably increased in the past decade. However, the concentration of the product is limited to 95% oxygen, because of the presence of argon in air, since these adsorbents present similar adsorption capacities for oxygen and argon**.[Santos,2007].**

Zeolites have the unique ability to adsorb N_2 more strongly than O_2 (i.e., by a factor of 2 or more in terms of pure component adsorption amounts). The main reason for this is the interaction between the quadruple moment of N_2 and the cation that is attached to the zeolite framework**.[Rege, et.al,1997]**.

Nitrogen and oxygen are, respectively, the second and third largest man-made commodity chemicals today. Since 1920s, N_2 and O_2 have been produced by cryogenic distillation of air. Since 1980s, adsorption (i.e., pressure swing adsorption or PSA) has been adopted rapidly and increasingly for air separation. Approximately 20% of air separation is presently accomplished by PSA**.[Rege, et.al,1997].**

Commercial PSA technology can be used to produce an oxygen-enriched stream containing 80-95% oxygen which finds application in biological wastewater treatment, medical use, enhanced combustion in furnaces and cupolas, etc**.[Sircar, et.al,1998]**.

Currently, design of PSA systems relies heavily on experimental data for the system of interest. Experiments are conducted over a wide variety of process condition (pressure, purge-to-feed rates, steps times, feed and product flow rate, etc.) for specified adsorbent and cycle.

The aims of the present work are:

1. The objective of this project is to determine whether or not it is feasible to build an oxygen supply device using 5A zeolites to separate oxygen and nitrogen from air, using two bed columns, packed with commercial 5A zeolite and its properties shown in **table(1) [Anant,et.al.2013].**
2. Studying the effects of adsorption pressure on the performance of PSA unit, using two columns 4-steps equalization modification cyclic operations. The Performance is characterized by O_2 and N_2 product purity, maximum operating pressure 6 bar.

EXPERIMENTAL WORK:

The experimental work includes two parts, one for air drying and another for oxygen and nitrogen separation from air using zeolite type 5A to produce pure oxygen and nitrogen. All the runs are conducted at ambient temperature.

Air Separation By Pressure Swing Adsorption (PSA) Process:

Devices;

Air separation by pressure swing adsorption to produce pure oxygen and nitrogen performed using two columns 4-steps equalization modification cyclic operations.
The equipment used in the present work consists of:

1- Two-tubes Adsorption columns of Aluminum type (a) of 6cm diameter and 70cm length.
2- Product flow meter (flow rate of 0.1 to 1 liter/min, AFR2000, XCPC2000).
3- The drying unit is composed of one galvanized steel columns, which are packed with activated alumina (2.395Kg) with properties shown in **table (2).** The length of column (L) is 27 cm and its diameter (D) is 12cm **fig.(6).**
4- Digital Oxygen meter with a polar graphic type probe with an incorporated temp. sensor which serves for precise Dissolved Oxygen(DO) and temp. measurement. Model : DO-5510HA with specifications shown in **table (3).fig.(7).**
5- Purge flow meters (Maximum flow rate 10L/min, Type YR-88, manufacture in china).
6- Pressure regulator (1 to 10 bar).
7- Solenoid valves on the feed line, (Model 2W-200-20,3/4" in size, 220V, 50Hz, 28VA, Temp (-5ºC-80ºC),H.A.K pneumatic).
8- Equalization valves (1/8" in size, 220V, 50Hz, Type122k232,30bar,Lucifer Switzerland.).
9- Pressure gauges (1-8 bar, china manufactured).
10- Control panel**(fig(8))** 4 steps, which is working as follow;

A-The first 20 seconds, V_1 (2 and 4 valve) is open. The remaining valves are closed.
B-For 10 seconds, V_2 (5 and 6 valves) are open. The remaining valves are closed.
C-For 20 seconds, V_3 (1 and valve 3) open. The remaining valves are closed.
D-For 10 seconds, (5 and 6 valves) open. The remaining valves are closed.

11- Each column contains 1.430Kg of zeolite 5A.
12- Flow diagram of PSA unit **fig.(9)** , PSA unit picture **fig.(10).**

Experimental Procedure:

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. It operates at near-ambient temperatures and differs significantly from cryogenic distillation techniques of gas separation. Specific adsorptive materials (e.g., zeolites, activated carbon, molecular sieves, etc.) are used as a trap, preferentially adsorbing the target gas species at high pressure. The process then swings to low pressure to desorb the adsorbed material.
Effect of higher operation pressure studied on Oxygen and Nitrogen purity in laboratory scale PSA unit from 1 to 6 bar using Zeolite 5A. In this system binary mixture (N_2/O_2) (79/21 vol %) used as a feed stream as following:

1- Air compressor started until the tank pressure reached the desired pressure (4bar for O_2, 1 bar for N_2).
2- Operate the control panel.
3- Then the air enters to dryer to drying from moisture and cleans it from impurities.
4- Regulate the air by the air regulator to the require pressure.
5- The air enters to the column no.1 (C1) from the top, the zeolite adsorbs nitrogen and the other gases and oxygen rich gas flow from the bottom.
6- The oxygen from column1 divided into two streams.
7- The second stream goes to the valve no.5 to equivalent pressure between the column no.1 and column no.2.
8- the third stream goes to the check valve no.1 that is reversal direction of it flow, therefore goes to the check valve no.3 that is the same direction of its flow and allow it to flow across it.
9- From check valve no.3 divided into two streams.
10- The first stream goes to the flow meter no.2, and the product oxygen goes to oxygen meter to measure its concentration and temperature.
11- The second stream goes to the flow meter no.1 then recycled.
12- The recycle is entering from the bottom of column no.1 to desorb the nitrogen from the zeolite to clean it, and to be ready to another adsorption process of oxygen.
13- The nitrogen out from the top of the column no.1, and valve no.1 is open then nitrogen out from it.
14- The processes from step 5 to 14 is the same process in the column no.2,but when the first column is adsorbed nitrogen and product oxygen the second column is desorbed nitrogen from zeolite by the oxygen recycle.
15- And when the second column is adsorbed nitrogen and product oxygen the first column is desorbed nitrogen from zeolite by the oxygen recycle.

Result and Discussion;

The separation of mixtures of fluids using zeolitic as selective adsorbents may be accomplished in three fundamentally different modes;

1-When the physical size and or shape of the molecules of the fluid materials to be separated are sufficiently different and a molecular sieve having a suitable pore size is available a separation is possible based on the acceptance-exclusion phenomenon.

2-When the physical size and or shape of the molecules to be separated are different and a molecular sieve is available having a pore opening through which the larger molecules pass only with difficulty, a separation is possible which is kinetically controlled. Some such separations are inverse to the separation effected when the molecules all can freely enter the pore system.

3-When the physical size and or shape of the molecules to be separated are not sufficiently different to either be separated by the acceptance-exclusion phenomenon or the kinetically controlled situation but all freely enter the pore system the separation depends on the forces of adsorption between the molecular sieve and the different molecules.

Pressure swing adsorption processes rely on the fact that under high pressure, gases tend to be attracted to solid surfaces, or "adsorbed". The higher the pressure, the more gas is adsorbed; when the pressure is reduced, the gas is released, or desorbed. PSA processes can be used to separate gases in a mixture because different gases tend to be attracted to different solid surfaces more or less strongly. If a gas mixture such as air, for example, is passed under pressure through a vessel containing an adsorbent bed of zeolite 5A that attracts nitrogen more strongly than it does oxygen, part or all of the nitrogen will stay in the bed, and the gas coming out of the vessel will be enriched in oxygen. When the bed reaches the end of its capacity to adsorb nitrogen, it can be regenerated by reducing the pressure, thereby releasing the adsorbed nitrogen. It is then ready for another cycle of producing oxygen enriched air.
Therefore, it is noted **fig.(12),** where the intersection of each of the oxygen production line and nitrogen, one point under the pressure of 2 bar while the intersection of two gas (N_2 and O_2) production line in **figs.(13.16)** with two points under the pressure of 3 and 6 bar sequentially and the intersection of the production of gases under the pressure of 5 bar in three points **fig.(15).**
Through practical experience shows that many factors influenced by the production of gases from the most important dimensional design own column absorption and surface area of the material adsorbent (zeolites 5A) where the pressures (2, 3, 5 and 6) bar were unsuitable to work.
Because of purity is increased with increasing of purge and after reaching to a peak, decreasing. As we know, purging the adsorption bed, help the adsorbent regeneration and increase its capability, but increasing the amount of this stream more than its sufficiency causes the adsorption of oxygen on the adsorbent because of its high vapor pressure in the column and the efficiency of adsorbent will be decreased.
Finally as we see from **fig.(14),** in short cycle time, high purity will be achieved. Optimum oxygen concentration 76.9%vol after 4 min operation time. Because there is not enough time for oxygen adsorption instead of nitrogen and verse reverse for nitrogen the optimum case is clear in **fig.(11)** which is will be 78.8% after 2 min under 1 bar operating pressure.

Conclusion and Recommendation

The following goals were met with the portable oxygen concentrator from the initial estimates;

- Purity: 76.9% oxygen,78.8% (from the first stage).

- Cost: $4200 (under $5000).

- Weight: 75kg.

- Small: Estimated .2m x 2m x 1m

Thus from the above information, it can be see that a competitive / light weight portable oxygen concentrator. It is useful for using in welding machine and it is small enough to take on an airplane. It is a good idea to study the effect of ozone on the oxygen and nitrogen production.

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Table (1): 5A Zeolite properties.

Chemical Name	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$
Pore Diameter	5Å
Mesopore Volume	0.062 cm^3/g
Micropore Volume	0.176 cm^3/g
Surface Area	571 m^2/g
Mass of Crushed Sample	2.046 g

Table (2): activated alumina properties.

Surface area , m^2/g	**330**
Total pore volume, $cm^3/100g$	**44**
Diameter of particles mm	**5**
Shape	**Sphere**
Bulk density, kg/m^3	**785**

Table (3): Oxygen Meter Model: DO-5510HA Specifications

Custom one – chip of microprocessor LSI circuit.		Circuit
Dual function meter's display, 13mm (0.5"). Super large LCD display with contrast adjustment for best viewing angle.		Display
0 to 20.0 mg/ L (liter).	Dissolved Oxygen	Measurement & Range
0 to 100.0 %	Oxygen in Air	
0 to 50 ºC	Temperature	
0.1 mg / L	Dissolved Oxygen	Resolution
0.1 % O_2	Oxygen in Air	
0.1 ºC	Temperature	
±0.4 mg / L	Dissolved Oxygen	Accuracy (23 ± 5 ºC)
±0.7 % O_2	Oxygen in Air	
±0.8 ºC / 1.5 ºF	Temperature	
The polar graphic type oxygen probe with an incorporated temperature sensor.		Sensor structure
0 to 50 ºC Automatic	Temperature	Probe Compensation & Adj.
0 to 39 % Salt	Salt	
0 to 3900 meter	Height (M.T)	
Records Maximum, Minimum and Average readings with recall.		Memory Recall

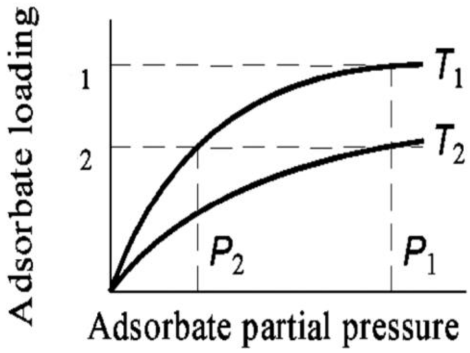


Figure (1): Temperature- swing and pressure-swing cycles.

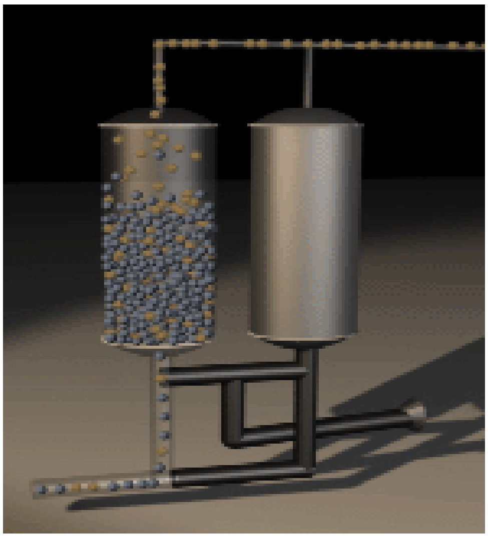


Figure (2): PSA Stage1

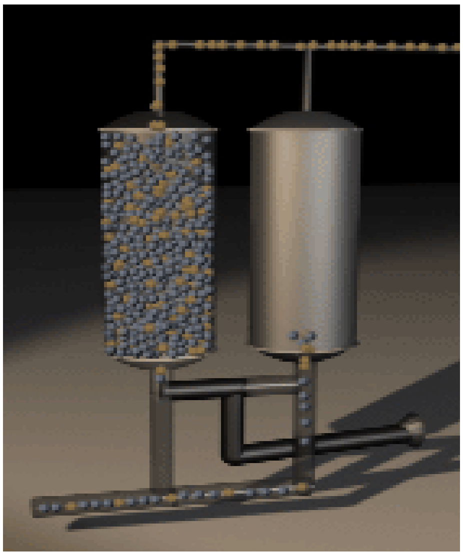


Figure (3): PSA Stage2

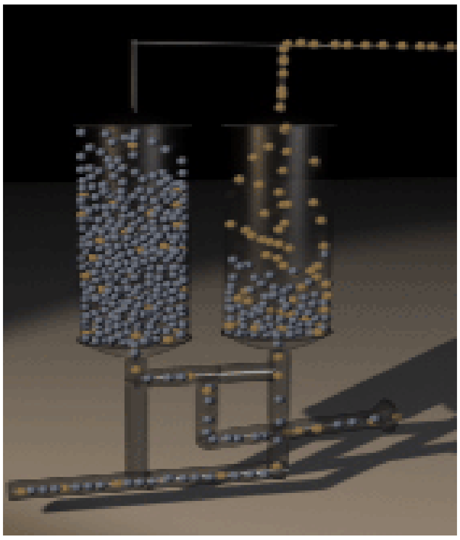


Figure (4): PSA Stage3

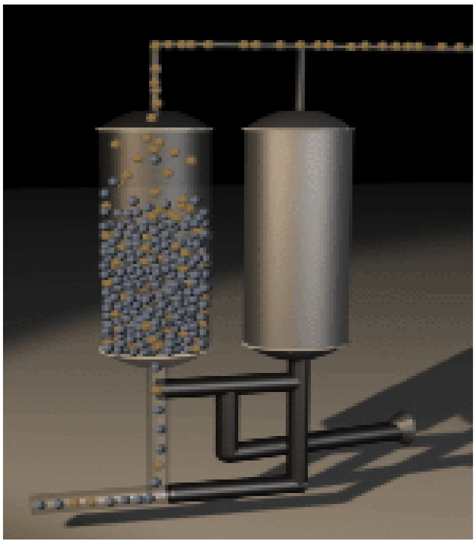


Figure (5): PSA Stage4

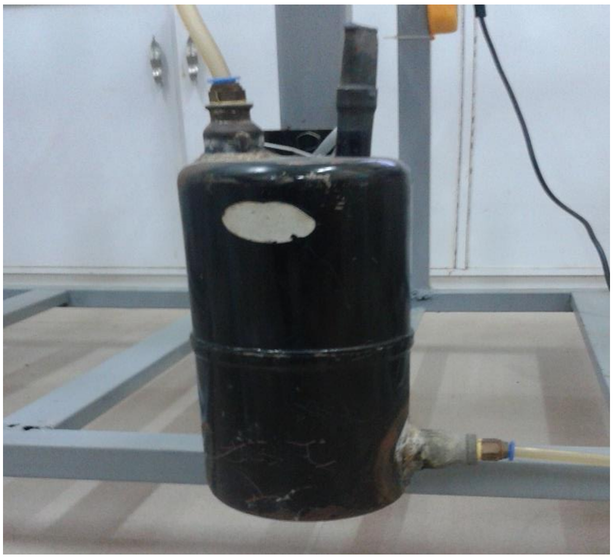


Figure (6): Drying unit.

Figure (7): Oxygen meter unit.

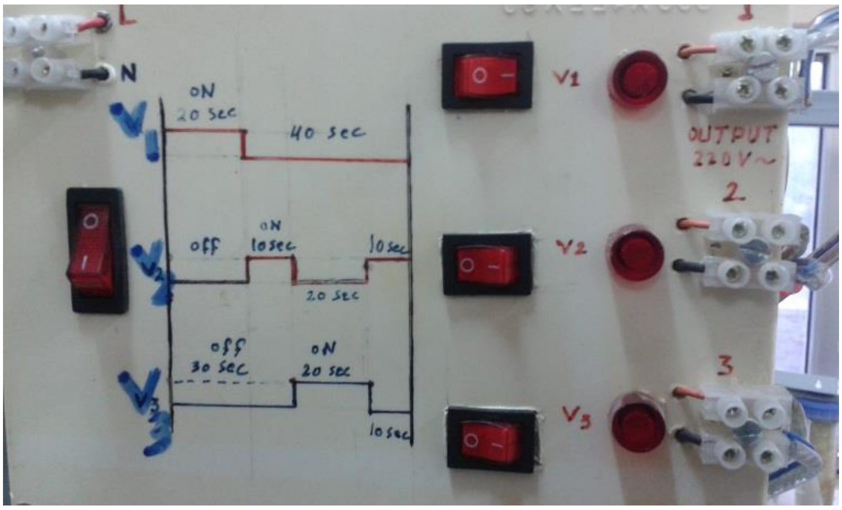
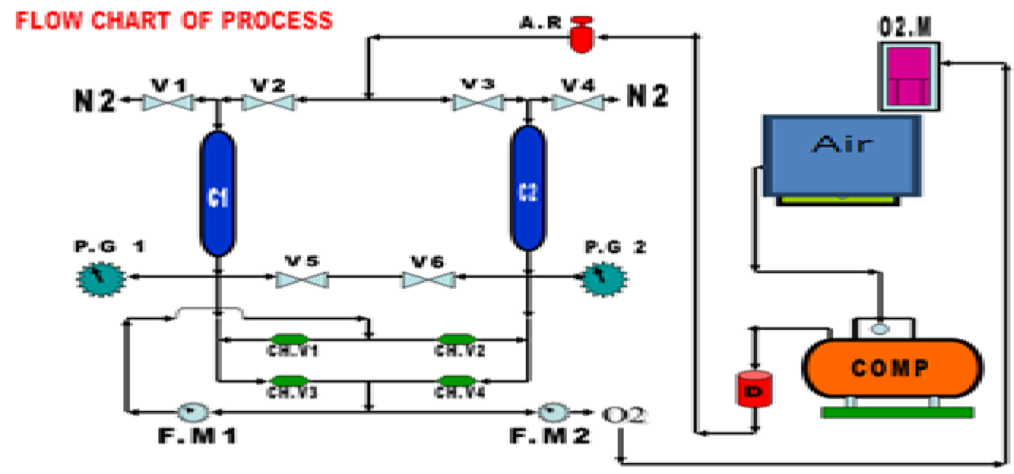


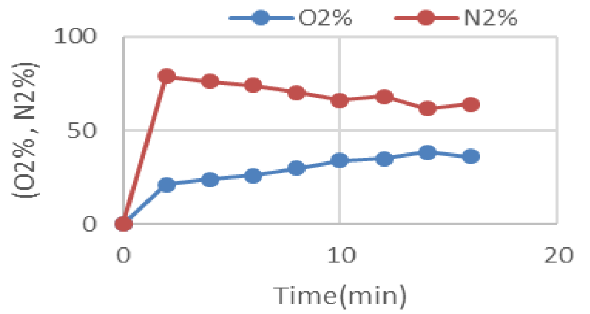
Figure (8): control panel 4 steps unit.



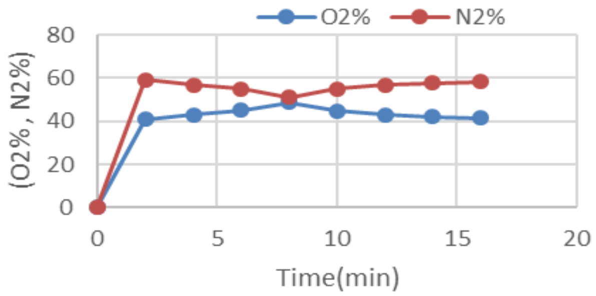
COMP	O_2.M	D	A.R	V	P.G	CH.V	F.M	C
Compressor	Oxygen meter	Dryer	Air regulator	Valve	Pressure gauge	Check valve	Flow meter	column

Figure (9): Flow diagram of PSA unit

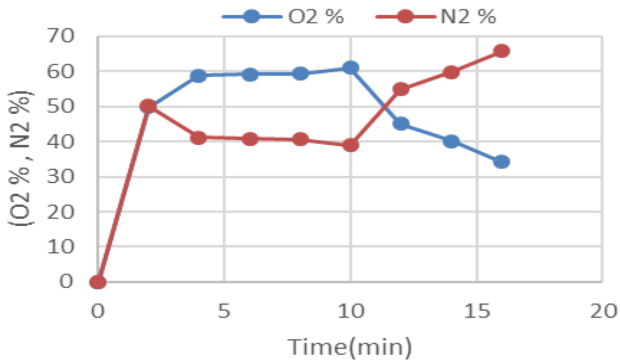
Figure (10): PSA unit



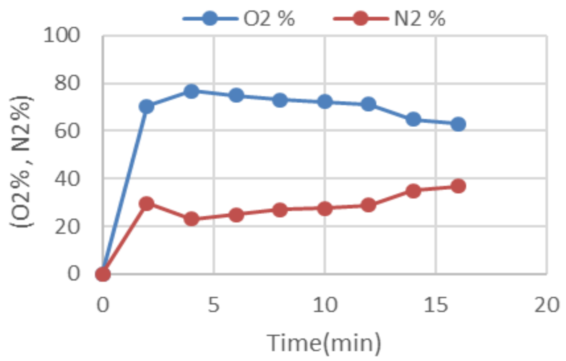
Fig(11) Purity variations versus time in a cycle of 16min and operating pressure of 1 bar and Qout=1 L/min,T=17.4c



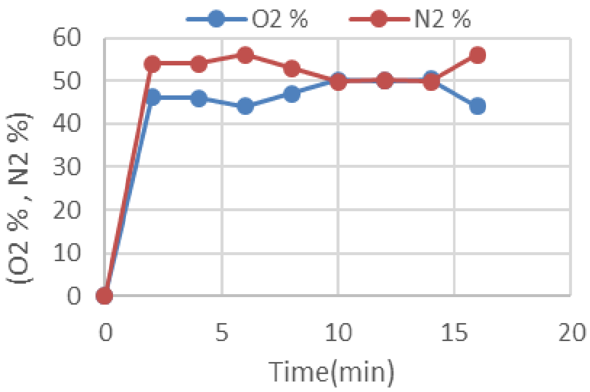
Fig(12) Purity variations versus time in a cycle of 16 min and operating pressure of 2 bar and Qout = 1 L/min, T=17.4c.



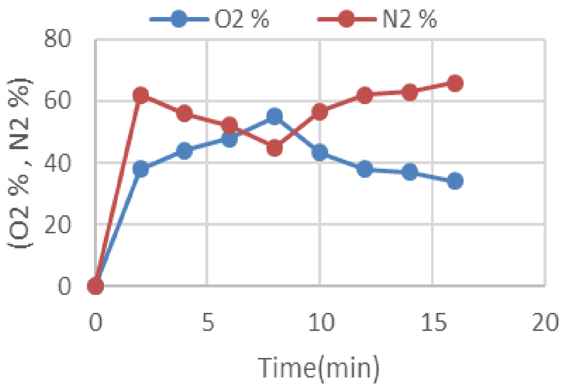
Fig(13) Purity variations versus time in a cycle of 16 min and operating pressure of 3 bar and Qout = 1 L/min, T=17.4c



Fig(14) Purity variations versus time in a cycle of 16 min and operating pressure of 4 bar and Qout = 1 L/min, T=17.4c.



Fig(15) Purity variation versus time in a cycle of 16 min and the operting prssuer 5 bar, Qout = 1 L / min and T = 14.7°C.



Fig(16) Purity variations versus time in a cycle of 16 min and operating pressure 6 bar, Qout = 1 L / min and T = 14.7°C.