

No_x Reduction In IC Engine Using Pressure Swing Adsorption Technique

N. Prasanna, S. Manikandan, P. Guruprasath, S. Mohan Baabu

Abstract: The reduction of NO_x emissions is a main goal of the Clean Air Act Amendments because of their known role in the formation of ground-level ozone. NO_x is a generic term for the nitrogen oxides that are most relevant for air pollution, namely nitric oxide (NO) and nitrogen dioxide (NO₂). These gases contribute to the formation of smog and acid rain, as well as affecting tropospheric ozone. NO_x gases are usually produced from the reaction among nitrogen and oxygen during combustion of fuels, such as hydrocarbons, in air; especially at high temperatures, such as occur in car engines. The facility that can reduce NO_x emissions from the combustion equipment, is using Pressure swing adsorption. 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. Specific adsorbent materials (e.g., zeolites, activated carbon, molecular sieves, etc.) are used as a trap, preferentially adsorbing the target gas species at high pressure. The air from the atmosphere is sent to the compressor and the air is compressed to 6 bar (approx.). the compressed air from the compressor is sent to the two reaction chambers where the two chambers are connected in parallel which works alternatively (when adsorption takes place in first chamber the desorption takes place in another chamber and vice versa). The connection between the two chambers is controlled by using valve. The nitrogen in the compressed air is adsorbed by the 13x zeolite and the remaining air from the reaction chamber is sent to the buffer tank where the air is stored for the continuous input to the engine, for maintaining constant pressure and to compensate the fluctuation in mass flow rate. A part of air is sent to the oxygen analyzer to know the amount of oxygen rich air which is sent to the engine. By using this method, the NO_x emission from exhaust is reduced and the performance is increased significantly.

Keywords: NO_x Reduction, Adsorption, Pressure swing adsorption, Zeolite, Emission control, bentonite, berl saddle.

1 INTRODUCTION

NO_x Nitrogen oxides are the most known cause for air pollution, namely nitric oxide (NO), nitrogen dioxide (NO₂) and nitrogen trioxide (NO₃). These gases are one of the reasons for the formation of smog and acid rain, as well as affecting tropospheric ozone. NO_x gases are produced due to the reaction with oxygen and nitrogen at high temperature during combustion of fuels, such as hydrocarbons, in air; especially at high temperatures, such as occur in car engines. In areas of vehicle traffic, such as in large cities, the nitrogen oxides emitted can be a major source of air pollution. NO_x gases are also produced naturally by lightning. Nitric oxide is produced during thunderstorms and lightning due to the extreme heating within a lightning strike. This causes stable molecules such as nitrogen and oxygen to convert into significant amounts of nitrogen oxide similar to the process that occurs during high temperature fuel combustion.

Scientists estimated that each flash from lightning on average in the middle altitude and tropical thunderstorms studied at 7 kg (15 lb) of nitrogen into chemically reactive NO_x. With 1.4 billion lightning flashes per year, multiplied by 7 kilograms per lightning strike, they estimated the total amount of NO_x produced by lightning per year is 8.6 million tons. NO_x emissions resulting from combustion of fossil fuel are estimated to be 28.5 million tons. Agricultural fertilizers and the usage of nitrogen fixing plants also contribute to atmospheric formation of NO_x, by promoting nitrogen fixation by microorganisms. The nitrification process transforms ammonia into nitrate. And the denitrification is basically the reverse process of nitrification. During the denitrification, nitrate is reduced to nitrite then NO then N₂O and finally nitrogen. By these processes, NO_x is emitted to the atmosphere.

A recent study conducted by the University of California Davis, found that adding nitrogen fertilizer to soil in California is contributing 25 percent or more to state-wide NO_x pollution levels. When nitrogen containing fertilizer is added to the soil, excess ammonium and nitrate not absorbed by plants can be converted to NO by microorganism in the soil, which enters into the air. NO_x is a main cause for smog formation which is already a issue in the state of California. In addition to contributing to smog, when nitrogen fertilizer is added to the soil and the excess is released in the form of NO, or leached as nitrate this can be a costly process for the farming industry.

The three primary sources of NO_x in combustion processes:

- Thermal NO_x
- Fuel NO_x
- Prompt NO_x

Formation of thermal NO_x, which is temperature dependent, is the most relevant source when burning natural gas. Fuel NO_x will be higher during the combustion of fuels, such as coal, etc. which have a higher amount nitrogen content, mainly when burned in combustors designed to reduce or minimize thermal NO_x. The contribution of NO_x is normally considered negligible. A another source, called feed NO_x is

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- The term NO_x is chemistry for molecules containing one nitrogen atom and one or more oxygen atom. It is generally meant to include nitrous oxide (N₂O), although nitrous oxide is a fairly inert oxide of nitrogen sprays and whipped cream. Nitrous oxide plays hardly any role in air pollution, although it may have a significant impact on the ozone layer, and is a significant greenhouse gas.

linked with the combustion of nitrogen available in the feed material of cement rotary kilns, at between 320 °C and 850 °C, where is considered as an minor contributor Thermal NO_x refers to NO_x formed by high temperature oxidation of the diatomic nitrogen found in air during combustion. The rate of formation is a main function of temperature and the residence time of N at that temperature. At high temperatures, usually more than 1600 °C, molecular nitrogen (N₂) and oxygen (O₂) in the combustion air separates into their atomic states and contribute in their series of reactions. Zeldovich was the first man to suggest the importance of the preliminary two reactions and the last reaction of atomic nitrogen with the hydroxyl radical was later added by Lavoie, Heywood and Keck contributed to the mechanism and to the formation of thermal NO_x. Bentonite is a clay generated frequently from the alteration of volcanic ash, consisting predominantly of smectite minerals, usually montmorillonite. Other smectite group minerals include hectorite, saponite, beidelite and nontronite. Smectites are clay minerals, i.e. they consist of individual crystallites the majority of which are <2µm in largest dimension. Smectite crystallites themselves are three-layer clay minerals. They consist of two tetrahedral layers and one octahedral layer. In montmorillonite tetrahedral layers consisting of [SiO₄] - tetrahedrons enclose the [M(O₅,OH)]-octahedron layer (M = and mainly Al, Mg, but Fe is also often found). The silicate layers have a slight negative charge that is compensated by exchangeable ions in the intercrystallite region. The charge is so weak that the cations (in natural form, predominantly Ca₂₊, Mg₂₊ or Na⁺ ions) can be adsorbed in this region with their hydrate shell. The extent of hydration produces intercrystalline swelling. Depending on the nature of their genesis, bentonites contain a variety of accessory minerals in addition to montmorillonite. These minerals may include quartz, feldspar, calcite and gypsum. The presence of these minerals can impact the industrial value of a deposit, reducing or increasing its value depending on the application. Bentonite presents strong colloidal properties and its volume increases several times when coming into contact with water, creating a gelatinous and viscous fluid. The special properties of bentonite (hydration, swelling, water absorption, viscosity, thixotropy) make it a valuable material for a wide range of uses and applications. Berl Saddles are early developed Tower Packings with special form of saddles. Having both internal and external surfaces entirely open, Distribution of Vapour-Liquid is entirely same at either sides. Comparing with Raschig Ring, Berl saddles create lower pressure on the column wall. Berl Saddles are often super posed each other while filling them into column because both inside and outside surfaces have the similar shapes. There are strategies for controlling NO_x emissions. Gas scrubbing is one of the most common forms of NO_x treatment, with sodium hydroxide being the conventional scrubbing medium. However, the absorbed NO_x is reborn to radical nitrate which may present wastewater disposal problems. Scrubbing solutions containing hydrogen peroxide are also effective at removing NO_x, and can afford benefits not available with NaOH. For example, hydrogen peroxide adds no contaminants to the scrubbing solution and so allows commercial products to be recovered from the process, e.g., nitric acid. In its simplest application,

H₂O₂ (0.5-1 wt.%) and Nitric acid (35-45 wt.%) are accustomed to scrub both nitric oxide (NO) and nitrogen dioxide (NO₂) -- the chief elements of NO_x from many industrial sources. The reactions are rapid at moderate temperatures (30-80 °C), with about 1.7 and 0.37 lbs hydrogen peroxide required per lb NO and NO₂, respectively. The chemistry controlling the process is outlined below:

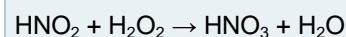
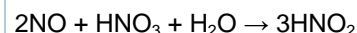


Table.1. Chemical reaction for controlling the process

A second advancement for controlling NO_x emissions involves its elimination at the source. This usually involves adding H₂O₂ on to HNO₃ contained in e.g., metal pickling baths, where the H₂O₂ reacts instantaneously with HNO as it is formed, thereby eliminating its decomposition to NO and NO₂. In this way, the nitric acid is regenerated in-situ without the expense of scrubbers. Compared to urea, which is also used for in-situ control, the hydrogen peroxide process affords true nitric acid recovery and doesnot degrade the standard of the finished product.

2 EXPERIMENTAL PROCEDURE

2.1 EXPERIMENTAL SETUP

The experimental setup is shown in the Fig.2.1, Zeolite 13X was prepared using bentonite as the raw material by alkaline fusion followed by a hydro-thermal treatment without adding any extra silica or alumina sources. Bentonite was mixed with NaOH powder at a 1:1.4 weight ratio. The resulting material was ground to a homogeneous mixture, and fused at 600 °C for 6 h. The fused mixture was cooled to room temperature, ground to a fine powder, and mixed with water at a weight ratio of 1:4, followed by vigorous stirring at room temperature for 24 hours. Finally, the mixture was aged in an oven at 80 °C for 12 h. The solid product obtained was filtered, washed with distilled water, and dried overnight. The morphological features and chemical composition of bentonite and zeolite 13X samples were examined by scanning electron microscopy. The surface areas of these samples were calculated using the Brunauer–Emmett–Teller (BET) method. The adsorption experiments were carried out using ultra high purity CO₂ or N₂ (U-Sung, 99.999%) at 25 °C over a pressure range of 0–1 bar. Required quantity of bentonite and sodium hydroxide is taken in beaker. Water is added to dilute the bentonite. Ultrasound from the ultrasound processor UP200HT is passed into the beaker at regular time intervals of 30 minutes for three times. Now the mixture look like homogenous slurry material. Then solution is dried at 110⁰c at hot air oven and the mixture is dry calcined at 600⁰c for 3 hours to remove impurities in muffle furnace. The powder obtained from the above process is mixed with borax and water to make it into a solution. Berl saddle made up of ceramic is dipped in the solution and air is passed over it for uniform spreading.

Then they are dried using muffle furnace and filled into the chamber.

2.2 PROCEDURE

The air from the atmosphere is sent to the compressor and the air is compressed to 6 bar (approx.). The compressed air from the compressor is sent to the two reaction chambers where the two chambers are connected in parallel which works alternatively, (when adsorption takes place in first chamber the desorption takes place in another chamber and vice versa). The connection between the two

chambers is controlled by using valve. The nitrogen in the compressed air is adsorbed by the 13x zeolite and the remaining air from the reaction chamber is sent to the buffer tank where the air is stored for the continuous input to the engine, for maintaining constant pressure and to compensate the fluctuation in mass flow rate. A part of air is sent to the oxygen analyzer to know the amount of oxygen rich air which is sent to the engine. By using this method, the NOx emission from exhaust is reduced and the performance is increased significantly. The experimental run has been done and the image is shown below (Fig.2.2)

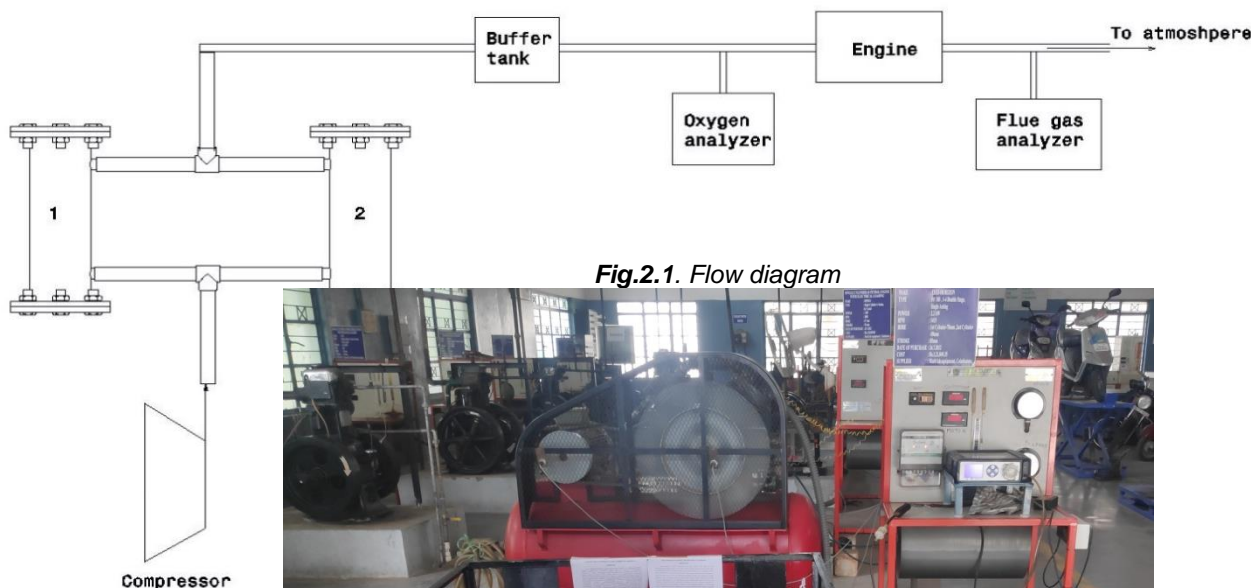


Fig.2.1. Flow diagram



Fig.2.2. Experimental run

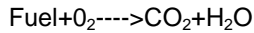
In our system we have mounted the chamber into a frame which we have made using the L angle rods of 25mm x 25mm and with a thickness of 3 mm. The frame has a plate to place the buffer tank and this plate is of thickness 5 mm and supports are also given under the base plate in order to withstand the heavy shock load and vibrations. Two plates are placed vertically for mounting those chambers and they are separated with a distance of 500 mm. The chamber is of height 300 mm and of diameter 50.8 mm. Therefore the volume is approximately $6.05 \times 10^{-5} \text{ m}^3$. We have used two valves at the two ends of the chambers for the alternative process for the adsorption and desorption. This chamber also has a separate valve for the draining of the air. The chamber is made of upvc and the ends are closed with the help of upvc caps at both ends. The pneumatic hose is used throughout the setup and these are closed with the help of gaskets. A brass tee joint is used to vary the

direction of the compressed air to be sent to the chambers. The hose is then mounted to a non return valve and therefore it helps to stop the return flow. And required couplings are used. The buffer tank is mounted with two way duplex ball valve for the outlet from the buffer tank.

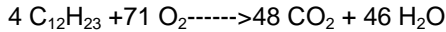
3 DESIGN CALCULATION

3.1 THEORETICAL CALCULATION

Petroleum-derived diesel is composed of about 75% saturated hydrocarbons (primarily paraffin's including n, iso, and cycloparaffins), and 25% aromatic hydrocarbons (including naphthalene's and alkyl benzenes). The chemical formula for diesel fuel ranging approximately from $C_{10}H_{20}$ to $C_{15}H_{28}$. The commonly used formula for diesel is $C_{12}H_{23}$. For any hydrocarbon fuel the combustion equation is given by,



Thus on balancing for diesel we get,



Thus theoretically 71 moles of O₂ or 2271.914g of O₂ is required for the combustion of 48 moles of CO₂ or 2112.456g of CO₂.

3.2 ACTUAL CALCULATION

For actual requirements we made the study on the Kirloskar diesel engine and the values are tabulated below:

S NO.	Applied Load (kg)	Time for 10cc of fuel consumption (sec)			Manometer reading (h) = h ₁ - h ₂ x 10 ⁻² m		
	L	t ₁	t ₂	t _{avg}	h ₁	h ₂	h
1	0	72	79	75.5	13.4	1	12.4
2	4	56	60	58	13.1	1.2	11.9
3	8	42	41	41.5	12.5	1.5	11.0
4	12	35	35	35	12.4	1.8	10.6

Table.3.2. Readings

SAMPLE CALCULATION

$$L_{max} = (BP \cdot 60000) / (N \cdot g \cdot C_b)$$

$$= (3.75 \cdot 60000) / (1500 \cdot 9.81 \cdot 0.94) = 16 \text{Kg.}$$

For 0 load:

$$A_o = ((3.14 \cdot d^2) / 4) = (3.14 \cdot .015^2) / 4$$

$$= 1.77 \times 10^{-4} \text{m}^2$$

$$\rho_a = (P / (R \cdot T_r))$$

$$= 101325 / (287 \cdot 303)$$

$$= 1.169 \text{Kg/m}^3.$$

$$h_a = (\rho_w \cdot h_w) / (\rho_a)$$

$$= (1000 \cdot 0.124) / 1.169$$

$$= 106.073 \text{m.}$$

$$V_a = \sqrt{2g \cdot h_a}$$

$$= \sqrt{2 \cdot 9.81 \cdot 106.073}$$

$$= 64.51 \text{m/s.}$$

$$Q_a = C_d \cdot a_o \cdot V_a$$

$$= 0.62 \cdot 1.77 \cdot 10^{-4} \cdot 64.51$$

$$= 6.799 \cdot 10^{-3} \text{m}^3/\text{s.}$$

$$m_a = Q_a \cdot \rho_a$$

$$= 6.799 \cdot 10^{-3} \cdot 1.169$$

$$= 7.949 \cdot 10^{-3} \text{Kg/s}$$

$$FC = ((\text{specific gravity} \cdot \text{volume of fuel}) / (1000 \cdot t_{avg}))$$

$$= (0.83 \cdot 10) / (1000 \cdot 75.5)$$

$$= 1.099 \cdot 10^{-4} \text{kg/s.}$$

S NO.	Applied load(kg)	Mass of air(g/s)	Mass of fuel(g/s)	Air fuel ratio
1	0	7.94	0.109	72.84
2	4	5.7	0.14	40.71
3	8	5.5	.2	27.5
4	12	5.4	.237	22.78

Table.5.2.2. Results

3.3 GRAPHICAL REPRESENTATION

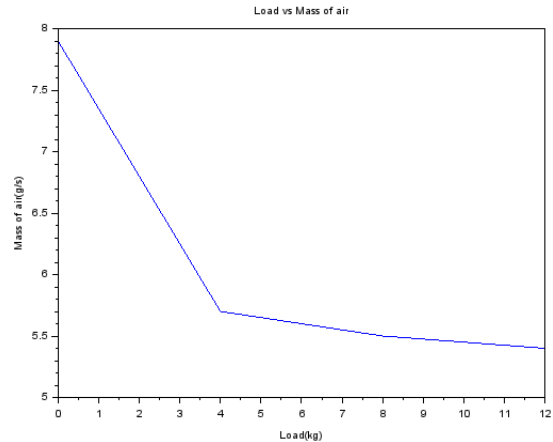


Fig.3.3.1. Graph between load and mass of air
 Fig.3.3.1. represents the graph between load and the mass of air. The load is plotted along x axis and the mass of air is plotted along y axis. Thus the graph shows that when the load increases the mass of air reduces

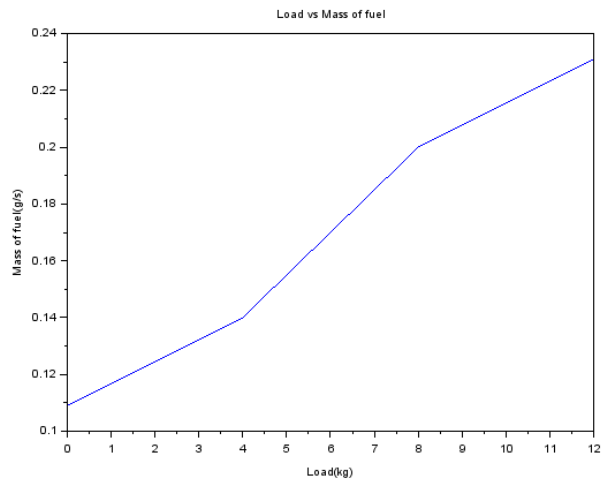


Fig.3.3.2. Graph between load and mass of fuel
 Fig.3.3.2. represents the graph between load and the mass of fuel. The load is plotted along x axis and the mass of fuel is plotted along y axis. Thus the graph shows that when the load increases the mass of fuel also increases.

Fig.3.3.3. represents the graph between load and the mass of air. The load is plotted along x axis and the mass of fuel is plotted along y axis. Thus the graph shows that when the load increases the air fuel ratio decreases and attains the optimum value for the diesel engine.

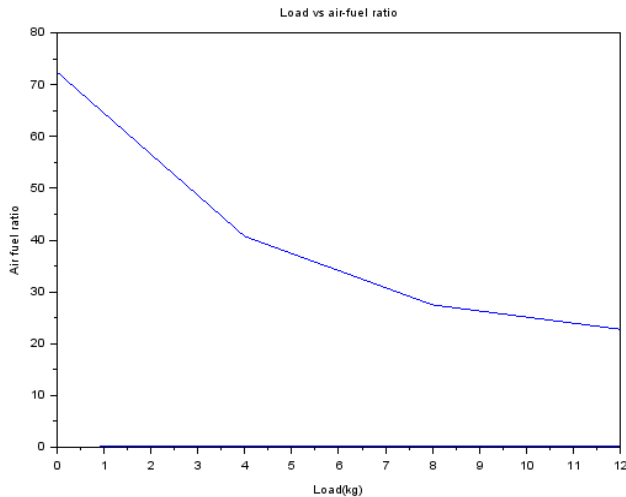


Fig.3.3.3. Graph between load and Air fuel ratio

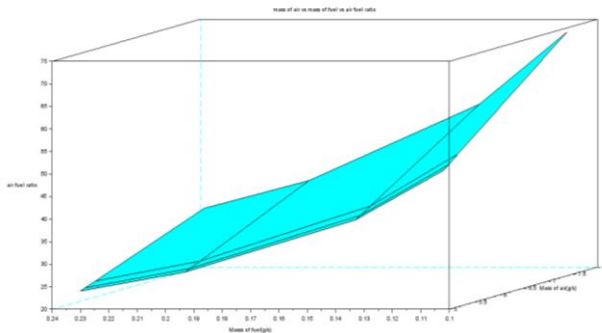


Fig.3.3.4. Graph between Mass of air, Mass of fuel and air fuel ratio.

Fig.3.3.4. represents the relationship between mass of air, fuel and air fuel ratio using 3d graph. Thus the graph clearly shows that when load increases the mass of air decreases, mass of fuel increases and air fuel ratio decreases.

3.4 DESIGN CALCULATION

According to American Standard of Mechanical Engineering, to withstand the pressure of 0-17 bar the L/D ratio should be below 6. Based on the concept of thick cylinders we designed the cylinder. Thick cylinder should have $t > D/20$.

Length=300mm, Diameter=50.8mm, Thickness=6mm L/D=5.90 and $t/D=0.119 > 1/20$. The formula for hoop stress is,

$$\sigma = \frac{Pr}{2t}$$

The hoop stress for the cylinder calculated is $2.14 \text{ N/mm}^2 < 5 \text{ N/mm}^2$.

3.5 COST ESTIMATION

Table.3.5. Cost estimation

S NO.	MATERIALS	SPECIFICATIONS	QUANTITY	PRICE (Rs.)
1	UPVC Pipe	Diameter=50.8mm Length=300mm Thickness=4mm	2	500
2	UPVC End cap	For 2" UPVC Pipe	4	160
3	Compressor delivery valve	1/4" Brass Valve	6	480
4	Frame	L Angle steel=9667.6mm 25x25 Steel plate=1000x606 & 760x150x2 Thickness=6mm	1	2400
5	Zeolite	13x	20kg	4000
6	Buffer tank	35 litres	1	2800
7	Gaskets	Brass	14	210
8	Hoses	2800mm	1	450
9	Others	Clamps, bolts, nuts, washers, etc.,	8 sets	150
Total				11,150

4 RESULTS

Thus the output, in the form of the adsorbed gas then stored from the buffer tank is analyzed with the oxygen analyzer. The input pressure is varied and the resultant oxygen volume is obtained as follows,

S NO.	PRESSURE (BAR)	OXYGEN VOLUME (%)
1	0	20.9
2	1	21.1
3	2	23.2
4	3	26.5
5	4	31.3
6	5	42.8
7	6	57.6
8	7	68.3
9	8	69.6
10	9	70.2

Table.4. Result table

The oxygen volumes increase gradually when the pressure supplied gets increased and the adsorption of nitrogen takes place effectively inside the chamber. This is because of the nature of the zeolite to adsorb at higher pressure. The adsorption is very effective till 7 bar after that the adsorption of the bed seems to be very low and gets saturated. The fig.4 represents the graphical graph between the obtained oxygen percentage to the supplied pressure

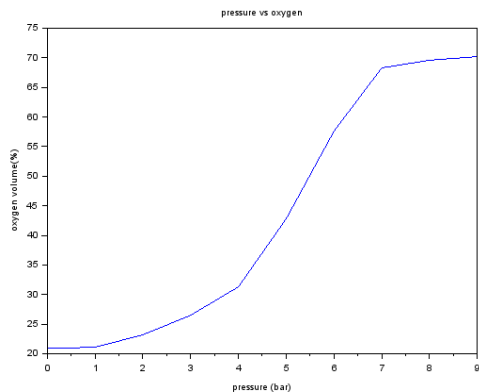


Fig.4. Graph between Pressure and Oxygen

The flow from the compressor is given to the chamber and it takes some time for the rise of the pressure. To overcome this the buffer tank is provided for the setup to have some safety for the continuous run

5 CONCLUSION

The zeolite 13x is used within the chamber to adsorb the nitrogen and this has been successfully carried out. From the experimental study we were able to obtain the following results,

- The packing material like berl saddle able to bind with the zeolite and can be used for the nitrogen adsorption.
- Zeolite with berl saddle are able to adsorb nitrogen and the oxygen content in the air can be increased upto 70% at the pressure of 9 bar.
- On the whole it can be concluded that zeolite 13X with berl saddle acts as an good adsorbent of nitrogen and the fabricated setup can has the capacity of holding the pressure requirements and supply the enriched oxygen. From the experimental we come to know that oxygen can be enriched upto 70% in the air.

Nomenclature

SYMBOLS	ABBREVIATIONS
NO _x	Nitrogen oxides
CO ₂	Carbo di oxide
O ₂	Oxygen
H ₂ O	Water
HNO ₃	Nitric acid
C ₁₂ H ₂₃	Hydrocarbon formula for Diesel
BP	Brake Power
N	Speed
B	Bore
SL	Stroke Length
C	Circumference
d	Diameter
A	Area
L	Load
t	Time

h	Height
m	Mass
Q	Volume flow rate
ρ	Density
Q	Vol. flow rate
R	Gas constant
p	Pressure
T	Temperature
V	Velocity
FC	Fuel consumption
ppm	Parts per million
°c	Degree celsius
°F	Degree fahrenheit
g	Acceleration due to gravity
SUBSCRIPT ABBREVIATIONS	
a	Air
r	Room
w	Water
avg	Average
max	Maximum
f	Fuel

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