

Separation of nitrogen from air to reduce NO_x emission from hydrogen engine

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Abstract- *The growing need to drastically reduce CO₂ emissions has led engineers and scientists to develop a clean, renewable and sustainable energy system. Hydrogen as a green fuel is a good choice since it does not emit any particulate like CO and CO₂, but it gives out NO_x emissions at exhaust of the engine. So to make eco-friendly or emission less engine which runs on hydrogen gas as a fuel, the nitrogen free air is to be supplied to carburettor inlet of hydrogen engine, which eliminates the NO_x emission at exhaust for reduction of the air pollution. Nitrogen separation from air would be done with the help of pressure swing adsorption method. In this method continuous separation of a nitrogen gas from atmospheric compressed air would be done by using zeolite 13X having maximum nitrogen adsorption capacity with low cost. Hence it is used as nitrogen adsorbent in a fixed bed column to supply nitrogen free air to carburettor inlet. The abstract idea of this paper is to eliminate NO_x emission and provide emission less hydrogen engine.*

Keywords- Zeolite, Pressureswing adsorption, Air separation, NO_x elimination etc.

I. INTRODUCTION

In recent years, many researchers have focused on the study of alternative fuels which benefit enhancing the engine economic and emissions characteristics. Among all fuels, hydrogen has been demonstrated to be the most promising green alternative fuel that can be used on SI engines. Besides, compared with traditional fossil fuels, hydrogen is a carbon less fuel whose combustion does not generate emissions such as HC, CO and CO₂. Thus, the application of hydrogen engines would alleviate concerns about toxic and green-house emissions from IC engines. This paper is related to the development of a new engine setup using pure hydrogen as fuel. Thus to develop the eco-friendly engine we need to separate nitrogen from air at carburetor inlet. Thus we have to specially design an air separator which separates Nitrogen gas from air. The main aim of this project is to develop the eco-friendly engine i.e. an engine which consumes hydrogen and air and emits minimum NO_x as an exhaust^[1]

The hydrogen engine can utilize hydrogen produced from any source, and since its fuel does not include a carbon

component, it is consequently one of the next generation engine systems that can simultaneously solve both the CO₂ and fossil fuel energy depletion problems. Among the hydrogen engines being developed, the hydrogen engine with an external fuel mixture is more efficient and durable than the direct injection type, and is considered capable of commercialization in a short period of time with low cost^[2]

The high adiabatic flame temperature of hydrogen resulting in the increased NO_x emissions can be thought as another barrier for the wide application of pure hydrogen engines. At present, the high costs of hydrogen production and the lack of hydrogen fuelling infrastructure also block the commercialization of hydrogen engines in the near future. Many studies of renewable energy have shown hydrogen is one of the major green energy in the future. This has led to the development of many automotive application of using hydrogen as a fuel especially in internal combustion engine. Global energy demand will continue to increase in the next decade as the world has been reeling from financial crisis and economic recession. Almost 80% of world energy is produced through the combustion of fossil fuels, including coal, natural gas, and oil, which have also been the primary source of the air pollutions and carbon emissions; the latter are believed to be the most important cause for the climate change. Society has been challenged to balance conflicting energy and environmental demands by decarbonizing our energy chain and finding a clean and viable source of fuel. In the past decade, the development of alternative fuels has drawn a significant attention from both governments and industries.^[3]

Amongst all the alternative fuels, hydrogen has long been considered one of the most promising candidates due to its high energy density (per mass) and lack of carbon emissions. Researchers have already demonstrated the feasibility of hydrogen and its applications in internal combustion engines to power vehicles as diverse as cars, aircraft, and rockets. However, several challenges including high fuel production cost, fuel transportation and storage, and safety issues have prevented hydrogen from widespread use especially in the transportation sector. Much research has been devoted to tackle these challenges in order to develop new technologies that can efficiently exploit the potential of hydrogen energy and economy.^[4]

In this experiment, a zeolite 13X is used to adsorb nitrogen from air with the help of pressure swing adsorption method. This nitrogen free air or oxygen enriched air is supplied at carburetor inlet of hydrogen engine. This results in reduction of NO_x emission from hydrogen engine.

II. LITERATURE REVIEW

Anson et al., studied the adsorption of argon, oxygen, and nitrogen were studied on silver exchanged titano silicate molecular sieve ETS-10 and the silver exchanged alumina silicate molecular sieve mordenite by inverse gas chromatography and volumetric adsorption isotherm measurements. Silver exchanged zeolites, especially silver-mordenite, have been noted to demonstrate some degree of selectivity for argon/oxygen. AgETS-10 is found to have a selectivity of 1.49 for argon over oxygen. From chromatographic, volumetric and gravimetric isotherm measurements, both Ag-ETS-10 and Ag-mordenite demonstrate adsorptive selectivity for argon over oxygen at 30 °C over a wide range of pressures. Both adsorbents demonstrate somewhat higher capacity for oxygen than for argon at atmospheric pressure (1.2–1.3 times).^[1]

Lee et al., this study investigated the applications of intake and exhaust valve timing variation and lean boosting to a hydrogen engine with SI and external mixture to identify the possibility of achieving high power, high efficiency and super low NO_x emission without backfire generation. The following conclusions were reached. The backfire that inevitably occurs by increasing the power of a hydrogen engine to the level of a gasoline engine could be controlled by the retardation of IVO, and the method above was confirmed to be effective along with the application of lean boosting. In addition, it was identified that EVC is not significantly effective in backfire control. The maximum temperature reduction rate of hydrogen from lean boosting is greater than those of other fuels due to the high specific heat of hydrogen at constant volume. However, hydrogen has a high lean limit which is capable of stable combustion, up to the super lean region around $\phi = 0.2$, in which the temperature could be reduced to below NO_x generation temperature. Almost pollution-free NO_x emission was achieved, even when operating at gasoline-level high power, with low temperature combustion supercharging super lean mixture.^[2]

Benjamin J. et al., studied and concluded the present work deals with the simulation of nitrogen production from air using a membrane module set with carbon molecular sieve membranes (CMSM). The diffusivities of N₂, O₂, CO₂ and water vapour on a CMSM made out of cellophane (Celo550) obtained via gravimetric and permeation experiments were

compared. The values of diffusivity found from the two methods were equal for nitrogen, but different for oxygen and carbon dioxide. This could be an indication that the dead-end pores existing in the membrane are not accessible to nitrogen, due to its larger kinetic diameter, but are accessed by oxygen and carbon dioxide. Assuming pressure-independent permeability in the simulations led to lower recoveries than considering pressure-dependent permeability, for the same purity. The use of a pressure independent permeability approach would therefore lead to an erroneous dimensioning of the membrane module. It was also concluded that higher feed to permeate pressure ratios, generally, favour the separation of nitrogen, allowing higher recoveries or smaller contact times for a given purity. In addition, an increase of feed pressure also improves the recovery of the process, but compromises the purity, for the same feed to permeate pressure ratio. It was also observed that increasing the pressure drop significantly impairs the separation. For this reason, pressure drop should be taken into account when designing the module or preparing the fibers. The work is that carbon molecular sieve membranes, prepared from pyrolysis of cellophane up to 550 °C, allow high purity nitrogen production from air with large recoveries (up to 65% for a purity of 99.9% and negligible pressure drop) and using an air feed with 100% RH.^[3]

Ingenito et. al., studied the goal of this paper was to identify key parameters for the NO_x reduction in order to define a technology for these pollutants abatement, keeping the engine performance. The strategy proposed is the Rich-Quick-Lean engine, whose characteristics, based on the NO_x behaviour at the different equivalence ratios, permit to reduce the nitrogen oxides formation. This combustor is namely divided into two stages, a rich and lean stage. The analysis of the effect of the residence time within each stage of the combustor has shown that the RQL strategy makes the combustor NO_x production independent on the overall residence time. The equivalence ratio in the rich stage has been shown to be a key parameter, affecting the quality of the mixing between the first stage exhausts and the secondary air and also producing a dramatic reduction of the NO_x formation. In fact, for the nominal SCIMITAR E.R. $\phi = 0.8$ it is possible to lower the NO_x EI from 576 g NO_x/kg fuel to 60 NO_x/kg fuel by assuming an E.R. higher than 10 in the rich stage. A fit of NO_x EI vs. the “rich stage” E.R. has located at 35.65 the equivalence ratio in the rich stage that will ensure an acceptable E.I. of 20.^[4]

Kacem et al., studied the purpose of this work was to evaluate the performance of activated carbons and zeolites adsorbents in terms of adsorption capacity, performance gas separation and material aging under PSA processes. The

adsorbents evaluated in this study showed adsorption capacities equivalent to those materials after literature. In particular, activated carbon-SC exhibits adsorption capacities at high pressure (8 bars) slightly better than those in the literature. Activated carbons generally have maximum adsorption capacities at high pressures (10–20 bars). Zeolites were efficient adsorbents at small pressure when the BET surface was totally using.^[5]

Chintala et al., studied the H₂ energy share improvement along with the NO_x emission reduction from a H₂ dual-fuel engine was studied using timed manifold water injection method. The following conclusions are drawn based on the experimental results; with base H₂ dual-fuel operation, the knock limited H₂ energy share was 20% without water injection at rated load and speed. The energy share increased to 32%, 36%, and 39% with SWC of 130, 200, and 270 g/kWh respectively for the same engine operating conditions. Degree of superheat of the water could be the major heat absorption source i.e., 63% of the total heat absorbed by the water among three kinds of heat energy. The SWC of 200 g/kWh with 36% H₂ energy share was selected as an optimum water quantity based on rate of pressure rise, COV in IMEP, better performance and lower emissions. Energy efficiency decreased slightly with water addition at rated load and speed, but it is still higher than the conventional CI engine. With water addition into the H₂ dual-fuel engine the in-cylinder peak pressure, peak temperature, and heat release rate decreased while ignition delay and combustion duration increased. A maximum of 37% reduction in NO_x emission could achieve with 270 g/kWh water addition with the penalty of a slight increase in carbon based emissions including HC, CO, and smoke. However, these HC and CO emissions could easily be decreased with the utilization of oxidation catalysts in the tail pipe. A study on the effect of water added H₂ dual-fuel engine with the use of after treatment device on performance and emission characteristics of the engine needs to be carried out in future for a complete solution.^[6]

Normann et al., studied the present study has demonstrated several methods to reduce NO_x emission in the oxy-fuel process. However, an economical evaluation or a system study to find out the optimum organization of NO_x capture still remains to be done. The survey has led to the conclusion that more knowledge is required in three key areas to optimize NO_x control in future oxy-fuel power plants.^[7]

Pengcheng et al., studied the cryogenic distillation, with high investment costs, is a well-developed and established technique for large-scale production (typically larger than 10 MMscfd of gas) of pure oxygen. Zeolite membranes were for the first time evaluated for separation at

cryogenic temperatures, for air separation. At each feed pressure, the membranes were quite oxygen selective in a narrow temperature range. For the first time, ultra-thin MFI membranes were evaluated at cryogenic temperature for air separation at low feed pressure down to 100mbar. The membranes were found to be oxygen selective at all the conditions studied. The observed O₂/N₂ selectivity and oxygen permeance were well above the upper bound in the 2008 Robeson selectivity–permeability plot. The permeance was nearly 100 times higher than that recently reported for promising polymeric membranes. The selectivity to O₂ should primarily emanate from O₂/N₂ adsorption selectivity. In addition, with decreasing feed pressure and temperature, the O₂/N₂ membrane selectivity was found to increase, which can most likely be attributed to greater O₂/N₂ adsorption selectivity at lower temperatures. The present work has therefore indicated the optimum conditions for air separation using MFI membranes, namely low feed pressures and low temperatures.^[8]

Ribeiro et al., studied the possibility of using a pressure swing adsorption process for the separation of a nitrogen and propylene mixture with the metal organic framework MIL-100(Fe) was assessed. The adsorption equilibrium measurements revealed that this material has a propylene/nitrogen selectivity of 40 for a 0.3/0.7 mixture at 2.5 bar and 70 °C and a propylene working capacity of 1.8 mol/kg between 0.75 and 0.1 bar at 70 °C. For the nitrogen recovery process nitrogen purity and recovery of respectively 99.9% and 81.5% were obtained. For the nitrogen and propylene recovery, a more demanding regeneration must be used. The products purities obtained were respectively 99.9% for nitrogen and 97.9% for propylene. The nitrogen recovery was 97.4%. The total power consumption was 36.6 W, a value that is lower than the ones reported previously in the literature for other technologies.^[9]

Tirzha et al., studied the reduction of carbon dioxide emissions from flue gases can be achieved using post-combustion capture technologies such as adsorption. In this paper, were port the continuous separation of a 15% mol/mol carbon dioxide–nitrogen mixture through the pressure swing adsorption (PSA) process. In this study, carbon dioxide–nitrogen separation applying the PSA process was investigated. Zeolite13X has high selectivity for CO₂ and is suitable for application in the CO₂/N₂ separation process. A model based on the LDF for the mass transfer, considering the thermal effects, was able to describe the process. An increase in the inlet temperature of the mixture CO₂/N₂ increases the CO₂ purity due to the greater difference between the capacities for the adsorption of N₂ and CO₂.^[10]

III. EXPERIMENTATION

A) Pressure Swing Adsorption Method

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 an affinity for an adsorbent material. It operates 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 trap, preferentially adsorbing the target gas species at high pressure. The process then swings to low pressure to desorb the adsorbed material.^[6]

B) Experimental Set Up

As shown in Fig. 1, the experimental system used in this research includes air compressor, silica gel column, two adsorption columns contain zeolite 13X, non-return flow valve, storage tank. 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. In this experiment air is passed under pressure through a vessel containing an adsorbent bed of zeolite 13X 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 absorb 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. In this experiment silica gel column is used to remove impurities and water vapour from compressed air. Using two adsorption columns allows near-continuous production of the target gas. It also permits so called pressure equalisation, where the gas leaving the vessel being depressurised is used to partially pressurise the second vessel. This results in significant energy savings.^[12]

C) Zeolites

Zeolite molecular sieves are crystalline, highly porous materials, which belong to the class of alumina silicates. These crystals are characterised by a three-dimensional pore system, with pores of precisely defined diameter. The corresponding crystallographic structure is formed by tetrahedrons of (AlO₄) and (SiO₄). These tetrahedrons are the basic building blocks for various zeolite

structures, such as zeolites A and X, the most common commercial adsorbents. Due to the presence of alumina, zeolites exhibit a negatively charged framework, which is counter-balanced by positive cations resulting in a strong electrostatic field on the internal surface. These cations can be exchanged to fine-tune the pore size or the adsorption characteristics. For instance, the sodium form of zeolite A has a pore opening of approximately 4 Ångstrom (4 x 10⁻¹⁰ m), called 4A molecular sieve. If the sodium ion is exchanged with the larger potassium ion, the pore opening is reduced to approximately 3 Ångstrom (3A molecular sieve). Ion exchange with calcium, one calcium ion replaces two sodium ions. Thus, the pore opening increases to approximately 5 Ångstrom (5A molecular sieve). Ion exchange with other cations is sometimes used for particular separation purposes. The pore opening of the sodium form of zeolite X (13X) is approximately 8 Ångstrom. Zeolite 13X, has the chemical formula Na₈₆[(AlO₂)₈₆ (SiO₂)₁₀₆]• H₂O. Zeolite is very efficient for two reasons.

Physical adsorption

When nitrogen is in close proximity to the exposed cations of the zeolite crystal, a charge induced dipole forms and the nitrogen is attracted into the zeolite crystal. Nitrogen is more polarisable than oxygen and the zeolite selectively adsorbs nitrogen allowing the oxygen gas to pass unrestricted. The internal surface area of zeolite is extremely large and so provides a high degree of adsorption per volume of zeolite.

Steric hindrance

The cage like structures of zeolite have been carefully designed to allow only nitrogen to pass to their inside and to exclude the larger oxygen molecules. That is, the holes in the side of the zeolite dice are large enough to allow nitrogen entry but small enough to exclude oxygen. The uniformity of the micro pores has been the major advantage of synthetically produced zeolites.^[16]

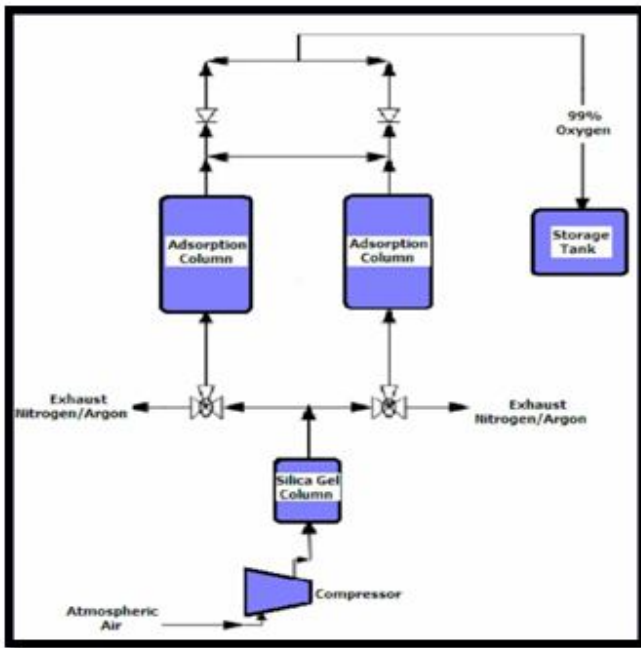


Fig. No.1 Pressure swing adsorption process (PSA)

d) Stages of pressure swing adsorption process (PSA)

Stage1- In the first stage of pressure swing adsorption process, air is compressed with the help of air compressor then this compressed air passed through silica gel column where moisture content present in air and impurities are adsorbed. Then compressed air is fed into the first adsorption column that is zeolite 13X bed. In this adsorption column, nitrogen molecules are trapped, while oxygen enriched air is allowed to flow through the adsorption column.^[6]

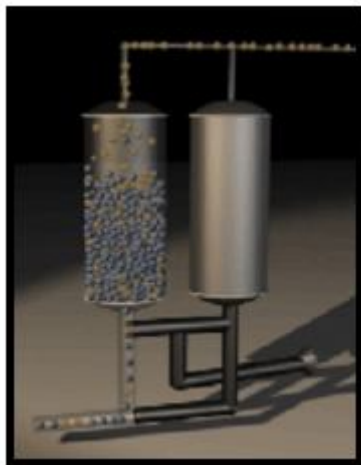


Fig. No.2 First stage of PSA process

Stage2- In the second stage of pressure swing adsorption process, the adsorbent in the first bed saturated with nitrogen molecules, and then airflow feed is directed into the second bed.^[6]

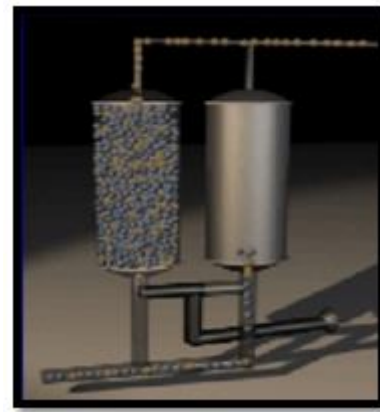


Fig. No.3 Second stage of PSA process

Stage3- In the third stage of pressure swing adsorption process, 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.^[6]

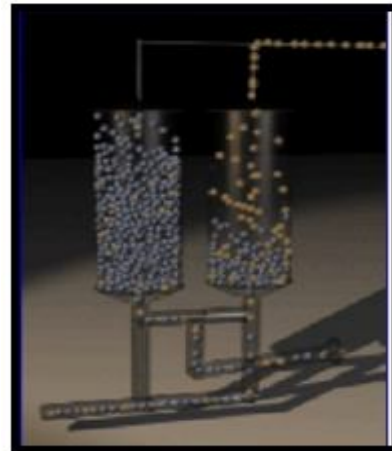


Fig. No.4 Third stage of PSA process

Stage4- In the fourth stage of pressure swing adsorption process, the process starts over. Compressed air is once again fed into the first bed. The second bed is depressurized releasing nitrogen molecules to the atmosphere.^[6]

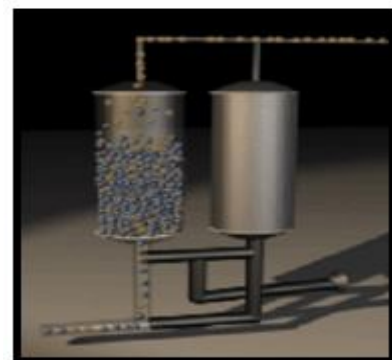


Fig. No.5 Fourth stage of PSA process

IV.CONCLUSION

The purpose of this work was to separate the nitrogen from air to reduced NOx emission from hydrogen engine. The pressure swing adsorption method is used to remove nitrogen. By using zeolite 13X nitrogen is adsorbed from air and oxygen enriched air is passed to the carburetor inlet of hydrogen engine and NOx emission are reduced.

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