

# A review of air separation technologies and their integration with energy conversion processes

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## Abstract

Cryogenic air separation technology has been successfully employed for many years to supply oxygen for the gasification of a wide range of hydrocarbon feedstocks to generate synthesis gas for the production of fuels, chemicals and other valuable products. Examples include the conversion of liquid and solid refinery waste streams into hydrogen for use within the refinery along with the coproduction of electricity, and the growing interest in gas-to-liquids (GTL) processes which convert natural gas into synthetic crude oil, waxes and fuels. Recently, increased attention has been focused on methods of integrating the oxygen production process with the downstream hydrocarbon processing units to reduce facility cost or increase efficiency. A review of traditional and developing processes to generate oxygen is presented, along with integration schemes to improve the economics of these facilities. © 2001 Published by Elsevier Science B.V.

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## 1. Introduction

Two questions frequently asked by industrial gas (oxygen, nitrogen, argon) consumers are:

- which technology is optimum for a specific rate, purity, pressure and use pattern?
- what are the integration opportunities between the air separation unit and other processes?

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This paper describes the processes for separating industrial gases from air and notes economic or other limits for each process. Integration opportunities for cryogenic and non-cryogenic industrial gas processes are presented for facilities incorporating gas turbines or having large amounts of excess heat or energy available as a byproduct. The processes associated with these characteristics are generally the oxygen-blown, partial oxidation, Fischer–Tropsch (F–T) plants producing chemicals, fuels, power, synthesis gas (syngas) or synthetic crude oil products. A brief review of integration solutions for cryogenic industrial gas plants and integrated gasification combined cycle (IGCC) power production facilities is presented as background information. A few conceptual integration opportunities for cryogenic and non-cryogenic industrial gas plants and energy conversion processes are described.

## 2. Non-cryogenic industrial gas processes

### 2.1. Adsorption

Adsorption processes are based on the ability of some natural and synthetic materials to preferentially adsorb nitrogen. In the case of zeolites, non-uniform electric fields exist in the void spaces of the material, causing preferential adsorption of molecules, which are more polarizable as those that have greater electrostatic quadrupolar moments. Thus, in air separation, nitrogen molecules are more strongly adsorbed than oxygen or argon molecules. As air is passed through a bed of zeolitic material, nitrogen is retained and an oxygen-rich stream exits the bed. Carbon molecular sieves have pore sizes on the same order of magnitude as the size of air molecules. Since oxygen molecules are slightly smaller than nitrogen molecules, they diffuse more quickly into the cavities of the adsorbent. Thus, carbon molecular sieves are selective for oxygen and zeolites are selective for nitrogen.

Zeolites are typically used in adsorption-based processes for oxygen production. A typical flowsheet is shown in Fig. 1. Pressurized air enters a vessel containing the adsorbent. Nitrogen is adsorbed and an oxygen-rich effluent stream is produced until the bed has been saturated with nitrogen. At this point, the feed air is switched to a fresh vessel and regeneration of the first bed can begin. Regeneration can be accomplished by heating the bed or by reducing the pressure in the bed, which reduces the equilibrium nitrogen holding capacity of the adsorbent. Heat addition is commonly referred to as temperature swing adsorption (TSA), and pressure reduction as pressure or vacuum swing adsorption (PSA or VSA). The faster cycle time and simplified operation associated with pressure reduction usually makes it the process of choice for air separation.

Variations in the process that effect operating efficiency include separate pretreatment of the air to remove water and carbon dioxide, multiple beds to permit pressure energy recovery during bed switching, and vacuum operation during depressurization. Optimization of the system is based on product flow, purity and pressure, energy cost and expected operating life. Oxygen purity is typically 93–95 vol.%. Due to the cyclic nature of the adsorption process, bed size is the controlling factor in capital cost. Since

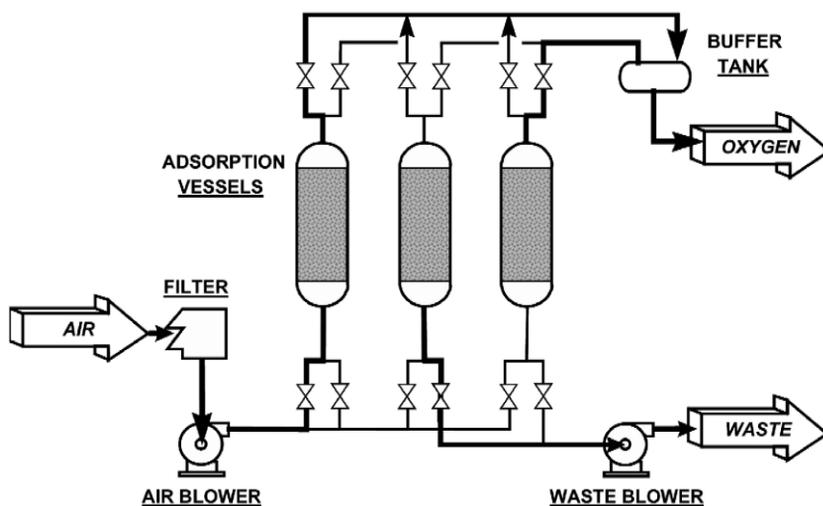


Fig. 1. Adsorption-based air separation process.

production is proportional to bed volume, capital costs increase more rapidly as a function of production rate compared to cryogenic plants.

## 2.2. Chemical processes

A number of materials have the ability to absorb oxygen at one set of pressure and temperature conditions, and desorb the oxygen at a different set of conditions. One such process that Air Products and Chemicals (Allentown, PA) investigated in the early 1990s was MOLTOX™, a molten salt chemical process depicted in Fig. 2. The process variation shown is based on absorption of oxygen by a circulating molten salt stream,

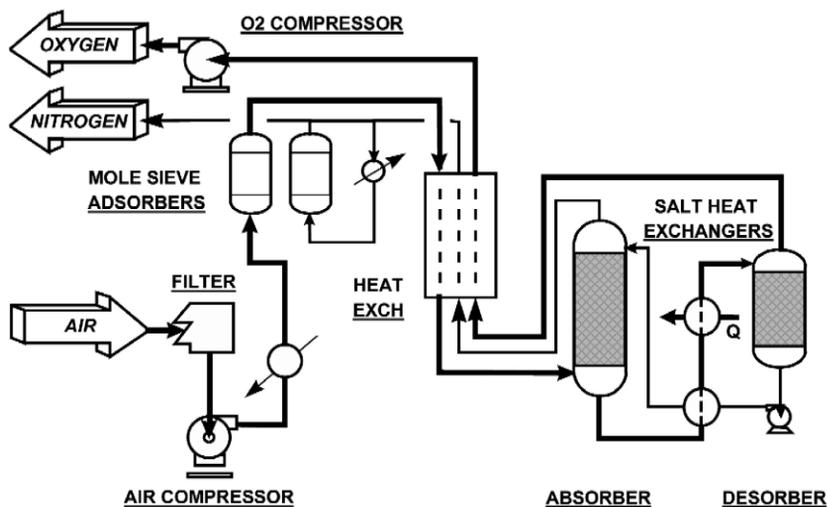


Fig. 2. Chemical air separation process.

followed by desorption through a combination of heat and pressure reduction of the salt stream. Air is compressed from 20 to 185 psia and treated to remove water and carbon dioxide in an adsorbent-based system. Water and carbon dioxide would both degrade the salt if not removed at this stage. Air flows through an adsorbent bed until bed saturation is reached. The beds are switched and the saturated bed is regenerated by dry nitrogen from the process. The clean, dry air is heated against returning product streams to between 900°F and 1200°F in the main heat exchangers. The hot air flows to the bottom of the absorber where it contacts molten liquid salt. The oxygen in the air reacts chemically with the salt and is removed with the liquid salt leaving the bottom of the absorber. The oxygen-bearing salt is heat interchanged with oxygen-free salt and further heated before being reduced in pressure and flowing to the desorber. Gaseous oxygen leaves the top of the desorber, while oxygen-lean salt is removed from the bottom of the desorber, heat interchanged and sent to the top of the absorber vessel to close the loop.

The hot oxygen and hot nitrogen streams enter the main heat exchanger and are cooled against feed air. The oxygen is compressed to delivery pressure, while a portion of the nitrogen is used to regenerate the air pretreatment system. The major process advantage of the TSA-based system is that air has only to be compressed to a pressure that overcomes pressure drop through the air pretreatment and heat exchanger, thus reducing the amount of air compression power compared to a cryogenic plant. A source of thermal energy must be available to liberate the salt via heating. Air Products and Chemicals operated a small-scale pilot unit that verified process conditions (99.9% oxygen purity at expected salt loading), however, corrosion of the salt/oxygen two-phase areas of the facility was determined to be an economic problem.

### *2.3. Polymeric membranes*

Membrane processes using polymeric materials are based on the difference in rates of diffusion of oxygen and nitrogen through a membrane which separates high-pressure and low-pressure process streams. Flux and selectivity are the two properties that determine the economics of membrane systems, and both are functions of the specific membrane material. Flux determines the membrane surface area, and is a function of the pressure difference divided by the membrane thickness. A constant of proportionality that varies with the type of membrane is called the permeability. Selectivity is the ratio of the permeabilities of the gases to be separated. Due to the smaller size of the oxygen molecule, most membrane materials are more permeable to oxygen than to nitrogen. Membrane systems are usually limited to the production of oxygen enriched air (25–50% oxygen). Active or facilitated transport membranes, which incorporate an oxygen-complexing agent to increase oxygen selectivity, are a potential means to increase the oxygen purity from membrane systems, assuming oxygen compatible membrane materials are also available.

A typical membrane system is shown in Fig. 3. A major benefit of membrane separation is the simple, continuous nature of the process and operation at near ambient conditions. An air blower supplies enough head pressure to overcome pressure drop through the filters, membrane tubes and piping. Membrane materials are usually assembled into cylindrical modules that are manifolded together to provide the required

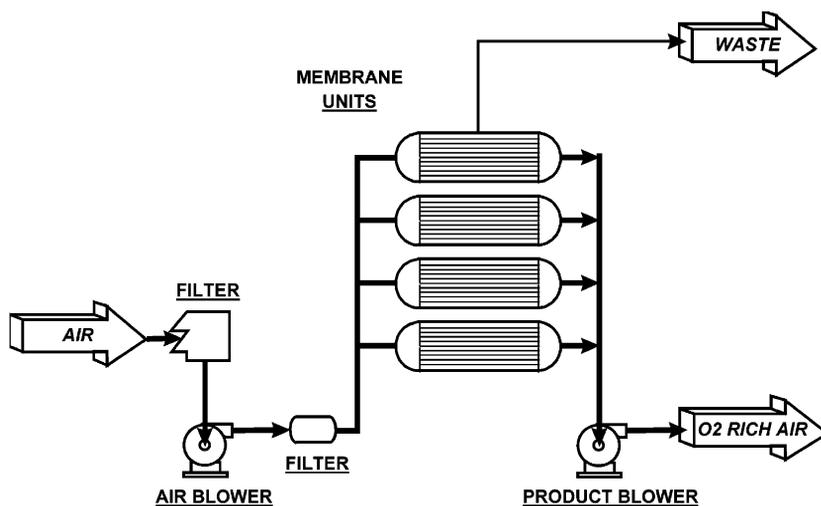


Fig. 3. Polymeric membrane air separation process.

production capacity. Oxygen permeates through a fiber (hollow fiber type) or through sheets (spiral wound type) and is withdrawn as product. A vacuum pump typically maintains the pressure difference across the membrane and delivers oxygen at the required pressure. Carbon dioxide and water usually appear in the oxygen enriched air product, since they are more permeable than oxygen for most membrane materials.

As with adsorption systems, capital is essentially a linear function of production rate and product backup is typically not available without a separate liquid oxygen storage tank and delivery support system. Membrane systems readily fit applications up to 20 tons/day, where air enrichment purities with water and carbon dioxide contaminants can be tolerated. This technology is newer than adsorption or cryogenics and improvements in materials could make membranes attractive for somewhat larger oxygen requirements. The fast start-up time, due to the near ambient operation, is especially attractive for oxygen-use systems than exhibit discontinuous usage patterns. The passive nature of the process is also appealing.

#### 2.4. Ion transport membrane (ITM)

ITMs are solid inorganic oxide ceramic materials that produce oxygen by the passage of oxygen ions through the ceramic crystal structure. These systems operate at high temperatures, generally over 1100°F. Oxygen molecules are converted to oxygen ions at the surface of the membrane and transported through the membrane by an applied electric voltage or oxygen partial pressure difference, then reform oxygen molecules after passing through the membrane material. Membrane materials can be fabricated into flat sheets or tubes.

For large energy conversion processes the pressure difference transport driving force is the method of choice. Membranes, which operate by a pressure difference, are

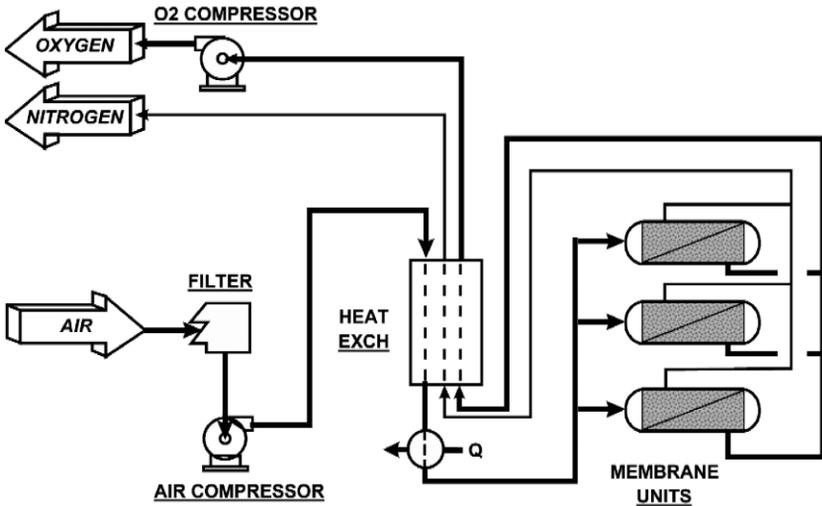


Fig. 4. Ion transport membrane air separation process.

referred to as mixed conducting membranes since they conduct both oxygen ions and electrons. The oxygen ions travel through the ITM at very high flow rates and produce nearly pure oxygen on the permeate side of the membrane. The oxygen can be separated as a pure product, or another gas can be used to sweep on the permeate side of the membrane to produce a lower purity product. If a reactive sweep gas is used, an oxidative product can be produced directly, e.g. natural gas methane sweep to make synthesis gas for gas-to-liquid (GTL) conversion.

A simple schematic of an ITM oxygen separation process is depicted in Fig. 4. Air is compressed and then heated to operating temperature by exchange against the hot process streams (non-permeate and oxygen product) and then auxiliary heat addition. In general, the heating of air can be done by either indirect heat exchange and/or direct firing of fuel. The oxygen stream is compressed to delivery pressure for use in IGCC or other applications. The pressurized nitrogen enriched non-permeate stream is used elsewhere in balance of the energy conversion process, for instance, expanded in an integrated gas turbine cycle to generate electric power.

The ITM oxygen process is suited to integration with power generation and energy conversion processes that require oxygen as a feedstock for combustion or gasification, or in any oxygen-based application with a need for power or an export power market.

### 3. Cryogenic industrial gas processes

#### 3.1. Overview of cryogenic processing

Cryogenic air separation is currently the most efficient and cost-effective technology for producing large quantities of oxygen, nitrogen, and argon as gaseous or liquid

products. An air separation unit (ASU) using a conventional, multi-column cryogenic distillation process produces oxygen from compressed air at high recoveries and purities. Cryogenic technology can also produce high-purity nitrogen as a useful byproduct stream at relatively low incremental cost. In addition, liquid argon, liquid oxygen, and liquid nitrogen can be added to the product slate for stored product backup or byproduct sales at low incremental capital and power costs.

Increasing the production rate from a single equipment train continues to be examined as a method of reducing unit costs through economies of scale. Fig. 5 demonstrates Air Products' experience in oxygen production from a single-train cryogenic ASU over recent years. Most of the facilities shown in Fig. 5 use traditional electric motor-driven equipment to compress the air feed to the ASU, as well as the oxygen and other product streams. Notably, the Buggenum (Demkolec) IGCC facility receives all of its air feed by air extraction from the gas turbine used in combined cycle generation of power from coal-derived synthesis gas. Market-driven requirements will extend single train size to 5000 short ton per day (sTPD) in the near future.

Fig. 6 illustrates the five major unit operations required to cryogenically separate air into useful products. An air pretreatment section downstream of the air compression and aftercooling removes process contaminants, including water, carbon dioxide, and hydrocarbons. The air is then cooled to cryogenic temperatures and distilled into oxygen, nitrogen, and, optionally, argon streams. Warming these product streams against the incoming air feed conserves refrigeration, with any deficit made up by expanding a small portion of pressurized air or nitrogen. Numerous configurations of heat exchange and distillation equipment can separate air into the required product streams. These process alternatives are selected based on the purity and number of product streams required; trade-offs between capital costs and power consumption; and the degree of integration between the ASU and other facility units. Characterization of the types of cryogenic processes used for air separation, hereinafter referred to as cycles, can be

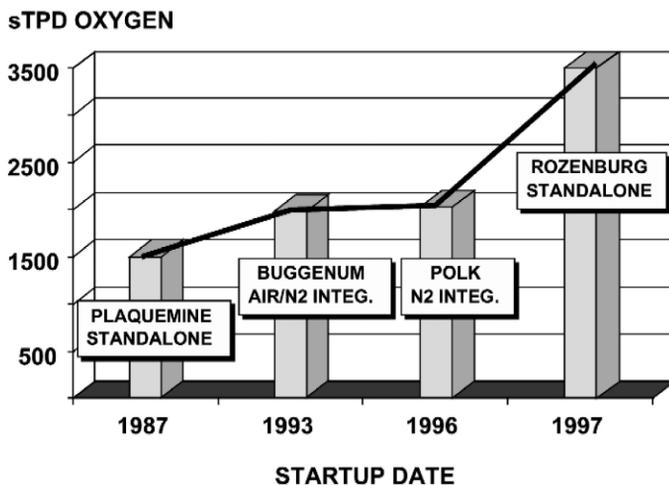


Fig. 5. The growth of single-train oxygen plant size.

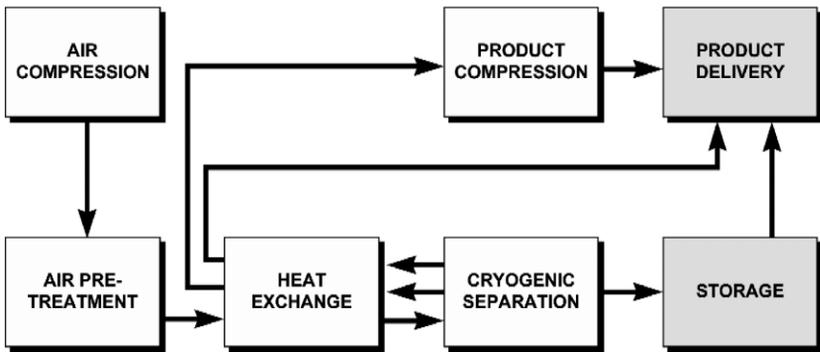


Fig. 6. Unit operations for a cryogenic air separation process.

based on the method of pressurizing the product stream(s) or on the air feed pressure to the ASU.

### 3.2. Compression cycles

Air separation processes typically produce gaseous product streams at slightly above atmospheric pressure and near ambient temperature. Typically the product oxygen leaves the main heat exchangers at low pressure, ranging from 0.5 to 10 psig, and a centrifugal compressor train with relatively high inlet volumetric flow rate delivers the product at the required pressure. Many hundreds of these plants operate worldwide.

### 3.3. Pumped liquid cycles

Liquid products can be pumped from the distillation section upstream of the cryogenic heat exchangers for vaporization and warming. These products may be pumped to the required delivery pressure or to an intermediate pressure. However, since producing a liquid product from the distillation system requires two to three times the power of producing a gaseous product, the cycle must efficiently recover the refrigeration contained in the pumped product stream. This is accomplished by condensing an air or nitrogen feed stream at high pressure against the vaporizing product stream in the cryogenic heat exchangers. The liquefied air or nitrogen feed returns the refrigeration to the distillation section.

Pumped liquid process cycles in which the product stream is pumped to an intermediate pressure at the ASU outlet are called partial pumped liquid cycles and require additional equipment to compress the product streams to the final delivery pressure. Full or partial pumping of product streams adds another degree of freedom in optimizing the cryogenic cycle, and can eliminate or reduce the size of oxygen compressors.

### 3.4. Low and elevated pressure cycles

Low-pressure (LP) ASU cycles are based on compressing the feed air only to the pressure required to reject the nitrogen byproduct at atmospheric pressure. As such, feed

air pressures will typically vary between 65 and 100 psia, depending on the oxygen purity and the level of energy efficiency desired. Elevated-pressure (EP) ASU cycles produce product and byproduct streams at well above atmospheric pressures and generally require smaller and more compact cryogenic components that can be cost effective. EP cycles typically use feed air pressures in excess of 100 psia. An EP cycle may be appropriate when all or nearly all of the nitrogen byproduct will be compressed as a product stream. In addition, an EP cycle is often selected for integration of the ASU with other process units such as gas turbines.

#### 4. Comparisons of process alternatives

Adsorption and polymeric membrane processes will continue to improve in both cost and energy efficiency through ongoing research and development of adsorbents and membrane materials. Neither technology is expected to challenge cryogenics for large tonnage production of oxygen, especially at high purities. Both adsorption and membrane systems produce byproduct nitrogen containing significant amounts of oxygen. If high purity nitrogen is required, an add-on deoxo or other purification system must be employed to upgrade the quality of the nitrogen. Neither process has the ability to directly produce argon or rare gases. Production of liquid oxygen or nitrogen for system back-up requires an add-on cryogenic unit or delivery of product from a merchant facility. On the other hand, adsorption and membrane processes are less complex and more passive than cryogenic technology.

Chemical processes offer the potential for continuous operation and economies of scale through large production output from single trains, but to date have not been able to overcome material corrosion problems. ITM technology is currently foreseen as the best candidate to challenge cryogenics for the production of high purity, tonnage quantities of oxygen. As with the other non-cryogenic processes, ITM has limitations in regard to production of pure byproducts and liquids for storage and backup. ITM is also at an embryonic state of development, so the potential for improvement is large.

Table 1 compares the merits of the various technologies based on the following categories. **Status** is the degree to which the technology has been commercialized, varying from mature for cryogenics through developing for ITM. **Economic Range** is the typical production range where the technology is currently economically feasible.

Table 1  
Technology comparison table

Process	Status	Economic range (STPD)	Byproduct capability	Purity limit (vol.%)	Start-up time
Adsorption	semi-mature	< 150	poor	95	minutes
Chemical	developing	undetermined	poor	99+	hours
Cryogenic	mature	> 20	excellent	99+	hours
Membrane	semi-mature	< 20	poor	~ 40	minutes
ITM	developing	undetermined	poor	99+	hours

The less efficient, but less complex adsorption and polymeric membrane systems are favored at the lower production rates. **Byproduct Capability** is a measure of the ability of the process to produce relatively pure nitrogen or argon streams without add-on deoxo or cryogenic systems. **Purity Limit** is the maximum purity that can be economically produced using the specific technology. All the technologies are capable of producing lower purities than the maximum by adjusting process conditions or by blending purer oxygen product with air. **Start-up Time** is a measure of the time required to restart the process and reach purity after a shutdown.

## 5. Proven integration concepts

Air extracted from a gas turbine's compressor can partially or fully supply the feed requirements of an ASU. In a simple configuration, the ASU distillation pressure will be set by the extraction air pressure. If the extracted air flow is less than the total ASU requirement, a supplemental air compressor will be used, and its discharge pressure will match the pressure of the extracted air. If the extracted air supply is about a quarter of the total ASU requirement, ASU distillation pressure can be independently established, and a pumped liquid process can be applied. High-pressure extraction air boils pressurized liquid oxygen and/or nitrogen in the cryogenic heat exchange area. The supplemental compressed air supply sets the distillation pressures in the ASU.

In another configuration, byproduct nitrogen from the ASU can be compressed, heated against extraction air, and injected into the gas turbine's combustor. Fig. 7 depicts the various integration schemes. The benefits of pressurized nitrogen injection into a gas turbine are well known [1] and include the following.

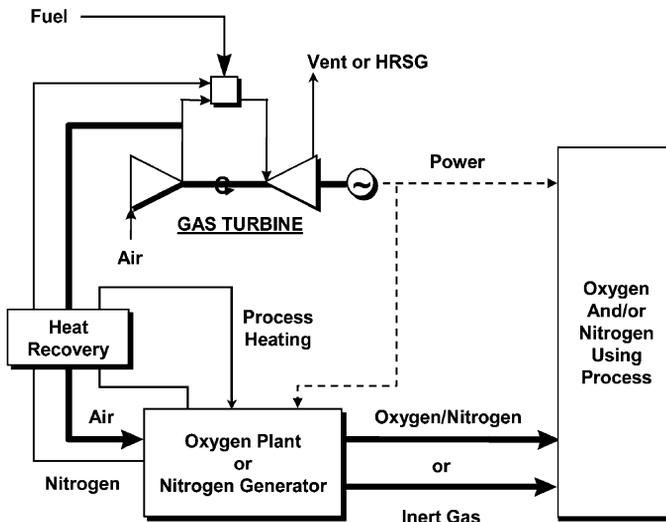


Fig. 7. ASU and gas turbine air and nitrogen stream integration.

- Efficient recovery of lower level heat (e.g., from an extracted air supply). Heat contained in extracted gas turbine air must be rejected before the air enters the ASU. This can be accomplished by transferring the heat to a pressurized nitrogen stream at close temperature approach and injecting the heated nitrogen into the gas turbine for recovery in the combined cycle process.

- Reduced NO<sub>x</sub> emissions. Injected nitrogen reduces the adiabatic flame temperature of the combustion products, thus reducing NO<sub>x</sub> formation in the gas turbine.

- Efficient increase in power output from the turbine. Injected nitrogen acts as a diluent that permits greater fuel consumption without exceeding turbine inlet temperature limits.

Fig. 8 summarizes the commercial ASU facilities provided by Air Products and Chemicals for a variety of gasification projects and including various levels of integration with gas turbines. Power production of the integrated options is a nominal 250-MW net electrical output.

- The standalone or non-integrated option generally uses a low air feed pressure ASU selected to reject waste nitrogen to the atmosphere.
- The nitrogen integrated design provided for Tampa Electric uses an elevated air feed pressure ASU, optimized for a combination of equipment cost and power consumption.
- The full air and nitrogen integrated option is designed around the air supply pressure from the gas turbine's air compressor. At the Demkolec facility, all the air for the ASU is supplied via extraction from the gas turbine.

Air Products and Chemicals' ASU built for Demkolec was the world's first fully integrated air separation facility. The 1960-sTPD oxygen plant serving Demkolec's coal

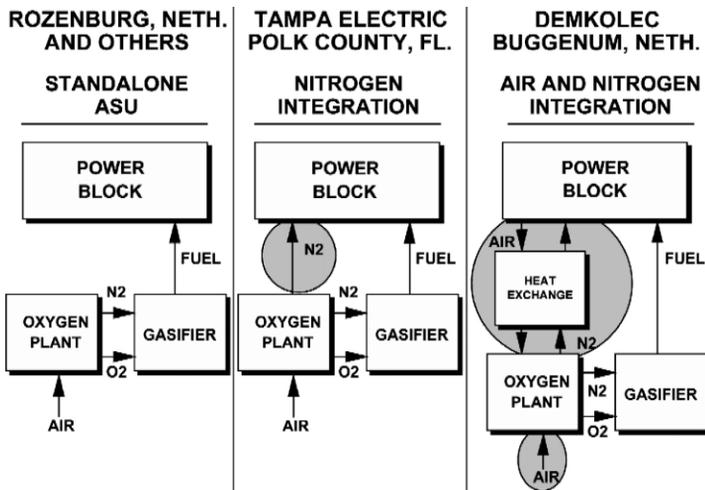


Fig. 8. Commercial integration experience.

gasification combined cycle facility in The Netherlands is an elevated pressure design, with all residual nitrogen compressed and returned to the combustion turbine.

**6. Other integration opportunities**

The following sections (Sections 6.1, 6.2, 6.3, 6.4 and 6.5) explore advanced concepts for integrating the oxygen generation process with partial oxidation processes or with gas turbines. In several cases the concepts apply to integration with non-cryogenic processes. ITM oxygen processes are not covered due to the many publications covering their application to partial oxidation facilities [2–4].

*6.1. Chemical air separation and partial oxidation process integration*

Partial oxidation of a hydrocarbon feed typically produces low and high level heat in excess of the requirements of the oxidation process. Past practice and current literature studies use cryogenic air separation processes to provide oxygen and nitrogen for use in the partial oxidation of hydrocarbon feeds into higher value hydrocarbon products. “Integration” between the air separation unit and the partial oxidation process (POX) is limited to the supply of steam or generated electric power within the POX process to drive the compression equipment of the ASU. It would be beneficial to use the high level heat from a POX process to drive the separation process and low level heat to provide required compression within the ASU. The operating temperature of the chemical-based ASU matches the temperature of process streams within many POX processes. Fig. 9 shows the integration of the major streams between the ASU and POX process.

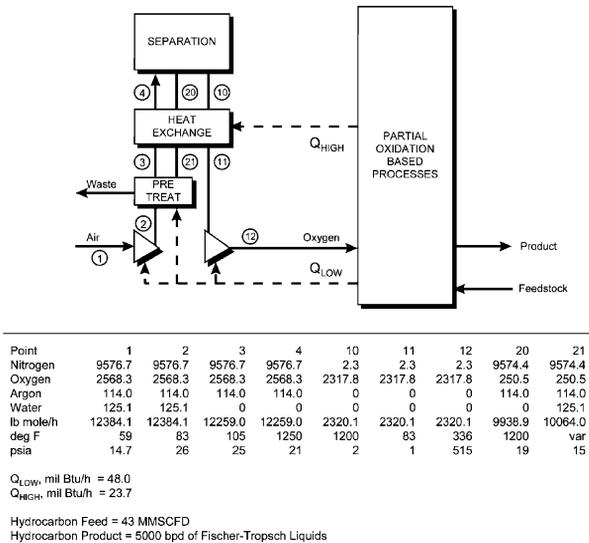


Fig. 9. PSA chemical air separation process at 890 sTPD oxygen and 500 psig.

A chemical ASU can use any compound that will absorb oxygen from an air feed stream at conditions T1 and P1, and release or desorb oxygen at conditions T2 and P2, where T2 is higher than T1 at essentially constant pressure or where P2 is less than P1 at essentially constant temperature. The alternates described are typically called thermal swing absorption or pressure swing absorption, respectively. In addition, a combination of thermal and pressure swing absorption can be practiced. An example of a chemical absorption/desorption process uses a molten mixture of alkali nitrates and nitrites [5]. Potential benefits of the chemical-based ASU over other processes for use in POX applications include:

- direct use of high level heat to operate the chemical ASU without conversion to steam or electricity.
- ability to construct large, single train units.
- use of lower level heat to operate ASU compression equipment.
- lower energy consumption leading to lower capital cost and smaller plant footprints.

An example comparison of a cryogenic and chemical-based ASU is presented based on conditions for a small scale gas-to-liquids process [6]. Using the data from Table 5 of Ref. [6], a 5000-bpd GTL facility using GHR technology requires 890 sTPD of oxygen at 500 psig. The 43 MMSCFD feed rate of natural gas to the process results in a high level heat duty of about 94 million BTU/h between 1800°F and 1000°F, and fuel gas that is available for combustion and low level steam generation. Any of several types of cryogenic processes can be employed to produce the required oxygen flow. A typical approach would be a full pumped liquid oxygen cycle which would consume about 12.5 MW of electric power, require 4840 gpm of cooling water and use 1750 lb/h of steam at 120 psig. Of the two types of chemical-based ASUs, PSA is probably the least capital-intensive since heat exchangers associated with the thermal swing operation are not required. Using data from Ref. [5], a PSA chemical-based ASU would consume about 10.5 MW of electric power, require 3322 gpm of cooling water and use 3654 lb/h of steam at 120 psig. Optionally, a TSA process could be used that would reduce ASU power consumption and make additional low level heat available for use within the facility or for export as power. Ultimately, the use of a PSA or TSA process and the air feed pressure to the ASU would be optimized based upon available amounts of the high and low value heat from the POX process and desired trade-offs between capital cost and operating efficiency. Fig. 9 contains additional information on the PSA process used for comparison purposes.

Other options include combusting fuel gas from the POX process for use as the high level heat source for the ASU process, or for production of steam for use within the POX process, or for low level heat production to drive the ASU compressors.

## *6.2. Extracted air heat recovery for solvent-based processes*

In a facility employing gas turbines, air may be extracted for a variety of reasons: as a feed to an air separation unit, as “bleed” cooling air for the turbine itself, or for other

requirements of pressurized air within the facility. The extracted air (Fig. 7) contains valuable heat that can be recovered at discrete temperature levels by boiling liquid fluids, or recovered by sensible heat transfer to another fluid(s). One class of applications for using the recovered heat is solvent regeneration in a process characterized by a gas/liquid absorption step followed by heat transfer to the liquid to desorb a gaseous product or contaminant. Examples of processes that could benefit from this heat integration include, but are not limited to, the following unit operations, which may be found in hydrocarbon gasification or hydrocarbon processing facilities.

- Regeneration of a liquid-based air pretreatment system that is part of a cryogenic air separation unit. A liquid-based absorption step for removal of contaminants in the air feed stream to an ASU could benefit from extraction air heat recovery. In one embodiment the hot air would be cooled against the liquid bottoms from an absorption column. The cooled air would enter the column and contact the liquid absorbent wherein the impurities in the air stream would be absorbed into the liquid. The air to absorbent heating step would desorb the contaminants from the absorbent liquid, which would then be sent back to the absorbent column. The absorbent system could consist of one or more fluids in several absorption steps for higher efficiency removal or to use specific absorbents to remove specific impurities in the air stream. Absorbent regeneration could include heating from other sources and use pressure reduction in combination with heating to desorb impurities.

- Regeneration of a gas cleaning solvent such as used in a syngas cleanup process. The use of absorption systems within POX facilities for removal of acid gases is well known. Extraction air heat could be used entirely or used to supplement other sources of heat for regeneration of the solvent.

- Regeneration of a solvent-based system to recover salable byproduct. A solvent-based system might be employed to recover a salable byproduct such as carbon dioxide from an off-gas stream within the facility. Again, the heat for liberating the product stream from the solvent would come totally or partially from heat recovered from the extracted air.

Several of these concepts can be combined as shown in Fig. 10. Heat from the extracted air may be recovered by indirect contact of the hot air with a process fluid or by heat transfer from the air to a working fluid such as steam, or an inert gas. In the example high level heat from the extracted air source is transferred to a nitrogen stream returning to the gas turbine. The extracted air is further cooled by contact with the rich bottoms from a absorption column used to pretreat air feed to the ASU. This heat transfer step could also be accomplished in other absorption systems within the POX or POX-product workup sections of the facility. Depending upon the solvent and material being absorbed, the high level heat recovery step might be eliminated and all the extracted air heat used for absorber regeneration. The extracted air can be combined with supplemental compressed air entering the pretreatment process, or it could be separately treated if the pressure was significantly different than the supplement air source. In this embodiment, carbon dioxide is recovered from the air pretreatment area as a byproduct. The carbon dioxide could be processed for sale as a byproduct or used internally in the facility. One example would be to return the carbon dioxide to the gas turbine as added diluent.

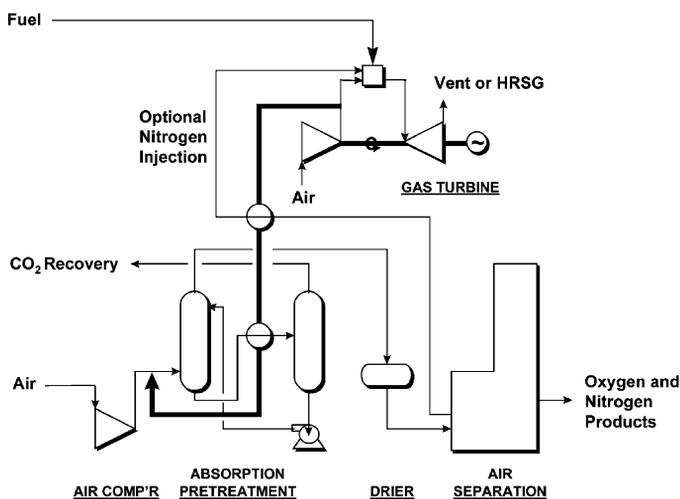


Fig. 10. Extracted air heat recovery application.

### 6.3. Extracted air heat recovery for adsorption-based processes

Analogously to the above, extracted air heat can be used to regenerate adsorption-based processes. The adsorption processes can be associated with the air separation system, POX gas treatment systems, or byproduct recovery systems. Purification recovery systems often use TSA or a combination of TSA and PSA cycles that typically require heat above 200°F for regeneration. Gas turbine extraction air is typically available in the 700–800°F range, making it a suitable regeneration heat source with or without a topping heat recovery step.

### 6.4. Power and inert gas generation

During the construction and start-up of industrial facilities, a source of power and inert gas are often required. In remotely located areas both of these items may have to be generated on-site. Power is required to operate machinery, run welding equipment and to supply light, heat and other utilities such as water to the construction site. Nitrogen is required for facility purging, inerting, pressure testing and line blowing prior to facility start-ups and during normal operation. Often, this requirement requires precommissioning and start-up of an oxygen plant at the facility for supply of the needed nitrogen. In addition, the start-up or transient nitrogen requirements may dictate sizing of the oxygen plant for requirements that are not needed during normal operation. As a result, capital cost and non-productive operating costs are incurred to provide the start-up, transient and precommissioning nitrogen.

One solution is to build a nitrogen generator that receives its air supply from a gas turbine supplying auxiliary power to the facility (Fig. 7). By utilizing extracted air from the gas turbine, the capital requirement for a separate air compressor is eliminated. Since

nitrogen generators supply most of the product stream at pressure, operation of the unit at the high air supply pressure from the gas turbine is optimum. Following facility start-up, the nitrogen generator may be shutdown or continue to operate depending on the nature of the continuous nitrogen requirement. It may be advantageous to supply high purity nitrogen requirements full time from the nitrogen generator and not burden the associated oxygen plant design with the production of high purity nitrogen. Or, the nitrogen generator can be held in reserve and operated when the oxygen plant is not available, as an alternative to supplying high-pressure gas or liquid storage as a backup source. The nitrogen generator can be adsorption-, cryogenic- or membrane-based.

### 6.5. Hybrid air purification system for large ASUs

A small footprint and reduced weight for large ASUs are critical success factors for developing technologies located on offshore platforms, ships or barges, or in remote locations. Pumped liquid process cycles are also of interest in reducing ASU cost. The following concept involves the use of reversing main heat exchangers to purify a low-pressure air stream that enters the distillation system, while using an adsorbent-based system for treatment of a higher pressure air used in the pumped portion of the cycle.

Current ASU design practice involves the compression of air to the operating pressure of the high-pressure (HP) distillation column. The air next enters an adsorbent-based air pretreatment unit to remove water, carbon dioxide and certain hydrocarbon contaminants. A portion of the treated air is further compressed and is condensed against pumped liquid product streams such as liquid oxygen (LOX) and liquid nitrogen (LIN). The size and the weight of the adsorption-based air pretreatment units is generally not an issue with land-based plants located in traditional areas. ASUs for use on offshore platforms, floating or landed barges, or in severe climates are required to have as small a footprint as possible and to weigh as little as possible due to the high cost associated with building plants on artificial structures. A different design concept would incorporate the size and weight benefits of reversing heat exchanger technology with the process cost benefits of a pumped liquid cycle.

In Fig. 11, air is compressed to the operating pressure of the HP distillation column, the majority of the air passes through reversing heat exchangers and into the distillation column. In reversing heat exchangers contaminants in the air stream are captured by desublimation within the heat exchanger passages. Periodically, the flow through the heat exchanger is “reversed” to allow a dry stream from the distillation system to flow through the air passages to sublimate, liquefy and sweep the contaminants from the system. A reversing heat exchanger and associated valving performs the combined duty of an adsorption pretreatment system and main cryogenic heat exchanger, thus saving footprint and weight.

A portion of the initially compressed air bypasses the reversing heat exchangers and is further compressed and intercooled before being treated in an adsorption-based system. Since this stream is typically in the 200–1200 psia range, it contains very little water vapor after being cooled. The reduced amount of moisture combined with the high pressure results in a small adsorption system for this duty and avoids the complication of using a reversing heat exchanger system for this duty.

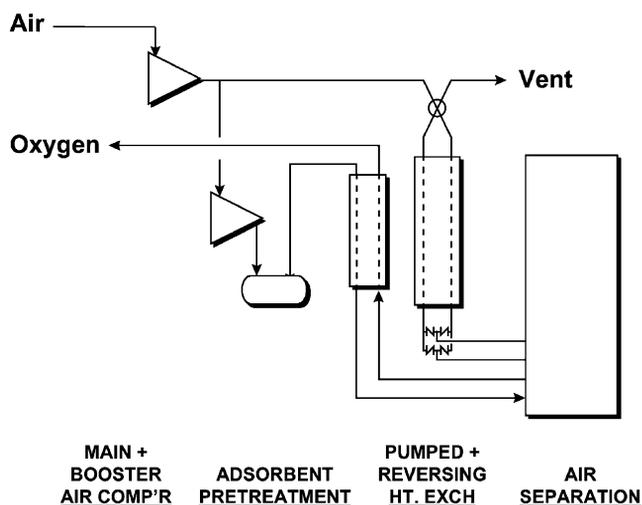


Fig. 11. Hybrid air purification scheme.

### 6.6. Nitrogen humidification using wastewater from partial oxidation processes

As noted earlier, nitrogen injection into gas turbines is a known method of increasing power output and decreasing NO<sub>x</sub> emissions. In very warm climates or at high altitudes, injecting the total amount of nitrogen available from an ASU associated with a POX process incorporating gas turbines for power production or mechanical drive may still not reach the full power output of the gas turbine(s). Humidifying the nitrogen to add mass and increase its temperature has been studied and is practiced at the Demkolec IGCC facility in the form of heating and saturating a combined stream of nitrogen and fuel gas. The methods of providing heat and moisture have always been based on using low level steam, boiler feed water or process heat as the source of moisture and heat to increase the water loading in the nitrogen.

An interesting concept is to use wastewater that results from treating syngas from a POX unit or water that is formed as a result of reacting syngas in a Fischer–Tropsch hydrocarbon synthesis step to humidify ASU nitrogen that is injected into a gas turbine (Fig. 12). Other aspects or integration features are listed as follows.

- The stripping action of nitrogen in contact with wastewater can simplify downstream water cleanup.
- Heat sources to increase the operating temperature of the humidification step and thereby increase the moisture content of the nitrogen could include cooling of extracted air from a gas turbine, cooling a standalone ASU air source compressed adiabatically, adiabatic heat of compression of nitrogen prior to humidification, as well as recovering heat from low level sources such as boiler feed water, slag coolers, syngas coolers, shift converters, synthesis reactors and other sources.
- Superheating of the moisturized nitrogen prior to injection into the gas turbine could be accomplished using some of the higher level heat sources described above.

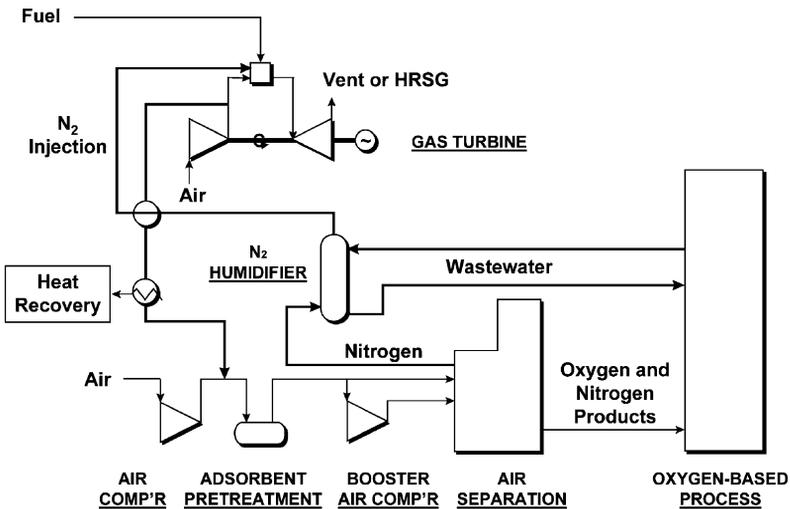


Fig. 12. Nitrogen humidification integration with a gas turbine and wastewater source.

### 6.7. ASU EP nitrogen refrigeration for LPG recovery in GTL plants

The use of EP ASUs can help achieve very large single-train sizes, minimize the number of ASU trains, and minimize footprint and weight. However, there may be no obvious use for the very large amount of pressurized nitrogen leaving the ASU. One use would be to expand the nitrogen to generate refrigeration (typically from  $-50^{\circ}\text{F}$  to  $-100^{\circ}\text{F}$ ) and use the refrigeration to recover LPG components ( $\text{C}_3$ ,  $\text{C}_4$ ,  $\text{C}_5$ ) from the natural gas feed and/or the tail gas from the Fischer–Tropsch process. This could be especially useful with highly associated natural gas, F–T catalysts formulated with a selectivity compromise, or for overall optimization of the F–T process.

### 6.8. Integrated gas-to-liquids coproduction facility for Fischer–Tropsch liquids and electric power

Coproduction in a GTL facility can be optimized by integrating a gas turbine combined-cycle unit with the ASU and the GTL process. The gas turbine receives nitrogen from the ASU and optionally supplies extraction air. The gas turbine combined-cycle receives tail gas, off-gas, wastewater, and steam from the GTL process and optionally supplies superheated steam to the gasifier.

Most of the work on GTL applications has focused on an all-liquids product, without export power. This is often the only feasible scenario for truly remote locations and many offshore circumstances. On the other hand, some opportunities will allow and even desire significant export power to accommodate growing external demand or facilitate additional petroleum/gas production facilities. In these latter circumstances, a GTL coproduction facility with integration features can optimally produce the Fischer–Tropsch liquids and electric power.



would allow a direct quench gasifier configuration, eliminating the expensive, high-temperature/high-pressure waste heat boiler.

## 7. Conclusion

The cryogenic process is today's preferred route for the supply of industrial gases to large facilities. Integration of heat, refrigeration, process and waste streams between the industrial gas process and other units within the overall facility can improve efficiency and decrease cost. Advanced concepts for heat integration could favor the use of chemical or ITM processes in the future. Niche opportunities exist to apply adsorption or polymeric membrane processes for generation of nitrogen requirements to satisfy remote location start-up needs and as a source of backup inert gas.

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