Industrial Gases

27

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Overview

Industrial gases may actually be used as gases, liquids, or cryogenic liquids. Industrial users generally accept them as those gases used primarily in their pure form in large quantities. Most of the gases we consider to be industrial gases have been in use for many years. Processes for the cryogenic separation of the air gases were developed as early as 1895, with commercial production of oxygen beginning in 1902. Nitrous oxide was used as an anesthetic as early as 1799. Carbon dioxide had been identified as a specific substance by 1608. Methane has been used as an energy source since the 1700s. Other gaseous compounds commonly used today for specific manufacturing processes (e.g., electronics/semiconductors, plastics) are discussed in other chapters of this Handbook related to those processes.

The reactivity of gases can be summarized into three classes: oxidizers, inert gases, and flammable gases. The gases that fall into the category of inert are nitrogen, argon, helium, and carbon dioxide. The oxidizers are oxygen, chlorine, and nitrous oxide. Acetylene, liquefied natural gas (LNG), and hydrogen are the flammable gases. These elements and compounds by no means encompass all gases considered to be industrial gases, but they represent the major gases used and produced in industry (see Table 27.1) [1].

The cryogenic air separation process, in which air is liquefied and separated into its major constituents (oxygen, nitrogen, argon) by the use of cryogenic technology, is the major source of nitrogen, oxygen, and argon produced for industry, as well as the noble gases krypton, neon, and xenon. Table 27.2 gives the cryogenic boiling point temperatures and concentrations for some of the gases present in the atmosphere.

The cryogenic air separation process starts with air entering the plant through air filters, where it is compressed and cooled. The air is passed through heat exchangers for further cooling and for removal of water vapor and carbon dioxide by liquid condensation. Solid adsorbents, such as molecular sieves, silicas, and aluminas, can also be used to remove the water and carbon dioxide by adsorption before separation of the air. When the air reaches a temperature of −338°F, it is sufficiently free of water and carbon dioxide and ready to be passed into the distillation column [6].

Separation occurs by distillation, which is the physical partition of compounds by the differences in their boiling points (see Fig. 27.5 below in the section "Argon"). The distillation method used is referred to as "double column," as it contains two separate distillation columns operated at two different pressures. The cooled air is fed to the bottom of the high-pressure column. Air is distilled in this column where the higher boiling temperature fluid oxygen stays at the bottom and the lower boiling temperature nitrogen boils to the top as a distillate product. The crude liquid oxygen from the high-pressure column is flashed into the low-pressure column as the two columns are thermally linked by a common reboiler/condenser.

Vapor is withdrawn from the middle of the low-pressure column and is passed as feed to the crude argon column. The vapor in that column is condensed and taken off as liquid crude argon. Pure nitrogen vapor is extracted from the top of the low-pressure distillation column, and liquid oxygen is taken from the bottom of this column. Figure 27.1 shows an air separation plant with a molecular sieve front-end cleanup and liquid storage tanks.

Alternatives to the cryogenic separation process include the membrane separation process and adsorption processes. The adsorption processes include pressure swing adsorption (PSA) [15] and vacuum swing adsorption (VSA). These methods are non-cryogenic and produce a vapor product only. This reduces the cost of production considerably when the local use of gas-phase product is the primary objective.

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Table 27.1 Properties of Industrail Gases

Gas Property		Helium-4 (He)	Para-hydrogen (p-H_2)	Normal Hudrogen (n-H_2)	Air	Nitrogen (N_2)	Oxygen (O_2)	Argon (Ar)	Carbon Dioxide (CO_2)	Acetylene (C_2)H_2)	Methane (CH_4)
Atomic/ molecular weight	4.00	2.016	2.016	2.016	28.975	28.01	31.9988	39.95	44.01	26.04	16.042
Normal boiling point	°F	−452.1	−423.2	−423.0	−317.8	−320.4	−297.3	−302.6	−109.33[c]	−103.4 (10 psig)	−258.68
										−118[c]	
Triple point	°F	−455.75	−434.8	−434.55	–	−346.0	−361.8	−308.8	−69.9	−116	−296.5
	psia	0.730[a]	1.021	1.045	–1.81	0.0216	9.99	60.4	17.7	1.69	
Critical point	°F	−450.3	−400.31	−399.93	−221.1	−232.4	−181.4	−188.1	87.9	96.8	−115.78
	psia	33.0	187.5	190.8	547	493	731.4	711.5	1070.6	907	673.1
Gas density at NTP	Lb/cf	0.0103	0.00521	0.00521	0.07493	0.072	0.08279	0.103	0.1144	0.0678	0.042235
Gas density STP	Lb/cf										
Vapor density at NBP	Lf/cf	1.0543[b]	0.084	0083	0.2805	0.2879	0.2795	0.3606	0.1462	–	0.1134
Liquid density at NBP	Lb/cf	7.802	4.42	4.43	54.56	50.48	71.23	87.02	73.5[d]	24.0 (70°F)	26.57
Specific heat at NTP	BTU/ tb-°F	1.24	3.555	3.425	0.241	0.249	0.2197	0.125	0.203	0.383	0.5271
Specific heat ratio at NTP	1.66	1.38	1.42	1.40	1.41	1.40	1.67	1.304	1.26	1.307	
Latent heat of vaporization at NBP	BTU/ lb	8.72	191.6	191.7	88.2	85.6	91.7	69.7	245.5[c] (C)	264	219.22
Ref: 8 *CGA Handbook*, 1999	p. 408	p.416	p.415	p.234	p.528	p.555	p.262	p.296	p.225	p.488	

NTP = 14.696 psia and 70°F; STP = 14.696 psia and 32°F; Lb/cf = pound per cubic foot.
[a]Lower lambda point; [b]NIST Technical Note 631, "Thermophysical Properties of Helium 4.", Nov. 1972; [c]Sublimation point; [d]Triple point. CGA References from NIST Technical Notes 1025 (1980), 1048 91982), 1079 (1985), 361, Monograph 168 (1981).

Table 27.2 Cryogenic Gases: Boiling Point and Concentration in Air

	Normal Boiling Point (°F)	Dry Air Concentration (% v/v)
Argon	−302.6	0.93
Nitrogen	−320.5	78.1
Oxygen	−297.3	20.94
Helium	−452.1	0.0005
Hydrogen	−422.99	0.00005
Neon	−410.7	0.0018
Krypton	−244.0	0.00011
Xenon	−163.0	0.000008

The membrane separation process is used to produce a number of gases for industrial use. Many membrane technologies have been developed over the last 10 years, including various polymer and pure carbon membranes [13, 17]. A common polymer membrane may consist of a microporous substructure of cellulose acetate and a thin layer of dense cellulose acetate (active layer) on the upper surface, resembling a sponge covered by a plastic film. The membrane is cast into a supporting cloth for added mechanical strength. The active layer serves as the separating barrier

Fig. 27.1 Air separation plant with a front-end cleanup, cold box tower and liquid storage tanks. (Courtesy Air Liquide.)

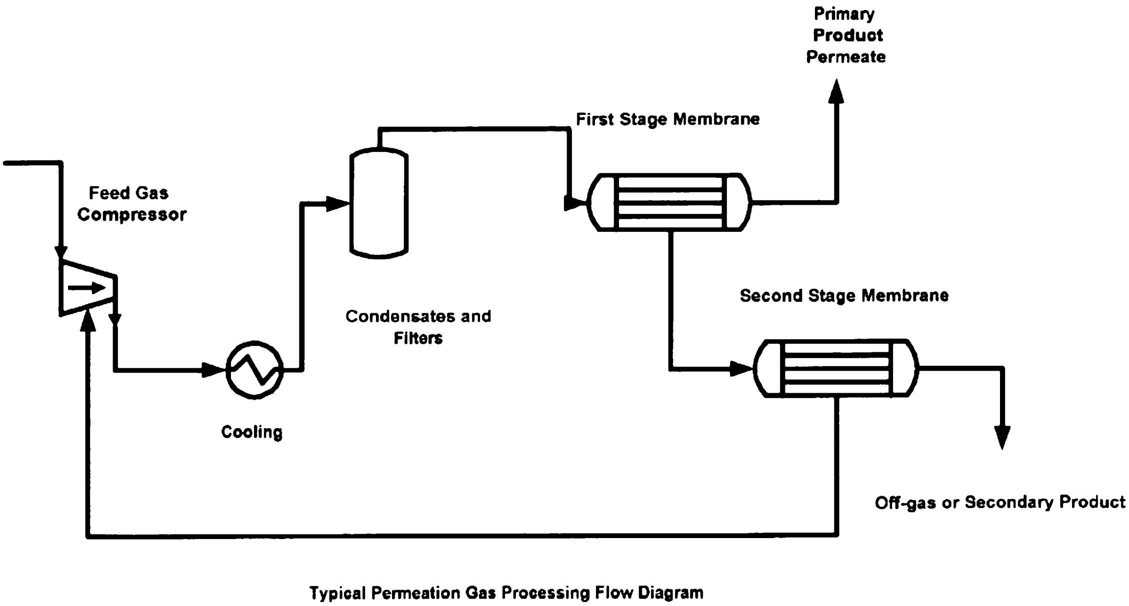

Fig. 27.2 Typical permeation gas processing flow diagram

and, because of its thinness, provides very high transport rates. The membrane selectively allows the smaller molecular-sized components to pass through the membrane substructure, thereby accomplishing the separation process. Carbon and zeolite-based membranes depend on the relative molecular size of the gases to effect the separation of the gases. A typical membrane separation flow system is shown in Fig. 27.2.

The VSA system is a non-cryogenic process that makes use of pressure that is less than atmospheric (vacuum) and adsorbents to separate nitrogen, and carbon dioxide from air. The PSA system is a similar process for producing a particular gas by passing a pressurized gas stream through a set of adsorbent beds. The impurities are selectively adsorbed using a molecular sieve or other selective adsorbents to trap the undesired components. In the production of oxygen using the VSA process, the VSA system separates air at ambient temperature by passing it through a column of adsorbent. The adsorbent, which is an inorganic crystal material, selectively adsorbs nitrogen molecules on its

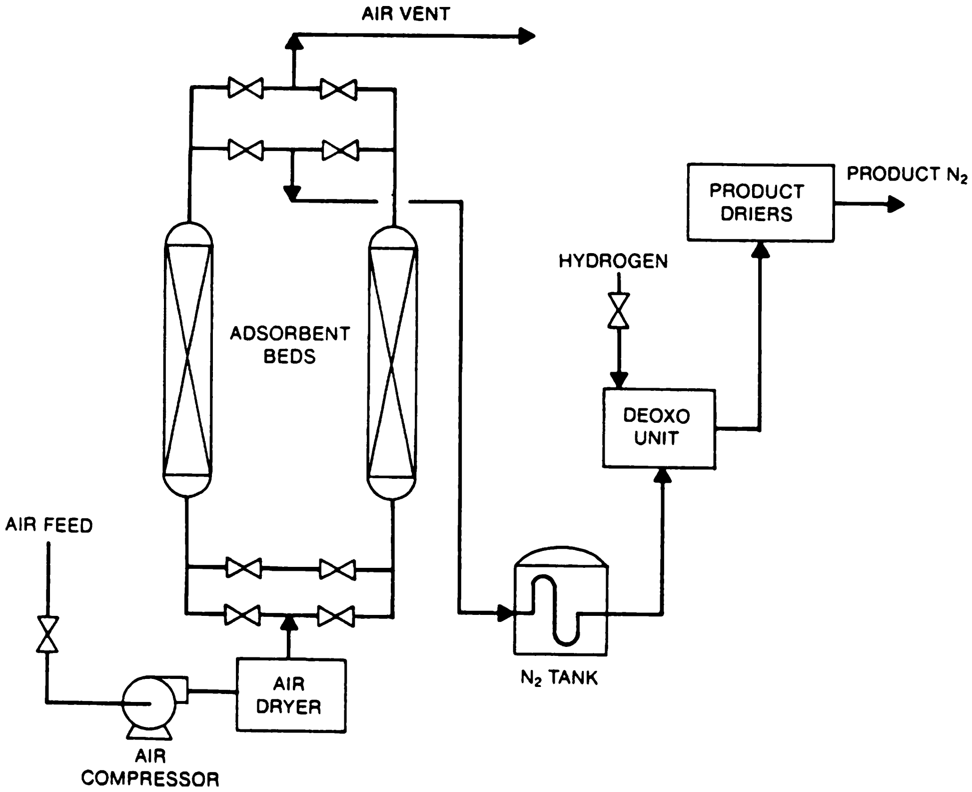

Fig. 27.3 Process diagram for nitrogen PSA system. (Courtesy Air Products and Chemicals, Inc.)

surface, while the oxygen molecules pass on through the adsorbent column.

The final oxygen product exits the adsorber column. The nitrogen adsorbed is released when the adsorber column is reactivated by use of differential pressure from a vacuum. Once the adsorber column is reactivated, the cycle is ready to be repeated. In the PSA system, compressed air is passed through a column of chemical adsorbent, which is a carbon-based material that essentially traps the oxygen molecules and allows the nitrogen molecule to pass through to the use point. Figure 27.3 shows the process flow of a PSA system, which can produce 98–99.5% pure nitrogen without the need for downstream purification. These adsorption systems usually are located at customer sites. See Fig. 27.4 for an example of an on-site PSA.

Small-volume users of the industrial gases are supplied by high-pressure gas cylinders filled with the desired product. These cylinders then are loaded onto flatbed trucks for delivery. For larger-volume gas transportation, long-length gas cylinders are permanently mounted on trailer frames. These high-pressure-cylinder vehicles commonly are referred to as tube trailers. The cylinders are constructed of alloy steels, and are designed, built, tested, and maintained in accordance with US Department of Transportation (DOT) regulations in the United States. Similar regulatory agencies in other countries define the requirements for safe transport and storage of compressed gases (e.g., Transport Canada, Ministère des Transports (France), Department for Transport (UK), and other national regulators). The typical small-volume cylinders are constructed to a DOT 3A or 3AA specification, and typically have rated service pressures from 2,015 to 2,640 psig and water volumes from 0.39 to 1.75 ft^3. The larger cylinders often have similar pressure ratings but water volumes of approximately 75 ft^3.

The containers used for transporting and storing the majority of cryogenic liquids are insulated cryogenic tankers, liquid cylinders (sometimes referred to as Dewars), and stationary storage tanks. These containers are similar in design to a Thermos® bottle. There is an inner vessel, which contains the cryogenic product, and an outer vessel. The space between the two vessels is under a vacuum and usually contains a wrapped insulation material such as aluminized Mylar, or it may contain a powdered insulation such as expanded perlite. The liquid cylinders, usually 160–250 L in capacity, are constructed to a DOT 4 L specification and operate with pressure up to 235 psig.

The cryogenic tank trucks may be constructed to a DOT MC-338 specification, and range in capacity from 3,000 to 14,000 gal, usually depending on the product. The operating pressures may range from 25 to 150 psig, and the vehicles often are equipped with cryogenic pumps used to deliver the

Fig. 27.4 An on-site nitrogen PSA supply system. The large vessels are absorbers and the smaller ones are dryers. (Courtesy Cirmac International, BY, Netherlands.)

product to higher-pressure storage tanks. The stationary storage tanks are designed and built to ASME standards, typically are constructed for pressures of 250 psig or less, and may range in capacity from 500 to 70,000 gal [3].

Nitrogen

Nitrogen makes up 78% of the earth's atmosphere. It is a colorless, tasteless, nontoxic, and relatively inert gas. Nitrogen does not support combustion nor does it support respiration; but it reacts with the more active metals such as lithium and magnesium to form nitrides, and at high temperatures it will combine with hydrogen, oxygen, and other elements. As a cryogenic liquid, nitrogen is nonmagnetic, stable against mechanical shock, and free from toxic or irritant vapor.

Nitrogen usually is produced by cryogenic air separation, liquefaction of atmospheric air, and removal of the nitrogen by distillation, as described earlier. Non-cryogenic adsorption technology, including PSA and VSA systems, economically provides nitrogen for requirements between 4,000 and 30,000 standard cubic feet per hour (SCFH) [13]. The development of more efficient membrane separation systems has happened in the last 10 years. The production of gaseous nitrogen for refinery instrumentation and vessel purging needs has shifted more to the use of membrane systems on site rather than cryogenic liquid in bulk storage due to significant cost savings.

Nitrogen has many applications, both as a gas and as a liquid. Gaseous nitrogen is widely used for inerting and pressurizing systems. Applications include the agitation of color film solutions in photographic processing; blanketing and deaeration of oxygen-sensitive liquids, volatile liquid chemicals, and nonferrous metals; and in the production of semiconductor electronic components, primary metals heat treating, and brazing of copper tubing. It is used to pressurize aircraft tires and emergency gas bottles to operate landing gear; and often to purge and pressurize pipelines, reactor vessels, or storage tanks throughout the petrochemical industry [1].

Gaseous and liquid nitrogen have applications in the foods industry in the areas of food processing and packaging. Liquid nitrogen is used for rapid freezing of expensive or highly perishable foods, such as shrimp and other meat products, as well as to refrigerate foods in long-distance hauling. A gaseous nitrogen atmosphere can help to retard the spoilage of some food products.

Liquid nitrogen is used in the cold-trapping of materials such as carbon dioxide and volatile organic carbons (VOCs) from gas streams, as a coolant for electronic equipment, for pulverizing plastics or rubber material, for deflashing of rubber tires, and for simulating the conditions of outer space. It is used to freeze liquids in pipelines during repairs to the pipeline. It can be used to generate very high-pressure gaseous nitrogen (15,000 psig) by liquid pumping. Liquid nitrogen is frequently used in medicine to remove skin blemishes in dermatology, and to preserve whole blood, livestock sperm, and other biological specimens.

Liquid nitrogen gas is transported in liquid cylinders, nonpressurized Dewars, cryogenic tankers, and trailers. Gaseous nitrogen is also transported in high-pressure gas cylinders and tube trailers. Both forms of nitrogen also are transported via pipelines when the sources are at economical locations and distances from the applications.

Oxygen

This gas, which occupies approximately 21% of the earth's atmosphere at sea level, has a number of very important uses. Oxygen is a colorless, odorless, and tasteless gas that is essential to the support of life. All elements except the inert gases combine directly with oxygen to form oxides. Oxygen is nonflammable, but is an oxidizer that readily supports combustion.

A large percentage of the oxygen produced commercially is made by cryogenic air separation. It may also be produced by PSA and membrane systems, as described in the production of nitrogen. Oxygen also may be made by the most common decomposition reaction, electrolysis of water.

Small quantities of pure oxygen may also be made by other chemical reactions. These reactions produce not only oxygen but by-products as well, and they are not usually as economical an alternative when compared with the other technologies.

Applications in enhanced combustion and life-support systems provide the majority of the demand for oxygen. It is used extensively in medical applications for therapeutic purposes, for resuscitation in asphyxia, and with other gases in anesthesia. Also it is used in high-altitude flying and deep-sea diving, and it is used for life-support and as a fuel oxidizer in the US space program [1].

For industrial applications, oxygen is in large demand for use with acetylene, hydrogen, and other fuel gases for purposes such as metal cutting, welding, hardening, and dehydrating. Oxygen enhances the capability of steel and iron furnaces. Oxygen is used in the production of synthesis gas–hydrogen–carbon monoxide mixtures from coal, natural gas, or liquid fuels; the synthesis gases are used to make gasoline, methanol, and ammonia. Oxygen may be used for the cracking of methane or natural gas by partial oxidation to produce acetylene, and in the production of nitric acid, ethylene, and other basic chemical feedstocks.

One of the largest commercial applications for oxygen is the Basic Oxygen Furnace (BOF) for refining iron and making steel. Another common application is its use in oxyfuel burners in the steel industry. It is used in electric arc furnaces, which melt scrap metals by passing an electric current through large graphite electrodes.

Oxygen enrichment is a process whereby oxygen is added to an air stream to improve a plant's efficiency. Combustion results in the generation of heat and gaseous by-products, usually carbon monoxide, carbon dioxide, and water vapor. Oxygen enrichment decreases the amount of nitrogen in the air stream, improving the combustion reactions while reducing the formation of undesired by-product gases. Oxygen enrichment is used in pulp mills to increase lime production from existing equipment and eliminate the need to purchase lime from other industries. It is also used in pulp mills to reduce airborne sulfur emissions to comply with federal environment regulations.

Gaseous oxygen is transported in high-pressure gas cylinders, tube trailers, and portable cylinder modules. Liquid oxygen is transported as a cryogenic fluid in liquid cylinders and insulated cryogenic tankers. Customer on-site storage is usually accomplished in large insulated cryogenic tanks.

Argon

Argon, a relatively scarce gas, is colorless, odorless, tasteless, and nontoxic. It forms no known chemical compound; thus it is extremely inert. Representing only 0.93% of the earth's atmosphere, it is the most valuable of the commodity air gases. Argon is utilized in a variety of applications. In the manufacture of lighting devices, it is used to fill lamp bulbs and to produce colors in display tubes for lighted signs.

Argon provides an inert atmosphere for the production of semiconductors and specialty metals, such as titanium and zirconium. It is often used to provide a protective shield for the growing of silicon and germanium crystals. Some metal welding and cutting applications require an inert gas shield, and argon gas often is used to fill this requirement [1].

Argon is manufactured in oxygen–nitrogen plants by means of fractional distillation after the liquefaction of air as described previously, in the cryogenic air separation process. In the distillation process where air is separated into oxygen and nitrogen, a stream of gas is withdrawn from the low-pressure column to enter the crude argon column. The argon content of the gas, initially 10%, is increased to 95% by subjecting the gas to several stages of distillation. This "crude" argon is further purified to yield the final pure argon product. Figure 27.5 shows a typical air separation process flow diagram. Argon is most economically shipped as a liquid. Liquid argon commonly is transported in liquid cylinders, cryogenic trailers, and portable tanks. Argon can be shipped in high-pressure gas cylinders and high-pressure cylinder trailers.

Hydrogen

Hydrogen, the lightest element known, is extremely flammable and is found in 0.00005% concentration in the air (0.5 parts-per-million). It has received notoriety in the late 1990s into the twenty-first century as a potential replacement for hydrocarbon fuels. This is because the actual combustion of hydrogen results only in the emission of water and the generation of heat which can be used in any of the existing forms of energy generation. However, as the subsequent discussion of hydrogen generation illustrates, there is much more to the carbon cycle of hydrogen use than the final combustion step [2].

The hydrogen molecule exists in two distinct forms: ortho and para, named according to their types of nuclear spins. *Ortho*-hydrogen molecules have a parallel spin, and *para*-hydrogen molecules have an anti-parallel spin. There is no difference in the chemical or transport properties of these forms, but there is a difference in the thermodynamic properties. *Para*-hydrogen is the form preferred for rocket fuels. Hydrogen consists of about three parts ortho and one part para as a gas at room temperature, which is referred to as normal or equilibrium hydrogen. The concentration of the para form increases with decreasing temperature until, for the liquid, the para concentration is nearly 100%. If hydrogen should

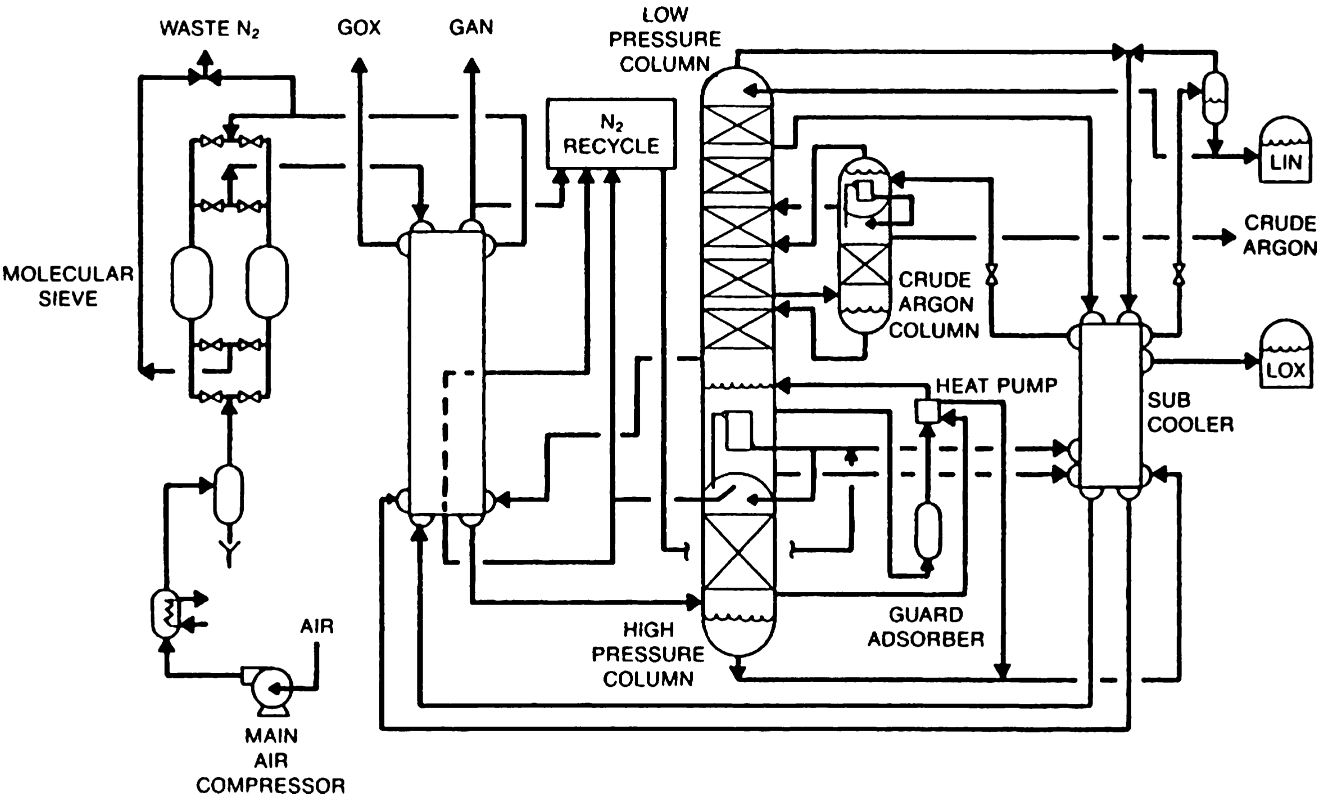

Fig. 27.5 Flow diagram for an air separation plant. (Courtesy Air Products and Chemicals, Inc.)

be cooled and liquefied rapidly, the relative three-to-one concentration of ortho to para would not immediately change [3].

Conversion to the para form takes place at a relatively slow rate and is accompanied by the release of heat. For each pound of rapidly cooled hydrogen that changes to the para form, enough heat is liberated to vaporize approximately 1.5 lb (0.68 kg) of liquid hydrogen. However, if a catalyst is used in the liquefaction cycle, para-hydrogen can be produced directly without loss from self-generated heat.

Hydrogen can be produced by steam methane reformation (the most widely used process) or by off-gas purification. Hydrogen can be produced at normal purity (95–98%) or at ultra-high purity (99.99%). The first step to obtain pure hydrogen in the steam reformer process when using a natural gas feedstock is to perform a pretreatment. There are small amounts of sulfur in natural gas that must be removed. Sulfur removal is done by preheating the natural gas to 700°F, and then sending it through a catalytic reactor. The catalyst inside the reactor adsorbs the sulfur. The second step is steam methane reforming. In this procedure, natural gas and steam are sent through a set of reformer tubes that are packed with a reforming catalyst. A furnace inside the reformer heats the reaction. The methane and steam react, and the results are 45% hydrogen, 40% steam, 8% carbon monoxide, and 7% carbon dioxide. The third step to obtain normal purity hydrogen is gas shifting.

Carbon monoxide, hydrogen, and steam are sent through a shift converter where the gas is heated between 400 and 700°F. The carbon monoxide and steam react to yield hydrogen and carbon dioxide. To produce pure hydrogen, the carbon dioxide must be removed. The gas passes through a carbon dioxide removal system, which contains a chemical solvent that selectively absorbs the carbon dioxide as the gas passes through the solvent [18]. Heat then is added to the solvent to discharge the carbon dioxide. The regenerated solvent is returned to the system to continue the removal of carbon dioxide (see also Chap. 22 for a detailed description of the water shift process).

To obtain ultra-pure hydrogen, a PSA [15] system may be used. In this process, the hydrogen, steam, and carbon dioxide are introduced to the system. At high pressure, the gas is passed through an adsorbent bed, and the adsorbent picks up the impurities and allows hydrogen to pass through the bed. In the regeneration process, the pressure is lowered to purge out the impurities. Then the hydrogen is used to rinse the adsorbent and repressurize the vessel. The efficiency of the hydrogen purification system is optimized at an operating pressure that allows use of a catalyst tube in the reformer. There are four other distinct processes by which hydrogen may be produced under the off-gas purification method: PSA, membrane separation, catalytic purification, and cryogenic separation. The cryogenic separation process uses

Fig. 27.6 A typical facility where liquid hydrogen is produced and stored. (Courtesy Air Liquide Canada.)

cryogenic principles to condense and separate the impurities from hydrogen. Impure hydrogen is introduced to the cryogenic system or "cold box." The impurities are condensed out, and pure hydrogen is obtained. Figure 27.6 shows a typical facility where liquid hydrogen is stored and produced. Membrane separation makes use of two layers of membrane material; the first layer is nonporous, and the second layer is porous [17, 19, 20]. A gas mixture under increased pressure is subjected to the surface, which allows a smaller molecule such as hydrogen to permeate faster than a larger molecule such as carbon dioxide.

The catalytic purification process requires the use of many catalysts to convert impurities into removable compounds. Hydrogen, chlorides, oxygen, and carbon oxides are passed through several catalytic reactors. In the first reactor, the chlorides are absorbed. In the second reactor, oxygen and hydrogen react to obtain water/steam, which is easily removed. In the third reactor, the carbon oxides react with hydrogen to yield methane, which would be considered an acceptable impurity in this particular hydrogen product stream. Some other sources of hydrogen are the dissociation of ammonia, steam reforming of light hydrocarbons, and by-product streams of chemical and petroleum processing. The "steam–iron" process is another method used to make hydrogen. Passing steam over heated, spongy iron reduces the steam to hydrogen with additional formation of iron oxide. There are several varieties of this process. The water–gas reaction is a reaction of steam with incandescent coke or coal; it is a source of hydrogen with carbon monoxide as an additional product. In the catalytic version of this reaction, excess steam breaks down to form more hydrogen while oxidizing the carbon monoxide to form carbon dioxide. Hydrogen frequently is obtained as a by-product of cracking operations using petroleum liquids or vapors as feedstock. Also hydrogen may be produced through the electrolysis of water.

Nearly all hydrogen production in the United States today is by steam reformation of natural gas. This, however, releases fossil carbon dioxide in the process and trades one relatively clean fuel for another, with associated energy loss, so does little to meet national energy needs. For high purity needs, a small amount of hydrogen is produced by electrolysis, but this again is only as good as the energy source used to produce the electricity used. Electrolysis can electrochemically split water into hydrogen and oxygen in essentially the reverse of the reaction in a fuel cell. To make sense for large-scale use, this process must use an inexpensive source of electricity. Because wind energy is currently the lowest cost renewable energy, it is the leading candidate. It is also a variable source that would benefit from being able to produce hydrogen when its electricity is not needed and to add fuel-cell generation when electricity demand exceeds what the wind turbines can provide. The combination also benefits because electrolyzers require direct current and wind turbine power is produced as direct current before conversion back to alternating current suitable for the electric grid [4].

In recent years, considerable research and interest has been given to the potential use of hydrogen as a nonpolluting energy source, in particular, the use of hydrogen in chemical fuel cells, in which the gas reacts with the oxygen from ambient air to directly produce an electric current. Although this has an immediate appeal for environmentalists, it remains to be seen whether the total production and use cycle can really achieve a lower environmental impact than the existing energy production methods.

Based on current production methods, which involve steam reforming of natural gas, hydrogen cuts carbon dioxide emissions for each kilometer driven by up to 30% compared with conventional petrol and diesel cars. A study sponsored by a European Union Commission and completed in 2010 shows that the 95% reduction target can be achieved by 2050 with the help of various hydrogen production methods, with an increasing share of renewable sources in the mix.

In its “balanced” scenario, the study assumes that fuel-cell vehicles will account for 25% of all cars on the road by 2050. This requires an investment of around three billion euros in a Europe-wide hydrogen refueling infrastructure by 2020. Expressed as a percentage of the total cost of ownership, this corresponds to a mere 5% [5].

Although the actual use of hydrogen in a fuel cell produces only energy and water as a by-product, it is in the actual production of hydrogen as previously discussed that the environmental effects of carbon dioxide and carbon monoxide releases are realized. With the current ability to use fuel cells with existing fuel sources such as methane and methanol, the pursuit of a purely hydrogen fuel cell may not be the environmental solution that is often implied by its proponents. However, the increased efficiency and use of renewable resources (including solar) to generate hydrogen may overcome this barrier.

It is estimated that the global hydrogen production capacity required to replace the entire current fossil fuel-based energy system would need to be of the order of about 2,500 Tg H_2 yr^{-1} [7]. The United States used about 177 billion gallons of gasoline for transportation in 2009 [8].Using one type of commercial electrolyzer, one can make 0.38 kg of gaseous hydrogen per gallon of water. Conversion of the current US light-duty fleet (some 230 million vehicles) to fuel-cell vehicles would require about 110 billion gallons of water/year to supply the needed hydrogen. For comparison, the United States uses about 300 billion gallons of water/year for the production of gasoline [9], about three times the amount needed for hydrogen. However, that amount is used and recycled, not consumed as it is in the hydrogen production process. Domestic personal water use in the United States is about 4,800 billion gallons/year.

For an estimate of the amount of water needed for hydrogen-powered fuel-cell vehicles, assume a vehicle fuel economy of 60 miles per kg of H_2 (the Honda FCX Clarity gets 72), that vehicle miles traveled $= 2.6 \times 10^{12}$ miles/year, and that you can make 0.38 kg of H_2 from 1 gal of water using Proton Energy System’s H6m Electrolyzer. Total water required for the US fleet $= (2.6 \times 10^{12}$ miles/year)(1 kg of H_2/60 miles)(1 gal H_2O/0.38 kg of H2) $= 1.1 \times 10^{11}$ gal of H_2O/year. This represents the water used directly for fuel. If one considers all water uses along the chain; for example, from construction of wind farms to the electrolysis systems (life cycle assessment), then the total water use would be in the range of 3.3×10^{11} gal H_2O/year.

For a detailed description of the electrolytic process of hydrogen generation, also see Chap. 22. The energy required to produce hydrogen at atmospheric pressure via electrolysis (assuming 1.23 V) is about 32.9 kWh/kg. A kilogram is about 2.2 lb. For 1 mole (2 g) of hydrogen the energy is about 0.066 kWh/mole. Compressing or liquefying the hydrogen would take additional energy. One company produces hydrogen through electrolysis at about 7,000 psi at an energy usage of about 60 kWh/kg Hydrogen.

Because a Watt is Voltage × Current, this is equivalent to Power × Rate × Time. The power in this case is the voltage required to split water into hydrogen and oxygen (1.23 V at 25°C). The rate is the current flow and relates directly to how fast hydrogen is produced. Time, of course, is how long the reaction runs. It turns out that voltage and current flow are interrelated. To run the water splitting reaction at a higher rate (generating more hydrogen in a given time), more voltage must be applied (similar to pushing down on the accelerator of a car; more gas is used to make the car go faster.) For commercial electrolysis systems that operate at about 1 A/cm^2, a voltage of 1.75 is required. This translates into about 46.8 kW-hr/kg, which corresponds to an energy efficiency of 70%.

Lowering the voltage for electrolysis, which will increase the energy efficiency of the process, is an important area for research [11].

The one possible solution to effective renewable energy from water may be in the current research centered around catalytic thermal decomposition of water using solar energy. In this process, first developed by the Solar Hydrogen Energy

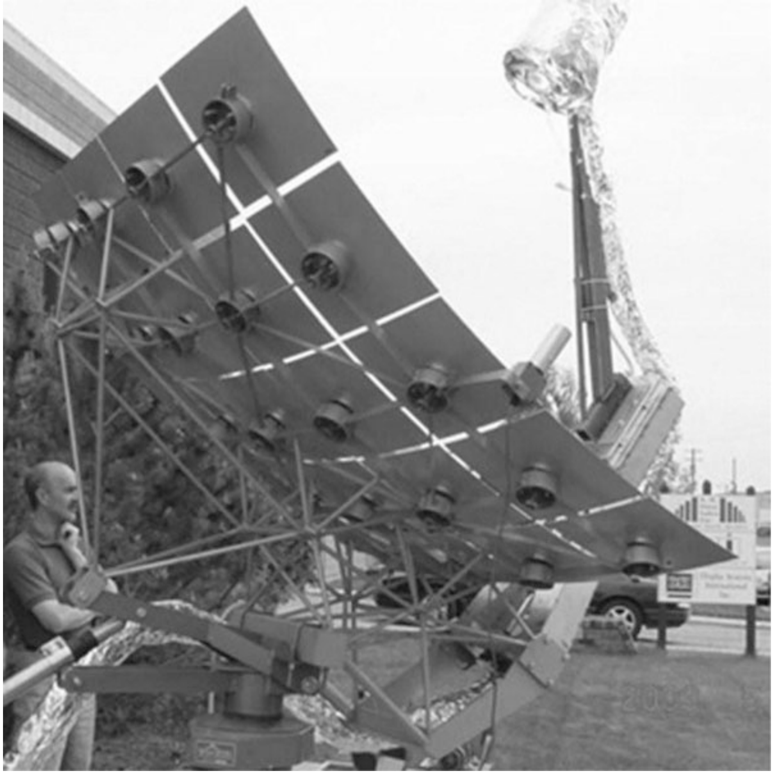

Fig. 27.7 Solar Hydrogen Catalytic Generator—small-scale prototype. (Courtesy of SHEC LABS.)

Corporation (SHEC) in Canada and now pursued in multiple laboratories, including the Global Photonic Energy Corporation in the United States, water is catalytically broken down into hydrogen and oxygen. The unique application of solar energy as the driving force, enhanced by the catalytic system, bypasses the usual thermodynamic barrier of standard electrolysis, which requires more energy (from a fossil fuel source) to generate the hydrogen than the energy that can be obtained from the hydrogen in a fuel cell (Fig. 27.7).

Other options proposed, such as the use of ammonia as a fuel, are still based on the production of hydrogen as the primary feedstock for the alternative fuels [12].

There are many applications for hydrogen. It is used to make fertilizers, as the active ingredient in detergents, and in the manufacture of polyurethanes. It finds application in the production of semiconductor devices, in the process of refining crude oil, in food processing for edible oils and shortening, and as fuel for the space shuttle. The hydrogenation of edible oils in soybeans, fish, cottonseed, and corn produces solids used in shortening and other foods. Many alcohols also are produced by the hydrogenation of the corresponding acids and aldehydes. It is possible to use hydrogen in low concentrations as a physiologically inert gas for a breathing atmosphere where multiple gases are involved. Hydrogen is an important gas in several semiconductor-manufacturing stages. It is used as a protective atmosphere in silicon crystal growth, as a reactant and carrier gas during semiconductor chip manufacturing, and as a reducing atmosphere for sintering and the bonding of leads to the finished chip [1].

The world economy currently consumes about 42 million tons of hydrogen per year. About 60% of this becomes feedstock for ammonia production and subsequent use in fertilizer (ORNL, 2003). Petroleum refining consumes another 23%, chiefly to remove sulfur and to upgrade the heavier fractions into more valuable products. Another 9% is used to manufacture methanol (ORNL, 2003), and the remainder goes for chemical, metallurgical, and space purposes (Holt 2003) [14].

Some recent worldwide hydrogen production totals are shown below [14]:

Origin	Amount in billions (Nm$_3$/year)	Percent
Natural gas	240	48
Oil	150	30
Coal	90	18
Electrolysis	20	4
Total	500	100

Each year, the United States uses more than nine million tons (about 90 billion normal cubic meters, 3.2 trillion standard cubic feet) of hydrogen, 7.5 million tons of which are consumed at the place of manufacture. The remaining 1.5 million tons are considered to be “merchant” hydrogen, or hydrogen that is sold. Today, most of this hydrogen is used as a chemical, rather than a fuel, in a variety of commercial applications [14]:

- Commercial fixation of nitrogen from the air to produce ammonia for fertilizer (about two-thirds of commercial hydrogen is used for this)
- Hydrogenation of fats and oils, in which vegetable oils are changed from liquids to solids; shortening is an example of a hydrogenated oil
- Methanol production, in hydrodealkylation, hydrocracking, and hydrodesulphurization
- Welding
- Hydrochloric acid production
- Metallic ore reduction
- Cryogenics and the study of superconductivity (liquid hydrogen)
- Preventing oxidation in the manufacturing of semiconductors
- Cooling turbines (hydrogen transfers heat very well)
- Hydrogen's main use as a fuel is in the space program. Today hydrogen fuels both the main engine of the Space Shuttle and the onboard fuel cells that provide the Shuttle's electric power.

Merchant hydrogen will remain the largest and fastest growing product in the US refinery chemical market. Advances will be driven by tightening sulfur standards for diesel fuels. Such environmental regulations promote the use of hydrotreating as a means of removing sulfur and other contaminants. As of 2010, diesel fuel must meet a 15 part-per-million (ppm) sulfur limit, and going forward, significant sulfur reductions are also expected for heating oil. Hydrocracking represents another growth application for merchant hydrogen, as US refineries continue to expand their hydrocracking capacity in efforts to boost gasoline and diesel fuel yields [16].

In the metals industry, hydrogen is used for applications such as annealing metals. It is also used as a fuel in underwater oxy-hydrogen torches and with oxy-hydrogen welding and cutting systems. Hydrogen serves as a nonoxidizing shield alone or with other gases in furnace brazing and in welding aluminum, magnesium, and lead. The temperature in the oxy-hydrogen flames is about 4,000°F, which is suitable for low-temperature welding and brazing. Oxy-hydrogen flames are used in the fabrication of quartz and glass, and hydrogen is used as a protective atmosphere in the float glass process whereby molten glass is floated on a pool of liquid tin. Atomic hydrogen welding is suitable for very thin stock and can be used with virtually all nonferrous alloys. In the process, an arc with a temperature of about 11,000°F is maintained between two nonconsumable metal electrodes. Molecular hydrogen fed into the arc is transformed into atomic hydrogen, which sends heat from the arc to the weld zone. At the surface of the welding area the atomic hydrogen recombines with molecular hydrogen, with the release of heat.

Liquid hydrogen is very important as a fuel for powering missiles and rockets. It is used in laboratory research on the properties of some materials at cryogenic temperatures, work often associated with studies of superconductivity. Liquid hydrogen can be used as a fuel, for either propulsion or heating.

Hydrogen gas is shipped in high-pressure gas cylinders and high-pressure cylinder trailers. Liquid hydrogen is shipped in insulated portable containers and in cryogenic tankers. The normal liquid hydrogen supply system utilizes a cryogenic stationary storage tank rated at 150 psig, just below the critical pressure of hydrogen. A cryogenic pumping station, which has a liquid hydrogen storage tank, a high-pressure cryogenic pump capable of supplying liquid hydrogen at 3,000 psig, and high-pressure gas storage tubes, often is used to supply large quantities at pressure above 150 psig.

Helium

Helium was discovered during a solar eclipse as an orange line in the spectrum of the sun's atmosphere. Physically, helium is colorless, odorless, and tasteless; and it is the second lightest element, second only to hydrogen. Helium is chemically inert and has only a 5 ppm concentration in the atmosphere (0.0005%).

Small amounts of helium are extracted from the atmosphere by fractionation methods, but not commercially because of the small amount of helium in the atmosphere. A number of natural gas wells contain helium, which can be recovered by a liquefaction and stripping process. Natural gas containing at least 0.2% helium has been found in the American Southwest, where the natural gas fields are the major US source of helium. Those helium-rich fields are within 250 miles of Amarillo, Texas; other helium-bearing fields have been found in Saskatchewan, Canada, and in areas near the Black Sea.

Helium cannot be synthesized; so conservation and cleanup recycle systems for "spent" gas are important means of preserving the earth's helium resources. One of helium's first uses was as a nonflammable replacement for hydrogen for inflation of lighter-than-air aircraft. Today liquid helium is vitally important in cryogenic research, as it is the only known substance to remain fluid at temperatures near absolute zero. It has a unique use as a refrigerant in cryogenics and is the only nuclear reactor coolant that does not become radioactive. Liquid helium is used extensively with superconducting magnets; in the medical field, it is used to cool the superconducting magnets for magnetic resonance imaging (MRI). It is used to purge and pressurize NASA vehicle liquid hydrogen tanks because it is the only gas that remains a vapor at liquid hydrogen temperatures.

Helium has a variety of other uses in welding and lighting. It is used as an inert gas shield in arc welding, for filling cold weather fluorescent lamps, and to trace leaks in refrigeration and other closed systems. Also helium is used for specialized purging and pressurizing applications. Helium can be used in place of or together with nitrogen as the inert portion of the atmosphere in sealed environments such as space vehicles, deep-sea submergence vehicles, and diving suits. The use of helium shield gas in a plasma arc furnace is a popular method for melting precious metal ores and scrap. Helium is very important for use in lasers and fiber-optic production, as well as in the production of germanium and silicon crystals for semiconductors.

Gaseous helium is stored and transported in high-pressure gas cylinders, high-pressure gas trailers, and portable cylinder modules. Liquid helium is transported in liquid cylinders, portable tanks, and cryogenic tankers. Because of the extremely low temperature of liquid helium and the cost of producing it, special design considerations must be given to storage containers in order to maintain the helium in the liquid phase. Some containers are designed to include a sacrificial liquid nitrogen shield that intercepts heat before it is transferred into the liquid helium.

Carbon Dioxide

The carbon dioxide market in the United States is served by gaseous, liquid, and solid carbon dioxide. The consumption of carbon dioxide gas is approximately 25 million tons per year with the enhanced oil recovery and urea production markets being the primary consumers. Liquid and solid consumption is about 7.5 million tons per year, serving primarily the food and beverage processing industries [21]. Carbon dioxide is used extensively in a variety of areas. It is used for pressurizing, and as a source of the bubbles and the acidic taste in soft drinks. Carbon dioxide is used to fill a type of fire extinguisher that literally depends on the inertness of the compound. Carbon dioxide is also used in freezing specialty and quality foods. Supercritical carbon dioxide (a dense, high pressure, single-phase form) is finding many new applications in pharmaceutical processing, plastics recycling, dry cleaning, flavor and fragrance extractions, and other solvent-based processes [1].

More specifically, each physical phase of carbon dioxide has uses in many areas. Gaseous carbon dioxide is used for pH control in water treatment and as a growth stimulant for plant life. It has been used successfully as a grain storage fumigant against pests and as a wide area mosquito lure to enhance chemical spraying effectiveness. Alone and in combination with other gases, carbon dioxide in food packaging extends the freshness and shelf-life of many products. It is second only to argon as a welding shield gas, and is used for flammable tank purging and inert blanketing of reactive liquids. Liquid carbon dioxide has multiple applications as a rapid, controllable refrigerant. It is used in one case as an expendable refrigerant for low-temperature testing of aviation, missiles, and electronic components. Carbon dioxide is also used in controlling chemical reactions and for stimulation of oil and gas wells. It is used extensively in food chilling and freezing applications, both in processing and in transportation.

Solid carbon dioxide, commonly called “dry ice,” is used extensively as a refrigerant for dairy products, meat products, and other frozen foods while in transit. It is also used as a cooling agent in many industrial processes such as grinding heat-sensitive materials, cold-treating metals, shrink-fitting machinery parts, in vacuum cold traps, in cryo-surgery, and specimen preservation and storage. It is used as a residue-free abrasive cleaner for many industrial equipment cleaning applications through the use of special air-driven particle blasting machines.

Carbon dioxide is usually nonreactive and nontoxic. At normal atmospheric pressure and temperature, it is colorless and odorless. Carbon dioxide will not burn, nor will it support combustion. Unrefined carbon dioxide gas is typically obtained from the combustion reaction of coal, coke, natural gas, and other carboniferous fuels. Other major sources are ethanol fermentation plants and the development of landfill gases as renewable sources.

The gas obtained is liquefied and purified by several different processes to a purity of about 99.99%. The major source of carbon dioxide is as a by-product of steam–methane reforming. The resulting reformer syngas may utilize one of the following three processes in the production of carbon dioxide. Recovery of pure carbon dioxide from reformer syngas has most often been accomplished through absorption by liquid solvents. The solvents used are monoethanolamine (MEA), diethanolamine (DEA), and methyl diethanolamine (MDEA).

A hot potassium carbonate solution may also be used in some applications (see Fig. 27.8 for the process flow diagram). In this process, the syngas stream from the reformer is sent to the stripper column where the carbon dioxide is absorbed by the solvent. The residual gas stream components are discharged from the stripper column. The carbon dioxide in solvent is sent to the regeneration column where the carbon dioxide is regenerated and discharged for further purification by compression dehydration and

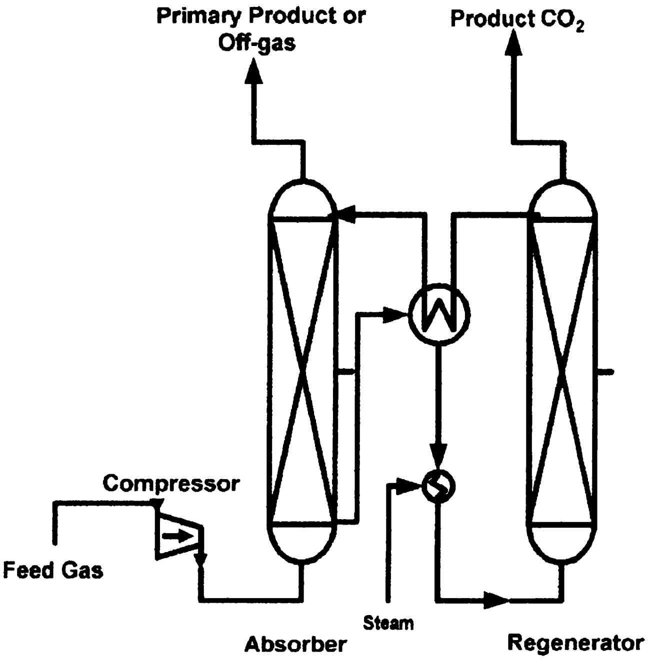

Fig. 27.8 CO_2 recovery by solvent adsorption process. (Courtesy Process Systems Consulting, Inc.)

refrigeration steps. The solvent is returned to the stripper column. The final product is essentially 99.99% pure.

Carbon dioxide may be manufactured at 95% purity by the membrane separation process from a similar gas or from natural gas [18, 19, 22]. In the recovery of high-purity carbon dioxide from the syngas or natural gas, and before any separations can occur, a pretreatment step removes any contaminants and any condensate liquids that may be present. The feed gas then enters the membrane system at 300–1,000 psig. The permeate gas is delivered at pressures between 50 and 150 psig and at a carbon dioxide purity of about 95%. The high-pressure residual gas containing 10–30% carbon dioxide enters a conventional treatment process such as MEA or DEA for a final cleanup. The carbon dioxide off-gas from the conventional treatment process is then elevated to the same pressure as that of the permeate gas from the membrane systems.

The combined streams may be further compressed to higher pressures, such as 2,000 psig for applications in carbon dioxide flooding in enhanced oil recovery. The third process used in the production of carbon dioxide is PSA. The feed gas usually contains approximately 20% carbon dioxide, 70% hydrogen, and the remainder methane, carbon monoxide, nitrogen, and water. The feed gas is typically under a pressure of 125–400 psig at temperatures of 80–120°F. The carbon dioxide and water are strongly adsorbed in the adsorb beds and the residual gas stream is depressurized for further recovery. The adsorber vessel is then evacuated through vacuum blowers where the carbon dioxide, which has been adsorbed by the bed, is released at purities of essentially 99%.

Carbon dioxide produced from ethanol fermentation plants or landfill gas may be recovered with similar processes. Unique to the fermentation plant is the ability to recover the carbon dioxide directly from the ethanol distillation tower, followed by a secondary water wash. Final purification and liquefaction stages then follow the normal process flow. Landfill gas recovery is unique in requiring essentially the removal of the methane and trace impurities [10, 23]. Several processes exist to provide two gas products (via membrane separation), a liquid methane and gaseous carbon dioxide stream (via the CryoFuel® system), or a gaseous methane and liquid carbon dioxide stream (via the Acrion® process). The Acrion® system is unique in that it uses the carbon dioxide as part of the purification process instead of relying on additional chemical treatments. Figure 27.9 shows the process flow diagram for the Acrion® system. Liquid carbon dioxide is normally stored in a foam-insulated tank that has a refrigeration unit to maintain the tank temperature and pressure.

Liquefied Natural Gas

(For Methane, or Compressed Natural Gas, See Chap. 20, Methane)

The primary advantage of LNG over gaseous natural gas is the cost and space savings due to the tremendous change in the product volume. Over 600 standard cubic feet of natural gas occupy only 1 ft^3 of space in its liquid form at −260°F and atmospheric pressure. This significant volume reduction reduces the storage and transport volume, and allows shipment of natural gas in areas where pipelines were never feasible.

The primary vehicle for transporting LNG is the cryogenic tanker. It also is transported in specially designed ships. LNG comes primarily from natural underground reservoirs. Significant quantities are now being recovered from both landfill sources and bioreactor sources around the world. LNG is composed predominantly of methane, which may contain minor quantities of ethane, propane, nitrogen, helium, and other components normally found in natural gas.

In the past the liquefaction of natural gas used a classic cascade cycle. The process required 120,000 hp for liquefaction of over 150 million standard cubic feet (mmscf) per day. Provisions are made for some of these cycles to use seawater for cooling. Later, baseload LNG plants utilized mixed refrigerant cycles, such as Air Products and Chemicals, Inc.'s propane precooled mixed refrigerant system. Baseload plant capacities range from about 70 mmscf/day to about 350 mmscf/day of LNG. Baseload plants move LNG from remote sites by ship to populated

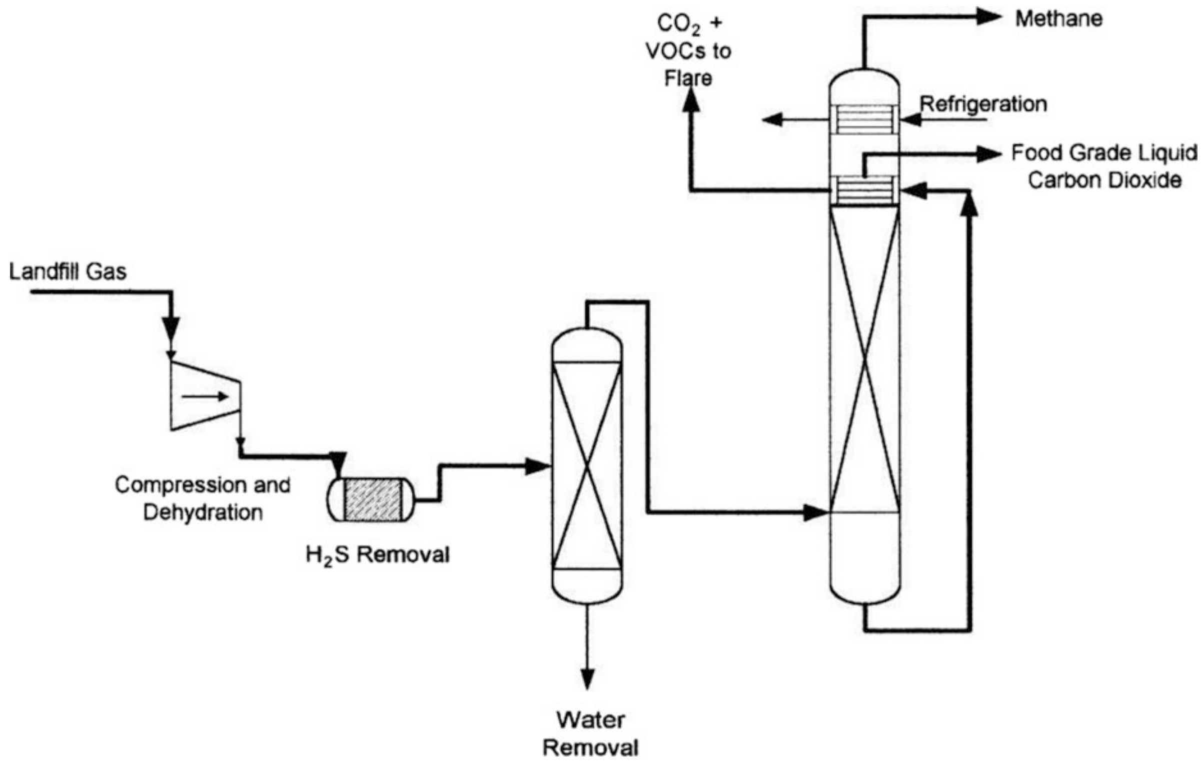

Fig. 27.9 Acrion CO_2 wash process flow diagram. (Courtesy Acrion Technologies, Inc.)

areas. For example, Indonesia and the United Arab Emirates supply LNG to Japan for electric power generation [10].

At baseload LNG production plants, natural gas enters the plant at near 85°F and 600 psig. The gas is treated to remove carbon dioxide and any sulfur compounds, and it is cooled with high-level propane refrigerant to remove as much water as possible. Dehydration to a dew point of about −100°F is done by carrying out regeneration with dried outlet gas by way of a high-pressure steam heater and a regeneration gas compressor. The dry, treated gas is passed through a stationary bed of activated carbon for removal of mercury, and is cooled with two successively lower levels of propane refrigeration. A scrub column flows to a fractionation train, which consists of a deethanizer, a depropanizer, and a debutanizer where relatively pure ethane and propane are produced. Excess ethane, propane, and butane from the fractionation process are reinjected into the main gas stream just prior to liquefaction. The overhead from the scrub column flows to the main heat exchanger for liquefaction to LNG. Figure 27.10 shows the process flow for an LNG plant [24]. For years LNG has been used for peakshaving purposes, which is the storage of excess capacity of LNG to be revaporized for the coldest days of the year [25]. In recent years LNG has been used in heating and vehicle propulsion. Also LNG is used to produce carbon black, which has applications in the manufacture of rubber products and printing ink. The burning of high-purity LNG (methane) is done to make carbon black for particular use in electronic devices.

Acetylene

Acetylene (C_2H_2) is a colorless and flammable gas. At 100% purity, acetylene is odorless, but at commercial purity it has a garlic-like odor. Acetylene can be liquefied and solidified with ease, although in both cases it explodes with extreme violence when ignited. Acetylene can be inhaled in rather high concentrations without chronic, harmful effects. In fact, it has been used as an anesthetic. However, it is a simple asphyxiant if present in concentrations high enough to deprive the lungs of oxygen and produce suffocation [1].

A primary method for the manufacture of acetylene is to react calcium carbide, the principal raw material, with water to produce acetylene with calcium hydroxide as a by-product:

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$$

Acetylene also is manufactured by thermal or arc cracking of hydrocarbons and by a process utilizing the partial

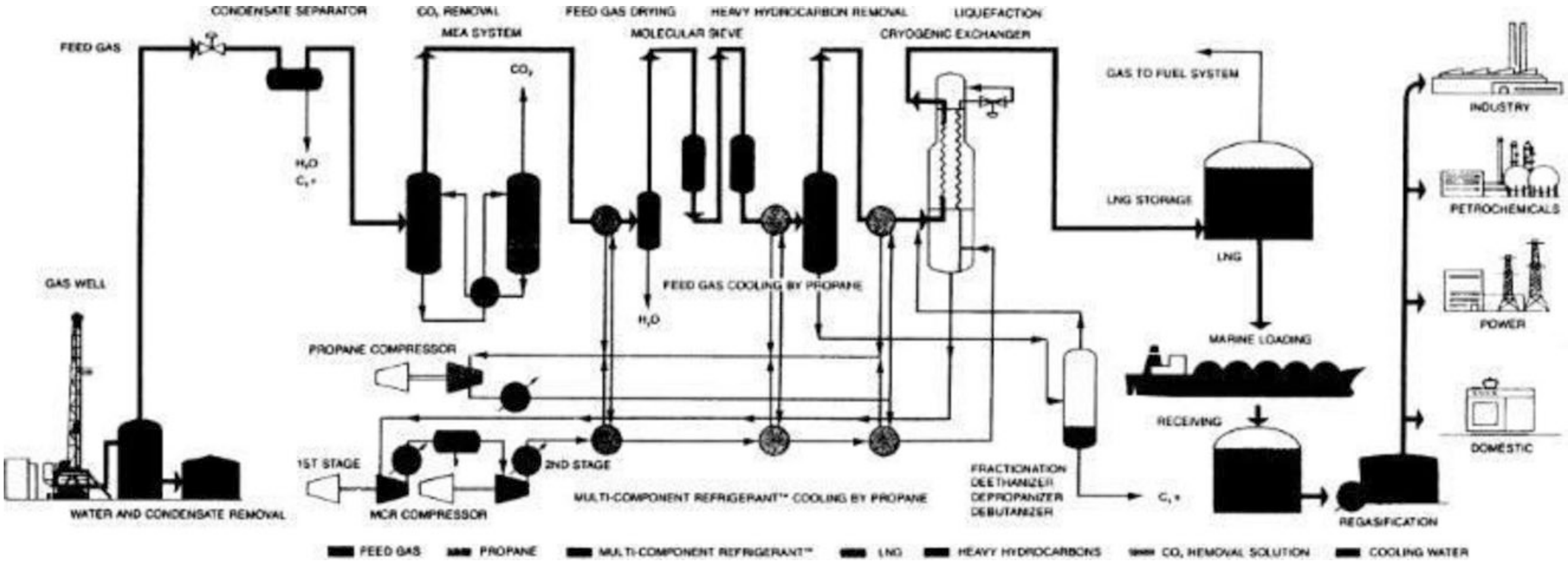

Fig. 27.10 Schematic of process flow for a baseload LNG plant. (Courtesy Air Products and Chemicals, Inc.)

combustion of methane with oxygen. The acetylene produced from calcium carbide is basically pure, with only water and air as impurities. Eighty percent of the acetylene produced is used for chemical synthesis.

Acetylene is an important raw material for a series of organic compounds such as acetaldehyde, acetic acid, acetic anhydride, acetone, and vinyl chloride. Those compounds are used to manufacture a large group of products, including plastics, synthetic rubber, dyestuffs, solvents, and pharmaceuticals, and in the manufacture of carbon black. The other 20% is used for oxy-acetylene welding, cutting, heat treating, lighting purposes, buoys, and beacons [1].

In the primary method for producing acetylene, calcium carbide is fed into a generator containing water. The resulting wet acetylene gas at 120–140°F is piped to a cooler condenser where it is cooled to 80–90°F and the water vapor is condensed. This is the first step in the drying process. The gas then goes to a low-pressure dryer filled with calcium chloride. The calcium chloride absorbs the moisture from the acetylene gas, which then enters a compressor, where the pressure is increased to 200–375 psig. An oil separator filters out excess impurities and oil. The gas next goes to a high-pressure dryer, where all remaining water is removed. The gas is then pumped into cylinders for shipment. The by-product, calcium hydroxide, is sent to a storage tank, where water is decanted off the top, and is recovered.

The only method of distributing acetylene, other than pipeline, is by means of portable steel tanks containing a porous solid filler saturated with acetone or other suitable solvent, in which the acetylene is dissolved under pressure. Acetylene alone is not handled at pressures higher than 30 psig because of its tendency to decompose explosively. Dissolved in acetone it may be stored at pressures of 150–250 psig.

Nitrous Oxide

Nitrous oxide (N_2O), commonly known as laughing gas, is a colorless and virtually odorless, tasteless, nontoxic gas. Nitrous oxide is an oxidizer that will support combustion, but it is a nonflammable gas. It is water-soluble; but when it is dissolved, its acidity does not change. The primary commercial method for producing nitrous oxide is by thermal decomposition of ammonium nitrate, with nitrous oxide and water in the primary reaction:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

The impurities formed are mostly high oxides of nitrogen and are highly toxic. After the water is removed in a condenser, the gas is washed in a solution of potassium dichromate to remove nitric oxide, in caustic to remove nitric acid, and finally in water. Nitrous oxide is an inhalant type of anesthetic or analgesic gas. It serves as a propellant for various aerosol products, particularly with foods such as whipped cream; and it is used as an oxidizing agent in blow-torches, atomic spectroscopy instruments, and in the manufacture of various compounds, both organic and inorganic. It also serves as fuel oxidant in rocket fuel and high-performance vehicles, and it is used as part of the working fluid in hypersonic wind tunnels that have been investigated recently. It has applications in cryosurgery similar to nitrogen [1].

Nitrous oxide is contained and transported in its liquid phase in high-pressure gas cylinders or in liquid cylinders. It is transported as a liquefied compressed gas under high pressure in cylinders and at lower pressures and reduced temperatures in refrigerated cargo tanks and insulated portable tanks. Nitrous oxide is stored in a foam-insulated tank accompanied by a refrigeration unit, which is similar to the tank used for carbon dioxide.

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