

Chapter 4

Industrial Gases

Industrial gases perform varied and essential functions in our economy. Some are raw materials for the manufacture of other chemicals. This is particularly true of oxygen, nitrogen, and hydrogen. Nitrogen preserves the flavor of packaged foods by reducing chemical action leading to rancidity of canned fats. Some gases are essential medicaments, like oxygen and helium. However, many of these gases, their liquids, and their solids have a common application in creating cold, by absorbing heat upon evaporation, by performing work, or by melting. In past decades, the outstanding examples of this have been liquid carbon dioxide and dry ice. On the other hand, with the modern expansion of industry, a new division of engineering has arisen called *cryogenics*.¹ This widely embracing term pertains to the production and use of extreme cold at temperatures below -100°C . The term has been applied very extensively during the last decade and is exemplified by the use of liquid hydrogen, oxygen, and fluorine in missiles for military and space projects. New cryogenic techniques have been worked out, reducing the cost of liquefaction, and improving and simplifying the equipment used for storage, handling, and shipment of very cold liquids and gases. The economic advantage of using cryogenic liquids is apparent when it is realized that a cylinder weighing 113 kg contains 169 kg of liquid oxygen (equivalent to 126 m^3 of gaseous oxygen at normal temperature and pressure). Eighteen small cylinders of gaseous oxygen contain a total of 166 kg of oxygen gas at a pressure of 15 MPa, but they weigh 1090 kg. Cryogenic liquids are stored and shipped in tanks or large tank cars² built on the multiple-walled vacuum bottle (Dewar) principle. The value of cryogenic³ gases, oxygen, nitrogen, argon, helium, and hydrogen (merchant only), amounted to \$1250 million in 1980. Of that total, oxygen accounted for \$500 million, nitrogen \$450 million, and hydrogen \$110 million.

These cryogenic, or supercold, temperatures cause fundamental changes in properties of materials. Cryogenics is being applied to rocket propulsion, infrared photoptics, and electronic data processing, with newer applications in magnetics and high-vacuum pumping. The major application of cryogenics to the chemical field is in the manufacture of nitrogen for ammonia production, and in metallurgy, where the use of oxygen hastens (by 25 percent or more) the production of steel in open-hearth furnaces, converters, and even in blast furnaces for pig iron. Cryogenics,⁴ in manufacturing low-temperature liquids, has long applied the

¹From the two Greek words meaning "the making of cold."

²New Tank Car Hauls Liquid H_2 from Florida to California, *Chem. Eng.* 69 (18) 66 (1961)

³Courtesy of Linde Division, Union Carbide Corp.

⁴See Perry, p. 11-10, 11-48 to 11-52, 12-49 to 12-53

following *fundamental principles*, and currently, most extensively to air and its constituents

1. Vapor compression with liquefaction if below the critical temperature of the gas in question
2. Interchange of heat in heat exchangers such as double-pipe units; refrigeration
3. Cooling of compressed gases by allowing them to perform work in expansion engines or turbines
4. Cooling of the liquids by evaporation
5. Separation of gases by difference in vapor pressure at the boiling point of the liquid mixture
6. Removal of contaminants by adsorption, freezing on surfaces, freezing followed by filtration of the cryogenic liquid, or by washing with an appropriate liquid

CARBON DIOXIDE

Carbon dioxide in liquid and solid forms has been known for over a century. Although Thilorier produced solid carbon dioxide in 1835 from the liquid material, it was not until 1924 that the solid product gained industrial importance through its first and still most important use for refrigeration. The production of merchant carbon dioxide in 1981 was about 3.6×10^6 t total for the gaseous, liquid, and solid forms.^{4a}

USES.⁵ By far the largest use of the solid form is for refrigerating and freezing ice cream, meat, and other foods. An added advantage is that a carbon dioxide atmosphere reduces meat and food bacteria spoilage. The solid form is also important as a source of carbon dioxide for inert atmospheres and occasionally for carbonated beverages. There are many other specialty uses, such as chilling aluminum rivets and shrink-fitting machine parts. The largest outlet of liquid carbon dioxide is for carbonated beverages. It is also important as a fire-extinguishing material. Gaseous carbon dioxide has many applications in the chemical industry, such as in the making of salicylic acid (Chap. 40).

Carbon dioxide has advantages over ordinary acids in neutralizing alkalies, because it is easily shipped in solid form, is noncorrosive in nature, and is light in weight. Chemically, it is equivalent to more than twice its shipping weight in sulfuric acid and about five times its weight in hydrochloric acid. It is finally gaining acceptance for pH control of wastewater after this use had been talked about for years.

With respect to food refrigeration, solid carbon dioxide is primarily a transport refrigerant. Its advantages cannot be attributed to any single factor but result from its dryness, its relatively high specific gravity, its excellent refrigerating effect, its low temperature, and the insulating and desiccating action of the gas evolved. Generally, about 450 kg of solid carbon dioxide will refrigerate an average car for a transcontinental rail trip without recharging. See Table 4.1 for a comparison of the properties of solid carbon dioxide and water ice. Liquid nitrogen has also entered this refrigerating field. The uses for all forms of CO₂, both merchant and captive, are: 40 percent for the production of urea, 35 percent for pressurizing oil wells for secondary oil recovery, 10 percent for refrigeration, 5 percent for beverage carbonation, and 10 percent for miscellaneous uses.

^{4a}t = 1000 kg.

⁵Yaws, Li, and Kuo, Carbon Oxides, *Chem. Eng.* 81 (20) 115 (1974); Key Chemicals, Carbon Dioxide, *Chem. Eng. News* 60 (29) 23 (1982).

Table 4.1 Comparison of Physical Properties of Solid CO₂ and Water Ice

Property	Solid CO ₂	Water Ice
Specific gravity	1.56	0.90
Sublimation point or melting point, °C	-78.5	0
Critical temperature, °C	30.9	365.6
Critical pressure, GPa abs.	7.38	19.72
Latent heat of fusion, kJ/kg	190.7	334.9
Latent heat of vaporization, kJ/kg	368.9	24.9×10^3
Weight of 1 m ³ of gas, kg	1.98	0.804
Weight of 1 m ³ of solid, kg	1441	913
Latent heat of sublimation, kJ/kg	576.8	
Refrigerating effect, kJ/kg	639.7	334.9

MANUFACTURE OF PURE CO₂.⁶ Although there are many sources of CO₂, the following four are the most important for commercial production:

1. Recovery from synthesis gas in ammonia production
2. Recovery as a by-product in the production of SNG (see Chap. 3)
3. Recovery from the production of ethanol by fermentation (Chap. 31)
4. Recovery from natural wells

An absorption system is used for concentrating the CO₂ gas to over 99% purity. In all cases the almost pure CO₂ must be given various chemical treatments for the removal of minor impurities that contaminate it. One of the reversible reactions long used for the concentration of CO₂ is



This reaction is forced to the right by increasing the partial pressure of the CO₂ and by reducing the temperature. It is forced to the left by heating the sodium bicarbonate solution. The absorption efficiency of 10 to 18% CO₂ is not very good. Other, usually more economical reversibly absorbing solutions are hot, concentrated potassium carbonate solution and monoethanolamine (Girbotol process, Chap. 3). The CO₂ available in these cases comes from the combustion of fuel oil in a boiler plant generating the required steam. To carry out this manufacture, the following principal sequences are employed:

Oil, natural gas, or coke is burned, giving heat for 1380 kPa steam and furnishing 10 to 15% CO₂ at 345°C.

Flue gas cooled, purified, and washed by passing through two water scrubbers.

CO₂ is removed by countercurrent selective absorption into an aqueous solution of ethanolamines.

CO₂-ethanolamine solution is pumped to a steam-heated reactivator.

CO₂ and steam leave the top of the reactivator passing through a CO₂ cooler to condense the steam, which returns to the tower as reflux.

⁶Perry, p. 16-36 and p. 16-42 for absorption of carbon dioxide, p. 3-162 for thermodynamic properties; ECT, 3d ed., vol. 4, pp. 725-742, 1978; Strelzoff, Choosing the Optimum CO₂-Removal System, *Chem. Eng.* 82 (19) 115 (1975).

CO₂ at about 200 kPa is purified from traces of H₂S and amines in a permanganate scrubber and dried.

CO₂ is compressed, cooled, and liquefied.

For "liquid" draw off from CO₂ receiver.

For dry ice:

Liquid CO₂ is reduced to atmospheric pressure, with consequent partial solidification. The evaporated gas returns through the precooler, and is recirculated, with recompression and recooling of CO₂.

CO₂ "snow" is compressed to form a cake.

Dry ice cakes are generally sawed to 25-cm cubes of approximately 23-kg weight.

A typical flowchart for continuously producing either liquid or solid and showing the sequences of these unit operations and chemical conversions is shown in Fig. 4.1. In the merchandising of liquid CO₂, the energy (hence expense) involved in handling the cylinders, full and empty, is so great that bulk cryogenic shipment of relatively low pressure liquid *cold* CO₂ is now being practiced to reduce container cost and weight. If heat exchangers are properly designed, it is necessary to buy little outside energy for solid CO₂ and none for liquid CO₂ (Fig. 4.1). The live steam generated by the boiler is sufficient to power the turbines for pumping and compression, and the exhaust steam from turbine-driven compressors boils off the CO₂ from the amine solution in the reboiler. The condensate from the reboiler is returned to the water boiler.

Another source of CO₂ is the fermentation industry, as described in Chap. 31. If yeast is used, alcohol and CO₂ are produced, and certain other microorganisms generate solvents and a gaseous mixture of H₂ and CO₂. The yield of CO₂ varies with the mode of fermentation. From 50 kg of starchy material such as corn, 17 L of 190-proof ethyl alcohol and 14 kg of CO₂ are obtained. The recovery and purification of CO₂ from fermentation differ from the absorption system in that the temperature seldom exceeds 40°C so that no special cooling is necessary and the CO₂ content of the gas usually starts above 99.5%. When the fermentors are sealed for the recovery of the gases, a purer and higher yield of CO₂ is obtained, and the yield of alcohol is increased by at least 1 percent by alcohol recovery from the CO₂ scrubbers.

A typical CO₂ recovery from fermentation is illustrated in the flowchart in Fig. 4.2. Here purification consists of oxidation of the organic impurities and dehydration by means of chemicals in liquid form. The gas from the fermentors is passed through three scrubbers containing stoneware spiral packing and on to the gasometer. The first scrubber contains a weak alcohol solution which acts as a preliminary purifier and removes most of the alcohol carried by the gas. The next two scrubbers, in which the scrubbing medium is deaerated water, remove almost all the water-soluble impurities. The scrubbing liquid is pumped either to the stills or to the fermentors for alcohol recovery.

From the gasometer the gas is conducted to a scrubber containing K₂Cr₂O₇ solution, which oxidizes the aldehydes and alcohols in the gas, and is then cooled. In the second scrubber, which contains sulfuric acid, oxidation is completed and the gas is dehydrated. The CO₂ leaving the acid scrubber contains some entrained acid which is removed in a packed tower over which a Na₂CO₃ solution is circulated. When the acid is neutralized, CO₂ is released. Before going to the compressor, the gas passes through a scrubber containing a small amount of glycerin, which absorbs the oxidized products and delivers an odorless gas to the compressor. The sulfuric acid, after being used for deodorization and drying, is pumped to the distillery, where it serves for pH control.

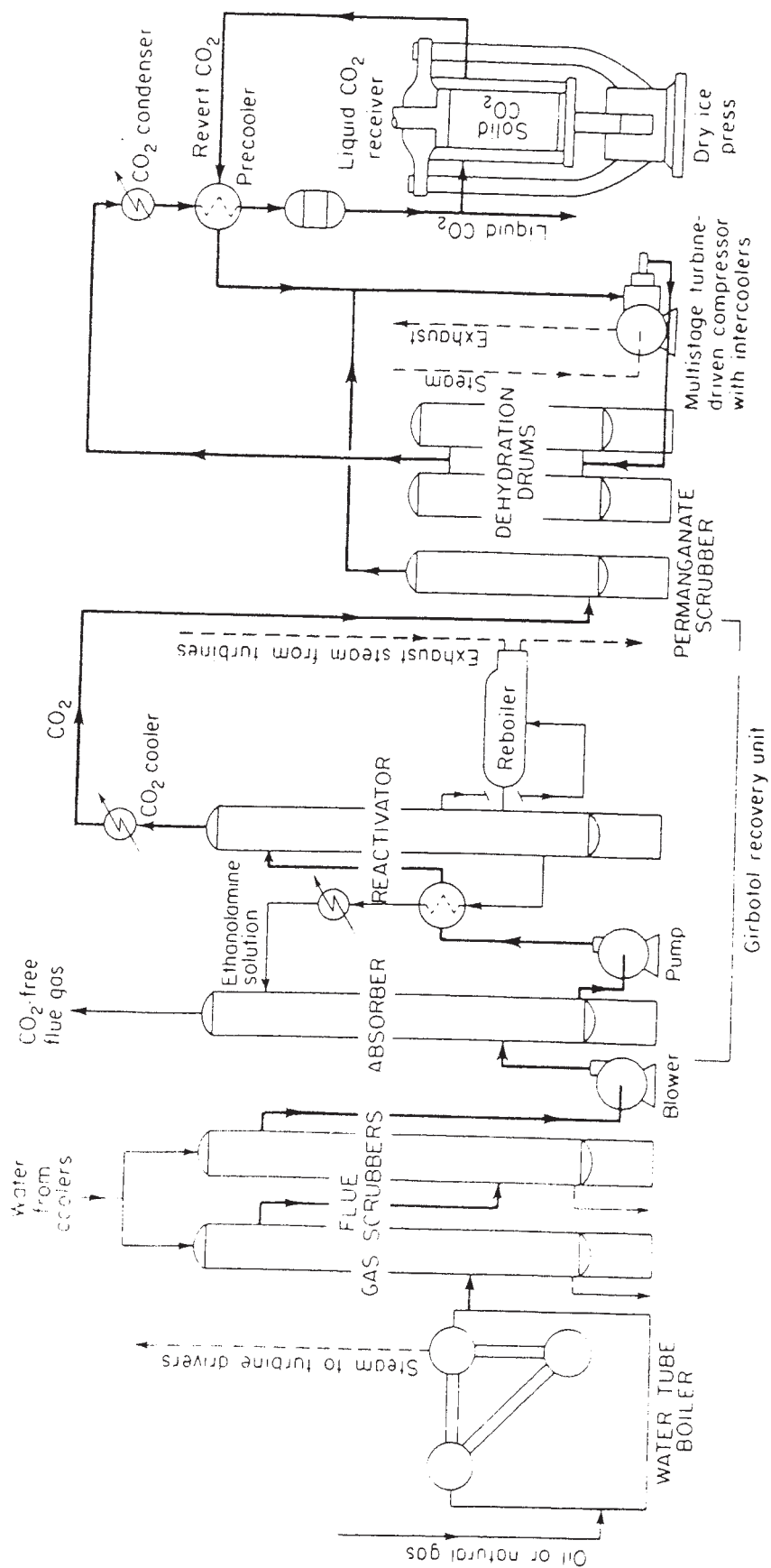
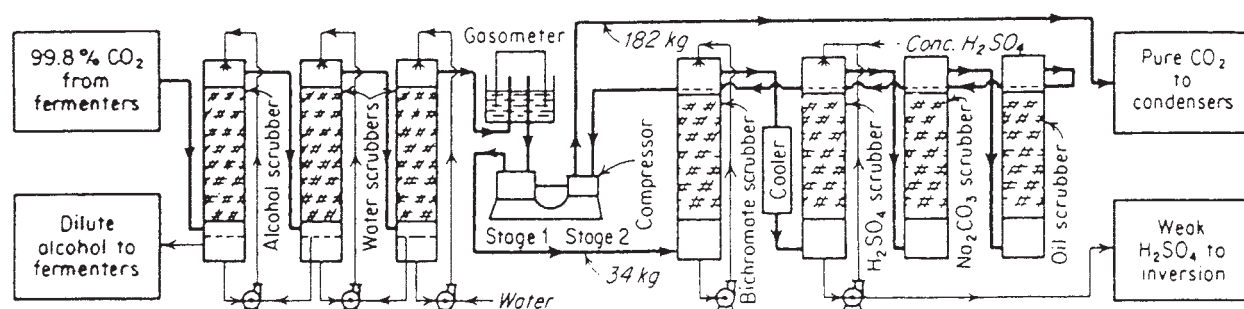


Fig. 4.1. Flowchart for CO₂ from fuel oil or natural gas (Girdler Corp.)



In order to produce 1 t solid CO_2 , the following materials and utilities are required.

Bichromate	180 g	Water	7600 L
Sodium carbonate	4.5 g	Electricity	17.8 MJ*
Oil	0.04 L	Direct labor	0.1 work-h
H_2SO_4 (66° Bé)	19 L†		

*Not including solid CO_2 compressing system.

†Weak H_2SO_4 all recovered for use in molasses fermentation.

Fig. 4.2. Flowchart for fermentation CO_2 purification.

HYDROGEN

USES AND ECONOMICS. Hydrogen has long been an important *gaseous* raw material for the chemical and petroleum industries. The annual production of merchant hydrogen is in excess of $3 \times 10^9 \text{ m}^3$ and is only a very small part of the total industrial production. Table 4.2 gives the hydrogen requirements for making some typical chemicals. Hydrogen is sold as gas and liquid. Liquid hydrogen is the most profitable, is produced by only three companies, and is shipped by tank car, truck, or barge. Gaseous hydrogen is made by many companies and is shipped in "tube trailers" holding about 4300 m^3 .⁷ The use of *metal hydrides* as *hydrogen*

⁷Key Chemicals—Hydrogen, *Chem. Eng. News* 59 (30) 19 (1981); The Changing Economics of Hydrogen, *Chem. Week*, 131 (24) 42 (1982); Snape and Lynch, Metal Hydrides Make Hydrogen Accessible, *CHEMTECH* 10 (9) 578 (1980); 10 (12) 768 (1980); Kelley, Escher, and van Deelen, Hydrogen Uses and Demands through 2025, *Chem. Eng. Prog.* 78 (1) 58 (1982); Hydrogen Economy Still in the Future, *Chem. Eng.* 89 (15) 17 (1982).

Table 4.2 Hydrogen Required for Typical Products

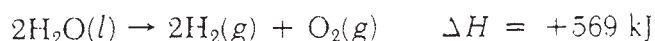
Raw Material to Be Hydrogenated	Product	Hydrogen Required at 150°C, m^3
Phenol	Cyclohexanol	787
Nitrogen	Ammonia	2645
Naphthalene	Tetralin	378
Olein	Stearin	82
Diisobutylene	Isooctane	1600
Carbon monoxide	Methanol	1715

SOURCE: Stengel and Shreve, Economic Aspects of Hydrogenation. *Ind. Eng. Chem.* 32 1212 (1940). All hydrogen requirements are per metric ton of product, except synthetic methanol and isooctane are per cubic meter.

sponges is increasing for storing hydrogen compactly at moderate pressure, that is 2 MPa, compared with 14 MPa of the common compressed hydrogen cylinder. The hydrides used are alloys of magnesium-nickel, iron-titanium, lanthanum-nickel, and misch metal-nickel.⁸

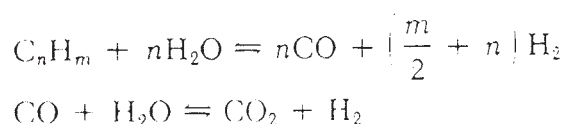
HYDROGEN MANUFACTURE. Hydrogen is derived almost exclusively from carbonaceous materials, primarily hydrocarbons, and/or water. These materials are decomposed by the application of energy, which may be electrical, chemical, or thermal. Examples include electrolysis of water, steam reforming of hydrocarbons, and thermal dissociation of natural gas (Chap 5). Hydrogen is also produced by partial oxidation of hydrocarbons and by such less important methods as the steam-iron process, water-gas and producer-gas processes, and separation from coke-oven⁹ gas and refinery off-gas streams. Diffusion through a palladium-silver alloy furnishes very high purity hydrogen.

Electrolytic Method.¹⁰ The electrolytic process produces high-purity hydrogen and consists of passing direct current through an aqueous solution of alkali, and decomposing the water according to the following equation:



The theoretical decomposition voltage for this electrolysis is 1.23 V at room temperature; however, because of the overvoltage of hydrogen on the electrodes and also cell resistance itself, voltages of 2.0 to 2.25 V are usually required. A typical commercial cell electrolyzes a 15% NaOH solution, uses an iron cathode and a nickel-plated-iron anode, has an asbestos diaphragm separating the electrode compartments, and operates at temperatures from 60 to 70°C. The nickel plating of the anode reduces the oxygen overvoltage. Most types of cells produce about 56 L (74.5 L, theoretically) of hydrogen and half as much oxygen per megajoule. The gas is about 99.7% pure and is suitable even for hydrogenating edible oils. The cells are of two types: the bipolar, or filter-press, type, where each plate is an individual cell, and the unipolar, or tank, type, usually containing two anode compartments with a cathode compartment between them. The unipolar cells may be open or closed tanks. In most installations the oxygen produced is wasted unless it can be used locally. Hydrogen is also obtained from other electrolytic processes, for example, electrolysis of salt brine (cf. Chaps. 10 and 11).

Steam-Hydrocarbon Reforming Process. This process consists of catalytically reacting a mixture of steam and hydrocarbons at an elevated temperature to form a mixture of H₂ and oxides of carbon. The following basic reactions occur:



⁸Misch metal is a mixture of crude rare-earth metals.

⁹New Nitrogen Plant, Geneva Works, Hydrogen Extracted from 252 Coke Ovens, *U.S. Steel Quart.* **11** (3) 1 (1957); U.S. Steel to Increase Chemicals Capacity: Hydrogen, etc., *Chem. Eng. News* **41** (41) 25 (1964).

¹⁰Pressure Lowers Electrolytic H₂ Cost, *Chem. Eng.* **67** (5) 60 (1960) (cell is operated at 3 MPa); Solid Electrolytes Offer Route to Hydrogen, *Chem. Eng. News* **51** (35) 15 (1973); *Chem. Eng.* **89** (7) 25 (1982).

Although the equations are shown for the general case of any hydrocarbon feed, only light hydrocarbons have been successfully used in commercial practice. Natural gas is most common, and propane and butane (LPG) are also frequently used. With the use of a specially prepared catalyst, naphtha is also a suitable feedstock.

The first reaction is the reforming reaction. It is highly endothermic, and the moles of product exceed the moles of reactant so the reaction goes to completion at high temperature and low pressure. Excess steam is normally used. Although the basic purpose is to prevent carbon formation, it also helps force the reaction to completion.

The second reaction is the water-gas-shift reaction. It is mildly exothermic and is favored by low temperature but unaffected by pressure. Excess steam also forces this reaction to completion and is so used. A catalyst is usually employed. Both these reactions occur together in the steam-reforming furnace at temperatures of 760 to 980°C. The composition of the product steam depends upon the process conditions, including temperature, pressure, and excess steam, which determine equilibrium, and the velocity through the catalyst bed, which determines the approach to equilibrium. A typical product contains approximately 75% H₂, 8% CO, and 15% CO₂; the remainder consists of nitrogen and unconverted methane.

For the production of additional H₂, the reformer is followed by a separate stage of water-gas-shift conversion. Additional steam is added, and the temperature is reduced to 315 to 370°C to obtain more favorable equilibrium conditions. A single stage converts 80 to 95% of the residual CO to CO₂ and H₂. Because the reaction is exothermic, the reactor temperature rises; this enhances the reaction rate but has an adverse effect on the equilibrium. When high concentrations of CO exist in the feed, the shift conversion is usually conducted in two or more stages, with interstage cooling to prevent an excessive temperature rise. The first stage may operate at higher temperatures to obtain high reaction rates, and the second at lower temperatures to obtain good conversion.

The process using propane is shown in Fig. 4.3, and the material requirements are listed in Table 4.3. This process¹¹ can be broken down into the following coordinated sequences:

Propane is vaporized by steam.

Propane vapor is desulfurized by contact with activated carbon to prevent deactivation of the catalyst.

Propane vapor mixed with steam is reformed (Fig. 4.4) over a nickel catalyst at about 815°C in alloy tubes in a combustion furnace (to furnish the heat for this endothermic reaction).

The gases H₂, CO, and some CO₂ are cooled to about 370°C, and the partial pressure of water increased by addition of steam or condensate, and passed over an iron oxide catalyst in the first-stage CO converter, where 90 to 95 percent of the CO is converted to CO₂ with more H₂. (This is the so-called shift,¹² or water-gas-conversion, reaction.)

These hot gases are first cooled by heat exchange with the gases leaving the first-stage CO₂ absorber before entering the second-stage CO converter, and finally by water to about 38°C.

¹¹Further details and other flowcharts as well as technical pamphlets on hydrogen should also be consulted. These are available from Girdler Corp., Louisville, Ky., Chemical Construction Co., New York, N.Y., and M. W. Kellogg Co., Houston, Texas; see also van Weenan and Tielrooy, Optimizing Hydrogen Plant Design, *Chem. Eng. Prog.* 83 (2) 37 (1983).

¹²Moe, Design of Water-gas Shift Reactors, *Chem. Eng. Prog.* 58 (3) 33 (1962). Rate equations for producing hydrogen.

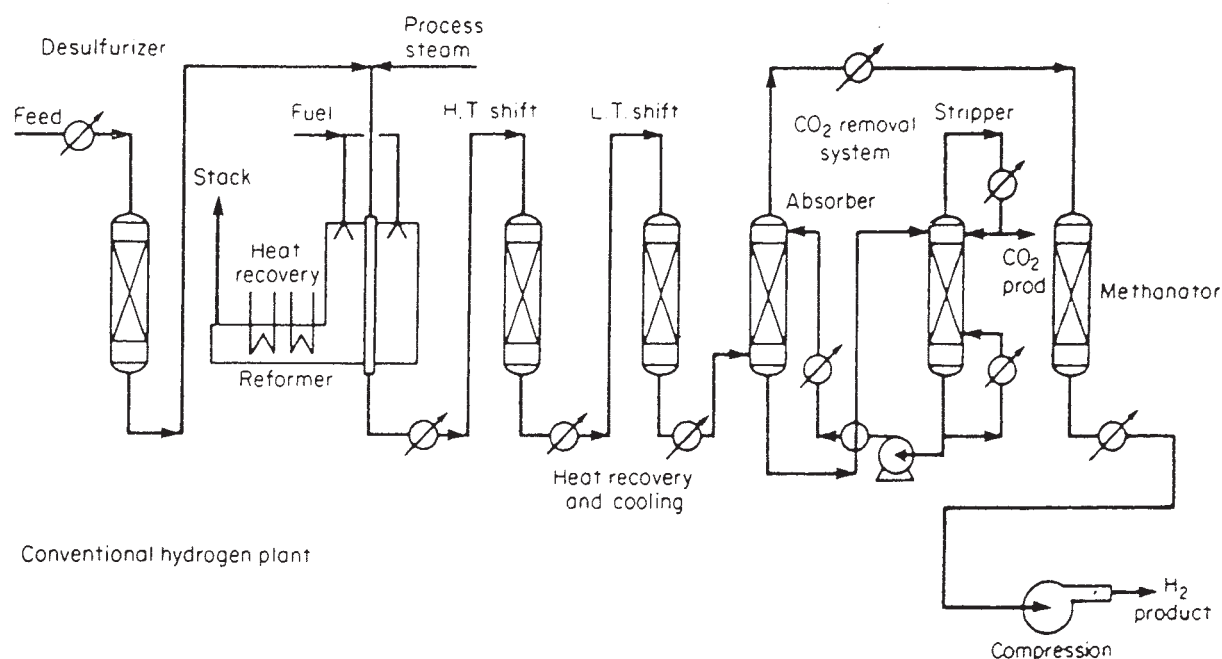


Fig. 4.3. Simplified hydrogen production processing train. (Union Carbide Corp., Linde Dto.)

The cooled gases are scrubbed with a monoethanolamine solution in the first-stage Girbotol absorber to remove essentially all the CO₂. Following this, the gases heated by exchange with the gases leaving the first-stage CO converter are passed through the second-stage CO converter, also followed by second-stage CO₂ absorber.

The gases low in CO₂ and CO are heated to about 315°C by exchange with gases from the second-stage CO converter and passed to the methanator over a nickel catalyst to convert essentially all the carbon oxides to methane by reaction with H₂.

The product H₂ gas from the methanator is cooled to 38°C (with water), leaving it pure except for saturation with water vapor. The lean amine solution from the Girbotol reactivator is first pumped through the second-stage CO₂ absorber to reduce the CO₂ content of the H₂ gas to a minimum and then pumped to the first-stage CO₂ absorber to remove the bulk of the CO₂ in the H₂ gas. The rich solution is returned to the reactivator through heat exchangers, and the CO₂ is stripped out by steam.

The CO₂, about 55 kg/100 m³ H₂, can be recovered for sale or use.

Catalysts. In many reactions connected with hydrogen manufacture, various catalysts are necessary, for example, nickel for steam-hydrocarbon reforming, iron oxide for CO conversion or the shift reaction, nickel for methanation, and nickel for ammonia cracking or dissociation.

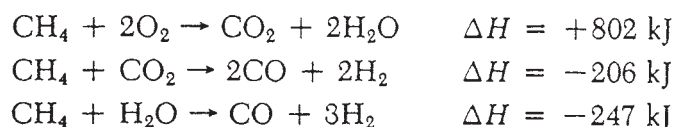
Partial Oxidation Processes. These rank next to steam-hydrocarbon processes in the amount of hydrogen made. They can use natural gas, refinery gas, or other hydrocarbon gas mixtures as feedstocks, but their chief advantage is that they can also accept liquid hydrocarbon feedstocks such as gas oil, diesel oil, and even heavy fuel oil. There are three commercial versions of the process. It was originally developed by Texaco, and variations were

Table 4.3 Product Analysis and Utility Requirements for Hydrogen Production by Steam Hydrocarbon Process*

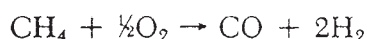
Product Analysis, Vol. %	Low-Pressure Reforming, Vol. %	Pressure Reforming, Vol. %
Carbon monoxide	0.001	0.001
Carbon dioxide	0.001	0.001
Methane	0.400	1.200
Hydrogen (minimum)	99.598	98.798
Raw Material and Utility Requirements, per 100 m ³ of hydrogen		
Process material		
Propane, sulfur free, L	36	37
Natural gas, 37 MJ/m ³ , m ³	25	25.3
Fuel, natural gas, propane, or oil, MJ	795	850
Steam, 480 kPa		
Propane for process, kg	445	238
Natural gas for process, kg	330	214
Cooling water, 17°C rise		
Propane for process, L	17,900	11,260
Natural gas for process, L	15,900	10,600
Power, exclusive of lighting, MJ	6.3	7.6

*The purification includes two stages of carbon monoxide conversion and carbon dioxide removal and one stage of methanation.

introduced later by both Shell and Montecatini,¹³ which differ primarily in the design and operation of the partial oxidation burner. All employ noncatalytic partial combustion of the hydrocarbon feed with oxygen in the presence of steam in a combustion chamber at flame temperatures between 1300 and 1500°C. When methane is the principal component of the feedstock, the reactions involved are:



The first reaction is highly exothermic and produces enough heat to sustain the other two reactions, which are endothermic. The net reaction is as follows:



This reaction is exothermic, and so the overall process is a net producer of heat; for efficient operation, heat recovery (using waste heat boilers) is important.

The product gas has a composition that depends upon the carbon/hydrogen ratio in the feed and the amount of steam added. Pressure does not have a significant effect on compo-

¹³ECT, 3d ed., vol. 12, pp. 939-982, 1980; Hydrogen Manufacture, *Hydrocarbon Process.* 58 (4) 168 (1979); The Search for Cheaper Hydrogen, *Chem. Week* 130 (9) 42 (1982); Hydro-

sition, and the process is usually conducted at 2 to 4 MPa, permitting the use of more compact equipment and reducing compression costs. The following composition is typical for a fuel oil feedstock:

	Mole Percent
H ₂	48.0
CO	46.1
CO ₂	4.3
CH ₄	0.4
N ₂ , etc.	0.3
H ₂ S	0.9
	100.0

This gas has a much higher carbon oxides/hydrogen ratio than steam reformer gas.

In the commercial application of the Texaco process, preheated oil is mixed, under pressure, with oxygen and preheated steam and fed to the partial oxidation burner. About 26 m³ of 95 to 99% oxygen is used per 100 m³ of H₂ + CO produced. The product gas is cooled by a direct-contact water quench followed by a water scrubber and a filter, all of which serve to remove unreacted carbon from the product gas. The carbon is removed from the quench water, for example, by filtering, for disposal or reuse, or it may be discarded as a water slurry.

The remaining process steps for conversion of the partial oxidation product gas to hydrogen are the same as for the steam-hydrocarbon reforming process: water-gas-shift conversion, CO₂ removal via monoethanolamine scrubbing, and methanation.

Coal Gasification Processes. Coal as a source of hydrogen will assume increasing importance in the future as reserves of gaseous and liquid hydrocarbon feedstocks decrease. Although coal was used in early water-gas and producer-gas plants for the manufacture of a H₂-CO mixture, these plants cannot compete with more modern processes. The various processes have been described in Chap. 6. The gases produced require the water-gas-shift conversion and subsequent purification to produce high-purity hydrogen. Table 4.4 shows a comparison of the four main processes for the production of hydrogen.

Cracked Ammonia. A mixture of nitrogen, 1 volume, and hydrogen, 3 volumes, may be prepared from the cracking or dissociation of ammonia. This mixed gas can be used for hydrogenation because the nitrogen is inert. The process consists of vaporizing the liquid ammonia from cylinders, heating it to 870°C, passing it over an active catalyst, and then cooling it in heat exchangers where the incoming gas may be vaporized. A single 68-kg cylinder of anhydrous ammonia will produce 190 m³ of cracked ammonia. This is equivalent to the contents of about 33 hydrogen cylinders.

HYDROGEN PURIFICATION

Carbon Monoxide Removal. High concentrations of carbon monoxide are commonly reduced by conversion to hydrogen via the water-gas-shift reaction; see Fig. 4.3. Removal by scrubbing in solutions of complex copper ammonium salts has been used commercially.

Carbon Dioxide and Hydrogen Sulfide Removal. Many processes for the removal of acid gases have been employed commercially.¹⁴

¹⁴Strelzoff, Choosing the Optimum CO₂-Removal System, *Chem. Eng.* 82 (19) 115 (1975).

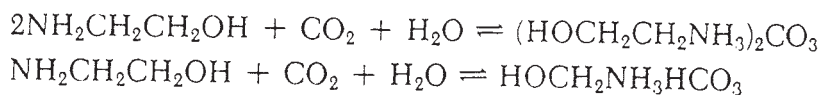
Table 7.4 Comparison of Hydrogen Production Alternatives

	Steam Reforming	Coal Gasification	Electrolysis	Thermochemical Decomposition
Appropriate overall thermal efficiency, %	70	60-65	32 (SPE)* 21-25 (KOH)	Upper limit 55
State of the art	Well-known technology	Mature technology available	Proven, reliable technology	Research stages
Environmental effects	Depletion of natural gas and other light hydrocarbons	Impacts of coal mining; air pollution likely to be less than via electricity from coal	Pollution problems with electricity generation	High efficiency means less resource use. Possible release of harmful chemicals
Advantages	Currently the cheapest method in the U.S.	Cheapest and most secure near-term alternative to methane reforming;	Small plant size; can use nonfossil fuel	Can use nonfossil fuel
Disadvantages	Scant long-term potential due to limitations on methane supply	Ultimate limitation is exhaustion of coal resources; requires large plant size	High cost, low net energy efficiency	Materials problems in reactant containment; large complex plant
Estimated hydrogen production costs,* \$/GJ product (1980 \$)	7.17	10.02	21.05	

*Solid Polymer Electrolyte (General Electric).

SOURCE: Chem. Eng. 87 (14) 80 (1980).

1. *Monoethanolamine (MEA) or Girbotol process.* A water solution of MEA is reacted with CO_2 in an absorber vessel under pressure at room temperature. The MEA solution is then heated and fed to a reactivation column where the $\text{MEA} \cdot \text{CO}_2$ complex is dissociated by stripping with steam at 90 to 120°C and near atmospheric pressure. The CO_2 and steam leave at the top of the reactivation column, and the regenerated solution leaves at the bottom, is cooled, and is pumped back to the absorber. The chemical reactions involved are:



Contrasted with physical absorption types of CO_2 -removal processes, the MEA process is capable of reducing the CO_2 concentration in the process gas to less than 0.01% by volume.

A major problem associated with the use of MEA solutions is their corrosive effect on process equipment. Corrosion is most severe at elevated temperatures and where the acid gas concentration in solution is the highest. Control of corrosion is achieved by using stainless steel at potential trouble spots, by limiting the concentration of MEA in aqueous solution in order to limit the CO_2 in solution, by excluding oxygen from the system, and by removing oxidation and degradation products using side-stream distillation. Another system uses a corrosion inhibitor (amine guard),¹⁵ which has greatly decreased corrosion as an operating problem even with increased CO_2 loadings.

2. *Hot potassium carbonate process.* This process, developed originally by the Bureau of Mines, is particularly useful for removing large quantities of CO_2 . Although it can remove CO_2 down to 0.1% by volume in the gas being purified, it is generally more economical at purity levels of 1% or greater. By absorbing CO_2 under pressure in hot solution close to its boiling point and regenerating it at the same temperature but at near-atmospheric pressure, steam consumption is reduced and heat exchangers are eliminated. Process improvements have been obtained through the use of catalytic additions and promoters to the solution, such as in the Giammarco-Vetrocok¹⁶ and the Catacarb processes.¹⁷

3. *Physical solvent processes.*¹⁸ These are processes in which CO_2 is removed by physical solution in a solvent, which is often proprietary. Examples of this class of process are the Rectisol process using cold (approximately -60°C) methanol, the Fluor solvent process using a nonaqueous organic solvent such as propylene carbonate, the Sulfinol process using an organic solvent, sulfolane (tetrahydrothiophene dioxide), the Selexol process using the dimethyl ether of polyethylene glycol, and the Purisol process using *N*-methyl-2-pyrrolidone. Aqueous ammonia solutions have been used for removal of CO_2 and H_2S , particularly in ammonia synthesis plants where ammonia is available. Water has also been used, but CO_2 solubility is poor, requiring high-pressure operation, and hydrogen losses, because of solubility, are high.

¹⁵Butwell, Hawkes and Mago, Corrosion Control in CO_2 Removal Systems, *Chem. Eng. Prog.* 69 (2) 57 (1973); Kubek and Butwell, "Amine Guard Systems in Hydrogen Production," paper presented at AIChE meeting, April 1-15, 1979, at Houston, Texas.

¹⁶*Chem. Eng.* 67 (19) 166 (1960) (flowchart)

¹⁷Eickmeyer, Catalytic Removal of CO_2 (Hot Carbonates), *Chem. Eng. Prog.* 58 (4) 89 (1962).

¹⁸Physical Solvent Stars in Gas Treatment/Purification (Selexol) *Chem. Eng.* 66 (13) 54 (1970).

Adsorptive Purification. Fixed-bed adsorption can remove such impurities as CO_2 , H_2O , CH_4 , C_2H_6 , CO , Ar , and N_2 , among others. One type of process is the thermal-swing process in which the impurity is adsorbed at a low temperature and desorbed thermally by raising the temperature and passing a nonadsorbable purge gas through the bed to aid desorption and carry the desorbed gas from the bed. For continuous operation two beds are necessary; while one bed is onstream, the second bed is being regenerated.

A second type of process is the pressure-swing adsorption process (PSA) in which the impurities are adsorbed by a molecular sieve under pressure and desorbed at the same temperature but at a lower pressure. A purge gas may be used. For continuous operation, at least two beds are required. Its principal advantage is that it can operate on a shorter cycle than the thermal-swing process, thereby reducing vessel sizes and adsorbent requirements. It is capable of purifying a typical crude hydrogen stream to a high-purity hydrogen product containing 1 to 2 ppm total impurities.

Integration of PSA technology into the steam-reforming process allows more than the removal of all the impurities¹⁹ from the hydrogen gas. In the conventional reformer the steam-to-carbon ratio is set to avoid carbon formation in the tubes, to provide enough steam for the low-temperature shift converter, and to provide a heat balance in the scrubbing section. With PSA the only constraint for the reformer designer is to provide a high enough steam-to-carbon ratio to avoid carbon deposition. This often allows a ratio as low as 3:1 compared with 5 to 6:1 in the scrubbing process.

Cryogenic Liquid Purification. An impure hydrogen stream can be partially purified by simply cooling to the appropriate cryogenic temperature,²⁰ where the impurities will condense and can then be separated as a liquid stream. This is often used for bulk removal of light hydrocarbons from hydrogen in a refinery off-gas. The product purity obtainable depends upon the vapor pressure of the impurity, and high purities are not readily attainable in most cases.

For additional purification, Linde removes low-boiling contaminants in a hydrogen gas stream at 2.1 MPa and -180°C by washing successively with liquid methane (to remove N_2 and CO) and liquid propane (to remove CH_4) to give 99.99% hydrogen. Final purification employs activated carbon, silica gel, or molecular sieves. Low temperatures for washing with liquid nitrogen or for fractionation are also used to remove impurities.

The parahydrogen content of bulk liquid hydrogen should be greater than 95%. The terms ortho and para refer to the direction of nuclear spin in the hydrogen molecule. Hydrogen normally contains 25% para at room temperature but slowly converts to nearly pure para at liquid temperature. During liquefaction, hydrogen should be catalytically²¹ converted from

¹⁹Large Quantities of High Purity Hydrogen, *Chem. Eng.* 86 (23) 90 (1979); Corr, Dropp, and Rudelstorfer, PSA Produces Low Cost High Purity H_2 , *Hydrocarbon Process.* 58 (3) 119 (1979); Simple Gas Adsorber Features Self-Regeneration, *Chem. Eng.* 88 (24) 71 (1981); Kaplan, Metal Hydrides Selectively Remove H_2 from Gas Streams, *Chem. Eng.* 89 (16) 34 (1982).

²⁰Haslain, Which Cycle for H_2 Recovery?, *Hydrocarbon Process.* 51 (3) 101 (1972); Lehman and VanBaush, Cryogenic Purification of Hydrogen, *Chem. Eng. Prog.* 80 (1) 44 (1976).

²¹Schmauch and Singleton, Technical Aspects of Ortho-Para Hydrogen Conversion, *Ind. Eng. Chem.* 56 (5) 20 (1964); Schmauch et al., Activity Data on Improved Para-Ortho Conversion Catalysts, *Chem. Eng. Prog.* 59 (8) 55 (1963); Lipman, Cheung, and Roberts, Continuous Conversion Hydrogen Liquefaction, *Chem. Eng. Prog.* 59 (8) 49 (1963).