256
4-23-81

①

Dr. 2552

ANL/CNSV-15

R-3151

MASTER

ARGONNE NATIONAL LABORATORY

Energy and Materials Flows in the Production of Liquid and Gaseous Oxygen

S. Y. Shen and A. M. Wolsky

ANL
EES

ARGONNE NATIONAL LABORATORY
Energy and Environmental Systems Division

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

prepared for
U. S. DEPARTMENT OF ENERGY
under Contract W-31-109-Eng-38

DISCLAIMER

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) among the U. S. Department of Energy, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona
Carnegie-Mellon University
Case Western Reserve University
The University of Chicago
University of Cincinnati
Illinois Institute of Technology
University of Illinois
Indiana University
The University of Iowa
Iowa State University
The University of Kansas
Kansas State University
Loyola University of Chicago
Marquette University
The University of Michigan
Michigan State University
University of Minnesota
University of Missouri
Northwestern University
University of Notre Dame
The Ohio State University
Ohio University
The Pennsylvania State University
Purdue University
Saint Louis University
Southern Illinois University
The University of Texas at Austin
Washington University
Wayne State University
The University of Wisconsin-Madison

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government or any agency thereof, nor any of their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes
Printed copy: A04
Microfiche copy: A01

Distribution Category:
Energy Conservation-
Industry (UC-95f)

ANL/CNSV-15

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

ENERGY AND MATERIALS FLOWS IN THE PRODUCTION OF LIQUID AND GASEOUS OXYGEN

by

Sin-yan Shen and Alan M. Wolsky

Energy and Environmental Systems Division
Special Projects Group

August 1980

work sponsored by

U.S. DEPARTMENT OF ENERGY
Assistant Secretary for Conservation and Solar Energy
Office of Industrial Programs

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

CONTENTS

TABLES

TABLES (Cont'd)

FIGURES

FIGURES (Cont'd)

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

PREFACE

This report is one of a series being prepared for the U.S. Department of Energy, Office of Industrial Programs, on energy and materials flows in energy-intensive industries. Each report gives an overview of the particular industry, including its products, corporate structure, and present and emerging technologies. Suppliers and customers of major energy-consuming industries should gain a better understanding of the effects of changes in the cost and availability of energy. In cases where firms can substitute one material input for another, the reports will help these firms take into account the impact of energy considerations on possible alternatives. Government analysts responsible for expediting industrial energy conservation should profit from having a compact and ready source of background information to help place proposed projects in perspective and to serve as a point of departure for specific evaluations. The industries studied to date and the current status of the corresponding reports are listed below.

The information presented in the report series is derived from previous reports, government and industry statistics, trade and technical publications, patents, textbooks, industry interviews, and plant visits. Some of these sources provide incomplete, out-of-date, or conflicting data; therefore, ANL staff perform additional research to supplement, update, and reconcile the sources.

Energy and Materials Reports

Industry	Status (as of Feb. 1981)	
Fabrication of aluminum products	Published 1979 (ANL/CNSV-3)	
Fabrication of iron and steel semifinished products	Published 1979 (ANL/CNSV-8)	
Olefins and their derivatives	Published 1980 (ANL/CNSV-9)	
Petroleum refining	Published 1981 (ANL/CNSV-10)	
Primary copper	Published 1981 (ANL/CNSV-11)	
Air products	Published 1981 (ANL/CNSV-15)	
Pulp and paper	Approved for publication	to be published in 1981
Cement	Approved for publication	
Primary aluminum	Draft	
Primary iron and steel	Draft	

ENERGY AND MATERIALS FLOWS IN THE PRODUCTION OF LIQUID AND GASEOUS OXYGEN

by

Sin-yan Shen and Alan M. Wolsky

ABSTRACT

Liquid and gaseous oxygen is produced in an energy-intensive air separation process that also generates nitrogen. More than 65% of the cost of oxygen is attributable to energy costs. This report analyzes energy use and materials flows for various air separation methods. Effective approaches to energy and material conservation in air separation plants include efficient removal of contaminants (carbon dioxide and water), centralization of air products user-industries so that large air separation plants are cost-effective and the energy use in transportation is minimized, and increased production of nitrogen. Air separation plants can produce more than three times more nitrogen than oxygen, but present markets demand, at most, only 1.5 times more. Full utilization of liquid and gaseous nitrogen should be encouraged, so that the wasted separation energy is minimized. There are potential markets for nitrogen in, for example, cryogenic separation of metallic and plastic wastes, cryogenic particle size reduction, and production of ammonia for fertilizer.

1 INTRODUCTION

Oxygen, the most widely used industrial gas, is produced in an energy-intensive, low-temperature process that separates air into its component gases. Energy costs account for about 65% of the cost of oxygen and other air products. Because oxygen is heavily used in the steel industry, its price affects that of steel and steel products. Nitrogen, the second most widely used industrial gas, is the main coproduct of oxygen produced in an air separation process. The energy efficiency of air separation is significantly influenced by the production ratio of oxygen and nitrogen, which can be varied. Industrial demand for oxygen and nitrogen is expected to increase steadily.

Section 1 of this report summarizes the characteristics of oxygen, the recent production history and markets for oxygen and nitrogen, and the structure of the air products industry. In Section 2, the theoretical operation of a machine that produces liquified gas is described. Section 3 discusses actual air separation processes in detail, and materials flows and energy use are considered in Section 4. Section 5 presents recommendations for energy conservation measures.

1.1 CHARACTERISTICS OF OXYGEN

Naturally occurring oxygen consists of three stable isotopes with atomic mass numbers 16, 17, and 18, having abundances in the proportion 10,000:4:20. The isotopic composition of the oxygen produced by air separation does not differ appreciably from this proportion. Molecular oxygen, O_2, is diatomic, except that in the condensed state there is some weak transient association of oxygen molecules, forming O_4, which is believed to cause the blue color of liquid and solid oxygen. There appears to be little or no molecular association in gaseous oxygen.

Oxygen is a normal fluid in most respects, its outstanding difference from most other fluids being its strong paramagnetism. The magnetic effects of its electrons do not exactly cancel. The paramagnetic property has been used in instruments designed to detect oxygen.

Because of its chemical activity, oxygen must be handled carefully. For example, ordinary hydrocarbon lubricants are dangerous to use in oxygen compressors and vacuum pumps exhausting oxygen. Also, valves, fittings, and lines used with oil-pumped gases are not used with oxygen. Serious explosions have resulted from the combination of oxygen with lubricants.

Various properties of oxygen, nitrogen, and air are listed in Table 1. The particular condition under which a substance can be present in any or all of the gas, liquid, or solid phases is known as the triple point (indicated in Figure 1, a typical phase diagram representing phase equilibria for the three states of a substance). The critical pressure, P_c, is the pressure below which a substance may exist as a gas in equilibrium with the liquid at the critical temperature. The critical temperature, T_c, is the temperature above which a gas cannot be liquefied by pressure alone.

1.2 INDUSTRIAL USES OF OXYGEN AND NITROGEN

1.2.1 Oxygen

Synthetic fuel programs of various magnitudes have been proposed by the federal government, industry, and public utilities. Depending on the processes and feedstocks used, the national synfuels production goals for the early 1990s could require three to five times the total current U.S. oxygen production of about 70,000 tons/day. The synthetic fuels industry will probably become the nation's largest user of oxygen before the year 2000.

Today, liquid and gaseous oxygen is used primarily in the steel industry, which accounted for about 65% of U.S. oxygen consumption in 1979 (see Table 2). During the past 15 years, steel technology has undergone a revolution. The industry is moving away from the open hearth furnace, which in some cases was modified to use oxygen, to the basic oxygen furnace. An open hearth furnace produces 250 tons of steel every 8-10 hours, while a basic oxygen furnace makes 300 tons of steel in 40 minutes.[2] The oxygen pumped into these furnaces must be of high purity to produce the best steel. Cost considerations, teamed with the advantages that pure oxygen offers in oxidation processes that formerly used air, have caused an upsurge in demand for large air separation plants.

Table 1 Cryogenic Properties of Oxygen, Nitrogen, and Air

Property	Oxygen	Nitrogen	Air
Molecular weight	31.999	28.013	28.96
Normal boiling point (°F)	-297.3	-320.4	-317.8 to -312.4
Triple point			
°F	-361.8	-346.0	NA[a]
psia	0.022	1.8	NA
Critical point			
°F	-181.1	-232.5	-221.3
psia	737	493	547
Density (lb/ft^3)[b]			
Gas at NTP	0.08281	0.07245	0.07493
Gas at STP	0.08921	0.07805	0.08072
Vapor at boiling point	0.279	0.287	0.280
Liquid at boiling point	71.27	50.46	54.56
C_p of gas at NTP (Btu/lb°F)[c]	0.220	0.247	0.240
C_p/C_v of gas at NTP[c]	1.40	1.41	1.40
Heat of vaporization (Btu/lb)	91.7	85.7	88.2
Heat of fusion (Btu/lb)	6.0	11.1	--

[a] NA = not applicable.

[b] NTP = normal temperature (70°F) and pressure (14.696 psia).
STP = standard temperature (0°C) and pressure (1 atm).

[c] C_p = specific heat at constant pressure.
C_v = specific heat at constant volume.

Source: Ref. 1.

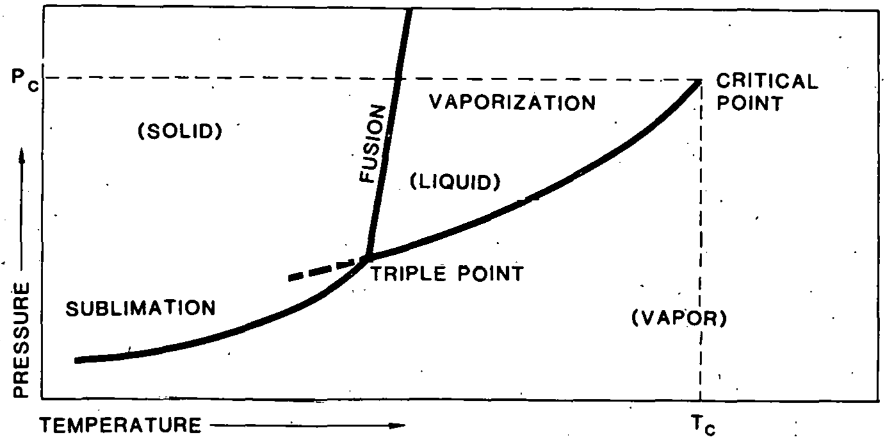

Fig. 1 Typical Phase Diagram of a Substance

The steel industry also uses oxygen in an oxy-acetylene flame, for scale removal from billets, and in oxygen lances, for cutting out imperfections. The oxy-acetylene flame also is heavily used in the fusion welding of metals such as cast iron, aluminum, and steel; the two gases are supplied to a special blowpipe in which they are mixed before combustion. The temperature of the inner core of the flame may reach about 4000°C, and suffices to locally melt the metal surfaces to be joined.

The nonferrous metals and chemical industries also are significant markets for oxygen. Oxygen is used in a variety of metal working applications and is used to enhance combustion in nonferrous metallurgical processes. The chemical industry uses oxygen to produce acetylene and ethylene oxide, to generate ammonia and methanol via partial oxidation of hydrocarbons, and to expedite coal gasification. In the continuous gasification of coal or other solid fuel, oxygen admixed with steam is passed into the fuel bed and maintains a sufficiently high temperature to allow the water-gas reaction to proceed smoothly.

Table 2 1979 Industrial Consumption of Oxygen

Industry	% of U.S. Consumption
Steel	
Basic oxygen process	39.6
Open hearth	9.3
Electric furnace	1.7
Other	14.8
Total	65.4
Nonferrous metals	3.0
Fabricated metal products	7.0
Chemicals	
Ethylene oxide	8.2
Acetylene	3.8
Titanium dioxide	2.8
Propylene oxide	2.3
Vinyl acetate	2.3
Miscellaneous	0.6
Total	20.0
Pollution control	3.0
Miscellaneous	1.6

In addition, oxygen is used in hospitals (to enrich air in respirators and to mix with anesthetics), aviation (for pilots' air supply), and pollution control. Wastewater streams can be aerated with oxygen in activated sludge processes. Pulp and paper mills, for example, are switching from an activated sludge process that uses air to one that uses oxygen. Using oxygen rather than air in the treatment of mill wastes lowers total treatment costs, reduces the land area required for sludge retention, produces less secondary sludge (and the sludge is easier to thicken, dewater, and settle), and enables the treatment system to better handle shock loads.[1]

During the 1960s, the space program was a major user of oxygen, consuming over 700,000 tons of liquid oxygen in 1962. This use has declined, however, since the completion of the Apollo program.

1.2.2 Nitrogen

Nitrogen is used primarily as a freezing agent and a blanketing agent. About 21% of nitrogen produced is used for freezing; the frozen hamburger industry is the biggest single user of liquid nitrogen. MacDonald's, for example, has five suppliers of hamburgers that each use 100-150 tons of liquid nitrogen per day. Other freezing applications include cryogenic size reduction of plastics, rubber, spices, and pharmaceuticals. About 33% of all nitrogen produced is used for blanketing, mostly in chemical processing and the electronics industry (14% each), with some application in the primary metals industry (5%).

Demand for nitrogen has been growing steadily in the liquefied industrial gases market and the chemical industry. In the aluminum industry, nitrogen has been replacing inert gas generators. The enhanced oil products industry also requires fairly large quantities of gaseous nitrogen. Nitrogen requirements for steel manufacture are modest and seldom exceed a small fraction of the oxygen flow. Some nitrogen also is used as the principal refrigerant in air separation cycles and as clean-up gas (to remove unwanted carbon dioxide and water).

Most chemical-fertilizer nitrogen is now derived from ammonia, which is synthesized from atmospheric nitrogen plus hydrogen. The hydrogen is made in most cases by reforming natural gas, naphtha, or other liquid and solid hydrocarbon fuels. Limited amounts of nitrogen are used in the form of calcium cyanamide, sodium, and potassium nitrate. A number of new processes for ammonia -- including production based on coal gasification and production based on heavy oil gasification -- designed to reduce the need for natural gas as the basic feedstock call for pure nitrogen (instead of nitrogen in air) as well as pure oxygen. The projected U.S. fertilizer nitrogen consumption in 1985 is about 16.5 million tons.[3] If gasohol production is accelerated, this number may be an underestimate. If ammonia technology moves away from natural gas (which is unlikely at this time), fertilizer nitrogen, which traditionally has not been derived from pure nitrogen, would represent a substantial market for nitrogen from air separation plants.

1.3 THE AIR PRODUCTS INDUSTRY

1.3.1 Oxygen and Nitrogen Production Levels

Among all chemicals produced in the United States, oxygen ranks third and nitrogen ranks fifth in total volume produced. Tables 3 and 4 show oxygen and nitrogen production trends between 1960 and 1979 and list the different forms of oxygen and nitrogen generated in 1977 and 1979. The per capita production of oxygen is plotted as a function of time in Figure 2.

Air separation plants can produce more than three times more nitrogen than oxygen, but the present market calls for a nitrogen-to-oxygen product ratio of 1:1 to 1.5:1. Nitrogen production increased an average of more than 11% annually from 1973 to 1979. At this growth rate, it will be a few years until nitrogen overtakes ammonia as the chemical with the fourth largest production volume. The market may never support full production of nitrogen by air separation plants.

The dollar value of shipments of oxygen is one-third that of all industrial gases, and nitrogen represents one-fourth of the total shipments of industrial gases. Annual production and shipments for industrial gases

Table 3 Recent U.S. Production of Oxygen and Nitrogen[a]

Year	Oxygen[b]		Nitrogen[b]	
	10^9 ft^3	10^6 tons	10^9 ft^3	10^6 tons
1960	58	--	19[c]	0.7[c]
1965	182	--	72[c]	2.6[c]
1970	284	--	151[c]	5.4[c]
1973	392	16.0	228	8.1
1974	390	16.0	243	8.7
1975	353	14.4	252	9.0
1976	388	15.7	290	10.4
1977	392	16.2	327	11.8
1978	430	17.8	383	13.9
1979	457	18.9	427	15.5

[a] All volumes in cubic feet are measured at normal temperature and pressure (NTP): 70°F, 14.696 psia.

[b] Density of oxygen is 0.08281 lb/ft^3 at NTP. Density of nitrogen is 0.07245 lb/ft^3 at NTP.

[c] Only high-purity nitrogen ($\geq$99.5% pure).

Source: Ref. 4.

Table 4 Types of Oxygen and Nitrogen Products, 1977-1979 (10^9 ft^3)[a]

Type of Product	1977		1978		1979	
	Oxygen	Nitrogen	Oxygen	Nitrogen	Oxygen	Nitrogen
Liquid produced for bulk delivery shipment to pipeline	7	6	12	9	14	11
Liquid and gas produced for cylinder shipment and bulk delivery	62	89	64	95	65	103
Liquid and gas produced for consumption in plant	52	27	51	49	52	44
Gas production for pipeline shipments	271	205	304	231	326	270
Total production	392	327	431	384	457	428

[a] Some totals do not match those in Table 3 due to rounding.

Source: Ref. 4.

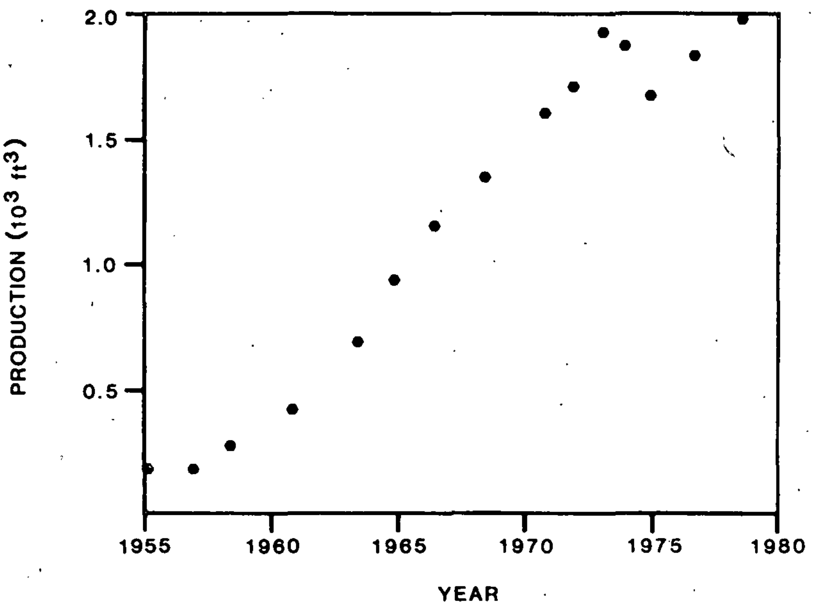

Fig. 2 Oxygen Production per Capita, 1955–1980

(SIC code 2813) are summarized in Table 5. The price of oxygen decreased steadily before 1973, and from 1973 to the present its deflated price has essentially stayed constant, as shown in Figure 3.

Oxygen, nitrogen, and other industrial gases are produced all over the United States. Two geographical regions, however, top the list in total number of plants producing oxygen and nitrogen. The east north central region (Ohio, Indiana, Illinois, Michigan, and Wisconsin) has 46 oxygen-producing plants out of 192 in the country and 45 plants that produce nitrogen, out of a total of 286. The west south central region (Arkansas, Louisiana, Oklahoma, and Texas) has 36 plants producing oxygen and 48 producing nitrogen. The number of establishments reporting production of industrial gases is

Table 5 Annual Shipment of Industrial Gases, 1976–1979

	Shipment Value ($\$10^6$)			
Product and SIC Code	1976	1977	1978	1979
Oxygen, high purity (28136)	337	354	433	502
Nitrogen, high purity (28135)	252	274	332	407
Acetylene (28132)	133	137	127	175
Carbon dioxide (28133)	74	104	113	130
Other elemental compressed and liquefied gases (28137)[a]	189	227	245	324
Industrial gases not classified elsewhere (28130)	32	39	44	55

[a] Such as argon, helium, and hydrogen.

Source: Ref. 4.

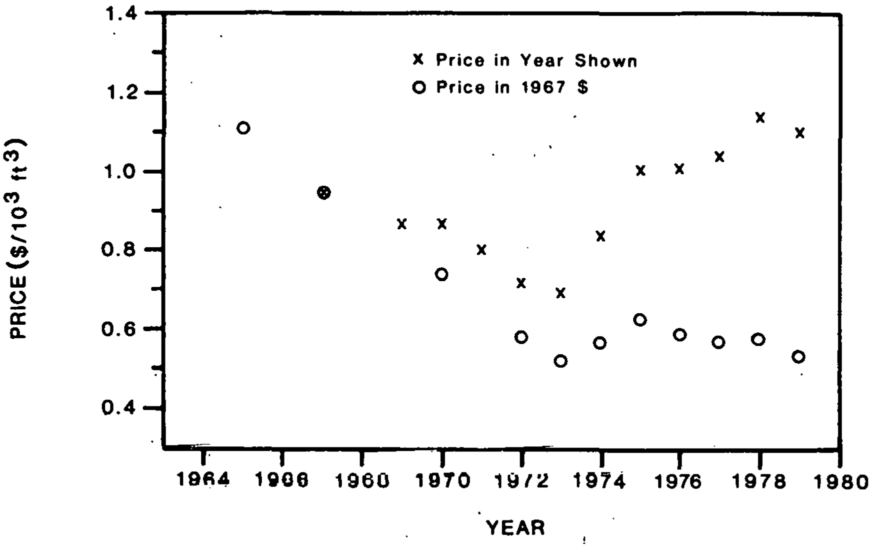

Fig. 3 Average Oxygen Prices, Including Transfers (Source: Adapted from Ref. 4)

summarized by state and geographical region in Table 6. Detailed breakdowns by geographic area of total production and shipments of oxygen and nitrogen in 1978 are given in Tables 7 and 8, respectively. The four major air products companies in the United States are the Linde Division of Union Carbide, Airco Industrial Gases, Air Products and Chemicals, and Liquid Carbonic Corporation, with Linde supplying about 60% of the market.

1.3.2 Structure of the Air Products Industry

Oxygen and other air products are produced in a cryogenic air separation process, described in detail in Sections 2 and 3. Because transportation of air products adds considerably to the cost, air separation plants usually are located close to the point of consumption. Large plants typically are planned with pipeline supply complexes designed to serve several industries in adjacent locations. In some cases, a number of customers are served by a single pipeline many miles in length, and oxygen producers assume many of the characteristics of a utility.

An air separation plant also may be located on one customer's premises and provide oxygen or nitrogen only to that customer. Such a plant is known as a "captive" facility. Alternatively, a small off-site plant can deliver the product by a short pipeline, usually to one customer. Union Carbide's Linde Division was the first company to design, build, and operate on-site plants (starting in 1949) for medium-size consumers in steel, chemical, and other industries. For example, Linde leases air separation plants with a minimum monthly output of 7.3 x 10^6 ft^3 of gaseous nitrogen. This production level is an indication of where the line is drawn between "medium" and "small" users.

The daily production of air separation plants varies from 25 tons to 2000 tons. The size of air separation plants has increased dramatically

Table 6 Number of Establishments Reporting Production of Industrial Gases in 1978[a]

Geographic Area and State	Oxygen	Nitrogen	Acetylene	Carbon Dioxide	Argon (refined)	Hydrogen	Nitrous Oxide
Total United States	192	286	189	80	89	118	8
New England	4	14	5	1	3	3	-
Connecticut	1	5	1	-	1	2	-
Maine	-	1	-	-	-	-	-
Massachusetts	3	6	3	1	2	1	-
Rhode Island	-	1	1	-	-	-	-
Vermont	-	1	-	-	-	-	-
Middle Alantic	29	43	19	4	13	7	-
New Jersey	3	9	4	1	2	2	-
New York	6	12	5	2	2	2	-
Pennsylvania	20	22	10	1	9	3	-
East North Central	46	45	33	15	19	28	1
Illinois	12	17	6	7	3	12	-
Indiana	6	5	5	3	5	3	-
Michigan	5	8	6	-	3	6	-
Ohio	22	13	13	4	8	7	1
Wisconsin	1	2	3	1	-	-	-
West North Central	5	14	16	12	1	5	1
Iowa	-	4	4	5	-	-	-
Kansas	-	1	4	4	-	1	1
Minnesota	2	1	3	2	-	-	-
Missouri	3	7	1	1	1	3	-
Nebraska	-	1	1	-	-	1	-
South Dakota	-	-	3	-	-	-	-
South Atlantic	21	50	26	12	9	14	1
Delaware	2	2	-	1	-	4	-
Florida	3	6	9	5	1	-	-
Georgia	2	5	5	2	2	3	1
Maryland	3	6	2	-	1	-	-
North Carolina	1	9	3	1	1	1	-
South Carolina	1	6	-	-	1	-	-
Virginia	3	3	3	2	1	2	-
West Virginia	6	13	4	1	2	4	-
East South Central	18	27	15	6	6	16	2
Alabama	7	6	3	-	3	4	-
Kentucky	4	5	3	2	-	3	-
Mississippi	1	1	2	1	-	1	1
Tennessee	6	15	7	3	3	8	1
West South Central	36	48	37	9	18	24	-
Arkansas	2	1	1	1	1	-	-
Louisiana	8	13	6	3	3	7	-
Oklahoma	1	2	3	1	1	-	-
Texas	25	32	27	4	13	17	-
Mountain	9	10	17	8	4	2	-
Arizona	1	3	1	2	-	-	-
Colorado	3	3	3	1	1	1	-
Idaho	-	1	2	-	-	-	-
Montana	1	-	3	-	-	-	-
Nevada	-	-	2	-	-	-	-
New Mexico	1	1	2	2	1	-	-
Utah	3	2	4	2	2	1	-
Wyoming	-	-	-	1	-	-	-
Pacific	24	35	21	13	16	19	3
Alaska	1	1	1	1	-	-	-
California	17	25	10	8	12	13	3
Hawaii	2	2	2	2	-	3	-
Oregon	-	2	4	-	1	1	-
Washington	4	5	4	2	3	2	-

---

[a] Hyphen (-) represents zero. The District of Columbia, New Hampshire, and North Dakota produce no industrial gases.

Source: Ref. 5.

Table 7 1978 U.S. Production and Shipment of Oxygen, by Geographic Areas

Geographic Area and State[a]	Production (10^9 ft^3)	Total Shipments Including Interplant Transfers: Quantity (10^9 ft^3)	Total Shipments Including Interplant Transfers: Value ($\$10^6$)
Total United States	430	379	433
New England	2	2	5
Middle Atlantic	59	58	71
New York	14	14	16
New Jersey	3	3	6
Pennsylvania	42	41	49
North Central	173	152	164
Ohio	42	42	43
Michigan	25	15	18
Other states	106	95	103
South Atlantic	46	45	47
East South Central	33	33	37
West South Central	88	60	69
Texas	62	48	52
Other states	26	12	17
Mountain	12	12	14
Pacific	17	17	26
California	15	15	20
Other states	2	2	6

[a]See Table 6 for identification of states in each area.

Source: Ref. 5.

in recent years. The reason is simple: the bigger the plant, the lower the cost of the oxygen and nitrogen furnished to customers.[6] For an on-site air separation installation, oxygen from a 200-ton/day plant costs \$27-34/ton in 1979 dollars, while oxygen from a plant producing 2000 tons/day or more costs less than \$23/ton. The delivered price to off-site users fed by pipeline is about 30-35% more. As demand increases, larger air separation plants are being built. The state-of-the-art design (such as Linde's T-2000 plant) produces 2000 tons/day of oxygen. In the first half of the 1970s, the largest air separation plant produced only about 1200 tons of oxygen daily. By the late 1980s, 6000-ton/day plants may be built.

Oxygen and nitrogen are most economically transported in liquid form, since the gas-to-liquid volume ratio is very large (see Table 9). Since liquid oxygen and nitrogen have very low boiling points, the methods and equipment used to distribute these liquids to customers must be highly efficient. Figure 4 shows a typical nationwide storage and distribution system.

Table 8 1978 U.S. Production and Shipment of Nitrogen, by Geographic Areas

Geographic Area and State[a]	Production (10^9 ft^3)	Total Shipments Including Interplant Transfers: Quantity (10^9 ft^3)	Total Shipments Including Interplant Transfers: Value (\$$10^6$)
Total United States	383	334	332
New England	6	6	11
Middle Atlantic	40	38	58
New York	11	10	15
New Jersey	11	11	15
Pennsylvania	18	17	28
North Central	102	78	70
Ohio	16	16	17
Illinois	11	11	16
Other states	75	51	37
South Atlantic	46	38	37
West Virginia	18	11	8
Other states	28	27	29
East South Central	26	23	22
Tennessee	8	6	7
Alabama	14	14	14
Other states	4	3	1
West South Central	126	115	83
Texas	97	92	60
Other states	29	23	23
Mountain	6	6	9
Pacific	31	30	42
California	28	28	38
Other states	3	2	4

[a] See Table 6 for identification of states in each area.

Source: Ref. 5.

The liquids are produced in centrally located production plants and kept in large storage tanks at the plants. In areas where large producing plants are not warranted, liquids are stored at the company's liquid storage points, where cylinders and high-pressure gas transports also can be filled. Liquid gases are distributed by railroad tank cars, liquid transport trailers, or mobile pumping units, which are special liquid-carrying trucks that can deliver either liquid or high-pressure gas from a liquid source. A popular size truck load of cryogenic fluid is 20 tons. Liquid gas transport units, like liquid storage units, are basically giant, insulated metal vacuum bottles. Liquid gas storage containers are insulated with a vacuum, perlite, or super-insulation (aluminized mylar). A typical liquid reservoir has a capacity of 200 x 10^6 ft^3. The inside container is usually made of stainless steel and sits on foamed glass blocks. The outside casing may be made of carbon steel. The boil-off is estimated at a few tenths of a percent per day.

Table 9 Selected Gas-to-Liquid Volume Ratios (at 1 atm, 290 K)

Substance	Ratio
Oxygen	843
Nitrogen	683
Argon	823
Helium	740
Hydrogen	833

Companies producing liquid gases also install liquid storage tanks on the premises of some large users who do not require a captive air separation unit. The tanks are filled from railroad tank cars or liquid transport trailers. Some users are supplied with gases from cold converters, which are filled with liquid from tank cars, transport trucks, or mobile pumping units, and which automatically vaporize the liquid as the user requires. Still other users are provided with gaseous storage receivers, which are filled from mobile pumping units. Smaller users are generally supplied by high-pressure cylinders or liquid-holding dewars, which are filled at storage points and delivered by cylinder trucks.

Almost all liquid oxygen produced today is used as a gas. Gaseous oxygen is delivered to steel mills at about 150 psi and to the chemical industry at a few pounds per square inch above atmospheric pressure. When production exceeds demand, oxygen is stored in "receivers" at 500-600 psi or, more economically, in liquid form.

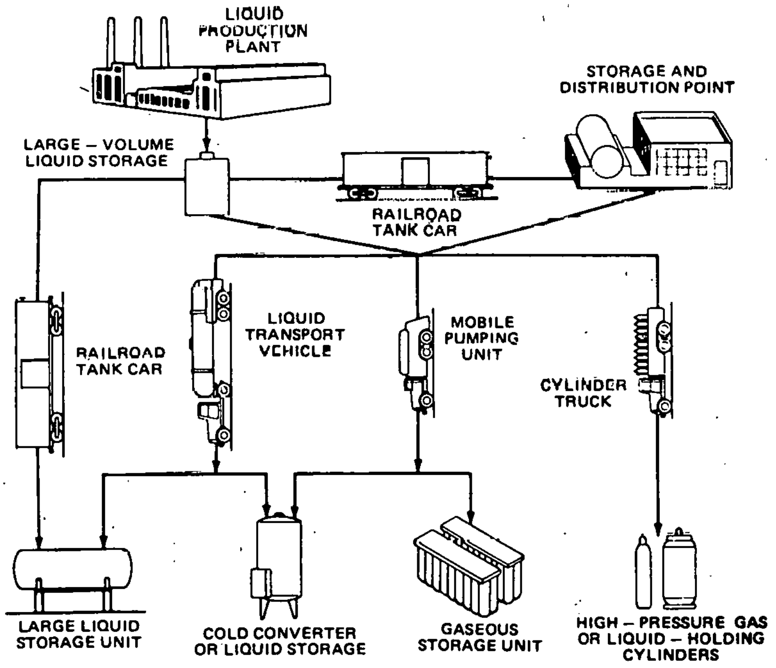

Fig. 4 Nationwide Liquid Storage and Distribution System (Source: Ref. 7)

2 THEORETICAL ENERGY USE IN LIQUEFACTION AND RECTIFICATION

Oxygen is produced principally by the liquefaction and rectification of air. The nine major constituents of air and some of their properties are listed in Table 10. Of these gases, all but carbon dioxide are found in unvarying concentrations and all but krypton and xenon are important commercially. While oxygen and nitrogen are the major products of air separation, the process also generates argon, helium, krypton, neon, and xenon.

To provide a standard of reference in calculating the efficiency and assessing the optimum mode of operation of a machine for producing liquefied gases, it is convenient to first consider an ideal refrigerative cycle for such a liquefier. If the gas to be liquefied has a critical temperature either above room temperature (or at least above a temperature that can be maintained readily), liquefaction by compression is possible. This is not the case for oxygen, which has a critical temperature of 154.7 K.

Consider the entropy (S) versus temperature (T) diagram for a typical liquid, represented by Figure 5, where the full lines are the pressure isobars ($p_2 > p_1$) and the broken curve is the limit of the heterogeneous two-phase region (liquid and vapor). Suppose that the temperature at which compression of the gas is to take place, T_2, is well above the critical temperature, T_c, and that T_1 is the boiling point of the liquid at $p_1 = 1$ atm. Now the following reversible refrigerative cycle, using the gas as a working substance, can be considered. First, starting at T_2 and p_1 (the point a), the gas is compressed isothermally to b. Then the gas is expanded isentropically and reversibly from b to c, such that the point c represents the condition of liquid saturation at the boiling point, T_1. Then at constant temperature, T_1, and constant pressure, p_1, the liquefied gas is evaporated until a saturated vapor is produced at d. This process of evaporation absorbs heat from the surroundings, at the low temperature, T_1, in an amount proportional to the liquid's latent heat of vaporization. Finally the gas is

Table 10 Composition of Moisture-Free Air

Gas	Volume (%)	Triple Point (K)	Boiling Point (K)	Critical Point (K)	Critical Pressure (atm)
Nitrogen	78.084	63.156	77.395	126.1	33.49
Oxygen	20.946	54.363	90.19	154.7	50.1
Argon	0.934	83.78	87.27	150.8	48.3
Carbon dioxide	0.02-0.04	216.6	194.68[a]	304.2	72.85
Neon	0.001818	24.55	27.07	44.4	26.9
Helium	0.0005239	none	4.216	5.20	2.26
Krypton	0.0001139	115.95	119.80	209.4	54.3
Hydrogen	0.00005	13.96	20.39	33.19	12.98
Xenon	0.0000086	161.3	165.05	289.8	57.64

[a] Sublimation temperature.

Source: Ref. 8.

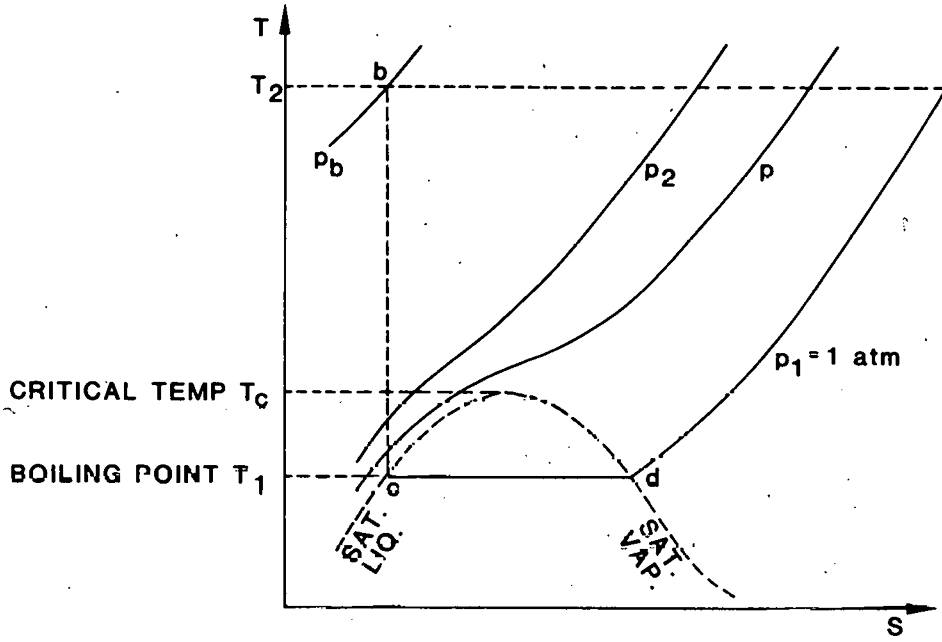

Fig. 5 Temperature-Entropy Diagram for a Typical Fluid, Showing Isobars (the cycle a→b→c→d is for theoretical refrigeration by ideal isentropic expansion)

allowed to warm up to temperature T_2 at constant pressure, p_1; the heat for this comes from the surroundings.

The heat absorbed at the low temperature, T_1, is:

$$Q_1 = L = H_d - H_c$$

where:

L = the latent heat of evaporation, and

H = the enthalpy corresponding to the subscripted point.

The heat evolved during isothermal compression at T_2 is:

$$Q_2 = T_2(S_a - S_b)$$

and the heat absorbed in isobaric warming from T_1 to T_2 is:

$$Q_3 = H_a - H_d$$

The net work done on one mole of the working fluid circulated in this reversible refrigeration cycle is:

$$W_{rev} = Q_2 - Q_1 - Q_3$$

since Q_1 and Q_3 represent the amount of "cold" the one mole of circulating fluid is able to offer. Thus:

$$W_{rev} = T_2 \; \Delta S - \Delta H$$

where:

$$\Delta S = S_a - S_b$$

$$\Delta H = H_a - H_c$$

are the differences in entropy and enthalpy between the gas at the high temperature, T_2, and the saturated liquid at the low temperature, T_1, when the pressure, p_1, is the same. The numerical values of ΔS and ΔH are determined once p_1 and T_2 are fixed. The minimum amount of work to liquefy one mole of gas is represented by W_{rev}.

The thermodynamic state functions and the corresponding thermodynamic potentials for oxygen can be read from the Mollier chart of oxygen (Figure 6) and are listed in Table 11. We find:

$$\Delta S = S_a - S_C = 26.5 \text{ cal/mole K}$$

$$\Delta H = H_a - H_c = 3100 \text{ cal/mole}$$

$$\begin{aligned} W_{rev} &= T_a \; \Delta S - \Delta H \\ &= (300 \text{ K})(26.5 \text{ cal/mole K}) - 3100 \text{ cal/mole} \\ &= 4850 \text{ cal/mole} = 160 \text{ kWhe/ton} \end{aligned}$$

Table 12 compares the energy (work) required in reversible liquefaction of air, nitrogen, oxygen, hydrogen, and helium.

The above estimate for the reversible work to liquefy oxygen begins with gaseous oxygen at 300 K and 1 atm. To obtain liquid oxygen from air, additional work is required to separate air into oxygen, nitrogen, and other components. The minimum separation energy can be calculated by considering an idealized process, using "semipermeable membranes," that removes the "entropy of mixing" (see Figure 7).

Table 11 Values Used to Calculate Reversible Work to Liquefy Oxygen

Point in Fig. 5	Temp., T (K)	Entropy, S (cal/mole K)	Enthalpy, H (cal/mole)
a	300	28.5	3250
b	300	2	--
c	90.19	2	150

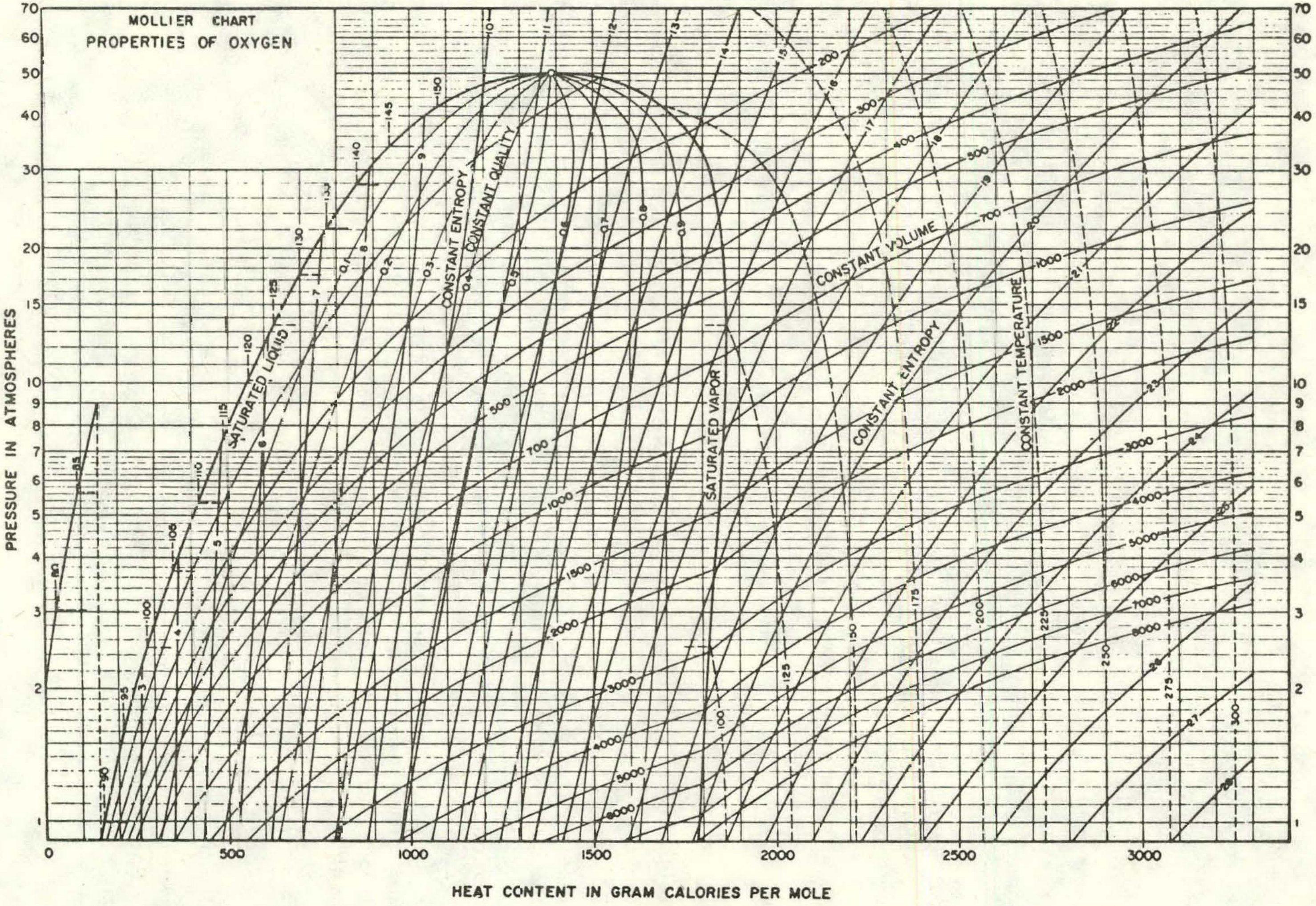

Fig. 6 Mollier Chart: The Properties of Oxygen (Source: Ref. 9)

Table 12 Work Required to Liquefy Selected Gases[a]

	Work			Thermal Energy	Electricity	
Substance	cal/mole	J/mole	Btu/lb	(Btu/lb)	kWh/lb	kWh/kg
Air	5,000	20,900	310	930	0.091	0.20
Oxygen	4,800	20,300	273	819	0.080	0.18
Nitrogen	5,100	21,400	328	984	0.096	0.21
Helium	6,500	27,200	2,935	8,805	0.86	1.89
Hydrogen	5,700	23,800	5,119	15,357	1.50	3.30

[a] Using ideal (thermodynamically reversible) process:
$W_{rev} = T_a \Delta S - \Delta H$, where T_a = 298 K (25°C), and P_a = 1 atm.

Note: The values given for each gas are equivalent amounts of energy (or work) expressed in several units of measure.

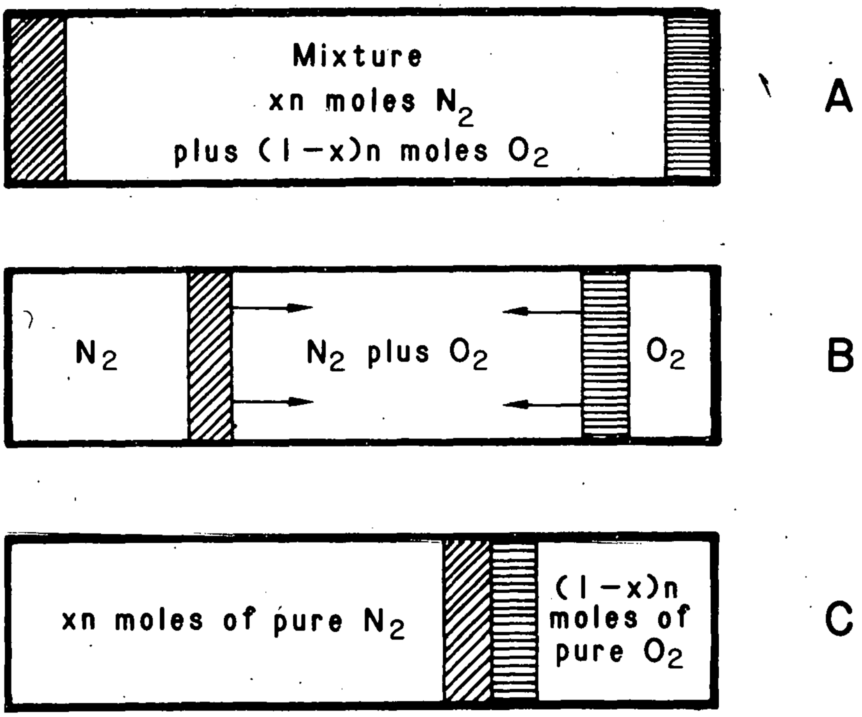

Fig. 7 Separation of Oxygen and Nitrogen Using Fictitious "Semipermeable" Membranes (Source: Adapted from Ref. 10)

Assume that a cylinder contains n moles of air, of which 79% is nitrogen and 21% is oxygen, at 1 atm. The partial pressures of oxygen and nitrogen will be 0.21 atm and 0.79 atm, respectively. The problem is to determine the least amount of work required to separate the mixture into pure nitrogen and pure oxygen, still at atmospheric pressure.

Suppose the container is fitted with two frictionless pistons, as shown in part A of Figure 7. Piston 1 is permeable only to nitrogen and piston 2 is permeable only to oxygen. Now the pistons are slowly moved, as shown at B, at relative speeds that will everywhere maintain the initial pressure. The end result will be C if we further assume that heat can flow out of the container and the process is isothermal.

The work required to compress the oxygen from the partial pressure of 0.21 atm to the final 1 atm is:

$$W_{O_2} = \int_{0.21}^{1} p\,dv$$

$$= -0.21\ nRT \ln p \Big|_{0.21}^{1}$$

$$= 0.21\ nRT \ln 0.21$$

For nitrogen:

$$W_{N_2} = -0.79\ nRT \ln p \Big|_{0.79}^{1}$$

$$= 0.79\ nRT \ln 0.79$$

The total work of separation for one mole of air is:

$$\begin{aligned} W_{O_2} + W_{N_2} &= 0.21\ RT \ln 0.21 + 0.79\ RT \ln 0.79 \\ &= RT\ (0.21 \ln 0.21 + 0.79 \ln 0.79) \\ &= (2.3095 \times 10^{-6}\ \text{kWh/K})(300\ \text{K})(0.328 + 0.186) \\ &= 3.56 \times 10^{-4}\ \text{kWh} \end{aligned}$$

This work is needed to produce 0.79 mole (2.438×10^{-5} ton) of nitrogen and 0.21 mole (7.408 x 10-6 ton) of oxygen. So the minimum separation work is:

$$(3.56 \times 10^{-4}\ \text{kWh})/(2.438 \times 10^{-5}\ \text{ton } N_2) = 15\ \text{kWh/ton of } N_2$$

$$(3.56 \times 10^{-4}\ \text{kWh})/(7.408 \times 10^{-6}\ \text{ton } O_2) = 48\ \text{kWh/ton of } O_2$$

3 OXYGEN PRODUCTION METHODS

Oxygen is produced by a variety of cryogenic processes; the basic methods are described here. In all these processes, air from which the carbon dioxide has been removed is liquefied by compressing it and allowing it to expand through a nozzle. In this expansion, work is done, heat is lost, and the temperature of the issuing gas falls. By a system of heat exchange, the cooled gas, which has been expanded, is made to cool the air still under pressure and the cumulative cooling effect thus obtained leads to liquefaction of the air.

The chief components of liquid air -- oxygen, nitrogen, and argon -- are separated by rectification of the liquid mixture. The liquid air is passed down a column fitted with numerous plates designed to give intimate contact between the column and the gas ascending it (gas produced by the evaporation of liquid air at the bottom). The result is that the more volatile nitrogen and argon are evaporated from the liquid and the less volatile oxygen is enriched in it. After a period of operation, liquid oxygen is obtained at the bottom of the column and nitrogen at the top.

A new method for air separation, developed during the 1970s, also is discussed in this section. Called pressure-swing adsorption, this process separates gas mixtures by adsorption/desorption on fixed adsorption beds, using gas pressure variation as the principal operating parameter.

3.1 THE SIMPLE LINDE LIQUEFIER

Instead of using the ideal isentropic expansion described in Section 2 to produce cooling, Linde and Hampson in 1895 independently used the cooling effect obtained in isenthalpic Joule-Thomson expansion to liquefy air. The success of their operations depended on the use of heat exchangers. Figure 8 is a schematic diagram of a simple "Linde" liquefier, and Figure 9 is the temperature-entropy diagram showing the cycle of operation.

The lettered points on both diagrams indicate the state of the air at various steps of the cycle. The process is carried out as follows. Air enters the compressor at pressure p_1 and temperature T_1 and leaves the compressor at p_2 and T_2. In practice, the compression itself is not isothermal, but nearly isothermal conditions can be obtained by employing a multistage compressor with appropriate intercoolers (using water, for instance) between stages and with a final after-cooler. The compression therefore takes the air from state a to state b.

The air then passes through the high-pressure side of the heat exchanger to the valve, V, where it is allowed to expand isenthalpically to pressure p_1. This Joule-Thomson expansion at V produces a cooling, provided the initial temperature, T_1, is below the inversion temperature. Since the inversion temperature for air is 603 K, an initial temperature of 300 K is satisfactory in an air liquefier. The cooled air, after leaving V, passes via the reservoir into the return low-pressure side of the heat exchanger and to the compressor. The valve continues to cool the air in the cycle until a steady state is reached with a fraction ε of the air flow being liquefied during the Joule-Thomson expansion.

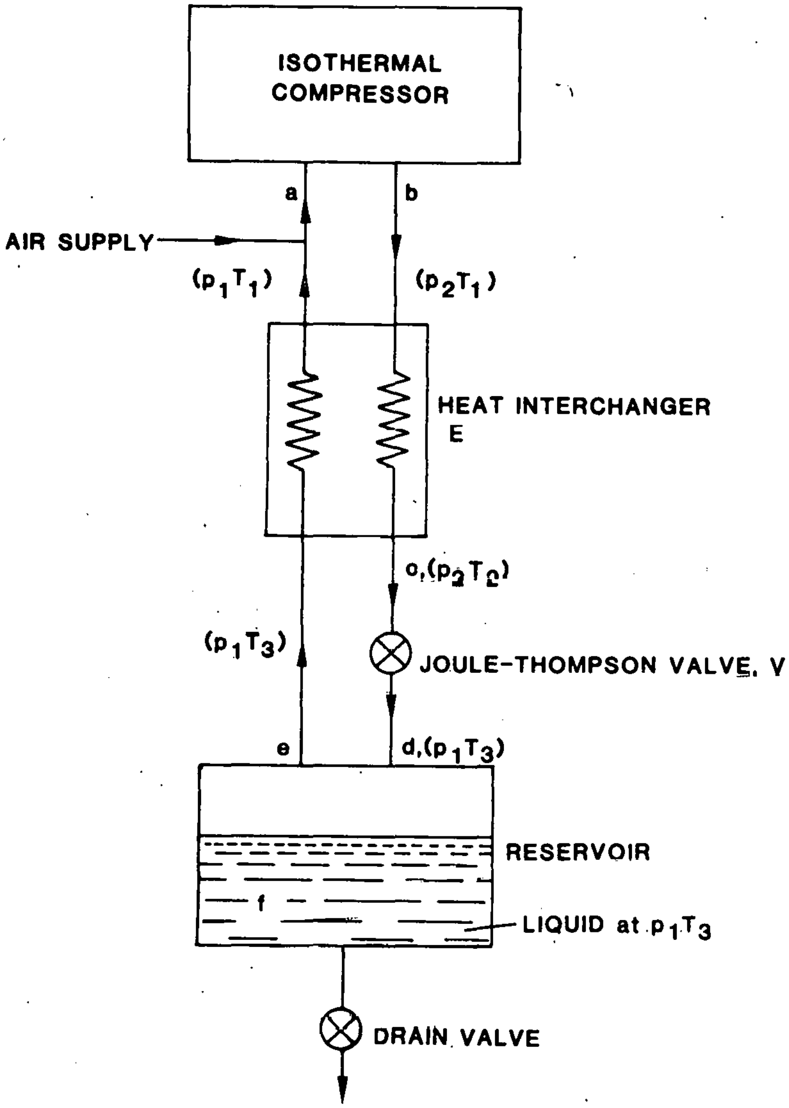

Fig. 8 Schematic Flow Diagram for the Simple Linde Air Liquefier

To determine the coefficient of liquefaction, ε, consider the heat balance of the whole plant behind the compressor in the steady state. Suppose a certain quantity of air is introduced at b in a certain time. Then:

$$H_b = \varepsilon H_f + (1 - \varepsilon)H_a$$

where H_i is the specific enthalpy in the i^{th} state and $\varepsilon = (H_a - H_b)/(H_a - H_f)$.

When the steady state is reached, the high-pressure gas enters the heat exchanger at p_2 and T_1 (point b) and leaves it at p_2 and T_2 (point c). The air expands isenthalpically through the valve V from p_2, T_2 to p_1, T_3, passing along the isenthalpic line from c to d. Points e and f represent that saturated vapor state and the saturated liquid state at the boiling point T_3 if p_1

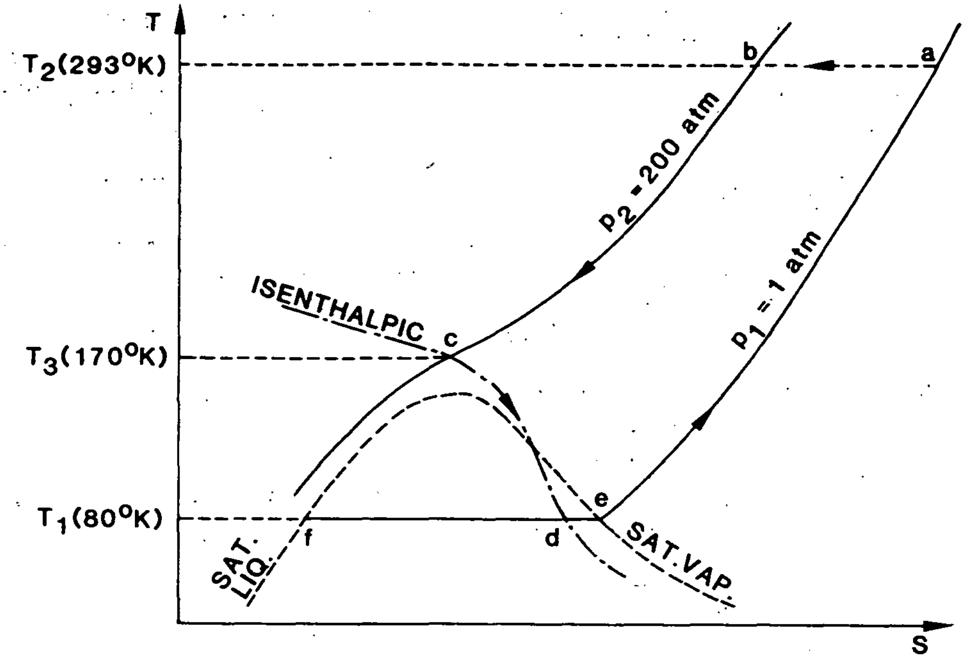

Fig. 9 Temperature-Entropy Diagram Showing Thermodynamic Cycle of Operation for Simple Linde Liquefier

is 1 atm. A fraction ε of liquid is collected in the reservoir at T_3 and p_1, and the remaining quantity of gas $(1 - \varepsilon)$, represented by the point e, enters the low-pressure side of the heat exchanger at T_3 and p_1 and leaves it at T_1 and p_1, having given up its cold to the downcoming high-pressure air.

To calculate the work required in the above process to liquefy one unit of gas, suppose, as in the ideal cycle, that an amount ε of the liquefied gas is evaporated in the reservoir, absorbing heat Q_1 at the low temperature, and that the air gains heat Q_3 as it warms up to temperature T_1. Under such a supposition, the refrigerative function of the machine is completely cyclical, having the same mass of air passing all points per unit time. An amount ε of gas is cooled from T_1 to T_3 by liberating heat to the exchanger and then is liquefied at T_3.

Between points a and b, the heat given out on compression is:

$$Q_1 = T_1(S_a - S_b)$$

Between points f and e, the heat absorbed in evaporating ε moles at T_3 is:

$$Q_2 = \varepsilon L = \varepsilon(H_e - H_f)$$

where L is the latent heat of air. From b to c, the heat given out to the exchanger is:

$$Q_3 = H_b - H_c$$

and for the step from point e to point a, the heat absorbed in the exchanger is:

$$Q_4 = H_a - H_e$$

The net work done is:

$$\begin{aligned} W &= Q_1 - Q_2 + Q_3 - Q_4 \\ &= T_1(S_a - S_b) - \varepsilon(H_e - H_f) \\ &\quad + (H_b - H_c) - (H_a - H_e) \end{aligned}$$

From the temperature-entropy diagram for air (Figure 10), the values of S and H can be read; these values are tabulated in Table 13.

Table 13 Entropy and Enthalpy Values for Points in the Simple Linde Liquefier when Liquefying Air

Point in Fig. 9	Entropy, S (cal/g K)	Enthalpy, H (cal/g)
a	0.9	122
b	0.525	114
c	0.31	65
d	0.53	65
e	0.58	67
f	0	23

The value of ε can be determined by:

$$H_b = \varepsilon H_f + (1 - \varepsilon)H_a$$

from which we have:

$$\begin{aligned} \varepsilon &= (H_a - H_b)/(H_a - H_f) \\ &= (122 - 114)/(122 - 23) \\ &= 0.081 \end{aligned}$$

The work to produce 0.081 g of liquid air is thus:

$$\begin{aligned} W &= T_1(S_a - S_b) - \varepsilon(H_e - H_f) + (H_b - H_c) - (H_a - H_e) \\ &= 300(0.9 - 0.525) \\ &\quad - 0.081(67 - 23) \\ &\quad + (114 - 65) - (122 - 67) \\ &= 103 \text{ cal} \end{aligned}$$

This corresponds to 1270 cal/g of liquid air or 1340 kWhe/ton of liquid air, with a Carnot efficiency of 13% when compared with reversible liquefaction, which requires 182 kWhe/ton of liquid air (see Table 12).

The same analysis can be performed using the temperature-entropy diagram for nitrogen (Figure 11). The values for S, H, T, and p for the process steps are shown in Table 14. The fraction liquefied, ε, is given by:

$$\begin{aligned} \varepsilon &= (H_a - H_b)/(H_a - H_f) \\ &= (2910 - 2690)/2910 \\ &= 0.076 \end{aligned}$$

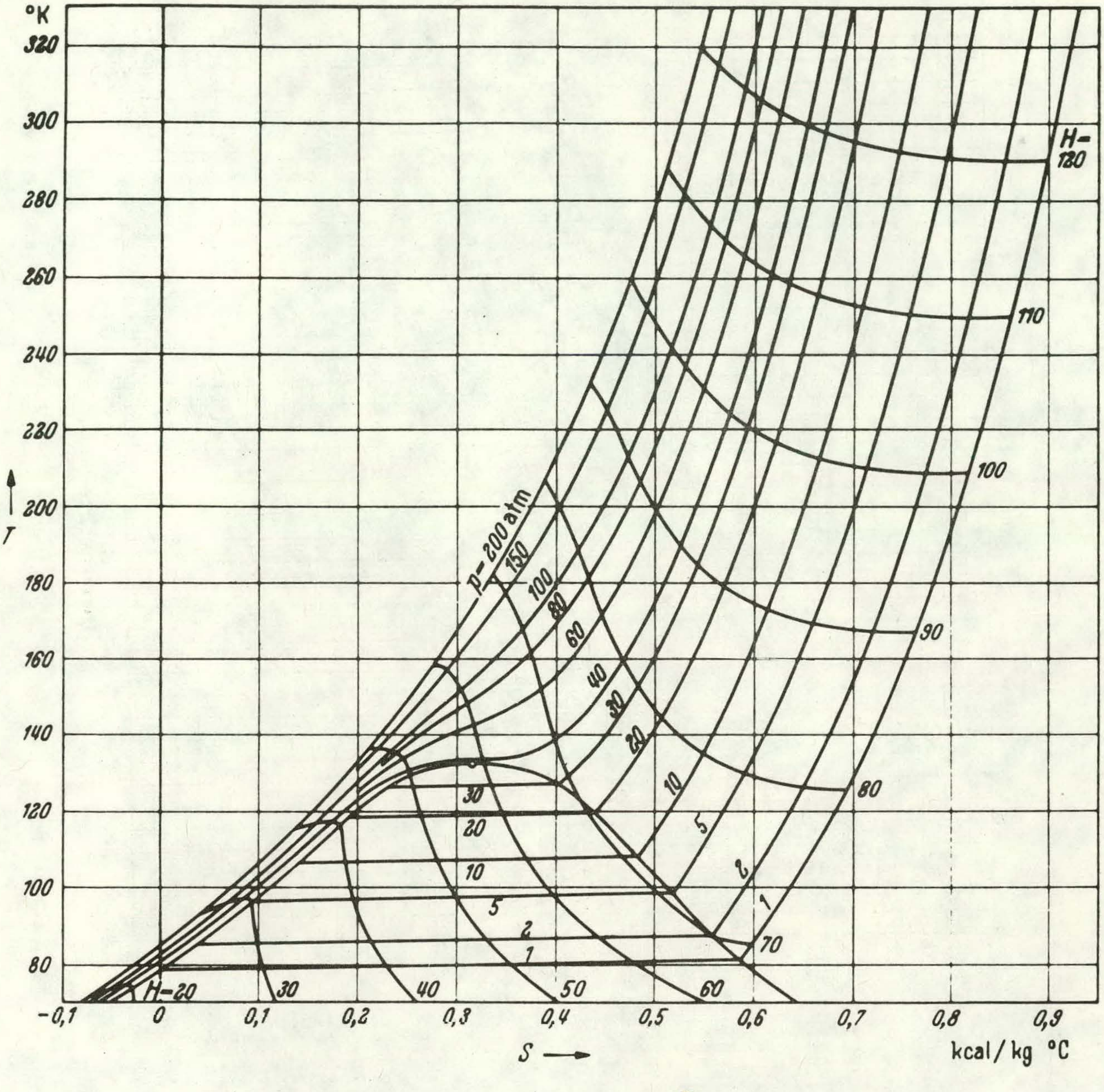

Fig. 10 Temperature-Entropy Diagram for Air (Source: Ref. 11)

The net work done to produce 0.076 mole of liquid nitrogen is:

$$
\begin{aligned}
W &= T_1(S_a - S_b) - \varepsilon(H_e - H_f) + (H_b - H_c) - (H_a - H_e) \\
&= 300(27 - 15.5) - 0.076(1310) + (2690 - 1300) - (2910 - 1310) \\
&= 3140 \text{ cal}
\end{aligned}
$$

So the energy use is 3140 cal per 0.076 mole or 41,316 cal/mole = 1476 cal/g = 1560 kWhe/ton. Compared with the reversible work of 192 kWhe/ton (see Table 12), this process is 12% Carnot efficient.

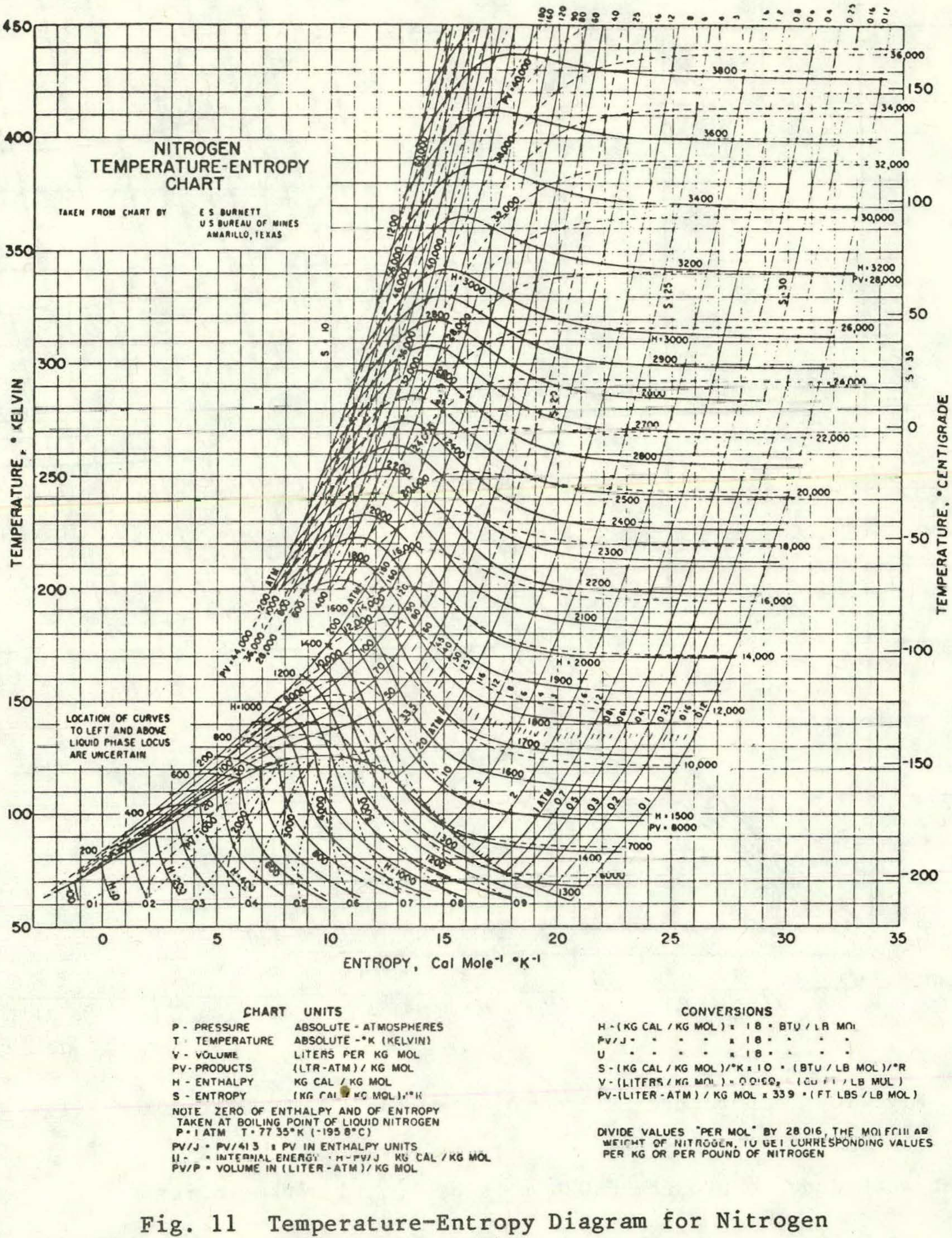

CHART UNITS

P - PRESSURE	ABSOLUTE - ATMOSPHERES
T - TEMPERATURE	ABSOLUTE -°K (KELVIN)
V - VOLUME	LITERS PER KG MOL
PV - PRODUCTS	(LTR-ATM) / KG MOL
H - ENTHALPY	KG CAL / KG MOL
S - ENTROPY	(KG CAL / KG MOL)/°K

NOTE ZERO OF ENTHALPY AND OF ENTROPY TAKEN AT BOILING POINT OF LIQUID NITROGEN P = 1 ATM T = 77.35°K (-195.8°C)

PV/J = PV/41.3 = PV IN ENTHALPY UNITS
U - = INTERNAL ENERGY = H - PV/J KG CAL / KG MOL
PV/P = VOLUME IN (LITER-ATM)/ KG MOL

CONVERSIONS

H - (KG CAL / KG MOL) x 1.8 = BTU / LB MOL
PV/J = " " " x 1.8 = " " "
U " " " " x 1.8 = " " "
S - (KG CAL / KG MOL)/°K x 1.0 = (BTU / LB MOL)/°R
V - (LITERS / KG MOL) = 0.0160, (CU FT / LB MOL)
PV - (LITER-ATM) / KG MOL x 33.9 = (FT LBS / LB MOL)

DIVIDE VALUES "PER MOL" BY 28.016, THE MOLECULAR WEIGHT OF NITROGEN, TO GET CORRESPONDING VALUES PER KG OR PER POUND OF NITROGEN

Fig. 11 Temperature-Entropy Diagram for Nitrogen
(Source: Ref. 8)

Table 14 Values Used to Calculate Work Required to Liquefy Nitrogen Using the Simple Linde Cycle

Point in Fig. 9	Entropy, S (cal/mole K)	Enthalpy, H (cal/mole)	Temp., T (K)	Pressure, p (atm)
a	27	2910	300	1
b	15.5	2690	300	200
c	9.5	1300	170	200
d	16.5	1300	77	-
e	17.3	1310	77	1
f	0	0	77	-

3.2 CRYOGENIC AIR SEPARATION PROCESSES

An air separation plant combines an efficient refrigeration system with a distillation process that depends on the difference in boiling points of oxygen and nitrogen. Both liquid and gas are produced using low-pressure air separation cycles. High-pressure cycles, used for liquid production in the 1950s, are based on reciprocating compressors available then. High-pressure cycles are becoming obsolete; they are more expensive and slightly more energy-efficient than low-pressure cycles. Plants that produce liquids have higher refrigeration requirements than those that produce gas; this accounts for the use of higher head pressures in early air separation plants.

Two principal types of equipment are required for an air separation plant: (1) equipment that operates at room temperature, including the compressors, inter- and after-coolers, oil separators, and water separators, and (2) the cold box, an insulated package of equipment operating below room temperature down to liquefaction temperature, which includes heat exchangers, clean-up equipment, expanders, and distillation columns.

3.2.1 Low-Pressure Cycle for Gas Production

The air separation cycle shown in Figure 12 is representative of the type used in low-pressure gas-production plants. Filtered air is compressed to approximately 75-85 psi in a centrifugal compressor and is after-cooled. After any liquid water is removed, the air enters the reversing heat exchangers and is cooled to nearly its dew point in counter-current heat exchange with the outgoing gaseous products. As the air cools, moisture is first condensed and frozen on the walls of the heat exchanger passage. At lower temperatures carbon dioxide freezes and also is deposited on the heat exchanger passage walls. The air emerging from the reversing heat exchanger is completely dry and has had over 99% of the carbon dioxide removed. Gas-phase, fixed-bed adsorption is used to remove the remaining carbon dioxide and, more importantly, any hydrocarbons entering with the air, which would be hazardous in the presence of liquid oxygen. The cleaned air is then fed to the bottom tray of the lower column of the double-column rectifier, as shown in more detail in Figure 13.

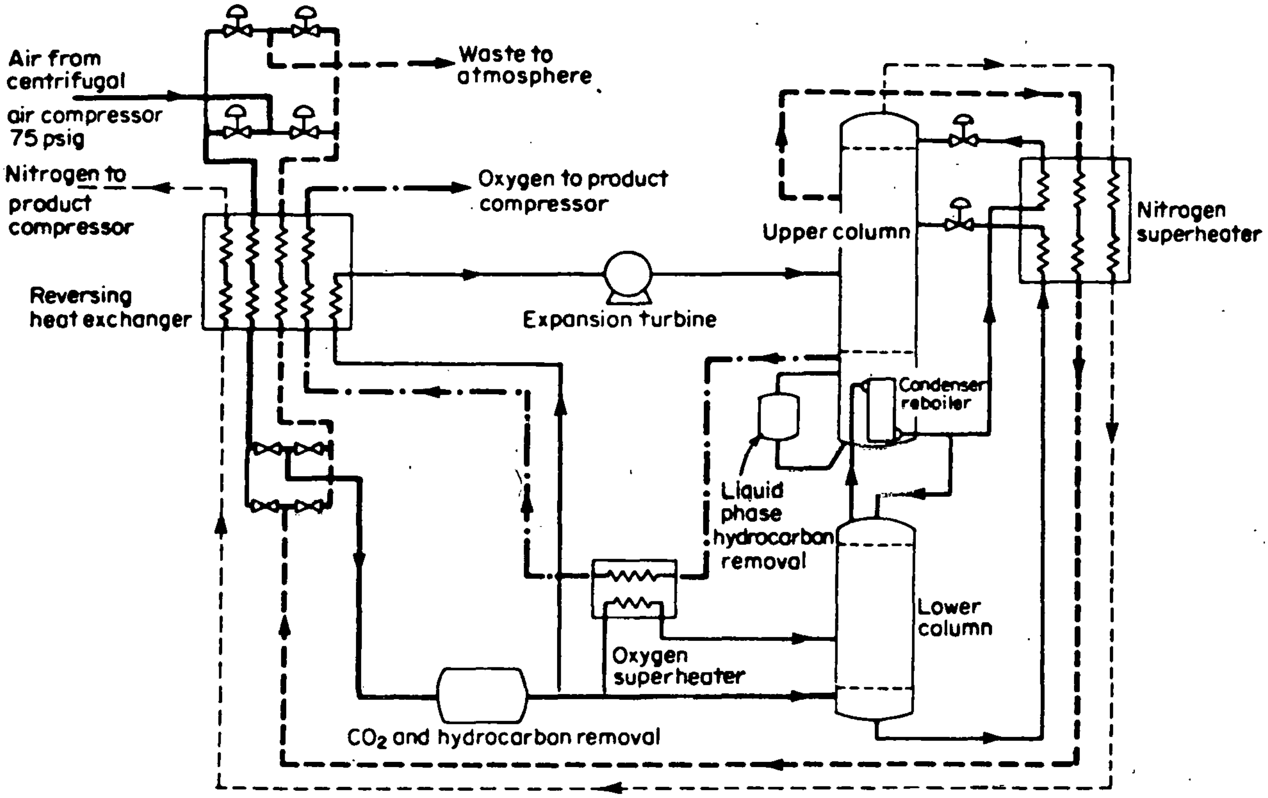

Fig. 12 Flow Sheet for Air Separation Plant Using Low-Pressure Cycle (Source: Ref. 7)

The double-column rectifier consists of two tray-type distillation columns that are thermally connected at the center through a heat exchanger that serves as a condenser for the lower column and a reboiler for the upper. Because nitrogen is more volatile then oxygen, it will ascend each column and oxygen will descend. Thus on the reboiler side of the upper column, there is a pool of high-purity, boiling liquid oxygen, while nearly pure nitrogen is condensed on the condenser side of the lower column. Because the normal boiling point of oxygen is 12.8 K higher than that of nitrogen, the pressure in the lower column must be high enough to raise the condensation temperature of nitrogen sufficiently to provide a positive temperature driving force in the main condenser.

To understand the energetics of this procedure, it must be recognized that the only refrigerant available is the liquid oxygen formed in the bottom of the lower column, which can be transferred to the main condenser. To use the liquid oxygen to rectify the liquid air, the column must produce liquid oxygen, apart from the vapor emitted from the bottom of the lower column. At 5 atm the boiling point of nitrogen is raised to 94 K, above the boiling point of oxygen at atmospheric pressure (90.2 K). Accordingly, an important step toward designing a plant that will yield pure oxygen and pure nitrogen simultaneously is to raise the pressure in the lower column to about 5 atm. This pressure requirement in fact necessitates use of a double instead of a single rectifying column.

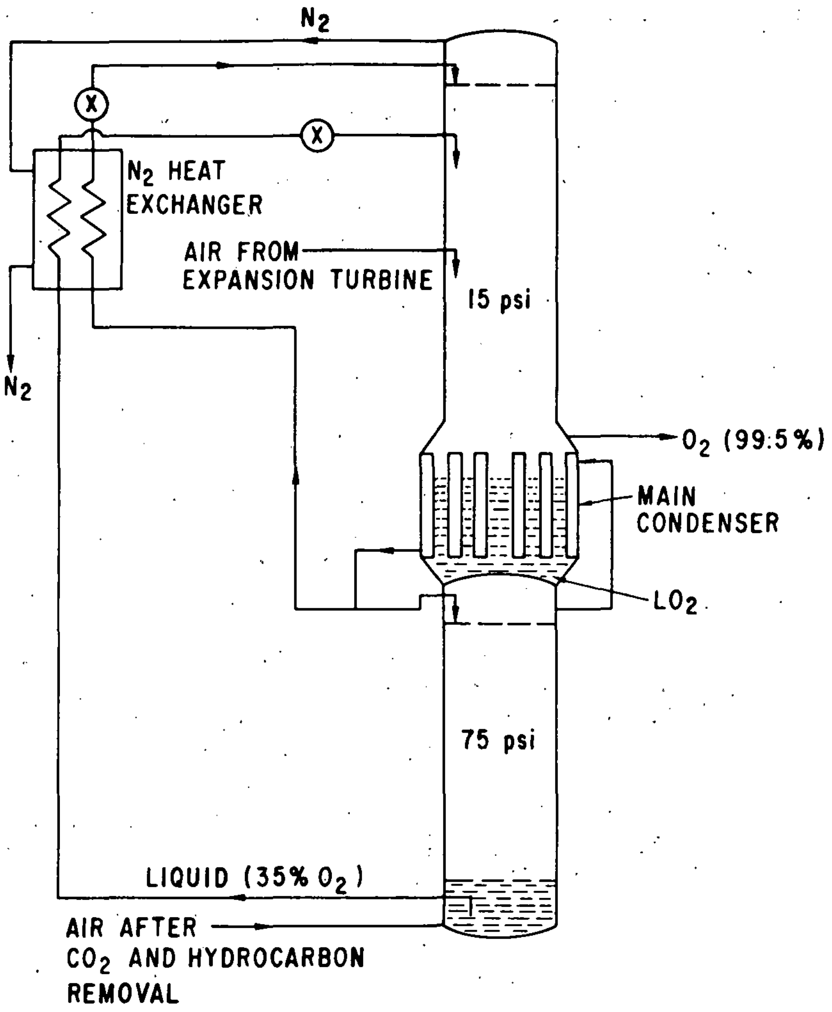

Fig. 13 Double-Column Rectifier Used in Gas-Producing Air Separators

The condensed nitrogen is split as it leaves the main condenser; one portion returns to the lower column as reflux, and the other is diverted to the upper column, through the nitrogen superheater, also for use as reflux.

An oxygen-rich (35%) liquid stream leaves the bottom of the lower column and, after being subcooled in the nitrogen superheater, serves as the main feed stream for the upper column. The two liquid streams entering the upper column are first subcooled to reduce flashing when throttled to the lower pressure of the upper column. The oxygen product is removed as saturated vapor from the main condenser, and a high-purity nitrogen product is removed as saturated vapor from the top of the upper column. The remaining gas is removed as a low-purity waste nitrogen stream several trays from the top of the upper column.

Carbon dioxide and light hydrocarbons tend to accumulate in the liquid oxygen in the main condenser. These constituents are removed by recirculating the main condenser liquid through a silica gel absorption trap.

The oxygen and two nitrogen streams are heated to approximately 100 K in their respective superheaters and are delivered to the reversing heat exchangers to be brought up to room temperature in heat exchange with the incoming air. The high-purity nitrogen and oxygen are warmed in separate nonreversing passages, while the waste nitrogen flows through passages that periodically reverse with the air passages. The waste nitrogen thus flows past the solid carbon dioxide and frozen moisture previously deposited from the air and causes the deposits to sublime. The waste nitrogen flow keeps the heat exchanger in a clean, operable condition.

The waste nitrogen stream has a purity of about 98% before entering the reversing heat exchanger. Demand for nitrogen has increased from 50% of total oxygen demand in 1973 to almost 100% of oxygen demand, but is still very low compared with the 4:1 nitrogen-to-oxygen ratio in air. It is therefore economically justifiable to use the waste stream for cleaning up the solid carbon dioxide and moisture deposits on the heat exchangers.

Refrigeration to overcome heat influx to the process is provided by expanding a portion of the air stream, for example through a centrifugal expansion turbine. Ideally, this is an isentropic process that reduces the enthalpy of the air being expanded and rejects energy from the process via the turbine shaft. Useful work can be recovered by coupling an electric generator to the turbine shaft. Clean, cold air for the turbine is withdrawn downstream of the carbon dioxide and hydrocarbon remover and reheated in a reversing heat exchanger to the proper temperature for introduction to the turbine. The reheating also controls the temperature pattern, helping maintain clean operation of the reversing heat exchangers. Air exhausting from the turbine is fed to the proper tray of the upper column.

Heat exchangers are usually of the very compact brazed aluminum plate-and-fin construction. Distillation trays may be either perforated or bubble cap. Construction materials for heat exchangers and distillation trays are aluminum, stainless steel, copper, and copper alloys. All low-temperature equipment is assembled, with piping, in one or more cold boxes heavily insulated with nonflammable materials.

3.2.2 High-Pressure Cycle

The cycle shown in Figure 14 is representative of the type used in high-pressure liquid oxygen and liquid nitrogen production plants. The refrigeration cycle for the forecooler is completely separate from the air cycle, with ammonia as the refrigerant. This is a conventional liquid expansion cycle consisting of an ammonia compressor, condenser, liquid throttling valve, and evaporator.

Atmospheric air initially compressed to about 2000 psi flows through separators that remove oil and water, which would freeze in the heat exchangers as the air is cooled. The air is then cooled in the precooler from room temperature to about 273 K (0°C) counter-current to the warming waste nitrogen stream, after which further cooling to 233 K (-40°C) is obtained in the ammonia-refrigerated forecooler.

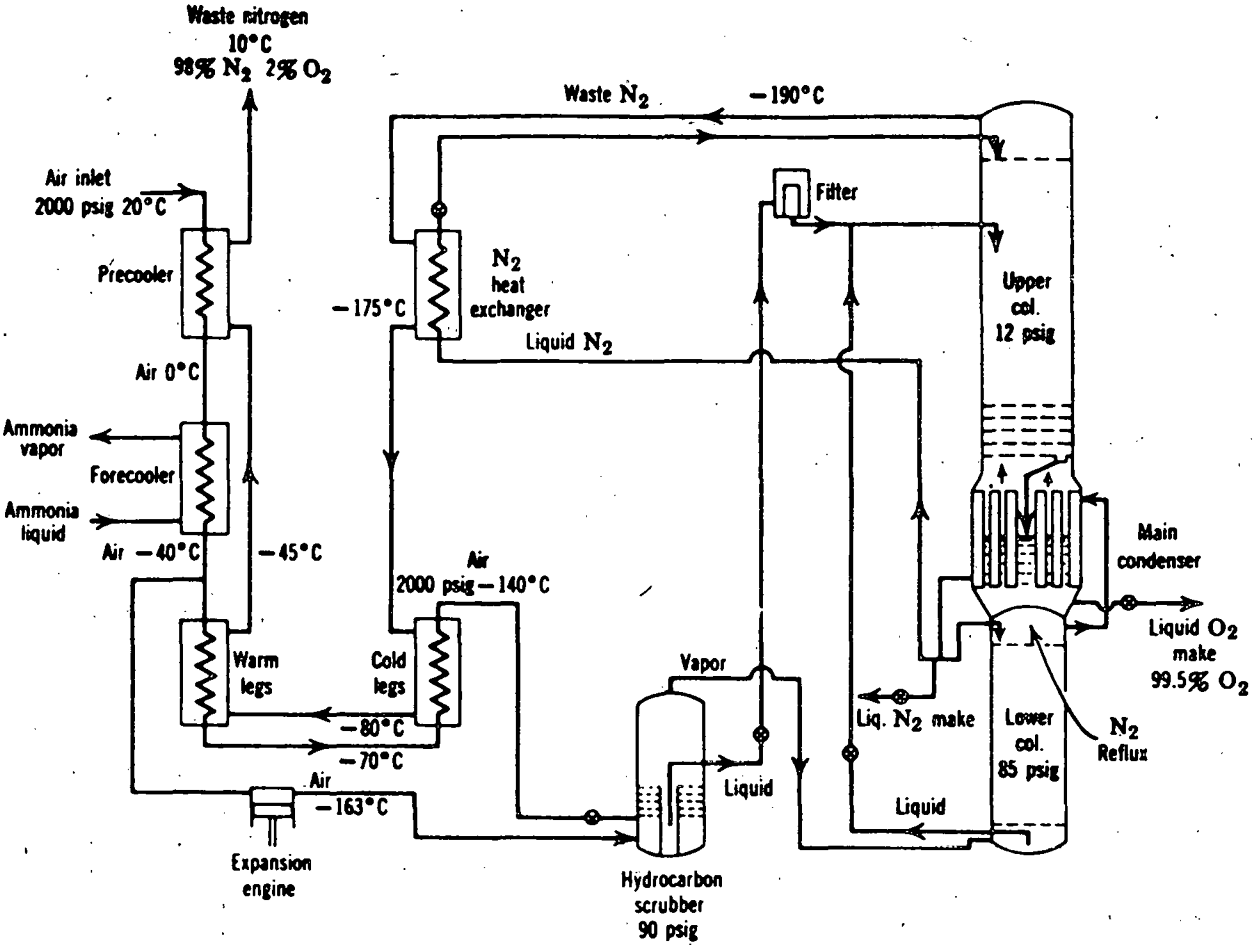

Fig. 14 Flow Sheet for High-Pressure Liquid-Producing Air Separation Plant (Source: Ref. 1)

The stream is then split into two parts, designated as "high pressure" and "expanded" air. The expanded air flows through the engine where, as the air expands doing external work, the temperature is decreased to 108 K (-165°C). This stream then flows to the hydrocarbon scrubber. The second stream of high-pressure air continues to be cooled to 133 K (-140°C) in the warm-leg and cold-leg heat exchangers counter-current to the warming waste nitrogen stream. Joule-Thomson expansion liquefies a portion of this stream, which then flows into the scrubber.

The remaining equipment in the process removes air contaminants and rectifies the feed into the liquid products. Additional information on the equipment is provided below.

Compressor. Centrifugal, axial-flow, or reciprocating units may be used. Usually, centrifugal or axial-flow machines are used in the high-capacity gas plants, whereas reciprocating machines are used in low-capacity gas plants or high-head-pressure liquid plants.

Oil Separator (no oil in centrifugal system, no piston ring). Oil from lubricated compressors must be removed since excessive carry-over into the heat exchangers can cause fouling, which may limit periods of continuous operation.

Water Separator. Cooling of the compressed air in the after-coolers results in appreciable condensation of water that also must be removed to prevent fouling of the heat exchangers. On an average summer day in a 500-ton/day oxygen plant, about four gallons of water per minute may flow into the process.[1] The water separator must be reliable and effective.

Precooler and Warm- and Cold-Leg Heat Exchangers. The precooler is a low-pressure-waste-nitrogen versus high-pressure-air, counter-current heat exchanger of conventional design. It cools the feed stream to about 273 K (0°C). Because of the high pressure of the air, the exchanger usually contains a relatively large number of small-diameter tubes. To increase heat transfer, the tubes may have extended surfaces. Water condensed in the precooler is removed by reversal of the air and nitrogen streams. The warm- and cold-leg heat exchangers operate in similar fashions.

Forecooler. Only liquid-phase oil and water are removed in the separators and precooler. Therefore, as the air is cooled to low temperatures, these contaminants will condense and solidify. The forecooler, refrigerated by the ammonia system, cools the high-pressure air to 233 K (-40°C) and is designed to handle the solids that are deposited. Two such units are installed so that one may be thawed while the other is in operation. Forecooling by a separate refrigeration system involves additional capital investment but reduces the amount of refrigeration that must be obtained by compressing the air. Without forecooling, it would be necessary to operate this cycle at a head pressure of approximately 3000 psi, which increases both plant equipment and operating costs. The decision whether or not to use forecooling is made on the basis of economics.

Expanders. Reciprocating and turbine-type expanders may be used. The reciprocating units are more adaptable to the high-head-pressure cycles of liquid plants, whereas turbines, with their inherent high capacity and more limited expansion ratio, are more frequently used with the lower-head-pressure gas-producing plants. Either type must have high adiabatic efficiency if a high overall cycle efficiency is to be achieved.

Hydrocarbon Scrubber. Air entering the hydrocarbon scrubber contains appreciable amounts of solid and gaseous carbon dioxide, residual amounts of solidified water and oil, and lesser amounts of other volatile hydrocarbons, such as acetylene, that are contained in the atmosphere. Within the scrubber, the impurities are washed from the vapor phase, which then flows to the distillation column. The wash liquid withdrawn from the scrubber flows through filters that remove the contaminants held in suspension but not those in solution. The filtered liquid is used as reflux in the distillation column. The quantity of solids collected in the filters requires that two filters be supplied and used alternately. Heavy residues that settle to the bottom of the hydrocarbon scrubber are blown down periodically through a drain.

Distillation Columns. The air feed may be fractionated in single or multiple columns. As outlined above, the two-column arrangement (Figure 15) with the lower column running at 5 atm is necessary for liquid oxygen production with provision for liquid nitrogen withdrawal. The operating pressures are so chosen that heat exchangers (known as the main condenser) can be interposed so that evaporation of liquid oxygen in the main condenser produces condensation of the nitrogen vapor in the lower column. All of the enriched liquid air and part of the liquid nitrogen produced by the lower column are pressure-transferred to the upper column. Here these reflux liquids flow down the trays against the reboiled liquid and become highly concentrated in oxygen. The remaining liquid nitrogen fraction, except for that withdrawn as product, is returned as reflux liquid to the top tray of the lower column.

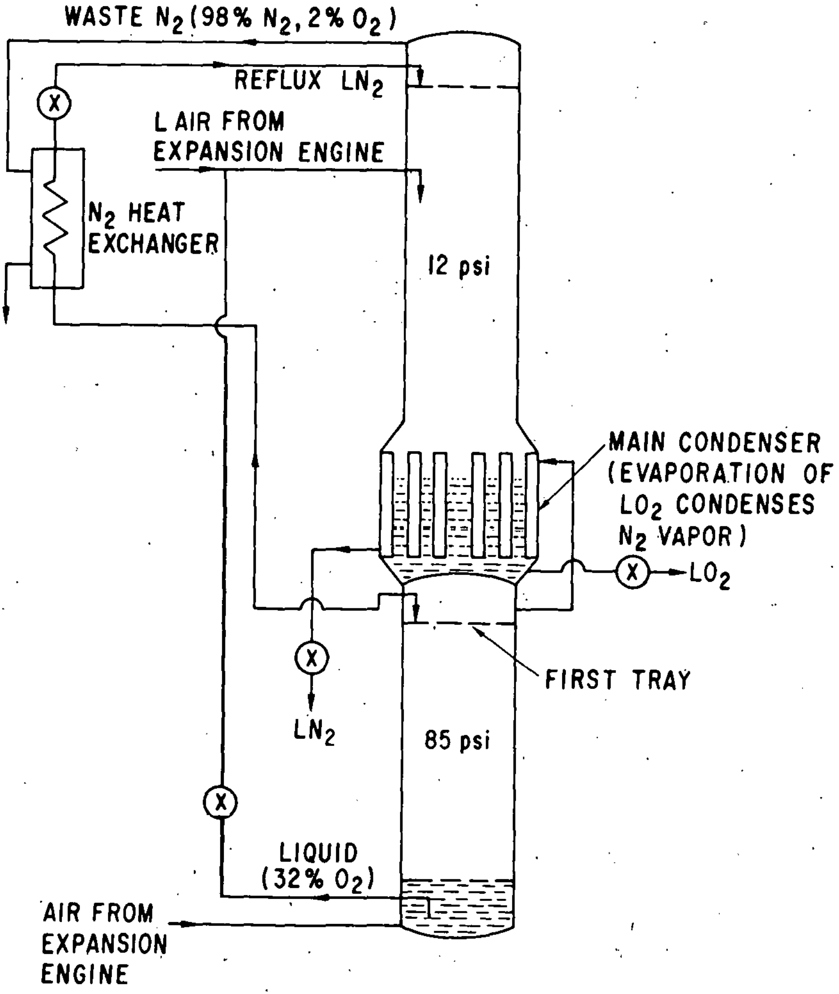

Fig. 15 Double-Column Rectifier Used in High-Pressure Liquid-Producing Air Separation Plants

3.2.3 Liquefying Oxygen at Low Pressure

Low-pressure cycles for production of liquid oxygen were developed by Union Carbide's Linde Division in the mid-1960s. These plants use a 150-psi (10-atm) liquefaction cycle instead of the high-pressure (2000-psi) cycle normally required in liquid-producing plants.

The low-pressure cycle has a number of advantages. In a typical high-pressure process, for example, the liquefaction cycle is based on a reciprocating compressor plus a booster-expander to bring air to about 2000 psi, and on a combination Joule-Thomson and engine expansion to provide refrigeration. The high-pressure equipment has a limited operating pressure range, is costlier to maintain and control, and its investment costs are high -- particularly for the heat exchangers.

In the low-pressure liquefaction cycle, the nitrogen remains in the gaseous state throughout its circulation, in contrast to other systems in which the refrigerant goes through two phase changes, i.e., during condensation and re-evaporation. The cycle can therefore be carried out at lower pressures by means of all-rotary compressors and work expanders, and it allows simpler controls and the use of low-pressure heat exchangers that do not cost as much as the high-pressure heat exchangers. Further, a high-pressure two-phase system that uses reciprocating compressors and expanders has the attendant control problems and possible lubricant contamination of the fluid being processed.

Linde's low-pressure circuit receives its feed of oxygen and nitrogen gas from the adjacent air separation unit. Optimum performance in the circuit is achieved by careful selection of the oxygen feed gas pressure, which, when combined with the nitrogen refrigerant pressure and recirculation rate, provides small temperature differences within the heat exchangers and permits maximum use of external forecooling. Increasing the condensing pressure of oxygen reduces its latent heat but increases the degree of subcooling needed. Hence, selection of the oxygen pressure is critical to maintain optimum economy between the latent heat and subcooling requirements.

Compressed to about 150 psi, the oxygen feed gas is first cooled to approximately 277 K (-46°C) in the warm-leg exchanger. It then enters a forecooler and is chilled to about 213 K (-60°C) with a counter-current stream of an externally supplied refrigerant (such as dichlorodifluoromethane). Further cooling to 133 K (-140°C) takes place against nitrogen gas in the cold-leg exchanger. Oxygen finally sent to the liquefier is cooled to saturation and totally condensed by a counter-current stream of low-pressure nitrogen gas. The liquid product is withdrawn and sent to phase separators where any vapor that forms prior to liquid storage is recycled to the compressors.

Expansion of compressed nitrogen gas provides nearly all of the low-temperature refrigeration needed in the circuit. Compressed to about 145 psi, nitrogen is cooled in parallel with the oxygen stream and countercurrently with the same stream after passing through the turbine, where it is expanded to a 6- to 10-psi range. Liquefaction of nitrogen is purposely avoided at this point to prevent reduced efficiency and possible erosion of the turbine-expander parts due to a mixed liquid-vapor flow. Also avoided is a two-phase flow in the heat exchangers and the resulting additional equipment such as entrainment separators and a liquid levels controller.

Expansion cools the nitrogen gases to about 86 K (-187°C) and provides power that is transferred directly to the boiler compressor by a high-speed shaft. During startup and cooling of the liquefier, the power developed by the work expander exceeds that which can be absorbed in the booster compressor, resulting in overspeeding of the compressor. This problem can be solved by installing a bypass in the nitrogen line to the turbine.

Another problem is the temperature "pinch" (i.e., a narrowing down of the temperature difference between the oxygen and nitrogen streams) that takes place in the liquefier at the point of condensation. This pinch -- which occurs when the recirculation ratio drops for any reason to 7.2 ft^3/hr (NTP) nitrogen per 1 ft^3/hr (NTP) oxygen liquefied -- becomes so severe that it limits the use of any additional refrigeration from the forecooler. High recirculation ratios are undesirable for opening the pinch because more refrigeration is then made available at the lowest temperature level than can be used, thus reducing overall cycle efficiency. According to Linde,[1] optimum performance with forecooling to 213 K (-60°C) is achieved with a recirculation ratio of 8.5 ft^3/hr of nitrogen per 1 ft^3/hr of oxygen liquefied and subcooled.

Linde[1] points out that this new low-pressure cycle is less expensive to build and operate, but it is slightly less energy-efficient than the high-pressure process. Its power costs are about 10% higher.

3.2.4 Large-Scale Oxygen Production

Oxygen plants are continually being made larger to satisfy industry's demands. An effort is made to increase the maximum commercial size of single-train components, so that the unit cost of oxygen can continue to be reduced as the plant size is increased. A present-day 2000-ton/day plant is depicted in Figure 16. In it, air is filtered and compressed to about 85 psig (a low-pressure cycle). The heat of compression is then removed in the water-cooled aftercooler before the compressed air enters the cryogenic equipment.

The air is cooled in the reversing heat exchanger, dropping in temperature from about 303 K to essentially the saturation temperature as it leaves the heat exchanger. During the cooling, water is condensed in the warmer part of the reversing heat exchanger and, at a lower temperature, it is frozen out on the heat exchange surface. In the colder portion of the heat exchanger, the carbon dioxide is solidified and also deposited on the internal surface of the reversing heat exchanger. After a short period, the air flow is reversed with the waste nitrogen flow. Waste nitrogen at low pressure can sublime the solid carbon dioxide and the ice, vaporize the liquid water, and carry them out to the atmosphere. Thus, the passage in the reversing heat exchanger is cleaned of contaminants, and the process can operate continuously in this cyclic fashion. For starting-up, the exchangers are reversed every 2 min to prevent contaminant build-up. The repetition is decreased to every 5 min and finally, at operation, to every 10 min.

Air at its liquefaction point leaves the cold end of the reversing heat exchanger and enters the bottom of the lower column. Air at this

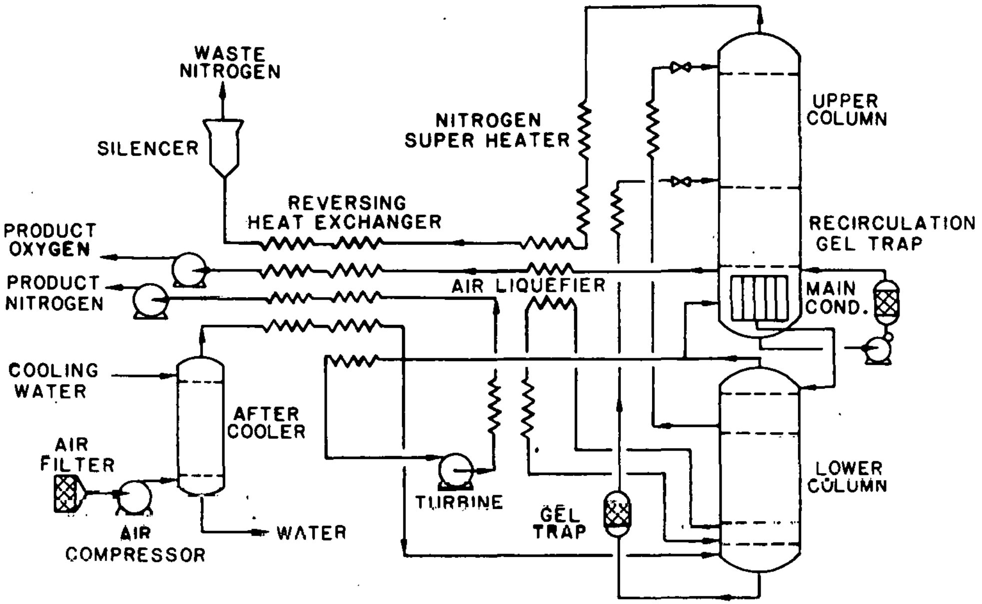

Fig. 16 Simplified Flow Diagram of a 2000-Ton/Day Oxygen Plant (Source: Ref, 1)

point contains an amount of carbon dioxide in equilibrium with the air, plus a small amount of solid carbon dioxide that has been physically displaced from the surface of the reversing heat exchanger. The lower set of trays of the lower column scrubs the carbon dioxide out of the vapor rising in the column. Thus, the liquid being removed from the bottom of the lower column will have a small amount of carbon dioxide with it. This will be removed in the kettle liquid gel trap by adsorption. Silica gel in this trap also removes any hydrocarbons from the liquid being transferred. The clean liquid is then transferred to the midpoint of the upper column. The carbon dioxide and hydrocarbons also could be removed in a gas-phase gel trap located at the cold end of the reversing heat exchanger.

Air is separated in the usual double-column arrangement. The lower column produces a stream of high-purity nitrogen vapor and a stream of liquid containing about 38% oxygen. The high-purity nitrogen vapor stream serves several important functions. It provides (1) a source of heat for vaporizing the liquid oxygen in the main condenser, (2) the reflux liquid for the upper portion of the lower column, (3) a clean stream to unbalance the reversing heat exchanger, and (4) a clean stream under pressure for expansion to produce refrigeration. It also becomes the high-purity nitrogen product stream after rewarming in the reversing heat exchanger. The reflux for the upper column is obtained a number of trays down from the top of the lower column. Both the kettle liquid stream and the nitrogen reflux stream are subcooled by the cold waste nitrogen stream leaving the top of the upper column. Both transfer streams are throttled into the upper column after passing through the subcoolers.

The upper column completes the separation of the streams into waste nitrogen and oxygen product. The high-purity oxygen liquid is collected at the bottom of the upper column. The difference in operating pressures between the lower and upper columns permits the main condenser to vaporize the liquid oxygen for the boil-up of oxygen vapor to the bottom of the upper column, and to vaporize the product gas by condensing the high-purity nitrogen on the other side of the main condenser.

Operational safety is of prime importance in the design of the main condenser. Small finned passages on the boiling side of the main condenser should be avoided because they are susceptible to plugging with foreign matter such as ice, solid carbon dioxide, or insulation. Once a passage is plugged, a flammable mixture can result if hydrocarbons are present in the boiling liquid, even when the condenser fin-stock is perforated and aligned. Two types of nonfinned, enhanced boiling surfaces have been developed by Union Carbide for use in main condensers. The oxygen passages in these reboilers are so large as to be virtually unpluggable.

Safe operation of the main condenser is assured by the continuous circulation of the liquid oxygen through the recirculation gel trap. Any carbon dioxide or hydrocarbons that manage to get into this liquid are adsorbed and removed from this system by the recirculation gel trap.

Product oxygen is warmed to essentially ambient temperature in a nonreversing pass in the exchanger. It is then compressed for delivery into the pipeline.

Refrigeration is provided by expansion of about 15% of the nitrogen product stream from the top of the lower column. Prior to expansion, the nitrogen is rewarmed in the cold leg of the reversing heat exchanger, thus adjusting the temperature difference in the cold leg to permit self-cleaning of the carbon dioxide deposits. The rewarmed nitrogen can then be expanded in the turbine without forming liquid in the wheel. This provides the necessary refrigeration to balance the cryogenic process. The expanded product nitrogen is then warmed in a nonreversing pass in the reversing heat exchanger. Warm product nitrogen is then compressed for delivery to the pipeline.

Waste nitrogen is partially warmed in the nitrogen superheater before it passes into the reversing heat exchanger to clean up deposits before passing into the atmosphere through the silencer.

Figure 17 shows some of the components of a 2000-ton/day plant. The larger-diameter cylinder on the right is the two-column rectification assembly. The smaller cylindrical system on the left actually has two components, an upper argon column and a lower storage vessel for product argon (see Section 4.1).

Air Compressor and Intercooling. The air compressor selected for a 2000-ton/day Linde plant is a single train axial-centrifugal machine. The unit consists of six axial stages followed by three centrifugal stages in a single casing. Integral intercooling takes place between the axial and centrifugal staging, and also between centrifugal stages. Two-stage suction filtering is used to ensure a properly cleaned air feed to the compressor. A suction silencer is also incorporated into the suction filter. Capacity control is provided through adjustable stator blading on all six axial stages.

Antisurge control is provided with the controller actuating a blow-off valve in the compressor discharge line. The driver of the compressor is a 39,000-hp, 1200-rpm brushless synchronous motor with forced air cooling. A speed-increasing gear couples the motor to the compressor with the 1200-rpm motor speed increased to a compressor speed of 4437 rpm. For noise attenuation, an acoustical hood houses the compressor and gear box. The compressor lower level also is totally enclosed, with the discharge line expansion joint, blow-down valve, and discharge silencer located in an isolated section of this enclosure. Compressor intercoolers and motor coolers also are located in sections of this enclosure.

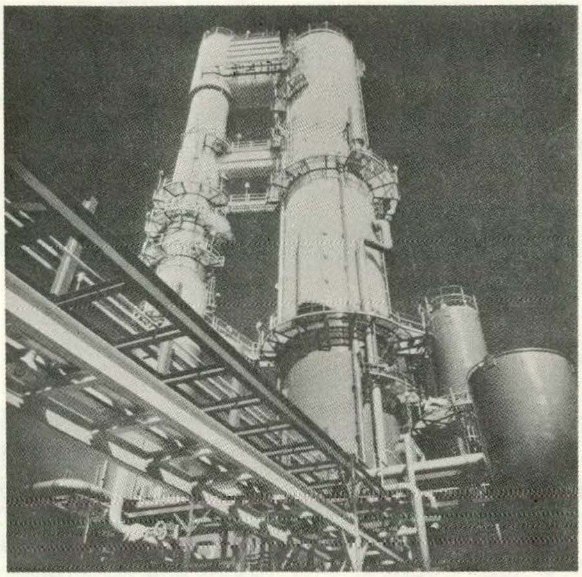

Fig. 17 A 2000-Ton/Day Air Separation Plant (Source: Ref. 1)

Cold Box Installation. Nearly all cold box components are made of aluminum. It is feasible to fabricate in the shop an entire set of cold box components: a complete turbine package, a gel trap package, one-piece rectification columns, a main condenser-reboiler, and four switching valve skids. The heat exchangers are of the brazed aluminum plate-and-fin type. Warm-end manifolding is prefabricated in the shop and field-mounted on foundations. The reversing heat exchanger cores are then welded in place. Prefabricated cold-end manifolding is completed in the field. All piping and manifold joints are welded. No mechanical joints are used within the cold box.

Tray Design. In the T-2000 plants of the Linde Division, both parallel-flow and cross-flow trays are incorporated into the design of the column. The parallel-flow tray is divided into two halves by a baffle. The liquid flows in opposite directions on each side of the baffle. On successive trays, however, the liquid on each half of the tray flows in the same direction. A bubbling promoter, shown in Figure 18, is used. The design of the promoter is such that the vapor flows preferentially through the promoter, adjacent to the inlet weir, initiating bubbling. Once initiated, the bubbling propagates across the tray deck; thus, the complete tray is active.

3.3 ADSORPTION TECHNIQUE FOR AIR SEPARATION

In the 1970s a new method for air separation, employing pressure-swing adsorption (PSA), appeared. Pressure-swing adsorption separates gas mixtures by short-time-cycle adsorption/desorption on fixed adsorption beds using gas pressure variation as the principal operating parameter.

Cryogenic air separation is generally more energy-efficient than PSA separation. But for small-tonnage productions, where the capital expenditure involved in cryogenic air separation may be too great, PSA offers an economical alternative. The breakpoint for cost-effectiveness in determining which cycle to use is about 20 tons/day. Below this production level, PSA has a shorter start-up time and lower equipment costs. The popular PSA units produce one, two, and five tons of oxygen a day.

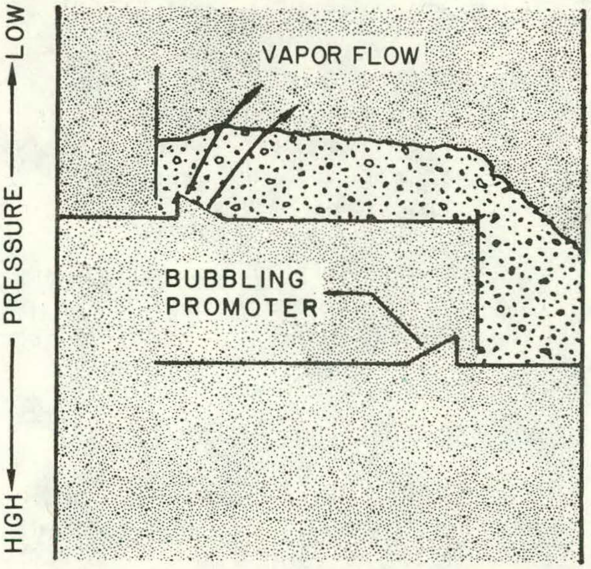

Fig. 18 Slotted Sieve Tray Bubbling Promoter used in 2000-Ton/Day Oxygen Plants (adapted from Ref. 1)

Historically, adsorption has been primarily employed in gas separation plants as an ancillary technique, e.g., for removing impurities such as water and carbon dioxide. At one time there was a certain amount of enthusiasm for the use of the "hypersorption" technique as a separation process, especially for hydrocarbon mixtures. Hypersorption employs moving beds of adsorbent that are recycled through zones maintained at different temperatures. It is in effect a continuous thermal-swing adsorption process. A notably successful application in the air separation industry has been the relatively large-scale separation of the krypton-xenon fraction from air separation units on moving beds of silica gel. In general, however, the problems associated with keeping considerable quantities of relatively friable solids in motion have inhibited the use of this technique.

Batch-type adsorption/desorption processes have been standard practice in the small-scale separation of gases. For example, the neon/helium by-product fraction has been separated into its components by fractional adsorption/desorption on a succession of charcoal beds cooled to liquid nitrogen temperatures. At a small scale, this technique can yield high-quality products.

The advent of commercial synthetic zeolite molecular sieve material has revolutionized the prospects for adsorption technology, not only in gas separation, but also in impurities removal, chromatographic analysis, and other fields. The exact geometry of zeolite molecular structures makes possible very high sorptive selectivity in cases where the molecules of only some components of a mixture have access to adsorption sites. This is the basis of the IsoSieve and similar thermal-swing techniques for separating straight-chain from branched hydrocarbons.

In addition to their true sieving capabilities, zeolites possess other structural properties that can create preferential adsorption effects, even among molecules of similar size. The case of air adsorption on a 5 Å sieve is a case in which all three main components are small enough to enter the sieve cage, but there is a higher capacity for nitrogen, which has a quadrupole moment, than for argon and oxygen, which do not.

3.3.1 Zeolite Molecular Sieves

Zeolites are crystalline, hydrated aluminosilicates of Group I and Group II elements (in particular, sodium, potassium, magnesium, calcium, strontium, and barium). The loosely held water in zeolites can be removed by heating and regained by exposure to a moist atmosphere, without destroying the crystal structure.

Structurally the zeolites are "framework" aluminosilicates based on an infinitely extending three-dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all of the oxygens. Zeolites may be represented by the empirical formula:

$$M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$$

In this oxide formula, x is generally equal to or greater than 2, since AlO_4 tetrahedra are joined only to SiO_4 tetrahedra, and n is the valence of the cation M.

Zeolites formed in nature occur in geodes, igneous rocks, and red clay and include chabazite, natrolite, mesolite, stilbite, heulandite, harmotome, phillipsite, etc. In synthetic zeolites, aluminum cations may be replaced by gallium ions and silicon ions by germanium or phosphorus ions. The latter necessitates a modification of the structural formula.

The structural formula of a zeolite is best expressed for the crystallographic unit cell as: $M_{x/n}[(AlO_2)x(SiO_2)y] \cdot wH_2O$ where M is the cation of valence n, w is the number of water molecules, and the ratio y/x usually has values of 1-5 depending on the structure. Occulsion of AlO_2 species within the zeolite structure may lower the ratio below one. The sum of x and y is the total number of tetrahedra in the unit cell. The portion of the formula in brackets represents the framework composition.

Although there are 34 species of zeolite minerals and about 100 types of synthetic zeolite, only a few now have practical significance as molecular sieves. Many of the zeolites, after dehydration, are permeated by very small channel systems that are not interpenetrating and that may contain serious diffusion blocks. In other cases, dehydration irreversibly disturbs the framework structure and the position of metal cations, so that the structure partially collapses and dehydration is not completely reversible. To be used as a molecular sieve, the structure of the zeolite after complete dehydration must remain intact.

3.3.2 PSA Oxygen Generation

Oxygen-enriched air can be produced by the selective adsorption of nitrogen on various zeolites, including calcium A, calcium X, and various types of mordenite. The selectivity for nitrogen, due to the quadrupole interaction, may be altered by varying the cation. Using this principle and a cycle based on a fixed-bed adsorption system, 95-98% pure oxygen may be produced when a polybed cycle (9-10 beds) is used.

Figure 19 shows the flow diagram of a LINDOX™ PSA oxygen generating system based on a three-bed adsorption scheme. During the adsorption step,

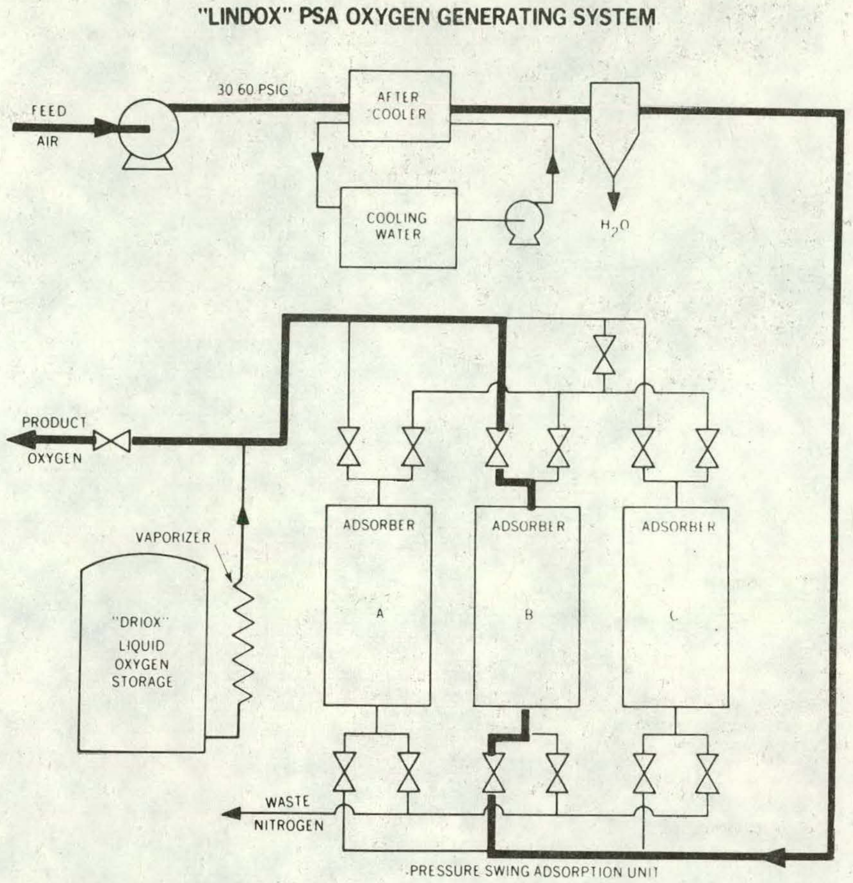

Fig. 19 Flow Diagram of a Simple PSA Air Separation System (Source: Ref. 1)

feed air flows through one of the adsorber vessels until the adsorbent is partially loaded. The feed is then switched to another adsorber and the first adsorber is regenerated in three steps: (1) depressurizing to atmospheric pressure, (2) purging with product oxygen, and (3) repressurizing to the adsorption pressure. In this figure, feed air is passing through adsorber "B." Oxygen that is 90% pure may be produced in such three- or four-bed systems operating between pressures of 55 psia and atmospheric pressure. As much as 55% of the oxygen introduced in the air feed is recovered as product oxygen. This process is used to produce oxygen for secondary sewage treatment.

Figure 20 shows a PSA plant for producing oxygen from air. The molecular sieve removes water, carbon dioxide, and nitrogen. This plant is used in conjunction with the Linde Division's UNOX™ system for wastewater treatment. The main components are a feed air compressor, PSA unit consisting of adsorber vessels pipe manifolded to sequencing valves, cycle control system, and instrument air dryer.

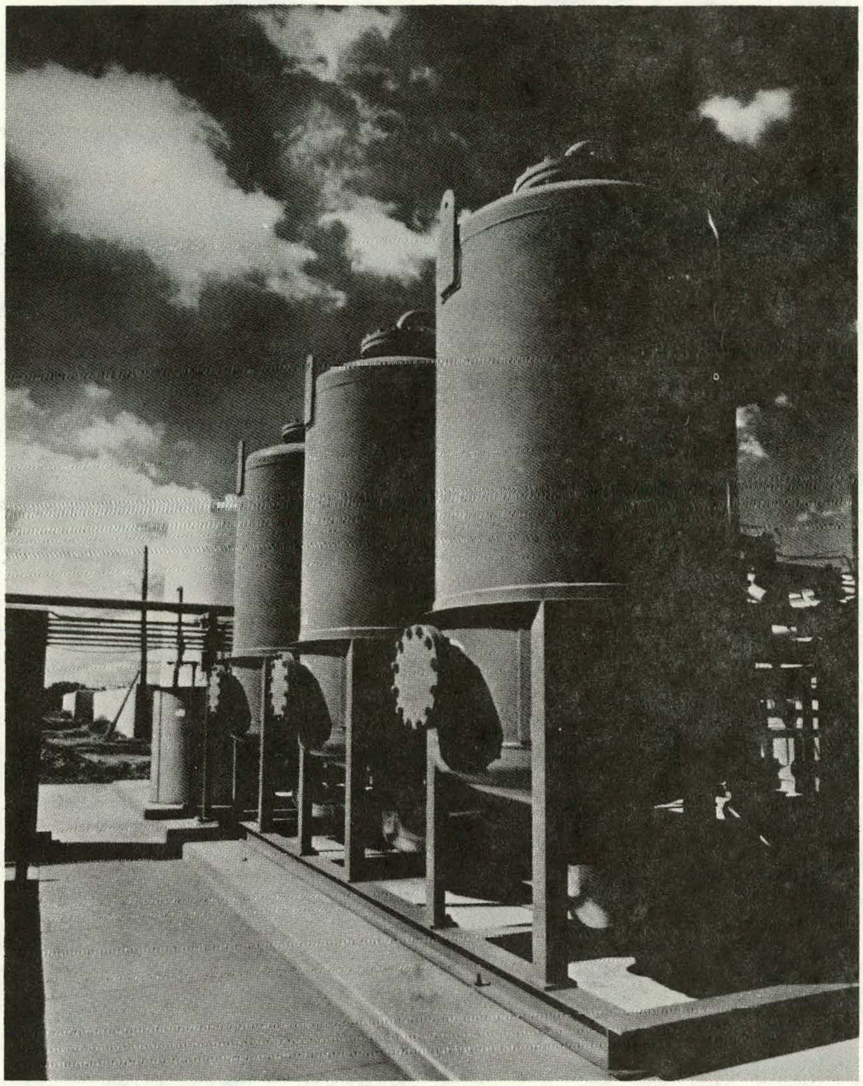

Fig. 20 Pressure-Swing Adsorption Plant for Producing Oxygen from Air (Source: Ref. 1)

3.3.3 Molecular Sieve Adsorption Processing

The separation processes employing molecular sieves are based on factors including the total sieving effect, a partial sieving effect, and relative adsorption selectivities. For obvious economic reasons, most adsorption separations today require a regeneration of the adsorbent after it becomes saturated with the adsorbate.

From a practical point of view, the adsorbent powder could be mixed into the fluid mixture and later filtered out. For most applications, however, separations are based on a fixed bed of agglomerated zeolite particles. The microcrystalline zeolite is mixed with an inert clay binder and shaped into pellets. The particle size, shape, and strength of these agglomerates determines the overall characteristics of the bed and the mechanical attrition (friction) resistance. Premature decrepitation of the zeolite pellets will produce a fine powder fraction that increases the pressure drop through the bed.

The usual configuration is vertical and flow through the beds may be either up or down. Horizontal beds also are used. A partial list of actual commercial separations that have been successfully achieved using molecular sieves is given in Table 15.

Table 15 Molecular Sieve Adsorption Applications

Air Products

Oxygen, nitrogen, argon

- Drying of air feed
- Carbon dioxide removal from air feed
- Nitrogen drying
- Argon drying
- Trace oxygen removal from argon
- Nitrogen oxides from air
- Nitrogen oxides from nitrogen
- Hydrocarbons from air feed
- Oxygen/nitrogen separation
- Trace methane from liquid oxygen

Inert gas

- Bulk carbon dioxide removal from flue gas
- Sulfur dioxide removal

Chemical and Petrochemical Industries

Ammonia

- Feed desulfurization
- Synthesis gas drying
- Synthesis gas purification
- Ammonia recovery from vent gas
- Bulk carbon dioxide removal
- Argon recovery from vent gas
- Hydrogen recovery from vent gas

Hydrogen

- Feed desulfurization
- Hydrogen drying
- Hydrogen purification
- Hydrocarbon removal
- By-product hydrogen upgrading
- Recovery from dissociated ammonia
- Bulk carbon dioxide removal

Sulfuric acid

- Sulfur dioxide removal from plant vent gas

Unsaturates

- Cracked gas drying
- Ethylene drying
- Propylene drying
- Butene drying
- Butadiene drying
- Isoprene drying
- n-Butene from isobutylene
- Carbon dioxide removal from ethylene
- Wulff furnace gas drying
- Acetylene drying
- Isoprene purification
- Propylene desulfurization
- Ethylene recovery from dementhanizer overhead
- Ethylene recovery from ethylene oxide blow-off gas
- Acetylenes from butadiene
- Olefin recovery from refinery off-gas
- Ethylene recovery from coke oven gas

Unsaturates (Cont'd)

- Ethylene recovery from styrene off-gas
- Methyl acetylene from propadiene

Biodegradable detergents

- n-Paraffin recovery from kerosene
- Kerosene drying

Aromatics

- Benzene drying
- Toluene drying
- Xylene drying
- Cyclohexane drying
- Solvent drying
- Styrene drying
- n-Hexane from benzene

Other chemicals

- Butanol drying
- Acetone drying
- Carbon dioxide drying
- Carbon tetrachloride drying
- Propylene dichloride drying
- Ethylene dichloride drying
- Fluorocarbon refrigerant drying
- Phenol drying
- Acrylonitrile drying
- Pyridine drying
- Ethanol drying
- 2-Ethylhexanol drying
- 2-Ethylhexyl chloride drying
- n-Butyl chloride drying
- Amyl acetate drying
- Dimethylformamide drying
- Diethyl ether drying
- Isopropyl ether drying
- Isopropanol drying
- Tetrahydrofuran drying
- Methylene chloride purification
- Propylene oxide drying
- Vinyl chloride purification
- Trichloroethylene purification
- Solvent drying
- Nitrogen oxides from HNO_3 off-gas
- Chlorine drying
- Peppermint oil drying
- Ammonia from dissociated ammonia
- Cable oil drying

Petroleum Refining

Catalytic cracking

- Unsaturate recovery
- Hydrogen recovery

Hydrocracking

- Recycle hydrogen drying
- Recycle hydrogen purification
- Feedstock purification
- Hydrogen upgrading

Table 15 (Cont'd)

Petroleum Refining (Cont'd)

- Alkylation
  - Feedstock drying
  - Feedstock desulfurization
  - Normal/iso separation
- Isomerization
  - Feedstock drying
  - Feedstock desulfurization
  - Normal/iso separation
- Catalytic reforming
  - Recycle hydrogen drying
  - Recycle hydrogen desulfurization
  - Feedstock drying
  - Regenerating gas drying
  - Normal/iso separation
  - Feedstock desulfurization
  - Feedstock denitrogenation
  - Hydrogen upgrading
- Catalytic polymerization
  - Feedstock desulfurization
  - Feedstock drying
- Vapor recovery
  - Adsorber oil drying
  - Refinery gas drying
  - Ethylene recovery
  - Propylene recovery
  - Hydrogen recovery
  - Hydrogen sulfide recovery
- Heavy products finishing
  - Transformer oil drying
  - Lube oil dewaxing
- Light products finishing
  - LPG drying
  - Butane drying
  - Pentane drying
  - Hexane drying
  - Heptane drying
  - Fuel oil drying
  - Jet fuel drying
  - Benzene drying
  - Xylene drying
  - Solvent drying
  - LPG sweetening
  - Butane sweetening
- Light products finishing (Cont'd)
  - Pentane desulfurization
  - Propylene recovery
  - Jet fuel desulfurization
  - Jet fuel upgrading
  - Diolefin removal
  - Peroxide removal
  - Hydrogen upgrading

Natural Gas Industry

- Production
  - Natural gas drying
  - Field condensate drying
  - Natural gas sweetening
  - Condensate sweetening
  - n-Paraffin recovery
- Processing
  - Natural gas drying
  - Condensate drying
  - Absorber oil drying
  - LPG drying
  - Butane drying
  - Pentane plus drying
  - Sour Canadian gas drying
  - LPG sweetening
  - Propane sweetening
  - Butane sweetening
  - Natural gas sweetening
  - Ethane-propane mix purification
  - Carbon dioxide removal from natural gas
  - Normal/iso separation
  - Natural gasoline sweetening
  - Bulk hydrogen sulfide recovery
  - Normal paraffin recovery
  - Ethane-plus recovery
  - Aromatics recovery
  - Bulk carbon dioxide removal
- Transmission and storage
  - Natural gas drying
  - Natural gas sweetening
  - LNG plant feed drying
  - LNG plant feed purification
  - Helium plant feed drying
  - Helium recovery

4 MATERIALS FLOWS

4.1 OUTPUT EFFICIENCY

The typical products of an efficient air separation plant consist of oxygen (99.5 mol % oxygen), nitrogen (containing 5 ppm oxygen), and argon and other rare gases. In a conventional air separation plant employing reversing heat exchangers and a double-column distillation system, the air and waste nitrogen flows are regularly interchanged. This interchange provides for condensation and re-evaporation of water and carbon dioxide over the full range from room temperature to the liquefaction temperature of air; by this means, water and carbon dioxide concentrations in the air are reduced below 1 ppm. The most important consideration in the design of this system is to obtain complete re-evaporation of the water and carbon dioxide into the waste stream. This completeness is a function of the relative pressures, temperatures, and flows of air and waste nitrogen. For a low-pressure plant using reversing heat exchangers approximately 6 m in total length and an air pressure of 5 atm, it is necessary to use a waste nitrogen flow that is 50-60% of the feed air flow.[12,13] This represents an output efficiency (output moles per input moles) of 40-50%.

The state-of-the-art air separator is a prepurifier type,[1] in which most of the unwanted contaminants such as carbon dioxide and water are removed from the air by adsorption in molecular sieves. The prepurifier air separator has an output efficiency of 80%, i.e., 0.8 mole of product can be obtained from 1 mole of air. The output efficiencies of three types of air separators are compared in Table 16.

Air separation is a relatively clean process; practically no chemical reactions take place in the distillation columns. Since air is 0.93% argon, which has a boiling point between those of nitrogen and oxygen, argon appears as an impurity in either the nitrogen or oxygen delivery streams (or in both). If argon is collected with oxygen, the latter will contain about 5% argon. If the argon is extracted with the nitrogen, the nitrogen will have about 1.3% argon as an impurity. As there is an extensive commercial demand for argon, many air separation facilities have an auxiliary column in which argon is concentrated. The argon refinery process, if used, consumes some

Table 16 Output Efficiency of Air Separation Plants

Type of System	Output Moles per Input Mole
Regenerator[a]	0.35
Reversing heat exchanger	0.50
Prepurifier	0.80

[a] Regenerators, historic heat exchangers (see Ref. 8), are included here for output efficiency comparison.

material, however. The crude argon stream, containing 15-20% argon, from the upper column is fed to the argon column, which produces 98% argon with 2% oxygen and a few parts per million of nitrogen. Hydrogen is added to this mixture to combust out the remaining oxygen, and the product is fed to the argon refinery column to remove the nitrogen and the excess hydrogen by distillation. The final product argon contains 5-10 ppm of oxygen and nitrogen.

4.2 EFFECT OF NITROGEN-TO-OXYGEN PRODUCT RATIO

As noted in Section 1.2, the primary use of oxygen has been in the manufacture of steel. Nitrogen requirements for steel manufacture are modest and seldom exceed a small fraction of the oxygen flow. While air separation plants can produce more than three times more nitrogen than oxygen, the present market calls for a nitrogen-to-oxygen product ratio of 1:1 to 1.5:1. However, in the chemical industry and the liquified industrial gases market, the requirement for nitrogen may substantially exceed that for oxygen. This section, therefore, examines the factors controlling the design of an air separation plant and discusses the process cycle choices that result from different product ratio requirements.

The high-pressure (lower) column of a conventional distillation system separates the gaseous feed air into a nitrogen stream and an oxygen-enriched stream. The latter is passed as a liquid to the low-pressure (upper) column and is further separated into oxygen and nitrogen. Oxygen reboil for the upper column is provided by condensation of nitrogen in the lower column; this condensed nitrogen is available as reflux for the two columns.

There are several restraints in this system. Minimum reflux in the high-pressure column can allow production of a nitrogen flow (at high pressure) that is 42% of the column feed air flow. This nitrogen may be used as gas, directly as nitrogen product, or to provide refrigeration by expansion in the turbine. In the latter case the nitrogen subsequently becomes available as a low-pressure product. Alternatively, the high-pressure nitrogen may be condensed and used as reflux to the low-pressure column. In this case approximately twice the reflux flow is available as a low-pressure nitrogen gas product from the low-pressure column.

Removal of nitrogen gas from the high-pressure column decreases the boil-up available in the low-pressure column and thus the oxygen product flow must be reduced to maintain purity. The distillation system in the low-pressure cycle is such that essentially all of the oxygen in the plant feed air may be recovered as product when no high-pressure nitrogen product is taken from the high-pressure column (at these conditions approximately 10% of the air flow is passed to the expansion turbine to maintain the plant refrigeration balance). As the flow of high-pressure nitrogen gas is increased, the air-to-oxygen flow ratio increases from approximately 5:1 to 8.4:1 at minimum reflux in the high-pressure column. To increase the nitrogen-to-oxygen ratio beyond about 3:1 (corresponding to an air-to-oxygen ratio of 4:1), part of the oxygen product must be discarded; thus the air-to-oxygen ratio increases rapidly.

For the case where gaseous nitrogen is removed only as a low-pressure product, the air-to-oxygen flow ratio remains essentially constant at 5:1

until the minimum reflux ratio in the high-pressure column is reached at a nitrogen-to-oxygen ratio of about 3.7:1. These relationships are shown in Figure 21.

As noted previously, with reversing heat exchangers it is necessary to use a waste nitrogen flow approaching 60% of the feed air flow. Figure 21 shows that the carbon dioxide clean-up limitation controls the low-pressure cycle design as follows. The minimum air flow required for a plant producing low-pressure nitrogen is determined by clean-up when the nitrogen-to-oxygen ratio exceeds 1.2:1. For a plant producing nitrogen at high pressure, the clean-up limit does not become a controlling factor until the product nitrogen-to-oxygen ratio exceeds 2:1.

The most convenient direct method of reducing the waste flow required for clean-up is to increase the air pressure in the heat exchangers. However, this may be uneconomical unless some further benefit, such as increased pressure of nitrogen and oxygen product, can be derived.

Use of the low-pressure cycle at nitrogen-to-oxygen product ratios above 2:1 necessitates that carbon dioxide and water be removed by adsorption. They are conveniently removed from air by adsorption onto a fixed bed of molecular sieves. Two beds can operate on a cyclic basis with one on-stream while the other is regenerated. Fifteen to twenty percent of the air flow is generally required to provide once-through open-circuit regeneration. This limitation is shown in Figure 21, where, for low-pressure nitrogen production, it controls the air flow to a low-pressure plant when the product ratio exceeds 3.3:1. A partially closed loop regeneration cycle can be used to avoid this limitation but increased reactivation temperature and capital cost result.

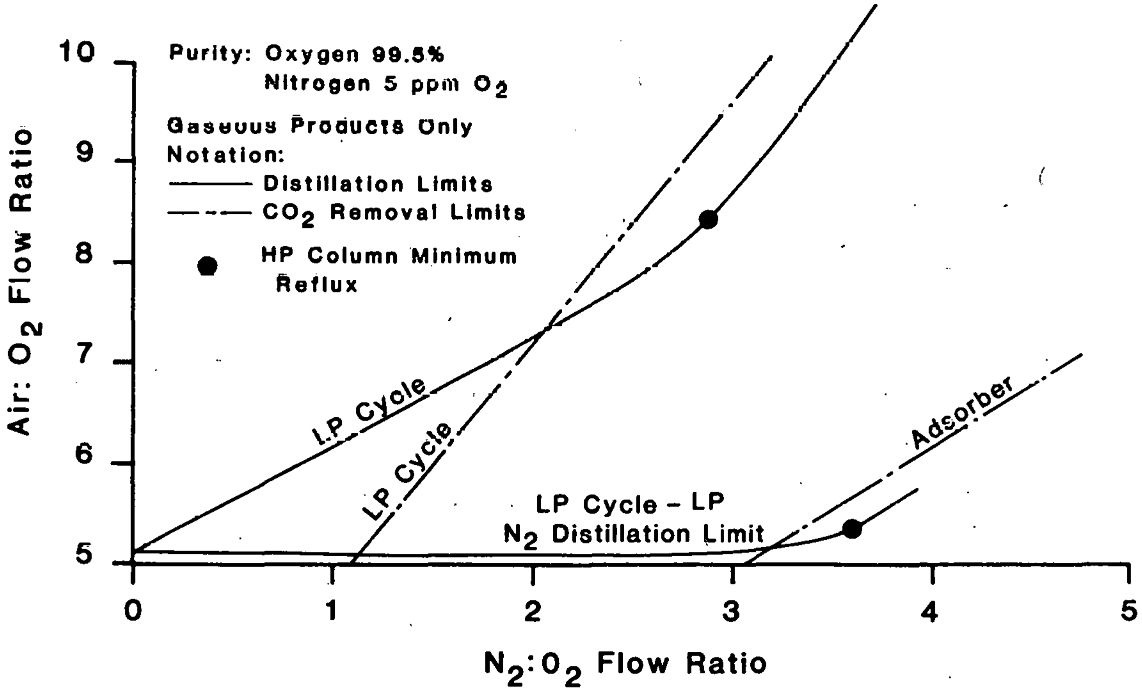

Fig. 21 Distillation and Carbon Dioxide Clean-Up Limitations in Air Separation Plants (adapted from Ref. 12)

Another important consideration is the concentration of oxygen in the reactivation gas. At oxygen concentrations above 21%, the risk of fire increases rapidly, especially in a system that requires electric heating. The limit corresponding to the 21% composition is a product ratio of 3.75:1.

5 ENERGY USE

5.1 ENERGY EFFICIENCY

In Section 3.1 we estimated that a liquefaction process using the simple Linde air liquefier is 13% Carnot efficient (1340 kWhe/ton of air liquefied). The efficiency of practical liquefaction processes has been reported to range from 7.5% (2560 kWhe/ton of liquid nitrogen) to at least 33% (582 kWhe/ton of liquid nitrogen).[14] Another source found the actual work to liquefy nitrogen in plants of moderate size to be about 860 kWhe/ton, and the separation work (in addition to the liquefaction work) to be about 100 kWhe/ton (for 65% isothermal compression efficiency).[15] The total work involved in separation and liquefaction was 960 kWhe/ton of liquid nitrogen.

The energy use in air separation consists of energy use (1) in compression, expansion, partial liquefaction, and distillation; (2) associated with cooling water pumps and auxiliaries; and (3) due to heat leaks, inefficiencies in the expansion engine, and compression of gaseous impurities. The energy used in the above three categories was reported[16,17] to be 176 kWhe, 15 kWhe, and 147 kWhe, respectively, for the production of one ton of air product which, in 1973, consisted of 33.5% by weight nitrogen, 65.7% oxygen (see Table 3), and 0.9% argon. The total air separation work was therefore 338 kWhe/ton of air product.

A more recent figure for the above air separation work is about 203 kWhe/ton of gas product;[1] most of the improvement can be attributed to an increase in plant size. A reasonable scheme of energy allocation is 60 kWhe/ton of nitrogen gas and 278 kWhe/ton of oxygen gas, both at normal temperature (70°F) and pressure (14.696 psia).[1]

Most gaseous oxygen is used under pressure. The Burns Harbor plant of the Linde Division, for example, pipes gaseous oxygen into the Chicago Complex pipeline network at an average pressure of 500 psig, and other plants in the complex pipe at about 350 psig. The Burns Harbor plant, however, supplies a major fraction of the oxygen to the pipeline system. The pressure of cylinder oxygen is typically about 2200 psig, but cylinder usage represents only a small share of the total oxygen market. A weighted average of the oxygen pressure is now 400-450 psig, and is increasing.[1] The average work to pressurize oxygen is about 117 kWhe/ton of oxygen at a compressor efficiency of about 62% isothermal.

The Burns Harbor plant pipes nitrogen at 295 psig, and a weighted average is about 200 psig. The pressurization work with a practical compressor efficiency of 65% is about 103 kWhe/ton of nitrogen. The compression of nitrogen is more efficient because oxygen compression equipment must be conservatively designed to ensure safe operation.

Figures for 1973 for liquefaction work were 630 kWhe/ton of liquid oxygen and 662 kWhe/ton of liquid nitrogen, about 25% and 29% Carnot efficient, respectively.[16] With Carnot efficiencies of 30% and 33%, the liquefaction work is estimated to be 525 kWhe/ton of liquid oxygen and 582 kWhe/ton of liquid nitrogen. The total energy consumed in the production of the liquids (separation plus liquefaction energy) is thus about 800 kWhe/ton of liquid oxygen and 640 kWhe/ton of liquid nitrogen. These figures are in excellent agreement with a recent production number of 760 kWhe/ton of air products.[18] The results of the analysis of energy use are summarized in Table 17.

5.2 ENGINEERING AND ECONOMIC COMPARISON OF CYCLES

For tonnage production of oxygen that is at least 99.5% pure, the low-pressure air separation cycle using reversing heat exchangers requires about 2% less power than the low-pressure cycle using regenerators, but the total volume of product gas (free of water and carbon dioxide) available increases from 35% to about 50% of the incoming air. The Linde Division's T-2000 model can output 93% of the total oxygen in the input air as product oxygen. Other cycles whose objective is not solely to produce oxygen gas produce more coproduct gases. A typical low-pressure cycle with molecular sieve prepurifiers outputs more than 80% of the input air as coproducts.

A recent study by Air Products and Chemicals, Inc., compared the capital investment and energy requirements of different air separation cycles, as shown in Table 18. An accurate comparison of capital costs for these cycles is difficult because differences between cycles are frequently overshadowed by site-related items, construction productivity, premiums for plant reliability, and the performance of the contractor. But relative energy requirements are determined by cycle thermodynamics and can therefore be compared with considerable accuracy.

For the production of high-pressure oxygen gas, the low-pressure-cycle plant with reversing heat exchangers is a clear economic choice. In cases

Table 17 Total Energy Used to Produce Oxygen and Nitrogen

Process, Product	kWhe/ton
Separation[a]	
Oxygen gas at NTP	278
Nitrogen gas at NTP	60
Liquefaction	
Liquid oxygen	525
Liquid nitrogen	582
Separation plus liquefaction[b]	
Liquid oxygen	800
Liquid nitrogen	640
Separation plus pressurization	
Oxygen gas at 425 psig	395
Nitrogen gas at 200 psig	163

[a] NTP = Normal temperature (70°F) and pressure (14.696 psia).

[b] Totals are not exact because of rounding.

Table 18 Capital Cost and Energy Comparisons for Three Air Separation Cycles (tonnage plant, 99.5% pure oxygen, pressure of 1200 psig)

Low-Pressure Cycle	Relative Energy Requirement	Capital Investment	Product O_2 and N_2 Available as % of Incoming Air
Reversing heat exchangers	100% (base)	100% (base)	50
Regenerators	102%	103%	35
Molecular sieve	106%	105%	80

Source: Ref. 19.

where very high percentages of pure and dry nitrogen are required, such as two to three times the oxygen requirement, a low-pressure cycle using molecular sieves as a prepurifier would be used. Some small oxygen plants and liquid oxygen and nitrogen plants serve users requiring a high nitrogen-to-oxygen production ratio. At present, for large-tonnage oxygen gas plants, the gaseous nitrogen requirement rarely exceeds the oxygen requirement, but this may not be the case when nitrogen demand increases, especially if nitrogen users select centralized locations, with oxygen users, for their plants.

Many different types of air separation plants have been designed to suit individual customers. The Chicago Complex of Linde, which accounts for a quarter to a third of U.S. oxygen production, uses two T-2000s (2000 tons/day) and eight T-1200s (1200 tons/day); three of the T-1200s are coproduct plants. Of the plants in this complex, which serves 30 users whose main need is for large quantities of gaseous oxygen, the most recent additions are the T-2000s, which are extremely efficient in producing oxygen but less efficient in terms of materials flow (less product oxygen and nitrogen are available as percentages of incoming air than in coproduct plants). The three coproduct plants, which use molecular sieves for cleanup to make 80% of the input available as product, are at one location, and their production represents only a minor fraction of the total production in the Chicago Complex. The reason for such distribution is simple: the overall industry is heavily oxygen-centered, and not all the nitrogen that is coproduced has a market. The overall product ratio of nitrogen to oxygen may be close to 1:1, but the usage ratio is considerably lower.

On the other hand, there are single-column nitrogen-producing plants, such as Linde's N-series plants. Here the distillation components consist of a single column with a condenser on top. The materials flow is designed so that the waste stream is air containing 35% oxygen. These plants are specially tailored for users who do not need much oxygen. However, most such users are not centralized, large-quantity users, and do not take full advantage of the nitrogen coproduced with pipeline oxygen.

5.3 SIZE OF AIR SEPARATION PLANTS

Air separation plants have been built with capacities of 1200-2000 tons/day. Small oxygen plants can be completely fabricated and packaged in the shop for delivery to the site. Costs of shop-fabricated units are generally lower than those of units built in the field. Large oxygen plants are built of several prepackaged units interconnected in the field. The maximum size of any one package is determined by what can be shipped. Primarily for economic reasons, air separation plants are being made larger and larger; the goal is to pack as much capacity into a single module as possible, at the lowest possible unit cost.

For very large plants (e.g., 2000 tons/day), the size of individual components determines the mode of construction and assembly. The objective again is to maximize the amount of work carried out in the shop and the size of components that can be shipped to the installation site. Individual components such as columns, condensers, and heat exchanger assemblies are set up, the interconnecting piping is installed in the field, and the cold box is then erected at the installation site.

The relative importance of power cost, cost of capital, and other operating costs (including maintenance) and labor as a function of plant size is shown in Figure 22. Power costs are assumed to be 3¢/kWh, an estimated average for 1979 using industrial electricity prices from the Monthly Statement of Electric Operating Revenue and Income published by the Federal Power Commission. The dominance of the cost of power at the larger plant sizes is clear.

Figure 23 is a plot of the overall cost of oxygen against plant size for a low-pressure-cycle tonnage plant, again using a 3¢/kWh power cost. Variances in scope of supply, cost of capital, oxygen pressure, site conditions, and product storage and back-up requirements generate the relatively broad cost range.

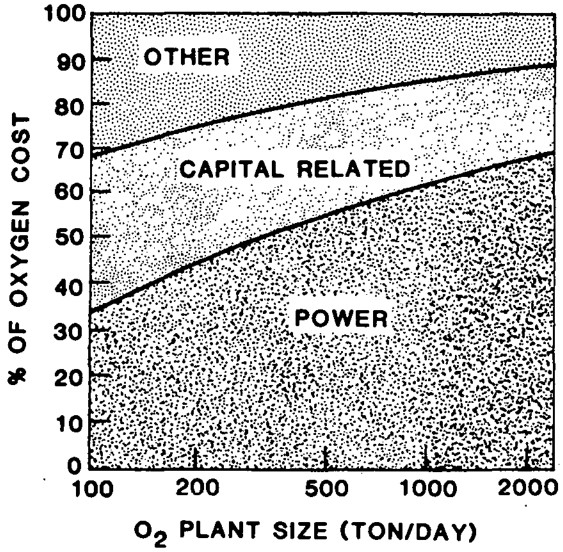

Fig. 22 Cost Components in Production of Oxygen versus Size of Air Separation Plant (oxygen product at 1200 psig; "other" includes labor and maintenance)

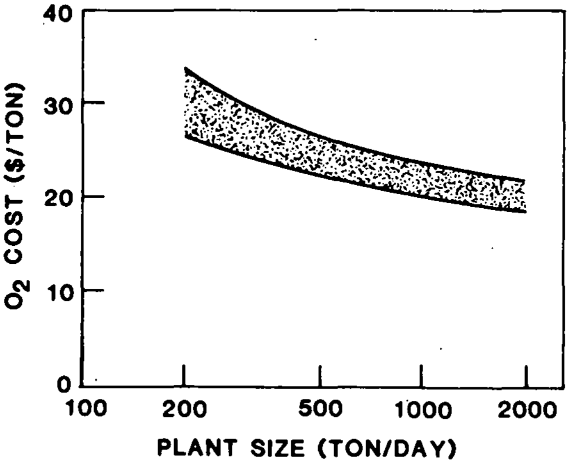

Fig. 23 Range of Oxygen Cost versus Size of Air Separation Plant

5.4 ENERGY COST ESCALATION

An interesting perspective on the impact of power cost escalation on oxygen cost is given in Figure 24. Assuming electric motor drive for the air and oxygen compressor of a 1200-ton/day low-pressure-cycle plant (built in 1979) with reversing heat exchangers and final oxygen compression to 1200 psig, the cost of energy represents 62% of the total cost of oxygen. If energy costs escalated at 8% annually, in 15 years power costs would represent 73% of the total cost of oxygen. Furthermore, if energy costs increased 12% annually, in 15 years power costs become 83% of the oxygen cost. This effect emphasizes the importance of selecting the right process cycle, the value of energy-saving equipment, and the need to monitor plant operations closely.

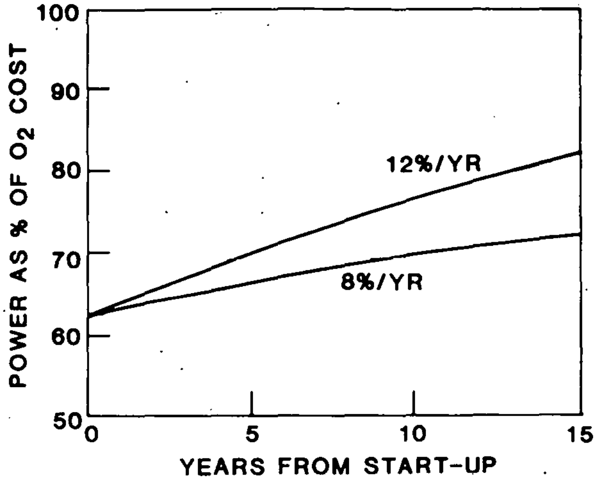

Fig. 24 Effect of Power Cost Escalation on Cost of Oxygen Produced by a 1200-Ton/Day Plant

6 CONCLUSIONS

Oxygen and nitrogen are coproduced by the separation of air, a highly energy-intensive process. In theory, air separation plants can produce more than three times more nitrogen than oxygen. In practice, the ratio is cut to about 1.5 times more nitrogen, which is still more than is needed to supply the existing market. At the present time, plant capacity utilization has no effect on nitrogen prices, except in a few isolated cases. Nitrogen is unlikely to ever be in short supply, except possibly in a few regions where there is more local demand for nitrogen than for oxygen. From a national energy standpoint, it is important to encourage (1) full utilization of nitrogen products, so that the wasted separation energy is minimized, and (2) geographic centralization of air product users, so that energy use in transportation is minimized.

Many potential users of liquid nitrogen as a refrigerant are prevented from using it because of the lack of specialized equipment on the market designed to process materials at extremely low temperatures and the general lack of knowledge about nitrogen as a cryogen. In some cases, ambient-temperature rather than cryogenic devices are used with liquid nitrogen, but they are not energy-efficient. Liquid nitrogen could be used more extensively and more efficiently if potential users had a better understanding of cryogenic equipment. The federal government could improve this understanding through workshops and other public information efforts.

Summarized below are nine specific areas in which further research, and goverment programs, could conserve energy and materials.

Oxygen Use in Waste Treatment. The use of oxygen in place of air in activated sludge treatment of municipal and industrial wastes (see Section 1.2.1) results in increased efficiency and energy savings. Oxygen for waste treatment can be generated by a pressure-swing adsorption unit or a cryogenic plant. In the case of the cryogenic process, nitrogen is produced in a purer state than is oxygen. For waste treatment, less-pure (90-95%) oxygen performs as well as pure oxygen. Therefore the energy required for cryogenically produced oxygen for this application may be less than that required for the oxygen needed by the steel industry. At the same time, the liquid nitrogen produced can be used for cryogenic separation of metallic and plastic wastes (see following text).

Cryogenic Separation of Plastic Wastes. The recycling of plastics, which are derived from petroleum, has been discussed for some time.[20,21] One difficulty is the separation of different types and grades of plastics. It is likely that by skillfully utilizing the different degrees of embrittlement of different plastics at cryogenic temperatures, a separation scheme can be designed. This would be an energy-efficient use of liquid nitrogen.

Cryogenic Particle Size Reduction. Cryogenic particle size reduction has been very successful in applications in the polymer area where particle size requirements are very tight, such as electrostatic and fluid bed powder coatings, rotational molding, dry blending, polymer solutions, and scrap polymer recycling. A major consideration in grinding a polymer is the heat generated as a result of friction, cutting, and impact action in the grinding chamber; this heat may be great enough to melt the polymer. Liquid carbon dioxide and dry ice have been used for cooling. At atmospheric pressure, liquid carbon dioxide flashes to a combination of a cold gas and a solid "snow," but liquid nitrogen vaporizes to a cold gas only. Heat transfer between solid carbon dioxide (195 K) and the material to be ground occurs slowly, and liquid nitrogen provides more-intimate contact and a lower temperature (77 K), which result in more-rapid heat transfer.

Thermoplastics are the most difficult polymers to reduce to fine powders (e.g., less than 30 mesh, or 600 microns) because of their toughness and elastomeric properties. Liquid nitrogen is necessary to cool the polymer below its embrittlement temperature before it is ground. In a typical operation, a cooling conveyor carries the polymer through a controlled cryogenic atmosphere offered by a liquid nitrogen spray. The embrittled material is fed into a size reduction mill, usually a high-speed hammermill or attrition mill. A second injection of liquid nitrogen, into the grinding chamber, removes the heat of grinding and keeps the polymer brittle until it is discharged as a fine powder. In the cryogenic shredding of discarded tires,[22] the steel and fiber do not shatter and can be separated from the rubber powder.

Many heat-sensitive materials can be ground at room temperature if a high air flow is used to dissipate the heat of grinding. These systems, however, require dust collection systems to separate the product from the air stream, to minimize material losses. When color or product changes are made, elaborate cleaning results in higher labor costs and decreased productivity, in addition to the capital investment in a dust collection system. Liquid nitrogen systems operate in a much neater fashion. With nitrogen produced as a coproduct of oxygen in air separation plants, the supply of the cryogen is not a problem. However, there have not been enough studies of efficient utilization of the "cold" embodied in the products during the overall operation. In an ideal pulverizing system, provisions would be made for heat exchange between a cold and a warm stream.

Manufacturing Atmospheres. Many materials, including spice seeds, leaves, and color concentrates, must be ground in a moisture-free or oxygen-free atmosphere. In addition to refrigeration, liquid nitrogen provides an inert atmosphere. However, cold ground powder in air can very quickly gather moisture. In an ideal system, one can collect the vaporized nitrogen (the insulation required for handling this gas should be minimal) and use it to provide a final moisture-free atmosphere for packaging, which would be highly desirable for pharamaceuticals, spices, etc. Such a system is energy and material efficient, does not produce dust, and should definitely be the direction for development.

Metals Recycling. Liquid nitrogen also provide methods for recycling metallic materials in household appliances, such as small motors in washing machines. A typical sequence of operation is a room-temperature process that pops out the motor by virtue of its inertia.[23] A cryogenic process then grinds up the motor. A magnetic separator recovers the steel and copper. Similar processing of gas water heaters recovers mostly copper.

New Technologies. An air separation system could produce pure oxygen and nitrogen for energy-efficient gasification facilities and ammonia production processes (see Sec. 1.2.1). While pure nitrogen is not now used to make fertilizer, future developments in fertilizer production technology could use the air separation process in a more energy- and materials-efficient fashion.

The Reversal of Pollution. Gaseous oxygen could also be used to improve water quality in rivers and lakes, in cases where the organisms that create normal ecological balance and destroy pollutants have died due to lack of oxygen. The ecosystem is disturbed when pollutants and organisms compete for oxygen. Lake or river water could be passed through a pipe and oxygen (low purity) injected at high pressure. The oxygenated water could then be reintroduced to the lake or river to revivify the water. Adequate treatment supplemented by reoxygenation can prove useful. The cost of in-stream oxygenation devices for water quality control should be studied.

Trash Incinerators. If incineration occurs in pure oxygen, instead of air, the flame temperature is higher; trash incinerators could operate more efficiently if pure oxygen were used. Carbon monoxide emissions would be eliminated, and nitrogen oxides arising from trash combustion reduced.

Preservation of Food. Waste of crops after they are harvested, especially cereal grains and legumes, is a problem in agricultural production, food transfers, and food processing. The removal of insects from cereal grain using inert atmosphere would be a simple alternative to chemical treatments in temperate and hot climates. For replacing the interstitial atmosphere of gas-tight storage bins, nitrogen gas is particularly suitable. It could be used effectively for short fumigations (approximately 20 days) and for protracted storage of dry cereals (years) and medium- to high-moisture-content cereals (months), since mold growth would be significantly retarded in the presence of low residual concentrations of oxygen ($<0.3\%$).[24]

About 20×10^9 lb of frozen food is consumed each year in the United States. Demand is expanding about 6%, or over 1×10^9 lb, per year. If liquid nitrogen were used to freeze 20% of the food produced to meet this increase in demand, 100,000 tons/year of liquid nitrogen would be required, assuming an average usage of one pound of liquid nitrogen for every pound of food. (Liquid nitrogen use varies from less than 0.5 lb per pound of dry food to 1.5 lb per pound of moist food).

The United States currently consumes about 38×10^9 lb of red meat each year. If 50% of present freezing were switched to light nitrogen freezing, and if 0.75 lb of liquid nitrogen were needed to freeze each pound of meat, the size of the new liquid nitrogen market would be 7 million tons/year.

REFERENCES

1. Pike, R., and C.D. Arrick, Union Carbide Linde Division, Tonawanda, N.Y., private communication (1980).

2. Finniston, H.M., opening address, in *Cryotech '73*, IPC Science and Technology Press, Guildford, England (1974).

3. *Environmental Considerations of Selected Energy Conserving Manufacturing Process Options: Vol. VII. Ammonia Industry Report*, U.S. Environmental Protection Agency Report EPA-600/7-76-034g (1976).

4. *Current Industrial Reports*, Series M28C, U.S. Department of Commerce.

5. *Current Industrial Reports*, No. M28C(78)-014, U.S. Department of Commerce.

6. Cuccione, E., *New Look in Air Separation Plants*, Chemical Engineering, *70*(9):150 (1963).

7. Shaner, R.L., *Production of Industrial Gases from the Air*, corporate publication, Union Carbide, New York City (1974).

8. Scott, R.B., *Cryogenic Engineering*, D. Van Nostrand, New York City (1962).

9. *Thermodynamic Properties of Oxygen and Nitrogen*, U.S. Bureau of Mines, Technical Paper 424 (1928).

10. Ruhemann, M., *The Separation of Cases*, Oxford at the Clarendon Press (1949).

11. Hausen, H., in *Forschung im Ingenienrwesen*, *274*:1 (1926).

12. Prentice, A.L., and R.M. Thoragood, *The Effect of Oxygen and Nitrogen Product Ratio on Air Separation Plant Design*, in Cryotech '73, IPC Science and Technology Press, Guildford, England (1974).

13. Duncan, V., East Chicago Plant, Union Carbide Linde Division, private communication (1979).

14. Smith, K.C., *Liquefaction of Gases*, in Encyclopaedic Dictionary of Physics, Pergamon Press, Elmsford, N.Y. (1961).

15. Vance, R.W., *Cryogenic Technology*, John Wiley & Sons, New York City (1962).

16. *Energy Use Patterns in Metallurgical and Nonmetallic Mineral Processing*, Battelle Columbus Laboratories, National Technical Information Service No. PB-245759 (1975).

17. Collyer, P.F., *Oxygen Supply Distribution and Storage with Reference to Iron and Steel Production*, Steel Times, *194*:435 (April 14, 1967).

18. Larson, S., Liquid Carbonic Corp., private communication (1979).

19. Scharle, W.J., *Large Oxygen Plant Economics and Reliability*, in Proc. Ammonia from Coal Symp., Tennessee Valley Authority (1979).

20. Gaines, L.L., and S.Y. Shen, *Energy and Materials Flows in the Production of Olefins and Their Derivatives*, Argonne National Laboratory Report ANL/CNSV-9 (1980).

21. *Cryogenic Recycling and Processing*, N.R. Braton, ed., CRC Press, Boca Raton, Fla. (in press).

22. Gaines, L.L., and A.M. Wolsky, *Discarded Tires: Energy Conservation through Alternative Uses*, Argonne National Laboratory Report ANL/CNSV-5 (1979).

23. Ito, R., Kurimoto Iron Works, Ltd., Osaka, Japan, private communication (1980).

24. Shejbal, J., *Preservation of Cereal Grains in Nitrogen Atmosphere*, Resource Recovery and Conservation, *4*:13 (1979).

BIBLIOGRAPHY

Bruges, E.A., *Available Energy and the Second Law Analysis*, Academic Press, New York City (1959).

Chemical Origins and Markets, Stanford Research Institute (1977).

Daunt, J.G., *The Production of Low Temperatures Down to Hydrogen Temperature*, in Handbuch der Physik, Springer-Verlag, Berlin (1956).

Davies, M., *The Physical Principles of Gas Liquefaction and Low Temperature Rectification*, Longmans, London (1949).

King, C.J., *Separation Processes*, McGraw-Hill, New York City (1971).

Latimer, R.E., *Distillation of Air*, Chemical Engineering Progress, *63*(2):35 (1967).

Pratt, C.J., *Trade and Trends in Fertilizer Raw Materials*, Chemical Engineering Progress, *63*(10):37 (1967).

Scharle, W.J., and K. Wilson, *Oxygen Facilities for Synthetic Fuel Projects*, presented at ASME Cryogenic Processes and Equipment Conf., San Francisco (Aug. 1980).

Shaner, R.L., and W.E. Sweeney, *Oxygen: 2000 Tons/Day*, Mechanical Engineering, *100*(1):38 (Jan. 1978).

Shreve, R.N., and J.A. Brink, *Chemical Process Industries*, McGraw-Hill, New York City (1977).

Smith, K.C., and J.W. Armond, *Adsorption as a Technique for Gas Separation*, in Cryotech '73, IPC Science and Technology Press, Guildford, England (1974).

Vance, R.W., and W.M. Duke, *Applied Cryogenic Engineering*, John Wiley & Sons, New York City (1962).

Westbrock, A.J., *Liquefaction of Oxygen, Nitrogen, and Hydrogen*, in Applied Cryogenic Engineering, John Wiley & Sons, New York City (1962).

ACKNOWLEDGMENT

The authors wish to thank Kathryn Macal for editing the manuscript.

Distribution for ANL/CNSV-15

Internal:

- J.G. Asbury
- L. Burris
- R.R. Cirillo
- E.J. Croke
- J.J. Dzingel
- A.R. Evans
- B.R.T. Frost
- L.L. Gaines
- W.J. Hallett
- W. Harrison
- A.S. Kennedy
- A.B. Krisciunas
- M.L. Kyle
- K.S. Macal
- W.E. Massey
- P.A. Nelson
- E.G. Pewitt
- J.J. Roberts
- N.A. Sather
- S.Y. Shen
- W.K. Sinclair
- T. Surles
- A.D. Tevebaugh
- A.M. Wolsky (265)
- ANL Contract Copy
- ANL Libraries (2)
- TIS Files (6)

External:

- DOE-TIC, for distribution per UC-95f (256)
- Manager, Chicago Operations and Regional Office, DOE
- Chief, Office of Patent Counsel, DOE-CORO
- President, Argonne Universities Association
- Energy and Environmental Systems Division Review Committee:
    - E. E. Angino, U. Kansas
    - E.N. Castle, Resources for the Future, Inc.
    - R.L. Clodius, National Assn. of State Universities and Land Grant Colleges
    - B.A. Egan, Environmental Research and Technology, Inc.
    - W.W. Hogan, Harvard U.
    - W.N. Poundstone, Consolidation Coal Company
    - L.H. Roddis, Jr., Charleston, S.C.
    - J.J. Stukel, U. Illinois
    - J.J. Wortman, North Carolina State U.
- J.H. Gibbons, Office of Technology Assessment, U.S. Congress
- D.E. Kash, USGS, Reston, Va.
- J.F. Collins, DOE, Chief Alternative Materials Utilization Branch, Office of Industrial Programs