CRYOGENIC TECHNOLOGY

1. Introduction

In present day usage, the word “cryogenics” refers to “all phenomena, processes, techniques, or apparatus occurring or using temperatures <120 K” (1). “Refrigeration” technology covers the temperature range of 120–273.1 K. The choice of these temperature ranges is somewhat arbitrary but has been accepted as an international standard. Around or below the temperature of 120 K, the “permanent” gases including methane, oxygen, argon, nitrogen, hydrogen, and helium can be liquefied at ambient pressure. A few relevant thermophysical properties for some gases at cryogenic temperatures are listed in Table 1.

Cryogenic technology has contributed greatly to scientific research and is widely used in many industrial applications. The ability to condense a gas such that it can be stored and shipped as a cryogenic liquid rather than as a pressurized gas has found several applications. Natural gas is stored and transported as liquified natural gas (LNG) to many countries in the world. Liquid hydrogen is used as fuel for space vehicles. Oxygen, nitrogen, and argon are shipped as liquids by truck and rail car to the point of end use.

Another major use of cryogenic technology has been to produce low cost, high purity gases through fractional condensation and distillation. Cryogenic air separation is used for the production of pure oxygen, nitrogen, and argon

Table 1. **Thermophysical Properties of Some Gases**[a]

	He	Ne	Ar	H_2[b]	CH_4	N_2	O_2	F_2	CO
normal boiling point, K	4.22	27.09	87.28	20.39	111.66	77.34	90.19	84.95	81.70
vapor density at bp, kg/m^3	16.76[c]	9.58[c]	5.78	1.34	1.82	4.84	4.47	5.63	4.37
liquid density at bp, kg/m^3	123.99	1203.88	1396.02	70.56	422.52	807.95	1141.89	1502.85	790.30
heat of vaporization at bp, J/g	20.82	85.19	161.16	444.74	509.34	198.77	212.05	172.47	214.14
triple point (tp), K		24.56	83.78	13.95	90.69	63.15	54.36	53.48	68.15
vapor pressure (solid at tp), kPa		43.300	68.700	7.220	11.696	12.520	0.150	0.252	15.400
heat of fusion at tp, J/g	12.49	16.26	29.59	58.09	58.68	25.70	13.88	13.43	30.02
critical temperature, K	5.20	44.40	150.86	33.19	190.56	126.20	154.58	144.12	132.92
critical pressure, MPa	0.228	2.653	4.898	1.313	4.599	3.400	5.043	5.172	3.499

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[a] Unless otherwise noted, the data source is American Institute of Chemical Engineers (AIChE) Design Institute for Physical Properties (DIPPR) Project 801, Evaluated Process Design Data, AIChE: New York, 1988.

[b] Normal H_2.

[c] Values computed using NIST equation of state.

(2). These gases are used in primary metals manufacturing (eg, steel), chemical manufacturing, glass manufacturing, electronic industries, partial oxidation and coal gasification processes, enhanced oil recovery and many other applications. Cryogenic methods are also used for the purification of hydrogen, helium, and carbon monoxide. Hydrogen and carbon monoxide gases are used in chemical manufacturing and some metal industries. Helium is used in welding, medicine, gas chromatography, and diving (3).

Cryogenic processes that provide low temperatures to refrigerate other materials or to alter their properties have been used in many applications (4). Liquid nitrogen is used for freezing food such as hamburgers and shrimp. Rubber tires and scrap metal from old cars are reclaimed using cryogenic cooling techniques to make them brittle for easier fracturing and component separation. Biological materials such as bone marrow, blood, animal semen, tissue cultures, tumor cells and skin are preserved by cryogenic freezing and storage.

Magnetic resonance imaging (MRI) uses cryogenics to cool high conductivity magnets for nonintrusive body diagnostics. Low temperature infrared (ir) detectors are utilized in astronomical telescopes. Cryogenic refrigerators have been applied industrially for cryopumping to yield high pumping speeds and ultrahigh vacuum. With the advent of high temperature superconductivity, it is anticipated that applications of superconductivity at near liquid nitrogen temperature will have great potential for electric power transmission, magnetic transportation systems, and magnets for energy generation in fusion processes.

2. Refrigeration Methods

Refrigeration for cryogenic applications is produced by absorbing or extracting heat at low temperature levels and rejecting it to the atmosphere at higher temperatures. Three general methods for producing cryogenic refrigeration in large scale commercial applications are (*1*) the liquid vaporization cycle; (*2*) the Joule-Thomson (J-T) expansion cycle; and (*3*) the engine expansion cycle. The first two are similar in that they both utilize irreversible isenthalpic expansion of a fluid, usually through a valve. Expansion in an engine approaches reversible isentropic expansion with the performance of work.

2.1. Liquid Vaporization Cycle.

In this process, a refrigerant fluid with the desired low temperature boiling point is compressed to a pressure at which it can be condensed with ambient air, cooling water, or another refrigerant fluid with a higher boiling temperature. The condensed, low boiling refrigerant is isenthalpically expanded to a suitable low pressure. Evaporation of the low pressure liquid provides the desired refrigeration. The evolved vapor is then commonly rewarmed prior to recompression. Heat rejection can be cascaded from very low temperatures to ambient level by use of several refrigerants with different boiling temperature characteristics.

2.2. Joule-Thomson Expansion Cycle.

In this process, a refrigerant fluid is compressed and precooled below its inversion temperature, ie, the temperature below which a pressure reduction results in a temperature decrease. The cold refrigerant fluid is isenthalpically (J-T) expanded to a lower pressure to produce the required low temperature. The low temperature fluid is partially rewarmed to provide cryogenic refrigeration and is usually then further warmed against the high pressure refrigerant fluid to provide the precooling.

2.3. Engine Expansion Cycle.

In this process, refrigeration is supplied by expanding a pressurized stream through a work-producing device (an engine). Whereas expansion though a J-T device does not cause the enthalpy of the stream to change, expansion though an engine causes the enthalpy of the stream to be reduced. This reduction in enthalpy produces the refrigeration for the process. In the refrigeration cycle, a fluid is compressed, optionally precooled, and expanded to a lower pressure through an expander. The expanded refrigerant fluid is warmed to provide cryogenic refrigeration then returned to the compressor to complete the cycle.

2.4. Other Refrigeration Methods.

Cryocoolers provide low temperature refrigeration on a smaller scale by a variety of thermodynamic cycles (4,5). The Stirling cycle follows a path of isothermal compression, heat transfer to a regenerator matrix at constant volume, isothermal expansion with heat transfer from the external load at the refrigerator temperature, and finally heat transfer to the fluid from the regenerator at constant volume.

Thermoacoustic and pulse tube refrigeration both use a closed refrigerant inventory (typically helium) to produce refrigeration by a thermodynamic cycle similar to that of the Stirling cycle. The thermoacoustic cycle operates at a sonic resonant frequency (6); the pulse tube cycle frequency is controlled by the induced rate of pressure oscillation.

The Gifford-McMahon cryocooler consists of displacer, regenerator, compressor, and intake/exhaust valves that can be staged to reach the required cryogenic temperatures (4,5).

Magnetic refrigeration uses the magnetocaloric effect to produce cooling. When ferromagnetic or paramagnetic materials are put into a magnetic field, their temperature rises: when removed from the field, their temperature falls. The amount of temperature change depends on the material, its temperature, and the strength of the magnetic field (4,5).

3. Applications

3.1. Air Separation.

A considerable number of cryogenic concepts were developed near the end of the nineteenth and beginning of the twentieth century to liquefy and separate air into its major constituents (composition of air: 78% nitrogen, 21% oxygen, and 1% argon by volume). By 1905, Carl von Linde's double distillation column process to produce practically pure oxygen and nitrogen was already known. Argon was produced industrially by 1912 (7). Trace quantities of other rare gases such as neon, krypton, and xenon are present in air and can be recovered by proper modifications to a cryogenic double distillation column air separation plant (3).

Figure 1 shows a cryogenic air separation process using a double distillation column of the Linde-type with a side rectifying column to recover crude argon (8). Feed air is compressed in a multistage compressor with interstage cooling to between 550 and 650 kPa. cooling. The compressed air is cooled in an aftercooler by cooling water and the condensed water is removed in an aftercooler separator.

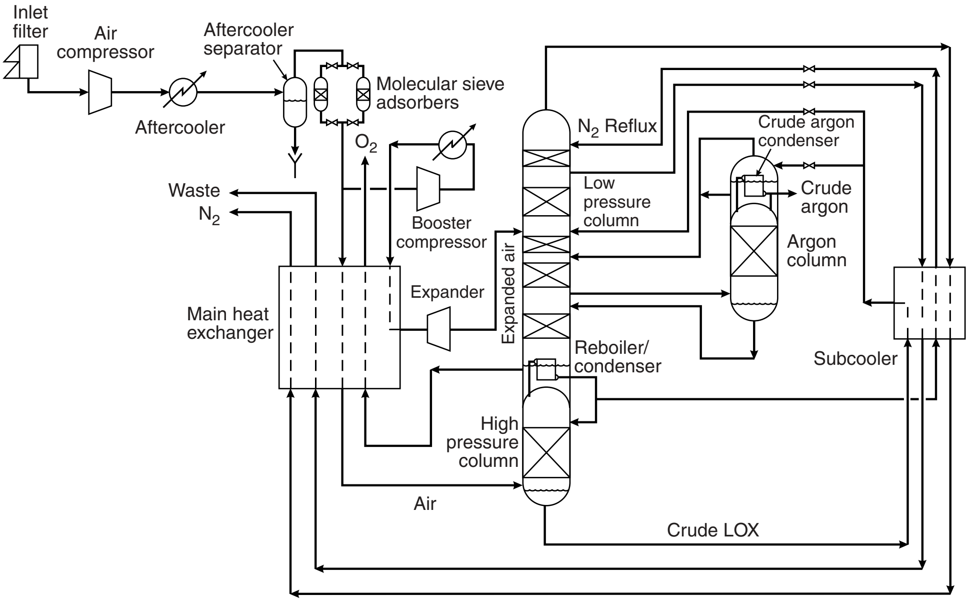

Fig. 1. Cryogenic air separation process.

To avoid freezing of water and carbon dioxide in the cryogenic part of the plant, the feed air is passed through an adsorbent bed of molecular sieve. Along with water and carbon dioxide, several trace impurities in the air such as acetylene, ethylene, butane, and other heavier hydrocarbons are also adsorbed. This alleviates some of the safety issues arising from the formation of hydrocarbon-oxygen mixtures in older plants that did not use molecular sieve adsorbers.

The purified air stream is split into two streams. One stream of ~7–12% of the total air flow is boosted in pressure by ~60–200 kPa in a booster compressor. The boosted air is cooled first by heat exchange with, typically, cooling water and then in the main heat exchanger against the returning cold product nitrogen and oxygen streams. The cooled air stream is work expanded to near atmospheric pressure and fed to the low pressure distillation column. This expander provides the needed refrigeration for the plant. Often the work extracted from the expander drives the booster compressor so that an additional source of energy is not required.

The major portion of the air stream is cooled in the main heat exchanger to near its dew point. Nitrogen and oxygen are separated by distillation in a two-stage distillation process. The first stage, the high pressure column, which operates at ~500–600 kPa, separates the feed air into nitrogen and an oxygen-enriched liquid (crude LOX) stream, which is eventually fed to the low pressure column. The low pressure column, which operates at close to ambient pressure, produces pure oxygen and nitrogen streams from its bottom and top respectively. Nitrogen reflux for both columns is generated at the top of the high pressure column. Nitrogen vapor at the top of the high pressure column is condensed against boiling liquid oxygen at the bottom of the low pressure column by heat exchange between the two streams in a reboiler condenser. The pressure difference between the two columns provides the temperature difference between the condensing and boiling fluids.

Since argon boils between oxygen and nitrogen, a peak in the argon concentration of ~7–15% occurs in the lower section of the low pressure column. A vapor stream is drawn from the low pressure column near the location of the peak argon concentration and is distilled in a third (argon) column. Typically, a vapor stream is drawn from the low pressure column at a point where the concentration of nitrogen is low [10–100 parts per million (ppm)] and the concentration of argon is 7–12%. Reflux for the argon column is provided by heat exchange between the vapor at the top of this column and a portion of the crude LOX stream in a crude argon condenser. The vaporized crude LOX is fed to the low pressure column and the condensed argon-rich stream is returned as reflux to the argon column. The liquid from the bottom of the argon column is returned to an appropriate location in the low pressure column. A crude argon stream containing 0.5–5% O_2 and 0.05–1% N_2 is withdrawn from the top of the argon column. The oxygen produced from the bottom of the low pressure column can easily have an oxygen purity of 99.5% or greater with the remainder being mainly argon. The nitrogen product from the top of the low pressure column can be produced with an oxygen concentration <5 ppm. As shown in Figure 1, a waste stream is sometimes drawn from a couple of stages below the top of the low pressure column. The withdrawal of this stream allows a better control of the purity of the nitrogen product from the top of the low pressure column. Any unrecovered oxygen and argon can now leave in this waste stream allowing the nitrogen product to have low levels of these elements.

The heat exchangers used in cryogenic air separation plants are generally brazed aluminum plate-fin heat exchangers. Since the early 1930s, sieve trays have been used predominantly for cryogenic distillation. Recently, the use of structured packing, to reduce the pressure drop per theoretical stage of separation, has become commonplace in the low pressure and argon columns. Its use in the low pressure column decreases the power consumption by the air compressor as the pressure of the feed air to the high pressure distillation column can be decreased by about 60 kPa. The use of structured packing in the argon column provides more theoretical stages of separation for the same permissible pressure drop between the bottom and top of the argon column. This allows argon production from the argon distillation column with oxygen impurity as low as 1 ppm, thereby either eliminating the need for, or reducing the size of, the expensive downstream processes that have been used in the past to produce pure argon product (9).

As depicted in Figure 1, the oxygen product is removed from the bottom of the low pressure column as a vapor then warmed to ambient. For most applications, oxygen is needed at an elevated pressure so oxygen product compression is required. An alternative to the approach of Figure 1 is to withdraw the oxygen product from the low pressure column as a liquid, pump the liquid to delivery pressure, then vaporize and warm the liquid by heat exchange with some suitable high pressure vapor stream. This approach, which is often referred to as “pumped-LOX”, is typically used in modern air separation plants and is shown in Figure 2 (2,10). The identity of the suitable high pressure vapor stream varies

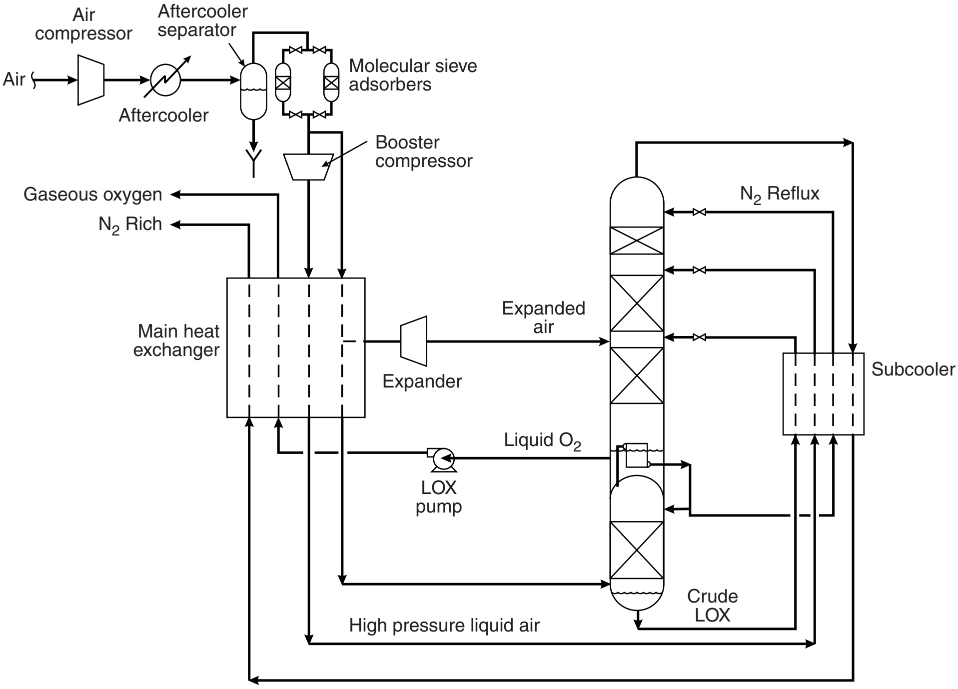

Fig. 2. Pumped liquid oxygen process.

but, as shown in Figure 2, is usually a compressed fraction of the incoming feed air.

In the field of semiconductor device manufacturing, on-going trends toward device miniaturization and the need for high production yield are leading to gas specifications with ultrahigh purities. This finding requires that the concentration of all impurities in each of the nitrogen, oxygen, and argon products be <10 parts per billion (ppb). It is widely felt that this impetus to decrease the impurity level will continue as the devices continue to advance and gases with parts per trillion impurity concentrations will eventually be desired. Ultrahigh purity (UHP) nitrogen is directly produced at the end use pressures of ~800–1000 kPa from the cold box (2). For this purpose, variants of a single distillation column process that directly produce nitrogen at the desired pressure are generally used (Fig. 3). Air typically consists of several impurities at ppm levels. Hydrogen is present in the range of 1–5 ppm; carbon monoxide is also present at similar levels. In order to avoid the presence of these impurities in the distilled nitrogen, both H_2 and CO impurities are removed prior to feeding the compressed feed air to the cold box. In one alternative, the compressed feed air is heated to a temperature of ~200°C and passed over a noble metal catalyst such as platinum to oxidize all the carbon monoxide and hydrogen. The resulting stream is then cooled and passed through a molecular sieve unit (Fig. 3). In an alternative process, layers of adsorbent catalysts containing noble metal are supplied within the molecular sieve unit to remove hydrogen and carbon monoxide impurities.

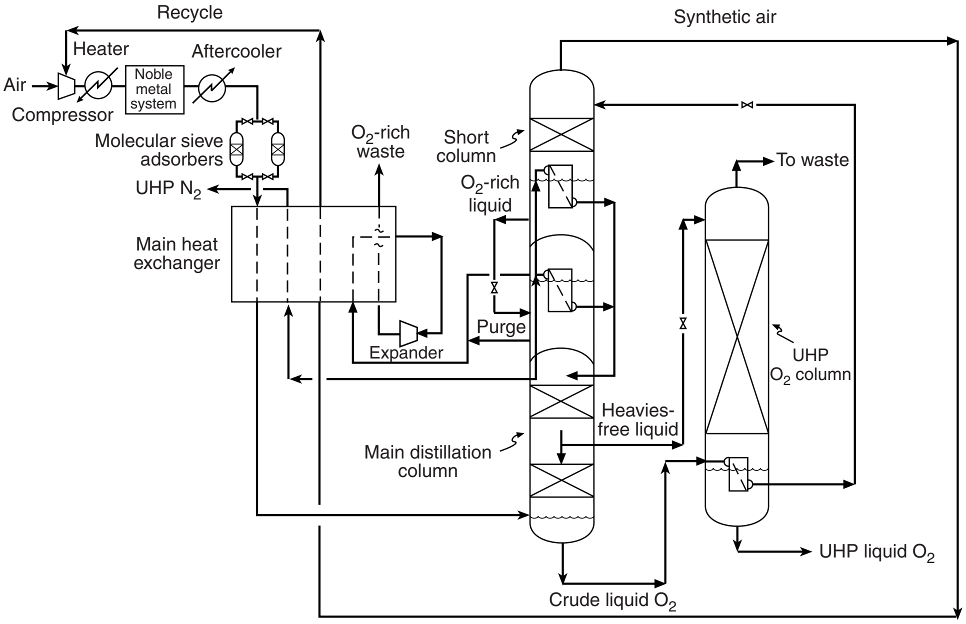

Fig. 3. UHP nitrogen process with UHP oxygen coproduction.

The impurities-free air is then cooled in the main heat exchangers and sent to the main distillation column of Figure 3 to produce UHP nitrogen from the top. A large number of separation stages (60–100) are used in this distillation column to reduce the oxygen concentration in the nitrogen product to a level of a few ppb. The crude liquid oxygen from the bottom of the main distillation column is eventually fed to the top of a short column containing four to six separation stages and operating at a pressure of ~400 kPa. The boilup at the bottom of this column is provided by condensing a portion of the UHP nitrogen from the top of the main distillation column. Not all liquid at the bottom of the short column is vaporized and an oxygen-rich liquid is withdrawn. Its pressure is further reduced to ~200–300 kPa and it is vaporized by condensing additional UHP nitrogen from the main distillation column. The vapor from this reboiler is partially warmed in the main exchanger and expanded in an expander to provide the refrigeration need of the plant. The expanded stream is discharged as a waste stream. A liquid purge stream is taken from the second reboiler to prevent the accumulation of hydrocarbons to unsafe levels. One interesting feature of this process is that the vapor stream leaving at the top of the short distillation column is close in composition to that of air and therefore, is referred as “synthetic air”. Since the synthetic air is at ~400 kPa it is recycled and mixed with the feed air stream. In Figure 3, it is recycled to an intermediate stage of the feed air compressor, which reduces the cost of buying a separate booster machine for the recycle of the synthetic air stream. The process shown in Figure 3 is quite efficient and economical for UHP nitrogen production (11).

Air contains several impurities that are heavier than oxygen—methane and higher hydrocarbons and nitrogen oxides are all present at ppm levels. A typical high purity oxygen produced from a process such as the one shown in Figure 1 contains all these heavier impurities at unacceptable levels to be considered UHP oxygen. Generally, the UHP oxygen requirement is ~1–5% of the UHP nitrogen production rate. The relatively small production rates for UHP oxygen are met by withdrawing a heavy impurities-free but oxygen-containing liquid stream from an intermediate location of the main distillation column in Figure 3 (2,12). The pressure of this liquid stream is then reduced and fed to the top of an UHP oxygen column containing 60–100 separation stages. Ultrahigh purity liquid oxygen product stream with concentrations of all impurities at a few ppb is recovered from the bottom of the UHP oxygen column. The boilup at the bottom of this column is provided by cooling crude liquid oxygen from the bottom of the main distillation column. Once again, this process is quite economical for the production of the desired quantities of the UHP oxygen.

3.2. Liquid Nitrogen, Oxygen, and Argon. Large quantities of liquid nitrogen are typically produced by liquefying gaseous nitrogen from an air separation plant. For this purpose, a gaseous nitrogen stream is compressed to a fairly high pressure and work expanded at successive lower temperatures to create colder temperatures for liquefying nitrogen. Figure 4 shows one such

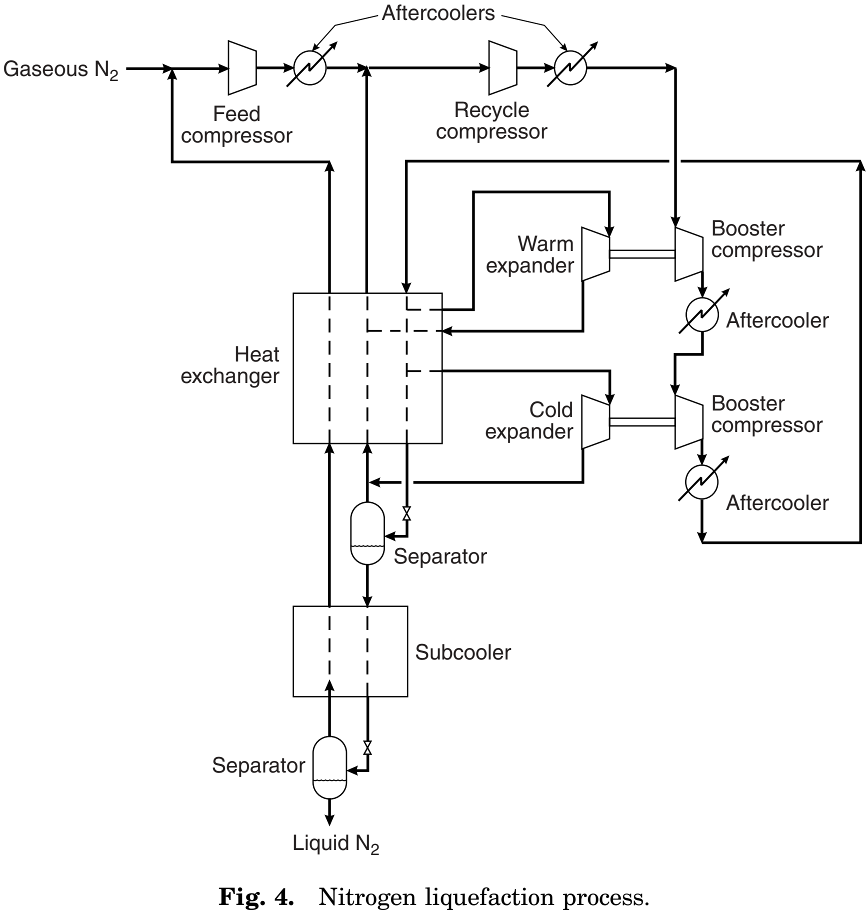

Fig. 4. Nitrogen liquefaction process.

process (1). Low pressure gaseous nitrogen from the air separation unit is combined with a recycle nitrogen stream and compressed to ~600 kPa in a feed compressor. The compressed nitrogen is combined with another recycle nitrogen stream and further compressed to ~3 MPa in a recycle compressor. Both the feed and recycle compressors are high efficiency, multistage centrifugal machines. The nitrogen stream is then further compressed in two booster compressors to ~4.5 MPa, which is above the critical pressure of nitrogen. Each of these booster compressors is linked to and driven by an expander providing refrigeration to the process. The final compressed nitrogen stream is then sent to a heat exchanger. Major portions of this stream are expanded in the two expanders and recycled while a smaller fraction is cooled to below the critical temperature of nitrogen by heat exchange with the expanded streams. The inlet temperatures to the expanders are chosen such that the temperature differences between the cooling and warming streams in the heat exchanger are minimized to reduce the liquefaction power requirement. The cooled high pressure nitrogen stream is then isenthalpically let down in pressure across valves in two stages to provide the desired liquid nitrogen product stream near ambient pressure.

Liquid argon can be produced directly from the crude argon condenser shown in Figure 1 by increasing the flow of air through the expander. However, refrigeration supply by expanding air into the low pressure column is not economical for production of large quantities of liquid oxygen. Typically, for this purpose, refrigeration is provided by adding liquid nitrogen from a nitrogen liquefier to the distillation system while liquid oxygen is withdrawn from the bottom of this column. Alternatively, when only a fraction of the oxygen and nitrogen product is desired as liquid, it can be sufficient to simply boost the incoming feed air to elevated pressure and, after cooling, expand vapor air into the bottom of the high pressure column.

3.3. Liquefied Natural Gas. Liquefied Natural Gas plants can be categorized as "peakshaving" or "base-load". Peakshaving LNG plants are built at the consumer end of natural gas pipelines to accumulate LNG in storage tanks for later vaporization and send out into the local grid during periods of peak demand. Base-load LNG plants provide a steady "base" supply of natural gas to utility companies, generally by transportation of LNG by ship from one country to another.

Peakshaving plants liquefy natural gas during the 125–200 day season of the year when excess supply pipeline capacity exists. Then, during cold weather periods of high demand, the LNG is pumped to distribution pressure, vaporized, and put into the local grid. This allows a higher yearly utilization of gas without expanding the production and transmission facilities. Peakshaving LNG plants range in size up to 1.4 million STP m^3/day, have LNG storage sufficient to hold one season's production, and send out capacity (pumps and vaporizers) to return the season's production to the grid during 5–15 days of cold weather.

Pretreatment of the natural gas before liquefaction is necessary to remove acid gases (CO_2 and H_2S) and water, which would freeze and plug the liquefaction equipment. The gas supplied to peak-shaving plants has been treated to pipeline specifications for acid gases and water before transmission. At the peak-shaving plant, residual acid gases are removed by absorption with monoethanolamine (MEA), methydiethanolamine (MDEA), or other amine solutions.

If there is sufficient regeneration gas available and the acid gas content is low enough, CO_2 and H_2S can be coadsorbed on beds of molecular sieve along with water. For base-load LNG plants, the acid gas content may be very high. MEA, MDEA, Sulfinol, Benfield, or other solutions are used, depending on the CO_2/H_2S partial pressures, the level of impurity removal, and economics.

The most commonly used refrigeration cycles for LNG peakshaving plants are (*1*) the cascade J-T expansion cycle; (*2*) the expander cycle; and (*3*) the multicomponent refrigerant cycle. The cascade J-T expansion cycle typically involves three separate working fluids (propane, ethylene, and methane) in individual refrigeration loops. Propane is compressed to a pressure at which it can be totally condensed against cooling water or air. The propane may be vaporized at several pressures while cooling the natural gas feed, ethylene, and methane streams. Ethylene is compressed to a pressure sufficient to be condensed by propane vaporizing in its lowest stage at a pressure near one atmosphere. Likewise methane is condensed against the lowest boiling stage of ethylene, which may also have several intermediate pressure (temperature) levels. Staging each of the propane, ethylene, and methane circuits to have intermediate vaporizing pressures reduces the refrigeration power requirement for LNG production by reducing the compression ratios of the refrigerant streams.

Expander cycles provide refrigeration by having a fluid perform work in an expansion engine. The fluid can be nitrogen, or natural gas. One variation of the expander cycle uses a relatively large quantity of available “flowby” gas that is normally throttled from transmission pressure to distribution pressure. Rather than reducing pressure across valves, the flowby natural gas is precooled and work expanded to provide refrigeration to liquefy a small portion of the natural gas. The flowby gas is then rewarmed and enters the distribution grid. Using this flowby gas reduces both capital and operating costs of the peakshaving plant.

The multicomponent (mixed) refrigerant cycle utilizes J-T refrigeration from a mixture that includes nitrogen and a blend of hydrocarbons from methane to butane or pentane. The mixture composition is optimized to obtain close temperature approaches to the condensing feed gas, and reduce the power for LNG production. The mixture is compressed to $\sim$3 MPa, partially condensed against cooling water, precooled, condensed, and subcooled in a heat exchanger, then reduced in pressure across a J-T valve to $\sim$0.3 MPa for vaporizing and rewarming to cool the natural gas feed and high pressure refrigerant.

Base-load LNG plants have predominantly used variations of the mixed refrigerant cycle, although some have utilized the cascade cycle. The mixed refrigerant cycle can be precooled by a high stage cycle that may be a propane refrigerator, a second separate mixed refrigerant cycle, or even an ammonia absorption system (13–16). The propane precooled mixed refrigerant cycle shown in Figure 5 has low energy requirements, characteristic of the cascade cycle, but a simpler equipment arrangement (17). Base-load plants generally recover propane and heavier components from the natural gas for internal use in charging the refrigeration systems, or for external use as LPG, butane, or natural gasoline. Single base-load LNG trains range in size from $\sim$3 to 20 million STP m^3/day LNG production. Machinery for the base-load plants comprise centrifugal or axial compressors driven by steam or gas turbines. Base-load LNG

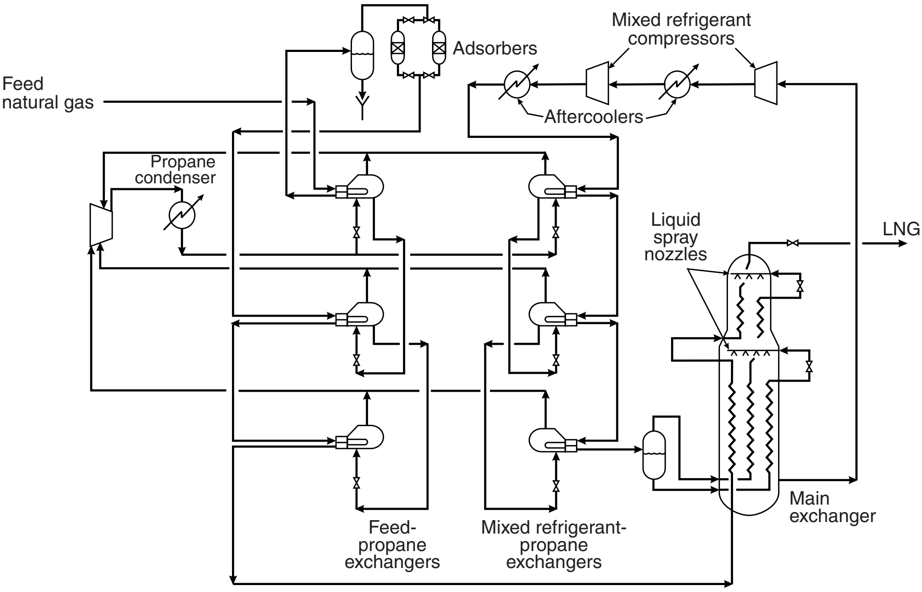

Fig. 5. Propane precooled mixed refrigerant process for natural gas liquefaction.

plants serve the trade to Japan, Taiwan, and Korea from Alaska, Malaysia, Borneo, Indonesia, Australia, Nigeria, Trinidad, the Persian Gulf, and North Africa.

3.4. Hydrogen Purification.

Cryogenic separation is used extensively for recovery and purification of hydrogen from refinery and petrochemical plant off-gases. The most common applications are in recovery of hydrogen from catalytic reformer gas, ethylene plant off-gas, hydrodealkylation (HDA) recycle gas, hydrodesulfurization (HDS) off-gas and methanol/ammonia synthesis purge gases (18). Hydrogen can also be coproduced when carbon monoxide is recovered by cryogenic separation of a steam-methane reformer off-gas.

The simplest form of cryogenic hydrogen purification uses partial condensation to condense light hydrocarbons and trace impurities such as argon, carbon monoxide, and nitrogen from the relatively noncondensable hydrogen. Due to the high relative volatility of hydrogen to light hydrocarbons, in the range of 100–300 for hydrogen/methane at separation temperatures of 135–100 K, cryogenic separation can easily attain a hydrogen purity of 90–96% without distillation. Product hydrogen is recovered at close to feed gas pressure, with typical hydrogen recoveries of 90–98%.

At optimum conditions, ie, feed gas rate of at least 5000 STP m^3/h, feed pressure of at least 2.8 MPa and feed hydrogen content <80%, all of the refrigeration requirements for the cryogenic hydrogen purification process can usually be obtained by J-T expansion of the condensed hydrocarbons. At less favorable conditions, auxiliary refrigeration is required. This refrigeration can typically be supplied by an inexpensive package such as a propane unit providing refrigeration at temperature levels of 250–210 K.

Compact brazed aluminum plate-fin heat exchangers can be used in most cryogenic hydrogen purification applications. The use of these relatively low cost heat exchangers, combined with low separation energy requirements, results in a highly economical process for hydrogen purification.

One of the most common applications of cryogenic hydrogen purification is to recover hydrogen and reject light hydrocarbons from the recycle loops within refineries. After pretreatment of the feed gas to remove water and aromatic impurities that would freeze at low temperatures, the feed gas is cooled to $\sim$120 K to condense most of the hydrocarbons and provide a product hydrogen purity of 90–92%. The condensed hydrocarbons are separated from the cooled stream and flashed to a low pressure, typically 200–500 kPa, revaporized and warmed for refrigeration recovery, and then sent to the plant fuel system. The uncondensed product hydrogen is rewarmed at pressure and recycled to the HDA unit.

It is worth noting that when hydrogen is produced by natural gas reforming followed by water gas shift reaction at low temperatures, the predominant impurities in the resulting hydrogen stream are nitrogen, unconverted carbon monoxide, unreacted methane and carbon dioxide. The most popular methods for purifying this stream are based on pressure swing adsorption process. All the impurities are removed by adsorption and hydrogen product with purities $>$99% is obtained. Similarly, hydrogen from ammonia purge gas is not generally recovered by a cryogenic process but by using membranes that have higher permeability for hydrogen as compared to other constituents in the purge gas. The varying nature of ammonia purge gas makes the use of membranes more attractive.

3.5. Hydrogen Purification with Light Olefins and Liquefied Petroleum Gas (LPG) Recovery. The relatively simple cryogenic purification process for hydrogen recovery can easily be adapted (19) to recover a crude light olefin or propane and heavier hydrocarbon (LPG) stream (Fig. 6). The pretreated feed gas is cooled to an intermediate temperature, in the range of 240–200 K for propylene/LPG recovery or 180–150 K for ethylene recovery. The uncondensed vapor is then further cooled to condense the remaining methane and residual heavy hydrocarbons. The two condensed hydrocarbon streams are flashed separately to a lower pressure, revaporized, and warmed with the product hydrogen stream for refrigeration recovery. A flash separator can be added to reduce the amount of light impurities in the crude olefin/LPG stream. A de-methanizer or de-ethanizer column can also be incorporated to provide a high purity olefin or LPG product, but this will require auxiliary refrigeration.

3.6. Hydrogen Liquefaction. Hydrogen can be produced from caustic/chlorine electrolytic cells, by decomposition of ammonia or methanol, by steam-methane reforming, or by partial oxidation of hydrocarbons. Hydrogen recovered by these methods must be further purified prior to liquefaction. This is generally achieved by utilizing pressure swing adsorption methods whereby impurities are adsorbed on a solid adsorbent.

Except for neon, which is too expensive to use, there are no gases having volatilities between nitrogen and hydrogen, so the cascading of refrigeration by condensing one fluid against another boiling at above ambient pressure is not feasible. Consequently, refrigeration $<$77 K is provided by expanders, or by

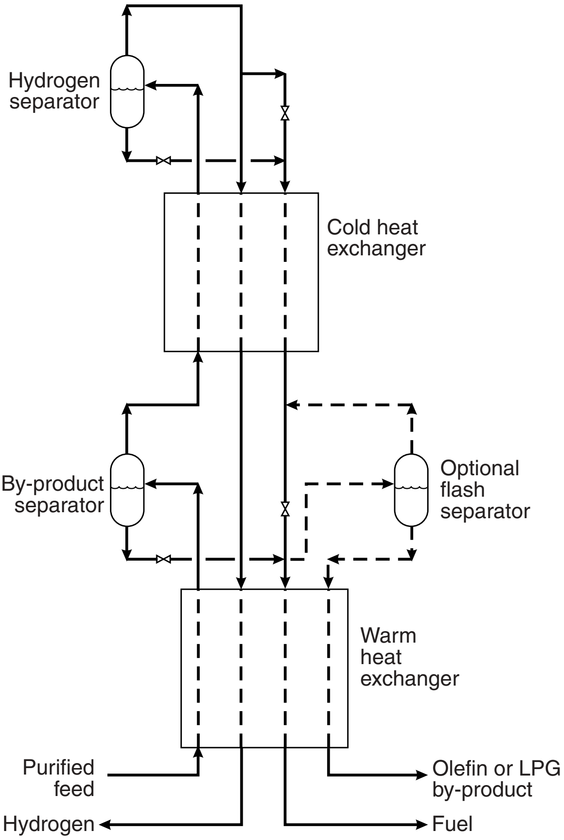

Fig. 6. Hydrogen purification process with by-product recovery.

vacuum nitrogen (triple point 63.2 K) in combination with expanders. A cycle utilizing only hydrogen expanders for refrigeration (no liquid nitrogen precooling) is shown in Figure 7 (20,21). Small hydrogen liquefiers may alternatively use closed-loop helium refrigeration cycles. As temperatures decrease, closer temperature approaches are needed in the heat exchangers to achieve low energy requirements. Consequently, temperature pinches in liquid hydrogen plants range from 1 K at 20 K to 6 K at 300 K.

Hydrogen has two coexisting isomers (ortho and para) that are present at equilibrium in a temperature-dependent ratio (22). The equilibrium para content of hydrogen is 25% at high temperature, 50.5% at 77 K, and 99.8% at 20.2 K. The ortho–para reaction is reversible, exothermic in the ortho–para (o/p) direction, and endothermic in the para–ortho (p/o) direction. “Normal” (25% para) hydrogen can be liquefied, but the conversion from ortho to para occurs in liquid hydrogen even without a catalyst. The heat of the o/p reaction causes a large amount of the liquid to boil away, due to the high heat of conversion (702.6 J/g converted) relative to the latent heat (445.5 J/g) (23). Having the heat of conversion enter the process at the lowest temperature is thermodynamically undesirable and

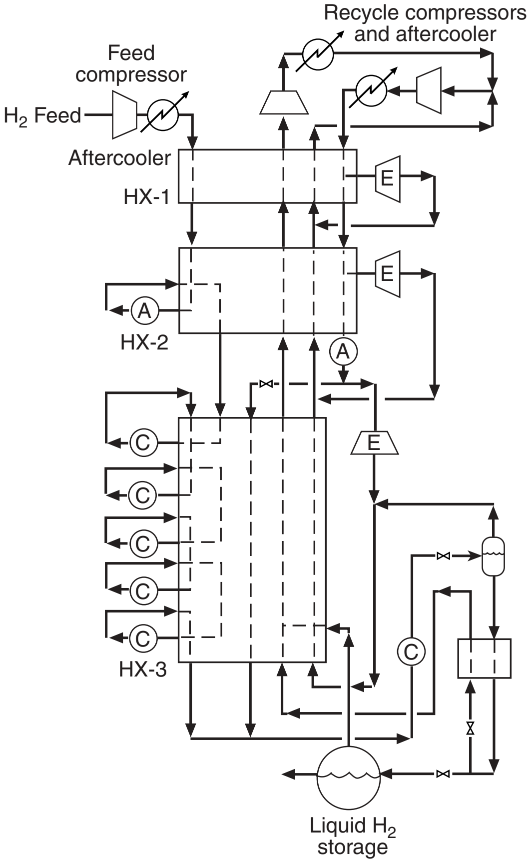

Fig. 7. Hydrogen liquefaction process. Key: A = adsorber, C = catalyst bed, E = expander.

results in high liquefaction energy. To avoid this and thereby reduce energy requirements, catalyst beds are used at various levels in the process so that the o/p reaction (with its heat of conversion) occurs at as high a temperature as possible, given the constraint of equilibrium. Hydrogen may contact catalyst continuously as it is cooled or in individual stages (20,21,24). Liquid hydrogen is usually produced as 95% para—an economic balance between the costs of liquid boiloff (power) and large catalytic converters.

3.7. Light Olefins and LPG Recovery. Even though the normal boiling point temperature of ethylene (169.4 K) is much >120 K, its recovery often requires much lower processing temperatures, particularly when high recoveries are needed.

As described above, light olefins and LPG can be recovered by making proper modifications to a hydrogen recovery process. Dephlegmators (fractionating condensers) can also be used for light olefin and LPG recovery (25,26). Dephlegmators are usually specially designed brazed aluminum plate-fin heat exchangers in which liquid condensed from an upward cooling vapor stream flows counter-currently within the heat exchanger to act as a reflux stream.

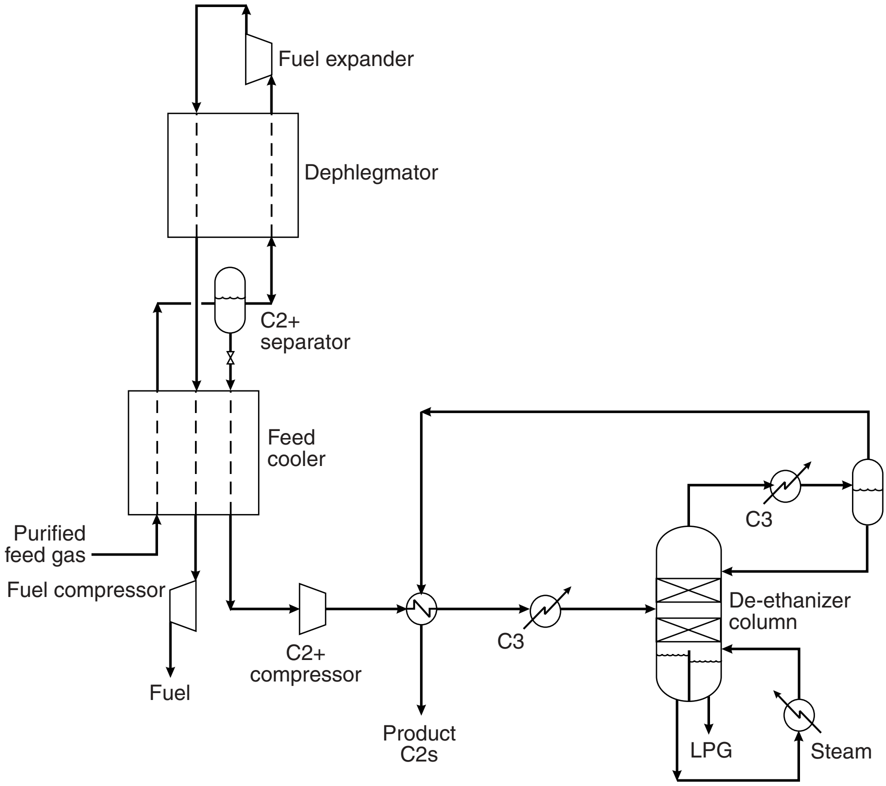

Fig. 8. FCC offgas ethane/ethylene recovery process.

The resulting mass transfer between the liquid and vapor, typically equivalent to 5–15 theoretical stages, produces a much higher purity liquid product than would a partial condensation process. Since less of the light components are liquefied, less refrigeration is required, and a higher recovery of the olefin/LPG products is economically justified.

A dephlegmator process can be used to recover ethylene/ethane and heavier hydrocarbons from fluid catalytic cracking (FCC) unit off-gas (Fig. 8). Pretreated feed gas is cooled to ~230 K and then further cooled and rectified in a dephlegmator to recover 90–98% of the ethylene, 99^{+}% of the ethane and 100% of the heavier hydrocarbons. Refrigeration for the cryogenic separation process is provided by revaporizing and warming the concentrated liquid C2+ hydrocarbon stream at low pressure and by work expanding the rejected light gases to fuel system pressure. The work extracted from this fuel expander can be used to drive a fuel compressor to recompress the warm fuel stream to a higher pressure.

The dephlegmator process recovers a substantially higher purity C2+ hydrocarbon product with 50–75% lower methane content than is possible with a partial condensation process. The C2+ product from the cryogenic separation process can be compressed and further separated in a de-ethanizer column to provide a high purity C3+ (LPG) product and a mixed ethylene/ethane product with 10–15% methane. Additional refrigeration for the de-ethanization process can be provided by a packaged system such as ammonia, propane or propylene refrigeration system.

3.8. Nitrogen Rejection and Helium Recovery. Cryogenic distillation has been used extensively in the processing of natural gas for nitrogen removal and for helium recovery (27–29). Three basic processes have been used for nitrogen rejection from natural gas; the single-column heat-pumped process, the double-column process, and the dual column cycle (29). Earlier processes utilized multistage flash columns for helium recovery from natural gas (30).

In the single-column heat-pumped process (Fig. 9), purified feed gas is cooled and fed to a high pressure column that operates at 2.1–2.8 MPa. Nitrogen vapor is withdrawn from the overhead of the column and natural gas liquids from the bottom. A closed-loop methane heat pump supplies reboiler heat and condenser cooling to effect the separation. The natural gas liquids stream is flashed to a low pressure, revaporized, and warmed with the rejected nitrogen for refrigeration recovery. The nitrogen rejected at high pressure is suitable for reinjection into oil reservoirs to maintain pressure and enhance oil recovery.

The double-column process (Fig. 10) is similar to the process described in Figures 1 and 2 for air separation. Pretreated feed gas free of water, carbon dioxide and sulfur compounds is cooled and fed to a high pressure column operating at 1–2.5 MPa. Nitrogen from the top of the high pressure column and a crude

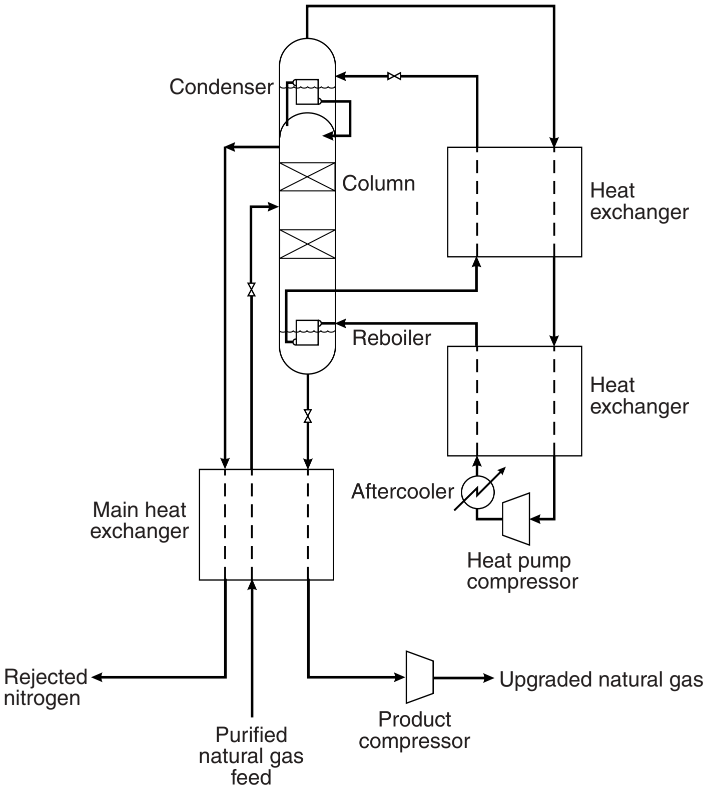

Fig. 9. Single column heat pumped process for nitrogen rejection.

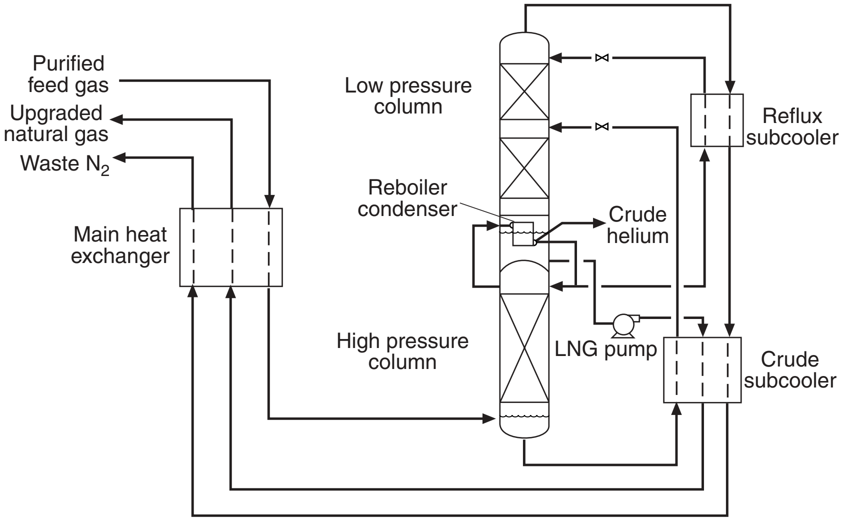

Fig. 10. Double column process for nitrogen rejection.

natural gas–liquid stream from the bottom of the high pressure column are further processed in a low pressure column at ~150 kPa to complete the separation. Reboiler heat for the low pressure column is provided by condensing nitrogen at the top of the high pressure column, which is then used to reflux both columns. The methane-rich liquid from the bottom of the low pressure column (LNG) is pumped to a higher pressure, revaporized, and warmed with the low pressure nitrogen from the top of the low pressure column for refrigeration recovery.

Crude helium (containing 50–70% helium, associated hydrogen and neon, 1–3% methane, and the balance nitrogen) can easily be obtained by minor enhancements to the nitrogen rejection unit, particularly with natural gases containing 0.5% or more helium. For example, by operating the double-column condenser in a partial condensation mode, a stream of uncondensed vapor at ~50% helium concentration can be obtained. This crude helium stream can be fed directly to helium purification and liquefaction units.

Natural gas liquids (NGL) recovery can also be integrated into a nitrogen rejection unit to achieve economies in equipment and operating cost (31). Integration of the heat exchange equipment and optimization of the refrigeration in the nitrogen rejection and NGL sections of the plant can provide significant overall savings. Typical ethane recoveries of 70–85% can be obtained.

3.9. Helium Purification and Liquefaction.

Helium, which is the lowest boiling gas, has only 1 K difference between its normal boiling point (4.2 K) and its critical temperature (5.2 K), and has no classical triple point (32,33). It exhibits a phase transition at its lambda line (running from 2.18 K at 5.03 kPa–1.76 K at 3.014 MPa) below which it exhibits superfluid properties (33).

Helium is commercially recovered from natural gas. If helium is present in a natural gas it usually occurs in concentrations between 0.2 and 2%, although it has been found in concentrations up to 8%. In the United States, significant quantities of helium exist in gas fields of Wyoming, the panhandle regions of Texas and Oklahoma, and in southwestern Kansas. Helium is also found in natural gas in Algeria, Canada, Poland, China, and the North Sea. As part of the United States helium conservation program of the 1960s, several plants were built to recover helium (typically processing 12 million STP m^3/day of gas), as well as a 400-km pipeline to collect their "crude" helium. Crude helium from this pipeline is stored in the Cliffside Reservoir near Amarillo, Texas for later withdrawal and processing. Helium from the Wyoming gas is liquefied without intermediate storage as crude helium.

Helium is normally concentrated in stages, first from the initial field concentration to crude, then to pure helium for liquefaction or sale as pure gas. As shown in the previous section, crude helium is easily recovered from a plant rejecting nitrogen from natural gas. Final upgrading of helium from crude to pure is typically done by Pressure Swing Adsorption (PSA) in combination with cryogenic partial condensation (34). Helium in natural gas streams is accompanied by neon and hydrogen, which cannot be separated from helium in the PSA unit; however, both must be removed to prevent their freezing in the helium liquefaction process.

A process for final upgrading (purifying) of the helium is shown in Figure 11 (34). Crude helium, which may be at low temperature from previous processing, is combined with PSA purge gas recycle, cooled to 80 K and partially condensed to provide a vapor stream of $\sim$90% helium concentration. Liquid from the partial condensation is warmed and separated to provide a waste stream and a nitrogen stream. The waste stream is used to regenerate the driers and a part of the nitrogen stream may be liquefied. The upgraded 90% helium stream, with air added to provide oxygen for catalytic combustion of the hydrogen, is preheated and passed over a hydrogen removal catalyst, then cooled to condense most of the water (Fig. 12). The upgraded-helium stream then flows through the PSA unit and to liquefaction. The PSA unit removes most of the remaining impurities (including water and nitrogen but excluding neon and unreacted hydrogen) to $<$10 ppm. The trace impurities are removed in an 80 K adsorber in the liquefier, and neon and any unreacted hydrogen are adsorbed in a 20 K adsorber. A portion of the pure product from the PSA is used to regenerate the PSA beds, then compressed, dried, and recycled to the inlet of the upgrader where it is combined with crude feed for high overall helium recovery.

Helium is liquefied by cooling to 80 K with either liquid nitrogen or the exhaust from a helium expander, then cooled below 80 K with refrigeration supplied by several helium expanders, followed by expansion through a dense-fluid "wet" expander. The number of expanders used in a liquefaction cycle varies with the plant capacity. Figure 13 shows a liquefier with 5 expanders (34). Helium is usually cooled at 2 MPa pressure, with the main flow from the exhaust of the expanders returning to compression at 0.2 MPa, and a small stream from liquid Dewar boiloff and liquid trailer loading returning at 0.1 MPa. Heat exchangers in the liquefier are brazed aluminum plate-fin type, designed for temperature approaches as tight as 0.1 K to minimize energy requirements. The helium expanders are usually centrifugal with either oil or gas bearings, and are braked by either an oil cup loader or a closed-loop helium compressor. The main recycle compressors are reciprocating or (more typically) oil-flooded screw machines.

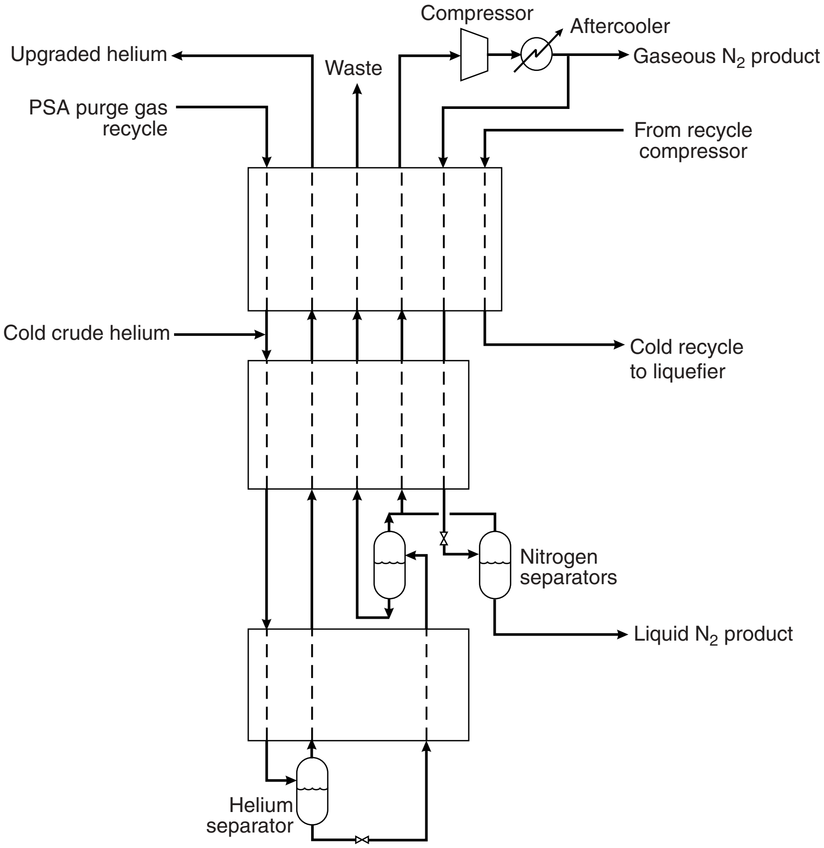

Fig. 11. Crude helium upgrading process.

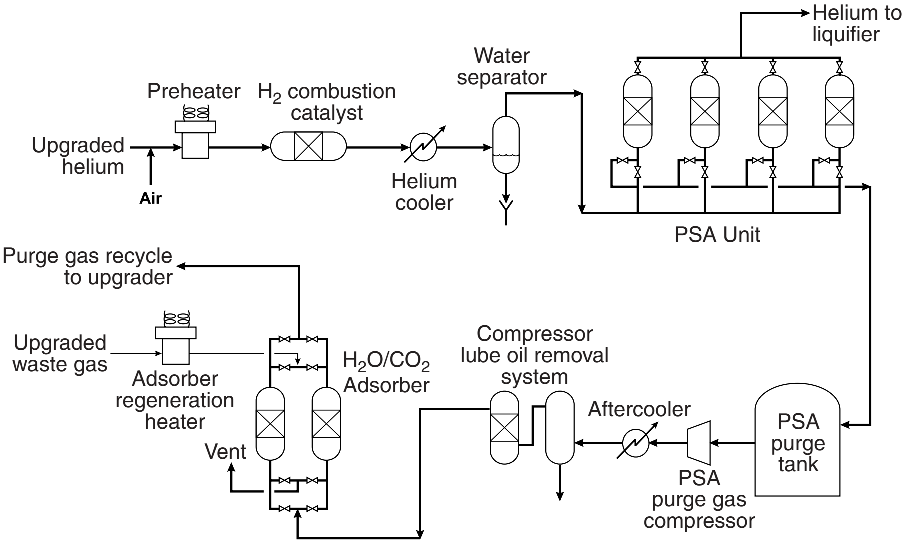

Fig. 12. Helium purification process.

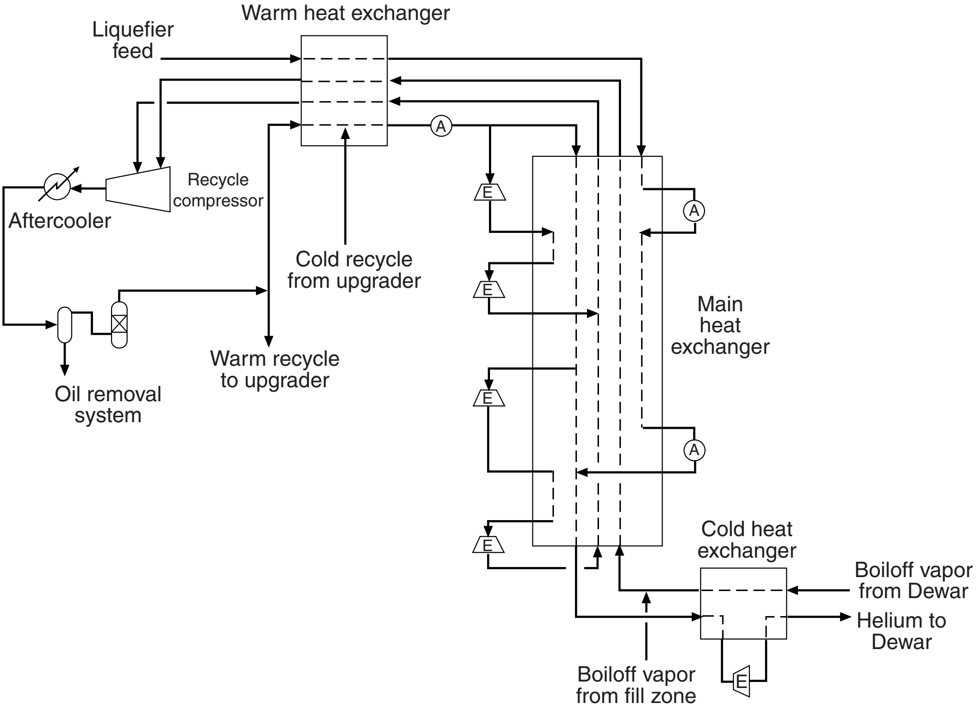

Fig. 13. Helium liquefaction process. Key: A = adsorber, E = expander.

Large helium refrigerators are used to cool superconducting magnets to 4.5 K in accelerators for high energy physics experiments (35). The process configuration for a helium refrigerator is similar to that for a liquefier, and the refrigerator may produce some liquid. The process flows will vary with the ratio of 4 K heat load relative to the liquid production rate, because a refrigerator has balanced flows cooling and warming, with the heat load at the cold end, whereas a liquefier heat load is distributed over the temperature range from 300 to 4 K. Temperatures <4.2 K are achieved by subatmospheric pressures maintained by cold compressors or by warm vacuum pumps. A refrigerator/liquefier can trade 100 W of refrigeration at 4 K for 1 g/s of liquid helium product. Liquid helium refrigerators are being considered for superconducting generators, transmission lines, and electric storage devices.

4. Equipment

4.1. Machinery. Compressor selection for a cryogenic process plant depends on the fluid, the volumetric flowrate, the pressures involved, the compressor efficiency, and the cost of energy and capital. Centrifugal compressors are lower in installed cost than reciprocating machines, and are preferred if the volumetric flows and pressures of the process allow them to be applied. For large volumetric flows, axial compressors are used. At very high pressures with small volumetric flows, reciprocating machines are required. Sometimes a combination of more than one kind of compression stage is used to yield the most cost effective and efficient system. For example, an oxygen compression system delivering oxygen at ~10 MPa might employ several centrifugal stages followed by several reciprocating stages.

Gases of low molecular weight are difficult to compress in centrifugal compressors, which results in a large number of stages being required to achieve a reasonable total pressure rise. Consequently, hydrogen and helium are seldom compressed using centrifugal compressors. Oil-flooded screw compressors are commonly used for helium processes operating at pressures under 2.4 MPa, which is typical for helium liquefiers and refrigerators. Oil removal equipment must be used following lubricated reciprocating compressors or oil-flooded screw compressors. Oil-flooded screw compressors also find application in small air separation plants for use in feed compression.

Axial compressors have been applied to base-load LNG plants, but currently the majority of those plants use centrifugal compressors.

Drivers for cryogenic plant compressors can be electric motors, internal combustion gas engines, gas turbines, or steam turbines.

Cold compressors are in use with suction temperatures ~4 K to provide temperatures <4 K by reducing the pressure under which helium is boiling. These cold compressors use magnetic bearings.

Expanders provide refrigeration by extracting work from a fluid, thereby reducing its enthalpy. Gas expanders can be either reciprocating or centrifugal, and can be loaded (braked) by electric generators, gas blowers or compressors, oil-film “cups”, or oil pump brakes. The extracted work can be usefully recovered in an electric generator or compressor. Centrifugal expanders are lower in first cost and in maintenance cost. Reciprocating expanders may be required for low volumetric flows and/or high expansion pressure ratios of low molecular weight gases. Bearings for gas expanders can be oil or gas bearing type (static or dynamic). Reverse-running liquid pumps have been used as liquid expanders. Isentropic efficiencies for gas expanders can be as high as 85–90% for machines with high discharge volumetric flow.

4.2. Heat Exchangers. The two most prominent types of heat exchangers used in cryogenic service are the coil wound, tube-in-shell exchanger and the brazed aluminum plate and fin (core) exchanger (36). Since cryogenic process efficiency is highly dependent on maintaining close temperature approaches between all the cooling and warming streams, these heat exchangers are normally designed to accommodate at least three, and as many as eight or nine, countercurrent streams in a single unit. Accurate thermodynamic and physical property data as well as accurate heat transfer and pressure drop correlations are required for the design of these types of heat exchangers. The design must provide for uniform flow distribution to achieve close temperature approaches and must account for longitudinal heat conduction.

The coil wound heat exchanger consists of multiple tubes helically wound on a mandrel, usually with spacers between each tube layer. The tubes are inserted into tube sheets at both ends of the tube bundle, with separate tubesheets to accommodate each tube circuit. The tube bundle is enclosed in a shell with inlet and outlet nozzles for the shellside fluid. Typical exchangers will have two or three tube circuits and a single shell-side circuit, which frequently contains an evaporating two-phase fluid. This type of heat exchanger is usually constructed of aluminum or stainless steel. Large aluminum coil-wound heat exchangers for base-load LNG plants may be >5 m in diameter, 60 m long, and weigh up to 300 metric tons.

The plate and fin heat exchanger consists of corrugated sheets (fins) stacked between flat sheets (plates). The corrugated sheets are usually perforated or serrated to enhance the heat transfer performance of the exchanger. The stack is brazed in a closely controlled vacuum furnace and headers and nozzles are then welded to the brazed stack to form the separate circuits of the unit. This type of heat exchanger is normally constructed of aluminum, but stainless steel units are also available.

4.3. Distillation Columns.

In a cryogenic air separation plant, distillation accounts for the major fraction of the total energy consumption. The low relative volatility characteristic of many cryogenic separations requires the use of many stages. Columns operating at low pressures are consequently designed for a low pressure drop per theoretical stage of separation. Sieve trays with small perforations (~1 mm) provide excellent efficiency at low tray spacing for the clean fluids of cryogenic distillation processes. The minimum pressure drop across distillation sieve trays is set by the requirement to maintain a stable biphase zone of gas bubbling through liquid, corresponding to ~35 mm of liquid per theoretical stage. A double column of the type shown in Figure 1 may use as many as 150 trays. Therefore it is important to keep the spacing between the trays as small as possible to minimize capital cost. Usually tray spacing is in the 10–20-cm range. Each major manufacturer has their own design of the tray geometry, including multipass cross-flow trays, split cross-flow trays and circular flow trays. Currently, low pressure drop structured packings are used instead of sieve trays in most sections of the low pressure column and the argon column of air separation units.

In some cryogenic hydrocarbon separation plants, such as a nitrogen rejection unit, both flowrate and feed composition may change over the life of the plant. This requires the use of valve or bubble cap trays with high turndown capability for distillation. In some applications, the presence of foaming or high froth liquids requires tray spacing as high as 60 cm.

4.4. Insulation.

Cryogenic insulation should economically reduce heat leak into the system so that its impact on the overall refrigeration requirement is minimized. Insulation can be categorized as unevacuated bulk type (eg, purged rockwool or perlite), rigid foam (eg, foam glass or urethane), vacuum-jacketed (VJ), evacuated powder (eg, perlite), and multilayer insulation (MLI) (eg, evacuated aluminized mylar).

Process equipment for small to medium sized cryogenic plants is often enclosed in a “cold box” consisting of a steel frame with panels. Large cryogenic plants typically enclose the distillation column in a field-erected “can” while the heat exchangers are contained within “boxes”. Regardless of the enclosure used, the void space within is filled with perlite or rockwool and purged with a gas that will not condense on the exterior of the equipment and piping. This method of insulation is commonly used on plants for air separation, hydrocarbon recovery, H_2 purification, and N_2 refrigeration. Equipment supports or suspension systems are designed for low conduction heat leak using materials with low thermal conductivity, long conduction paths, and small cross-sections. Small refrigerators commonly use evacuated MLI. For the large equipment sizes of base-load LNG plants, individual equipment items and piping are separately insulated with urethane. Lines to transfer liquid cryogens can be insulated with rigid foam, vacuum, evacuated MLI, or evacuated MLI with heat shield, depending on the impact of heat leak and the frequency of cooldown. Bayonet fittings and valves for VJ lines are designed for low heat leak using long conduction paths with small cross-sections.

Storage tanks for large volumes (>1000 m^3) of LNG, liquid nitrogen, and liquid oxygen often use unevacuated perlite insulation that is pressurized with boil-off gas from the tank's liquid. Tanks for similar volumes of liquid H_2 are usually insulated with evacuated perlite. Smaller tanks for LNG, liquid nitrogen, and liquid oxygen use evacuated perlite insulation. Tanks for liquid helium and smaller ones for liquid hydrogen are insulated with evacuated MLI, and the liquid helium tanks usually incorporate a heat shield using boil off vapor or liquid N_2 to intercept part of the heat leak.

Transport vehicles for cryogenic liquids have an inner vessel holding the liquid and a surrounding vacuum perlite or MLI insulation, all enclosed within an outer vessel. Liquid helium vehicles are insulated between the inner and outer vessels by vacuum MLI and a heat shield cooled by liquid nitrogen which is carried on board. These liquid helium containers can be filled with liquid helium in the United States and transported by ship to Europe or Asia without venting helium for 45 days (37). Barges and railcars to transport cryogens are in everyday service in the United States in support of the space program. LNG ships of 125,000-m^3 cargo capacity use rigid foam insulation.

5. Safety

The possibility of an uncontrolled release of a cryogenic fluid such as liquid oxygen, methane, or hydrogen from storage and during handling must be carefully considered during the design of a cryogenic facility. The level of risk may be reduced by providing dikes for secondary containment of liquid spills. Procedures to protect personnel from cryogenic burns and asphyxia and to protect the nearby equipment from embrittlement failure must be carefully considered and followed. When trace impurities in the feed streams can lead to the combination of an oxidant with a flammable cryogen (eg, solid oxygen in liquid hydrogen) or a combustible with an oxidant (eg, acetylene in liquid oxygen), special precautions must be taken to eliminate them. Many materials react with pure oxygen, so care must be taken in the selection of any materials that may be in contact with oxygen and in the cleaning of oxygen systems prior to use. Potential ignition sources must be minimized, particularly in oxygen compression and in systems for handling oxygen at elevated pressures (10,38).

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Rakesh Agrawal
D. Michael Herron
Howard C. Rowles
Glenn E. Kinard
Air Products and Chemicals, Inc.