

Ammonia Synthesis Can Be Argon Source

Expanding uses and trends in various markets for argon are starting to show an impact on current source—air liquefaction. Potential is seen for two processes to recover argon from ammonia purge gas.

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Argon, the use of which is expanding currently in several important markets, could be recovered economically from the purge gas from ammonia synthesis plants.

The gas is presently a by-product of the production of oxygen by air liquefaction and distillation. The market for argon, however, has been growing twice as fast as that for oxygen, and it is approaching the point at which the incremental cost of recovery will begin to rise. In the case of the approach by using purge gas from ammonia synthesis, processes that enrich the argon content of that purge gas enhance the economics of potential argon recovery.

Two such processes are discussed in this article, one depending upon cryogenic treatment and the other on absorption in liquid ammonia. The article opens, however, with a brief discussion of the air liquefaction route.

Argon has been finding increased use in many markets, particularly metallurgical. Among applications in that field have been the following: shielding for welding, brazing, and soldering; inert atmosphere for high temperature refining, preparation and fabrication; inert purge for degassing molten metals; and inert atmosphere for semiconductor fabrication. It has also been finding major uses as a light source, in filling of incandescent and fluorescent lamps, and in lasers.

It may be readily understood how the development of the exotic metals and the semi-conductor industries has led to the expansion of the market for argon. In 1972, that market exceeded 3,700 million cu. ft., having grown by 25% over the previous year, and at an average rate of 16% annually for the previous decade. (1).

As is indicated in Table 1, argon is the most important minor constituent of air. Air separation by liquefaction and distillation to manufacture oxygen and nitrogen has argon as a relatively inexpensive by-product.

Air separation plans follow numerous different process schemes (2, 3, 4), but all have many features in common. A typical flow sheet, taken from a text by Cook (2), is presented in Figure 1.

Table 3. Constituents of air
(vol.-% and boiling pts., °K.)

Constituent	vol.-%	b.pt.
Nitrogen	78.	77°K
Oxygen	21.	90°K
Argon	0.94 . . .	87°K
Hydrogen*	0.01 . . .	20°K
Neon	0.0015. .	26°K
Helium	0.0005. .	4°K
Krypton	0.0001. .	120°K
Xenon.	0.00001.	166°K

* Fraction is variable.

Air is compressed and cooled by heat exchange with water, with refrigerant, and with product and reject gas streams. In the course of cooling, water and carbon dioxide condense as solids which are removed periodically by reversing flows. Part of the stream may be expanded through a turbine or other engine. However, most of the liquid is

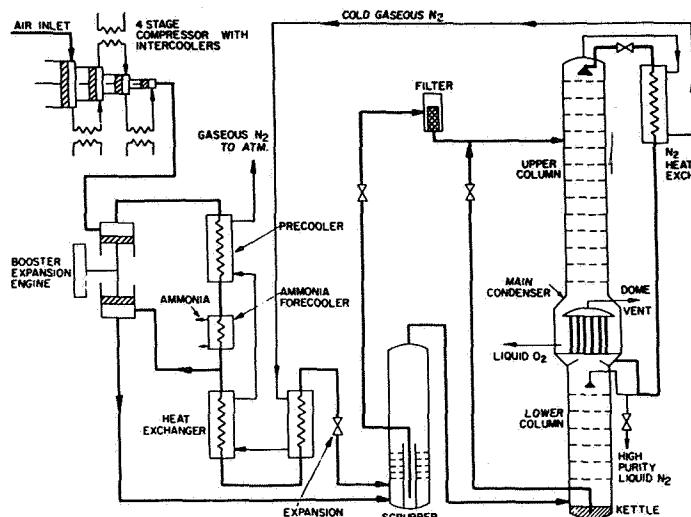


Figure 1. High-pressure air separation cycle.

obtained by Joule-Thompson expansion through a valve to avoid the complications of having both gas and liquid flowing through moving equipment.

The distillation step is carried out in two columns built one on top of the other. The lower operates at relatively high pressure, about 70-100 lb./sq. in. gauge, and acts solely as a rectifying section. It produces pure nitrogen as a top product. Enriched oxygen (34-40%) leaves the bottom as a two-phase mixture which is flashed to the pressure of the upper column, about 10 lb./sq. in. gauge, and fed at an intermediate point. Nitrogen and argon are stripped out in the section below the feed, giving a relatively pure oxygen as the bottoms product. The reboiler of the upper column serves as the condenser of the lower column, possible because of the pressure difference. Part of the liquid nitrogen from the lower column is used to provide reflux for the upper column. Impure nitrogen leaves the top of the upper column and is returned to the atmosphere after heat exchange.

The pressure to which the inlet air is compressed and the amount of auxiliary refrigeration which is required are functions of the form in which the product streams leave the process. If both are desired as gases, then energy requirements are relatively low, and a pressure of approximately 100 lb./sq. in. gauge sufficient. If both are to be sold as liquids, pressures of 1,000-2,000 lb./sq. in. gauge are common. Low pressure plants producing liquid oxygen are a recent development (3). The energy requirement of the plant, provided either in the compression of the feed or in the auxiliary refrigeration, thus increases as the enthalpy of the products goes down.

Argon recovered in low-pressure column

Because argon is intermediate in volatility between oxygen and nitrogen, it builds up to a maximum concentration on the intermediate plates of the low-pressure column. This concentration is typically of the order of 12%, the remainder being primarily oxygen.

As seen in Figure 2, a side stream of vapor from this region of the column is taken as the feed to the argon recovery unit. In the first column of this unit most of the oxygen is taken out the bottom and returned to the air separation column. The liquid from the high-pressure column provides the cooling for the reflux. The "crude argon" from this column contains about 1% of both nitrogen and oxygen.

In the purification scheme shown in Figure 3 crude argon is first distilled again to remove nitrogen and then passed through molecular sieves to remove residual oxygen. Alternative means to remove oxygen include reaction with hydrogen and reaction with metallic copper. The refined liquid argon has a purity of 99.996% or better, corresponding to a total impurities content of about 40 ppm.

Because the source of the feed to the argon recovery unit is a side stream from the low-pressure column, the cost of argon recovery will be quite sensitive to the fraction of argon which is recovered from the feed to the air separation plant. As this fraction increases, the concentration of argon in the side stream will necessarily decrease and the separation in the crude argon column will become correspond-

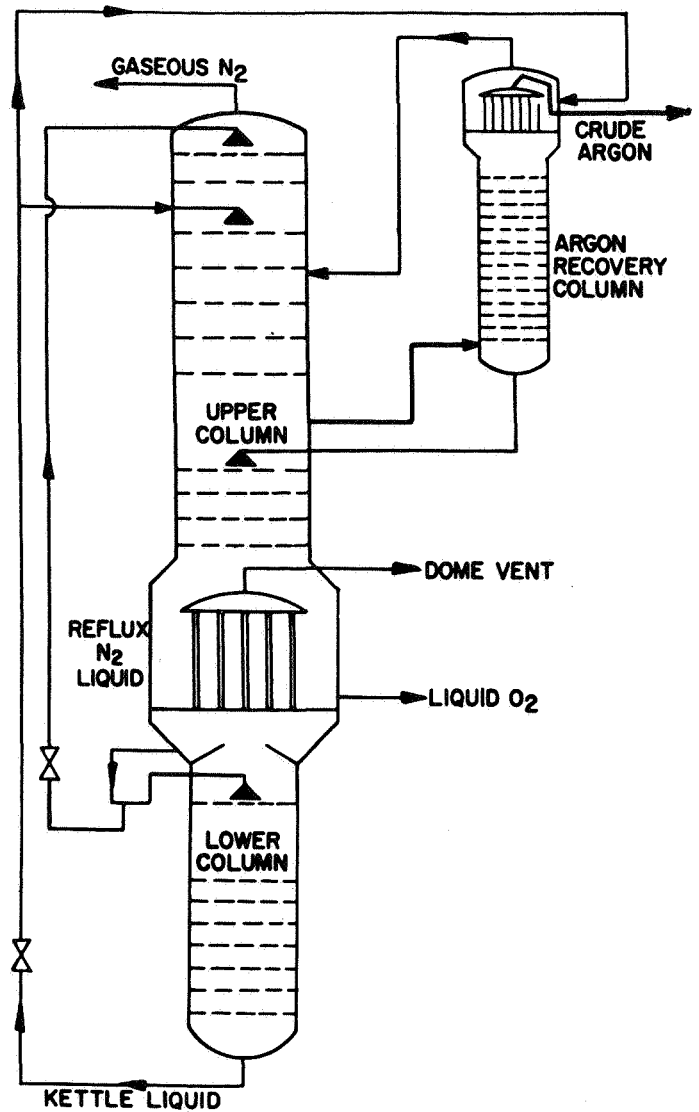


Figure 2. Argon recovery system.

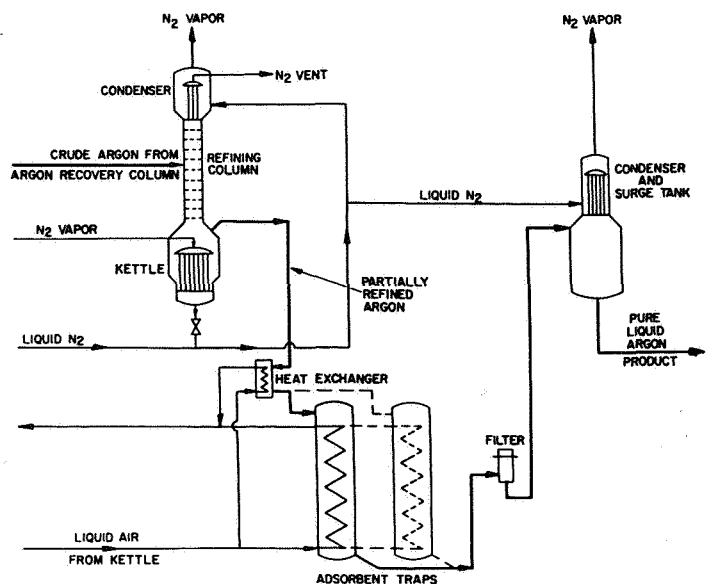


Figure 3. Argon purification with absorption of oxygen.

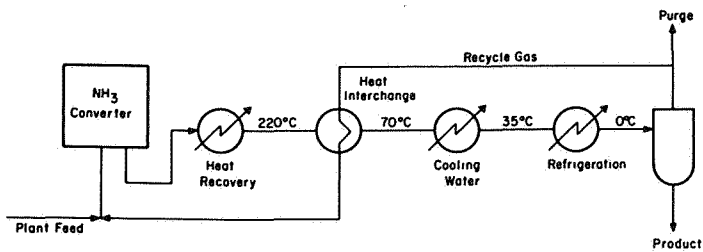


Figure 4. Conventional ammonia recycle loop.

ingly more difficult. As the market for argon continues to grow relative to that for oxygen, alternative sources will become increasingly attractive.

A greatly simplified flow sheet for a conventional ammonia synthesis loop is shown in Figure 4. The system pressure is usually 200-300 atm., and the temperature of reaction is 450-500°C. Because conversion of nitrogen and hydrogen to ammonia is only 20-25% per pass and is limited by thermodynamics, economics dictates that the effluent stream be cooled to condense ammonia and be recycled to the reactor.

The hydrogen in the feed stream is obtained by reforming methane or other hydrocarbon; the nitrogen comes from the air. As a result, the feed stream typically contains about one-quarter of one per cent argon and three to five times that amount of methane. These gases are inert in the process, but accumulate with continued recycle. Their presence reduces the conversion in the reactor, necessitating their removal from the system.

This is accomplished in conventional plants by purging a fraction of the recycle stream. The resultant loss of hydrogen and nitrogen typically amounts to 5-7% of the feed. The purge stream contains 2.5-3% argon and 10-12% methane. This argon level is rather low for economic recovery, and little or none is produced from the purge stream of conventional ammonia plants.

Two processes have been proposed to reduce the amount of ammonia production which is lost because of the purge. One is based on cryogenic processing of a somewhat increased purge stream, a substantial portion of which is returned to the recycle loop without significant loss of pressure. The other utilizes liquid ammonia at relatively high temperature to absorb the inert gases from a side stream of the recycle loop.

In both cases a purge stream is produced which is significantly smaller in volume and correspondingly richer in argon content. The economics of the subsequent recovery of argon as a by-product of ammonia production would thereby be enhanced.

Cryogenics finds role in handling purge stream

While a number of cryogenic processes have been designed for handling ammonia plant purge streams, we are indebted to the M. W. Kellogg Co. for the following description of a process which they offer on a turn-key basis (5). A schematic view of the plant layout is shown in Figure 5. The feed stream to the cryogenic unit is about 140% greater than a conventional purge. About 66% of this stream is returned to the recycle loop, after been cooled to cryogenic

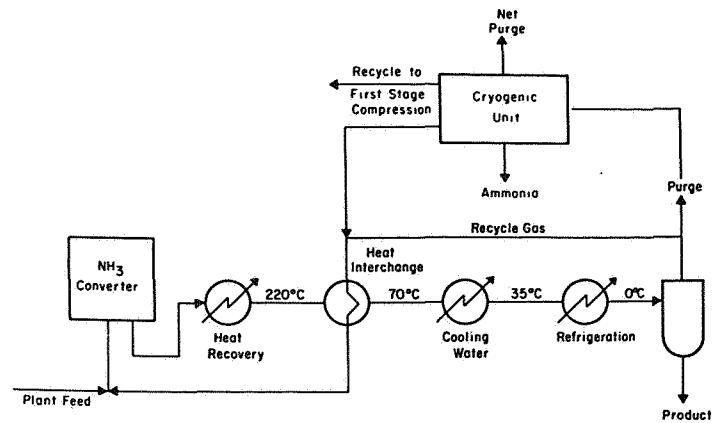


Figure 5. Kellogg cryogenic purge treatment.

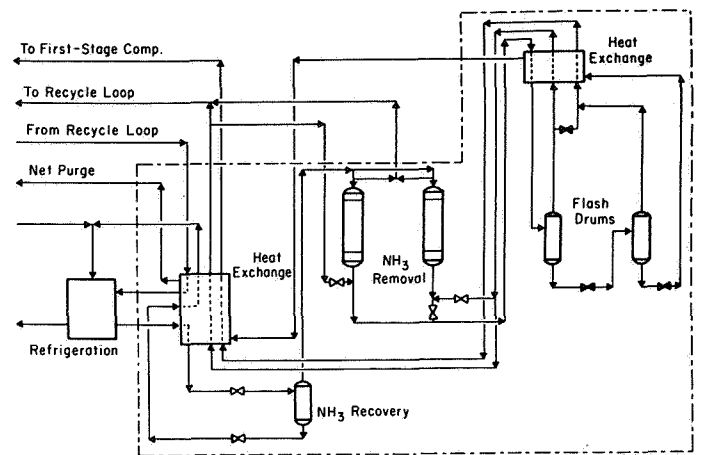


Figure 6. M.W. Kellogg cryogenic unit.

temperatures, without substantial loss of pressure. Another 6% is combined with the low pressure feed to the primary compressor. The rest is purged to the hydrogen plant furnace.

Looking the "cold box" (Figure 6) we see a system of heat exchangers and flashing steps which is reminiscent of the air liquefaction plant. The high-pressure purge stream is cooled by ammonia refrigeration and by heat exchange with the product streams to cryogenic temperatures. Most of the ammonia is removed first by condensation, and the residual is picked up on a molecular sieve. About three-fourths of the nitrogen and the bulk of the argon and methane condense from the high-pressure stream and are separated in a knock-out drum. After heat exchange the high pressure stream is returned to the recycle loop. The liquid is then flashed to about 600 lb./sq. in., the gas formed being about 90% hydrogen which is returned as feed to the primary compressor.

The remaining liquid contains 70% of the nitrogen, almost 80% of the argon, virtually all of the methane, but only about 5% of the hydrogen entering the cryogenic unit. It constitutes the net purge from the system and is sent to the hydrogen plant furnace after flashing and heat exchange.

yet been fully realized. One might well conclude that one of the more significant aspects of such a system at this moment would be the recovery of the gas for synthesis rather than the potential argon recovery.

LYNN: Do you happen to know what fraction of the argon your plant recovers?

BALL: I wouldn't have that figure with me at the moment, no.

CLAY HALE, Adtek, Inc.: You mentioned that the solubility of the gas in the ammonia was higher at the higher temperatures than at lower pressure level. Where was this data obtained and at what pressure levels was data available?

LYNN: We have obtained this from nine different sources in the literature. We have a great deal of binary data and some ternary data and we used this information to develop a calculational procedure which lets us compute the five-

component equilibrium as a function of temperature and pressure. This computer program was used for the plate-to-plate column calculations in the flow sheet which I discussed.

HALE: Would this also be true at low pressure? You're talking about 1500 to 2000 pounds? Would this apply at the low pressure also?

LYNN: Yes, it will apply at relatively low pressure. Of course you have to operate above the vapor pressure of ammonia. Since you want to absorb the inert gases in a relatively small amount of ammonia, however, you want a large partial pressure of the inert gases in the absorption column. This means that it is advantageous to operate the column at the maximum available pressure. The increase in solubility between 0° and 90°C is roughly a factor of 10 for these gases, which is the reason for operating the column at the higher temperature.