CRYOGENIC CONSULTING SERVICE , INC.

CRYOGENIC ARGON PRODUCTION

A Technology Review Paper for Presentation at the
1999 Modern Air Separation Plant Technology Conference
July 26 -- 27, 1999 at Chengdu, People's Republic of China
By Joseph T. Bernstein, Cryogenic Consulting Service Inc.

Air Separation Background

The major components of atmospheric air include nitrogen (78.12%), oxygen (20.95%) and argon (0.93%). Argon is produced as a byproduct of cryogenic air separation for the production of pure oxygen or pure oxygen and nitrogen.

Depending on whether product oxygen and nitrogen are low pressure gas or high-pressure gas or liquids, cryogenic air separation processes may take various forms. The Low Pressure Cycle (Figure 1) utilizes air compressed to approximately 6 atma; heat exchange to cool air to near condensing temperature (utilizing cooling from product oxygen, nitrogen, etc.) and distillation Towers to separate air into pure oxygen and nitrogen.

In the "Split Cycle" process shown in Figure 2, some air is compressed to a higher pressure to allow liquid oxygen to be pumped to a product pressure and evaporated in the product -- air exchanger. Many other process variations exist, but all ASU cryogenic systems include:

- air compressor or compressors
- means of removing the freezable impurities, water and CO2
- means of producing low temperature refrigeration (expander)
- feed -- product heat exchangers
- distillation Towers

The various approaches to air separation will be discussed in other conference papers. In this presentation, we will focus on the elements, which relate to argon production.

The separation of air into oxygen and nitrogen almost always utilizes the "double tower" system (Figure 3) in which air is first separated into a pure nitrogen liquid and an enriched oxygen liquid (35% -- 39% oxygen) in a "high-pressure" column at about 6 atma. The liquid N2 produced in the "high-pressure" tower solves a problem of providing liquid nitrogen reflux at the top of the upper (low pressure) tower, which accomplishes the final separation into oxygen and nitrogen products at about 1.4 atma.

The double tower system utilizes liquid oxygen at the bottom of the low pressure tower to condense nitrogen gas at the top of the high-pressure column. The pressure of the boiling liquid oxygen at the bottom of the low pressure tower determines its boiling temperature, which in turn determines the condensing temperature and pressure for the nitrogen vapor at the top of the high-pressure tower.

Typical temperature and pressure relationships of the double tower system are shown in Table 1. Two cases are shown in Table 1, a plant utilizing trays (usually sieve trays) and not employing techniques for minimizing temperature differences or pressure drop is shown on the left, and a plant utilizing packing for the "low pressure" column, and other techniques for minimizing pressure and temperature differences is shown on the right side. The high-pressure drop or low pressure drop design may reflect different economic conditions such as power cost and plant size. In general, very large plants make low pressure drop economically attractive.

The pressure at the bottom of the low pressure tower results from the pressure drop through the low pressure tower itself and the feed -- product heat exchangers and other equipment until the "waste" nitrogen is vented to atmospheric pressure. The result is a requirement for air entering the high-pressure column to be at a pressure of about 5 or 6 atma.

The low pressure tower functions mainly to produce oxygen product and nitrogen product and/or waste nitrogen, but since argon has a boiling temperature between that of oxygen and nitrogen (see Figure 4, oxygen, nitrogen & argon vapor pressure) there will be a significant build-up of argon in the low pressure tower (as long as oxygen is produced as a relatively pure product). Figure 5 shows a typical concentration profile for oxygen, nitrogen and argon vapor within a low pressure tower producing pure oxygen. Figure 5 shows that although argon is less than 1% of the air composition, it may build up to 10% or even 20% in the trays in the middle of the low pressure tower (below the enriched air feed point). The extent of the build-up of argon is determined by the purity of the oxygen and nitrogen products, and by the number of distillation stages and L./V. rates in the low pressure column.

Argon Production

The production of argon involves connecting a "side arm" column, which receives a feed vapor from the low pressure column at a point near the maximum argon concentration, but also at a point where nitrogen concentration is still low. The typical argon "side arm" column connected to a double tower system is shown in Figure 6.

The side arm column utilizes condensing provided by partially evaporating the approximate 38% oxygen liquid "enriched air" feed to the low pressure column. Figure 6 shows typical temperature and pressures in the low pressure tower and argon side arm tower. The pressure at the top of the argon side arm (crude argon) tower has a lower limit of about 1.1 atma or 1.05 atma.

This lower limit is set by two factors:

a.) the available temperature for condensing which is set by the pressure and composition of the evaporating "enriched air" liquid, as determined by the conditions of the double tower system.

b.) the fact that the "crude argon" product from the top of the side arm column should be delivered at a pressure slightly above atmospheric pressure after warming to ambient temperature in a heat exchanger.

Both of these factors limit the minimum pressure at the top of the crude argon side arm column to about 1.1 atma (or at the extreme 1.05 atma).

Therefore, as shown in Figure 6, the maximum available pressure difference from the bottom to the top of the argon side arm column is about 0.35 atma. Utilizing distillation trays with a pressure drop equivalent to about 4 cm of liquid (approximately.005 atma) the maximum number of trays in the crude argon tower is 0.35 atma/.005 atma = 70 trays. In typical practice, the tray type of crude argon side arm column will have 40 -- 60 distillation trays.

Because the relative volatility of argon in argon -- oxygen mixtures is low (see Figure 7), the typical traditional argon side arm column (with 40 -- 60 trays) will produce a "crude argon" product containing about 1% -- 2.5% oxygen, as well as some nitrogen. In order to remove all oxygen (to 1 ppm or less) about 150 -- 200 stages would be required in the argon side arm column.

Figure 7 allows us to understand the Liquid and Vapor flows within the crude argon column. In Figure 7, L./V. = 0.96 and V. -L. is the crude argon product quantity. Figure 7 shows that, for an argon -- oxygen feed mixture containing about 12% to 16% argon, the L./V. ratio must be at least about 0.96, or slightly higher. Assuming (V. -L.) =.008 (of .0093 argon in 1.0 unit of air), and solving the two equations, V. =0.008/.04= 0.2 or 20% of the air feed for the assumed L./V. and V. -L. (.008 Argon product is assomed for mathematical simplicity, but typical argon recovery in a large, modern ASU may exceed 95%.) Of course, the exact L. and V. rates may vary slightly, but Figure 7 illustrates that the argon -- oxygen equilibrium does not allow for much variability of the L./V. ratio in the crude argon side arm column. For instance, if L./V. = 0.98, by the same mathematical relationships, V. = 40%. The increase of L./V. from 0.96 to 0.98 would have only a small effect in reducing the number of stages required, since L./V. is already close to 1.0. However, this increase of L./V. to 0.98 would double the amount of vapor flow in the crude argon column and double the condensing requirement at the top of the crude argon column. In fact, in most cases a vapor flow in the crude argon column equivalent to 40% of the air feed would normally exceed the condensing duty available from the rich air liquid, since the low pressure column cannot operate if too much of the rich liquid feed is vaporized. So in practice, L./V. in the crude argon column is limited to about 0.96 -- 0.97.

Because of the high relative volatility of nitrogen, essentially all of the nitrogen entering the crude argon tower leaves with the product crude argon at the top. So, if the nitrogen in the crude argon product is to be 1%, in the feed it must be 1% x.008/.20 =.0004 mol fraction, or less. So the connecting point on the crude argon side arm tower must be chosen carefully to allow a high argon concentration, but provide a low nitrogen concentration (typically about 100 ppm). If there is too much nitrogen at the crude argon column condenser, the condensing temperature becomes lower for a mixture with more nitrogen, and the crude argon column condenser (with a fixed temperature on the cold side) may stop working.

Because the "traditional" argon side arm column "crude argon" product contains 1% -- 2.5% oxygen and also 1% -- 2% nitrogen, the traditional argon production system must include additional equipment for removing the residual oxygen and nitrogen. The traditional cryogenic argon system consists of three major elements (see Figure 8):

1.) The crude argon side arm column

2.) A catalytic "deoxo" system which burns the remaining 1% -- 2.5% oxygen by catalytic reaction with H2 .

3.) A final "pure argon" tower which removes nitrogen (and H2) to make high purity Argon.

The catalytic "deoxo" system receives the crude argon gas after warming, at near atmospheric pressure. The crude argon is compressed, heated to approximately 400 C. H2 is added in a controlled quantity to provide a slight excess after reaction with oxygen. After reaction of O2 + H2, the hot argon is then cooled, and the water vapor resulting from the hydrogen -- oxygen reaction is removed, usually in a dual bed adsorber drier system. A detailed flowsheet of the deoxo system (Figure 9) shows that the deoxo system can be complex, and requires operational attention, some maintenance, and involves the cost of supplying hydrogen.

Improved Argon System

Because the limitation of the crude argon tower is based on available pressure drop, it is possible to consider low pressure drop devices, such as packing, instead of distillation trays. Before 1980, the very few commercial installations with packing were generally not successful because of difficulty in maintaining good distribution of liquid in a large, long packed tower.

Beginning about 1980, the Sulzer Company developed the so-called "structured" packing with a regular shape of corrugated metal or wire mesh. This packing achieved good distribution of liquid, even in large diameter columns. The structured packing was tried in cryogenic applications, and by about 1990 the Linde Company described the

use of a crude argon side arm column with structured packing to achieve almost complete removal of oxygen. (1)

Figure 10 shows the situation with packing in both the low pressure column and the side arm crude argon column, (although the low pressure column could be either trays or packing). The pressure at the enriched air feed is essentially the same (or slightly lower for the case of packing) in the low pressure tower whether packing or trays are used, giving about the same condensing temperature and pressure limitation at the top of the crude argon column. When packing is used in the low pressure column, the pressure at the feed to the crude argon column is slightly lower, giving an available pressure difference of about 0.27 atma from the feed point to the top of the crude argon tower. At an approximate pressure drop of 0.0007 atma per stage for packing (about 15% of tray pressure drop) more than 350 stages could be possible if all of the available pressure drop in the crude argon tower were used. In practice, about 150 to 200 stages are required in the crude argon tower to reach an oxygen level below 1 ppm, depending on L/V ratio in the crude argon tower.

The result of this approach is the elimination of the "deoxo" system. The packed towers containing about 150 -- 200 theoretical stages are quite tall, and are usually divided into two separate towers, and require pumps between the two towers and also usually to return liquid from the bottom of the side arm column to the feed point at the low pressure column, as shown in Figure 11. Even with a good liquid distribution in structured packing, liquid re-distributors are utilized approximately every four or five meters of height. The design of liquid distributors is important for successful operation of structured packing towers. The initial feed vapor distribution is also important.

Because the pressure at the top of the crude argon column is still rather low (1.1 -- 1.2 atma) the product is usually produced as a liquid, and the height of the crude argon tower condenser is used to provide pressurization of the feed to the pure argon tower by means of an elevation difference. When the crude argon product is vapor (if pressure allows) this has an advantage in venting N2 at the top of the crude argon tower,

References

1. Rohde, W.J., IOMA Broadcaster, Sept.-Oct. 1991, p, 5.

LIST OF FIGURES & TABLES

TABLE 1.1
TYPICAL LOW PRESSURE OXYGEN PLANT CONDITIONS

	Plant with Tray Tower	**Large Plant with Packing Optimized For Low ΔP**
Atmospheric Pressure for Waste Nitrogen Leaving Process	1.0 ATMA	1.0 ATMA
Pressure drop of Waste N2 in Piping, exchangers, valves plus Pressure drop in upper column	0.5 ATMA	0.33 ATMA
Pressure of oxygen boiling at Bottom of LP column	1.5 ATMA	1.33 ATMA
Boiling Temperature of O2 at 1.5 ATMA / 1.33 ATMA	-179 Deg C	-180.1 Deg C
Reboiler/Condenser Temperature Difference	2.8 Deg C	1.0 Deg C
Condensing Temperature of N2 at Top of Lower Tower	-176.2 Deg C	-179.1 Deg C
N2 Condensing Pressure @ Temp.	6.2 ATMA	4.97 ATMA
Pressure drop in Lower Tower, Exchangers, Piping & Valves	0.44 ATMA	0.44 ATMA
Air Compressor Discharge Pressure	6.7 ATMA	5.41 ATMA

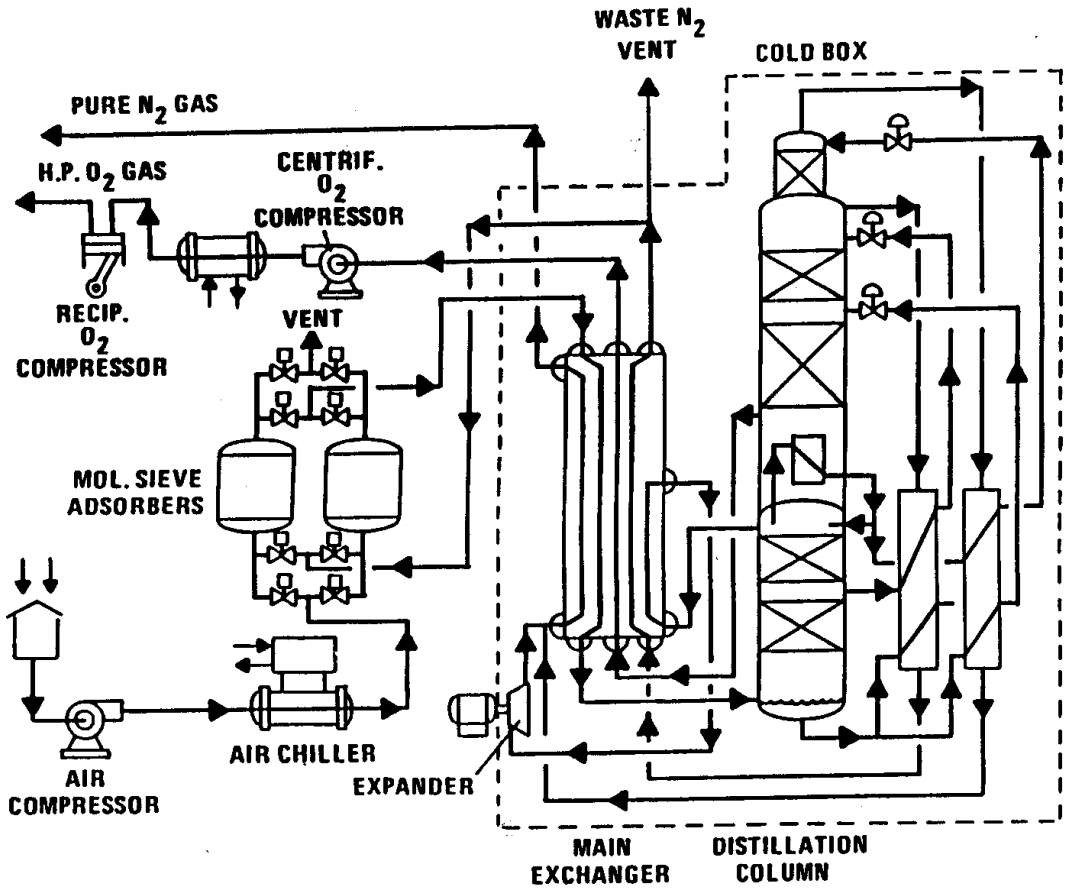

FIG. 1 - LOW PRESSURE CYCLE
WITH FRONT END ADSORBERS
AND OXYGEN COMPRESSION

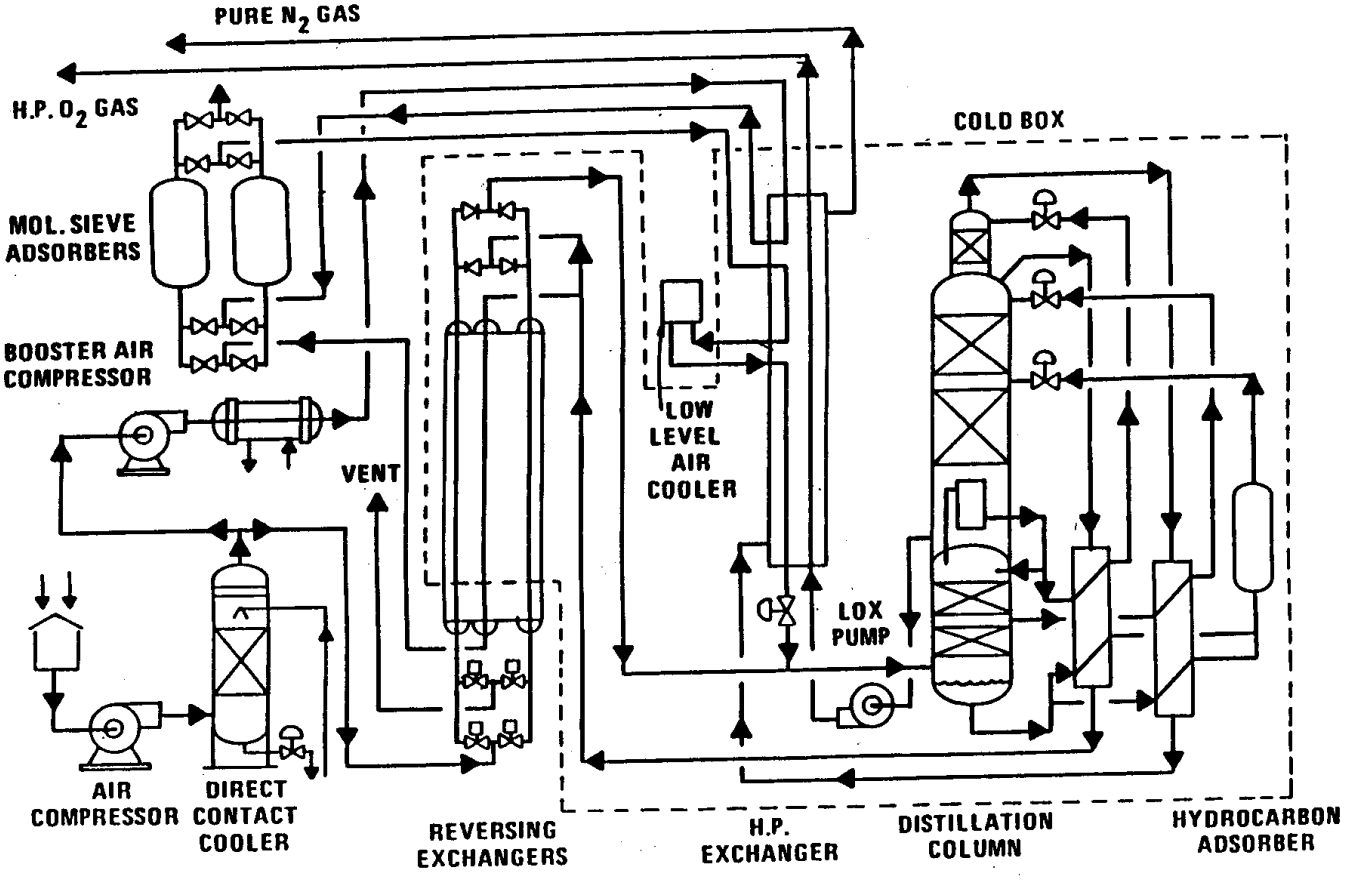

FIG. 2 – PUMPED LIQUID OXYGEN CYCLE
WITH SPLIT AIR

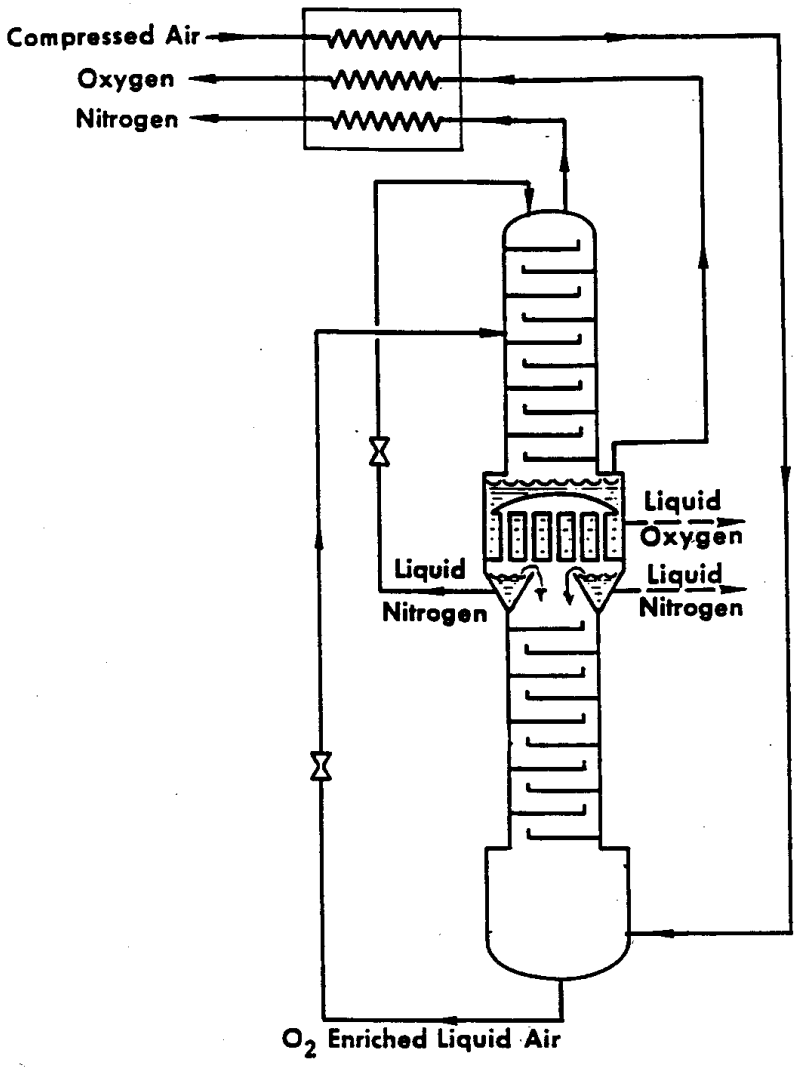

FIG. 3 – LINDE DOUBLE COLUMN AIR SEPARATION SYSTEM

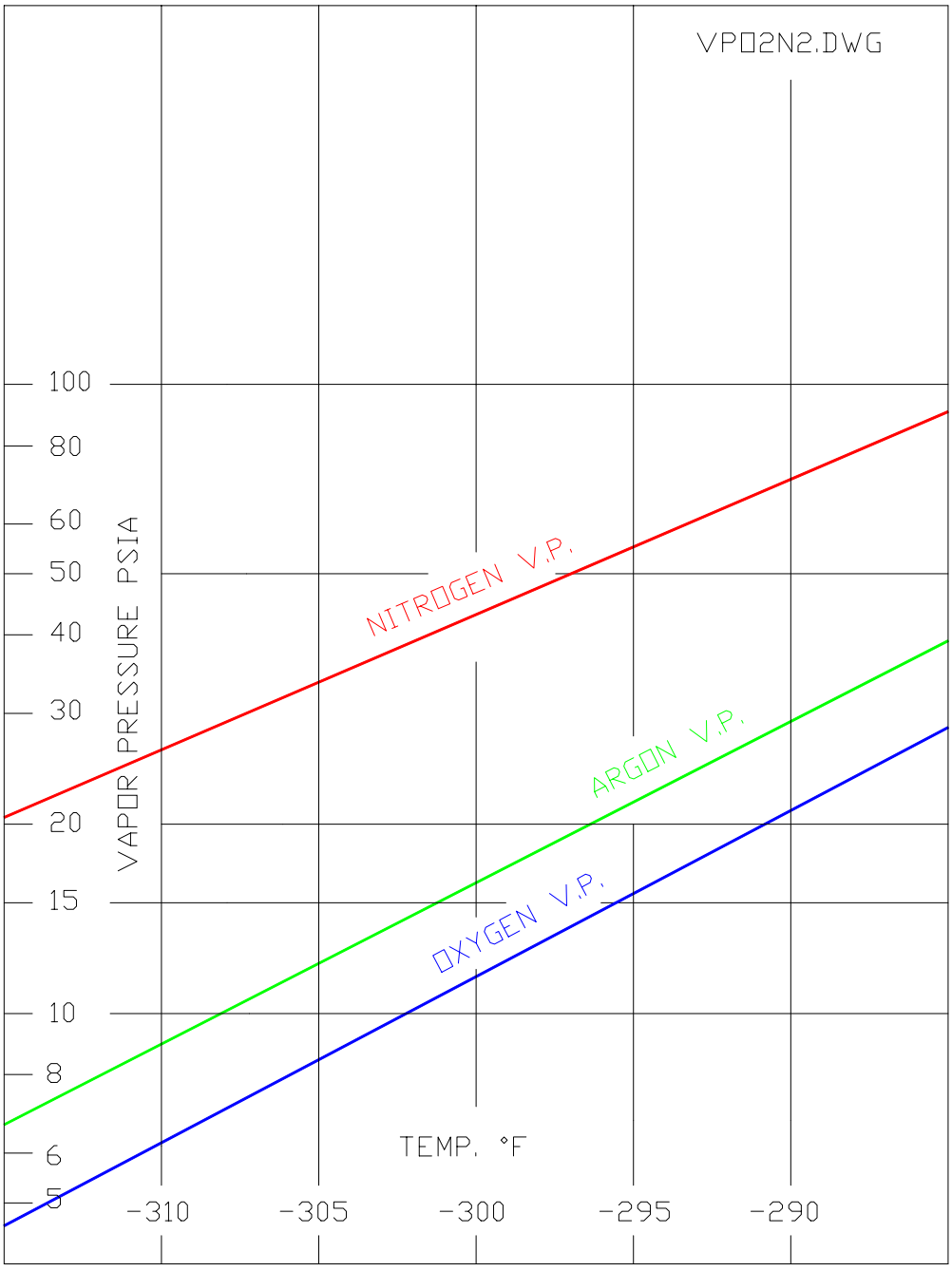

FIGURE 4 O2, N2, ARGON VAPOR PRESSURE

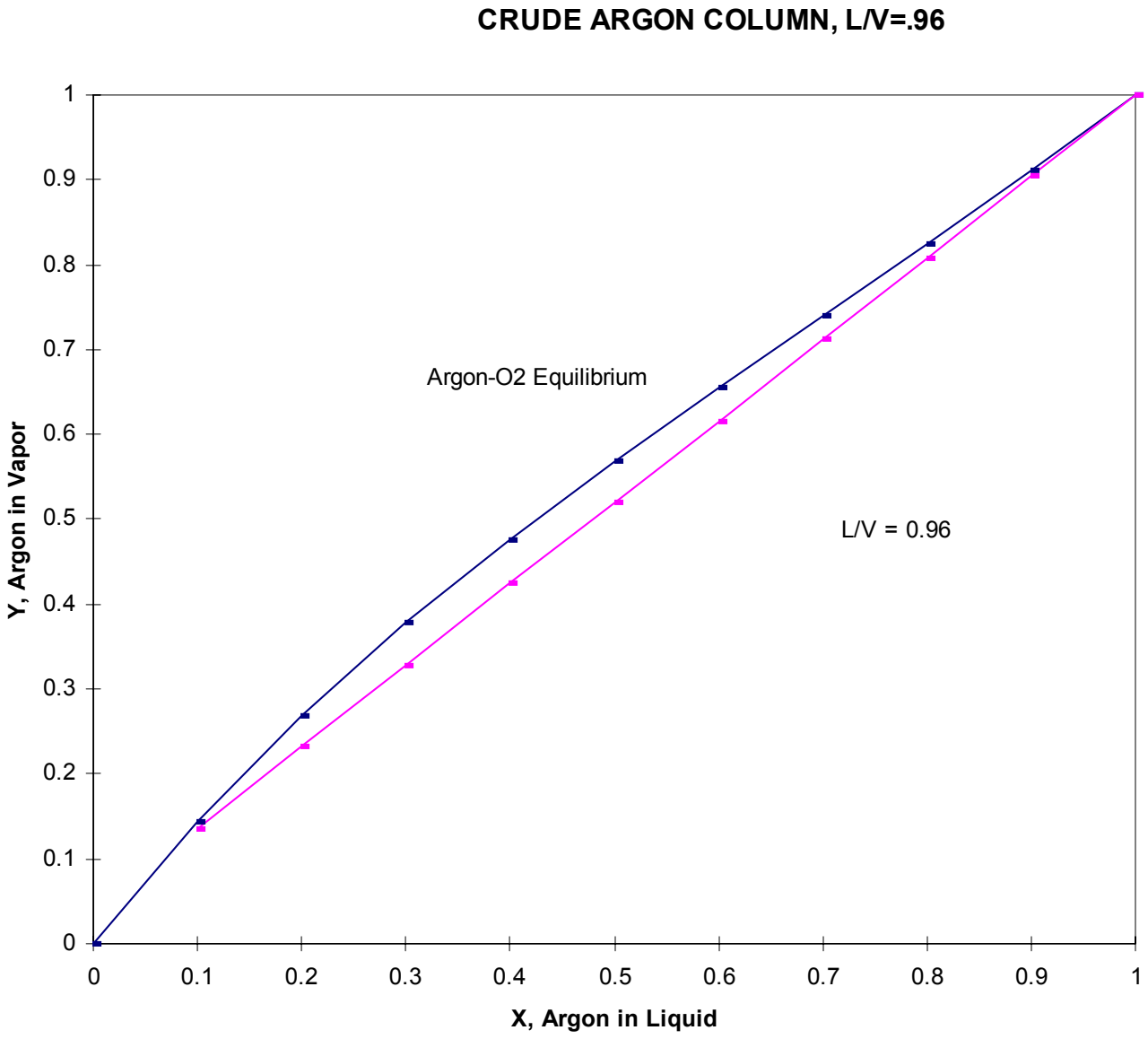

FIGURE 7 CRUDE ARGON X-Y DIAGRAM

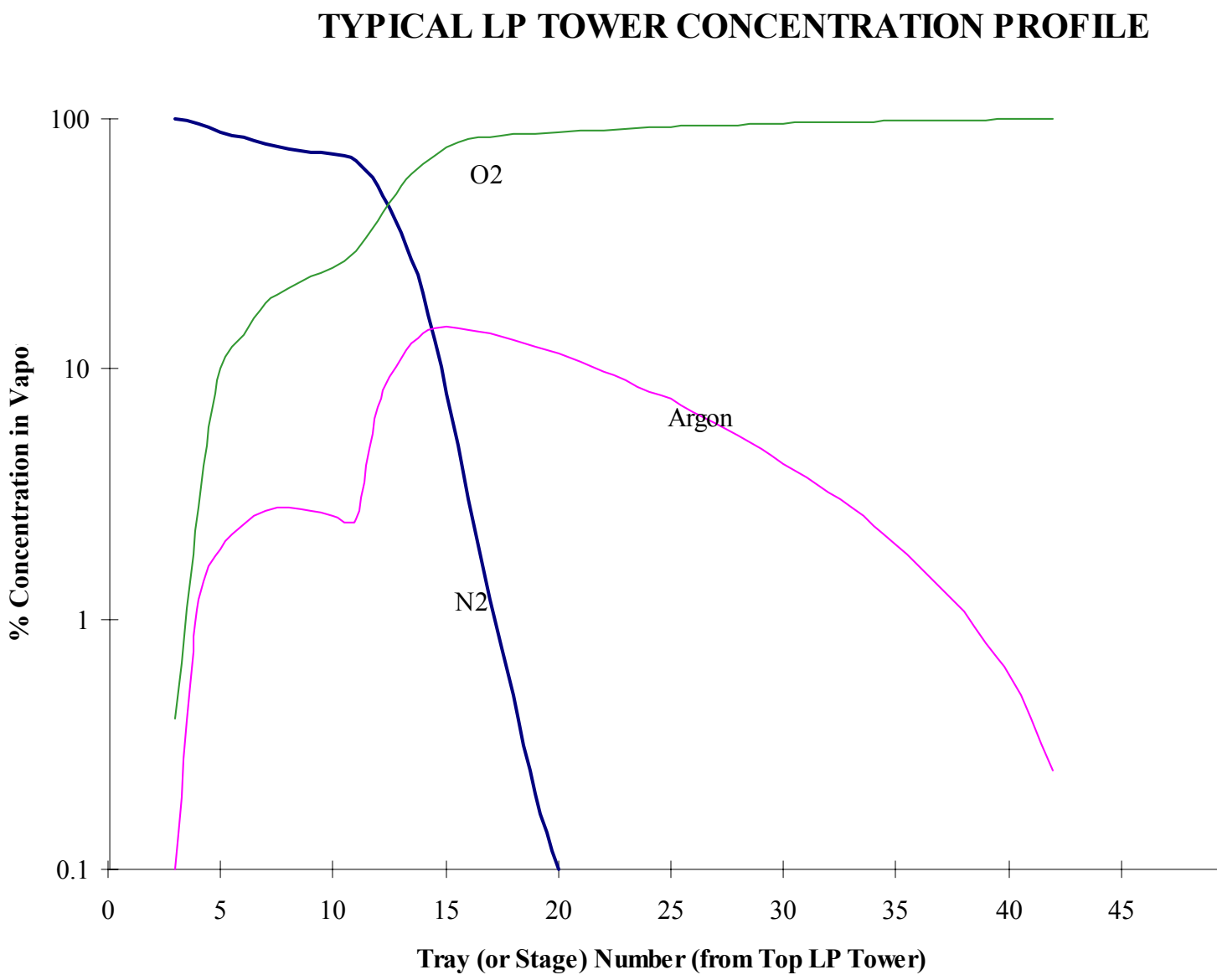

FIGURE 5 TYPICAL CONCENTRATION PROFILE IN LP TOWER

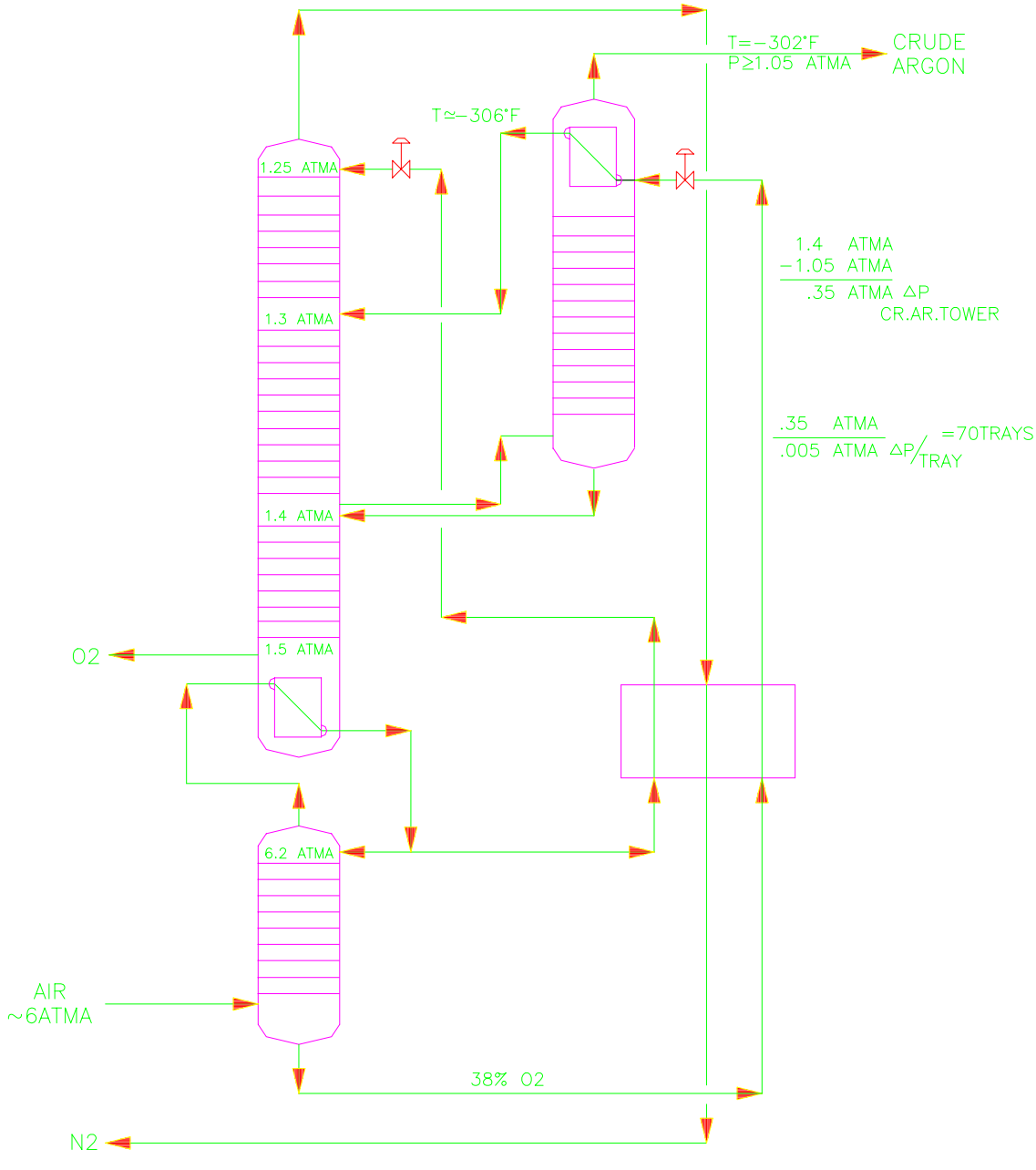

FIG.6 DOUBLE TOWER AIR SEPARATION WITH CRUDE ARGON TOWER

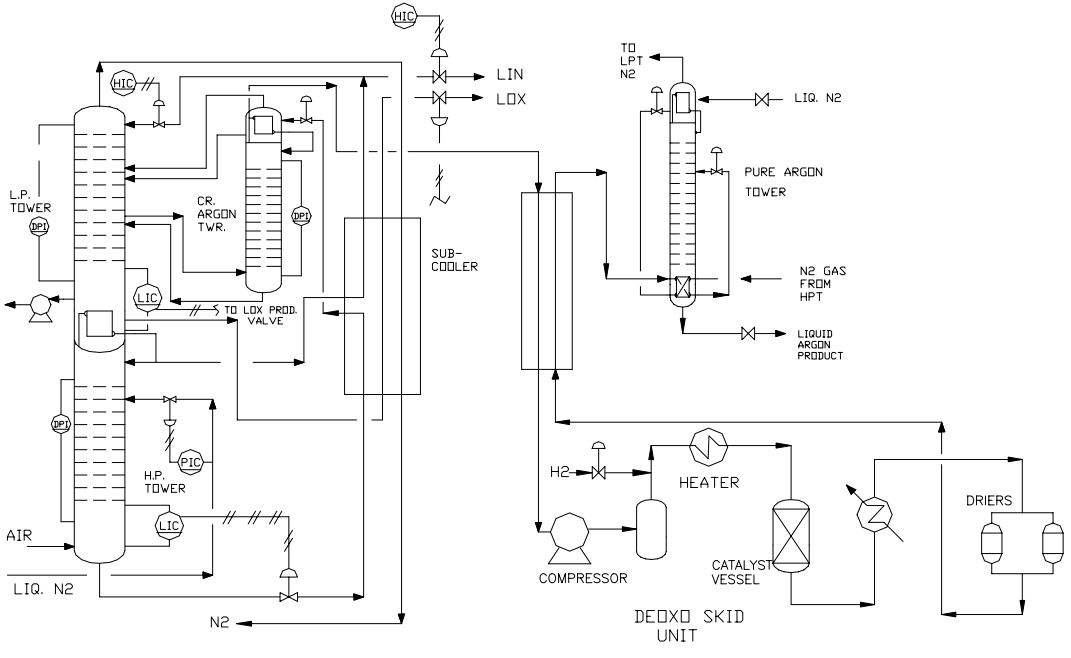

FIG. 8 TRADITIONAL ARGON SYSTEM FILE: 628-8.DWG

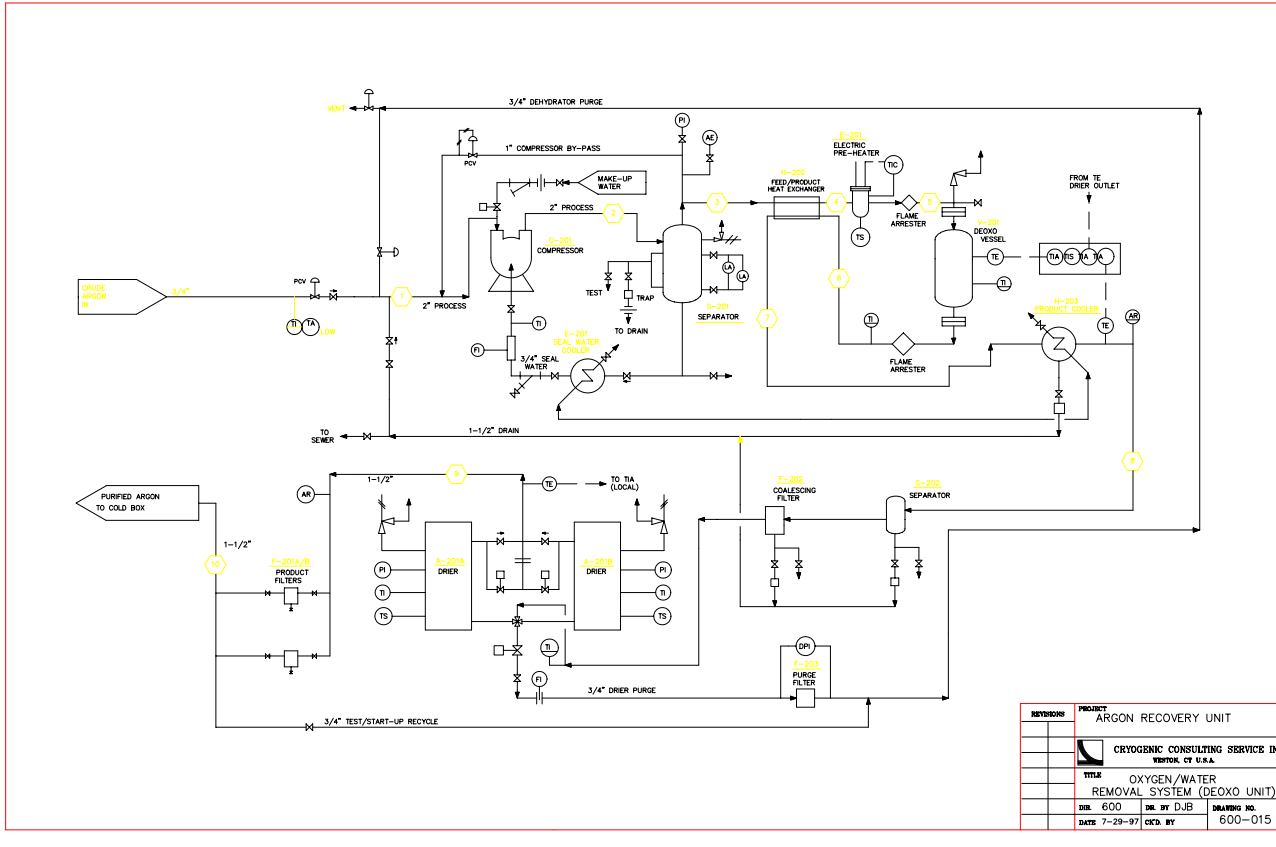

FIGURE 9, DEOXO SYSTEM FLOWSHEET

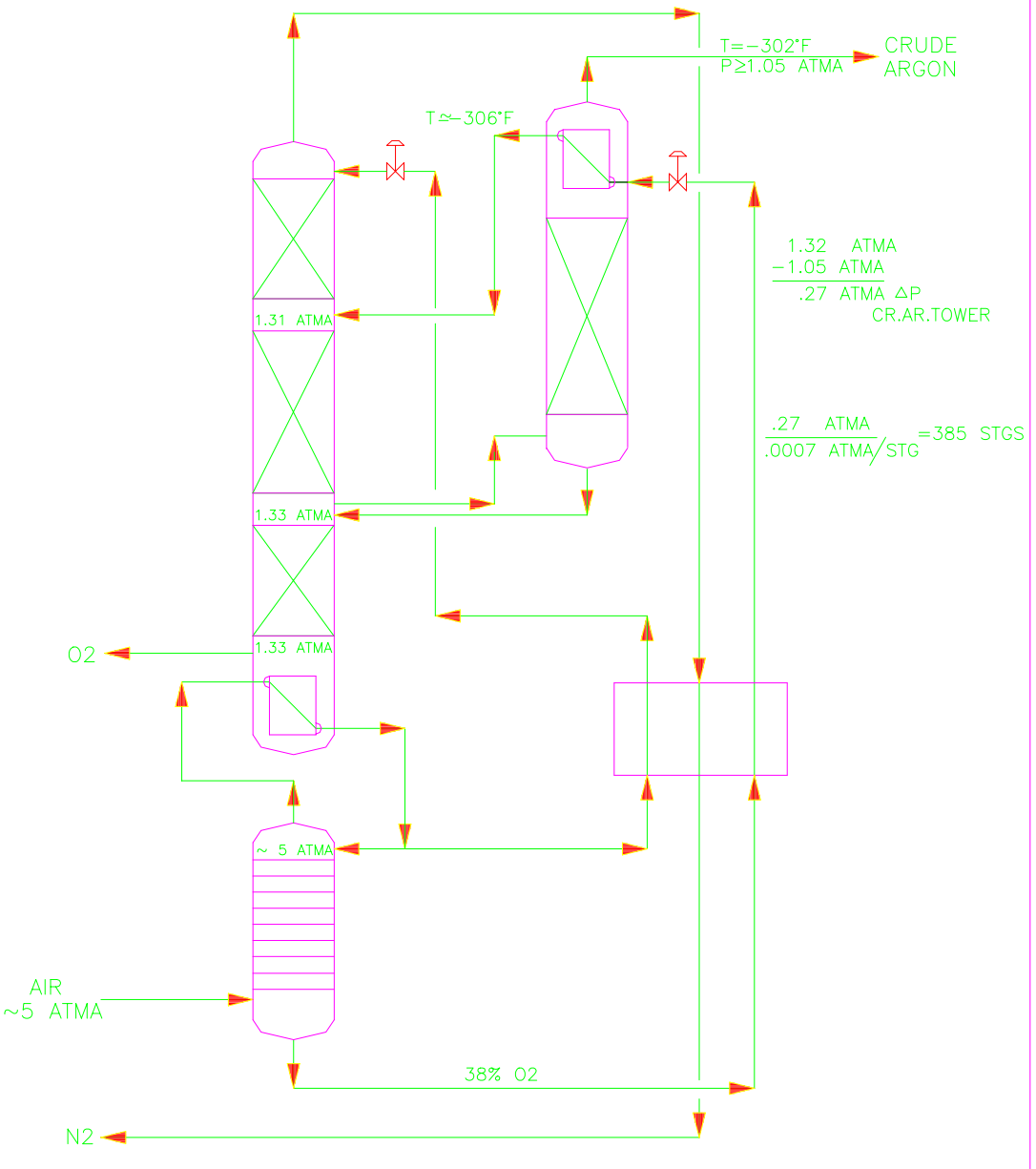

FIG.10 DOUBLE TOWER AIR SEPARATION WITH CRUDE ARGON TOWER

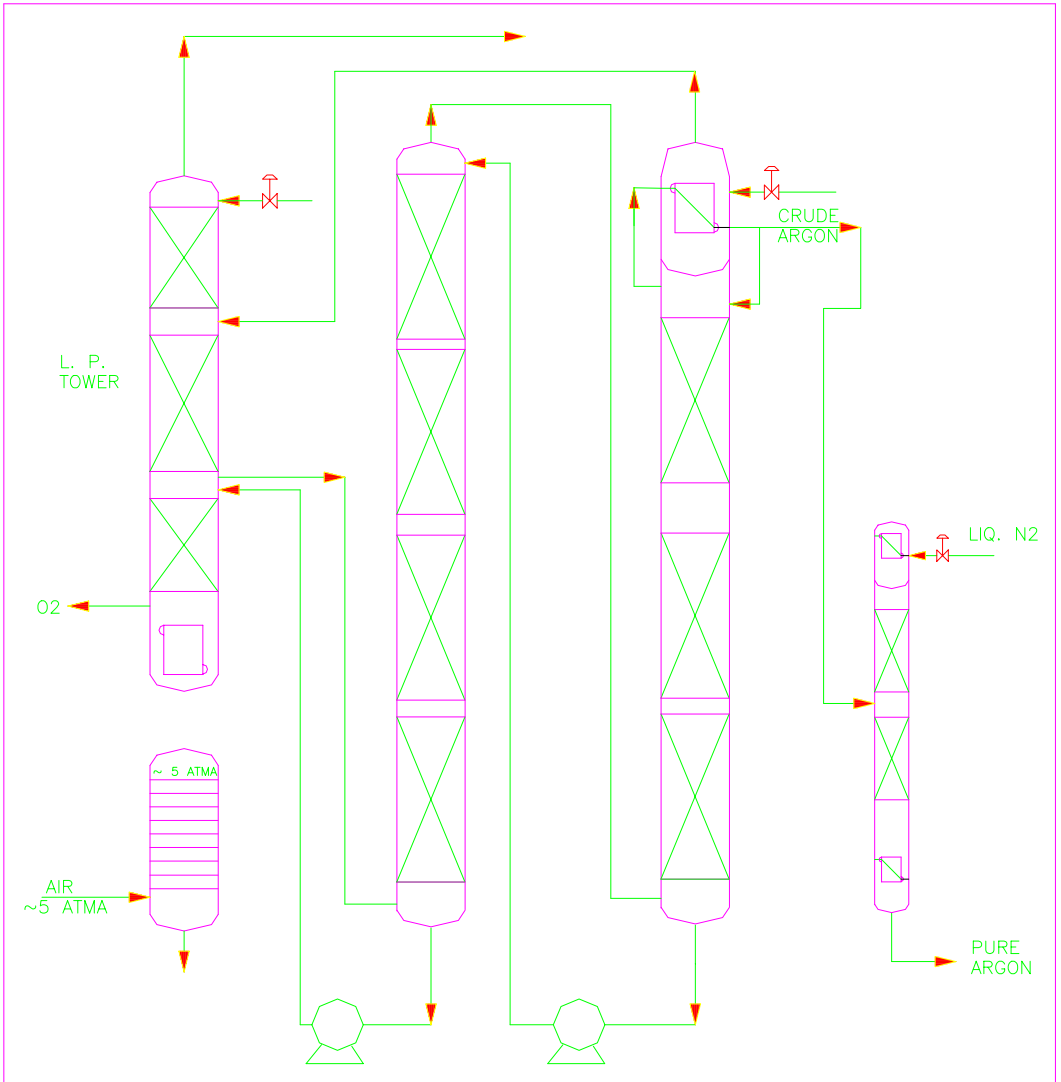

FIG.11 CRUDE ARGON TOWERS WITH PACKING, NO DEOXO SYSTEM