SAFETY ASPECTS of modern air separation plant cycles

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The conditions which have given rise to mishaps in air plants are of great interest to all who design, own, and operate these plants. Now that there have appeared in *CEP* (*1, 2*) two articles dealing with more or less specific approaches to the solution of the mishap problem, it now seems timely to correlate the various phases of the subject in a very general manner. This is particularly important so that those who are capable of contributing to the better understanding or to techniques aiding in the solutions of the technical problems involved, but who may not be directly connected with air separation plants in their modern form, may gain a better perspective of the problem.

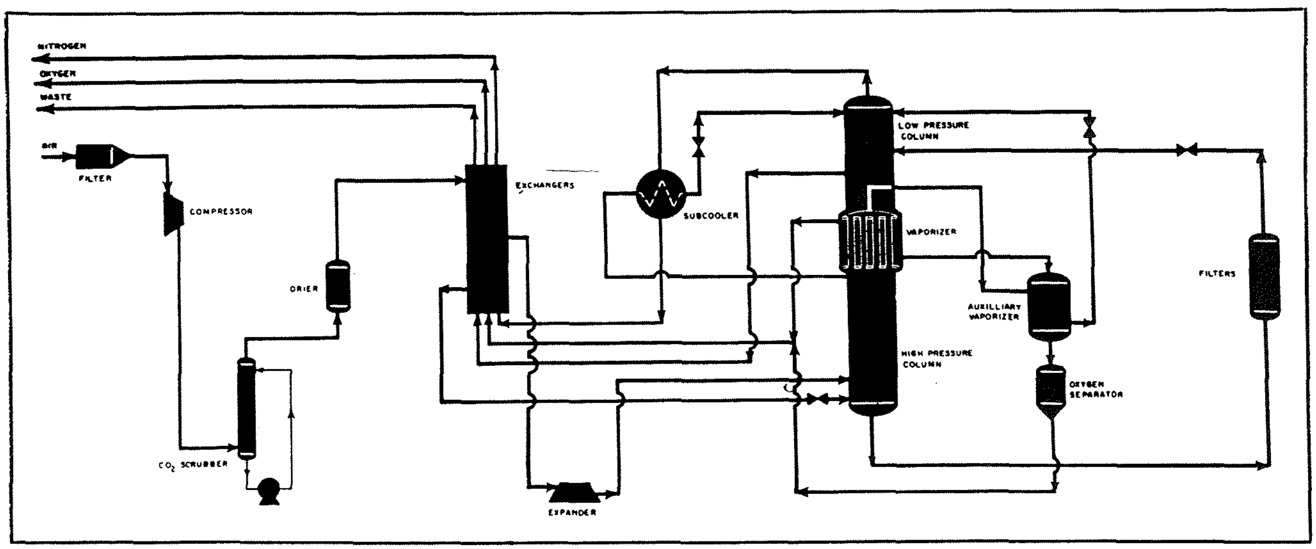
Standard Medium Pressure Cycle

First, consider the various cycles in use today. Figure 1 shows a standard medium pressure air separation plant using the best known classical cycle, one which has been used from the beginning of the industry. Briefly, its operation is as follows:

An air compressor supplies air at a pressure which may vary from 150 to 400 lb./sq. in. gauge; this compressed air passes through a standard caustic scrubbing unit which reduces the CO_2 content to 5 p.p.m. or less. The air then passes through a standard desiccation unit which reduces the water content to less than 1 p.p.m.; the purified air now enters the low temperature unit proper where it is first cooled down by heat exchange through standard shell and tube exchangers, liquefied, and finally separated into its components in a double fractionation column. The refrigeration is supplied by expanding a large portion of the air through either a reciprocating expansion engine or expansion turbine.

The above-described air separation unit is the most popular and the most extensively used air plant in the world because it can be built in a wide range of capacities and can produce simultaneously oxygen, nitrogen, and argon with very high purities and very high recoveries. No other air separation cycle can match the performance of this plant for all-around product recovery, product purity, and economy. Unfortunately, experience has shown that the medium pressure air separation cycle is the most susceptible to mishaps. This may be explained by the simple fact that contaminants may find themselves in the main condenser or vaporizer where a large quantity of liquid oxygen vaporizes slowly at almost atmospheric pressure. Unless proper precautions are taken both in design and operation, the contaminants

Fig. 1. Schematic flow diagram of a standard medium pressure air separation plant.



may build up beyond their solubility limit and trouble will ensue.

To overcome the problem arising from slow evaporation at nearly atmospheric pressure, designers have offered various modifications of the basic design of the main vaporizer so that purging could be effected, and have even added a second or auxiliary vaporizer which handles liquid oxygen withdrawn from the bottom of the main vaporizer. However, the auxiliary vaporizer does not stop explosions, but merely confines them in a different location. There is also indicated how various designers looked into different designs of vaporizers in order to effect a better heat exchange and vaporization and at the same time reduce the risk of high contaminant concentrations.

Results of tests of solubility of acetylene in liquid oxygen, plotted with the data of Fedorova and carried out by our own Research Laboratory, are shown in Figure 2. These curves indicate quite conclusively that designers of air plants should not accept a solubility limit for acetylene in liquid oxygen greater than 5 cc. per liter at the temperature level of liquid oxygen (−183° C.). Furthermore, the maximum solubility of acetylene in liquid nitrogen is 2.28 cc. per liter at the temperature level of liquid nitrogen. In checking our figures with those indicated by Fedorova (*3*), it is clear that Fedorova is even a little more conservative. In other words, designers should not, under any circumstances, assume figures in excess of those indicated above.

It is possible to show in graph form (Figure 3) what happens to the effective capacity for acetylene removal by silica gel filters if the latter are contaminated by foreign matter. For example, let us assume that the acetylene content of the air is 2 p.p.m. and that the silica gel filters have been designed to remove 97.5 per cent of the total acetylene entering the air plant during a given period of time. If the silica gel filter is contaminated by other foreign matter or improperly regenerated, then the effective capacity of the filter is sharply reduced. For instance, if the filter's effective capacity for the removal of acetylene is reduced to, say, 50 per cent, then the acetylene content permissible in the air must be reduced to 0.1 of 1 p.p.m. The above-described conditions hold true for a plant without an auxiliary vaporizer.

So far, reference has been made to a standard medium pressure air separation unit which has the advantage of supplying high purity products combined with high recoveries. As already stated, this is the most popular plant used in the production of high purity oxygen and also in the production of high purity nitrogen for most ammonia plants. On the other hand, because oxygen is vaporized at an atmospheric level in a large vaporizer, this air separation cycle is susceptible to an accumulation of contaminants in the main vaporizer and may give rise to trouble unless operated properly. This condition has been explained in detail (*1*).

Standard Low Pressure Cycle

Another air separation cycle that is used extensively in the metallurgical and petrochemical industries is the standard low pressure plant (Figure 4) which operates at an air pressure of 70 or 80 lb./sq.in. gauge and wherein regenerators or cold accumulators replace the shell and tube heat exchangers. This air cycle has certain definite advantages. It uses oil-free air blowers; the regenerators reduce the air temperature to almost its dew point, which means that the regenerators not only freeze out water and carbon dioxide, but also freeze out a great portion of the dangerous contaminants. This air cycle also offers oxygen at a very low cost because of lower horsepower. The regenerators themselves may be packed with either aluminum or other material, or may take the form of extended-surface aluminum exchangers with reversing passages. While this low pressure cycle is, from a design standpoint, considerably safer than the standard medium pressure cycle, it has the disadvantage of not being able to produce any appreciable quantity of very pure nitrogen plus another disadvantage of delivering oxygen at atmospheric pressure, which means the use of oxygen compressors with their inherent problems.

High Pressure Cycle

A few years ago, another air plant cycle was developed to overcome some of the problems of oxygen compression and at the same time deliver sufficient quantities of high purity nitrogen for use in ammonia synthesis. This plant is commonly known as the high pressure plant (Figure 5) wherein the compressors deliver the air at approximately 600 lb./sq.in. gauge. An external purification system is used for complete removal of carbon dioxide and water; the purified air enters the low temperature separation unit which is identical to that of any other air plant. However, the excess refrigeration due to the higher than normal pressure of the incoming air permits the oxygen to be withdrawn as a liquid away from the air unit proper and vaporized as well as compressed in a high pressure liquid oxygen pump; the vaporized oxygen then re-

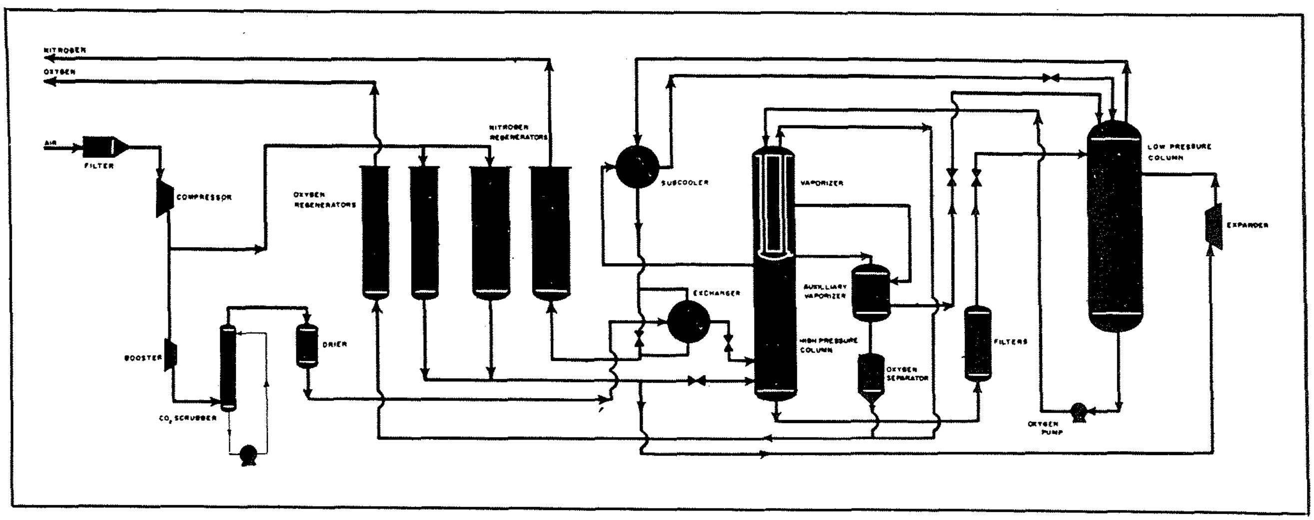


Fig. 4. Schematic flow diagram of a standard low pressure air separation plant.

enters the low temperature unit through a series of exchangers for cold recovery. This type of cycle has the advantage of using small inexpensive and trouble-free liquid oxygen pumps for oxygen compression and from a safety standpoint the oxygen is always withdrawn as a liquid from the main vaporizer which in reality acts only as a heat exchanger. On the other hand, the high pressure cycle has the disadvantage of requiring reciprocating compressors with their problems of lubrication and contamination and the other disadvantage of having a high horsepower consumption per ton of oxygen.

Double Cycle

More recently, in order to arrive at a compromise between a trouble-free plant and an efficient plant, a double cycle (Figure 6) unit has been built.

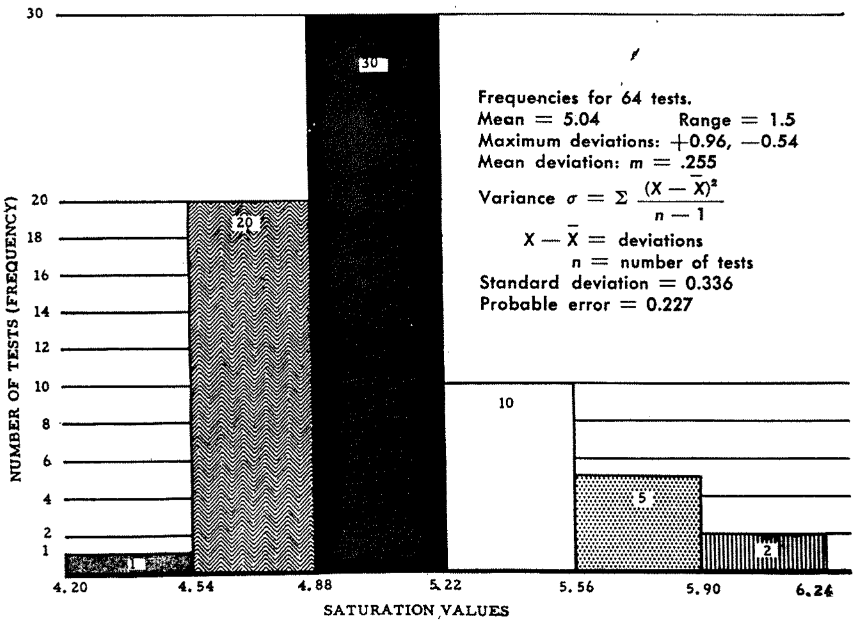


Fig. 7. Frequency distribution curve for solubility of various hydrocarbons in oxygen.

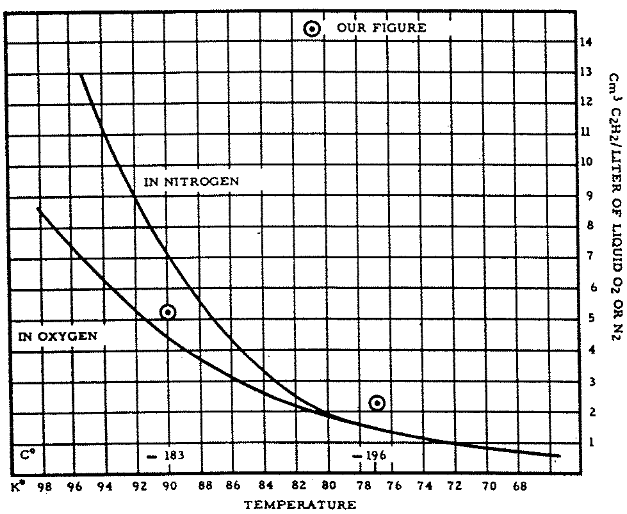


Fig. 2. Solubility of acetylene in liquid oxygen and nitrogen.

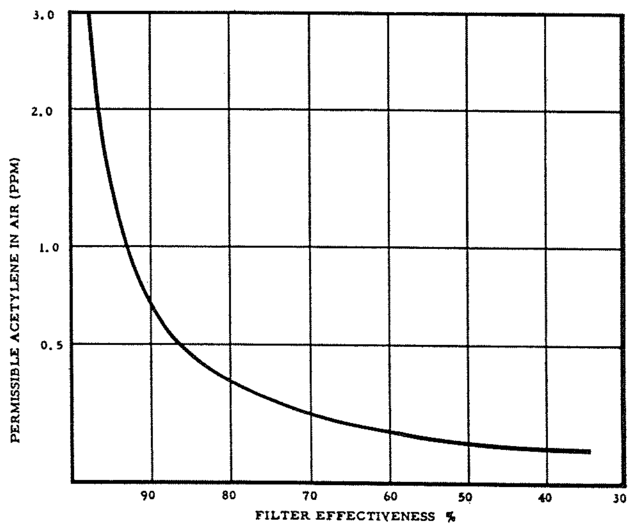


Fig. 3. Acetylene removal capacity of silica gel filters contaminated with foreign matter.

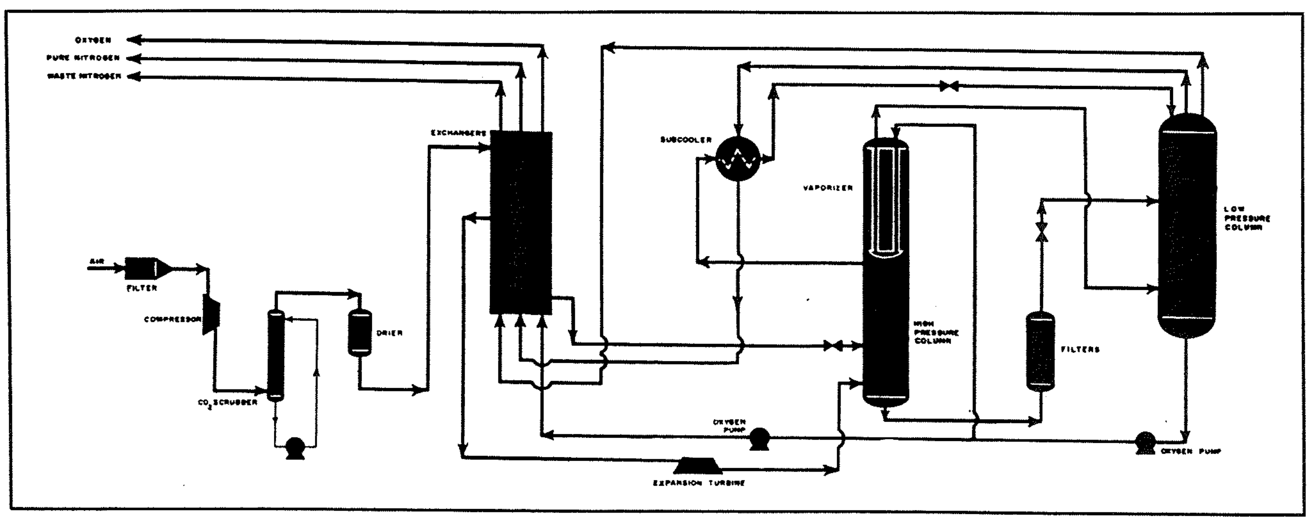


Fig. 5. Schematic flow diagram of a high pressure air separation plant.

All the air is compressed in an oil-free blower to 70 or 80 lb./sq.in. gauge. The greatest portion of the air enters standard regenerators or reversing extended surface exchangers which clean the air of contaminants as well as CO_2 and water. The balance of the air is boosted in an auxiliary compressor to a higher pressure; after pre-purification for CO_2 and water removal, the auxiliary air stream enters standard shell and tube heat exchangers. This double cycle air plant may be used in conjunction with liquid oxygen pumps for oxygen compression and at the same time produces an appreciable quantity of high purity nitrogen which can be used directly for ammonia synthesis. The advantages of this cycle are: a large portion of the air is comparatively free from contaminants; the oxygen is withdrawn as a liquid from the main vaporizer; oxygen compression is obtained from trouble-free liquid oxygen pumps. Concerning horsepower expenditure, the energy consumed by this cycle is only slightly higher than that consumed by a standard low pressure plant combined with gaseous oxygen compressors. Furthermore, even the other disadvantage of permitting the smaller portion of contaminated air to enter the unit may be offset by an inexpensive purification system in the auxiliary cycle.

Contaminants

Concerning contaminants, this discussion has so far been concentrated on acetylene, which is definitely known to be troublesome and with which we are familiar enough to offer some solutions. However, during the past few years, we have had definite case histories on plant mishaps wherein no acetylene was found either before or after the explosion. Furthermore, analyses carried out after some of the mishaps showed considerable traces of oxides of nitrogen and hydrocarbons other than acetylene. In other words, we cannot assume that acetylene is the only troublesome contaminant. We must investigate the roles of other contaminants and the conditions under which these contaminants will prove troublesome.

Just what final solution will render all air separation units absolutely trouble-free is still a question mark.

1. Very large silica gel filters can be designed, to be operated with daily switching. This may prove effective. However, it is still not absolutely foolproof and it is certainly not economical from an energy standpoint.
2. A liquid air reflux to scrub out incoming air before the latter enters the low temperature section proper may be used. This has been tried out; but it is not economical because it entails a relatively high purge loss. This system may be satisfactory in a plant producing high purity oxygen sold at so much per cubic foot; but it is not economical for a plant producing oxygen which must be assessed at the lowest possible cost per ton.
3. An air pre-filter system operating at low temperatures may be used. This system is effective, but has a relatively high investment cost and may not prove economical for plants producing over 100 tons per day of oxygen.
4. One may also consider the introduction of inhibitors. If certain substances have the capacity to lower the explosive limits of hydrocarbons, we may well introduce other substances which will serve as inhibitors. However, this idea, though reasonable, may prove questionable.
5. The best solution may ultimately prove to be the catalytic oxidation of the air prior to the latter's entry into the low temperature unit. However, this system requires more investigation regarding the type of catalyst, catalyst life, and overall costs.

What About the Future?

Concerning a future program or plan of action, the following recommendations are proposed:

1. A rapid and accurate method of analysis of air for:
   a. total hydrocarbons;
   b. concentration of individual contaminants.
2. A rapid and accurate method of analyzing for various contaminants within certain sections of the air separation unit.
3. A more accurate examination of the solubility limits of various hydrocarbons in liquid oxygen. (See frequency distribution curve, Figure 7.)
4. A more accurate determination of vapor pressure of various hydrocarbons.
5. A closer study of the reactions of hydrocarbons at low temperature levels to determine their explosive limits and conditions for explosions.
6. A more thorough study of various adsorbents for contaminant removal capacity and regeneration of adsorbing material.
7. A better design of air separation units to combine maximum safety with better economy.

The major designers of air separation plants already have research programs following in a general manner the above recommendations. To fulfill a program of this type, however, requires considerable time and money. To be of greater service to the industry, all design groups should sit together periodically to consider a joint program so that the above recommendations may be brought to a successful conclusion quickly, economically, and for the benefit of all. The results of such a program could easily be made available through the program and publications services of the A.I.Ch.E. So far as users are concerned, we ask only for their co-operation in supplying designers with field data from plant operations. This information is necessary and must be given freely if designers are expected to fulfill the requirements of safe design.

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3. Fedorova, M. F., *J. Phys. Chem. (U.S.S.R.)*, **14**, 422-6 (1940).

Fig. 6. Schematic flow diagram of the double cycle air separation plant.