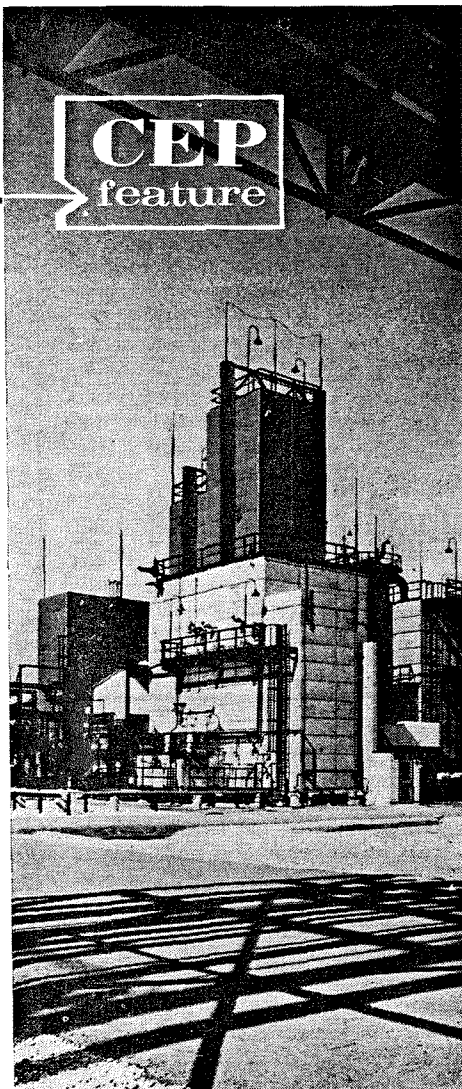


The industry speaks on . . .

Safely operating that low temperature plant

Pooling of individual knowledge is the key to future progress in safely operating low temperature plants. With this in mind, engineers and plant personnel sought the answers to advance the technology for the benefit of the whole industry at the annual "Safety in air and ammonia plants" Question and Answer session held at the A.I.Ch.E.'s national meeting in Tulsa. Of particular concern was the hydrocarbon contamination problem, techniques for removal of trace impurities, and methods of analysis. Here is another candid report of the discussions of operating personnel responsible for safely operating the low temperature plants.



American Air Liquide's air separation unit producing 400 tons/day of oxygen for the Rohm & Haas plant at Deer Park, Texas.

Impurity control in air separation plants

Control hazardous hydrocarbon levels by using adsorption filters and catalytic oxidation units.

DESIGNERS OF AIR SEPARATION UNITS can not completely predict and eliminate the hazards of dangerous contaminants by process separation alone. They still lack sufficient data on the effects of all the presumed harmful constituents, whether the constituents are harmful singly or in combination, on the conditions necessary for reaction, and finally the cause of ignition. Designers have relied on methods external to the process separation such as adsorption filters and catalytic

oxidation units which, unfortunately, are still in the experimental stage.

Problems involving many unknown and variable factors can not be solved immediately and completely by simple deduction. Laboratory data must be combined with sufficient field observations to reduce the unknown factors so that safe design can be achieved. The operating experience of American Air Liquide, Inc., while not complete by any means, may serve as an addition to the general

knowledge in this field.

A schematic of the air separation plant showing the location of the adsorbers, the catalytic oxidation unit, and the main sampling points for chemical analysis is shown in Figure 1.

Rich-liquid adsorbers

The use of silica gel adsorbers for rich liquid to remove C_2H_2 has been

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American Air Liquide, Inc.
AND J. T. HUGILL*
Air Reduction Sales Co.

Table 1. Desorption tests showing time measured from the injection of a small amount of impurity into the carrier gas flow ahead of a given gas purification column to the signal given by the first trace of impurity coming out of the column.

IMPURITY	FLUSHING GAS	TIME PERIOD, SEC.		
		194 °F	302 °F	338 °F
C ₂ H ₂	N ₂	606	227	—
	Air	639	211	149
C ₂ H ₄	N ₂	370	156	—
	Air	312	—	122
C ₂ H ₆	N ₂	1491	326	—
C ₃ H ₈	N ₂	ND	809	—
C ₄ H ₁₀	N ₂	5680	753	—
	Air	4200	674	405
C ₂ H ₆	N ₂	ND	7082	—
N ₂ O	N ₂	247	148	—
NO+NO ₂	N ₂	183	141	—

ND means no desorption.

standard practice in the industry for the past twenty years. There is no question that this safety feature has markedly reduced the number of accidents in air separation units due to high concentrations of C₂H₂ and possibly other hydrocarbons. Recent experience has demonstrated that the use of rich-liquid silica gel adsorbers alone does not provide enough protection, especially when the unit is installed in industrialized areas where the air contamination would normally be at a continuous high level.

Rich-liquid adsorbers have always been designed for the removal of trace amounts (air inlet content of less than 1 ppm) of C₂H₂ only. For this specific purpose the adsorbers, as designed, have done an adequate job. For many years, however, designers were unaware of the influence of other contaminants on the adsorption capacity of these filters. The design of the adsorbers in many cases was not based on any quantitative formula, but followed a "rule of thumb" based on analytical procedures which are now recognized as completely inadequate for anything but C₂H₂. Only with the advent of chromatography and other analytical methods have we had a more complete knowledge of what goes on in rich-liquid adsorbers, Table 1 and Figure 2.

Designers have now accepted the fact that rich-liquid filters should be designed only for C₂H₂ removal and the capacity of the filter should be sufficient to handle a steady rate of 1 ppm (by volume) of C₂H₂ in the air to be treated. If the concentration is increased beyond 1 ppm, or if other harmful hydrocarbons are present, then any attempt to control all the contaminants, including C₂H₂ by

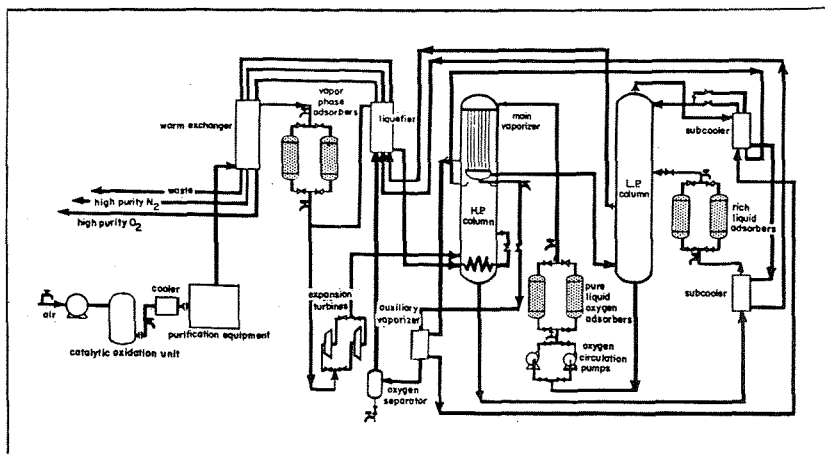


Figure 1. Flow sheet of medium air separation unit showing location of adsorbers.

rich-liquid adsorbers alone makes the design of the adsorbers cumbersome, expensive, and imposes a serious drain on refrigeration.

Vapor-phase adsorbers

To improve the removal of dangerous impurities (particularly oxides of nitrogen and hydrocarbons) in the air stream, additional adsorbers were considered for the initial vapor-phase section of the plant. Vapor-phase adsorbers have been installed in six large air separation plants which have been in operation from three to five years. The main conclusion derived from these applications is that vapor-phase adsorbers have been highly effective in stopping oxides of nitrogen and trace hydrocarbons other than CH₄ and C₂H₂. Three of the applications have been in refinery areas and treat air which is heavily contaminated.

In view of the many unknown fac-

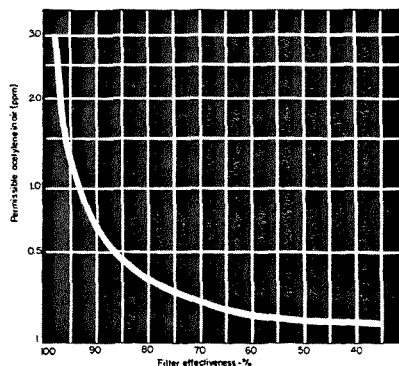


Figure 2. Permissible C₂H₂ in air in relation to filter effectiveness when vaporizer contains 5 cc of C₂H₂/liter of liquid oxygen. This shows the reduction in capacity of rich-liquid filters due to contaminants other than C₂H₂. Air separation unit has no auxiliary vaporizer.

tors, all of the units were designed with ample adsorption capacity. In one case where the contamination is very high, the adsorbers are switched every ten days. In other areas the adsorbers are switched anywhere from two to four weeks, depending on prevailing conditions.

Figure 3 demonstrates the effectiveness of vapor-phase adsorbers in stopping oxides of nitrogen. A similar graph is obtainable for the removal of trace hydrocarbons.

The reactivation procedure for these filters is similar to that for rich-liquid filters. In fact, it is simpler because no liquid is involved and the reactivation temperatures are generally lower. The desorbing medium can be either N₂ or air.

Correlation and evaluation of the results obtained from the first applications was difficult because of problems in making quick, positive, and precise analysis of the incoming and outgoing trace contaminants and the ever changing atmospheric conditions. All existing adsorbers, therefore, had to be designed with a high safety factor, and the switching frequency had to be determined in the field on a trial basis. With more precise analytical instruments being developed, it is becoming possible to calculate the optimum size of the vapor-phase adsorbers with a fair degree of accuracy.

An important advantage of the vapor-phase adsorbers is that they can be installed in medium or high pressure air separation plants using oil lubricated reciprocating compressors. This should be of special interest to the ammonia industry which is the principal user of this type of plant for the production of high purity N₂.

Some interesting data on various forms of vapor-phase adsorbers has

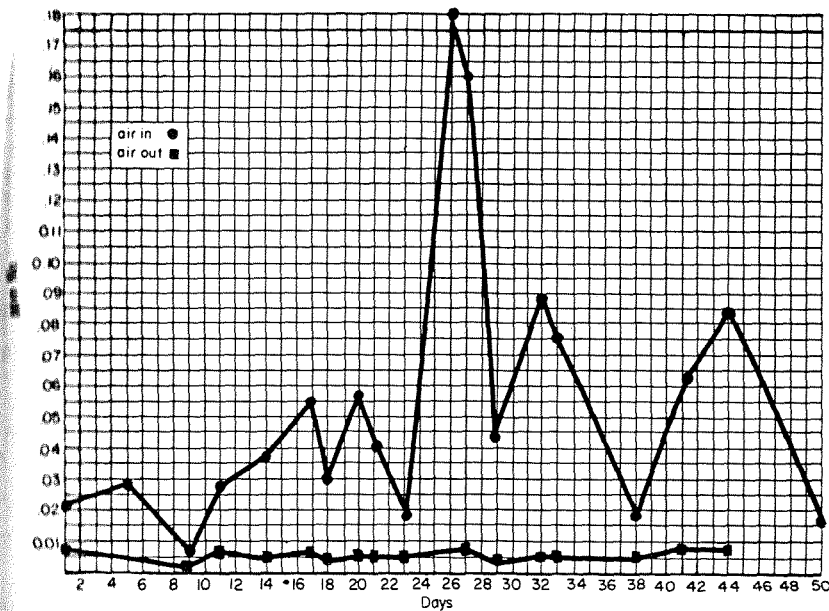


Figure 3. Effectiveness of vapor-phase adsorbers in removing oxides of nitrogen.

been published (1), but more information is needed. In general, laboratory information is confirmed by plant experience for the silica gel adsorbers.

Pure liquid oxygen adsorbers

On an experimental basis, low temperature adsorbers have been placed on the pure liquid O_2 stream entering the main vaporizer. This application is possible only in large plants employing a specially designed film-type vaporizer, wherein the liquid O_2 product is recirculated in the vaporizer by a low pressure centrifugal pump. Needless to say, the adsorber is placed at the discharge end of the pump. In this manner any small traces of contaminants which passed through other safety units are pre-

vented from entering the main vaporizer.

Figure 4 shows the effectiveness of this type of adsorber. While initial observations from two plants show satisfactory results, it is felt that because of the lack of precise analytical instruments it is too early to draw any final conclusions.

Catalytic oxidation of air

In areas where heavy concentrations of C_2H_2 in the atmospheric air could be expected (much greater than 1 ppm), some means had to be found to deal with this problem other than the vapor-phase and liquid-phase silica gel adsorbers. Considerable investigations were undertaken to develop a method, which could be placed

on the air stream before or after the compressors, which would completely eliminate or reduce to manageable proportions the concentrations of impurities before the low temperature separation unit proper.

It was known that MnO_2 under certain temperature conditions promoted the air oxidation of relatively low concentrations of hydrocarbons. One plant erected in Europe had a special unit to remove heavy concentrations of C_2H_2 from the air using a large charge of crude MnO_2 . This unit, although very expensive and requiring relatively high temperatures, proved very satisfactory in reducing C_2H_2 from dangerously high concentrations down to less than 0.1 ppm.

On the suggestion that MnO_2 was the main ingredient of Hopcalite, the Mine Safety Appliance Co. was approached. They agreed that the problem might be solved with a suitable promoted catalyst of the Hopcalite type. Tests showed that with moderately elevated temperatures such as would occur immediately after average air compression, the catalyst would effectively remove all the C_2H_2 and several other hydrocarbons in the expected concentrations. The final design, complete with necessary catalyst cartridges, was not too expensive. The results, providing the correct temperature for operation could be obtained without serious effects on the turbo compressor, merited proceeding with the design and installation of the equipment.

One serious limitation with this particular catalyst is that the air must be oil free. This limits the application to air units where the compression is by a centrifugal compressor or where a relatively expensive oil removal sys-

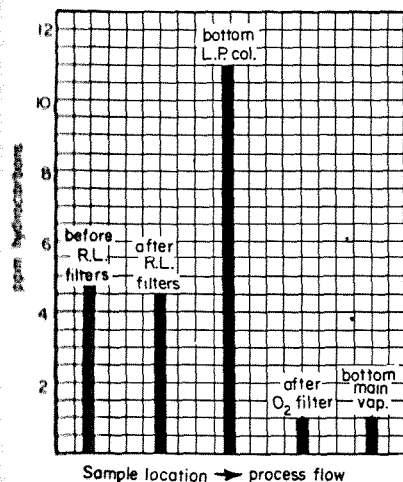


Figure 4. Effect on hydrocarbon removal of silica gel adsorber on pure liquid O_2 stream.

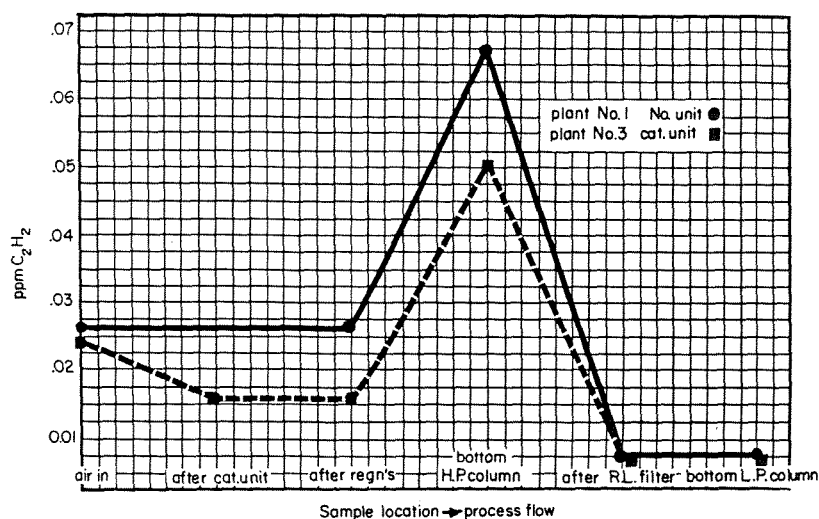


Figure 5. The effect of the catalytic oxidation on C_2H_2 removal from process.

tem is installed. There is also the question of the necessary temperature level (minimum 300°F) being obtained with the reciprocating compressors. The air must be heated if this fails.

These units have been installed in three plants to date. While detailed information is lacking, a careful study of one unit indicates that the oxidation equipment is performing in the specified manner. Accurate data are difficult to obtain because of the unavailability, until just recently, of a satisfactory and accurate method of analyzing low concentrations (less than 0.05 ppm) of C_2H_2 and other hydrocarbons, particularly in the presence of H_2O and CO_2 . Available data, Figure 5, shows that the expected high concentrations of C_2H_2 have not materialized, thus it is difficult to prove categorically that the unit works exactly as expected.

Instrumentation trends

Tremendous strides have been made by the instrument manufacturers during the past year or two for making quick and precise analyses of very small trace amounts of contaminants. We feel confident that by close cooperation between the two industries



Kerry



Hugill

F. G. Kerry has been in charge of the American Air Liquide Co. in New York and Sales Mgr. of the Eng. and Const. Div. since 1949. Has engineering degree from McGill Univ. and Graduate Degree from Inst. of Gas Research of Paris, France. He is also a member of A.I.-Ch.E., CGA, and International Acetylene Assoc.

J. T. Hugill, presently Manager of Tonnage Products Sales of Air Reduction Sales Co., was formerly Manager Field Operations of Air Liquide, Montreal. Graduated from R.M.C., has M.Sc. in Ch.E. from Alberta, and Ph.D. from McGill (1946).

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we may soon be in a position to control completely all of the known dangerous contaminants.

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Questions and answers

J. LAWRENCE—U. S. Industrial Chemical Co., Tuscola, Ill.: Many air plants have an argon system where you feed liquid air. Has any thought been given to that small amount of air, and whether it can pile up in the argon condenser where it feeds? Should this be a problem? We run a continuous purge from our condenser.

F. G. KERRY: Are you referring to the stream that enters the sidarm attachment?

LAWRENCE—U. S. I.: The stream of liquid air that by-passes the rich-liquid filter and enters the argon system, the argon boiler coil, the condenser, etc.

KERRY: Actually, that stream is very small, isn't it?

LAWRENCE—U. S. I.: Yes.

KERRY: I do not think we have, but maybe other people have given special attention to it.

W. R. ROCKWOOD—Union Carbide Chemicals Co., Brownsville, Texas: You mentioned the effectiveness of the vapor phase with Sovabead as highly effective for the oxides of nitrogen and traces of hydrocarbons, except CH_4 and C_2H_2 .

KERRY: In other words, we do not design them for C_2H_2 removal. We feel that if we can remove most of the contaminants other than C_2H_2 , then our rich-liquid filters can handle C_2H_2 . We try to separate the C_2H_2 from the other contaminants. Obviously, some C_2H_2 may be picked up in the vapor-phase filters, but we are not at all interested in that. What we want to do is to make sure that only C_2H_2 will enter the rich-liquid filters. Then we know how to design the rich-liquid filters in order to handle it.

ROCKWOOD—Union Carbide Chemicals: You said N_2 is usually used in desorbing. Could you expand upon that and compare the use of N_2 with air for desorption?

KERRY: We have tried both and prefer N_2 if available. Even if we design an air plant for N_2 scrubbing, we generally over-design so as to have enough excess N_2 for desorption purposes. If it is impossible, then we can use air for the vapor-phase filters.

R. F. BOLLEN—Dow Chemical of Canada, Sarnia, Ont.: We have a vapor-phase O_2 plant, and I think we

were one of the plants referred to that has a catalytic oxidation unit in service. It went into operation in July. So far sufficient data to make a full report have not been compiled. However, I do have some comments.

The unit operated quite well on start-up immediately after getting into service, and our hydrocarbon level was quite low. Shortly after that, the wind changed to the direction from which we normally pick up high hydrocarbons. Our hydrocarbon analyzer indicated an increase to about 800 ppm hydrocarbon. We were disappointed with our catalytic filter, until we realized that the hydrocarbons that we were picking up were mostly CH_4 , C_2H_6 , and C_3H_8 . In order to get these particular hydrocarbons out with any oxidation unit, you have to have a high temperature. Our unit was designed for 400°F. At that level we can get most of the unsaturates and about 80% of the propane, but we can not touch the CH_4 or C_2H_6 . Thus, the unit was operating according to design. We do not feel that we have too much to worry about with these higher unsaturated hydrocarbons, because, according to the literature, hazardous levels exist around concentrations of 50,000 ppm.

We took the unit out of the system to see whether it was doing anything at all for us. The result was that we picked up a little C_2H_2 for the first time since operating the unit.

KERRY: Some time ago, when we were first experimenting with the catalytic oxidation filter, we tried its use on quite a few hydrocarbons in our lab. We found that at normal operating temperatures at the discharge end of a compressor (300°-350°F) C_2H_2 could be removed very effectively. For other contaminants, we had to go to higher temperatures. For example, to remove CH_4 or C_2H_6 we had to go to 500 and 550°C to get either 100% or 90% removal. The effectiveness of removal changes with the space velocity of the gas going through the catalyst. Fortunately, we are not too concerned with CH_4 because it boils off quickly. Thus, catalytic oxidation is normally recommended only for C_2H_2 removal if the concentration in the air is very high.

K. B. KNOX—St. Paul Ammonia Products Inc., St. Paul, Minn.: On rich-liquid filters it is rather difficult, if not impossible, to regenerate to 300°F. It would be easier probably to reach 300° on the vapor phase. If that were done, would it give you the protection that you recommend?

KERRY: Yes, the only reason for 300° is to make sure you drive off other

hydrocarbons and C_2H_2 . Acetylene alone can be driven off at much lower temperatures. For example, we find that by the time the rich-liquid filter reaches an ambient temperature of about $15^\circ C$ practically all the C_2H_2 is off. But we always carry on beyond that to drive off anything else which may still be adsorbed. In other words, the vapor-phase filter gives you extra added safety.

N. H. WALTON—SunOlin Chem. Co., Claymont, Del.: Last year Ray Walton told us about an experience with the filter at the Rohm & Haas plant, which had some pressure drop problems. Have these been eliminated?

C. R. WALTON, JR.—Rohm & Haas Co., Pasadena, Texas: Yes, it has. About a year and a half ago, we went into the vessel itself and metallized the vessel and connecting piping. This has solved our problem. We took the plant down in June of this year, and I personally looked at the filters, and they looked very well. The pressure drop, in fact, is less than 2 pounds at the design rate.

H. GARRICK—Mine Safety Appliances Co., Pittsburgh, Pa.: The temperatures mentioned seem to be a little high. We've been trying to oxidize the oil-lubricated compressors, and preliminary studies have shown that we have been able to oxidize CH_4 at much lower temperatures if some other fuel is present, such as a high percentage of some unsaturate. We found that we could oxidize CH_4 at $500^\circ F$, but further studies are planned.

KERRY: When we were first experimenting with different types of catalysts about three years ago, we had to go to very high temperature levels. Since then, I am sure that considerable work has been done by manufacturers of catalytic agents.

M. A. WILLIAMS—Union Carbide Chemicals, Texas City, Texas: You mentioned that you had some of these vapor-phase filters in service for five years. Have you changed silica gel in those filters during that period?

KERRY: I cannot tell you because they are not our plants. As far as I know, some of the earlier ones have not been changed. As a matter of fact, the first vapor-phase filters installed in air plants were not for the purpose of removing hydrocarbons, but for the purpose of preventing CO_2 particles from entering the high-speed expansion turbines. However, after making analyses on the filters, we found that they were picking up hydrocarbons, and that led the way to try them out for hydrocarbon removal. The units which were designed primarily for

hydrocarbons have been in operation for about three years.

WILLIAMS—Union Carbide Chemicals: Do you have any particular test whereby you check the silica gel to see if it should be changed?

KERRY: We have not. You might say it is strictly how much, or how many hydrocarbons remain after regeneration. In other words, if after a regeneration you are still adsorbing and desorbing in a normal manner, there's no point in changing the silica gel.

P. S. HEPP—Sun Oil Co., Marcus Hook, Pa.: At one point it was indicated that the silica gel adsorbers in the low pressure O_2 stream require a pump. We have a pair of these adsorbers in the product O_2 reboiler system operating without a pump, the only driving force being a thermosiphon to the reboiler. They are working quite well.

KERRY: We do not require a pump, but the pump is already there. In very large plants we depart from the classical design of columns, one sitting on top of the other, and we split the two columns placing them side by side. We use a low pressure circulating pump to take the liquid O_2 and recirculate it through the specially designed vaporizer that we use. Since the pump was available, it was only natural to put adsorbers after the pump.

HEPP—Sun Oil: We've run efficiency tests on these adsorbers after a year

and a half of operation, and we regenerate them to about $120^\circ F$. First, we found that the usual adsorbers ahead of the low pressure tower were removing about 33% of all the C_2 -plus hydrocarbons reaching the main adsorbers ahead of the low pressure column. I would like to point out that the analysis included 29% C_5 and 18% C_6 materials, which is pretty deep in the process for such heavy hydrocarbons. The guard adsorbers, as we call them, in the low pressure column bottoms removed 86% of the C_2 -plus materials reaching the low pressure tower. Here again, 25% of these were C_5 materials and 17% were C_6 's, almost the exact same analysis. Apparently there was very little change in the composition distribution as it went through the plant. The feed air composition at this time was about 3.5 ppm of hydrocarbons.

I have a comment concerning the industry survey on this subject. The average regeneration temperature of everyone reporting on low pressure tower feed adsorbers was 195° . Actually, only 20% go to the 300° that you recommended.

KERRY: We took some rich-liquid filters from one of our own plants and we carried a very serious and intensive desorption test, which included vacuuming. We actually pulled out traces of white oil, which we normally would never dream of finding at the rich-liquid filters.

ERNST KARWAT
Linde Co. (Germany)

Hydrocarbon control in air separators

Adsorption at cold end of regenerators is effective; precombustion methods also offer advantages.

AN EXPLOSION IN A LINDE-FRÄNKEL apparatus in which the presence of sufficiently large quantities of acetylene was definitely excluded gave cause for a renewed investigation of the behavior of C_2 and C_3 hydrocarbons in air separators. The results showed that primarily C_3H_8 is unaffected by the conventional safety measures and consequently constitutes a potential source of danger.

This article deals with known and

novel safety measures, especially with regard to whether C_3H_8 present in the air can be rendered innocuous in the separator or prevented from entering the separator.

What caused the explosion

The explosions occurred as liquid O_2 was being run off from the separator into a bucket, resulting in severe damage to pieces of electric apparatus and electric switchgear. Somewhat