

ERNST KARWAT
Linde Co. (Germany)

Hydrocarbon control in air separators

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

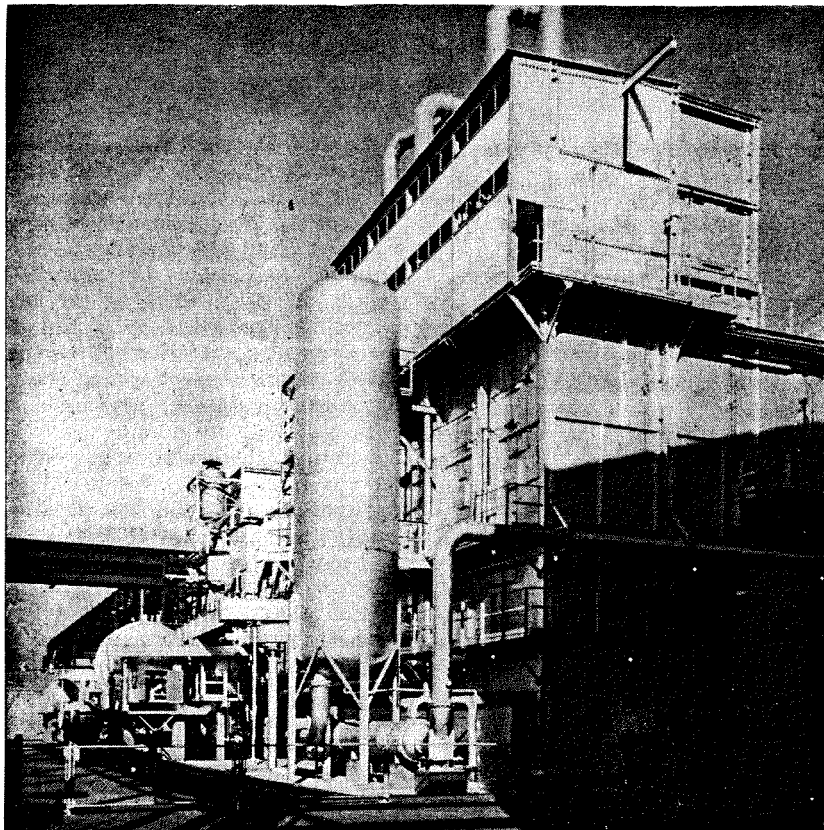
AN EXPLOSION IN A LINDE-FRÄNKEL apparatus in which the presence of sufficiently large quantities of acetylene was definitely excluded gave cause for a renewed investigation of the behavior of C_2 and C_3 hydrocarbons in air separators. The results showed that primarily C_3H_8 is unaffected by the conventional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



Typical oxygen plant of Linde (Germany).

less violent was the explosion inside the C_2H_2 separator which stretched the separator about 11 cm. and destroyed a number of tubes of the auxiliary vaporizer.

For weeks before the explosion, analytical checks of the main condenser O_2 had shown only C_2H_2 contents of a few hundredths ppm. Higher C_2H_2 contents could not be detected at the time of the explosion in a number of air separators operating in the same plant. Hence, there was no doubt that the force of the explosion was attributable to hydrocarbons other than C_2H_2 even though the presence of small quantities of solid C_2H_2 acting as a triggering substance did not need to be excluded.

Subsequently, over the course of several weeks, the impurities in the main condenser, in the gaseous O_2 , and in the C_2H_2 separator were determined, the values for which are listed in Table 1. There were very small quantities of dissolved hydrocarbons which, in the light of earlier investigations (1) may be regarded as harmless. C_3H_8 and C_2H_2 are practically absent in the main condenser, although the air behind the regenerator and the high-pressure column liquid contained both. In addition, C_2H_6 , C_3H_8 , and C_2H_4 are present.

It is worthy of note that about 40-80% of the C_2H_6 and C_2H_4 introduced into the auxiliary vaporizer is removed by the gaseous O_2 . A liquid

phase in equilibrium with this gaseous O_2 (pressure, 1.1 kg./sq. cm.; content, 2 ppm C_2H_4) should contain about 650 ppm C_2H_4 . The liquid found in the C_2H_2 separator, however, contained only 70 ppm C_2H_4 . Apparently this liquid must be regarded as a mixture of C_2H_4 -rich evaporation residues with C_2H_4 -poor surplus liquid, just as the final content of 2 ppm C_2H_4 for gaseous O_2 may be considered as having emanated from a mixture of gas streams of varying C_2H_4 content.

Propane concentration hazardous

The C_3H_8 content of the gaseous O_2 is below the limits of detection. This is understandable, for at the saturation limit (9800 ppm C_3H_8) the tension of the C_3H_8 from the saturated solution amounts to only a few hundredths ppm, and is several hun-

Table 1. Contents of condensed hydrocarbons in ppm.

	A	B	C	D
C_2H_6	0.7	2	1	30
C_2H_4	3	5	2.5	70
C_3H_8	0.2	0.5	0	20
C_3H_6	0.45	0.01	0	1
C_4H_{10}	<0.1	—	0	1
C_2H_2	0.3	0.005	0.003	~0.1

A in the O_2 -rich liquid of the pressure column.

B in the liquid O_2 of the main condenser.

C in the gaseous O_2 after the separator.

D in the unevaporated surplus liquid of the separator.

dred times lower over solutions containing only $\frac{1}{2}$ to 30 ppm C_3H_8 . On the other hand, the partial pressures of C_2H_4 and C_2H_6 from their solutions are about 10 to 100 times higher.

In early investigations, we tried to judge whether such hydrocarbons are retained in the auxiliary vaporizer by hydrocarbon material balances around the auxiliary vaporizer. We concluded, however, that the sums of all the errors deriving from sampling, gas chromatography, and fluctuations in the hydrocarbon content of the processed air make such calculations unreliable.

Therefore, after operating periods of different lengths, we sealed off the inlet and outlet of the auxiliary vaporizer and then heated its tubes from outside. We subsequently flushed the O_2 evaporating chambers with N_2 , and measured the impurities carried out by the flushing gas. In the case of eight measurements, no C_2H_4 or C_2H_6 could be found but C_3H_8 was always present in varying quantities up to 400 liters. As far as the explosive potential (free energy of combustion) is concerned, such a quantity of C_3H_8 is enough to be considered a hazard. This situation is rendered less serious, however, by the fact that simultaneously there was always present several kg. of CO_2 in the auxiliary vaporizer (1).

During the tests, surplus liquid in the auxiliary vaporizer amounted to 1% of the quantity of vaporized O_2 . In no case of such supervised deriming was a large enough quantity of hydrocarbons found in the auxiliary vaporizer and C_2H_2 separator that the force of the explosion could be explained by their presence alone.

Particularly it could not be proved that the exploded hydrocarbon was C_3H_8 , but investigation had shown that of all the C_2 and C_3 hydrocarbons only C_3H_8 has a tendency to accumulate in the auxiliary vaporizer and C_2H_2 separator. Scarcely any C_3H_6 is present, and the two C_2 hydrocarbons, C_2H_4 and C_2H_6 are comparatively highly volatile.

Hydrocarbon adsorption study

Investigations of adsorption in the liquid and gaseous phases were undertaken to gain an understanding of the basic relationships in order to better consider safety measures. This data supplements earlier measurements of vapor pressure, solubility, and explosiveness of the hydrocarbons (1).

position, which renders the explosion-probability (1) of C_3H_8 less than that of C_2H_2 (provided that no C_2H_2 is admixed to the C_3H_8). On the other side, the lower adsorbability in gaseous or dissolved state of C_3H_8 compared to C_3H_6 and its lower fugacity compared to C_2H_4 and C_2H_6 compel us to classify C_3H_8 as more dangerous than the C_2 -hydrocarbons. In our opinion, it would be best to keep C_3H_8 away from O_2 -rich liquids.

It is of interest to compare the safety properties of C_4H_{10} with those of C_3H_8 . The vapor pressure of C_4H_{10} is only 1% and the solubility in liquid O_2 only 2% of those of C_3H_8 . The adsorbabilities are nearly the same. It enters the rectification set-up mainly by entrainment. We classify C_4H_{10} in the same class as C_3H_8 relating to its safe handling.

The safety measures we tried to evaluate are as follows:

Method 1. Intensified flushing of the auxiliary vaporizer with surplus liquid prevents the accumulation of vaporization residues. When the surplus amounts to 2% of the O_2 output it becomes necessary to recycle the liquid surplus through an adsorber to avoid impermissible refrigeration losses. A properly functioning C_2H_2 adsorber retains C_2H_2 and C_3H_8 almost completely, thus the circulating liquid contains chiefly C_2H_4 , C_2H_6 , and C_3H_6 . The conditions for adsorption in the circulation-type adsorber are favorable since the concentrations of the hydrocarbons in question have increased due to the preceding boiling of the liquid O_2 in the auxiliary vaporizer or are raised by the circulation. As can be seen from Figure 1, the adsorptivity of the gel increases with the concentration of C_3H_8 . As a result of sorption displacement, C_2H_6 breaks through fairly quickly, C_3H_8 concentration rises slowly, and C_2H_4 does not break through until near the end of the adsorbers period of operation. With an ample circulation of liquid, such a system gives improved safety in the auxiliary vaporizer and the separator.

Method 2. Removing hydrocarbons from the air before the high pressure column by washing with small quantities of liquefied air was evaluated. The high solubility of C_2H_6 , C_2H_4 , and C_2 -hydrocarbon (3000 to 120,000 ppm) allows limiting the quantity of washing agent to 0.2% of total air throughput. The washing liquid can be vaporized without risk over hot water outside the separator with sacrifice of its refrigeration value. If pre-washing is intended to prevent C_2H_2 from entering the rectification columns, the

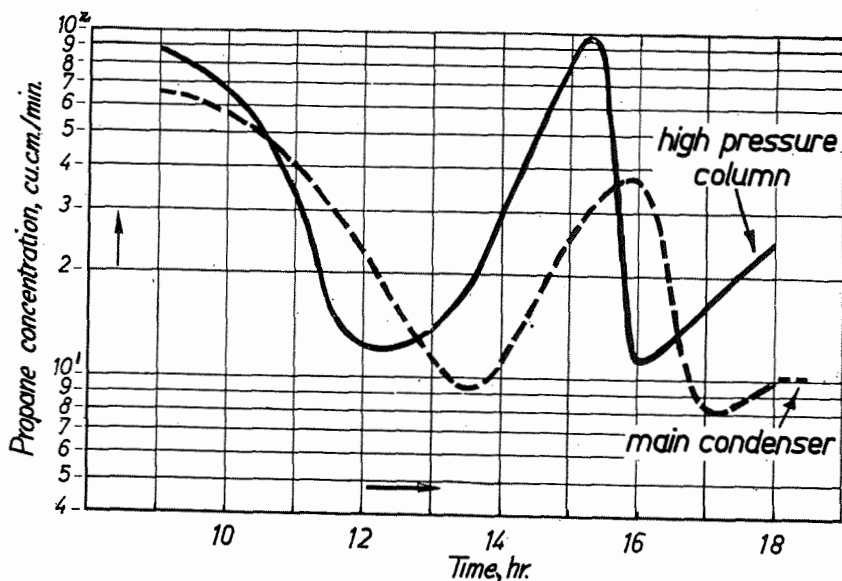


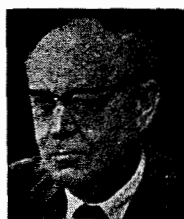
Figure 2. Fluctuations of the propane content in the oxygen-rich liquid of the pressure column and in the liquid oxygen of the main condenser.

theoretical minimum quantity of washing agent is about 4% of air throughput. If the air is saturated with C_2H_2 behind the regenerator, the quantity of washing agent will have to be at least doubled to avoid saturated C_2H_2 solutions. The cold content of such a large quantity of liquid cannot be sacrificed.

The liquid must be purified with an adsorber which would contain roughly about 75% of the quantity of gel used in the usual C_2H_2 adsorber for the high pressure column liquid. C_2H_6 , C_3H_8 , and C_2H_4 will break through just as quickly as in the customary adsorber. On the whole, pre-washing presumably would not increase safety as compared with the usual adsorption between the high- and low-pressure columns.

Better methods needed

A disadvantage of the first two



Ernst K. Karwat received grades of "Diplom-Ingenieur" and "Doktor-Ingenieur" as a physical chemist in 1920 and 1923 from the Technische Hochschule, Breslau, Silesia. He joined the Chemical Department of the German Linde Corp.

and became Head of the Department in 1939. He has worked on basic scientific problems as well as developmental work in the fields of low and high temperatures, in the use of oxygen for metallurgical and gasification processes. Since 1956 he has been working with the A.I.Ch.E. Committee on safety problems in air and ammonia plants.

methods is that all the fluctuations in the hydrocarbon content of the air, especially its content of C_2 hydrocarbons and C_3H_8 (the fluctuations in the content of C_2H_2 and C_3H_6 are damped by the acetylene adsorber), would markedly show in the main condenser, the vaporizer, and adsorber cycle. The frequent variations in analytical findings would probably make supervision rather difficult.

In the trend of technological development O_2 plants will soon be automated, and then the measures taken relative to hydrocarbons in air separators will have to be such that hydrocarbons, with the exception of CH_4 and C_2H_6 , are no longer encountered where there are liquid, O_2 -rich mixtures. This requirement is not satisfied by the two safety measures described.

Method 3. Hydrocarbons can be removed more effectively with an adsorber located in the gaseous phase between regenerator and pressure column. In gas-phase adsorption the gel extracts a large multiple of the hydrocarbons removed by adsorption in the liquid phase. The identical concentrations of 0.2 ppm C_3H_8 in gaseous air or 0.4 ppm in O_2 -rich liquid air are in equilibrium either with a load of 50 cu. cm. or 0.04 cu. cm. C_3H_8 /gm. of silica gel, or about thousand times more in the case of gas-phase adsorption.

An adsorber for the air behind the regenerator will have a fairly large cross section and also a large quantity of gel. It gives excellent protection against penetration of C_2H_2 , C_3H_6 , and also C_3H_8 . The C_2H_6 breaks

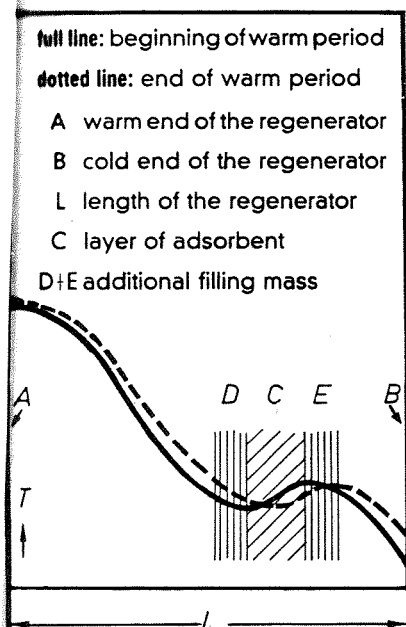


Figure 3. Temperature curve in the regenerator with a gel layer.

through after a short time, and the C_2H_4 a little later. Operational periods of several months can be achieved up to the break-through of C_3H_8 and even longer periods for C_2H_2 and C_3H_6 .

Method 4. The most effective way of removing all air impurities is by gel layers located near the cold end of the regenerators (2). The impurities adsorbed from the air during the warm period are taken up during the cold period by the stream of N_2 passing over the gel. This method of regenerative adsorption and desorption was investigated in the laboratory and in full-scale tests. The chief measurements on the full-scale regenerator concerned the thermal variations resulting from the introduction of gel, while chemically, only the adsorption and desorption of CO_2 was observed. The laboratory measurements dealt with the behavior of the hydrocarbons.

In the regenerator, the gel layer achieves equilibrium with the pressurized air during the warm period and with the stream of N_2 during the cold period. In the warm period, an O_2 -rich O_2-N_2 mixture is taken up by the gel, this mixture being given off again when the pressure is reduced and during the ensuing cold period. The respective quantities of adsorption and desorption heat are distributed between the gel and the gas. Heat taken up after leaving the gel layer is given off by the air to the filling mass, and from there it is taken up again by the recycled N_2 ,

thus compensating for part of the desorption heat which causes the N_2 to be cooled over the gel. These are the reasons why the temperature curve in the regenerator at the gel layer is S-shaped, Figure 3. An appropriate quantity of heat storing material must be placed adjacent to the gel layer for the exchange of adsorption and desorption heat. The quantity of O_2 taken up by the gel and given off to the N_2 stream amounts to about 0.5 to 0.75% of the production.

To check the behavior of the hydrocarbons in regenerative adsorption and desorption, air at a pressure of 5 atm.; a temperature of 100°K; and containing about 1 ppm C_2H_2 , 1 ppm C_2H_4 , 0.3 ppm C_3H_8 , 0.7 ppm C_2H_6 , and a surplus of CO_2 was passed over a layer of alumina gel or sovalbeds in one direction for a period of 15 min. Subsequently the same quantity by weight of pure N_2 at the same temperature and about atmospheric pressure was passed over in the opposite direction. These operations were repeated alternately over the course of several weeks. The air remained practically free from hydrocarbons. The hydrocarbons, with the exception of small amounts of C_2H_2 , were found in the recycled N_2 . We concluded from these experiments that it is possible by this

method to achieve maximum possible purification of the air in full-scale plants.

Method 5. Total combustion of the hydrocarbons before the air enters the separator should reduce the C_3H_8 to 0.02 ppm (10% of the concentration that would pass through the cold end of the regenerators). This requirement is high, but is possible if the initial content of C_3H_8 in the air does not exceed 10 ppm.

If the bulk of the C_2H_6 is to be converted, the temperature must be set 50 to 100°C higher than usual for the combustion of C_2H_2 , C_3H_6 , and C_2H_4 . This will not be difficult if heat exchangers for outlet and inlet air can be built cheaply enough.

A great advantage of the precombustion method would be that the air separation processes could be subjected to changes in gas and liquid flow to obtain desired results, without having to devise new safety measures in each case. The safety measures discussed under previous methods do not fulfill this requirement.

LITERATURE CITED

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G. T. WRIGHT

Dominion Foundries and Steel Ltd. (Canada)

Oxygen plant vaporizer explosion

An analysis of the causes led to plant changes for improving safe operation.

HIGH PURITY OXYGEN SUPPLIED by three units with a total capacity of 350 tons/day is required by the Dominion Foundries and Steel, Ltd. for producing steel. At 8:10 P.M., September 30, 1959, the vaporizer in No. 2 unit exploded, wrecking the vaporizer and surrounding parts of the cold box, Figures 1 and 2. No one was injured and production loss was minimized because the No. 3 spare 150 ton unit had gone on stream three weeks earlier.

Plant description

The No. 2 plant is a 100 ton/day

split cycle-type. The intake air is filtered through a 10-ply paper filter and then compressed to 75 lb./sq. in. gauge in a turbo compressor. It is water scrubbed to remove soluble impurities. Two thirds of this air passes through aluminum-filled regenerators, then into the high pressure column. The rest of the air is compressed to 350-550 lb./sq. in. gauge, goes through caustic scrubbers, heat exchangers, then through an expansion engine, and into the high pressure column. Rich liquid, produced in the high pressure column, then passes through silica-gel filters into the low