### 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-FRÄNKL 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.

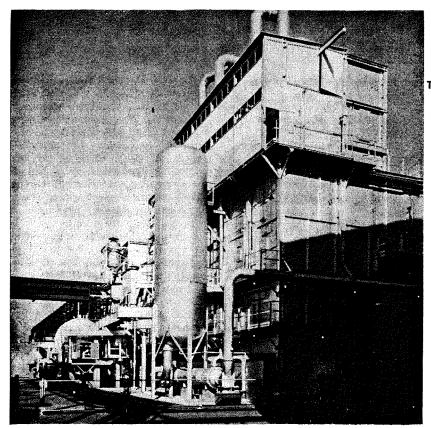
This article deals with known and

novel safety measures, especially with regard to whether  $C_sH_s$  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

No. 4)



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.  $C_3H_6$  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.	Cont	ents	of	condensed	hy-
drocar	bon	s in	ppm	-		-

	Α	в	С	D	
C₂He	0.7	2	1	30	
C₂H₄	3	5	2.5	70	
C₃H₃	0.2	0.5	0	20	
C₅H₀	0.45	0.01	0	1	
C4H10	< 0.1		0	1	
C₂H₂	0.3	0.005	0.003	~0.1	
A in	the Outloh	liquid	of the n		

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.

Typical oxygen plant of Linde (Germany).

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. с

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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<sub>3</sub>H<sub>8</sub> 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<sub>3</sub>H<sub>8</sub> 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<sub>2</sub> 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 (I).

The load curves of various hydrocarbons in Figure 1 show the standard cu. cm. of a hydrocarbon adsorbed (ordinate) by one gram of widepored silica gel from a liquid-O2 solution of that hydrocarbon as a function of the concentration in the solution in ppm (abscissa). According to these curves the hydrocarbons are divided into two groups: in the group of unsaturated hydrocarbons (C2H2, C3H6, and  $C_2H_4$ ) the adsorptivity varies much less with their concentration in the solution than in the group of the saturated hydrocarbons  $(C_3H_8)$  and  $C_2H_6$ ). In the range of concentrations most frequently encountered in practice, namely 0.1 to 5 ppm, wide-pored silica gel takes up almost 1000 times more unsaturated hydrocarbons than  $C_3H_8$  or  $C_2H_6$ .

The load curves in Figure 1 end (in circles) with the maximum adsorptivity of the gel at the saturation point of the solution. At this point the solution, the pure hydrocarbon, and its vapor are in equilibrium with the gel. Hence, at this quadruple point the amount of hydrocarbon adsorbed from the solution is identical with that adsorbed from the gaseous phase. This indicates that such hydrocarbons, which emerge at the cold end of the regenerator with dew point concentration can be more efficiently adsorbed there from the gaseous phase than from their solution after total liquefaction, *i.e.*, from the  $O_2$ -rich liquid in the high pressure column. From the equilibriums it follows that a layer of gel saturated in contact with the gaseous phase can be desorbed by washing it with pure liquid  $O_{2}$ .

#### Mixtures influence sorption

In the air separator we always have to deal with hydrocarbon mixtures, not with individual hydrocarbons. Consequently the adsorption of mixtures was subjected to investigations which showed the highly important influence of sorption displacement. Consider a liquid-O<sub>2</sub> solution of a mixture of 40 ppm each of C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, and  $\tilde{C}_{3}H_{6}$  passed over gel until the same mixture passed out the exit side. When the gel was desorbed, the components of the mixture were not in proportion to their adsorbability as shown in Figure 1, but in entirely different proportions: 83% C<sub>3</sub>H<sub>6</sub>, 10% C<sub>2</sub>H<sub>4</sub>, 5% C<sub>3</sub>H<sub>8</sub>, and 2% C<sub>2</sub>H<sub>6</sub>. The C<sub>3</sub>H<sub>6</sub> has practically completely prevented the adsorption of C2H6, very much restricted the adsorption of C<sub>3</sub>H<sub>8</sub>, and considerably impaired the adsorption of C<sub>2</sub>H<sub>4</sub>.

We have also investigated the interaction of the hydrocarbons with the constantly present air impurities  $N_2O$ and  $CO_2$ , both during the equilibrium measurements and with respect to the break through of the various substances. From these studies we could understand the observations made during the practical operation of the  $C_2H_2$  adsorber of an air separator.

The first  $C_2H_6$  passes through a freshly regenerated  $C_2H_2$  adsorber only 15 min. after being put into operation. Propane is found from 30 to 45 min. later in the main condenser, and from this point onwards all the fluctuations of the  $C_3H_8$  content in the  $O_2$ -rich liquid of the pressure column are encountered half an hour later in the main condenser.



Figure 2 shows the concentration of  $C_3H_8$  in the enriched liquid air of the high pressure column and in the main condenser. Hills and valleys of the two lines follow each other in  $\frac{1}{4}$ -hr. distance. The increase in  $C_2H_4$  behind the adsorber takes somewhat longer than that of  $C_3H_8$ , but it also ended long before the first traces of  $C_2H_2$  and  $C_3H_6$  breaking through make it advisable to change the adsorber.

In the gas-phase adsorption of the various hydrocarbons, the usual phenomena are encountered: extensive independence of the gel's adsorptivity for a hydrocarbon on temperature and pressure along the hydrocarbon's vapor pressure curve (i.e., at its dew point), but marked diminution of the gel's adsorptivity when the temperature is raised above dew point temperature while maintaining a constant partial pressure. The sequence in which the hydrocarbons displace each other from the gel is somewhat different from that observed in the case of liquidphase adsorption. Here, too,  $\hat{C}_2H_6$ passes from the adsorber most quickly, and then is followed by  $C_2 \bar{H}_4$  and carbonic acid, and then by C<sub>3</sub>H<sub>8</sub>.

The various substances according to the degree of adhesion with which they are bound by the gel and the sequence of their break-through for liquid-phase adsorption are as follows:

$${\rm C_2H_2\!-\!C_3H_6\!-\!CO_2\!<\!}^{\rm N_2O}_{\rm C_2H_4}\!\!>\!{\rm C_3H_8}$$

 $-C_2H_6$  (first to break-through)

For gas phase adsorption, these are as follows:

$$\begin{array}{c} C_3H_6 \\ C_2H_2 \end{array} > C_3H_8 - N_2O - C_2H_4 - \\ C_2H_2 \\ C_2H_6 \quad (\text{first to break-through}) \end{array}$$

It is remarkable that in gas-phase adsorption  $C_3H_8$  relative to other hydrocarbons is bound stronger than in liquid-phase adsorption.

#### **Evaluation of safety methods**

We tried to evaluate various safety measures, some of known and some of a novel nature, particularly with regard to  $C_3H_8$ . Focussing attention on  $C_3H_8$  does not mean we classify it as the number two enemy behind  $C_2H_2$ . The free energies of combustion and the destructive power of explosive oxidation reactions of both do not differ greatly. However, there is a great difference in spontaneity of self-decom-

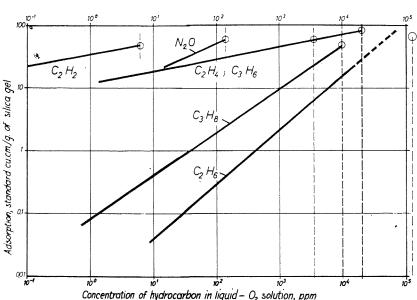


Figure 1. Adsorption of various hydrocarbons dissolved in liquid oxygen on wide-pored silica gel.

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.у, 1гposition, which renders the explosionprobability (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  $C_2H_4$  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 adsorbabilites 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 O2 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  $C_3H_6$  almost completely, thus the circulating liquid contains chiefly C2H4, C2H6, and C3H8. 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 O2 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.H. 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  $C_3$ -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

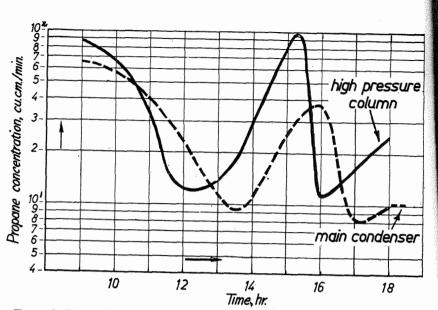


Figure 2. Fluctuations of the propane content in the oxygen-rich liquid of the pressure column and in the liquid oxygen of the main condenser.

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.  $C_2H_8$ ,  $C_3H_8$ , 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 highand 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 De-

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<sub>4</sub> 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

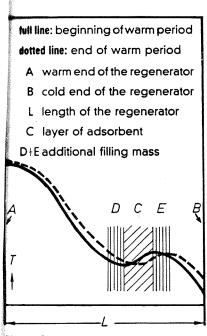


Figure 3. Temperature curve in the regenerator with a gel layer.

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<sub>3</sub>H<sub>8</sub> 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 N2 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<sub>2</sub> 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 laver is given off by the air to the filling mass, and from there it is taken up again by the recycled N<sub>2</sub>,

thus compensating for part of the desorption heat which causes the N2 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 O2 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 CO2 was passed over a layer of alumina gel or sovabeds in one direction for a period of 15 min. Subsequently the same quantity by weight of pure N2 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

## LOW TEMPERATURE

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 C3H8 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  $\check{C}_2H_2$ ,  $C_3H_6$ , 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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- 1949

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## 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 Do-minion 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

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