

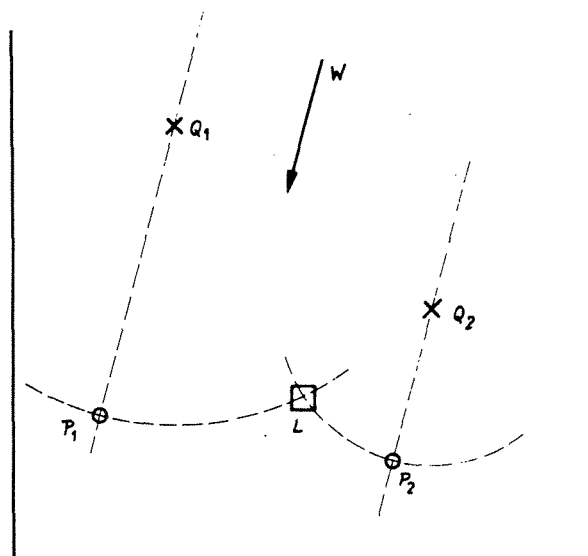
PRESENT STATUS OF THE HYDROCARBON SITUATION IN AIR SEPARATORS

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In our former work done on the hydrocarbon-safety problem, numbers about the amount of hydrocarbons in the feed air, with which one has to reckon in reality, were lacking. Today we know considerably more in this domain owing to the increasing use of gaschromatography. Average and maximum values found in 85 samples drawn from the air in 16 industrial plants are given in Table 1. This gives the values separately for each plant, and in the last two lines also the total averages from 85 samples and 16 plants. The air samples were taken at a place in the plant area downwind of a suspected source of hydrocarbons and at a distance from this source equal to the distance of the air separation plant from it, Figure 1.

It was somewhat surprising that with great regularity the average values of all hydrocarbon concentrations were found to be lower than 0.1 ppm and even the maximum values lower than 1 ppm with one single exception. In one of the plants controlled (plant 4, table 1) previously considerable higher concentrations particularly of propane had been observed. The figures as listed for plant 4 are already the result of systematically closing various sources of C_2 and C_3



- L = Location of existing or future air intake
- W = Wind direction on day of sample
- Q_1, Q_2 = Suspected sources of air contamination
- P_1, P_2 = Location at which sample is taken when wind direction is W

Figure 1. Air sample taking in the plant area.

hydrocarbons like blowing down, flaring and so on. It would seem desirable to revise the statements hitherto made on the safety of our air separators in the light of these figures and of recent experience in the field. This will be done here firstly for usual tonnage plants with a rich liquid adsorber, secondly for a modified plant type with gas phase adsorber between regenerators and pressure column. The basically favorable result of such review is, that if in usual tonnage plants the feed air shows the concentrations of Table 1 there is no cause for concern about the hydrocarbon concentrations in the liquid oxygen of the main condenser and of the acetylene separator (naturally with the exception of acetylene). This result coincides with the experience that very rarely hydrocarbons other than acetylene could be proven to have been the cause of an explosion.

Hydrocarbon concentrations

Table 2, line 1, gives the hydrocarbon concentrations in the main condenser calculated from the average values of Table 1 penultimate. For non-adsorbable hydrocarbons like C_2H_6 , C_2H_4 , C_3H_8 the concentrations are sixfold of Table 1 while for the other hydrocarbons the figures are based on the assumption that 98% of them have been retained in a rich liquid adsorber.

If subsequently the liquid oxygen of the main condenser is boiled down to a remainder of 1% in the residual liquid, then in the residual liquid the hydrocarbon content should increase to 100-fold because according to the nonfugacity of most of the hydrocarbons from their solution (the acetylene excepted) almost nothing is transferred to the gas phase. Such enrichment however is practically never found in the residual liquid because the reality differs considerably from this assumed scheme.

In three plants, A, B and C, we measured the concentrations in main condenser, acetylene separator and gaseous oxygen. The results are listed in Table 2, lines 2-9. The liquid in the separator shows a small enrichment only in hydrocarbons. Its composition fluctuates frequently. This fluctuation has perhaps something to do with the pressure wave which, during switching of the regenerators, drives somewhat more liquid through the vaporizer. It may well be that it also flushes down carbon dioxide and propane deposited meanwhile on the tubes. Such depositions have been identified. Beyond this the figures of lines 4 and 7 of Table 2 disclose interesting things about the mechanism of evaporation in the additional vaporizer. Contrary to the usual assumption that the gaseous oxygen separates itself well from the liquid remainder it is observed that the gaseous oxygen carries with it about 50-80% of the ethane and ethylene, fed to the vaporizer

TABLE 1. HYDROCARBON CONCENTRATIONS (ppm) IN AIR SAMPLES FROM VARIOUS PLANTS

plant	number of samples		C ₂ H ₆ ppm	C ₂ H ₄ ppm	C ₃ H ₈ ppm	C ₂ H ₂ ppm	C ₃ H ₆ ppm	C ₄ H ₁₀ ppm	C ₄ H ₈ + C ₅ ppm
1	5	average	0.020	0.020	0.005	0.011	0.008	0.068	0.016
		maximum	0.060	0.050	0.019	0.036	0.036	0.200	0.050
2	4	average	0.006	0.038	0.004	0.040	0.005	0.032	-
		maximum	0.010	0.090	0.007	0.110	0.017	0.050	-
3	20	average	0.047	0.043	0.028	0.088	0.099	0.036	0.112
		maximum	0.167	0.280	0.090	0.089	0.045	0.085	0.348
4	5	average	0.015	0.092	0.011	0.041	0.022	0.011	0.015
		maximum	0.034	0.300	0.037	0.076	0.034	0.018	0.030
5	6	average	0.130		<0.020	<0.020	0.090	<0.020	-
		maximum	0.300		-	-	0.170	-	-
6	7	average	0.490	0.130	0.115	0.01	0.036	0.155	0.200
		maximum	1.273	0.509	0.321	-	0.087	0.488	0.568
7	3	average	0.102	0.170	0.004	0.007	0.015	0.005	0.010
		maximum	0.144	0.290	0.010	0.009	0.032	0.008	-
8	6	average	0.245	0.371	0.016	0.079	0.039	0.006	0.033
		maximum	0.380	0.590	0.024	0.330	0.058	0.007	0.125
9	2	average	0.050		0.050	0.030	0.050	0.030	-
		maximum	-		-	-	-	-	-
10	2	average	0.004	0.003	0.002	0.002	<0.001	<0.002	<0.002
		maximum	-	-	-	-	-	-	-
11	3	average	0.07	-	-	0.03	-	0.005	-
		maximum	0.09	-	-	0.04	-	-	-
12	6	average	0.05	-	0.015	0.03	0.01	-	-
		maximum	0.12	-	0.042	0.11	0.02	-	-
13	4	average	0.03	<0.002	0.003	0.008	<0.01	<0.01	-
		maximum	0.12	-	0.007	0.012	-	-	-
14	4	average	0.05	-	-	0.01	-	-	-
		maximum	0.09	<0.002	<0.002	0.02	<0.01	<0.01	-
15	3	average	0.015	0.009	-	-	-	-	-
		maximum	0.033	0.01	<0.001	0.001	<0.001	0.001	-
16	5	average	0.005	0.002	-	0.013	-	-	-
		maximum	0.007	0.003	<0.001	0.020	0.001	-	-
Total	85	average	0.10	0.08	0.03	0.04	0.02	0.03	0.08
Total	85	maximum	1.27	0.59	0.32	0.33	0.17	0.49	0.57

from the main condenser. The small fugacity of hydrocarbons from their solutions can hardly be doubted and there remains only the conclusion that during boiling down, the liquid rest forms a spray which is not separated but entrained and carried to the regenerators where the droplets then evaporate. These droplets are apparently not retained at the cold end of the regenerators because otherwise a hydrocarbon cycle back to the column would be set up and the hydrocarbon level in the main condenser would increase steadily. This however was not observed.

"Boiling down to dryness"

The entrainment can also be caused by the fact a considerable number of tubes of the auxiliary vapor-

izer boil down the liquid oxygen in a way which is close to "boiling down to dryness." Herein, under certain conditions, hazards may be involved especially at insufficient and irregular flooding of the vaporizer. As a remedy, abundant rinsing of the vaporizer together with cycling of the unvaporized portion of the liquid through an adsorber, is recommended, Figure 2 and Figure 3. In both cases we have liquid bleeds for removing non-adsorbed hydrocarbons like C₂H₆, C₂H₄, C₃H₈ from the cycle. If the bleed is 1% of oxygen production, the concentration of non-adsorbed hydrocarbons in the cycle may rise to 600-fold of the concentration in the air to 60 ppm C₂H₆, 50 ppm C₂H₄ and 18 ppm C₃H₈ with the limitation however, that acetylene, propylene and butylene are lacking entirely, owing to the effect of the cycle adsorber. Therefore the liquid in the cycle can be considered harmless. We see the main improvement

TABLE 2. HYDROCARBON CONCENTRATION IN LIQUID AND GASEOUS OXYGEN

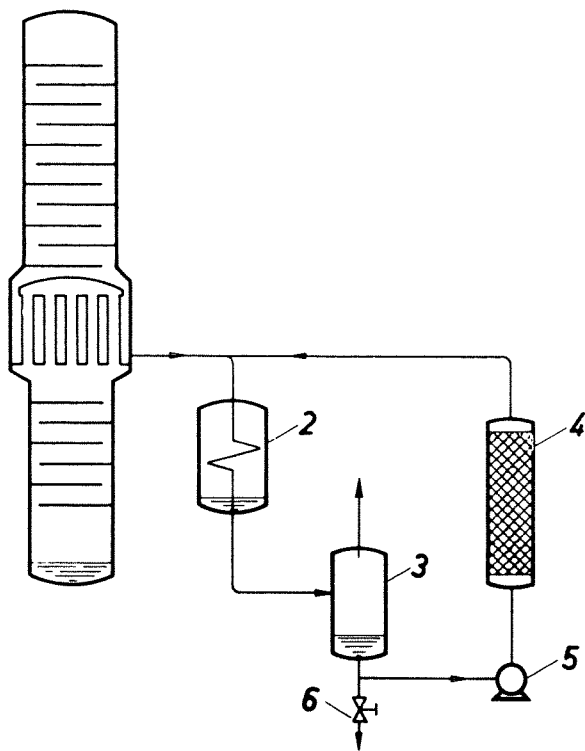
Pos.	C ₂ H ₆ ppm	C ₂ H ₄ ppm	C ₃ H ₈ ppm	C ₄ H ₁₀ ppm	C ₂ H ₂ ppm	C ₃ H ₆ ppm	C ₄ H ₈ ppm		
1	0.6	0.5	0.2	0.18	0.005 to 0.1	0.003 to 0.1	0.1	main condenser	calculated from table 1
2	2	5	0.5	-	0.005	0.01		main condenser	measured in: plant A
3	30	70	20	1	0.1	1		acetylene separator	
4	1	2.5	0	0	0.003	0		gaseous O ₂	
5	0.9	0.012	0.009		0.025			main condenser	plant B
6	0.75	0.026	0.55		0.025			acetylene separator	
7	0.5	0.005	-					gaseous O ₂	
8	0.16	0.013	0.002		0.025			main condenser	plant C
9	1.9	0.16	0.09		0.025			acetylene separator	

in the fact that there can no longer be dry-operation of the additional vaporizer. It is, of course, not possible to foresee whether chemical plants will continue to have air with the low hydrocarbon concentrations as shown in Table 1, or whether we will advance to concentration

levels for the evaluation of which we have no experience yet. Such complications would however easily be overcome by gas phase adsorption. Gas phase adsorbers in the stream of the cold air were hitherto in use, e. g., for elimination of extreme high concentrations of acetylene. In tonnage oxygen plants arranged behind the regenerators they are useful for protecting the rectification column also from other hydrocarbons. The temperature of adsorption is adjusted to slightly above the dew point temperature of the passing air; thus detrimental contact with preliquefied air is avoided. The hydrocarbons enter the gel with the air as a mixture.

To get an insight into the mechanism of adsorption at the very low temperatures and the extremely low hydrocarbon concentrations of the air at the cold end of the regenerators we had an adsorption vessel supplied with sampling tubes each 10 or 20 cm, and used it to adsorb the air impurities under conditions of pressure and temperature similar to those of a cold-end-adsorber.* The hydrocarbon contents of the samples were plotted in percentage of the initial concentration against the length of the gel layer. The decrease of concentration along the gel layer is shown by separate curves for each hydrocarbon. Figure 4 represents the distribution of the hydrocarbons the 13th day after the start of the fresh adsorber. What had happened since the start is somewhat similar to combined effects of multicomponent frontal chromatography and displacement desorption.

At constant operation-conditions the various hydrocarbons move through the gel in always the same succession, each hydrocarbon with its characteristic velocity. Independent of the type of hydrocarbon the concentration front moves at low concentrations, e. g., 1% with greater speed than at higher concentrations (e. g., 10% or 50%) but the low concentration-speed and the high concentration-speed respectively are constant. As a consequence, the front lines (concentration drop curves) become the more flat the deeper a substance has penetrated into the gel or the more time has passed since the start of operating the adsorber.



- 1) rectification column
- 2) additional vaporizer
- 3) acetylene separator
- 4) adsorber
- 5) pump
- 6) liquid bleed

Figure 2. Recycling of surplus liquid from an additional vaporizer.

*The experimental work has been done by Dr. G. Klein.

Break-through curves

A strongly adsorbed hydrocarbon like propylene or acetylene moves very slowly through the gel, e. g., the 1% concentration point of the propylene front line with a velocity of about 15 mm per day as compared to 11 cm daily progress of an ethylene front line. The break-through curves appear as the inverse function of the front lines; that means the break-through is the smoother the longer the gel layer, and/or the stronger a hydrocarbon was adsorbed. Thus the various impurities unite behind the adsorber stepwise. First, methane arrives and quickly grows up to its initial concentration at the exit of the adsorber. Somewhat later the ethane joins the methane and so on in an order depending on the adsorptivities.

It is of great advantage continually to supervise analytically the purified air at the exit of the adsorber and to proceed to the deriming of the adsorber at the very moment an undesired hydrocarbon, e. g., propane, reaches the exit, thus keeping it off from the rectification zone with full precision. This working method is deemed to be a satisfying solution of our hydrocarbon problem.

Theoretically the concentration of any hydrocarbon behind the adsorber is never zero. Therefore the liquid oxygen of the main condenser is circulated through a gel trap which may take up any traces especially of acetylene, Figure 2 & 3. During deriming of the gas-phase-adsorber, this gel trap, if great enough will serve as a sufficient cleaning device for the rectification system. Finally there will be described a very simple device for taking samples of liquid oxygen from a bath of liquid, e. g., the main condenser, for its continuous automatic analytical control, Figure 5.

Sampling arrangement

The conventional sampling arrangement usually comprises a tube from which a liquid sample is drawn from the container for the liquid with the sample then being passed through a throttling valve into an evaporator. This arrangement does not operate satisfactorily because an uncontrollable evaporation of the liquid occurs in the tubing before the liquid has reached the throttling valve. As a result, the gas and liquid flow alternately and intermittently through the throttling valve into the evaporator. The composition of this sample, as ultimately received by the analysis apparatus, is therefore not identical with the composition of the liquid contained in the storage tank from which the so-called sample was taken.

The sampling arrangement shown in Figure 5 essentially comprises a filter chamber (1) positioned

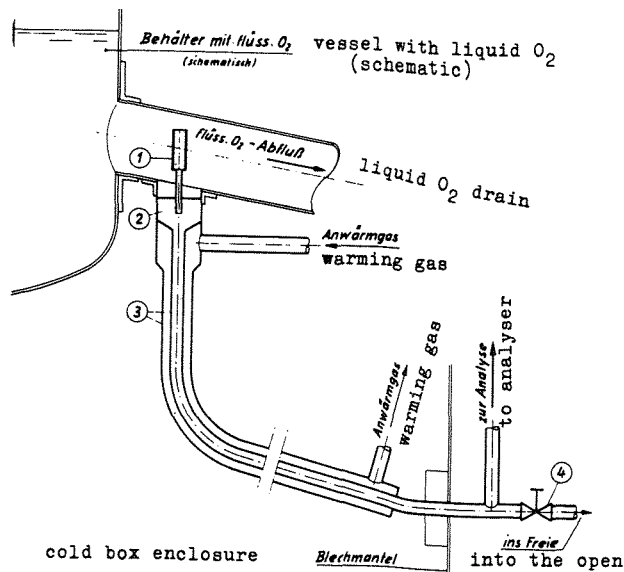


Figure 5. Sampling arrangement for liquid gases.

within the body of liquid gas and having a capillary tube (2) extending from the filter chamber through the body of liquid gas so that one end of the tube projects outwardly from the wall of the tank for a short distance. The projecting end of the tube is connected to one end of a tubular evaporator (3) having a relatively large cross section so as to present relatively little resistance to the flow of gases therethrough. A warm dry gas, air or nitrogen serves as a heating means. The lower end of the evaporator is provided with a control valve and is connected to a gas analyzer, such as a gas chromatograph.

In the operation of this arrangement, a thin stream of liquid gas flows through the filter chamber and the capillary tube into the evaporator. The thin stream of liquid is completely evaporated within the evaporator and then flowed to the gas analyzer. The liquid will not evaporate in the capillary tube since the outer wall of the capillary is cooled by the liquid surrounding it.

The speed of the sample is controlled by valve (8) so that the pressure within the evaporator (6) is at no time greater than the pressure in the storage tank (1). The flow of the liquid is then always directed from the tank (1) towards the valve (8). As a result, the flow of the gas sample admitted to the analyzer is uniform, homogeneous in its composition and identical to the composition of the liquid gas contained in the tank (1).