EXPLOSION OF CONDENSERS IN AN OXYGEN PLANT

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The Sasol Co., located in South Africa, experienced explosions in the additional condensers on two units in one of its oxygen plants. The plant where these incidents occurred consists of six units of 375 ton each, producing gaseous oxygen, with regenerators for oxygen and nitrogen, Figure 1. The plant uses a normal high and low pressure process. The pressure column operated at about 60 lb./sq.in. pressure, the upper column at about 5 lb./sq.in.

Additional condenser

The vessel where this accident happened is the additional condenser. It is fed with liquid oxygen from the main condenser. Normally these plants are run in such a way that the oxygen is vaporized in the additional condenser, while a small surplus remains in liquid form and is collected in a trap, the acetylene separator. The additional condenser actually is designed according to the shell and coil type. It has a large number of tubes. In this case, it contains about 750 tubes.

The acetylene analyses, which normally have been made of the liquid in the main condenser, always showed less than 0.025 ppm acetylene. Occasional



Figure 1. Production of gaseous oxygen with additional condenser.

checks on other hydrocarbons did not show more than traces quantities. The original recommendation was to always collect a certain quantity of liquid in the trap, and to drain this liquid and vaporize it instantaneously in a water bath.

This quantity was later reduced because it was not believed necessary to drain such a quantity of liquid due to the low air contamination. Actually, for some time the additional condensers normally were flushed once per day, by a temporarily increased flow of liquid oxygen, opening a valve from the main condenser. In the time between these flushes they were running practically dry.

In this plant the prevailing winds are northern and supply very pure air. Only occasional southerly winds were carrying contamination from other chemical plants.

This plant was in operation about 10 years. Each unit generally is shut down for a total derime every year. The additional condensers have an operating time of 2 weeks.

Explosions in units 4 and 5

The incidents occurred on two neighboring units, numbers 4 and 5. The air intakes of the air compressors of the units are situated near a corner which is formed by compressor building, i.e., by the building itself, and by a rectangular protruding extension of this building. During the 24 hours before the incident, there were southerly winds of low velocity blowing. On one unit a minor explosion occurred immediately after opening the liquid oxygen valve for flushing, i.e., the valve for the liquid coming from th main condenser.

The oxygen side of the additional condenser was leaking after this explosion and the vessel had to be isolated. Later it was found that the flange connection of the oxygen pipe between the additional condenser and the trap was blown up. This additional condenser was in operation for 5 days at the time of this explosion.

About $1 \frac{1}{2}$ hours later a larger explosion occurred on the neighboring unit, number 4, on which the additional condenser had been flushed at about the same time as the other one.

The center of this explosion obviously was the bottom of the trap. This vessel was torn completely, several pipes and supports were damaged. Fortunately, no persons were injured.

Accumulation of hydrocarbons

The explosions were obviously caused by the accumulation of hydrocarbons; the reacting quantities were not very large. From a calculation of the explosive force which was necessary to tear the trap in the second case, about 35 grams of combustible material, plus an adequate quantity of liquid oxygen, was required, altogether about 150 grams. It is possible to collect such quantities within the available time, even from low concentrations of hydrocarbons in the liquid oxygen, if the liquid oxygen is completely vaporized and the coils are running dry.

Chromatographic analyses of samples which had been taken, after the explosions, from the main condenser liquid of other units in operation, show a considerable amount of C_2 hydrocarbons, very little C_3 , and no trace of C_4 . There was some suspicion of butadiene because a synthetic rubber plant was just being put into operation. From this plant probably some butadiene had been vented at this time. This plant is about half a mile distant from the oxygen plant. During the several hours before the explosions, the wind was blowing from this direction.

Hydrocarbon vapor pressure

The vapor pressures of the C₄ hydrocarbons at the temperatures at the lower end of the regenerators are so extremely low that this theory does not seem reasonable. In the principal flow diagram, the heat exchanger shown represents the regenerators. Actually, the temperature at the lower end of these regenerators would be about 100° K. The vapor pressure of the C₄ hydrocarbons at this low temperature is in the range of 10^{-8} atmospheres. This is extremely low; acetylene has a vapor pressure of 10^{-6} atmospheres at this temperature.

One, therefore, does not think that it is possible for butadiene to enter the actual low temperature section and to collect in sufficient quantities. It is thought that other hydrocarbons might have been the explosive, and that they had been ignited by acetylene. Even when one has less than 0.025 ppm of acetylene in the liquid of the main condenser, it is still possible that some acetylene might collect when this liquid is vaporized completely in the coils of the additional condenser.

Preventing similar incidents

Whatever hydrocarbons may have formed the combustible material, the only remedy for preventing similar incidents seems to be an adequate continuous flushing of the tubes of the additional condensers. Therefore, it was arranged, immediately, not to vaporize about 0.5 to 1% of the oxygen production in the ad-



Figure 2. Additional condenser with recycling adsorber.

ditional condenser tubes, but to collect it in the liquid state in the trap. From here the liquid oxygen is drained to a warm evaporator and vaporized instantaneously at ambient temperature. The quantity drained can be measured in gaseous state downstream from this evaporator.

For increasing operational safety of a unit with such a design, it is now recommended that one install a recycling adsorber.

Recycling adsorber

Figure 2 shows what is called a recycling adsorber, or an adsorber with a recycling pump. One has the additional condenser (2) and the trap (3). One is adding a pump (5). From the pressure side of this pump the liquid oxygen is returned to an adsorber (4), into the main condenser, or into the line leading to the additional condenser.

When one designs the pump with a capacity such that the same quantitity as it is taken from the plant is recycled through the adsorber, then one can be sufficiently sure that the pipes of the coils are always internally filled with liquid and, hence, no hydrocarbons accumulate.

DISCUSSION

LARUE—Spencer Chemical: Did the plant, in question, employ any hydrocarbon analyzers on the inlet air stream or the recycling line? If analyzers were provided, did they operate on a continuous basis?

LANG: In this plant there was no continuous hydrocarbon analyzer. We have recommended arranging for a program of chromatographic analysis, not by an analyzer of an automatic type. The samples for this are taken from the main condenser liquid and occasionally from the liquid in the traps. LARUE: In the recirculation circuit for rich air, is silica gel used in the adsorber?

LANG: No, it's an adsorber of the same type as a rich liquid adsorber, filled with silica gel.

GLASS-Monsanto: Dr. Lang, was there any other guard adsorbers in your circuit that were not shown?

LANG: Yes. These plants have the normal rich liquid adsorbers for the liquid coming from the pressure column to the main column.

GLASS: Are these two units in parallel where you are able to take one out of service for regeneration?

LANG: Two units in parallel, right.

GLASS: What is the frequency of changing or regenerating your beds?

LANG: Normally, one week.

GLASS: Have you had any experience on monitoring the effluent, or both the feed and effluent from these beds, for hydrocarbons?

LANG: I can only refer to some publications which have been made by our company and which I will be glad to send to you if you would be interested. We generally know that there are some hydrocarbons which are not so well adsorbed, but as to butadiene, I remember that we talked about this, and we are of the opinion that this would be adsorbed better than, for instance, carbon dioxide.

GLASS: The question in my mind really is this: although you may monitor or take a sample from time to time on both the feed and the effluent from these beds, a certain surge or a sudden intake can over-range these beds in a very short time. It has been our experience that you have to monitor them quite closely, otherwise you can exceed their capacity and bleed hydrocarbons into your system, and they can accumulate to dangerous levels in your liquid oxygen pool. We monitor both the cold end air and our liquid pool; we do this on a continuous basis in an effort to keep tabs on what's coming in and what's accumulating in our pool.

LANG: Do these questions refer to the recycling adsorber?

GLASS: No, I'm talking about the main rich liquid adsorber. It appears to me that it is very possible that you could have had an over-ranging of your silica gel bed that was in service at the time that you had this event. LANG: I can only say that before these explosions, there have been made, only from time to time, checks for hydrocarbons other than acetylene, because it did not appear necessary.*

GLASS: Do you anticipate installing a continuous analyzer to monitor your system?

LANG: This is not our responsibility. So far as I know, there is a process chromatographic analyzer available, with a flame ionization detector, the instrument which usually is used for these purposes; the only question is where the samples are taken from. My company, as you probably know, has recommended a special type of sampling device, which also has been published by Dr. Karwat and Dr. Klein.

SIMMS—Phillips Petroleum: Dr. Lang, did I understand you to say that the ignition source may have been less than 1/2 part per million acetylene?

LANG: No, I only wanted to say that with even a very low content of acetylene, for instance, not more than 0.01 ppm acetylene in the liquid of the main condenser, if we would boil down this liquid and collect the whole quantity of acetylene which is contained in this, then we would be able to collect some—several grams—which would perhaps have acted as ignitors for this explosion.

*After reconsidering this point, I would like to make the following additional remarks:

It is necessary to distinguish between the poorly adsorbable hydrocarbons as methane, ethane, ethylene, propane, propylene and the adsorbable acetylene.

In <u>Chemical Engineering Progress</u>, Volume 57, No. 4 (April, 1961), p. 43, Dr. Karwat describes a case of a rich liquid adsorber with propane breaking through within a few hours although the adsorber was retaining acetylene for more than one week. According to our experience an adsorber for the oxygen enriched liquid from the pressure column or an adsorber for liquid oxygen generally is an efficient means for removing acetylene, but it is of little use for removing the poorly adsorbable hydrocarbons. The hydrocarbons which are not adsorbed should be removed with oxygen purged from the air separator in liquid state.