AIR SEPARATION PLANT INCIDENT

Unusual occurrence involved reaction in hydrocarbon absorbers of air separation plant.

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A reaction occurred in September, 1967, in the hydrocarbon adsorbers of an air separation plant. In presenting a report on this event, I'm including a specific request that if anyone has experience with similar such reactions that they communicate with the author.

By way of background, the air separation plant was put into operation in late 1956. It is a conventional high pressure cycle system which supplies liquid nitrogen for a hydrogen wash column, nitrogen for the synthesis gas stream, and in addition provides an oxygen stream to facilities across the fence.

Preparing for a turnaround

At the time of the incident the entire facility was being prepared for an annual turnaround. The wash column itself had been shut down. As the oxygen demand across the fence continued, the air plant was still in operation. As this mode of operation produced excess refrigeration, the excess liquid in the low pressure column was being dumped from the plant. The defrost system was being used, as the regular dump system was not sufficient to carry the additional load. This excess liquid was being purged thru the defrost header and then to a vent stack, or candy cane, which is about eight in. in diameter and about 20 ft. high. There was considerable liquid, as it would appear that the candy cane was completely filled and was actually bubbling and spilling over the top. At the same time one of the adsorbers was being reactivated. The reactivation outlet from the adsorber went into the same header and the same vent system as was being utilized to dump the excess liquid from the columns. The outlet temperature on the adsorber was believed to be about plus 50 °F. at the time of the reaction. The nitrogen purity for the reaction was well within bounds. There was no column upset that would have affected the nitrogen purity. Nitrogen purity was also being monitored because this was from the same process stream supplying nitrogen to the syn-gas stream.

Audible, but not noticeable

The reaction was audible to the operators that were there in the plant. Except for the bulging of one of the jacket panels there was no outward physical evidence. The plant operation itself was not affected and the plant continued to operate for several hours before being shut down in an orderly fashion. It was noted that the adsorber reactivation outlet temperature dropped within two to three minutes from the approximately plus 50 °F. to about minus 200 °F.

After the box was opened it was found that the first elbow from the top of the adsorber was ruptured. As the normal feed to the adsorber bottle was from the top downward, the top connection would have been the outlet for the reactivation stream. A visual inspection of the inner surfaces of the elbow indicated heavy washing and loss of metals as from a flame. There was a ductile pipe failure as there was appreciable thinning of the metal and the edges of the failure were very sharp.

The adsorber vessel had a double bulge in the top half that gave it a faint appearance of an hourglass. The maximum bulge was about 7/8ths of an inch on the diameter. The lower half of the vessel was undisturbed. The filter design to keep the silica gel inside the adsorber consisted of a perforated metal tube at both the outlet and the inlet of the vessel which was then backed up on the inside by a fine mesh stainless steel screening. At the top connection this perforated metal tube was completely shattered and pieces were found both inside the adsorber as well as outside in the packing of the box. There was also evidence of the pieces being thrown up into the outlet piping as there were very sharp cuts and markings in the area of the failure of the elbow. The fine mesh screen in this top outlet could not be found at all. At the bottom of the vessel, the perforated metal had been forced downward over the support section for the screening, causing it to split in several places.

Frozen balls were found

One factor that was very important was that when the adsorber was opened up a number of small frozen balls, ranging in size up to about one inch in diameter, were found. These were identified as trichloroethylene. The plant had been solvent washed in 1964 and the silica gel in both of the adsorbers had been changed in 1965.

In considering these various facts, it was speculated that the liquid oxygen being dumped through the vent system had slugged back from the vent header into the reactivation system. The solvent, possibly left in the piping system or in the vent system from the washout in 1964 or possibly in washouts prior to that, had been injected into the adsorber during this reactivation or past reactivations.

The possibility of small hydrocarbon concentrations being formed by the evaporation of the liquid oxygen of course can't be overlooked, although no evidence could be found that this had occurred. A discussion of ignition energy sources would be largely speculation, but it's quite obvious that the pressure and flow in the adsorber at the time of the reaction could be described as very unstable.

Corrective steps taken

With regard to corrective actions that are being taken, the liquid dump from the column or any of the process piping is being completely separated from the vent systems that would be utilized by any of the reactivation systems. The solvent wash procedures set up by the plant are being completely reviewed and revised. The reactivation procedures and maximum outlet temperature are also being reviewed with the possibility of some piping

changes and additional heat to the reactivation.

A dead leg was found in the assembly holding the inlet screening. As this dead leg contained a portion of the screening, it is probable that the designer was trying to reduce pressure drop. However, as the safety problem associated with dry boiling liquid oxygen on each reactivation was considered to outweigh any slight increase in pressure drop, the dead leg was eliminated.

As this, to our knowledge, is the only reaction that has occurred in a hydrocarbon adsorber, we'd be particularly interested to know if anybody else had experienced a reaction of this type.

Discussion

Q. What do you think was the major fuel that participated in the reaction?

BALL: As there was considerable solvent left after the reaction, it would appear probable that the solvent was the main fuel present. The possibility exists of some other hydrocarbons being left or deposited in the adsorber because of the oxygen being slugged into the warm bed evaporating and leaving a residue behind. The very unstable pressures and flow conditions in themselves could have been the energy source necessary for ignition.