

# LIQUID OXYGEN DISPOSAL VESSEL EXPLOSION

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Symposia on air separation and ammonia safety at these A.I.Ch.E. National Meetings during the past seven years have attracted wide general interest and industrial participation.

Detailed presentations of air separation plant explosions have brought a new awareness to safety hazards of compression systems, notably reciprocating air compression systems, and the urgency for detection and control of hydrocarbon contaminant concentrations in oxygen rich streams. At Monochem we believe that we have benefitted substantially by the relatively free exchange of information on these subjects in these meetings. It has unquestionably influenced our plant design criteria and our operating procedures such that we have a far safer operating plant than would otherwise have been the case.

I would like to be able to say that we have capitalized 100% on these published incidents and have experienced, therefore, no foreseen or unforeseen safety incidents of our own. My presence here obviously speaks for the fact that this is not the case. The incident which I will detail to you shortly occurred only very recently in our tonnage oxygen plant. We believe it to be of interest because (1) it involved an explosion or detonation of hydrocarbons and (2) it occurred in what is generally accepted to be a well-designed liquid oxygen disposal system, under conditions which have not previously been recognized to give cause for concern over safety.

## Process design

The process design of our oxygen plant is not unusual. In fact, it is rather typical of that used in many recently designed low pressure tonnage oxygen plants. Most of those present, I am sure, are familiar with the general process design. However, for the benefit of those few who are not, I'll take a moment here to point out some of the highlights which are related to this incident.

Figure 1 depicts only the major vessels and streams involved. Many of you will note, for example, that all the subcoolers have been omitted.

Air from our centrifugal air compressor delivers air to a packed column (1); here it is cooled by direct contact with a recirculated stream of cooling tower water. The compressed ambient temperature air then enters the cold box through a set of reversing heat exchangers (2). These serve to cool the incoming air to near its dew point by countercurrent heat exchange with outgoing cold process streams. Reversing

passages are provided for the air and waste streams only. All other process streams flow through fixed passages.

Air near its dew point enters the high pressure column (3). Here it is fractionated into an overhead stream of relatively pure nitrogen, which is either condensed for reflux or used as "unbalance nitrogen" which is then expanded through the turboexpander (4) to provide the refrigeration required by the process.

The bottom stream from the high pressure column is rich liquid; it is this stream in which the hydrocarbons first concentrate. The rich liquid is passed through silica gel adsorbers (5), called rich liquid filters which serve to remove the hydrocarbon contaminants, notably ethylene and acetylene.

The rich liquid then enters the low pressure column (6) where it is fractionated to an overhead pure nitrogen stream and a bottom pure liquid oxygen stream. The pure liquid oxygen is pumped through the main condenser-reboiler (7) where it is partially vaporized to provide the vapor boil-up for the low pressure column. The main condenser-reboiler simultaneously condenses nitrogen as liquid reflux for the high pressure column.

A portion of the liquid oxygen not vaporized is sent to an auxiliary condenser-reboiler (8) where 98 to 99% is vaporized to become the product oxygen stream

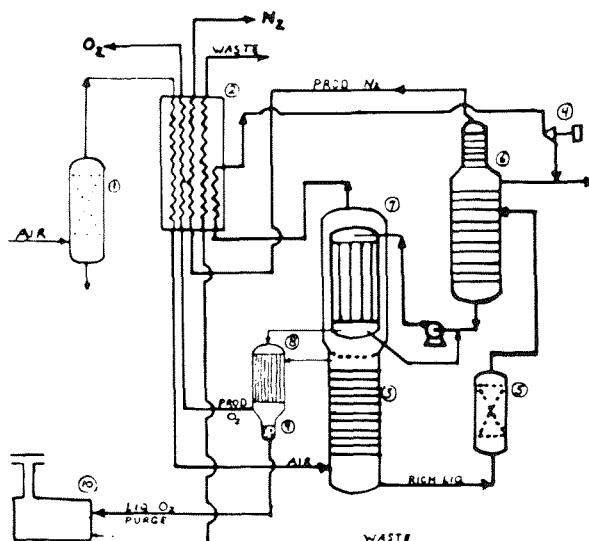


Figure 1. Simplified process flow diagram.

having 98 to 98 1/2% purity. The 1 to 2% liquid oxygen which remains unvaporized contains concentrated hydrocarbons; it flows into the separator (9) from which it is continuously purged to the liquid oxygen disposal tank (10).

## Sequence of operations

The incident which I am here to report occurred within the liquid oxygen disposal tank. It occurred during the first part of a regeneration of a rich liquid filter. The sequence of operations which preceded the explosion are as follows:

1. The rich liquid flow was redirected from the "A" rich liquid filter to the spare "B" rich liquid filter.
2. The liquid contents of the "A" rich liquid filter were drained and vaporized in the liquid oxygen disposal tank.
3. A flow of approximately 200 std. cu. ft./min. of heated nitrogen was established in a downward direction through the "A" rich liquid filter and out the purge header to the liquid oxygen disposal tank.

One should note here that meanwhile a small continuous purge of liquid oxygen was also flowing from the separator to the liquid oxygen disposal tank. Its weight rate of flow approximately equalled that of the regeneration nitrogen.

After approximately two hours the normal liquid level in the separator was lowered to a minimum by increasing the rate of flow of liquid which normally flows from the separator to the liquid oxygen disposal tank. This action is a routine function preparatory to a one per shift deliberate flushing of the auxiliary condenser-reboiler. (In explanation, the latter involves the rapid dropping of about 1% of the liquid level in the main condenser-reboiler, so that sufficient liquid oxygen will flow through the auxiliary condenser-reboiler to well irrigate all the tubes. We hope that this procedure accomplishes the flushing out of any hydrocarbon deposits which may inadvertently collect in the auxiliary condenser-reboiler, for example, in tubes which unintentionally run dry.)

At the time when the separator level had reached the minimum an explosion occurred. Inspection disclosed that the explosion was confined to the outer end of the liquid oxygen disposal tank. Quite fortunately there were no personal injuries, and the cost of repairing the physical damage was minor.

## Engineering sketch

Figure 2 shows an engineering sketch of the liquid oxygen disposal tank involved. Superheated steam enters at one end through a sparger nozzle located beneath a corrugated tray. In the figure, the corrugated plate slants downwards from the left towards the right and the sparger steam nozzle is located beneath it at its upper end. Steam flows under the full length of the corrugated tray before passing to the atmosphere with vaporized oxygen through a vertical T-shaped stack. Liquid oxygen to be vaporized enters at the end of the vessel opposite the stack and must flow downward the full length of the sloped corrugated tray. Steam is always flowing at a rate sufficient to fully vaporize the liquid oxygen. Although some steam condensate does form, it is not present in sufficient quantity to become materially significant either at the drain point indicated or as droplets falling out of the gas emitting from the stack. We believe that

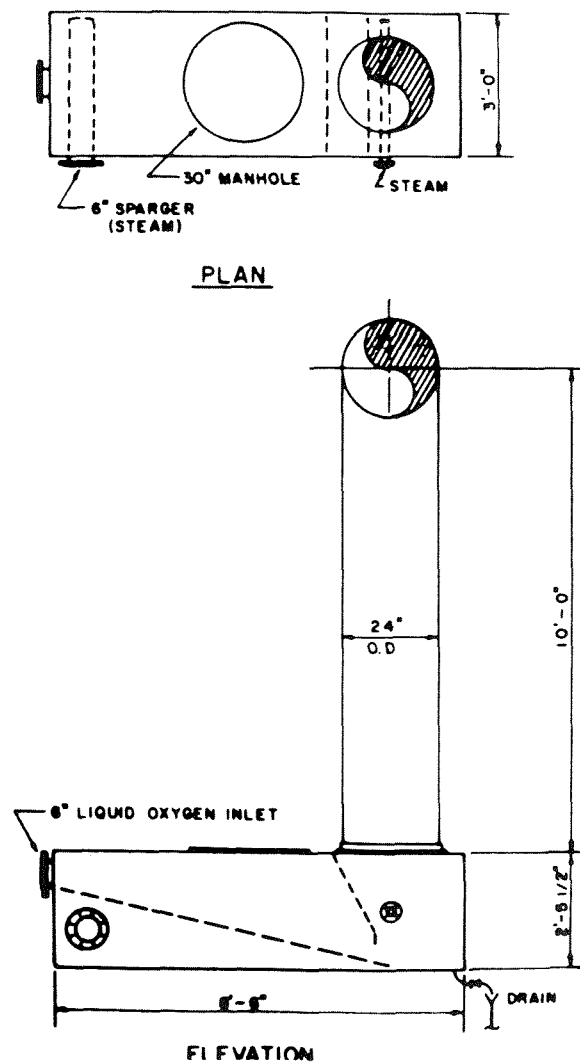


Figure 2. Engineering sketch of the liquid oxygen disposal vessel.

this liquid oxygen disposal tank design, or variation thereof, has been generally assumed to be safe for disposing of liquid oxygen heavily contaminated with hydrocarbons, particularly acetylene.

## Repaired unit

Figures 3 and 4 are pictures of the liquid oxygen disposal tank after it was repaired. Figure 3 is a view from the end that was ruptured. The weld line for the channel that holds the corrugated plate is visible, slanting from the right to the left. Figure 4 is a view from the opposite side. You can see the steam header and the frosted oxygen line entering the disposal tank. The tank is located a safe distance from the control room. The cold box is between the control room and the tank.

Figure 5 is two pictures of the tank as it appeared immediately after the explosion. Note that the rear end has blown out, but the vessel as a whole is relatively undamaged. There was no significant damage to the T-shaped stack, to the vessel sides, or to the bolted manhole cover. There was also no important damage to the corrugated tray, but it was deformed sufficiently to force its lower end downwards and out of the retaining side rails. The baffle is completely missing.

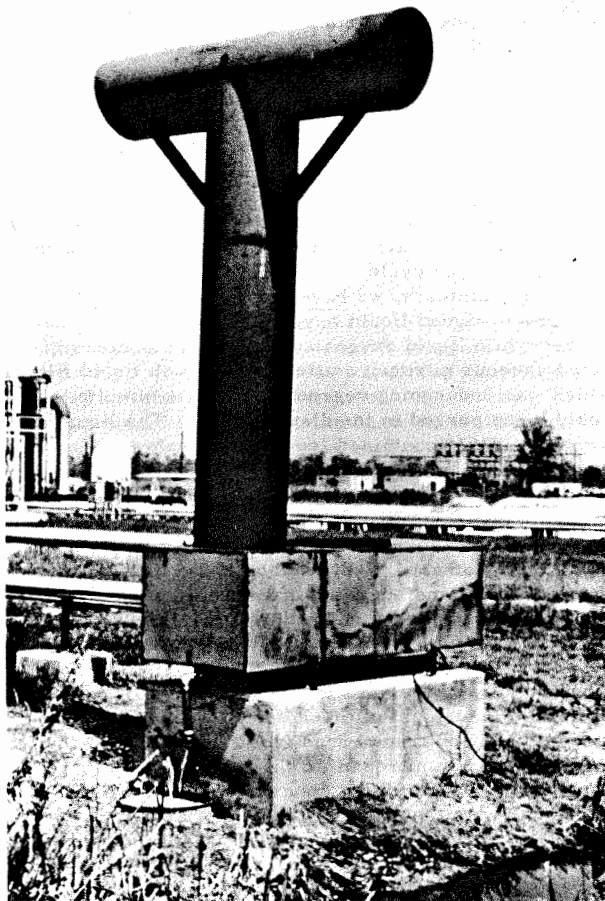


Figure 3. View of liquid oxygen disposal tank from the end that was ruptured (after repair).

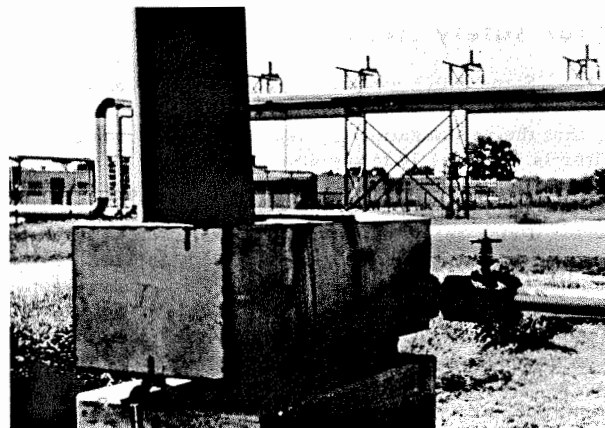


Figure 4. View of liquid oxygen disposal tank from opposite end (after repair).

## Detonation Source

From these observations we have concluded that the explosion occurred at the lower end of the corrugated tray, that it probably was in the form of a detonation and that the explosion force was directed primarily in line with the flow of steam and vaporized oxygen, at right angles to the stack, towards the end of the vessel.

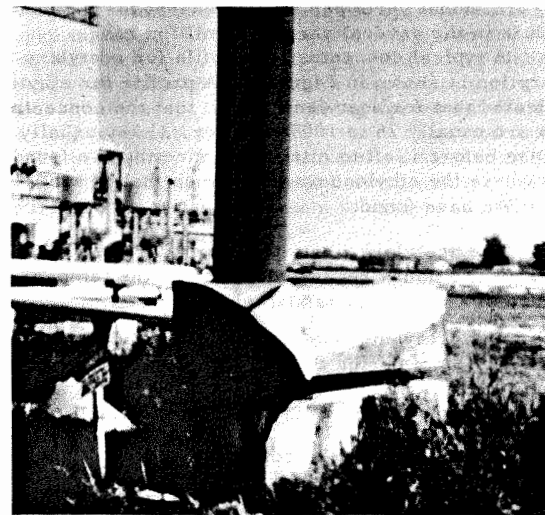


Figure 5. Two photographs of tank as it appeared immediately after the explosion.

The obvious postulation that could be made from this incident is that the source of the combustible hydrocarbons was the regeneration gas stream and that the ignition was made possible because it was brought into contact with a stream of liquid oxygen on a hot plate. We offer no other explanation. However, our analytical data indicate that the hydrocarbon concentrations were very likely surprisingly low and of sufficient interest to comment upon.

## Hydrocarbon content

A question for which we have a very good answer is what contaminant concentrations were present in liquid oxygen which was being continuously purged from the separator? Fortunately we had a hydrogen flame chromatograph that was analyzing this stream every 9 to 11 min. for parts per million content of hydrocarbons. Analyses recorded for several hours before and after the explosion were within limits of normal operation. These limits are listed in Table 1. These concentrations in themselves are so low as to at least generally be accepted as giving no cause for concern.

What then was the hydrocarbon content of the purging regeneration gas? Quite frankly we don't know. However, we have since analytically monitored

TABLE 1. HYDROCARBON ANALYSIS FOR PURGE LIQUID OXYGEN.

Constituent	Concentration, ppm
Methane	10-40
Ethane	1-10
Ethylene	< 0.1
Propane	0.1- 5
Acetylene	< 0.05
Propylene	< 0.05
Butane	< 0.2

a number of subsequent rich liquid filter regenerations, and now have at least some idea as to what the contaminant concentrations might have been at the time of the explosion. Time does not permit a complete presentation of these data. Suffice it to say we have found the concentrations of all other components other than acetylene and ethylene to be apparently insignificant, being fractional parts per million except for methane which is in the several parts per million range.

A typical concentration profile for acetylene desorption is shown in Figure 6. A profile for ethylene duplicates that for acetylene except that the concentrations are usually 25 to 100% greater. (I say usually because before I left to attend this meeting, we found a case where the ethylene was ten times that of acetylene.) We have found:

- (a) that the acetylene first appears in derime gas after about two hours regeneration, while the temperature of the exit gas is still about  $-290^{\circ}\text{F}$ .
- (b) that the acetylene concentration rises to a peak of 20 to 50 ppm during the next 30 to 40 min. and then tails off slowly to a nondetectable level in about 4 to 5 hr.

The peak acetylene concentration occurs approximately when the exit derime gas temperature is about  $-170^{\circ}\text{F}$  to  $-200^{\circ}\text{F}$ . Surprisingly to us, the acetylene concentration is still several parts per million even when the exit regeneration gas temperature has increased to  $0^{\circ}\text{F}$ .

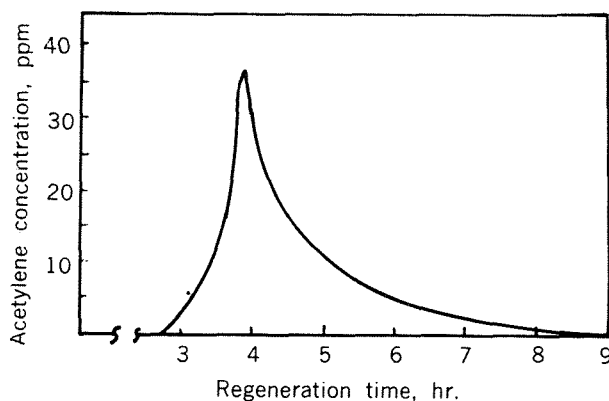


Figure 6. Typical concentration profile for acetylene.

## How does the data fit

How does this data fit with the known condition of regeneration at the time of the incident? The regeneration had proceeded for a sufficient time for acetylene and ethylene to appear in the exit regeneration gas stream. While we do not know the exact temperature of this gas at the time of the explosion, we did record its temperature shortly thereafter as  $-250^{\circ}\text{F}$ . Referring to our data for the subsequent regenerations, we have found no case where the acetylene concentration was greater than 7 ppm at that point in the regeneration cycle.

In summary, we have experienced an explosion in a well designed liquid oxygen disposal tank. It occurred while liquid oxygen and hydrocarbon contaminated gaseous nitrogen exiting from a rich liquid filter which was undergoing regeneration while simultaneously being purged to the disposal tank. The liquid oxygen initially contained less than 50 ppm total hydrocarbons and at most only parts per billion unsaturated hydrocarbons. The regeneration gas probably contained less than 7 ppm acetylene, less than 20 ppm ethylene, and negligible other hydrocarbons other than methane. Hydrocarbon concentrations of these two streams suggests that the liquid oxygen actually being evaporated on the hot corrugated tray of the disposal tank could initially have contained, at most, several parts per million acetylene and ethylene; and this, of course, would necessitate that a substantial portion of the weight of these components in the gas stream had been transferred from the gas phase (exiting regeneration nitrogen) to the liquid phase (purge oxygen) while they flowed concurrently through the purge piping to the disposal tank. The explosion occurred then under conditions of very low hydrocarbon concentrations in liquid oxygen, concentrations which are not unusual for many air separation plants, particularly those located near areas heavily populated with petrochemical plants, particularly acetylene plants.

## Prior safety steps

Steps which we have taken to prevent a recurrence of this incident are: (1) piping modifications so that the regeneration gas leaving the rich liquid filter is fed directly to the atmosphere or alternately to the stack of the disposal tank; (2) improved electrical grounding of the liquid oxygen disposal tank.

Prior safety steps worthy of mention were: (a) instrumentation design to permit, remotely within the control room, operation of the valve which dumps purge liquid oxygen from the separator, (b) location of the disposal tank away from the operating area and in such orientation that in the event of an explosion flying debris would be away from the area where an operator might normally be standing.

In conclusion we recommend that all others operating air separation plants review their purging procedures so as to be sure that they are not unintentionally incurring conditions in their disposal systems which in view of our explosion incident could be considered hazardous.

## DISCUSSION

SVOBODA—Dow Chemical: We have a similar installation. Our oxygen purge comes from an oxygen separator where the hydrocarbons build up to 150 to 250 ppm, primarily methane, ethane, and some propylene and ethylene. I would suggest that you check your steam source. Can you feasibly get oil in the steam from your steam-generating source which drops out in the disposal tank? We solvent wash the disposal tank by totally flooding it with chloroethane or some other similar solvents anytime the air plant is down for derime.

BOYNE: My only comment might be that there was not a visible evidence of carbon deposits lying on the bottom which would have led us to believe that oil had collected underneath the corrugated tray. Second, and I am guessing, had this been the case, it would have been more likely that the corrugated tray might have been blown upwards rather than downwards.

I think that point, although I went over it very quickly, is of sufficient interest to be stressed. The corrugated tray was blown downward at its lower end and the wave front travelled primarily in line with the stream flow. The manhole that is on top of this vessel would have taken very little pressure to have blown it loose. The sides of the vessel just bulged somewhat. The damage is all in one end, in one direction.

I might add to my report here that our routine analytical procedure, this chromatographic method,

essentially never shows any acetylene to be present in the liquid leaving the separator. The rich liquid filters are taken off-stream for regeneration every four days, which may be a shorter cycle than others practice, but this has been an excellent way of our keeping acetylene from getting past them.

We have calculated the average concentration of acetylene in the incoming air which would correspond to that found in the regeneration gas stream during the period of regenerating the filter. You may be surprised to learn that this number is only 3 ppb.

ANDRES—Canadian Industries: Have you done anything about changing the rate of regeneration on the derime of these rich liquid filters in the early part of the cycle?

BOYNE: No. In the particular incident, when we had the explosion, we were deriming with nitrogen which was heated from the beginning of the cycle. Heating the nitrogen is not our normal procedure, but was the case during this incident. We have repeated heating since, and find very little change in the concentration of hydrocarbons except that everything comes out faster when the regeneration nitrogen stream is heated from the very beginning. We find that the hydrocarbons first appear in the exiting regeneration stream at the same temperature level and also seem to disappear at about the same temperature.