SAFETY IN DISPOSAL OF LARGE QUANTITIES OF LIQUID OXYGEN

T. Ŗ. McMurray Linde Co., Div. of Union Carbide Corp. Tonawanda, New York

The major hazard covered in this article is encountered because of oxygen's affinity for hydrocarbons. The hydrocarbon hazard is not confined to external sources of contaminants alone. The reason for disposing of the liquid may be a high hydrocarbon concentration within the oxygen of the main reboiler itself. The A.I.Ch.E. "Questionnaire on Air and Ammonia Plant Safety" indicated the industry's average shutdown limits were 1.4 ppm acetylene and 290 ppm of other hydrocarbons. At these limits, which are considerably above what the author considers to be best practice, a total of 12 pounds of hydrocarbons would be present in a reboiler containing 800,000 cu. ft. NTP of oxygen. These hydrocarbons have a total heat of combustion approximately equal to the contained energy in 75 pounds of nitroglycerine. While it is improbable that total combustion of these hydrocarbons would occur, it may readily be seen that care must be taken to prevent their concentration and detonation, and above all, to avoid providing additional fuel from external sources.

This problem is not limited to the disposal of liquid oxygen alone. In the draining of oxygen-rich liquids, or even air, slow evaporation in a "pot" will gradually enrich the oxygen content. Oxygen purities above 98% are readily attainable, as the last liquid vaporizes, if the boiling is slow enough for equilibrium conditions to exist. Thus, the mere presence of nitrogen in the liquid does not eliminate the hazard or permit careless disposal techniques. On the contrary, where transfer line gel traps or their equivalent are used, the oxygen-rich liquid taken before the traps may present a far greater disposal hazard than the clean liquid oxygen from the reboiler. This greater hazard being created by concentrating both the hydrocarbons and the oxygen as the liquid evaporates.

Drain line design

The first item in any liquid disposal system that must be considered is the design of the liquid drain piping from the main oxygen reboiler or other vessel to the point of liquid disposal. There are a few general considerations to be kept in mind during the design of this piping. Drain valves should be leak tight to prevent maintaining an oxygen atmosphere within the pipe where there may be accumulated hydrocarbons from previous drainage. For the same reason, provisions must be made to purge the line with nitrogen following operation and, in multiplant installations, continuous purging is recommended. Gare must also be taken to ensure that valves, safety devices, and piping do not become inoperable through freezing and plugging with ice.

Oxygen drain lines should preferably be run outside of buildings or other confined spaces to minimize the danger of oxygen concentrations in the event of a leak. The piping should be routed away from walkways, roadways, and other areas that will be frequently utilized by operating personnel. It should not be run in a piping trench but rather above a surface of concrete or clean gravel so that the area around it may be maintained free of combustible materials. It should be installed with a downward slope from the outside face of the cold box to the vaporizer. This will minimize the formation of liquid pockets in which hydrocarbons might collect following the disposal of oxygen.

The piping must also be mechanically suitable for the service for which it is intended. The piping should be designed for the maximum working pressure of any vessel connected into the drain disposal system. It should be fabricated from materials that are suitable for the low temperature service and, wherever possible, welded or brazed joints are used throughout the piping. Soft solder is not permitted because of its tendency to develop leaks. Mechanical joints of all types, such as screwed or flanged joints, are minimized as they are also a potential source of leaks. Expansion joints and flexible hoses are avoided by using flexible pipe configurations that will withstand the full temperature cycle within acceptable design stresses. The piping and drain valves should be adequately supported throughout and protected from sources of mechanical damage.

Vaporizer design

Several methods of disposing of the liquid oxygen have been tried in the past years by Linde Company including the use of large tanks, gravel-filled drain "pits," and various styles of heat exchangers. While clean tanks may be considered a safe means of holding the liquid until it vaporizes from natural or supplied heat leak, under some conditions the gradual concentration of hydrocarbons, particularly acetylene, can make this method potentially dangerous. This hazard is more serious with contaminated oxygen-rich liquids since the slow boiling increases both the oxygen and hydrocarbon concentrations. This method has had a fairly good service record, but it should be avoided where possible.

The hazard of slow vaporization of liquid within a tank can be eliminated by filling it with clean gravel.

CUTAWAY VIEW OF DIRECT CONTACT STEAM VAPORIZER



Figure 1. Cutaway view of direct contact steam vaporizer.



Figure 2. Oxygen vaporizer with direct steam contact.

The large mass of gravel provides heat to quickly flash oxygen at a relatively warm temperature and avoids the accumulation of acetylene. The gravel bed must be sized to vaporize the maximum quantity of liquid to be drained, as otherwise its benefit will be lost. This method has worked very well for both clean oxygen and contaminated oxygen-rich liquids. Needless to say, where both liquids are handled, separate gravel beds must be provided for each to prevent oxygen from contacting oil or other residues from the contaminated rich liquid. The main drawback of this type of vaporizer is that it is relatively hard to keep clean from atmospheric contamination. For this reason, as well as to avoid combustible residues on the gravel, the bed must be changed and the tank cleaned regularly.

The best method

The best method of vaporizing liquid oxygen is in a vaporizer in which the oxygen is flashed to gas at ambient or higher temperature. This ensures that the hydrocarbons, and especially acetylene, are also vaporized instantaneously and cannot accumulate to hazardous proportions. The heat exchanger in Figure 1 is a direct contact steam vaporizer. It is essentially a tank containing a spiral baffle and a large gas outlet at the top. Steam is admitted at the bottom of the spiral baffle and flows upward through the vaporizer. Liquid oxygen is admitted on top of the baffle and attempts to flow down countercurrent to the steam. The oxygen is



Figure 3. Oxygen vaporizer in operation.



flashed on contact with the steam and flows through the top outlet and up the stack. Openings at the bottom of the stack provide entry for approximately 1 cu. ft. of air for every cu. ft. of oxygen vaporized. Thus, the oxygen is diluted to a 60% oxygen mixture before entering the atmosphere. This vaporizer is normally supplied with 150 psi saturated steam, in quantities up to 5,000 pounds per hour. At this steam rate, the vaporizer will handle 400,000 cu. ft. (NTP) per hour of liquid oxygen, discharging it to the atmosphere at essentially ambient temperature.

Direct contact

In operation, the steam is turned on and the vaporizer is heated to steam temperature. At this point, liquid oxygen is admitted to the system. A temperature switch is provided in the bottom head of the vaporizer and the liquid oxygen flow is automatically stopped should the temperature at this point fall below 125°F. Thus, it would be impossible for liquid oxygen to form a pool within the vaporizer or to leave by the condensate drain. In practice, very little condensate drains from the unit as the high internal velocities entrain it with the vaporized oxygen.

A picture of a typical direct contact steam vaporizer installation may be seen in Figure 2. In this, the steam line will be seen entering the bottom right of the vaporizer and the liquid oxygen line at the top. The temperature indicating bulb and control, and air admission ports in the stack, are also shown. Operation of this unit is shown in Figure 3, and it will be noted that the high velocities blow the oxygen considerably above the top of the stack before it is mixed with the atmosphere.

Recommended system

The recommendations presented above for the safe disposal of large quantities of liquid oxygen can best be summarized by referring to Figure 4. On this, it will be noted that the liquid drain line is conventionally trapped within the cold box to prevent the liquid standing against the casing wall. Once outside the casing, it passes first through a control or drain valve for regulating the flow of liquid to match the steam rate in the vaporizer. Following this is the automatic shutoff valve controlled by the temperature bulb within the vaporizer. The line then slopes down to the vaporizer which is kept remote from normal operating areas.

The vaporizer is installed above grade for cleanliness of its surroundings, hence a vertical rise in the drain line cannot always be avoided. Where it must be used, the rise is located adjacent to the vaporizer to minimize trapped liquid and keep it away from operating personnel. The liquid in this pocket is subsequently vaporized by purging the drain header with warm nitrogen.

The normal 150 psi steam supply is regulated to below the design pressure of the vaporizer and, in the event of a steam failure, the temperature control will prevent draining liquid oxygen. After vaporization, the oxygen is diluted with air and vented at an elevation well above any surrounding equipment. This system has been used in many Linde plants and permitted rapid disposal of large quantities of liquid oxygen without danger to operating personnel.

DISCUSSION

<u>VANWINKLE</u> — American Oil: I take it that you don't use this type of device for continuous purging of small quantities of liquid oxygen?

<u>MCMURRAY</u>—Linde: No. As Mr. Shaner mentioned this morning, we recirculate liquid in our reboiler through silica gel. We do not purge. If you wanted to do it on a continuous basis, I see no reason why you couldn't run out an insulated line.

VANWINKLE: You don't usually insulate lines that well.

MCMURRAY: It depends on how much you are trying to drain. On a very small plant, this is probably quite true—that you couldn't insulate it that well. But as long as you had a liquid flow through the system, I wouldn't see that you would concentrate hydrocarbons.

SEFTON: What is the temperature of the effluent at the top?

MCMURRAY: It is above 32 F. We can tell that because when you drop below, you get a snow storm.

SEFTON: Is there any possibility that you might get a cold "zone" in the vaporizer at say minus 150 or below?

MCMURRAY: The oxygen inlet is certainly at liquid temperature, but no liquid pool can form due to the physical configuration. At the bottom of the vaporizer, the temperature is above 125°F hence, no liquid pool can form to concentrate hydrocarbons.

ANONYMOUS: How do you control the oxygen flow to the vaporizer? Do you insulate the drain line? If not,

do you require high pressure or pumps to force the liquid through the vaporizer?"

MCMURRAY: We open the steam valve wide and control the oxygen flow manually to match. We don't normally insulate the line. There is no need to on an intermittent basis. It would only be if you want a continuous drainage for some purpose. As far as getting enough pressure to drive it out, the only restriction you have is a four-foot vertical rise which in liquid oxygen would be about two pounds. So any pressure source of about four or five pounds on your "thaw" system is enough to drive your liquid out.

<u>BOLLEN</u>: Is this a patented design and, if so, is your company marketing this device?

MCMURRAY: As far as I know, there are no patents on it. We are not selling it.

BOLLEN: And there is nothing to stop anyone from making up a similar type of vaporizer?

MCMURRAY: No. Not as far as I know.