SAFE HANDLING OF OXYGEN IN HYDROCARBON SYSTEMS

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The purpose of this paper is to discuss an incident that took place at the Brandenburg-Doe Run Plant in one of our hydrocarbon oxidation units about a year and a half ago. The area of the occurrence was in the mixing chamber where oxygen is added to a process stream prior to the oxidation step. The mixing of oxygen and hydrocarbons has always presented an interesting challenge to designers and instrument engineers. From the standpoint of the mixing chamber design, one must obtain a high degree of turbulence so that potential eddying or small gas pockets are eliminated completely.

Control of oxygen concentration must take into account a specific knowledge of the system with which one is dealing, particularly with respect to its flammable envelope characteristics. Safe operation is achieved only if one operates outside of this envelope. Generally speaking, in oxygen systems one operates below the flammable envelope or limit. However, in some cases, operations are controlled above it.

Process sensing points

Most oxidation processes have one or more process sensing points which are used to control the oxygen flow, or, in extreme cases, are used to initiate a complete shutdown of this flow. Typical control instrumentation could involve chromatographic equipment. This could be either in the form of continuous field chromatographs similar to those that have been discussed in other air plant applications, or they might involve periodic sampling by the operating unit and submission of the sample to a control laboratory. Some operations also use orsats. Whatever the sensing mechanism might be, it all amounts to about the same— you must control your oxygen concentration relative to the mixture into which you're injecting it.

In the event that a process monitor dictates a complete shutdown of the system, it generally should be accomplished automatically. It is important that when a shutdown is indicated, all valves in the shutdown system function reliably and quickly. For at that stage absolutely no further flow of oxygen should be tolerated into the hydrocarbon stream.

In general, therefore, it can be stated that from a safety standpoint the success of an oxidation operation depends upon the controlled addition of oxygen into a flammable hydrocarbon stream. Obviously, a certain degree of danger is associated with operations of this type, even though reactant rates are controlled so that the oxygen content is always out of the flammable envelope.

Elaborate mixing devices

In order that maximum safety in plant operating areas might be maintained, elaborate mixing devices or systems are used such as one which will now be described, Figure 1. One can see from the diagram that oxygen is regulated by means of the flow recorder that receives its impulse from a process signal.

Mixing devices may vary in design, however their functions are all similar in that they provide a means of injecting oxygen into a turbulent hydrocarbon stream, thereby insuring efficient mixing. A multiplicity of orifice- or nozzle-type injectors are usually involved. The orifice or nozzle is sized so that a specific pressure differential exists between the oxygen and hydrocarbon side. This pressure differential is monitored by suitable instrumentation which activates a shutdown of this entire station if the oxygen pressure drops or approaches the hydrocarbon pressure. Usually the process has other monitors which sense trouble within the oxidation unit itself, which also activate the complete shutdown system.

This particular system is a generalization of others that have been reported in literature: J. M. Robertson of the Celanese Corp. reported a system very similar to this in a December, 1960, Chemical Engineering Progress article. Obviously, each system has differences which are tailored to meet its specific process needs. But in general they all function in a similar manner.

Functioning of shutdown system

Whenever a shutdown of the system is activated, both oxygen feed valves (Nos. 1 and 2 in Figure 1) close and the vent and inert sweep valves (Nos. 3 and 4, Figure 1) open. The inert sweep prevents hydrocarbons from backing into the oxygen line, and the vent provides a double block and bleed to insure complete isolation of the oxygen and hydrocarbon systems.

In addition, manual block valves (Nos. 5 and 6) on either side of the control valves are closed by the operator in charge of that particular area after each "fail safe" shutdown, to insure the isolation of the oxygen and hydrocarbon systems.

Let us stop a moment and look more specifically at the relative timing of the above-mentioned valves. Let us assume for the purpose of the discussion that for one reason or another the source of oxygen becomes marginal. This would be sensed, in this particular case, by a drop of differential pressure across the mixing system (D/P cell, No. 7). As the dif-

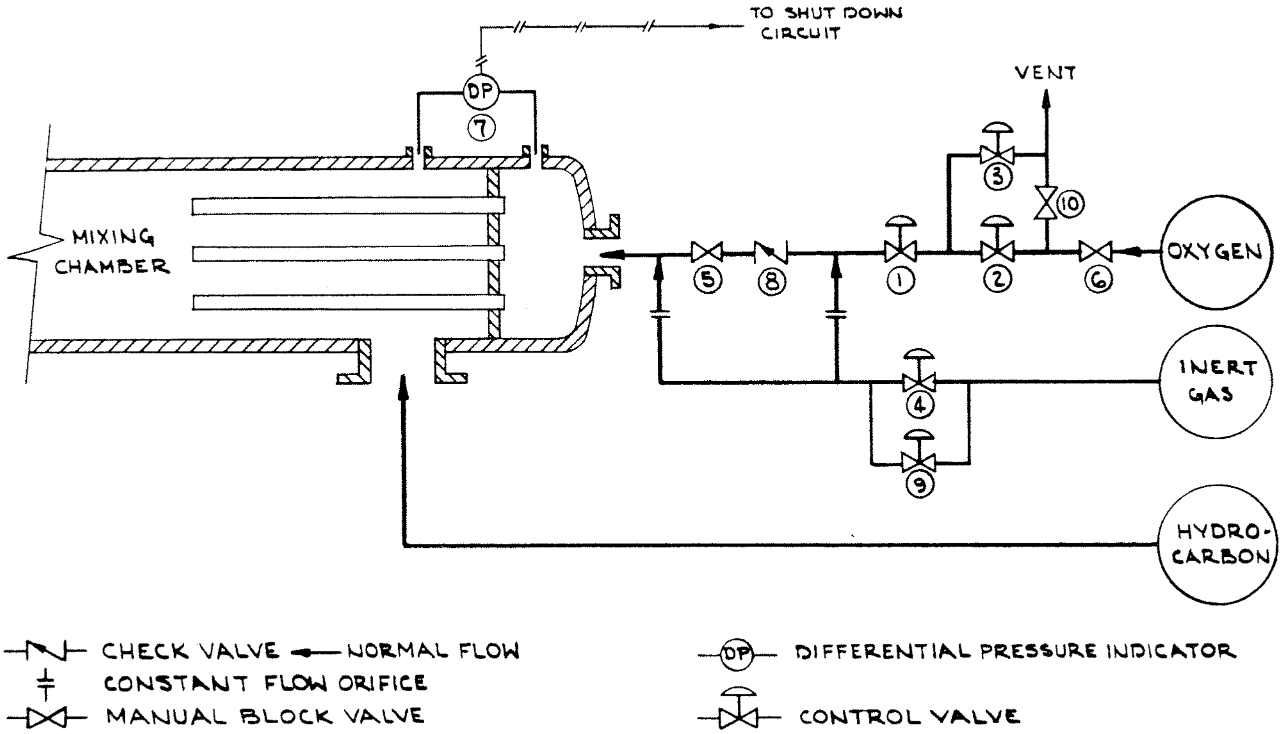

Figure 1. Typical oxygen mixing station and related control valves.

ferential pressure between the oxygen and hydrocarbon systems drops to some preset level, the shutdown system would become activated and valves Nos. 1 and 2 would quickly close. The reliability and speed of these valve closures is extremely important. The vent valve (No. 3) would then open to insure an area of no pressure between the oxygen and the hydrocarbon supply. Next, inert gas purge valve (No. 4) would open, allowing an inert gas (nitrogen, steam, or any other compatible material) to automatically purge the region just downstream of the last block valve (No. 1), thus, insuring a positive flow into the mixing chamber which in turn prevents a backflow or edding of hydrocarbons into the oxygen feed system.

Explosion involving mixing station

As previously stated, in December, 1962, an incident occurred at the Doe Run plant that involved an oxygen mixing station similar to the one just described. Our control operator detected a drop in oxygen flow which caused the mixing station differential pressure to drop. The process shutdown system was activated and a routine shutdown should have followed. In this particular case, several minutes after the shutdown presumably was activated, an explosion occurred in the area of the mixing chamber. Other related pipe lines containing flammable materials ruptured, thus, adding additional fuel to the ensuing fire. The fire lasted approximately 30-45 minutes.

Timely efforts by the plant fire crew contained the fire to that specific area. The resultant damage consisted primarily of the following:

1. Spalling of the reinforced concrete structures.
2. Considerable insulation damage.
3. Complete gutting of all the pneumatic and electronic lines in that area.
4. Little or no mechanical equipment damage outside of the mixing chamber and the associated control valves.

Review of all aspects

An investigation team was chosen to review all of the aspects of the mishap and to see whether or not they could piece them together and come up with a logical explanation of why the failure took place. One of the team's observations was that the oxygen flow to the mixing chamber had dropped off for no apparent reason prior to the explosion.

In this particular case, when the oxygen flow dropped back, the operator in charge made an immediate check of the oxygen compression system. It was found to be in order, yet the oxygen flow continued to drop. An automatic shutdown of the system followed. This should have resulted in the opening of the vent and the inert gas purge valves along with the closing of the two oxygen valves. However, within a short period of time after the shutdown sequence had been started, we experienced the explosion and fire.

A review of the equipment after the mishap indicated that the instrument air lines to the vent valve were damaged, (tiny pin holes). Also check valve No. 8 (Figure 1), which gives additional insurance in the double block and bleed system, was found to be inoperative due to excessive wear of the internal hinge, thereby, allowing the check or clapper to drop down below the seat face in the valve body. This situation then allowed a potential hydrocarbon backflow condition to exist.

Theory of explosion

In attempting to pinpoint the specific cause of the explosion, the following theory was advanced: A partial failure in the instrument air line to the vent valve permitted it to open partially. Let us now follow through with this assumption for a moment and picture the consequence. One can easily see that oxygen would leak out through this vent unnoticed. This condition could then become severe enough to the point where all of the available oxygen was passing out through the vent valve. Under these conditions, one could experience the drop in oxygen flow observed above. This in fact could have allowed a slight backflow of hydrocarbon into the oxygen piping. It is felt that this might have permitted a condition whereby the reaction was allowed to take place within rather than outside of the flammable envelope. Further it is felt that a small explosion or detonation occurred which ruptured the lines, thereby, supplying large quantities of fuel.

As a result of our investigation, several changes were made to the shutdown system. Let us again look at the purging system for a moment (Figure 1). The inert gas sweep system now employs dual control valves. Originally we had a single control valve which was activated by the shutdown control system. Also, there was a rotameter in parallel with the control valve, which an operator could manually activate if he was experiencing a low flow condition. This inert supplement was used, if in the operator's or supervisor's opinion, he was not experiencing adequate flow velocities in the mix chamber. This, you will note, then left it entirely up to the discretion of operations.

Rotameter use

There was evidence in reviewing these circumstances and others that this rotameter was not used as often as it might have been in the past. It was, therefore, decided to add control valve No. 9 in place of the rotormeter and interlock it with the oxygen flow. With this scheme, any time the oxygen flow drops down below a predetermined level, control valve No. 9 opens and a supplemental sweep is introduced. If a shutdown situation were to develop, both sweep valve No. 9 and the original valve No. 4 would open.

Another change that was made was in the action of vent control valve No. 3. The initial concept was that all valves would be simultaneously activated. However, let us assume for a moment that vent valve No. 3 is extremely fast and that oxygen control valves Nos. 1 & 2 are relatively slow. In this case, whenever a shutdown condition occurs, an area of low pressure is created in the oxygen pipeline, thereby, causing a possible backflow or "hiccup" of hydrocarbons back into this feed system. It was felt that this was potentially an undesirable situation. Therefore, a time delay mechanism has been introduced into the vent valve (No. 3) operation scheme which holds it closed until oxygen valve No. 1 is fully closed.

As a further safeguard, a position indicator has been added to No. 3 vent valve stem. In this way, an inadvertent opening of the valve may be detected and consequently can trigger a fail safe shutdown.

Speed of valve operation

A review of the speed with which these valves operated indicated that they were relatively slow. As indicated earlier, the reliable closure of these valves and a rapid response time is extremely important. Let us now consider a typical diaphragm control valve. These valves originally operated from a full-open to a full-closed position in 8 or 9 sec.—not bad for normal control applications, but no good for this application. These valves were modified to varying degrees so that response times could be shortened.

Pad gas pressure at the top of the diaphragm might normally be about 40 lb./sq.in. gauge. One of the first things we did was to use larger buffer springs to give a quicker snap action or response time. In valves where positioners were used, additional venting devices were placed in parallel on the lower side of the diaphragm so that instrument air could be exhausted more quickly. Also, a higher pressure instrument air supply was used on top of the valve diaphragm to give the closure more driving force.

Solenoid valves unsatisfactory

In order to insure a fast high capacity exhaust of instrument air from the lower diaphragm, solenoid activated pneumatic control valves were used instead of standard solenoid valves. It was found that most solenoid valves were not satisfactory in this capacity range. Therefore, by incorporating the features of a high volume, high velocity release of instrument air on the lower side of the diaphragm, and a simultaneous injection of higher pressure instrument air on the top side of the diaphragm, a very low response time valve was created.

We have been successful using this approach on the valves in question. Valve response times were reduced from the 8 to 9 sec. previously mentioned to approximately 0.1 sec.

Including the time delay that was incorporated into the vent valve, we have decreased the response time of the system from approximately 9 sec. to an overall of about 0.4 sec.

DISCUSSION

LARUE—Spencer Chemical: I am wondering if you are not creating a potential hazard in your effort to design a supersafe system. A serious situation could result if oxygen leaks back through the control valve into the purge gas header. Someone could then start purging a vessel or line with what he though was nitrogen, only to discover to his sorrow that it was in fact oxygen. This appears to be a weak point in your system.

PAPENFUSS: Are you suggesting the possibility of a contaminated source of purge gas?

LARUE: That's correct.

PAPENFUSS: I think this is certainly possible but not likely. Our source of purge gas (nitrogen) is very closely monitored. The nitrogen, which is supplied from an adjacent air plant, is monitored continuously for oxygen content. Our limits are less than 30 ppm oxygen in the nitrogen.

Our standard operating practice in the air separation plant is to notify all users when the oxygen content exceeds 100 ppm. When the impurity level exceeds 1,000 ppm, the nitrogen compression facility is shut down and a source of high purity standby or backup nitrogen is used until the purity problem is corrected.

The two plants are run under common supervision, so I think there is close coordination on the quality of the purge. I think your point is valid, however, where a close control of purge quality is not practical.

HANLEY—DuPont: The other day I heard someone talk about using pure oxygen in a secondary reformer application. Is such a complicated system as this used in that case? Do you still have purge, etc.?

PAPENFUSS: I will refer your question to someone involved in reformer operation. This is not the application you refer to. I don't know what they use in those applications.

HANLEY: I realize that you're not talking about flammable limits, and he is.

WALTON—SunOlin: I was the one you mentioned. We have a system almost identical to this. There's a bypass around this purge source control valve with a fixed orifice in it, and we use steam, and so we always have steam, a steam purge going in here. But other than that, the system is almost identical to this.

LARUE: Have you experienced any accidents or overheating problems with the injection of pure oxygen into the secondary reformer?

WALTON: No problems so far.