

SAFE LEVEL OF OXYGEN IN NITROGEN COMPRESSION SYSTEMS

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Compressing nitrogen, even when several percent oxygen is present, would seem at first glance to be an operation free of explosion hazards. After all, inerting a fuel system with nitrogen to prevent combustion, or an explosion, is a common and very effective practice. The least amount of oxygen required to support combustion for a given fuel gas can be found in such references as Bureau of Mines Bulletin 503, "Limits of Flammability of Gases and Vapors." For most hydrocarbons this minimum oxygen concentration is in the range of 10 to 12%. Purging to 20% below the index (as recommended by the A.G.A.) ensures a safe system at ambient temperatures and pressures.

Temperature and pressure

The key here, of course, is temperature and pressure. The range of flammability is increased for most mixtures of gases in a straight-line relationship with increasing temperature. Increasing pressure, however, does not have a uniform effect on all flammable mixtures and is specific for each flammable mixture.

In an air separation plant, nitrogen compressors may be used either in product nitrogen service delivering gaseous product to a customer or to another processing operation, or in a nitrogen recycle service which is an auxiliary refrigeration system. Although our company has not had any difficulty in this particular area, available data would indicate that the problems associated with compressing nitrogen may be similar to the flammability problems associated with the compression of air in oil lubricated reciprocating compressors. There have been several incidents in the industry with nitrogen recycle compressors that support this approach and a literature survey shows that combustion and explosion can occur at the proper temperature and pressure conditions with as little as 1-1/2 to 2% oxygen.

Product purity requirements would appear to preclude a combustion reaction in a product nitrogen compressor and no record has been found of a reaction in this service. A nitrogen recycle system, on the other hand, may operate at an oxygen level of from 2 to 5% and as this stream is coming directly from the top

of the low pressure column it is immediately affected by changes in the column operation.

Description of a failure

A brief description of an actual failure will help illustrate the problem. This particular machine in nitrogen recycle service compresses in four stages to 2200 lb./sq. in. The second stage normally ran at about 180 lb./sq. in. The oxygen concentration normally fluctuated between 1 and 3-1/2% and three-quarters of an hour before the incident was 3-1/2%. The reaction occurred in the piping between the second and third stages rupturing it in two places. The reaction could be classed as a detonation as a hole was punched in a blind flange with a pressure rating of 8,000 lb./sq. in. and a static rupture pressure of 22,000 lb./sq. in.

In another instance a series of detonations occurred in the discharge piping of a similar machine also in nitrogen recycle service. The compressor was being started up at the time and the discharge pressure was about 800 lb./sq. in. The first rupture occurred in the 1-1/4-in. nominal size discharge pipe about 50 ft. from the compressor and 3 ft. downstream of the after-cooler and separator. The second rupture was about 4 ft. further downstream and the third rupture about 15 ft. beyond that. This compressor had originally been lubricated with Mobile A-30 but had been changed to DTE-105 sometime before the reaction. The oxygen content had risen above 5%, which was the limit of the analyzer, at the time of this incident.

Flame temperatures

Some experimental work has been done which relates to this problem. A paper, "Flame Temperatures of Limit Mixtures," by M. G. Zabetakis, S. Lambiris, and G. S. Scott presented at the 1958 Seventh Symposium on Combustion discusses the effect of pressure alone and temperature alone on the flame temperatures of limit mixtures. The effect of pressure on the adiabatic flame temperature of natural gas-air limit mixtures is shown in Figure 1 which is taken from this report.

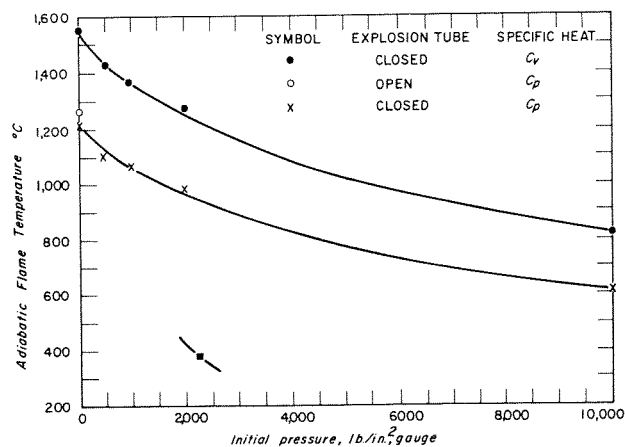


Figure 1. Adiabatic flame temperatures of limit natural gas-air mixtures as a function of pressure.

The upper two lines in Figure 1 are the adiabatic flame temperatures for lower limit mixtures and the lower point is the flame temperature at 2,000 lb./sq. in. gauge for upper limit mixtures. The calculations for the top line assumed a constant volume process in a closed tube. The same limit data were used to calculate the closed tube constant pressure flame temperatures shown in the next curve and the single point at atmospheric pressure for an open tube constant pressure process. The experimental work was done in closed tubes, and in actuality the pressure does not remain constant, and the volume of unburned gas decreased as the flame propagated up the tube. As this paper points out,

"although flame propagation does not occur under constant pressure or constant volume conditions in closed tubes, use of the former condition (constant pressure) results in flame conditions that are more nearly correct as a first approximation."

This is borne out by the fact that in an open tube at atmospheric pressure the flame temperature falls much closer to the value obtained in a closed tube at 1 atm. if a constant pressure rather than a constant volume process is assured.

At atmospheric pressure, upper limit mixtures have flame temperatures approximately the same as those of the corresponding lower limit mixtures. However, as shown by the single point in Figure 1 at 2,000 lb./sq. in. gauge and less than 400°C, the flame temperatures fall quite rapidly as the pressure increases.

Minimum oxygen requirements

Figure 2 below shows the minimum oxygen requirements for flame propagation through various combustible-inert gas-air mixtures at 27°C as a function of pressure. As can be seen, the minimum oxygen required for combustion decreases markedly with pressures up to about 500 lb./sq. in. gauge.

Unfortunately one has little data that combine the simultaneous effects of high pressure and high temperature on a flammable mixture. In correspondence on this subject Dr. Zabetakis made the following comment.

"For example, at 27°C the minimum oxygen requirements for flame propagation through methane-nitrogen-air mixtures decrease from 12% at 1 atm. to about 8.5% at 2,000 lb./sq. in. gauge; I would expect these figures

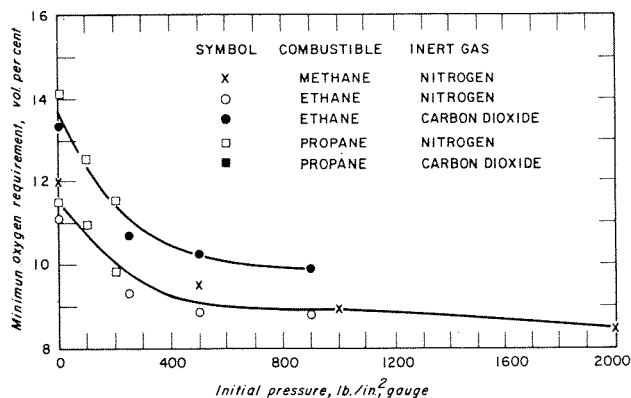


Figure 2. Minimum oxygen requirements for flame propagation through various combustible inert gas-air mixtures at 27°C as a function of pressure.

to decrease by about 1% if the temperature were raised by 100°C." In other words, at 2,000 lb./sq. in. gauge and 127°C the minimum oxygen requirement would be about 7.5%, at 227°C it would be about 6.5%, etc.

Dr. Zabetakis also stated,

"It is interesting to note that we have auto-ignited hydrocarbon fuels at initial pressures below 100 lb./sq. in. gauge in nitrogen-air atmospheres containing 2% oxygen at about 500°F; ignitions were obtained in atmospheres containing less oxygen at still higher temperatures."

Ignition mechanisms

Consider ignition mechanisms for a moment. Valve failure, with resultant high temperatures from recompression, or frictional or spark energy from impact of broken pieces have been the usual ignition energy for fires and explosions in air compressors. It would appear that valve failure in nitrogen service could also provide the necessary ignition energy. It has also been speculated that peroxides and pyrophoric deposits might be involved. With the normal elevated cylinder operating temperature and a deficiency of oxygen, oxidation of the lubricating oil could produce peroxides. Pyrophoric materials could result from the wearing of, and friction between, moving parts in the high nitrogen atmosphere. A sudden increase of the oxygen content, as from a column upset, could start a chain reaction beginning either with the pyrophoric materials or the peroxides, resulting in a fire or explosion.

Operating procedures

There obviously is a need for additional experimental data before precise conclusions can be drawn. In the meantime, certain operating procedures can be utilized to reduce the possibility of a reaction.

1. Keep the oxygen content as low and as constant as is compatible with the system.
2. Protect the compressor against a sudden increase of the oxygen content by appropriate monitoring and shutdown devices.
3. Do not change from nitrogen to air service without cleaning or passivating the compressor system.