Nitrogen Blanketing for Methanol Storage and Transportation

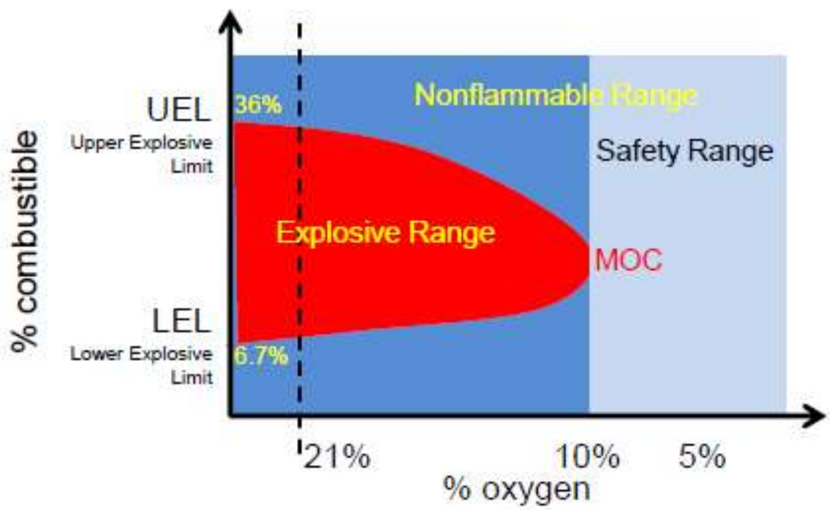
Overview

Air is the enemy of many materials. Not only can oxygen cause safety concerns and product degradation, but moisture, dirt, hydrocarbons and exhaust gases can also negatively affect products stored in tanks and vessels. In the case of methanol storage and transportation, the flammability of this highly volatile solvent is a major concern. The purpose of this paper is to describe the use of nitrogen blanketing as a "best practice" method for safe storage and transportation of methanol.

Advantages of using Nitrogen

Safety

- Nitrogen is an inert gas in most instances. This means that it is non-flammable and in most cases, does not react with other substances. It can be used to inert combustible substances. By providing the proper level of nitrogen in the system, methanol can be kept below the minimum oxygen concentration (MOC) of <10% and in the safety range. It is Air Liquide's practice to inert systems to half this value, i.e. 5% oxygen in the case of methanol.



- The lowest concentration of a gas or a vapor in air that is capable of producing a flash or fire in the presence of an ignition source is called the lower explosive limit (LEL) or the lower flammability limit. The highest concentration of a gas or vapor is the upper explosive limit (UEL). Concentrations of gas or vapor above the UEL are "too rich" to burn. These levels depend on temperature, pressure and the concentration of the oxidizer (oxygen). In the case of methanol, the LEL is 6.7 % and the UEL is 36% (percentage by volume of methanol vapor in air at atmospheric pressure).

Quality

Nitrogen can be used to blanket a product and reduce the oxygen concentration. It can also be used to displace air and its associated moisture content. The replacement of moist air with dry nitrogen will prevent water contamination of the product. This water can sometimes lead to corrosion of vessels and piping. The purity of nitrogen is also important in maintaining the quality of the stored product.

Environment

With nitrogen blanketing, the headspace of a vessel is flushed in order to prevent methanol vapors from being released to the environment. The vapors can then be collected into a system that will allow them to be thermally oxidized or possibly recovered for reuse. Sometimes it is cost effective to use liquid nitrogen and its ability to condense and recover volatile organic compounds (VOC's). The evaporated liquid nitrogen can then be reused to blanket the tank farm.

Regulations

The National Fire Protection Association (NFPA) 69 (www.nfpa.org) is the standard on explosion prevention systems. The NFPA addresses MOC but uses the term limiting oxidant concentration (LOC). The limit for methanol is 10%. However, Air Liquide´s practice is to inert flammable systems to half the LOC value.

Oxygen sources

Any liquid that moves into and out of the vessel acts like a syringe:

- Emptying the vessel draws air or blanket gas into the tank
- Filling the vessel forces air or blanket gas out of the tank

Thermal in-breathing and out-breathing (vent/de-vent) also happens due to ambient temperature and barometric pressure changes (e.g. a 21,000 gallon vessel can in-breathe 500 scfh of air). The American Petroleum Institute (API) (www.api.org) has published the Standard 2000, that describes how to safely vent atmospheric and low pressure storage tanks.

State of the art solutions

Tank blanketing, or padding, refers to applying a cover of gas over the surface of a liquid, in this case methanol. Its purpose is either to protect or contain the stored product or prevent it from harming personnel, equipment, or the environment. Nitrogen

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is supplied as very pure and dry gas. It is usually stored as a very cold liquid and vaporized before use for blanketing. Large consumers of gaseous nitrogen may be supplied via pipeline from an Air Separation Unit (ASU) or nitrogen generation plant.

The efficiency of nitrogen utilization depends on the condition of the system and if the method of application is suitable for the product and concerns of the customer. The optimal method of nitrogen utilization can be determined during an audit carried out by the nitrogen supplier. The audit will also establish the optimal nitrogen volume required for the specific vessel and is based on the typical pumping of liquid in and out. The audit also gives suggestions for the proper equipment. Part of the audit is an analysis of the system safety but also includes a Worker Safety/ Nitrogen Hazard Orientation that ensures all health, safety and environmental topics are covered.

Methods of applying nitrogen fall into five primary configurations and are dependent on the needs and logistics of the actual process being controlled. These five application methods are further detailed below:

Method 1 - Continuous Pressurized Purging or Manual Pressure Control

A key point in blanketing a liquid is to maintain the volume of nitrogen in the headspace. To do so, the vapor space must be pressurized or swept with nitrogen gas. The pressure of the headspace gas must be precisely maintained to ensure proper blanketing, for safety.

This should also be measured against cost considerations. To that end, the blanketing pressure should be kept very low. The blanketing pressure is normally well below the normal tank venting pressure. This prevents the unnecessary loss of blanketing gas and also reduces the amount of material lost from the sweeping of product that has been vaporized due to vapor-liquid equilibrium in the headspace of the vessel.

One way to achieve this is continuous purging. In continuous purging, nitrogen is introduced into the tank as a continuous flow exits through a vent. This method consumes a high volume of the blanketing gas and does not always reliably maintain an inert atmosphere. A pressure-reducing valve (PRV) is used to blanket the tank. Traditionally, these devices are the best suited to a continuous flow rate. One of the issues with a PRV is that they must throttle pressure over a wide flow range which can impact the controlled pressure significantly due to droop and lockup conditions.

Sometimes the pressure can swing as much as 30 percent below or 20 percent above a setpoint. This can lead to the loss of the necessary atmosphere within the tank. When using this method the gas pressure must be controlled at a pressure slightly above atmospheric pressure. The best choice of equipment are regulators such as conservation vents or tank-blanketing valves. These are typically used for their low cost and

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ease of operation. The photo above is a Vacu-Gard® Tank Blanketing Valve and is typical of a manual installation.

Method 2 – Automatic Pressure Control

In many industrial plants that employ digital control systems (DCS), the blanketing technique consists of the necessary controls and valving to sense and maintain the set pressure within the tank to as close as ± 0.25 inch w.c. [water column] (± 0.009 psi). Set pressures of 0.5 inch w.c. are possible and common.

In this type of system, the DCS will sense the tank pressure, control the inlet blanketing gas pressure if required and, through a main control valve, regulate nitrogen into the tank. Further, the system may also include a control valve to allow the reduction of pressure by opening a vent valve to allow gas to escape to the plant's flare system.

Most of these systems utilize a back-flow prevention in the form of a check valve or by ensuring that the supply pressure is higher than the pressure that can be generated by the process. A DCS installation may also monitor tank pressure and perform alarm or control functions in response to over- or under-pressure conditions.

This type of system is often the most costly due to the high number and complexity of components.

Method 3 – Oxygen Control

Barometric pressure changes can result in the movement of air into and out of an atmospheric pressure vessel. Also the hydraulic effect of removing product from the vessel creates a vacuum that must be filled by air or nitrogen. This method of application incorporates the use of oxygen analyzers to determine the oxygen content in the headspace of the vessel being inerted. A stream of headspace gas is drawn into an analyzer and the oxygen concentration is determined and the results are fed back to a proportional controller. The controller then sends a setpoint to the valve which opens or closes appropriately. This method allows for very tight control of conditions and a very efficient use of nitrogen. Design concerns are expensive equipment and expensive implementation, the oxygen analyzer must be maintained and calibrated, and analyzer lines can become fouled. The photo at left shows an oxygen control (Air Liquide's VESTAL™-O).

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Method 4 – Dual Control: Oxygen & Pressure

Sometimes it may be necessary to control two variables in the process to ensure the highest quality products. As in the previous two cases, the pressure is monitored and controlled and gas is drawn into an analyzer that looks at the oxygen content. The flow of nitrogen is adjusted by an automatic control system until the percent oxygen reaches the acceptable limits. Again this allows for very tight control and high efficiency for the use of nitrogen. It also prevents the ingress of air when product is moved out of the vessel. Concerns are the same for this method as for the previous methods; however, because of the added control a higher degree of complexity is required in the programming logic. The photo at right shows a Dual Control (Air Liquide's VESTAL™-OP).

Method 5 – Other Variable Control

There may be other variables that can affect the integrity of the product or system. Blanketing and inerting systems can be designed to utilize other measurable variables such as percent moisture. Again this can allow for tighter control, more efficient usage and may eliminate the need for monitoring of other things. Concerns remain the same as methods 2 and 3. The photo at left show some examples of Air Liquide's various VESTAL™ units.

Conclusion

Methanol can be stored and transported under a nitrogen blanket in a safe and cost efficient manner by using state of the art equipment. This complies with technical requirements and safety standards (NFPA, API). After analyzing the specific conditions, nitrogen flows can be optimized to maximize savings. Finally, nitrogen blanketing also helps protect equipment and products from the negative effects of the presence of higher levels of oxygen as well as moisture.

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