CHEMICAL ENGINEERING TRANSACTIONS
VOL. 31, 2013
Guest Editors: Eddy De Rademaeker, Bruno Fabiano, Simberto Senni Buratti

ISBN 978-88-95608-22-8; **ISSN** 1974-9791

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at: www.aidic.it/cet

DOI: 10.3303/CET1331105

Safe Design Against Explosions of Emission Collecting Systems

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Each industry in which flammable gas and liquids are handled has the problem to collect in a safe way the vent of the equipments to a suitable emission treatment unit (thermal oxidizer, cryogenic condenser, scrubber).
Historically, a lot of accidents happened inside emission collecting systems of batch plants because of the contemporary presence of flammable vapours, air, and effective ignition sources in operations such as:

- Liquid transfer by pump or nitrogen/air pressure
- Vent of equipment due to heating, distilling or gas release during reactions

In the first part of this paper two accidents happened inside emissions collecting systems will be analyzed in order to define consequences and typical causes.
In order to avoid these accidents two different ways of safety design are usually proposed:

- Diluted emissions collecting systems
- Inerted emissions collecting systems

The emissions systems in dilution are more common. The basis of safety, in this case, is to have flammable vapours concentration inside pipelines and manifolds below Lower Explosive Limit (LEL). This, normally, is guaranteed by an additional air stream given by a fan or a blower.
In the second system the basis of safety against explosion is given by assuring an atmosphere with oxygen content lower than Limiting Oxidant Concentration (LOC) of the flammable vapours. In the paper we will show the reasons why the use of inerted emissions collecting systems should be preferred.
High emissions flows are dangerous both for explosion risk and for ambient pollution and economically expensive thus this section will be followed by suggestions on emission flow optimization and reduction.
In conclusion, for both type of collecting system, some recommendations about avoidance of ignition sources and guidelines for safe connection of process equipments to emission ducts will be presented.

1. Introduction

Kidam et al. (2010) in their review of the Failure Knowledge Database about accidents happened in chemical process industry showed that:

- The majority of accidents (73%) were due to technical and engineering faults
- In piping systems failures are more frequent (16 % from 364 cases)

In general when piping systems are analyzed for safety assessment, pipelines systems containing liquids or pressurized gas are object of the analysis and principal hazard is the release of the flammable or toxic substance outside the pipelines.
In this paper, instead, it is discussed the safe design of emission collecting systems containing flammable gas and vapours where the principal hazard is the formation of flammable atmosphere inside the pipelines.
The scope of this paper is to propose inherently safe design solution to prevent accidents in this section of the plant.

1.1 Chemical process industry batch plants emissions to treatment units

An incomplete list of typical process operations that affect emissions flow rate and concentration in off-gas conveying systems is:

Please cite this article as: Mentasti M. and Crippa T., 2013, Safe design against explosions of emission collecting systems, Chemical Engineering Transactions, 31, 625-630 DOI: 10.3303/CET1331105

- Transportation of liquids between different equipments
- Equipments venting and nitrogen blanketing
- Centrifuges inertization
- Filters drying with gas flow
- Vent of vacuum pumps
- Equipments heating
- Distillation operations
- Reactions emitting incondensable gases

All these operations contribute to the total flow and flammable gas/vapours concentration inside the emission collecting system with a duration that may change from few seconds to hours. This leads to a flow and concentration profile that consists in a base line with peaks resulting from the listed operations.

2. Explosions inside emission collecting systems

2.1 Accidents case study 1. API plant with emission system containing tetrahydrofuran

Accident happened in Italy in July 2002 – Explosion inside a pipe with sizes from DN 200 to DN 400 in polypropylene and stainless steel used to collect emissions sent to washing columns and to a thermoxidizer. The explosion destroyed over 100 m of pipe, alkaline and acid washing columns and two polypropylene blowers. Nobody was injured. The emissions collecting system was about 7 years old and had a previous similar accident.

To investigate the formation of an explosive atmosphere a complete review of actual productions was performed. The system conveyed into emission collecting system either process emissions (e.g. vents from vessels and reactors inerted with nitrogen) and spot ventilations (e.g. local exhaust ventilation in air), this operation mixes air with organic vapours with a high probability in some parts of the piping to stay inside the explosive range.

Just before the explosion the vent of a reactor containing high volatile and flammable Tetrahydrofuran (THF) was open. It was calculated that, after dilution, concentration of THF in the emission system was about 6.3 % v/v, inside the flammable range. The polypropylene pipe, columns and blowers were not antistatic and probably the ignition was due to electrostatic ignition source.

The thermal oxidizer was not damaged but could not be modified to receive separately process emissions and spot ventilations. The company decided to improve safety using all antistatic piping and controlling dilution of the process emissions with air at all piping points. To verify dilution six LEL probes were placed at strategic points of the collecting system and if LEL values were higher than 25 % the emissions had to be sent directly to atmosphere after the washing columns.

2.2 Accidents case study 2. API plant with emission system containing hydrogen

Accident happened in Italy in July 2006 – Explosion inside an antistatic polypropylene pipe used to collect emissions sent to washing columns and to a regenerative thermoxidizer.

During the inspection two different damage spots on the polypropylene pipe were detected:

- At the connection point of process emissions with spot ventilation collecting system
- At the bypass tee of columns to emergency (totally destruction of the pipe upstream the first column)

Damages to the washing columns were the following:

- First column (acid): opening of the cylindrical body with spillage of the content
- Second column (basic): damages to the bigger nozzles and to the upper bottom
- Third column (basic): damages to the bigger nozzles and to the upper bottom

Carbon steel pipes upstream polypropylene pipes and the thermoxidizer were not damaged.

During accident, the LEL monitor (hydrogen FID detector) had not detected abnormal concentrations of flammable gas/vapours providing nor alarm, nor flow deviation to emergency. Thus, investigation of which productions were in place at that moment was made and it resulted that hydrogen was a by-product of a synthesis. Hydrogen is not detectable by the FID as it is fed by this same gas, thus hydrogen emission has been identified as likely cause of the accident. Flammable atmosphere has probably been created because of accumulation of the reactant (Diethyl Malonate) that subsequently reacted and caused an higher hydrogen concentration than normal that could not be enough diluted by spot ventilation air. Pipes were antistatic but a layer of organic material and dust, revealed during inspection, may have compromised the antistatic properties.

The company decided to improve the safety by installing a separate chimney dedicated to hydrogen emissions that are diluted with a forced air flow and to establish cleaning procedures of the emission collecting system during maintenance.

3. Preventing flammable atmosphere inside emission collecting systems

3.1 Systems working below LEL by air dilution

It has been, historically, the most common basis of safety inside off-gas conveying systems because in the past nitrogen blanketing was hardly used and not assured on all equipments using volatile organic substances. This method is very difficult to implement with sufficient safety level.

The reason is that a sufficient air flow mixing with each emission point must always be present to dilute the flammable gas/vapours content into the emission below LEL.

Safety margin should apply to the concentration of flammable gas/vapours in dilution under LEL. Standard NFPA 91 (2004) requires that concentration inside systems conveying flammable gas/vapours/mists should not exceed 25% of LEL. Standard NFPA 69 (2008) permits concentrations up to 60 % when automatic instrumentation with safety interlock is provided.

The main problems related to this technology are the following:

- In multipurpose plant, different flammable liquids may be used in different equipments. In the emissions ducts different flammable vapours may meet with synergy difficult to predict in terms of LEL of the final mixture.
- It is very difficult to define worst case peak conditions of flammable gas/vapours flow rate and concentration in normal process because emission flows in vent line are not constant and homogeneous during the normal life of the plant. Air dilution flow rate should be defined in order to manage the worst case peak conditions, otherwise there may be transitory in which all the flow is inside flammable range
- It is even more difficult to define worst case peak conditions of flammable gas/vapours flow rate and concentrations due to faults or human errors. Many of the operation that may affect flow rate and concentration profile of flammable gas/vapours may depend on human fault
- In presence of highly volatile flammable vapours inside the vessels (eg. gasoline, acetone, ethers, THF as in the previous accident example, etc) or, for example in hydrogenation process in which the concentration of flammable gas/vapours may be higher than Upper Flammability Limit (UFL), in the collecting system there will be a volume in which, for sure, the flammable range is passed through.

The experience shows that this system of preventing the formation of explosive atmospheres is often out of control and many ducts explosions have this origin. Accidents investigations demonstrate that the origin of the explosive atmosphere in most cases was the insufficient air dilution.

In addiction, the large air flow required for effective dilution may require larger emissions treatment systems, either by combustion or by cryogenic condensation. Also the use of scrubbers becomes more expensive with increasing flow rates and emissions abatement less efficient because of dilution.

3.2 Systems working with oxygen concentration lower than LOC

When nitrogen blanketing become a common practice to warrant the safety into the process equipment, some chemical industries started to control the emissions ducts explosion risk by maintaining the oxygen concentration below Limiting Oxidant Concentration.

NFPA 69 (2008) shows LOC for most common flammable gases and vapours used in process industry. Following the safety margin proposed by this standard, oxygen concentration inside ducts must stay below 2-3 % v/v depending on the presence of a continuous concentration monitoring system. This value is defined in case of presence of H_2 which has the lowest LOC reported – 5 % v/v. Since it is technically difficult to reach this value, general practice is to reach 6-7 % v/v oxygen concentration that is still lower than most flammable vapours LOC and to avoid the presence of substances, like hydrogen, that have lower LOC in the off-gas system.

For the streams containing these substances, specific vent solution and treatment shall be designed.

This way of design solves all the problems related to the peak of emissions released in the vent line and to the presence of highly volatile flammable vapours. Precautionary oxygen content inside the pipeline should be designed and checked in order to guarantee to stay below LOC also in presence of mixtures of flammable vapours.

This method is not easy to implement because:

- It requires the correct inertization of all the equipment connected to off-gas system

- Emissions ducts are generally kept at a design pressure lower than atmospheric and therefore all the system must be air tight.
- It is necessary to monitor the oxygen concentration in the emission pipelines in order to guarantee to stay below LOC even in presence of problems in inertization of the single equipment.

Number and position of Oxygen detectors shall be defined on the basis of the complexity of the system. General guideline may be to put them in the general manifold and in the principal branches in order to define where air is coming inside the system.

Oxygen detector shall be connected to nitrogen purge in different sections of off-gas system in order to keep the oxygen concentration below hazardous level.

If there is not air dilution, emissions flow rates are lower, but may change because of discontinuous operation. The system must be sized for peaks and the highest peaks are generally produced when an equipment that has been operated with nitrogen pressure, is vented to the duct for example during transferring from a vessel to another by nitrogen pressure or at the end of a filter dryer filtration or washing step and discharging the nitrogen pressure to the mother liquor receiver.

Good operating practice, with operators training, may reduce these peaks to avoid the need of an over sizing of emissions ducts and emissions treatment.

3.3 Emission flow optimisation

High emissions flows are dangerous for ambient and economically expensive.

This is a list of some good practice rules to avoid high flows of flammable gas/vapours to emission collecting systems:

- Use of pumps instead of nitrogen pressure to transfer flammable liquids.
- Condenser cooling liquid must have sufficient flow for complete condensation and with temperature lower than condensing vapours dew point. An automatic control on cooling media using the temperature difference between inlet and outlet to control the media flow optimizes condensation and media use.
- Do not fully open vacuum valves when starting evacuation of a vessel but do it gradually.
- Control nitrogen flow during filter panels drying using calibrated orifices.
- Limit exhaust flow from mother liquors vessels when discharging nitrogen pressure from filters using orifices.
- When loading liquids from drums or bins use pumps instead of vacuum.
- Use nitrogen blanketing of equipments without nitrogen continuous flow but using a pressure balance control system.
- Do not oversize equipment vent piping, in case of operational mistakes or failures there is the risk of high pressure inside the vessel before the safety device opening and the outlet flow from the vent may be very high.
- Every time the manhole is opened the vessel requires a new inertization operation. If performed by vacuum/nitrogen or nitrogen pressure procedure the outlet flow has a high oxygen concentration and therefore explosion risk. Manholes should be kept closed whenever possible, solids loading and sampling should be done using specific devices.
- Emissions containing hydrogen should be treated separately as it is very difficult to keep oxygen concentration lower than its LOC.

4. Reducing the ignition risk

4.1 Ignition sources analysis

If it is not possible to prevent the explosive atmospheres, then ignitions sources must be avoided.

Standard UNI EN 1127-01 (2008) shows possible ignition sources for flammable atmospheres. In the list below the possible presence of each ignition source proposed in the standard has been assessed:

- Hot surfaces: if the emissions treatment is by thermal oxidation particular care must be taken at the connecting point between the system and the thermal oxidizer. For emissions ducts designed with air dilution: the safety devices normally used are a LEL analyzer that deviates emission to atmosphere in case of high concentration and a detonation lock near the thermoxidizer. Detonation locks must be kept clean otherwise they may give very high pressure drop or catch fire themselves. For emissions ducts designed for low oxygen level: the safety devices used are an oxygen analyzer that deviates emission to the atmosphere if the oxygen concentration is higher than set point and an ejector used as emissions compressor. The safer ejector motor is normally steam at medium pressure that gives a gas speed inside the ejector throat higher than any flame speed. Of course steam pressure must be constant.

- Flames and hot gases (including hot particles): same as above point.
- Mechanically generated sparks: emissions ducts do not normally have moving parts. Only exception may be related to the presence of blowers and fans. It is better to avoid that explosive atmosphere pass trough these equipments. If this is not possible, blowers and fans must be designed and certified compatibly with the inside and outside the area classification.
- Electrical apparatus: All the electrical devices must be certified following UNI EN 1127-01 (2008) requirements on the basis of hazardous area classification of the volumes inside and outside the emission conveying system following the European Standard IEC EN 60079-10-1 (2008).
- Stray electrical currents, cathodic corrosion protection: piping must be grounded to a certified installation.
- Static electricity: in several accidents inside emission collecting systems electrostatic discharges were found to be the most likely ignition source. Lerena and Suter (2010) suggest that ignition sensitivity to static discharges shall be assessed defining Minimum Ignition Energy (MIE) of the flammable gas/vapours present inside the pipelines. Values found in literature are considered reliable for the case flammable gas/vapours by the same authors. Britton (1999) presents MIEs of most common flammable gas/vapours and the values are generally lower than 0.001 J. Several electrostatic discharges proposed by Standard NFPA 77 (2007) may be effective to ignite these flammable atmospheres. The same electrostatic standard proposes solutions for avoiding electrostatic discharges. Construction material for emissions piping shall be dissipative and pipelines shall be grounded. Most common material used is antistatic polypropylene, easily recognized because of its black color due to the carbon load. Any other construction material shall be dissipative and resistant to corrosion from all the compounds that may be present into the emissions. Into some production buildings polymeric combustible materials are not allowed for piping, in this case the construction material may be stainless steel for organic and alkaline compounds and antistatic Teflon lined carbon steel piping for acidic corrosive compounds. Particular care must be taken about ducts cleaning; even if the pipes are antistatic a thin layer of organic powders or organic fluids may insulate the construction material from the emissions flow. Static electricity cannot be produced by a clean gas flow but can be generated if inside the gas there are not electro conductive powders or mist. Some vacuum pumps are lubricated continuously with small quantities of oil that are emitted with gases as a mist. Lubricating oils are highly insulating fluids and tend to wet the inner wall side of the pipe that may become not antistatic. A mist separator is highly recommended when using this type of vacuum pumps.
- Lightning: generally rare, very difficult to protect when outside buildings.
- Radio frequency (RF) electromagnetic waves from 10^4 Hz to 3×10^{12} Hz: not applicable, generally not present.
- Electromagnetic waves from 3×10^{11} Hz to 3×10^{15} Hz: not applicable, generally not present.
- Ionising radiation: not applicable, generally not present.
- Ultrasonic: not applicable, generally not present.
- Adiabatic compression and shock waves: not applicable, generally not present.
- Exothermic reactions, including self-ignition of dusts: often inside emissions ducts there are chemical reactions between gases or vapours that produce solids or tars inside the pipes. These reactions generally do not give ignition risk because of the high dilution of the reactants. In case of highly reactive compounds a specific scrubber or other abatement installation should be used.

5. Guidelines to connect process equipments to emission collecting systems

The following is a list of general recommendations on how to connect several process equipments to the emissions ducts.

- Multipurpose reactors: to safely operate they should have an automatic nitrogen blanketing system, preferably with a pressure balance control.
- Storage tanks: underground tanks with closed circuit vent line connected to the tank car generally do not need venting to an emission treatment facility because temperature inside the tank remains constant all day. Above ground tanks have temperature changes during the day and night, they suck nitrogen by night and emit nitrogen saturated with vapours during the day heating and therefore they must be connected to an emission duct. If the tank has a nitrogen blanketing system it is sufficient to install a check valve that maintains positive pressure inside the tank on

the emission pipe. If the tank hasn't got nitrogen blanketing, it cannot be connected to a low oxygen concentration emission duct, but it can be connected to an air dilution emission collecting system if the air flow into the duct is sufficient to lower the flammable concentration sufficiently below LEL. Of course nitrogen blanketing is strongly recommended.

- Fluid bed driers: these equipments have many different operating conditions. They are intrinsically unsafe if they operate with hot air whilst drying powders wet with flammable solvents. In this case in the normal operating condition the dryer can't be connect to a low oxygen concentration emission duct. It can be connected to an air dilution emission system, but just after checking that the flammable concentration during initial drying time is kept sufficiently below LEL of the flammable gas/vapour in use.
- Centrifuges: If filtering is from solids suspended in flammable solvents, centrifuges must have an automatic nitrogen blanketing system with pressure control system that maintains pressure inside the machine at values higher than atmospheric and an oxygen analyzer to check that oxygen concentration is below LOC with an adequate safety margin.
- Vacuum pumps: they can be connected to any emission duct, but care should be taken not to suck air together with vapours otherwise they may discharge an explosive mixture into the pipe.
- Flow mixing: solvents generally do not react with other solvents but care should be taken when using aldehydes, ketones, olefins or other compounds that may react or polymerize into emissions ducts.

6. Conclusions

The hazards related to conveying flammable gas and vapours to emission abatement systems in chemical batch plants were discussed.

Literature shows that often accidents in the chemical process industries happen in piping systems because of poor design. Two accidents happened in Italy were proposed as starting point of the analysis.

It was demonstrated that dilution of flammable gas/vapours concentration under LEL is a common basis of safety in which it is often very difficult to guarantee that flammable range is not passed through in the entire stream conveyed from process equipment to emission treatment system even in normal operations.

It was showed that nitrogen inertization with control of oxygen concentration below LOC is a safer technique to prevent flammable atmosphere inside emission collecting systems pipelines. This technique, to be effective, requires the inertization of all the equipment connected to the emission collecting system, oxygen concentration monitoring in the vent line and some specific design and operative features to reduce the likelihood to increase oxygen concentration in the off-gas system.

Some recommendations about avoidance of ignition sources were then presented.

All the guidelines proposed to prevent the flammable atmosphere and reduce the likelihood of presence of effective ignition sources show that it is possible to reduce the risk of explosion inside the off-gas pipelines by good design of the system, good operating practice, operators training and good cleaning and maintenance standards on the pipelines.

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