VOC ABATEMENT AND VENT COLLECTION SYSTEMS

"A structured approach to safe design" or "Do the safety risks outweigh the environmental benefit"

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An increasing number of environmental improvement initiatives are being implemented to meet environmental emissions limits for Volatile Organic Compounds (VOCs), using "end of pipe" abatement techniques. To achieve these limits Vent Collection Systems are typically required to collect the pipe vents and feed them to the abatement unit. Where vents contain flammable or reactive vapours, complex safety and operational problems can be encountered in terms of fire, deflagration, detonation or chemical reaction of mixing vent streams.

This paper will cover a number of deflagration / detonation incidents from vent collection systems.

This paper will also address initial consideration of VOC losses and whether they can be eliminated/minimised which is key to the selection of the Best Available Technique (BAT) for abatement, as well as achieving the design of a safe vent collection system. The paper will then cover a structured methodology to achieve a "Basis of Safety" for vent collection systems.

To illustrate the application of this approach to vent collection systems the following case studies will be used:-

(a) Multiproduct Batch Plant, where the chemical inter reactivity of mixing vent streams was evaluated to develop a safe design.
(b) Carbon Monoxide Vent collection system on a Titanium Dioxide plant waste gas stream where the approach was applied to develop a comprehensive basis of safety for operation.
(c) Monomer production plant where following a number of explosions in the vent collection system, the basis of safety was re-evaluated and as a result, inerting was used to reduce oxygen concentration to avoid formation of a flammable mixture in the header.

In all cases the installation of a vent collection system to achieve environmental compliance can result in significant safety risks. These risks must be evaluated to ensure the continued safe operation of sites and to consequently meet the environmental improvement objectives.

Keywords: VOC, Vent Collection, Deflagration, Detonation, Safety, Risk, Reactivity, Fire

INTRODUCTION

Air Quality Standards in Europe have been increasingly tightened over the years. Some of the most important industrial emissions are Volatile Organic Compounds (VOCs).

VOCs emissions result in photochemical ozone creation in the lower atmosphere which have both human health effects and can lead to damage to crops and vegetation. VOCs are classified according to their Photochemical Ozone Creation Potential (POCP) referenced to a standard of 100 for ethylene.

In 1993 the UK Government set out how it expects its obligations to be met under the United Nations European Committee on the Environment (UNECE) VOCs protocol to reduce its emissions by 30% (based on 1988 levels) by 1999. A 65% reduction is forecast for the chemical sector based on the application of environmental improvement programs. Also under review is the proposed VOC Solvent Emissions Directive which aims to cut VOC emission by 67% by 2007, compared to 1990 levels. VOCs are produced/consumed in a wide range of industry sectors including power, food, chemical, petrochemical, finechemicals, pharmaceutical, manufacturing, electronic and automotive. For large companies to small and medium sized enterprises/ (SME)to achieve environmental compliance for Volatile Organic Components (VOC) emissions as part of their improvement program, end of pipe abatement can often be the only practical option. This would typically follow a Best Available Techniques Not Entailing Excessive Cost (BATNEEC) and Best Practicable Environmental (BPEO) option assessment.

In many cases, to meet the EA IPC Guidance Note emission limits for VOCs, vents are collected and fed to an abatement unit.

Techniques for VOC abatement can be broadly characterised as :

Recovery and Re-use Techniques

- Absorption
- Adsorption
- Condensation

Destruction Techniques

- Thermal oxidation
- Catalytic oxidation
- Biological
- Flares

Where vents contain flammable or reactive vapours there are complex safety and operational implications from the deflagration, detonation and chemical reactivity risks. These hazards are a particular problem on VOC abatement vent collection systems which feed thermal oxidisers or where other ignition sources are present. Activated Carbon VOC abatement systems are also known sources of ignition from hot spots being formed by high heat of absorption, Reference 14.

This paper will outline some of the risks related to vent collection systems, and detail a structured methodology to achieve 'A Basis of Safety' which is applicable to both batch and continuous processes. This approach will be illustrated by a number of case studies.

BACKGROUND

In order to collect process vent materials from process vessels (including reactors and storage tanks) a vent collection system is typically required.

On many installations the vent collection has been considered as just another pipe system. Hazards have not been assessed in the Hazard Studies, no basis of safety detailed and the system not managed / operated as a main plant item. The interactions with the plant normal pressure relief system have also not been considered.

However vent collection systems present significant risk such as :-

- The vent can contain flammable or reactive components
- Ignition of flammable mixture within the vent header can lead to deflagration or detonation hazards
- Transmittal of fire / explosion to other areas of plant via vent system
- Vent collection systems also expensive to install and operate

INCIDENTS

There are many examples of hazardous events in vent collection systems involving deflagration / detonation. A great deal of the early work in the 1960's was in the American oil industry where environmental legislation led to vapours being collected from ship offloading facilities and fed to incineration systems. This, plus the increasing environmental pressures on the process industries, has resulted in a number of incidents, including:-

- Reference 24 A Waste Gas incinerator near Houston experienced a pressure wave in the suction vent pipe resulting in extensive damage. A well designed system was overcome by an "unforeseen" combination of failures. Through a combination of automatic and operator responses to shut off the waste gas feed, a fuel rich stream was suddenly introduced to the incinerator. The flame front generated a pressure wave which blew apart the flame arrestor, piping etc. The damage could have been minimised with an in line detonation arrestor.

- Reference 22 This discusses an incident which resulted in the destruction of a large fluid hydroformer, and 63 tanks. Investigators were unable to trace the propagation of detonation through the piping system but the velocity was estimated at 1000 - 2000 ms^{-1} with pressures up to 28 barg.

- Reference 35 In a vent system connected to an incinerator, a flash back occurred. The inline flame arrestor failed with a subsequent fire in the dump tank.

- Reference 39 A waste gas incinerator experienced a flash back with a pressure wave in the suction vent gas system. This resulted in extensive damage to the vent system fan, valves, arrestor and piping.

- Reference 31, 32, 33 An incident in August 1991 highlighted the risk of vent collection systems. Terminal Pty Limited, Coode Island, Melbourne operation on "Site A" Compound with 45 tanks with a total capacity of 45,000 m^3. The tanks were connected by a vapour recovery system. An explosion occurred in Tank 80, causing the tank wall and roof to be propelled approximately 20m in the air. The subsequent fire propagated through the vent collection system. Figure 1 shows the site before the incident and Figure 2 after the event which gives an indication of the scale of destruction. Ignitions in tanks are not uncommon with a recent incident at Shell Rotterdam Reference 37 being yet another example

Figure 1: Site 'A' Plan View Coode Island, Melbourne

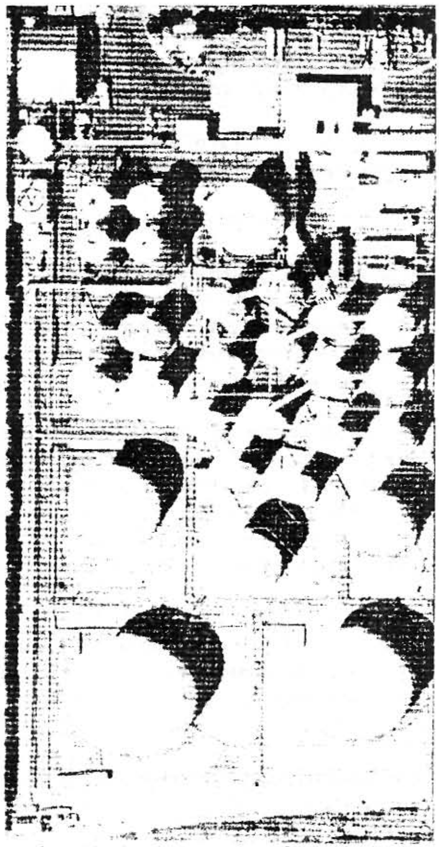

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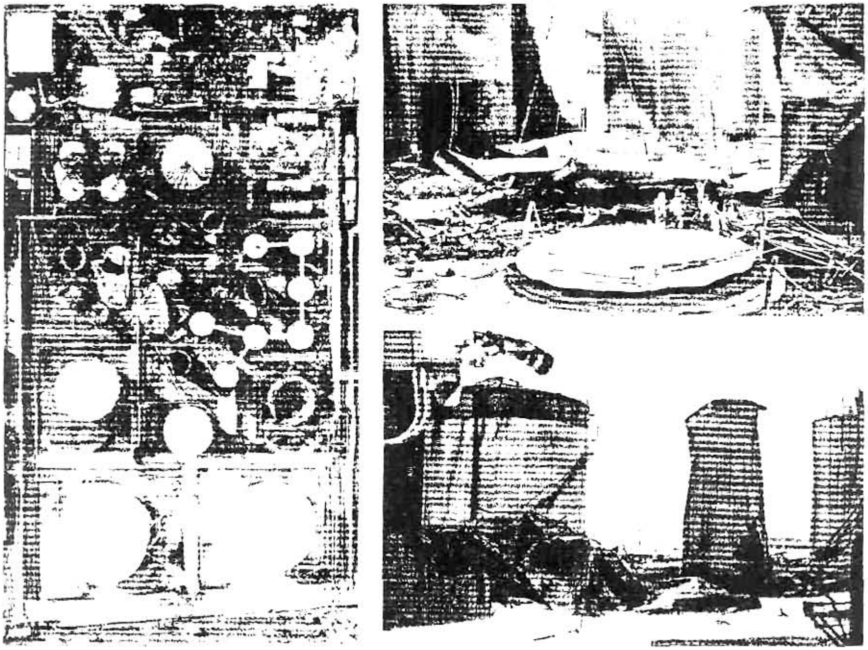
Figure 2. Coode Island - Explosion Damage



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- Reference 29 details a number of incidents.

The number of vent collection system problems and incidents are on the increase with environmental pressures resulting in more end of line abatement systems being installed.

Where vent collection systems feed thermal oxidiser systems, a risk a they also present due to unburnt gas accumulation and ignition, which can be transmitted back to the plant.

VOC ABATEMENT

The need for vent collection systems, as described previously, can arise from the need for VOC abatement. A typical approach to VOC abatement is detailed in Figure 3.

Vent Collection can lead to significant risk, and where possible, attention should be given to eliminate, minimise and locally abate "VOC emissions" before a vent collection system is considered. In undertaking this, low/no solvent technologies should be considered to reduce or eliminate the requirement to use VOCs. Vent collection and end of line abatement, also represent a significant investment in capital, and ongoing operational costs. They have also been the cause of reduced plant reliability due to blockage, pressure control problems etc.

Before embarking on a VOC abatement project, whether it is based on source reduction or end of line abatement, it is imperative that vital preliminary data on vent emissions is collected in a systematic and structured fashion, Reference 33. This can be a time consuming exercise, especially for large sites with a significant number of emission points. It can also be equally complex for a Batch Process due to variation in cycle times, process operations and products. Establishing accurate emission data is essential to assess minimum, maximum and normal emissions at each step of a Batch cycle.

The approach normally consists of developing a model of emissions, to establish an accurate mass balance of VOC emission from all sources. Any errors, or inaccurate assumptions, at this point can lead to unsafe design, inappropriate selection of abatement techniques and high capital / operating costs.

Figure 3. Typical Approach To Environmental Improvement for VOCs

Review Drivers
- Environmental compliance
- Business needs
- Process optimisation

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Data Collection
- Identify Emission Points, Normal and Emergency
- Update Plant Flowsheet and Line Diagram
- Identify all compounds
- Collect physical data
- Consider fugitive emissions

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Quantification of VOC losses by
- Site mass balance
- Theoretical calculation
- Measurement of losses

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Comparison To Environmental Agency Requirements

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Structured Source Reduction Study
- Eliminate emission points: closed system
- Review choice of solvent (eg low volatility / water based)
- Common or back venting
- Inert blanketing storage tanks
- Purging reduced
- Evaluate most effective options

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Evaluation Of VOC Abatement Technique For BATNEEC And BPEO

Destruction
- Thermal oxidation
- Catalytic oxidation
- Biological

Recovery and Re-Use
- Condensation
- Adsorption
- Absorption

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Process Design And Specification Of Solutions
- Source elimination and reduction modifications
- VOC abatement plant

VENT COLLECTION SYSTEM METHODOLOGY TO DEVELOP A BASIS OF SAFETY

In order to achieve safe design of a vent collection system, a structured methodology is required.

As a result of significant experience in the safe design of Vent Collection systems over a range of projects, Eutech has established a structured methodology as defined in Figures 4 and 5.

This will provide the information to develop a "Basis of Safety" and then assess the risk with a full Hazard Study program being be applied to any proposed design.

Figure 4. "Basis of Safety" Development for vent collection systems

Vent Collection System
- Identification of vents
- Quantification of emission
- Model vent sources, organics, oxidants, inerts

⇩

Application of Techniques for Minimisation of Losses
Is a Vent Collection System Necessary?

⇩

Component Flammability Data Collection
- Lower Explosive Limit(LEL)
- Upper Explosive Limit(UEL)
- Minimum Oxygen Content(MOC)

⇩

Identification of Operating Scenarios
- Normal
- Maximum / Minimum
- Start up / Shutdown

⇩

Modelling and Tabulation of Combined Vents
- Flammability
- Chemical Reactivity

⇩

Identification of Hazards
- Burnback
- Deflagration
- Detonation

⇩

Assess Primary Basis of Safety Options Based on Prevention
- Inert operation to below 25% MOC
- Air dilution to below 25% LEL
- Operate Fuel rich

In order to maintain and/or monitor the vent stream, an oxygen or flammable gas analyser(to monitor concentration as % LEL) is typically installed. Having established a proposed primary 'Basis of Safety' for the vent collection system (eg inerting, air dilution) it is necessary to carry out a risk assessment to establish whether the level of risk is acceptable versus the subsequent consequences

Figure 5. Vent Collection System Risk Assessment

Proposed Primary Basis of Safety

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Identify The Potential Flammable Mixture in Header from Oxidant Ingress Using
- Hazard Study
- Process Hazard Review techniques.

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Model Oxidant Ingress Cases to Assess Flammable Mixture Potential.

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Hazard Analysis to Develop Fault Trees and Evaluate Frequency.

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Consider Requirement for Secondary Protection
- Explosion relief
- Deflagration/detonation arrestors
- Containment
- Suppression systems.

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Consequence Assessment of Vent System Deflagration / Detonation.
- Loss of containment
- Fragmentation
- Fire transmittal

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Ignition Source Assessment
- Friction
- Electrical
- Static
- Hot surfaces
- Chemical reaction

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Evaluate Total Risk Versus Consequences

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Finalise Basis Of Safety Document

As an outcome of this approach, it is also necessary to develop operating and maintenance procedures, taking into account identified hazards for safe commissioning and operation of the Vent Collection System. The final outcome should include a fully documented design, mass balance and quantified risk assessment.

For operation of the vent collection system, an owner of the process should be identified who is responsible for safe operation, design changes and maintenance.

DEFLAGRATION / DETONATION CONSEQUENCES

Ignition of a flammable mixture in a vent collection system can result in burn back from the point of ignition and run up to deflagration / detonation.

Deflagration

Deflagration is defined as a combustion wave, propagating at a velocity less than the speed of sound, (as measured at the flame front), which propagates via a process of heat transfer.

The consequences of ignition of a flammable mixture in a vent collection system, can result in deflagration with a pressure ratio up to 10 times initial pressure and maximum propagation velocities of typically 10 - 300 m/s. See Figure 6.

Deflagration to Detonation Transition

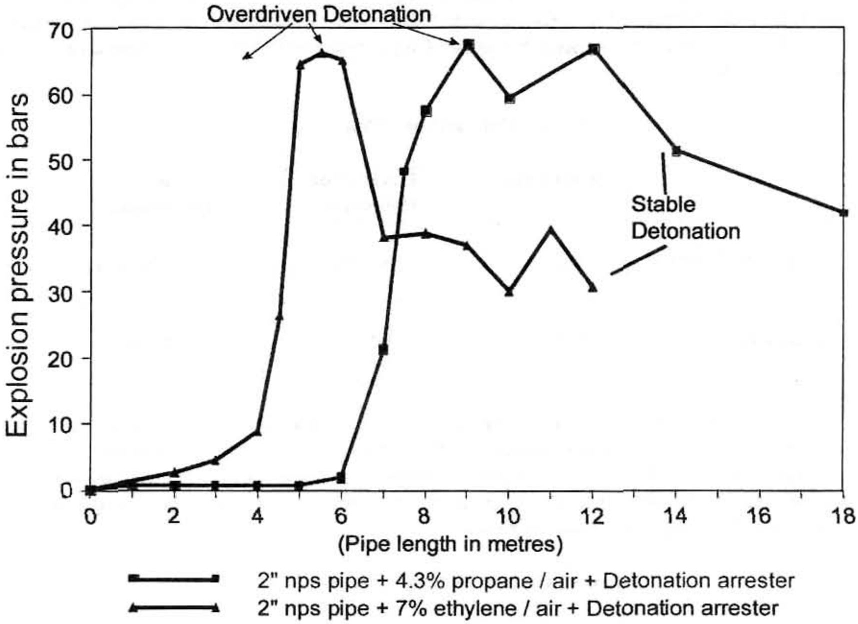
Following deflagration it is possible to achieve Deflagration to Detonation Transition (DDT) which results from acceleration of a deflagration flame to detonation via combustion generated turbulent flow and compressive heating effects. During DDT, overdriven detonation peak pressures of up to 100 barg can be observed, assuming the initial start pressure is atmospheric.

Overdriven detonation pressures cannot easily be estimated as they are dependant on many factors such as pipe layout , surface roughness etc. For example from a range of tests carried out by IMI AMAL assessing run up distances in 2" nominal diameter piping (Figure 6), the results indicated peak pressure from overdriven detonations in a pipe, were in the region of 70 to 80 barg for propane air and ethylene/air mixtures with a duration from microseconds to milliseconds. From IMI AMAL tests in 6" nominal diameter piping pressures up to 150 barg have been recorded. References 24 and 40 quote overdriven detonation pressures of up to 100 barg based on initial atmospheric pressure. However the pressures are only very short lived pulses, applying momentary stress on the walls and, hence, unlikely to lead to failure. These pressures are also supported by References 26 and 32.

Stable Detonation

This is the fully developed detonation wave, propagating at a constant velocity of typically 1600 - 1900 ms^{-1}. IMI AMAL test data, Figure 6, indicates typical stable detonation pressures of 20 - *50 barg and 20-30 barg for propane, based on a range of tests. Reference 24 advises on stable* pressures of 18 - 30 barg and Reference 19 20 - 24 barg.

Figure 6. Experimental Effect of Run up length on Detonation Pressure
(IMI AMAL specific test results)



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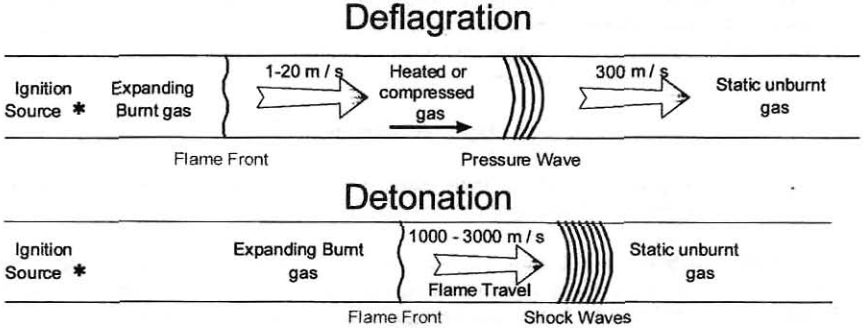


Conclusions

The available literature data for the ignition of a flammable mixture in a vent system indicates that there is the potential for deflagration and acceleration to detonation. In a vent collection system the presence of obstructions, bends and flanges promote turbulence, and therefore provide *increased acceleration.*

Table 1. Typical Deflagration - Detonation Phenomena

	Deflagration	**Overdriven Detonation**	**Stable Detonation**
Maximum Pressure	~10 barg	~150 barg	~20 - 50 barg
Timescale	Millisecs	≤1 Millisecs	>1 Millisecs

At present, it is virtually impossible to predict the potential for detonation and run up distances. Typically, a worst case design basis needs to be assumed or experimental work must be carried out on the likely vent mixtures to establish a design basis and potential for loss of containment. Investigation into the phenomena of detonation in pipework is ongoing at the Department of Physics, University of Wales.

DEFLAGRATION / DETONATION PROTECTION

In many cases, it is not practical to eliminate ignition sources and prevent all sources of oxygen ingress to the header, hence options for deflagration/detonation protection need to be assessed. *The options available to protect the vent collection systems in the event of a* deflagration/detonation include:-

Containment

This method would require constructing the whole plant to withstand deflagration, overdriven detonation and stable detonation pressures as defined in the previous section. Although this approach can be used it can be expensive and often not practical except in small diameter pipes which can contain to pressures > 100barg

Deflagration Protection

This would arrest propagation of a flame in its incipient stages, (ie during subsonic flow) and can be achieved in a number of different ways.

Passive Flame Arrestor. *Installed to quench the flame before Deflagration - Detonation* Transition (DDT) can occur. Flame arrestors utilise a property known as Maximum Experimental Safe Gap (MESG) which is the largest gap through which a flame will not transmit when tested in accordance with test standards. Arrestors are designed with cells to be smaller than the MESG, such that as the flame front travels through each cell there is a transfer of energy between the flame front and the cell walls. This heat transfer through the boundary layer to the cell wall results in cooling of the burning gases to below the autoignition temperature of the unburnt gas ahead of the flame front (34, 36). Current UK guidelines for testing of deflagration and detonation arrestors are covered in BS 7244, and the draft European standard Pr EN12874. The US Coast Guard (USCG) standard covers detonation arrestors only.

Design of Flame arrestor elements is based on the gas groupings in BS7244 1990 as follows:

Group IIA	MESG >= 0.9mm
Group IIB	MESG = 0.5 to 0.9mm
Group IIC	MESG <0.5mm

Group IIA comprises the majority of hydrocarbon gas, Group IIB more reactive gases/vapours such as ethylene, whilst Group IIC contains the most reactive gases such as hydrogen and acetylene. For a single gas/vapour the MESG can easily be found. However for mixtures, it is more difficult unless mixture data is available otherwise the component with the smallest MESG has to be considered. The concept of endurance burning is also an important issue in the use of flame arrestors. Under certain conditions, a flammable mixture in a header could ignite, burn back and then form a stable flame on the arrestor. Under this condition the arrestor element can gradually heat up to the Auto ignition temperature (AIT) of the inlet gas/vapour -this is the "Safe burning time" which can vary from 2 hours for small units to 15 mins for larger, although burning tests of greater than 15 mins are considered optimistic.

Explosion Venting. The explosion vent is a weak membrane in the pipework to relieve pressure and discharge the flame to atmosphere.

Vents should be placed at intervals less than the predicted run up distance to detonation. Great care is needed on location of a vent due to the flame and pressure which is vented. Explosion vents will reduce the effects of pressure, but will not stop the flame continuing past the vent. The main problem is identifying a safe location into which relieve the vented products/flame.

Explosion Suppression. Explosion Suppression involves the detection and extinguishing of the flame in its incipient stages by rapid injection of chemical suppressants (eg Kidde or Fike type system) and arresting the propagation of the flame front. The distance between detection and suppression must be less than the run up to detonation or a combination of detectors, suppressant and slam shut valves would be required. These have been used on vent collection systems. (Reference 25)

Hydraulic Arrestor. This is based on a liquid seal to act as an arrestor. It has the advantage of not being affected by blockage. The disadvantages are increased pressure drop, operational problems, and reliability. In addition extensive instrumentation is required including level measurement to maintain water level, Gas flow-to ensure design flow is not exceeded and Temperature to detect if burnback deflagration/detonation has occurred

Explosion Isolation. Explosion isolation involves the activation of mechanical valve or chemical barrier to arrest the propagation of flame in a pipe. Valves or chemical barriers are effective when located near potential ignition sources and present no restriction to flow.

Conclusions on Deflagration Protection. For deflagration protection it is necessary to have identified the point of DDT, pressures etc, as covered in the previous section. If however ,it is not possible to quantify this or locate the arrestor close to the ignition point, it is assumed that run up to detonation could occur and detonation rather than deflagration protection is required. The requirement for effective detonation protection is to arrest the propagation of a detonation, limiting the potentially destructive force of the pressure shock waves and transmittal eg a flame front to the main plant.

Detonation Protection

Passive Detonation Arrestor. These are passive bi or uni–directional arresting devices used to quench or destroy the transverse structure of the detonation flame front and are inherently safe. The problem with an arrestor is that it acts as a filter and is subject to blockage.

Active Detonation Arrestor. These are systems that detect the propagating flame front and activate rapid response valves and suppressors to prevent the propagation of a flame. There are high integrity trip systems designed specifically for the duty.

Suppressors and valves are located in strategic positions and supplemented with vents. These systems should be considered where blockage is a problem and have been installed on a number of vent systems (25, 28).

Conclusion. Passive detonation arrestors present an inherently safe simple solution with no moving parts when compared to an active system. This is on the basis that acceptable plant on-line time is possible due to potential blockage problems and that particulate build up has no effect on the integrity of the arrestors.

OTHER ISSUES ASSOCIATED WITH THE DESIGN OF VENT COLLECTION SYSTEMS

In the design of vent collection systems, other factors need to be taken into account including:-

a) Liquid condensation/freezing: Liquid collection in the vent pipe work can require knock-out pots to prevent carry over to the abatement system. Lagging and/or trace heating may also be required to prevent condensation in the vent pipe work. (Reference 35)

b) Fouling: Potential for blockage from solids or liquid build up in the vent, deflagration/detonation arrestors needs to be assessed in terms of operation of the plant and is a particular problem for Group II arrestors with their smaller and longer quenching cells. In cases of fouling problems, a parallel arrestor may be required so one arrestor is in service while the standby one is cleaned (see Figure 7 and 8 which shows a parallel arrestor installation.) An interlocked valving system must be used to ensure the header cannot be isolated which could result in over pressure of the plant.

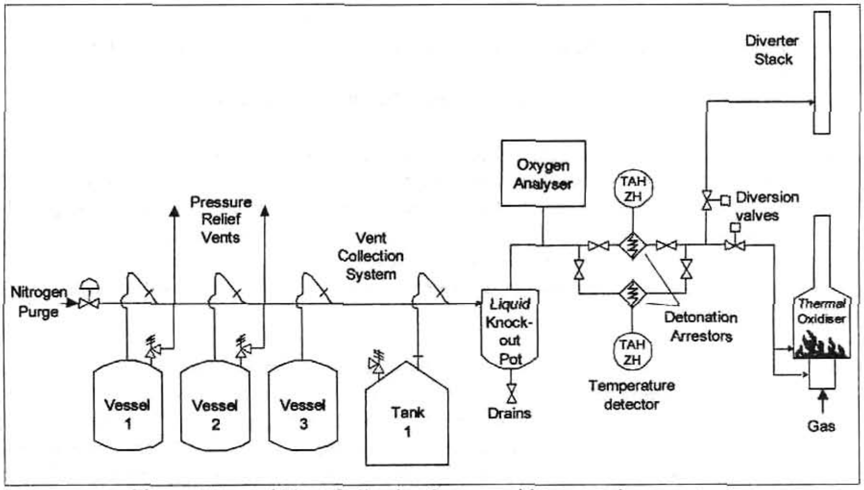


Figure 7 Inerted Vent Collection System with Detonation arrestors

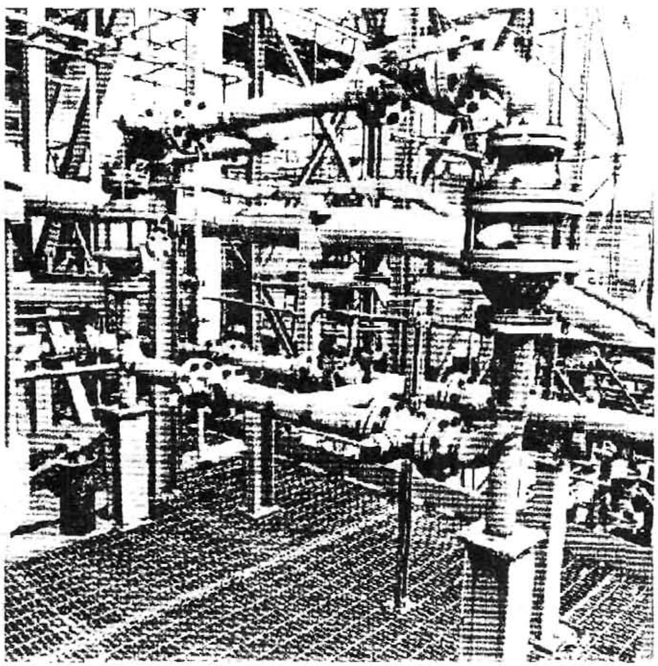


Figure 8 Detonation arrestor with installed standby

c) Pressure Relief: VOC Vent collection systems are typically designed for normal vent losses. Pressure relief for relief as a result of fire, thermal expansion, reaction should be a totally separate system which could be individual relief vents or vents to a relief header. Any relief system design should follow a structured process from initial identification of relief cases to consideration of final vent discharge and disposal eg flaring / absorption etc.

d) Pressure Drop: Operation of vent collection systems are usually such that they do not affect the main process. A vent system can operate at slight positive pressure which has the advantage of preventing air ingress or slight negative pressure where a fan is often required to overcome pressure drop in the vent system with a pressure control loop. Design and control of such a system can be complex and require modelling to assess operating scenarios. The reduced MESG for more reactive gases/vapours ie Group II B/IIC can result in high pressure drops, for arresters

e) Divert Stack: Vent collection systems typically require a stack to divert flow into during startup / shutdown conditions when the vent stream may be in the flammable range; during fault conditions or in cases of abatement plant malfunction. The risks need to be considered as part of the risk assessment and discussions held with the Environment Agency to ensure the effect on the environment is understood. Diversion is often automated and linked to the plant control system (IPS).

CASE STUDIES

The structured approach to Vent Collection System design has been applied by Eutech to a number of studies.

Case study 1:Vent Collection System Design for a Multiproduct Batch Plant

At their factory at Seaton Carew, Oxford Chemicals manufacture a range of over 400 flavour and fragrance intermediates. Chemicals are processed in any of twenty-two reaction vessels, which range in size from 20 to 2500 litres, and are constructed from QVF glass-lined steel or stainless steel. Expansion and future development plans to incorporate a biofilter stimulated a review of process venting. An internal study quickly determined that the final vent treatment systems were adequate. The common vent collection system, however, was identified as an area of concern, as it had developed over the years with some undesirable interconnections between vessels that handle chemicals that can react violently if mixed.

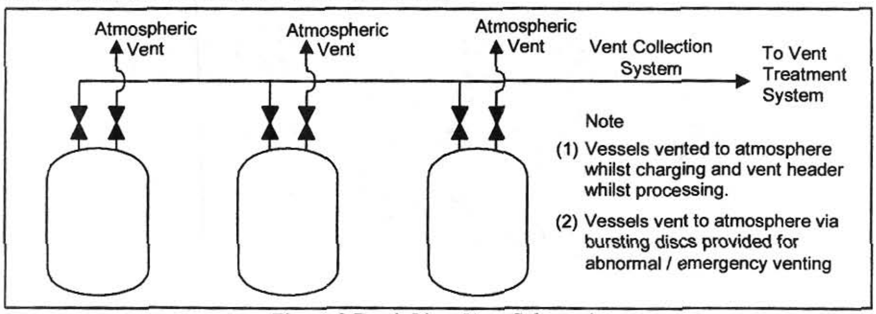


Figure 9 Batch Plant Vent Schematic

Liaising closely with Oxford Chemicals production and technical staff, data was collected on potential hazards in two areas - chemical reactions and potential flammable mixtures. By applying a reaction matrix it showed that no dangerous reactions would be introduced; action was needed, however, to protect against the possibilities of fire or explosion.

This conclusion was backed by detailed flammability studies, using knowledge-based analysis of the chemicals and mixtures involved.

Eutech proposed two possible control measures, inert gas purging or air dilution. Inert purging required the oxygen concentration in the header to be diluted with nitrogen to a design concentration of 2 per cent, with an action level of 5 per cent, representing an alarm point at which, if the oxygen level continued to rise, the header fan and vessel agitators would shutdown. This was based on operating at 25% of the minimum oxygen concentration (MOC) of organic chemicals.

Air dilution of the vent vapours, the other option, provided for the concentration of flammable vapours to be 25 per cent of the lower explosive limit of the worst case chemical. An additional advantage of dilution is that at very low concentrations, the risk of chemical reaction is insignificant. The design included proposals for sizing the new header, on air and nitrogen flows, and on elimination of ignition sources.

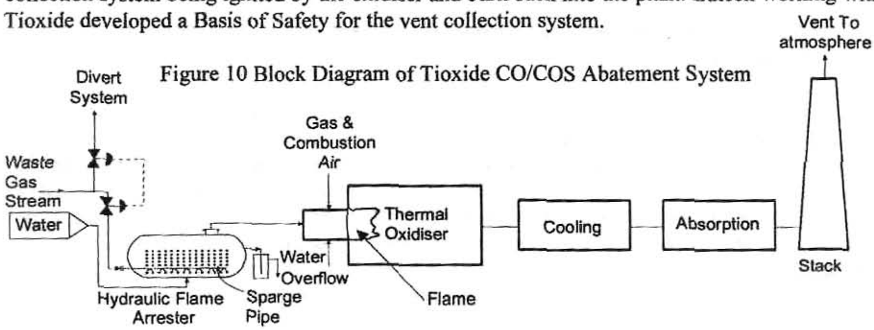
Oxford Chemicals selected air dilution with a flammable gas analyser for the replacement vent collection system which is now operating. This incorporates a large fan to draw air through the system continuously, an approach which has the added advantages of preventing leaks, and avoiding back pressure which could expand and stress the vessels.

Case study 2: CO/COS Vent Collection System, Tioxide

Tioxide's ICON Titanium Dioxide plant at its Greatham site produces Carbon Monoxide (CO) and Carbonyl Sulphide (COS) as waste gas from the process. In order to comply with agreed consent levels ,abatement options were evaluated by Tioxide .

The selected option was a thermal oxidiser with down stream cooling and absorption Figure 10. This raised concern about the potential for flammable mixture formation in the vent collection system being ignited by the oxidiser and burn back into the plant. Eutech working with Tioxide developed a Basis of Safety for the vent collection system.

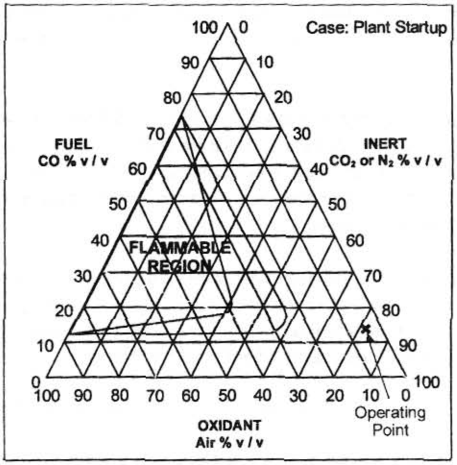
Figure 10 Block Diagram of Tioxide CO/COS Abatement System



The vent components consisted of N_2, CO, COS, H_2O, Cl_2, CO_2. The hazard identified was the potential for CO/COS air mixture to be ignited by the Thermal Oxidiser which could run up to Deflagration/Detonation. The methodology as detailed in "Vent Collection System Design Methodology" was applied as defined in Figure 4 & 5.

The vent flows were quantified and modelled on a spreadsheet for all potential operating conditions, eg peak rates, start up, shut down etc, with Le Chatelier's Equation used to assess the mixture flammability limits and these were plotted on a Flammability diagram Figure 11. The flammability data was collected for all components as well as data on deflagration/detonation potential for CO.

Figure 11 Flammability Diagram



A hazard assessment, lead by a Eutech Hazard Study Leader, was carried out with a plant team to assess potential for air ingress for normal, abnormal, startup / shutdown situations. Cases were eliminated that would not lead to a significant air / oxidant ingress which might approach the MOC, with the remaining cases being evaluated to quantify the frequency of a flammable mixture being established.

The study also considered ignition sources from the thermal oxidiser, vent fan and static from the GRP pipework.

The Basis of Safety for the Vent Collection system was established as operating at less than 25% MOC, with a slight positive pressure to minimise potential air ingress. Due to the potential for particulates in the waste gas, a hydraulic arrestor was selected as opposed to a standard detonation arrestor and designed to prevent burn back as a result of ignition of the vent gas steam. A hydraulic flame arrestor design is based on the velocity of gas through the sparge pipe, where the flame propagation will be stopped at the water surface because the water layer between rising bubbles prevents ignition transfer and flash back through the flame arrestor. Increasing the gas flow rate above the maximum gas flow will cause ignition transfer between bubbles and flash back.

The quantified risk assessment established the likely frequency of a flammable mixture being formed and defined recommendations to reduce this to achieve an acceptable level of risk.

Case study 3: Monomer Plant Vent Collection System Design

Following an explosion incident, as a result of liquid carry over to the oxidiser and a second incident of deflagration/detonation in the vent system, a comprehensive study was undertaken to achieve safe design and operation. The study assessed the two hazards considered ie liquid carry over to the thermal oxidiser and burn-back to deflagration/detonation.

A comprehensive study was carried out to accurately quantify vent losses from the plant to establish an accurate mass balance. Early in the study, considerable design effort was focused on elimination and minimisation of vent losses at source. This had the benefit of reducing flammable potential and blockage problems from monomers. The methodology, as defined in Figure 4 and 5, was followed with inert operation to give O_2 at less than 2% vol ie <25% MOC selected as the basis of safety. The vent system also had a divert stack system which would act as a safe location to divert vent flow on start up or shutdown. Consideration was given to the divert stack design and location to ensure dispersion of the vent gases such that acceptable flammability of less than 25% LEL and odour criteria were met at the site boundary. Dispersion modelling was undertaken to evaluate this.

The study addressed, in a structured way, the potential for air ingress from normal and abnormal cases. These were modelled on a spreadsheet and used to assess deviations, with Le Chateliers Law being applied to quantify mixture flammabilities. As part of the hazard analysis (HAZAN), fault trees were developed to establish the frequency of a flammable mixture being formed and subsequent ignition and deflagration/detonation potential.

A significant part of the study focused on the potential for run up to detonation potential, detonation pressures and consequences. Due to the complexity of the pipework and line length, the detonation was considered a risk.

In order to evaluate the consequences following detonation, detailed piping stress calculations were carried out on the proposed vent pipe; these indicated that the 4" Sch 40 had a failure pressure >200 barg and 6" >160 barg. The study also addressed the requirements for Bi-directional detonation arrestors and their optimum location. In order to overcome the risk of a stable flame being formed on the arrestor and subsequent burnback, temperature probes were to be installed on the relevant face. These would be used to trip feeds to the divert stack system and initiate a Nitrogen quench flow. It was also necessary to establish the system response time to ensure burn-through could not occur. Endurance burn requirements are defined in BS 7244 and USCG; AMAL advised that for the proposed arrestors, 15 minutes should be taken as the action point. The Quantified Risk Assessment was finalised to take into account risks versus consequence.

CONCLUSIONS

From the paper it can be seen that installation of vent collection systems can present significant risks in terms of safe operation of a plant or process. Elimination or minimisation of emissions at source should be the first priority and vent collection systems with end of line abatement should be avoided where possible. The safety risks include the potential for ignition in a vent collection system leading to deflagration/detonation and subsequent destruction. They are also costly to install and operate and can lead to reduced plant reliability.

To achieve safe design of a vent collection system, it is vital to have accurate data on vent sources as errors in this can lead to incorrect assessment of flammable potential and safe vent collection system design.

In summary, a structured approach is required to achieve safe design of a vent collection system and we should ask

'Do the Safety Risks outweigh the Environmental Benefits'?.

ACKNOWLEDGEMENTS

I would like to thank Oxford Chemicals and Tioxide for their kind permission to publish details of their study.

I would also like to thank Terminal Pty for the information provided on the Coode Island incident.

DEFINITIONS

BATNEEC. Best Available Technologies Not Entailing Excessive Cost.

BPEO. Best Practical Environmental Option.

Flame Arrestor. A device that permits gas flow, but prevents flame propagation beyond it in a flow system. The most common type is the dry flame arrestor. It consists of a matrix of small diameter holes or channels that permits the flow of gas, but quenches flame that propagates into it Other kinds of arrestors are the liquid seal, and high speed shut off valve types.

Deflagration. A flame front that propagates by the transfer of heat and mass to the unburned gas ahead of the flame front in a flammable gas mixture. Flame speeds can range from less than 1 m/s to (based on the unburned gas temperature) greater than 350 m/s (supersonic) for very high pressure, turbulent flames. Peak overpressures can range from a very small fraction to as much as twenty times the initial pressure.

Detonations (Gaseous). A flame front that propagates by shock wave-compression ignition in a flammable gas mixture. Flame speeds are supersonic (based on the unburned gas temperature) with Mach numbers ranging from 5 to 15. The pressure of a stable detonation usually ranges from about 20 to 30 times the initial pressure but can achieve compression ratios in excess of 100 at the moment of transition from deflagration to detonation.

Run-Up System. The flow system - pipes, bends, valves and any other flow devices - that a flame *front travels through from the point of ignition to the flame arrestor.*

End-of-Line Flame Arrestor. This type of flame arrestor is used where the potential ignition source is located outside of the vessel or flow system that is being protected. One end of the unit is open to the atmosphere directly or through a vent valve, cowl or a short length of open ended straight pipe. It is also referred to as a vent flame arrestor.

In line Flame Arrestor. A flame arrestor that is installed within a run-up system that does not vent to the atmosphere directly. The flow system between the potential ignition source and the flame arrestor is made through lengths of pipe that exceed end-of-line limitations and/or contain bends, tees, valves, or any other flow restricting or turbulence generating fittings.

Quenching Diameter. The largest diameter of a tube which will just quench a flame front in a particular fuel/air mixture. If the diameter is increased any further, the flame front can propagate in the tube without being quenched.

Maximum Experimental Safe Gap (MESG). The maximum gap between equatorial flanges in a spherical volume that will just prevent flame transmission from the vessel to the flammable gas mixture surrounding it.

Minimum Oxygen Concentration (MOC). This is defined as the lowest concentration of oxygen which will just support the combustion of fuel.

Burning Velocity. The fundamental burning velocity is the velocity with which flame moves, normal to its surface through the adjacent unburned gas.

Lower Explosive Limit (LEL). The minimum concentration of gas or vapour in air below which the propagation of a flame will not occur in the presence of an ignition source.

Upper Explosion Limit (UEL). The maximum concentration of a gas or vapour in air above which the propagation of a flame will not occur in the presence of an ignition source.

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