MITIGATION OF VAPOUR CLOUD EXPLOSIONS BY CHEMICAL INHIBITION

Dirk Roosendans[a], Pol Hoorelbeke[b], Kees van Wingerden[c]
[a]PhD Fellow, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Elsene, Belgium
[b]Total, Rue de l'Industry 52, B-1040 Brussels
[d]GexCon AS, Fantoftvegen 38, 5892 Bergen, Norway

The oil industry operates installations and processes with important quantities of flammable substances within a wide range of pressures and temperatures. A particular hazard for this type of installations is an accidental release of a large quantity of flammable material resulting in the formation of a flammable cloud within the installation. Historical evidence has shown that the ignition of such a cloud can lead to a devastating explosion and a total destruction of the installation. Such accidents are commonly named "Vapour Cloud Explosions" (VCE).

Recently, a novel innovative technique to mitigate the overpressure effects of a vapour cloud explosion was developed (Hoorelbeke, 2011). The mitigation technique consists of injecting dry chemicals into a vapour cloud. It was the first time that dry chemicals were extensively tested for this application. The research by Hoorelbeke (2011) is being continued and this paper gives an update on the achievements towards the development of a practical implementation of the chemical inhibition technology on an industrial scale.

KEYWORDS: Vapour Cloud Explosion, Chemical Inhibition

INTRODUCTION

The influence of various chemical substances on combustion characteristics is a wide area of research and this since many years. An example of research results on combustion inhibition is given in Figure 1 (V. Babushok et al.). The work of V. Babushok et al. suggests that metallic compounds including Fe, Pb and Cr are the most effective and that inhibition action is related to a specific atom or atom-groups and is relatively independent of its surrounding ligands.

Despite the fact that a lot of research is available on combustion suppressants, not a lot of research has been done on the use of solid chemical inhibitors in the context of mitigation of vapour cloud explosions resulting from the non-controlled release of large amounts of flammable hydrocarbons. Specific research in this area was performed by Hoorelbeke (2011).

Figures 2–5 give some research obtained by Hoorelbeke in experiments in a 20 l vessel and in a 50 m^3 test module. In these experiments, the inhibitors were used in the form of finely dispersed particles. The following agents were tested:

- Potassium carbonate
- Sodium bicarbonate
- Sodium chloride
- Potassium bicarbonate
- Calcium sulphate
- Manganese (II) carbonate
- Magnesium carbonate

The following flammable mixtures (gas/air) were used in the experiments:

- Methane
- Ethane
- Propane
- Propylene
- Butane
- Butene
- Acetylene
- Hydrogen.

The work of Hoorelbeke concentrated on the use of carbonates and bicarbonates as inhibitors and this for the following reasons:

- Some carbonates and bicarbonates are very efficient as chemical inhibitor for mitigation of Vapour Cloud Explosions;
- Most carbonates and bicarbonates are commercially available in large quantities at a low cost (unlike some other metal based inhibitors);
- Most carbonates and bicarbonates are not toxic, even at relatively high concentrations;

The above properties (effectiveness, availability, toxicity) are important characteristics for possible application of inhibitors as VCE mitigating agents on an industrial scale.

CONTINUED RESEARCH ON INHIBITORS

The research of Hoorelbeke (2011) on the selection of effective and industrially applicable agents with inhibiting properties for Vapour Cloud Explosions is being continued by Roosendans. This research is focusing on the following areas:

- Testing of additional types of inhibitors;
- Investigation of the influence of particle size and particle concentration on the effectiveness of known inhibitors;
- Testing of some commercially available chemicals with known inhibiting properties;

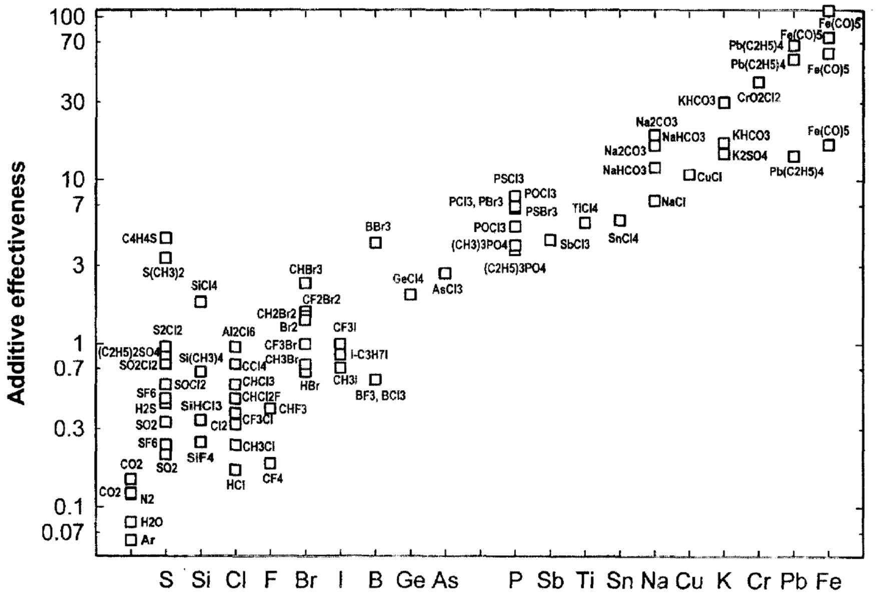

Figure 1. Relative inhibitor effectiveness (relative to CF_3Br)

- Mixtures of agents with known inhibiting properties;
- Study of aqueous solutions of inhibitors injected in the form of a mist;

The experiments are conducted in a 20 l vessel (see Figure 5). This vessel is an explosion resistant hollow sphere made of stainless steel. The vessel has a

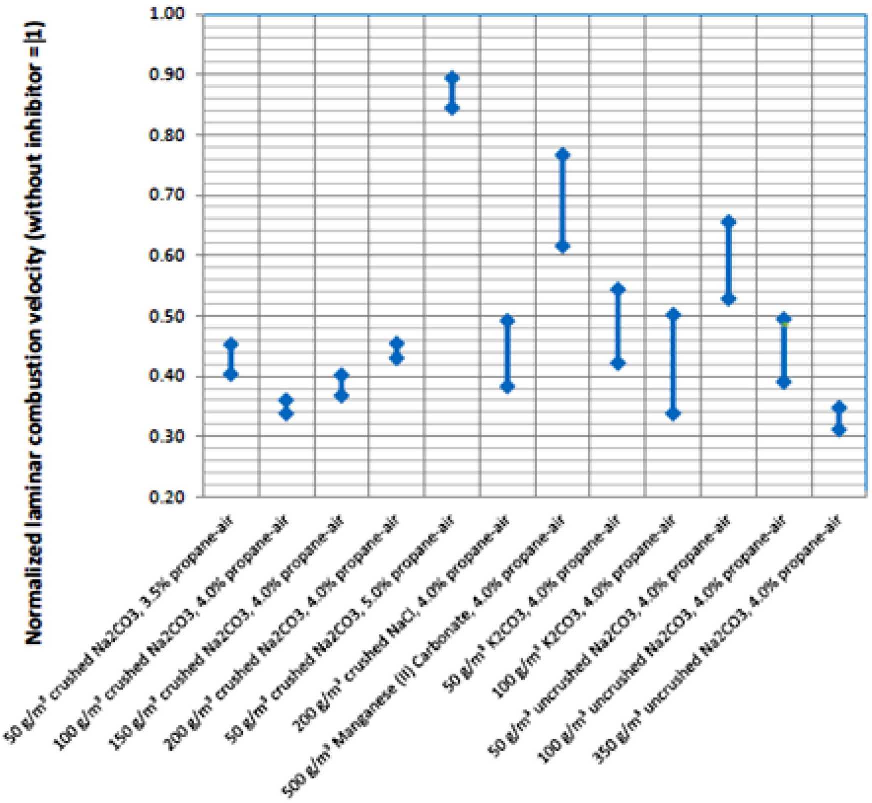

Figure 2. Influence of inhibitors on normalized laminar combustion velocity (propane/air mixtures)

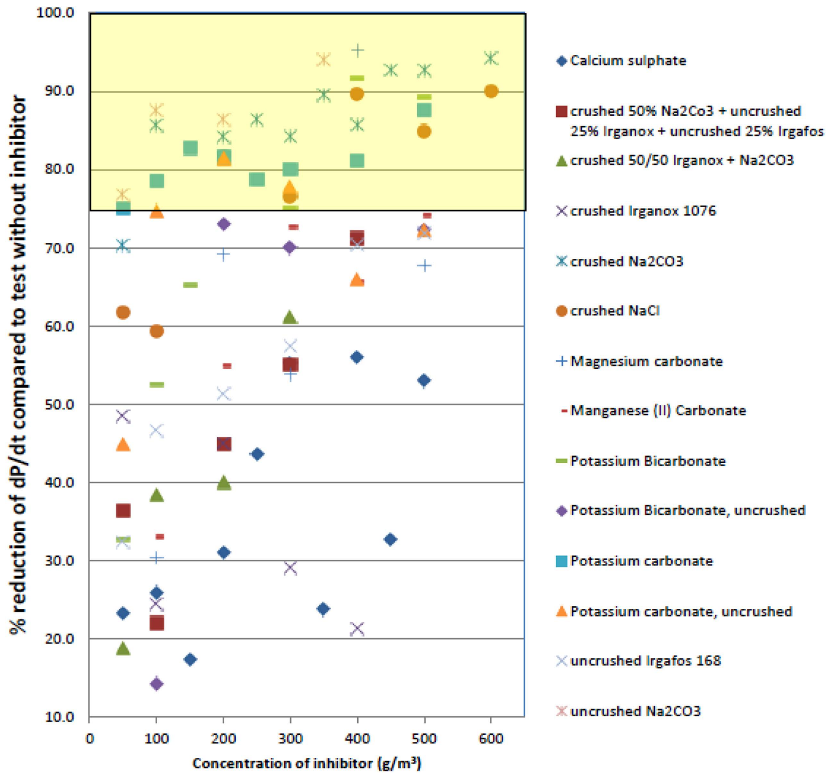

Figure 3. Pressure rise reduction for different inhibitors (propane/air-mixtures)

double wall. In between the walls a water jacket serves to cool the inner wall for heat generated by the explosions (initial temperature for all tests is approximately 20°C).

For testing, the vessel is first evacuated. The desired amount of gas is introduced via a valve and controlled by a pressure monitoring system (concentration determined on

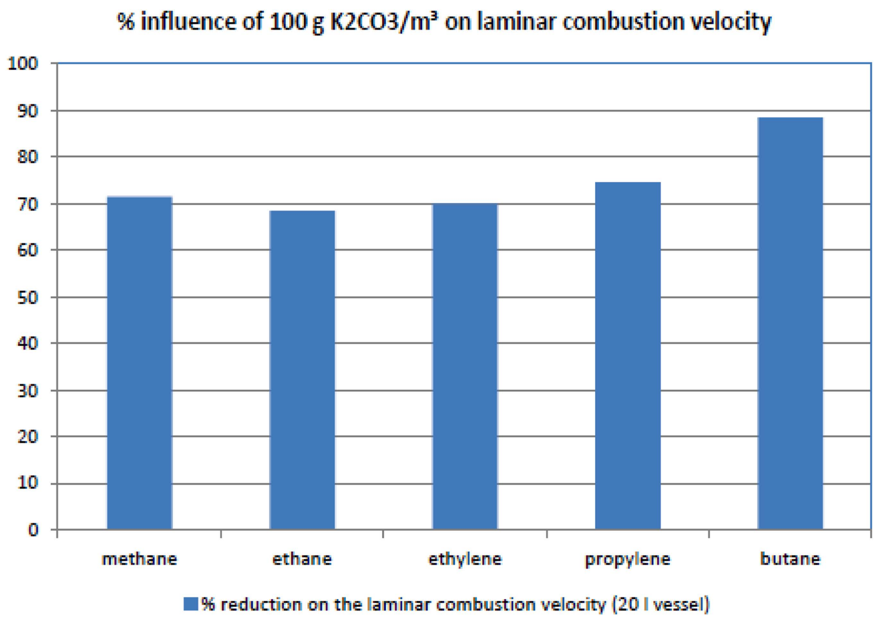

Figure 4. Influence of fuel type on inhibitor efficiency

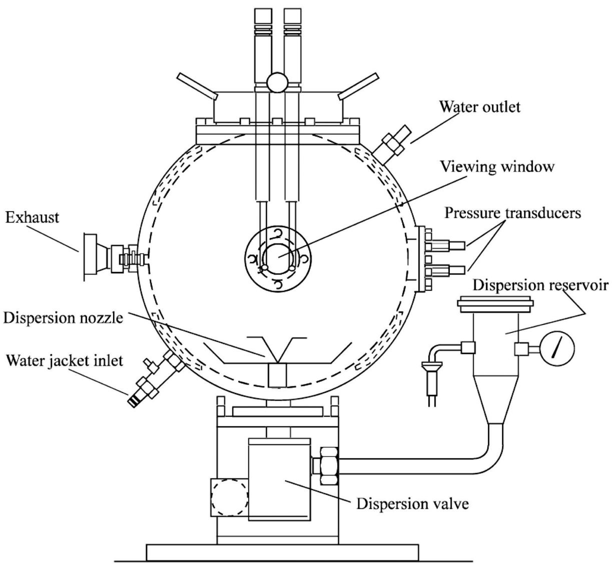

Figure 5. 20 l vessel

the basis of the method of partial pressures, assuming a final pressure of 1 bar absolute after dust dispersion). Next air is introduced until the pressure in the sphere is 0.4 bar absolute.

The desired amount of flame inhibitor is dispersed into the sphere from a pressurized container via a fast acting valve and a rebound nozzle. The fast acting valve is pneumatically opened and closed by means of an auxiliary piston. After injection of the flame inhibitor the pressure in the 20-l sphere is equal to 1 bar absolute.

The valves for the compressed air are activated electrically. The ignition source is located in the centre of the sphere. Ignition is effected 60 ms after injection of the flame inhibitor started. The ignition source was a chemical igniter (ignition energy 100 J). The pressure measuring system includes two pressure sensors; recording and control equipment. The tests were performed varying the flame inhibitor concentration.

Some of the experimental results are shown and discussed in the sections below.

INHIBITING PROPERTIES OF POTASSIUM CHORIDE

Potassium chloride (KCl) was preselected as a possible VCE inhibiting agent based on the proven effectiveness of sodium chloride in the research by Hoorelbeke (2011) and based on the results of the work by Babushok et al. The experiments with KCl as inhibitor were conducted in a 20 l vessel.

Due to the significant influence of particle size distribution, the solid KCl was crushed before use to improve the flame inhibiting properties. The KCl particle size distribution after crushing is given in Table 1.

Test were performed using lean (3.5% v/v), stoichiomeric (4.0% v/v) and rich (5.0% v/v) propane-air mixtures.

Table 1. KCl particle size distribution

Particle size range	%
> 500 μm	1.6
< 500 μm	98.4
< 250 μm	85.1
< 125 μm	50.3
< 63 μm	26.0

The results of the experiments are summarized in Figure 6.

For lean mixtures, the flame does not propagate (i.e. is quenched) when the concentration of potassium chloride exceeds 100 g/m^3.

For stoichiometric mixtures, potassium chloride yields a reduction of laminar flame velocity by almost 90% for concentrations above 100 g/m^3.

Also for rich mixtures, potassium chloride has a good mitigation effect, reducing the laminar flame velocity by about 70% for concentrations above 100 g/m^3.

Figures 7–9 compare the performance of KCl as inhibitor against the performance of the combustion inhibiting agents NaCl and K_2CO_3.

For lean concentrations, potassium chloride has slightly worse mitigation properties compared to potassium carbonate. Potassium carbonate did not yield any flame propagation at 100 g/m^3, while 200 g/m^3 potassium chloride was needed to fully stop flame propagation.

However, for stoichiometric and rich propane-air mixtures, the mitigation effect of potassium chloride was better than for both potassium carbonate and sodium chloride with significantly lower laminar flame velocities even for moderate inhibitor concentrations of 50–100 g/m^3.

Another benefit of potassium chloride is that it does not seem to have the same hygroscopic properties as for example potassium carbonate, making it much easier to handle and use in practice as part of an industrial real-scale explosion mitigation system.

STUDY OF THE INFLUENCE OF PARTICLE SIZE AND PARTICLE CONCENTRATION ON THE EFFECTIVENESS OF POTASSIUM CARBONATE AS INHIBITOR

In the research of Hoorelbeke (2011), the focus was directed towards potassium carbonate and potassium bicarbonate as inhibitors because of their effectiveness as inhibitor together with their non-toxic properties, relatively low cost and commercial availability in large quantities.

Some more research was conducted on the impact of particle diameter and particle concentration on the inhibition effectiveness of potassium carbonate.

The results indicate that the inhibition effectiveness is similar for particle diameters below 100 μm for inhibitor concentrations above 50 g/m^3 (see Figure 10).

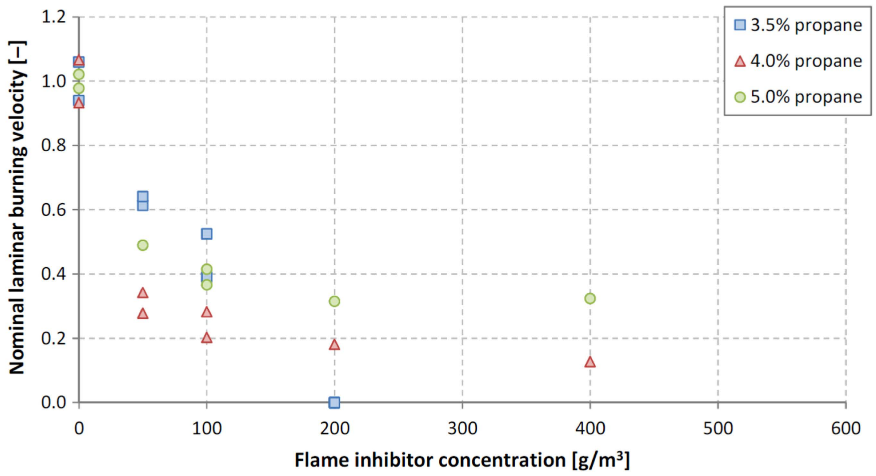

Figure 6. Nominal laminar burning velocities for tests with KCl in lean, stoichiometric and rich propane/air-mixtures

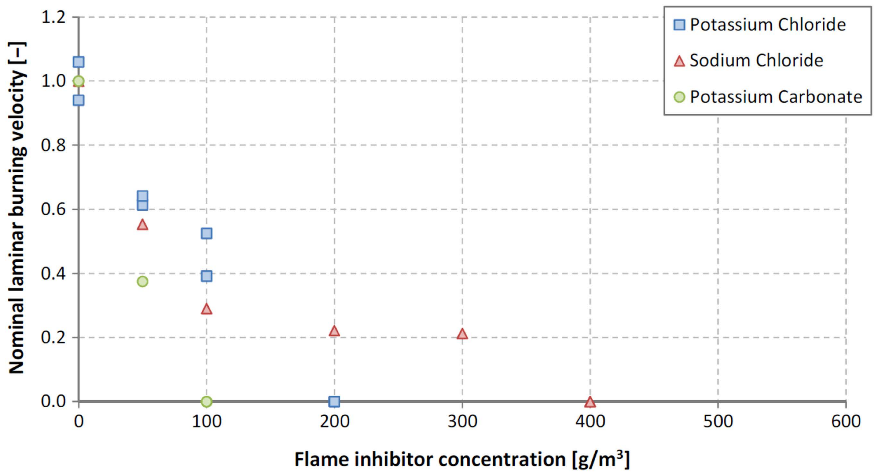

Figure 7. Nominal laminar burning velocities for tests with KCl NaCl and K_2CO_3 in a lean propane/air-mixture

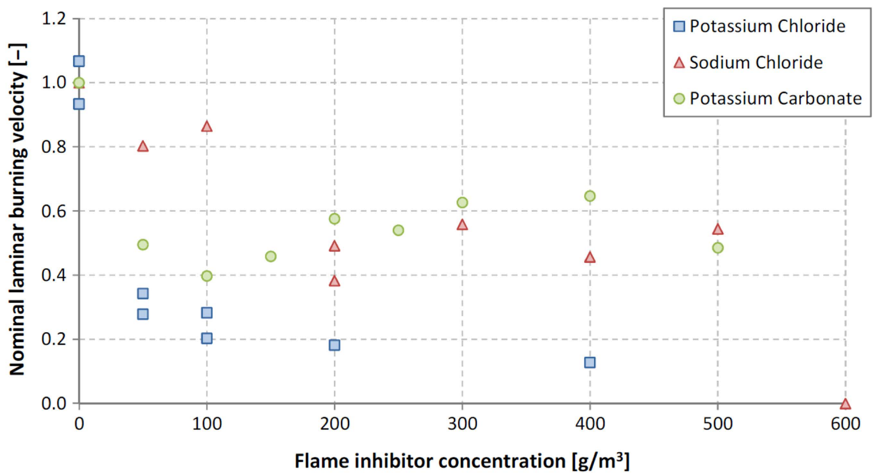

Figure 8. Nominal laminar burning velocities for tests with KCl NaCl and K_2CO_3 in a stoichiometric propane/air-mixture

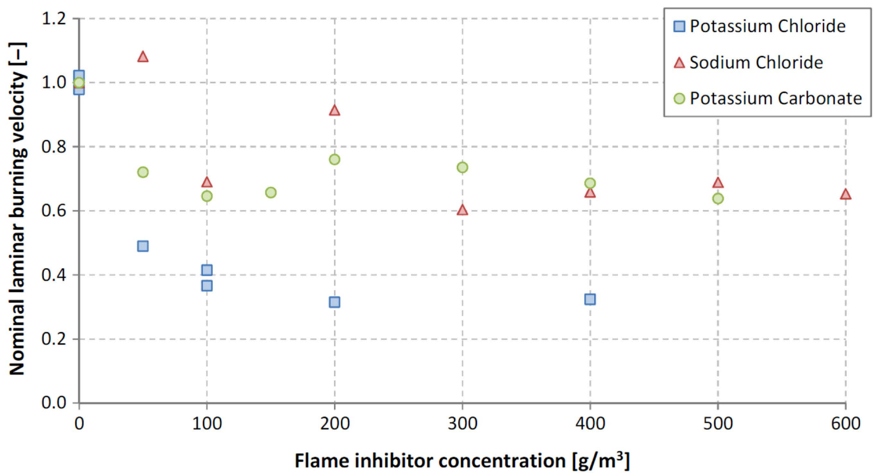

Figure 9. Nominal laminar burning velocities for tests with KCl NaCl and K_2CO_3 in a rich propane/air-mixture

STUDY OF BI-EX AND PURPLE K AS VCE INHIBITING AGENTS

The experiments to study the inhibiting properties of potassium carbonate and potassium bicarbonate were done using pure potassium carbonate and pure potassium bicarbonate. However, due to the hygroscopic properties of K_2CO_3 and $KHCO_3$, it proved difficult to develop a good dispersion system for these substances. Such a dispersion system is needed for the development of an industrial application of the inhibition technology. Therefore, the VCE inhibiting properties of some commercial fire extinguishing powders were investigated. Two different fire extinguishing powders were tested, namely Bi-Ex and Purple K.

Bi-Ex consists mainly of sodium bicarbonate while Purple K 80 consists of potassium bicarbonate. Besides the bicarbonate, Bi-Ex and Purple K 80 include some other products to reduce coagulation and ageing of the product and to improve its fluidization properties.

The experiments were performed in a 20-l spherical explosion vessel described above for lean, stoichiometric and rich mixtures of propane-air.

The particle size distribution for Bi-Ex and Purple K used in the experiments is given in Table 2.

Test were performed using lean (3.5% v/v), stoichiometric (4.0% v/v) and rich (5.0% v/v) propane-air mixtures.

The results of the experiments are summarized in Figures 11 and 12.

For lean mixtures both 100 g/m^3 Bi-Ex and 100 g/m^3 Purple K 80 reduces the laminar flame speed by about 80%. Bi-Ex quenched the flame with concentration above 200 g/m^3.

For stoichiometric mixtures 100 g/m^3 of Bi-Ex yielded a reduction of the laminar flame speed of almost 80%, while 100 g/m^3 of Purple K 80 reduced the laminar flame speed by approximately 70%.

Both 100 g/m^3 of Bi-Ex and 100 g/m^3 of Purple K 80 reduced the laminar flame speed in a rich mixture of propane air by about 55%.

For rich and stoichiometric mixtures Bi-Ex was a more efficient inhibitor than Purple K 80 with dust concentration of 100 g/m^3 and more, while Purple K 80 tends to be a more efficient inhibitor with lower dust concentrations. Bi-Ex is the most efficient inhibitor for lean mixtures at all dust concentrations.

Figures 12–14 compare the performance of Bi-Ex and Purple K 80 as inhibitor against the performance of the previously tested inhibiting agents KCl and K_2CO_3.

For lean concentrations Bi-Ex is the most efficient inhibitor up to 100 g/m^3 of dust concentration. From this concentration potassium carbonate is the most efficient inhibitor, quenching the flame at 100 g/m^3.

For stoichiometric and rich mixtures potassium chloride is equally efficient as Bi-Ex and Purple K 80. It should be noted that both Bi-Ex and Purple K 80 has a larger mass fraction of particles smaller than 63 μm. This could have a significant impact on the efficiency of the inhibitor.

It must be emphasised that in order for the inhibitor to work, it must be in its ion form. The inhibitor will have to melt as well as undergo other chemical reactions such as the reaction from bicarbonate to carbonate. Therefore, as it has been seen in previous work, [5], the contact time between the salt and the inhibitor is crucial for an effective reduction of the flame speed. This relationship is shown in van Wingerden, M. et al. [5]. The effect of the Bi-Ex and Purple K 80 should therefore also be investigated in large scale experiments in order to quantify the effectiveness in this turbulent time scale.

DEVELOPMENT OF A DISPERSION SYSTEM FOR PRACTICAL APPLICATION OF THE INHIBITION TECHNOLOGY ON AN INDUSTRIAL SCALE

The practical use of the VCE inhibition technology on an industrial scale does not only require study and selection of the most appropriate chemical substance in terms of inhibition power and compatibility with the external

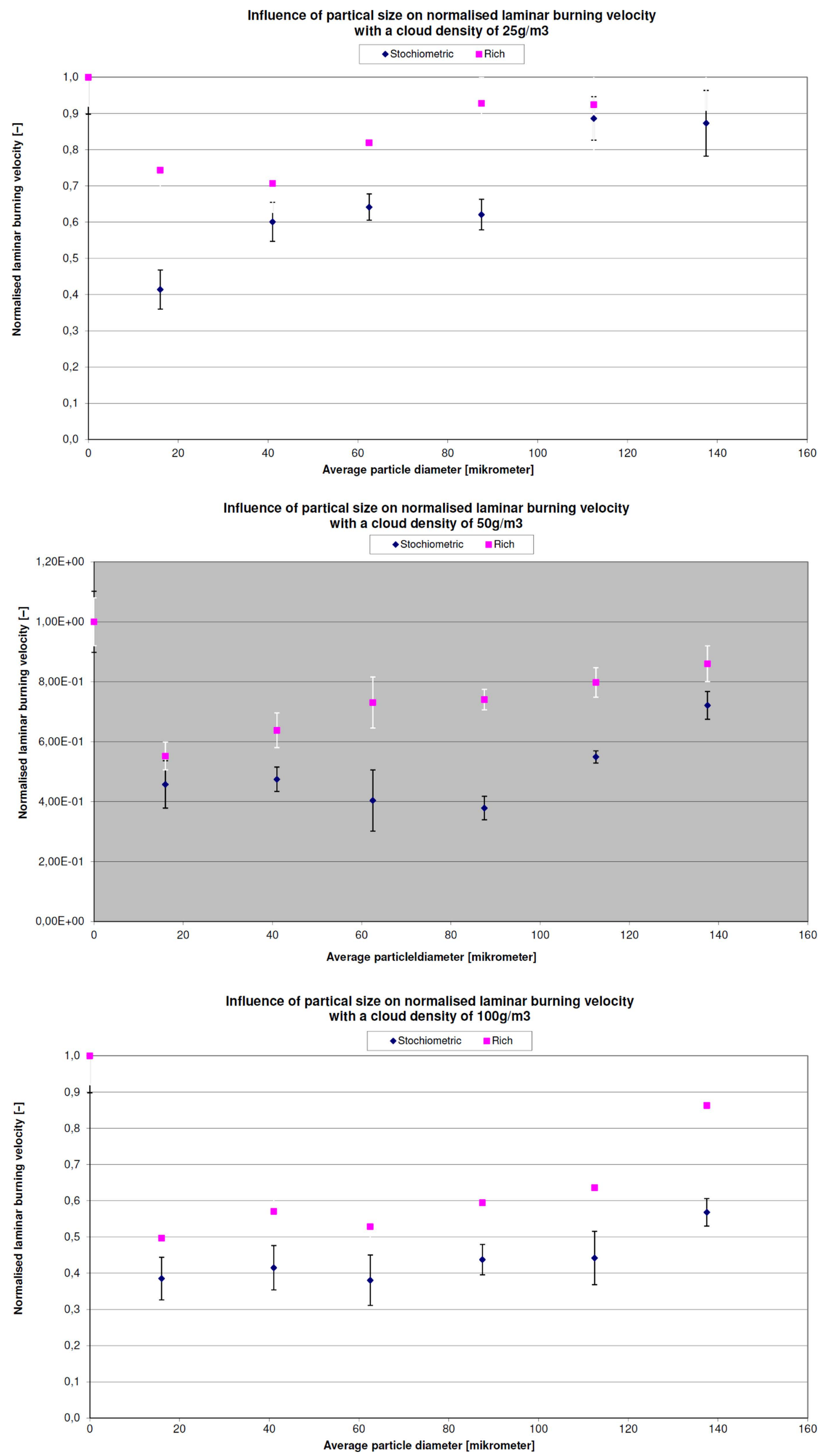

Figure 10. Influence of particle diameter and particle concentration on the inhibition effectiveness of potassium carbonate in propane/air-mixtures

Table 2. Particle size distribution (in %) for Bi-Ex and Purple K 80

Particle size range	Bi-Ex	Purple K 80
> 500 μm	–	–
< 500 μm	–	–
< 250 μm	–	–
< 125 μm	99	–
< 63 μm	79	75
< 40 μm	53	–

environment (stability in time, toxicity, availability, cost, corrosive properties, conductivity), but also the development and selection of the most appropriate technology to inject and disperse the solid inhibitor particles into a flammable hydrocarbon cloud.

SELECTION OF INHIBITOR INJECTION SYSTEM

The decision was taken to develop a modular injection system consisting of individual autonomous injection skids. Such a design is much more flexible and adaptable than a fixed system which is designed for a specific application and a specific environment.

The following design criteria were identified for a single powder inhibitor injection skid:

- The size of the volume to be protected must be in the order of 1.250 m^3 (footprint of about 300 m^2) per skid;
- The injection system must ensure a concentration of inhibitor in the cloud in the order or 100 g/m^3 during at least 5 minutes;
- The inhibitor cloud must be available within 10 seconds after activation of the injection skid;
- The injection skid can be used in a highly congested environment (size limitations);
- The throw length of inhibiting powder (= maximum horizontal distance reached) must be large enough to ensure the creation of a well dispersed inhibitor cloud.

A review was conducted of commercially available injection systems against the above mentioned design criteria. The purpose of this exercise was to select the most appropriate injection technology for the development of a VCE mitigation system by chemical inhibition.

Different commercially available systems for injection of solid inhibitors were studied. These systems included:

- Explosion suppression systems
- Powder fire extinguishing modules
- Fixed piped dry powder system
- Fixed dry powder monitor
- “Impulse storm”
- Mobile powder extinguishing system.

Figures 16–21 show examples of the above mentioned injection technologies.

A review of the above mentioned technologies for injection of dry inhibitor powders indicated that the mobile powder extinguishing systems were the most compatible with the design requirements for a single powder inhibitor injection skid.

The latter technology was selected as a basis for development of an inhibitor injection system. A modified version of a mobile powder extinguishing system was used to perform experiments to study the dispersion behaviour of large clouds of solid inhibitor particles in congested and confined process units.

The modifications to the commercially available mobile powder extinguishing system included:

- Installation of pressure measurements at several locations of the system
- Addition of a dispersion nozzle

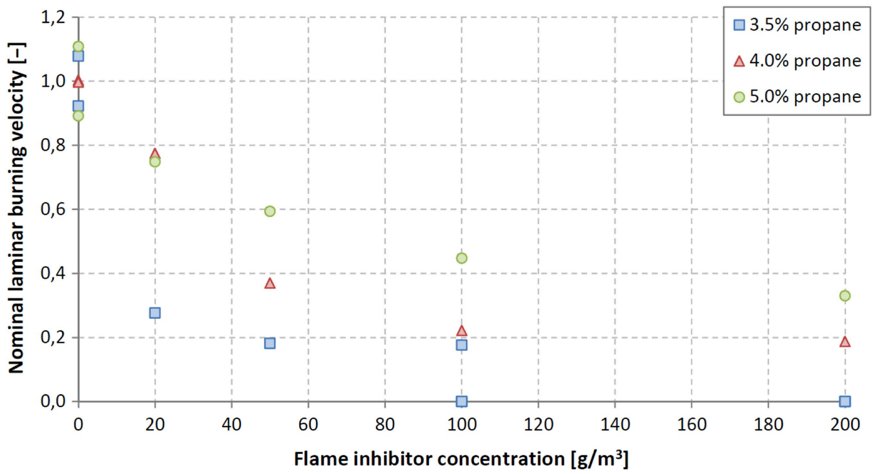

Figure 11. Nominal laminar burning velocities for tests with Bi-Ex in lean, stoichiometric an rich propane/air-mixtures

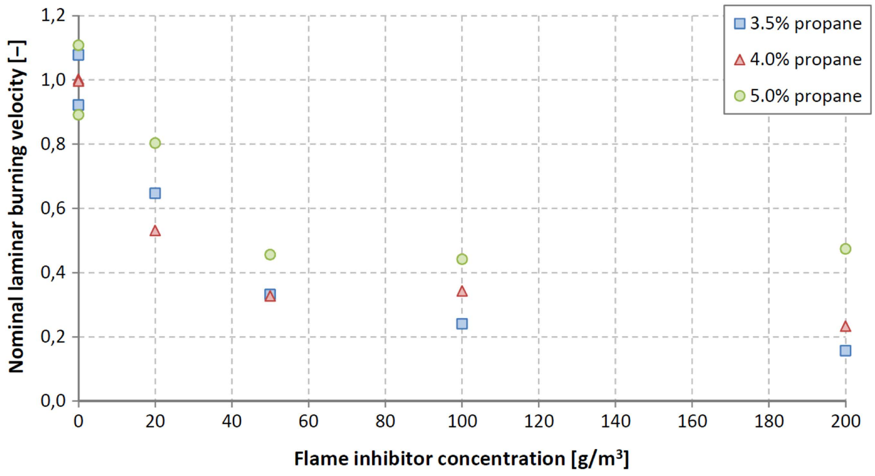

Figure 12. Nominal laminar burning velocities for tests with Purple K 80 in lean, stoichiometric an rich propane/air-mixtures

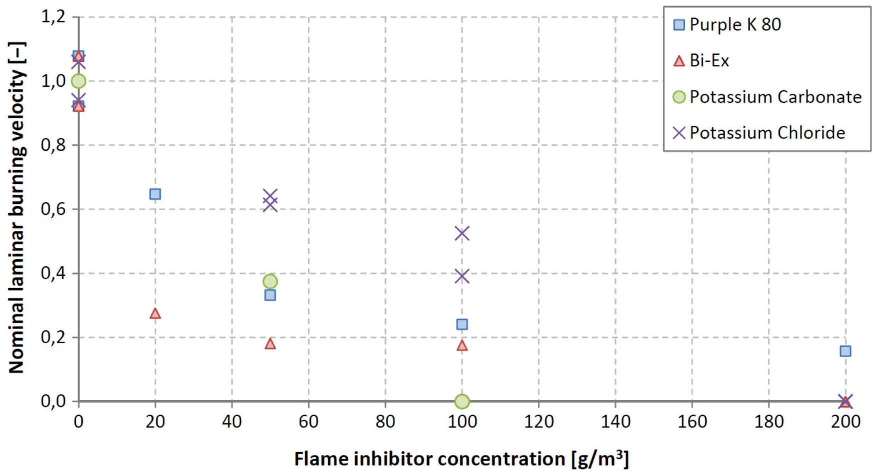

Figure 13. Nominal laminar burning velocities for tests with Bi-Ex, Purple K 80, KCl and K_2CO_3 in a lean propane/air-mixture

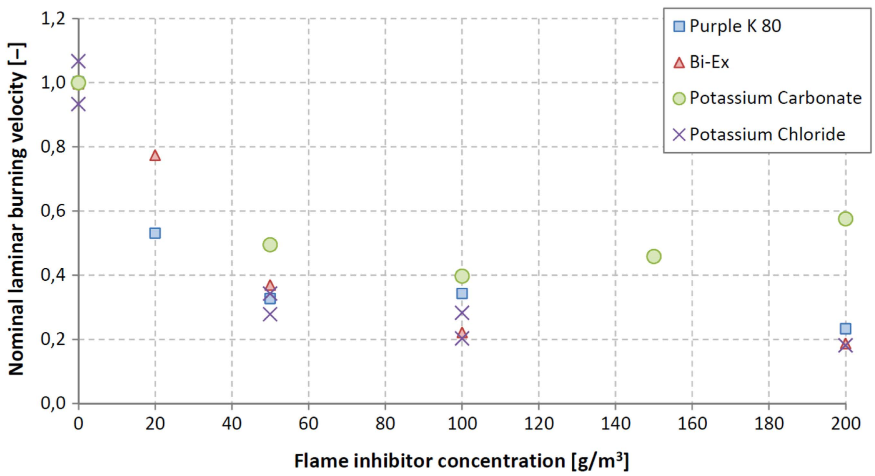

Figure 14. Nominal laminar burning velocities for tests with Bi-Ex, Purple K 80, KCl and K_2CO_3 in a stoichiometric propane/air-mixture

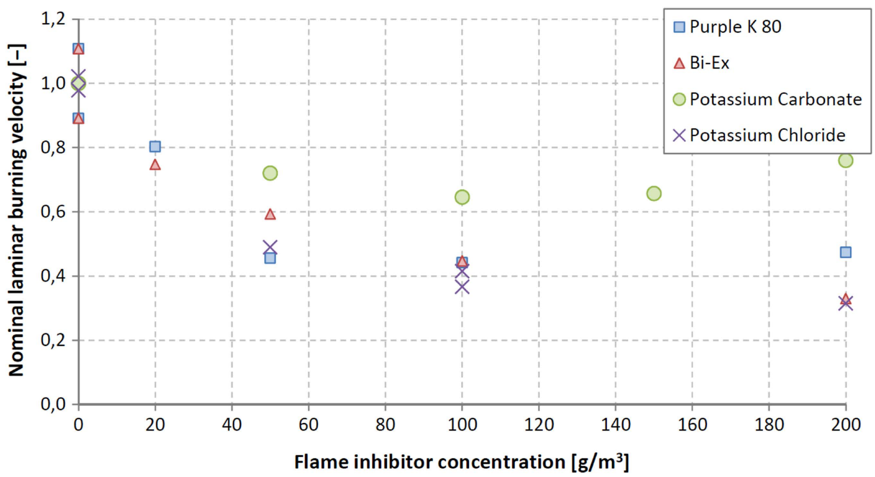

Figure 15. Nominal laminar burning velocities for tests with Bi-Ex, Purple K 80, KCl and K_2CO_3 in a rich propane/air-mixture

- Installation of PLC controlled valves to control the inhibitor injection sequence and duration
- Installations of load cells for measurement inhibitor mass flow rates.

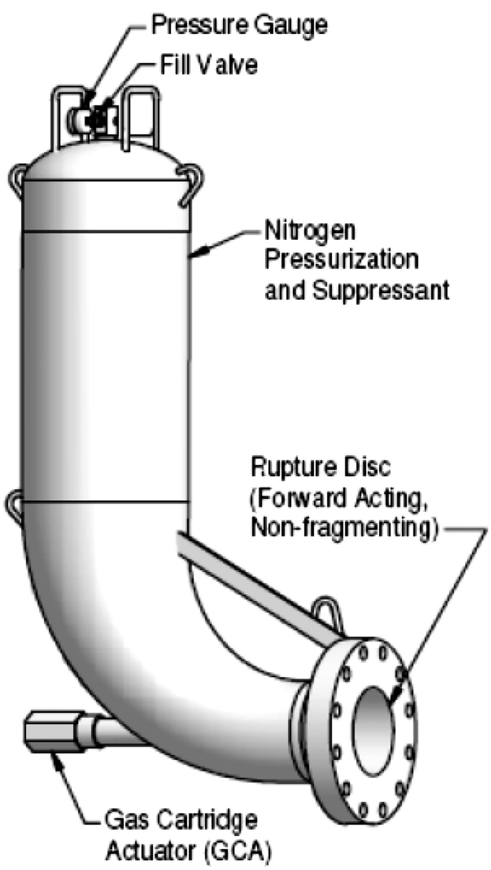

Figure 16. Example of explosion suppression system

The modified mobile powder extinguishing system used in the inhibitor dispersion experiments (see below) is shown in Figure 21.

Some characteristics of a single injection skid are listed below:

- Mass of inhibiting powder per skid: 5000- 1.000 kg
- Type of inhibitor: Bi-Ex (with 97% sodium bicarbonate) with a D50 of 40 μm
- Footprint of skid: about 1 m^2
- Height of injection nozzle: about 4 m above ground
- Inhibitor vessel pressure: 16 barg (using a 15 Nm^3 N_2 bottle at 300 barg)
- Inhibitor injection sequence: 15 shots of 5 seconds (total time: 300 s) with a 15 to 30 second cloud settling time between individual injection shots
- Mass flow rate of inhibitor during injection shots: 5 to 15 kg/s.

Figure 17. Example of powder fire extinguishing module

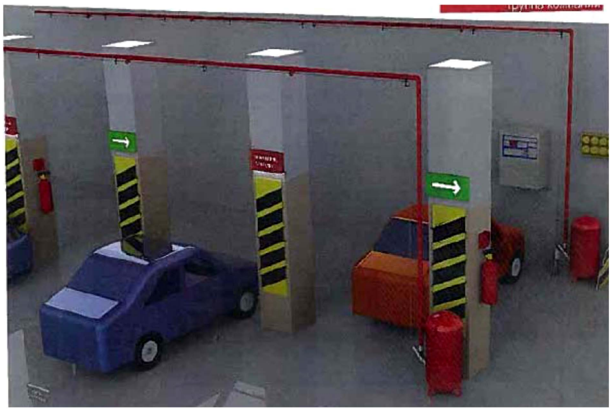

Figure 18. Example of fixed piped dry powder system

Figure 19. Example of fixed dry powder monitor

DISPERSION BEHAVIOUR OF LARGE CLOUDS OF SOLID INHIBITOR PARTICLES

The effectiveness of a VCE mitigation system by chemical inhibition depends on the ability to create a cloud of solid inhibitor particles meeting the following requirements:

- The inhibitor particle cloud has to be large enough (covering a volume of at least 1.250 m^3 per injection skid);
- The inhibitor concentration in the cloud must be high enough (at least 20 to 40 g/m^3)
- The inhibitor particle cloud must be present for a long enough time (at least 5 minutes).

The verification of the above requirements is being performed in large scale dispersion tests of solid inhibitor powder.

The dispersion experiments were performed in a dismantled petrochemical facility in the east of France (see Figure 23) using the modified mobile powder extinguishing system discussed above.

Figures 24 and 25 show pictures that were taken during these dispersion tests.

Figure 20. Impulse Storm

Figure 21. Example of a mobile powder extinguishing system

The large scale dispersion tests resulted in the following findings:

- During one of the dispersion tests, pure micronized potassium carbonate (D50 = 10 μ) was sticky and caking occurred in the vessel. Only 50% of 170 kg was discharged and nitrogen channelling occurred in the bulk of the powder inside the vessel. These findings indicate that inhibitors are difficult to use in practical applications without additives to avoid caking and without additives to improve fluidization properties.
- Very small inhibitor particles (i.e. D50 ≤ 10 μm) drifted upward and outside the process unit by the

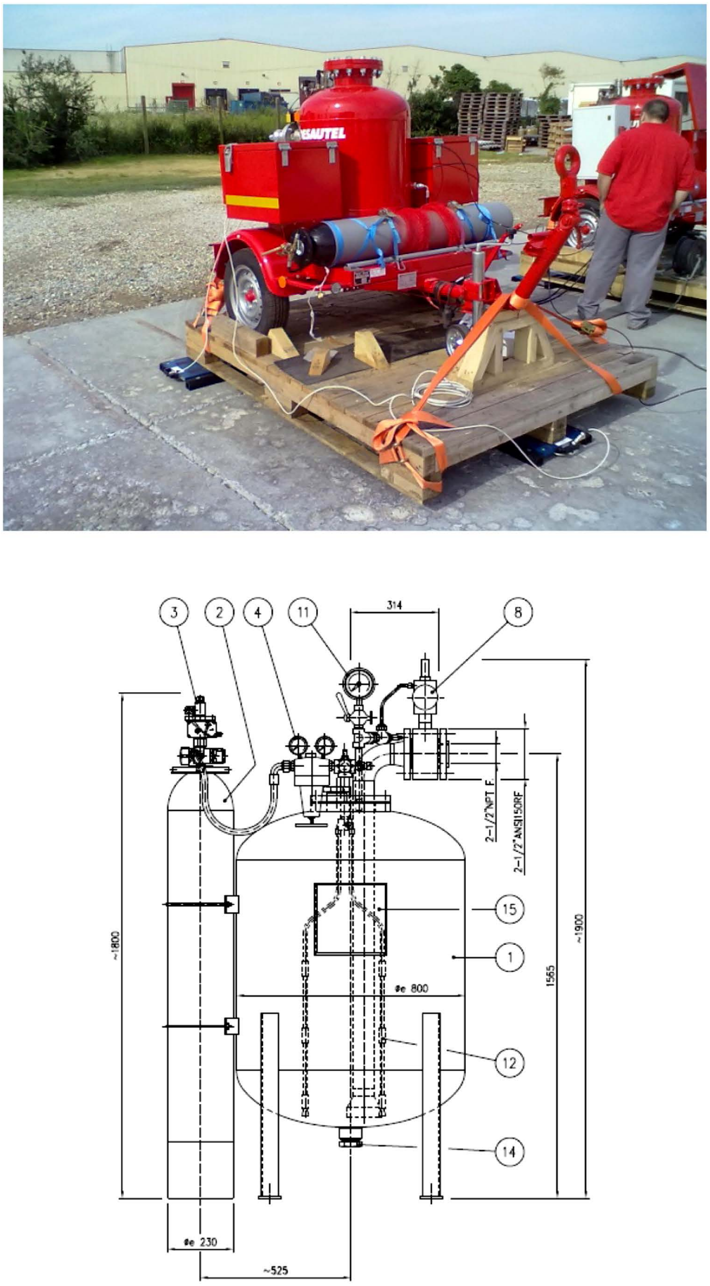

Figure 22. Modified mobile powder extinguishing system for use in dispersion experiments

wind (see also Figure 25). An appropriate particle diameter range for application in a VCE mitigating system seems to be D50 = 20–40 μm.

- Fouling of the lenses of the optical concentration measurement probes has lead to uncertainty on inhibitor concentrations. An efficient flushing system to keep the optics clear of inhibitor deposits needs to be foreseen (see also Figure 26).
- Measurements of inhibitor concentration at various locations in the inhibitor cloud indicate that inhibitor concentrations are in the range of 100 g/m^3 or more for a duration of about 60 seconds.
- A multi shot sequence with an inhibitor injection of about 8 kg/s during 5 seconds a 15 second settling time between injection shots appears to be a fair basis for design of the injection skid.
- The inhibitor cloud size during the dispersion tests was about 1.250 m^3, which is in line with the preset requirements for the individual inhibitor injection skid performance.

Figure 23. Petrochemical facility used for large scale dispersion experiments

- With the current design for the individual injection skid, the minimum time between activation of the system and the presence of an inhibitor cloud covering a volume of about 1.250 m^3 is about 25 to 30 seconds.
- Optimization of the injection skid design and operation is needed to extend the duration of the inhibitor particle cloud to minimum 5 minutes. Additional dispersion tests are needed for this purpose.

An example of one of the measured inhibitor concentration profiles at a given location in the inhibitor cloud during the dispersion tests is given in Figure 27. The vertical blue bars in this figure indicate the period during which injection of inhibitors takes place. In the period between the blue bars, the inhibitor particle cloud is allowed to settle and disperse.

The grey area between the concentration profiles indicate the uncertainty in measured values due to fouling of the optics of the concentration measurement system as discussed above.

Figure 24. Large scale dispersion test of solid inhibitor particle cloud

Figure 25. Large scale dispersion test of solid inhibitor particle cloud

ONGOING RESEARCH

Research in the chemical inhibition of Vapour Cloud Explosions is being continued. Especially the following aspects are being investigated in more depth:

- Study of the interaction of inhibitors on the chemical reaction mechanism (reaction equilibrium and reaction kinetics);
- Experimental study of the efficiency of chemical inhibition to mitigate vapour cloud detonations;
- Influence on chemical inhibition on Deflagration to Detonation Transition (DDT);
- Experimental study of the efficiency of mixtures of solid inhibitors;
- Study of aqueous solutions of inhibitors injected in the form of a mist;
- Optimization of inhibitor injection system (by experimental research on injection technology, injection sequence, injection flow rate, injection pressure etc.) to guarantee the presence of an inhibitor particle cloud of large enough size, high enough concentration for a long enough time.

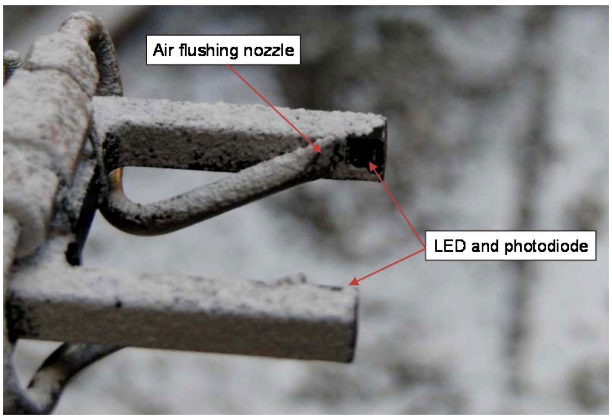

Figure 26. Fouling of the optics of the concentration measurement probes with inhibitor powder

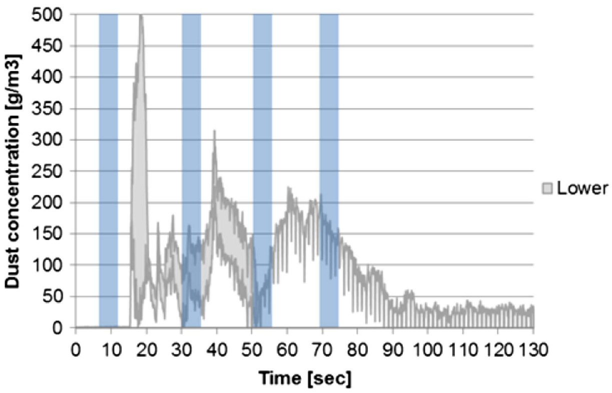

Figure 27. Inhibitor concentration profile measured in large scale dispersion test

- Development of a scheme to optimize the inhibition injection system as a function of local parameters (type of hydrocarbons present at the site, available detection systems. . ..)

Finally, the feasibility of large scale explosion tests (1.000–5.000 m^3) is being investigated to test the optimized VCE mitigation system on an industrial scale.

CONCLUSION

A novel technique to mitigate the consequences of Vapour Cloud Explosions was proposed by Hoorelbeke (2011). The technique is based on the injection of solid inhibitor particles in a flammable hydrocarbon cloud. The inhibitors interact with the combustion reaction mechanism to suppress partially or completely the combustion reactions.

In this paper, additional research results in the area of mitigation of Vapour Cloud Explosions by chemical inhibition are presented.

Testing of additional species with combustion inhibiting properties indicate that potassium chloride and the commercially available fire extinguishing agents Bi-Ex (based on sodium bicarbonate) and Purple K 80 (based on potassium bicarbonate) have superior inhibition characteristics compared to potassium carbonate, especially for stoichiometric en rich mixtures. Furthermore, some more research was conducted on the impact of particle diameter and particle concentration on inhibition effectiveness of potassium carbonate. The test results indicate that the inhibition effectiveness is similar for particle diameters below 100 μm for inhibitor concentrations above 50 g/m^3.

The above results are useful in the selection and engineering of the most effective inhibitor for application in VCE mitigation systems.

Besides research to optimize the nature of the inhibitor, research was done on the level of the most appropriate inhibitor injection system.

A set of design criteria were developed for a system to act as an effective Vapour Cloud Explosion mitigation system.

Various commercially available designs for inhibitor injection systems were reviewed and compared against the predefined design criteria. One of these designs was selected and modified for the purpose of the development of a VCE mitigation system.

The performance of the modified system was tested in some large scale inhibitor dispersion tests. The results of the dispersion tests indicate that the implementation a large scale industrial application of a VCE mitigation system based on chemical inhibition is possible and realistic. Further testing needs to be performed to optimize the effectiveness of such a system.

REFERENCES

1. Hoorelbeke, Numerical and Experimental Study of Vapour Cloud Explosions – Mitigation by Inhibitors, PhD Thesis, Brussels University (2011).
2. V. Babushok, W. Tsang Inhibitor Rankings for Alkane Combustion Combustion and Flame, Vol. 123, Vol. 4, 488–506 (2000).
3. Hoorelbeke P, Helschger G, Wilkins B, Mitigation of Vapor Cloud Explosions by Inhibitors, 3rd World Conference on Safety of Oil and Gas Industry, China, Beijing, 27–28 Sept 2010.
4. Lee JH, Hoorelbeke P, Roosendans D, Van Wingerden K., Mitigation of Vapor Cloud Explosions by Inhibitors – an update, 4th World Conference on Safety of Oil and Gas Industry, South-Korea, Seoul, 27–29 June 2012.
5. van Wingerden, M., van Wingerden K. and Andersen, C.T., Extended Experimental Determination of the Effect of Flame Inhibitors on the Laminar Burning Velocity of Propane-Air Mixtures GexCon report no. GexCon-10-F44147-RA-1, rev 00, 2010.