Industrial System for Chemical Inhibition of Vapor Cloud Explosions

Process Safety Conference
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Prof. dr. ir. D. Roosendans
TOTAL S.A., Paris, France
Project Characteristics

- Start of project in 2004
- > 2 M€ of research (2005 – 2018)
- International collaboration with institutes & specialized organizations
- So far 3 PhD thesis dedicated to the project
  - P. Hoorelbeke (2011)
  - O. Dounia (2017)
  - D. Roosendans (2018)
- Internal and external awards
Outline of Presentation

1. Context of Vapor Cloud Explosions

2. Principles of Combustion and Flame Inhibition

3. Experimental Study on Flame Inhibition by dry inhibitor powders

4. Industrial Application of Flame Inhibition Technology by Dry Powders of Alkali Metal Compounds
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Context of Vapor Cloud Explosions

6 kg of natural gas
Refinery Units and Petrochemical Units in the World

<table>
<thead>
<tr>
<th>Region</th>
<th>Refinery units</th>
<th>Petrochemical units</th>
</tr>
</thead>
<tbody>
<tr>
<td>NAM</td>
<td>1707</td>
<td>1693</td>
</tr>
<tr>
<td>SAM</td>
<td>634</td>
<td>619</td>
</tr>
<tr>
<td>EUROPE</td>
<td>1869</td>
<td>2382</td>
</tr>
<tr>
<td>ME</td>
<td>450</td>
<td>737</td>
</tr>
<tr>
<td>AFRICA</td>
<td>460</td>
<td>219</td>
</tr>
<tr>
<td>NE ASIA</td>
<td>2065</td>
<td>5380</td>
</tr>
<tr>
<td>ASIA PACIFIC</td>
<td>808</td>
<td>1732</td>
</tr>
<tr>
<td>FSU</td>
<td>926</td>
<td>571</td>
</tr>
</tbody>
</table>

Refinery units: 8919  
Petrochemical units: 13333  
TOTAL: 22352
Are Vapor Cloud Explosions a problem of the past?
BayernOil (Vohburg, Germany), 1 September 2018

- Pressure drop reactor D-3401A gasoline desulfurization (140°C, 25 bar)
- Crack of approx. 1.5 m in length, starting directly at the support claw suspension (80 m³ reactor)
- Gas alarm: in a few seconds increase to 20/40% LEL and beyond...44 seconds afterwards...vapor cloud explosion...
- CAT Cracker/gas plant, De-hexanizer, DIP, ETBE, gasoline desulfurization plant (OATS) field completely destroyed
- Proximity blast proof container for employees (nothing happened!) max 30-50 m
- Neighboring old control room destroyed (moved to BP Texas in new control room, but cable/junction over old control room) -> process control system completely lost

Vapor Cloud Explosions are not a problem of the past!
## Vapor Cloud Explosion Probabilities

<table>
<thead>
<tr>
<th>Unit Type</th>
<th>Source</th>
<th>VCE probability (1/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkylation unit</td>
<td>API</td>
<td>5.10 \times 10^{-4}</td>
</tr>
<tr>
<td>Cat cracking unit</td>
<td>API</td>
<td>6.50 \times 10^{-4}</td>
</tr>
<tr>
<td>Cat reforming unit</td>
<td>API</td>
<td>2.60 \times 10^{-4}</td>
</tr>
<tr>
<td>Crude unit</td>
<td>API</td>
<td>4.90 \times 10^{-4}</td>
</tr>
<tr>
<td>Hydrocracking unit</td>
<td>API</td>
<td>5.60 \times 10^{-4}</td>
</tr>
<tr>
<td>Hydrotreating unit</td>
<td>API</td>
<td>2.00 \times 10^{-4}</td>
</tr>
<tr>
<td>Average all refinery units</td>
<td>API</td>
<td>4.30 \times 10^{-4}</td>
</tr>
<tr>
<td>Ethylene unit</td>
<td>Total Petrochemicals</td>
<td>&lt; 10^{-2}</td>
</tr>
<tr>
<td>Standard process unit</td>
<td>BP</td>
<td>1.30 \times 10^{-4}</td>
</tr>
<tr>
<td>Chemical/refinery high pressure unit</td>
<td>BPI</td>
<td>1.30 \times 10^{-3}</td>
</tr>
</tbody>
</table>

Average probability of VCE: +/- 5.10^{-4}/yr
Number of process units in TOTAL RC: +/- 200
Probability of major VCE in TOTAL RC: Once every 10 years

La Mède, 1992
Buncefield, 2005

Low probabilities? (once every 10,000 years per unit)
## Barriers against Vapor Cloud Explosions

<table>
<thead>
<tr>
<th>System</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isolation systems</td>
<td>Take time to be effective</td>
</tr>
<tr>
<td>Depressurization systems</td>
<td>Residual vapor cloud to be considered</td>
</tr>
<tr>
<td>Water curtains</td>
<td>Limited efficiency</td>
</tr>
<tr>
<td>Water deluge</td>
<td>Time needed for full deployment</td>
</tr>
<tr>
<td>Blast walls</td>
<td>Not always practical</td>
</tr>
<tr>
<td></td>
<td>Limited efficiency</td>
</tr>
<tr>
<td>Blast design</td>
<td>Expensive</td>
</tr>
<tr>
<td></td>
<td>Sometimes difficult to achieve</td>
</tr>
<tr>
<td>Reinforced buildings</td>
<td>Expensive</td>
</tr>
<tr>
<td></td>
<td>Sometimes difficult to achieve</td>
</tr>
</tbody>
</table>

Today, there are no effective active mitigating barriers to protect against the occurrence and consequences of Vapor Cloud Explosions.

There is a need for active mitigating barriers!
Principles of Combustion and Flame Inhibition

1. Context of Vapor Cloud Explosions

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Moses Gomberg, a chemistry professor at the University of Michigan, discovered organic free radicals in 1900.
Radicals and Combustion Reactions

- Combustion reactions are radicular chain reactions. These chain reactions depend on the presence of flame radicals in sufficient amounts. Without these radicals, the chains are broken and combustion reactions cannot continue.

- Consider the combustion of hydrogen ($H_2$) in oxygen ($O_2$): $2H_2 + O_2 \rightarrow 2H_2O$

Examples of reactions intervening in the combustion of $H_2$

- **Initiation** (= creation of radicals)
  - $H_2 + M \rightarrow 2H\cdot + M$
  - $H_2 + O_2 \rightarrow HO_2\cdot + H\cdot + M$

- **Propagation & Branching** (= multiplication of radicals)
  - $HO_2\cdot + H_2 \rightarrow H_2O_2 + H\cdot$
  - $H\cdot + O_2 \rightarrow O\cdot + OH\cdot$
  - $O\cdot + H_2 \rightarrow O\cdot + OH\cdot$
  - $O\cdot + H_2O \rightarrow OH\cdot + OH\cdot$
  - $OH\cdot + H_2 \rightarrow H_2O + H\cdot$

- **Termination** (= elimination of radicals)
  - $H\cdot + H\cdot + M \rightarrow H_2 + M$
  - $H\cdot + OH\cdot + M \rightarrow H_2O + M$
Inhibition of Vapor Cloud Explosions? How?

Vapor Cloud Explosion

But... difficult to eliminate all hot surfaces and ignition sources

But... oxygen available in ambient air

But... large quantities of fuel in case of major leakage

Let us try to disturb the chemical chain reaction!

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Perturbation of Radical Reactions involved in Combustion

- Disturb chemical chain reaction! But how?
- Promotion of radical termination reactions!
  
  → Cooling of flames (but a lot of thermal agent needed)
  
  → Adding radical scavenging species (inhibitors)
  
  → Both (cooling + radical scavenging)
Experimental Study on Flame Inhibition by Dry Powders

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Experimental Program 2008 - 2010

- **Purpose:**
  - To determine the relationship between inhibitor characteristics (concentration, type, etc.) and flame combustion velocity of a fuel-air mixture (20 l vessel)
  - To verify the effectiveness of inhibitors in medium scale conditions (50 m³)

- **Number of tests:**
  - 316 experiments in a 20 l vessel
  - 103 experiments in a 50 m³ modules
Carbonates and bicarbonates of sodium and potassium are effective flame inhibitors!
## Influence of Particle Size

<table>
<thead>
<tr>
<th>Particle material</th>
<th>Flame Type</th>
<th>Particle diameter (µm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>Laminar non premixed counter flow methane/air flame</td>
<td>15 - 20</td>
<td>Seshadri (1978)</td>
</tr>
<tr>
<td>water</td>
<td>Turbulent flames</td>
<td>10</td>
<td>Van Wingerden (2000)</td>
</tr>
<tr>
<td>water</td>
<td>Turbulent flames</td>
<td>30</td>
<td>Acton et al (1990)</td>
</tr>
<tr>
<td>water</td>
<td>Turbulent flames</td>
<td>18</td>
<td>Sapko et al (1977)</td>
</tr>
<tr>
<td>water</td>
<td>Counter diffusion methane flame</td>
<td>~ 20</td>
<td>Lentati and Chelliah (1998)</td>
</tr>
<tr>
<td>NaHCO₃, KHCO₃</td>
<td>Laminar propane/air counter flow non-premixed flame</td>
<td>&lt; 38</td>
<td>Fleming et al (1998)</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>Laminar non-premixed counter flow methane/air-flame</td>
<td>0 – 10</td>
<td>Chelliah et al (2002)</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>Turbulent flame inhibited by NaHCO₃, KHCO₃, Na₂CO₃, K₂CO₃</td>
<td>&lt; 20</td>
<td>Hoorelbeke (2011)</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>Simulation of hydrogen/air flame at $\phi = 0.5$ (burning velocity of 50 cm/s) and $\phi = 1.4$ (burning velocity of 300 cm/s)</td>
<td>&lt; 17 µm, &lt; 3 µm</td>
<td>Mitani (1983)</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>Premixed methane/air flame ($\phi=1.2$)</td>
<td>12 - 28 µm</td>
<td>Iya et al. (1975)</td>
</tr>
<tr>
<td>NaOH solution</td>
<td>Laminar non-premixed methane/air flame</td>
<td>10 – 20</td>
<td>Lazzarini et al. (2000)</td>
</tr>
<tr>
<td>NaOH solution</td>
<td>Laminar premixed and non-premixed opposed flow flames</td>
<td>10 – 20</td>
<td>Wanigarathne et al. (2001), Chelliah et al. (2002)</td>
</tr>
<tr>
<td>NaOH solution</td>
<td>Counter diffusion methane flame (modeling)</td>
<td>15</td>
<td>Lentati and Chelliah (1998)</td>
</tr>
</tbody>
</table>
Flame Inhibition by Aqueous Solutions of $\text{K}_2\text{CO}_3$

For effective inhibition, the size of droplets must be very small (< 10 – 20 µm)
Experimental Program: tests in 50 m³ module
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Development of Inhibition Technology

- **2011**
  - First powder dispersion tests
  - Desktop study of existing technologies

- **2012**
  - Large scale powder dispersion tests
  - Desktop study of existing technologies

- **2013-2014**
  - Further development of engineering solution

- **2015-2016**
  - Preparation and execution of large scale explosion tests (California, US)

- **2017-2018**
  - Development of industrial implementation in the context of projects
Development of Inhibition Technology: Technology Selection

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Development of Inhibition Technology: Dispersion Testing

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Industrial System for Chemical Inhibition of Vapor Cloud Explosions

Power jet

3 test campaigns in 2012
Development of Inhibition Technology: Dispersion Testing

4 meters high

30 m

40 m
Development of Inhibition Technology: Final Solution

- Inhibitor: KHCO$_3$ or K$_2$CO$_3$, D$_{50}$ = 20 - 30 µm
- Volume protected per skid: ~1250 m$^3$
- Storage pressure: 16 barg
- Nitrogen volume: 15 Nm$^3$ @ 300 barg
- Surface plot: ~1 m$^2$
- Continuous injection of inhibitor (2 kg/s)
- Pre-ignition strategy
- Dispersion of the cloud of inhibitor: 20 s after the start of the leak
- Concentration of the inhibitor in the volume to be protected: 100 g/m$^3$
- Sustained cloud of inhibitor during at least 5 minutes
Large Scale Testing (Livermore, US)

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Industrial System for Chemical Inhibition of Vapor Cloud Explosions
Large Scale Testing (Livermore, US)

Slow deflagration, no inhibition
Detonation
Large Scale Testing (Livermore, US)

Detonation, inhibition with KHCO$_3$
Large Scale Testing (Livermore, US)

Deflagration, inhibition with KHCO₃

-9.315 ms
Large Scale Testing (Livermore, US)

![Graph showing flame front velocity vs position (m/s)]

- **Test 16**
- **Test 17**

- **15.7 bar**
- **50 mbar**
Industrial Application of the Technology
Industrial Application of the Technology

- 2 confirmed projects:
  - Steam cracker project in South Korea
  - Steam cracker project in United States
- Several potential other projects

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Thanks for your attention

For more information, please contact:

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