Workshop
Saint Dénis La Plaine, November 2006

Explosion Science

Federal Institute for Materials Research and Testing (BAM)
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Working Group "Safety Related Properties of Gases"
Division II.1 "Gases, Gas Plants"
History, Trends and Challenges

Beginning of explosion science
Prevention of explosive atmospheres
Ignition of explosive atmospheres
Flame propagation in explosive atmospheres
Protection against the consequences of flame propagation
Final statement
Beginning of explosion science

• The development of human culture is closely linked to the use and exploitation of fire by mankind.

• Even today more than 90 % of the energy used comes from combustion processes (apparently decreased in recent decades).

• A remarkably high degree of operational safety has been achieved over thousands of generations in using combustion processes.

• Of course there is never 100 % safety.

• We occasionally hear of accidental fires and explosions, of combustion processes running out of control, and of undesired processes that happen completely unexpectedly.

• Even though their share of the total volume of combustion is generally very small, their local effects can be disastrous.

• It is therefore truly worthwhile to ensure that such events are avoided.
Mining disasters

• **The Oaks explosion**, Barnsley, Yorkshire, (March 1847): 73 killed
• **Courrières mine disaster**, Courrière, France, (March 1906): 1099 killed (Worst mine disaster in Europe)
• **Consol No. 9 Mine Mining Disaster**, Farmington, West Virginia, USA (1968): 78 killed, 21 survivors (very gassy mine, 200,000 to 250,000 m³ CH₄ per day:... a concrete cap was placed on both shafts....to reduce the amount of intake air...sustaining the mine fire...November 22 at 2:45 a.m. an explosion occurred....and blew the cap off the shaft opening. After the concrete cap blew off, both shafts were filled with limestone....)
• **Liaoning mine disaster**, Fuxin, People's Republic of China (February 14, 2005): 210 killed
• **Sago Coal Mine Disaster**, Tallmansville, West Virginia, USA (January 2, 2006): 12 killed, one survivor
Consol No. 9 Mine Mining Disaster (http://www.msha.gov/DISASTER/FARM/FARM1.asp)

Explosion 5.30 am

Flames after explosion (9.30 am)

Concrete cap was blown away in a second explosion two days later (installed one day after explosion)
Beginning of explosion science

Coal Mining Disaster Incidents and Fatalities, 1900-2004

(A mining disaster is an incident with 5 or more fatalities)

Data source: MSHA

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Beginning of explosion science

Gas explosion disasters

- **New London School explosion**, New London, Texas, USA (March 18, 1937): 300 killed (natural gas leak)
- **Cleveland East Ohio Gas explosion**, Cleveland, Ohio (October 20, 1944): 130 killed, one square mile area destroyed (LPG vapour) Refinery in Feyzin, Isère, France (January 4, 1966): 18 killed (BLEVE)
- **Flixborough disaster**, North Lincolnshire, England (June 1, 1974): 28 killed (cyclohexane oxidation)
- **San Juan Ixhuatepec explosion**, México State, Mexico (November 19, 1984): 500 killed (LPG BLEVE), Petroleum storage facility
- **Piper Alpha explosion**, North Sea, Scotland, (July 6, 1988): 167 killed (leakage of natural gas condensate)
- **Phillips Petroleum Co.**, Pasadena, Texas, USA (October 23, 1989): 23 killed (isobutane UVCE)
- **Guadalajara sewer explosion**, Jalisco, Mexico (April 22, 1992): 296 killed (gasoline explosions in a sewer system)
Beginning of explosion science
Beginning of explosion science

Piper Alpha, 06.06.1988
First rescue craft

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New water pipes, made of zinc-coated copper, were built too close to an existing steel gasoline pipeline. The underground humidity caused these metals to create an electrolytic reaction, which eventually caused the metal to corrode, creating a hole in the pipelines that caused gasoline to leak into the ground and into the main sewer pipe.
History, Trends and Challenges

Beginning of explosion science

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Final statement
Prevention of explosive atmospheres

An explosion can take place only if a reaction can propagate in the mixture. For the evaluation of the flammability (explosibility) the following characteristics are used:

- Explosion limits,
- Other characteristics of explosion regions,
- Temperature and pressure limits for instability,
- Explosion point,
- Flash point.
Explosion limits

mixture too lean  mixture explosible  mixture too rich
First reported explosion limits of methane by Davy (1816, 100 cm³ narrow necked bottle, top ignition via candle flame):
LEL = 6.2 (burning without explosion)  
LEL = 6.7 (diminished violence)  
UEL = 14.3

History of methane explosion limits
**Explosion limits**

Flame propagation criterion according to EN 1839, method „T“

Flame detachment (ignition, height min. 100 mm)

Aureole (no ignition, except height of aureole is 240 mm)

Presentation of Volkmar Schröder!
Explosion limits

fuel rich NH₃/air mixture

14,7 mol-% NH₃ in air

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Newer aspects:
Explosion limits of various fuels in N$_2$O atmosphere (instead air) 
→ follow-on project

<table>
<thead>
<tr>
<th>Fuel</th>
<th>LEL (mol.-%)</th>
<th>UEL (mol.-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ammonia</td>
<td>4,4 (15,4)</td>
<td>65,0 (33,6)</td>
</tr>
<tr>
<td>n-butane</td>
<td>0,7 (1,4)</td>
<td>27,0 (9,3)</td>
</tr>
<tr>
<td>ethane</td>
<td>1,3 (2,1)</td>
<td>33,0 (15,4)</td>
</tr>
<tr>
<td>ethylene</td>
<td>1,4 (2,3)</td>
<td>40,5 (32,4)</td>
</tr>
<tr>
<td>carbon monoxide</td>
<td>9,5 (11,0)</td>
<td>86,0 (77,0)</td>
</tr>
<tr>
<td>methane</td>
<td>1,5 (4,4)</td>
<td>45,9 (16,5)</td>
</tr>
<tr>
<td>propane</td>
<td>0,7 (1,7)</td>
<td>27,0 (10,9)</td>
</tr>
<tr>
<td>propylene</td>
<td>0,8 (2,0)</td>
<td>29,5 (11,0)</td>
</tr>
<tr>
<td>hydrogen</td>
<td>2,9 (4,1)</td>
<td>82,5 (77,0)</td>
</tr>
</tbody>
</table>

BAM-Annual report 1986
Explosion limits

Pressure-time histories of propane/N₂O explosions → follow-on project
Other characteristics of explosion regions

Reducing the explosion range by inerting the gas system

MOC: maximum oxidizer content
MXC: maximum permissable amount of combustible
MAI: minimum required amount of inert gas
IAR: minimum inert gas / air (oxidizer) ratio
ICR: minimum inert gas / combustible ratio
Temperature and pressure limits for instability

C₂H₂ decomposition reaction
(1.5 bar, 20 °C, 500 f/s):
\( p_{ex} = 11.7 \) bara

Pressure limits of stability for C₂H₂/NH₃ mixtures at 20 °C and 100 °C (measured and calculated)
**Explosion point, Flash point**

**Scheme of a flash point apparatus**

1. Sample (liquid phase)
2. Sample (vapour phase)
3. Ignition source
4. Stirrer
5. Thermometer reading the flashpoint
6. Thermometer regulating the heater
7. Thermostating device
8. Lid

**Correlation between explosion limits, explosion points and flash points: vapour pressure versus temperature**

- **A** = not explosive (to lean)
- **B** = explosive
- **C** = not explosive (to rich)
- **D** = hybrid mixtures possible

**Diagram Notes:**
- **A** = molar amount
- **B** = upper explosion point
- **C** = lower explosion point
- **D** = flash point
- **UEL** = upper explosion limit
- **LEL** = lower explosion limit
- **vapor pressure curve**
- **vapor pressure**
- **temperature**
The knowledge of the flash point may lead to a wrong safety impression due to possible reactions on liquid surface and in foams of bubbles (Hattwig, Stehen: "Handbook of Explosion Prevention and Protection")

→ Possible topic for follow-on

Methanol at -20 °C (flash point at 1 bara: 9 °C, increases with initial pressure) and 5 bara O₂
Outline

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Ignition of explosive atmospheres

If an explosive mixture is present, the question arises whether it is ignitable by a certain ignition source or not. For the evaluation of the ignitability the following characteristics are used:

- Minimum ignition energy,
- Minimum ignition current,
- Autoignition temperature.
Ignition of explosive atmospheres

Examples of possible ignition sources:

- Fire, flames, smoldering material
- Hot surfaces
- Static electricity (spark discharge)
- Static electricity (brush discharge)
- Electrically generated sparks
- Mechanically generated sparks
Ignition of explosive atmospheres

Definition of the minimum ignition energy

Presentation of Max Weiss!
Typical blue flames at ethers:

Ignition of an ether vapor - air mixture on a hot surface (PTB)
Determination of Autoignition Temperature according IEC 79-4

1. Ignition chamber (Erlenmeyer flask 200 ml)
2. Oven
3. Metering device
4. Mirror

\( T_1 \) Thermocouple reading the auto ignition temperature
\( T_2 \) Thermocouple regulating the oven
Ignition process is strongly dependent on the reaction mechanism!
→ Presentations of John Griffith and Christian Liebner
Outline

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If a combustible mixture can be ignited, the question arises how the explosion can propagate under given conditions. The following characteristics describe the reaction propagation:

- Detonation limits,
- Propagation speed of deflagrations,
- Maximum experimental safe gap.
# Flame propagation in explosive atmospheres

<table>
<thead>
<tr>
<th>Explosion</th>
<th>Deflagration</th>
<th>Detonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_f/S_S )</td>
<td>( 10^{-4} &lt; S_f/S_S &lt; 3 \times 10^{-2} )</td>
<td>( 5 &lt; S_f/S_S &lt; 10 )</td>
</tr>
<tr>
<td>( S_{behind}/S_{ahead} )</td>
<td>( 4 &lt; S_{behind}/S_{ahead} &lt; 6 ) (acceleration)</td>
<td>( 0.4 &lt; S_{behind}/S_{ahead} &lt; 0.7 ) (delay)</td>
</tr>
<tr>
<td>( p_{behind}/p_{ahead} )</td>
<td>0.98 (slight expansion)</td>
<td>13 &lt; ( p_{behind}/p_{ahead} ) &lt; 55 (compression)</td>
</tr>
<tr>
<td>( \rho_{behind}/\rho_{ahead} )</td>
<td>( 0.06 &lt; \rho_{behind}/\rho_{ahead} &lt; 0.25 )</td>
<td>( 1.7 &lt; \rho_{behind}/\rho_{ahead} &lt; 2.6 )</td>
</tr>
<tr>
<td>( T_{behind}/T_{ahead} )</td>
<td>( 4 &lt; T_{behind}/T_{ahead} &lt; 16 ) (heating)</td>
<td>( 8 &lt; T_{behind}/T_{ahead} &lt; 21 ) (heating)</td>
</tr>
</tbody>
</table>
50-dm$^3$ spherical autoclave designed for pressures up to 1.100 bar (investigation of detonations)
Flame propagation in explosive atmospheres

Different explosion regimes
(deflagration, heat explosion, detonation)

**Yellow range:** possibly heat explosion

Propene $\text{C}_3\text{H}_6$ [Vol.-%]

O$_2$ [Vol.-%]

$\text{N}_2$ [Vol.-%]

- Range of deflagorative explosion, 5 bar abs, 25 °C
- Soot is formed here (43 vol.-% up to 69 vol.-%)
- Stoichiometric $\text{C}_3\text{H}_6 + 1.5 \text{O}_2 \rightarrow 3 \text{CO} + 3 \text{H}_2$
- Stoichiometric $\text{C}_3\text{H}_6 + 3 \text{O}_2 \rightarrow 3 \text{CO}_2 + 3 \text{H}_2\text{O}$

Presentation of Peter Schildberg!
Flame propagation in explosive atmospheres

Determination of MESG (maximum experimental safe gap) according to IEC 79-1A

1 Inner explosion chamber (20 ccm)
2 Outer explosion chamber (2.5 l)
3 Gap
4 Window
5 Ignition source
6 Screw
Flame propagation in explosive atmospheres

Maximum Experimental Safe Gap

- Alkane
- Alkene
- Alkyne
- Hydrogen
- Ammonia
- Carbodisulfid

number of C atoms

maximum experimental safe gap (mm)
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If an explosion propagates the question arises how its effects can be estimated. For the evaluation of the effects of an explosion, the following characteristics are used:

- Explosion pressure and maximum explosion pressure,
- Pressure rise and maximum rate of pressure rise, $K_G$-value,
- Pressure effects during detonations.
Protection against the consequences of flame propagation

Explosion pressure ratios for hydrogen/oxygen and hydrogen/air mixtures (measured and calculated)
Protection against the consequences of flame propagation

$K_G$-values for hydrogen/oxygen and hydrogen/air mixtures (measured and calculated)

Presentation of P. Schildberg and K. Holtappels!
Protection against the consequences of flame propagation

Examples of constructional measures

- explosion-resistant construction
- explosion venting
- isolation
Protection against the consequences of flame propagation

Pressure venting:
\( \text{C}_3\text{H}_8/\text{N}_2/\text{air at 1 bara (rupture foil opened at 20 mbar overpressure)} \)
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Final statement

Many aspects (trends, challenges...) have been combined in the SAFEKINEX-project.
Important trends and challenges not presented:

- vapour cloud explosions and their consequences
- quantitative risk assessment of explosion hazards
- Security (terrorism)
- modeling (reactive flows in closed/confined/open spaces, safety characteristics, kinetics)
… The way we blind ourselves to honest assessment of risk goes back a long way. …

… As individuals, we may learn from close shaves and warnings; as a society, we only learn from blood. …

*Risk Management and Technology* by Roy Brander, Calgary, Alberta
*Presentation to the National Defense Industrial Association Conference, Vancouver, 29 February 2000*
Thank you very much for your attention. If there are any questions left don`t hesitate to ask me.