Experimental Research on Gas Phase Detonations

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CV of H.-P. Schildberg

1957  Born in Neumünster, Schleswig-Holstein, Germany

1988  PhD in Physics at the Institut Laue-Langevin, Grenoble, France


1994 – today  Work in the Safety Engineering Department of BASF in Ludwigshafen

Main fields of expertise

• Gas phase deflagration / detonation
• Structural response of plant components to gas phase detonations
• Incendivity of ignition sources
• Electrostatics (with regard to producing incendive discharges)
Overview

- Brief background info: deflagrative and detonative explosions in gaseous mixtures
- Motivation for research on gas phase detonations
- Detonations in pipes
- Detonations in empty vessels (i.e. no turbulence enhancing elements inside)
- Detonations in vessels filled with dry packings
- Detonations in vessels filled with irrigated packing
- Detonations in bubble swarms rising upwards in a liquid
- Particularly dangerous geometries in context with detonations
- Detonation-like reactions by adiabatic compression in Block-and-Bleed units and replaced pipe sections
- Present status of adopting the pipe results in regulation, guidelines, standards etc.
Gas Phase Explosion
(Self-sustaining flame front)

\[ v_{\text{flame}} < v_{\text{sound}} \] (typically: 0.5 – 10 m/s)

Deflagration

\[ v_{\text{flame}} > v_{\text{sound}} \] (typically: 1600 – 2800 m/s)

Detonation

- Occurrence of shock wave: no
- Mechanisms for triggering the reaction in the unburnt mixture:
  - transfer of heat from flame front to unburnt mixture
  - diffusion of radicals from flame front into unburnt mixture
- Propagation speed of pressure \( v_{\text{pressure}} \):
  - \( v_{\text{pressure}} = v_{\text{sound}} \)
- Pressure venting:
  - possible
- Explosion pressure ratio \( r = p_{\text{ex}}/p_{\text{initial}} \):
  - \( r \leq 25 \)
- Influence of geometry of enclosure on \( r = p_{\text{ex}}/p_{\text{initial}} \):
  - no
- Spatial pressure distribution:
  - same pressure at any location (\( \Rightarrow \) no net force on containment)
- Adiabatic compression by shock wave heats up gas mixture to \( T \gg T_{\text{autoignition}} \)
  (flame front is coupled to shock front)
- Yes, substantial differences between pressures at different locations (huge net forces on containment)

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Example: Deflagrative and potentially detonative explosion regime of n-Butane/O\textsubscript{2}/N\textsubscript{2} at 1 bar abs, 20 °C

- Mixtures in region with magenta background can undergo the transition to detonation.
- Mixtures in region with orange background only deflagrate.
- Mixtures in region with blue background are not explosive.
Practical demonstration: Transition from deflagrative to detonative explosion of a gaseous mixture in a long pipe

Deflagration to Detonation transition in almost stoichiometric propane/air-mixture at about $90^\circ\phi_i$ distance to point of ignition (=1.8 m), 3 bar abs, $15^\circ\text{C}$, pipelength = 4 m, $\phi_i = 20$ mm

4.9 vol.-% C$_3$H$_8$, Versuch 9, slow motion
4.9 vol.-% C$_3$H$_8$, Versuch 9, real time
4.03 vol.-% C$_3$H$_8$, Versuch 7, slow motion
4.03 vol.-% C$_3$H$_8$, Versuch 7, real time

Note: stoichiometric concentration of propane in air is 4.03 vol.-%
**Experimental conditions:**
- Gas mixture: stoichiometric propane/air (4.03 vol.-% propane)
- \( p_{\text{init}} \): 3 bar abs; \( T_{\text{init}} \): 15°C
- Inner tube diameter: 20 mm
- Length: 4 m, \( L/D = 200 \)
- Frame rate: 85000 fps (frames per second)
- Time between successive frames: 11.76 µs

**Relative time [µs]** (DDT at 0 µs)

- \( v = 168 \text{ m/s} \)
- \( v = 367 \text{ m/s} \)
- \( v = 677 \text{ m/s} \)
- \( v = 1129 \text{ m/s} \)

**Acceleration [m/s²]**

- \( a = \Delta v/\Delta t = 552 \text{ m/s}/588 \mu s = 0.93 \times 10^6 \text{ m/s}^2 \)

**V. detonation = 2040 m/s**
Parameter important to assess probability of DDT: the detonation cell size $\lambda$

- $\lambda$ characterizes the microstructure of the detonation front with respect to pressure distribution.

- Values of $\lambda$ of stoichiometric combustible/air- and combustible/O$_2$-mixtures at $p_{\text{initial}} = 1$ bar abs and $T_{\text{initial}} = 20$ °C:

<table>
<thead>
<tr>
<th>combustible</th>
<th>detonation cell size $\lambda$ [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>oxidant = air</td>
</tr>
<tr>
<td>H$_2$</td>
<td>16</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>305</td>
</tr>
<tr>
<td>C$_2$H$_2$</td>
<td>4</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>28</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>40</td>
</tr>
<tr>
<td>C$_3$H$_6$</td>
<td>52</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>55</td>
</tr>
<tr>
<td>n-C$<em>4$H$</em>{10}$</td>
<td>50-62</td>
</tr>
<tr>
<td>C$<em>6$H$</em>{14}$</td>
<td>51</td>
</tr>
</tbody>
</table>

Note:

a) $\lambda$ is proportional to the inverse of $p_{\text{initial}}$
b) $\lambda$ is in good approximation proportional to $T$ [K]

References:

Meaning of the detonation cell size $\lambda$

- **Theoretical contemplation [1]:**
  In a pipe with an internal diameter $\phi_i < \lambda/3 \equiv \lambda/\pi$ a detonation can never propagate, even if the incoming reaction front is a detonative one.

- **Experimental finding [2]:**
  In a pipe with an internal diameter $\phi_i < \lambda$ a deflagration will not transition to a detonation.

- **Experimental finding [3]:**
  In a packing (Pall-rings, Raschig-rings) with ring diameter $\phi_i < \lambda/3 \equiv \lambda/\pi$ a deflagration will not transition to a detonation and, presumably, an incoming detonation can never propagate.

- **Experimental finding:**
  If the inner diameter of a pipe, which ends in a larger vessel, is less than $13 \cdot \lambda$, the detonation coming in from the pipe will revert to a deflagration upon entering the vessel ("13-$\lambda$ rule"). Otherwise the detonation coming in from the pipe continues as detonation inside the vessel.

References:
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Brief background info: deflagrative and detonative explosions in gaseous mixtures

Motivation for research on gas phase detonations

Detonations in pipes

Detonations in empty vessels (i.e. no turbulence enhancing elements inside)

Detonations in vessels filled with dry packings

Detonations in vessels filled with irrigated packing

Detonations in bubble swarms rising upwards in a liquid

Particularly dangerous geometries in context with detonations

Detonation-like reactions by adiabatic compression in Block-and-Bleed units and replaced pipe sections

Present status of adopting the pipe results in regulation, guidelines, standards etc.
Motivation

- In chemical process plants **detonable gas mixtures do occur** and effective ignition sources can, in general, not be ruled out with certainty.

- The sole safety concept in this case is **explosion pressure proof design** of the affected plant components.

- Worldwide there are **no guidelines published** by standardization organizations or interest groups (ISO, NFPA, ASME, CGA, CEN, EIGA, BSI, DIN, VDI) for explosion pressure proof design against the load generated by gas phase detonations.

- Scientific literature:
  - **Focused** mainly on the explosive mixture itself, **not on the interaction mixture-enclosure**
  - Pressure/space/time profiles only understood for the two most simple detonative pressure scenarios with lowest pressure generation. **No systematic classification of the remaining scenarios, not to mention their pressure/space/time profiles**

BASF started research in 2008 aimed at developing a guideline for detonation pressure proof pipe design.
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Publications with Experimental Results


Publications giving a General Overview

[7] H.P. Schildberg, Gas phase detonations in pipes: the 8 possible different pressure scenarios and their static equivalent pressures determined by the pipe wall deformation method. (part 1), Chemical Engineering Transactions, 48, 241-246; DOI:10.3303/CET1648041

[8] H.P. Schildberg, Gas phase detonations in pipes: the 8 possible different pressure scenarios and their static equivalent pressures determined by the pipe wall deformation method. (part 2), Chemical Engineering Transactions, 48, 247-252; DOI:10.3303/CET1648042

[9] Technische Regel für Gefahrstoffe 407 (TRGS 407), Tätigkeiten mit Gasen – Gefährdungsbeurteilung,
Note 1: In the attachment A4 (page 48 – 56 of TRGS 407) the pressure scenarios in long pipes and their static equivalent pressure are for the first time mentioned in a guideline (here only related to detonative decompositions of acetylene).
Note 2: The TRGS 407 is published by German Bundesministerium für Arbeit und Soziales (Federal Ministry for Work and Social Affairs).
Main results of the work on detonations in pipes

- Detonations in pipes can be described by **8 distinctly different pressure scenarios**:
  - 4 Scenarios in “long” pipes
  - 4 Scenarios in “short” pipes

- **6 scenarios are design-relevant**

- An experimental method ("pipe wall deformation method") was established to determine the "**static equivalent pressures \( p_{\text{stat}} \)" of each detonative scenario
  - **Direct** correlation between input parameters (mixture composition) and the desired result \( p_{\text{stat}} \).
    There are no complex intermediate steps and approximation involved by which the desired results are derived from other parameters measured during the experiment as it is the case with the hitherto used method of making tests at initial pressures low enough that all loads remain in the elastic regime of the pipe wall and, consequently, trigger a large number of vibrational modes.
  - Strain rate hardening is automatically included
  - Knowledge of detonative pressure/time profiles not needed

- Once the static equivalent pressures are know, the classical pressure vessel formulae, which can only cope with static loads, can be applied for detonation pressure resistant design

- Results can be generalized to apply to any combustible/O\(_2\)/N\(_2\) mixture by a parameter \( R \), whose typical variation over the entire explosion triangle is provided.
Help to visualize the different detonative pressure scenarios

1st step: trigger an explosion with transition to detonation inside a pipe

2nd step: record the maximum pressure ratios found in the pipe at any axial position during the course of the explosion
Maximum pressure ratios found in a long pipe at different axial positions in the course of an explosion involving a transition from deflagration to detonation (schematic)

- Scenario 1: DDT (predetonation distance, combustion in deflagrative mode)
- Scenario 2: unstable detonation, overdriven detonation
- Scenario 3: stable detonation
- Scenario 4: reflected stable detonation

ignition at x = 0
Example: local pressures of scenarios 1 and 4 made visible by residual plastic deformation in wall of long pipe

**Test 7:** 12.2 bar abs, 20 °C, stoichiometric H₂/air (H₂:O₂:N₂=29.56:14.78:55.66 [vol.-%])
48.3 x 2.6 pipe, material: 1.4541

**Test 19:** 35 bar abs, 20 °C, H₂:O₂:N₂=50:25:25 [vol.-%], 48.3x2.6-pipe, material: 1.4541

**Test 19:** 10 bar abs, 20 °C, CH₄ : O₂ = 11.25 : 88.75 [vol.-%], 48.3 x 2.6 pipe, material: 1.4541
Maximum pressure ratios found in a short pipe at different axial positions in the course of an explosion involving a transition from deflagration to detonation (schematic)

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>DDT (predetonation distance, combustion in deflagrative mode)</td>
</tr>
<tr>
<td>6</td>
<td>Unstable detonation</td>
</tr>
<tr>
<td>7</td>
<td>Reflected unstable detonation</td>
</tr>
<tr>
<td>8</td>
<td>Coalescence of 5 and 7 under omission of 6, i.e., DDT occurs directly ahead of blind flange</td>
</tr>
</tbody>
</table>

Ignition at x = 0
Example: local pressures of scenarios 5, 7, 8 made visible by residual plastic deformation in wall of short pipe

**Test 26:** 4.5 bar abs, 20 °C, $\text{H}_2:\text{O}_2:\text{N}_2=28.6:14.3:57.1$ [vol.-%]

**Test 30:**
4.0 bar abs, 20 °C, $\text{H}_2:\text{O}_2:\text{N}_2=28.6:14.3:57.1$ [vol.-%]

**Test 28:**
4.5 bar abs, 20 °C $\text{H}_2:\text{O}_2:\text{N}_2=28.1:14.05:57.85$ [vol.-%]
Example: bulging in short pipes (scenario 8)

**Test no. 28:**
4.5 bar abs,
14.05 vol.-% O₂
in stoichiometric
H₂/O₂/N₂

**Test no. 29:**
4.63 bar abs,
14.175 vol.-% O₂
in stoichiometric
H₂/O₂/N₂
### Static equivalent pressures for the 8 detonative pressure scenarios in pipes

<table>
<thead>
<tr>
<th>Type of pressure scenario</th>
<th>Static equivalent pressures for any detonable gas mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>no.</td>
<td>pipe name</td>
</tr>
<tr>
<td>1</td>
<td>long pipe</td>
</tr>
<tr>
<td>2</td>
<td>unstable detonation</td>
</tr>
<tr>
<td>3</td>
<td>stable detonation</td>
</tr>
<tr>
<td>4</td>
<td>reflected stable detonation</td>
</tr>
<tr>
<td>5</td>
<td>short pipe</td>
</tr>
<tr>
<td>6</td>
<td>unstable detonation</td>
</tr>
<tr>
<td>7</td>
<td>reflected unstable detonation</td>
</tr>
<tr>
<td>8</td>
<td>coincidence of DDT and reflection</td>
</tr>
</tbody>
</table>

**Note:**
- \( \alpha = 0.7 \) (valid in general)
- \( p_{\text{CJ \_r}} \) of the mixture can be calculated (based on combustion enthalpy, mean molar mass and \( c_p/c_v \)-values)
- 2.4 applies for reflection of the stable detonation and is assumed to also apply for reflection of unstable detonations and DDT's
- \( R \) must be determined experimentally (ratio between effective load at DDT and effective load for stable deto.)
- justification for using factors 1.5 and 2 -&gt; backup slides to this lecture

\( p_{\text{stat}} \) are valid for any other explosive gas mixture at any \( p_{\text{initial}} \) and \( T_{\text{initial}} \).
Variation of $R$ over the explosive range of a ternary mixture of type combustible/O$_2$/N$_2$ (tentative)

- Mixtures in the region with blue background are not explosive.

Example: static equivalent pressures measured for detonations of stoichiometric Ethylene/air mixtures at 15°C

<table>
<thead>
<tr>
<th>Type of pressure scenario</th>
<th>( p_{\text{stat}} ) (expressed as multiple of ( p_{\text{initial}} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>no.</strong></td>
<td><strong>pipe</strong></td>
</tr>
<tr>
<td>1</td>
<td>long pipe</td>
</tr>
<tr>
<td>2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>short pipe</td>
</tr>
<tr>
<td>6</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
</tr>
<tr>
<td>8</td>
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- Present status of adopting the pipe results in regulation, guidelines, standards etc.
Fundamental problem when deflagration to detonation transitions occur in empty vessels

If there is a transition from deflagration to detonation in the vessel, precompression will almost always occur, because the diameter is usually not much larger than the predetonation distance. **The precompression factor may attain the highest possible value, i.e. the deflagration pressure ratio.**

Note: The detonation propagates faster than the speed of sound in the reaction gases, i.e. pressure relief into the central section of the vessel occurs after the wall has „seen“ the detonative pressure peak.
If a DDT occurs at this time instant, maximum pressure loads can be expected, because the unreacted mixture is almost precompressed to $r \cdot p_{\text{initial}}$.

$r$ denotes the deflagration pressure ratio, $p_{\text{initial}}$ the pressure in the vessel at the moment of ignition.

**Note:** The detonation propagates faster than the speed of sound in the reaction gases, i.e. pressure relief into the lower section of the vessel occurs after the wall in the upper left section has “seen” the detonative pressure peak.
Mixtures which undergo a DDT inside vessels

**Example:**
Propene/O₂/N₂, 5 bar abs, 25 °C

- Mixtures in region with blue background are not explosive

- Range of detonative explosions in a 20 l sphere.
- In a 2.5 m³ vessel with L/D ≈ 4.5 the range is slightly larger.

(experiments by BASF)

**Note:**
Largest pressures are generated by mixtures close to the border of the detonative range, not by mixtures in the center !!!!!

**Example:**
Propene/O₂/N₂, 5 bar abs, 25 °C
Pressure/Time recordings of explosions of Propene/O$_2$-mixtures at 5 bar abs, 20°C in a 20 l sphere (1/2)

Common pressure-time recording of a deflagration

Pressure/Time recordings of explosions of Propene/O₂-mixtures at 5 bar abs, 20°C in a 20 l sphere (2/2)

Propene = 23 vol.-%  
O₂ = 77 vol.-%  

no precompression, DDT directly at ignition source

Propene = 38 vol.-%  
O₂ = 62 vol.-%  

precompression by a factor of 20 before DDT occurs

Fundamental questions when quantifying hazards associated with potential detonations in vessels

- Under what conditions (mixture composition, $p_{\text{initial}}$, $T_{\text{initial}}$, volume, $L/D$) do we have to assume that a DDT occurs?

- What is the largest conceivable value of the static equivalent pressure $p_{\text{stat}}$ in comparison to $p_{\text{stat}}$ of the pipe scenario no. 8
  Note: This must be evaluated in the limiting case that the dynamic load factor is 2, i.e. the wall can respond fast enough to the exciting pressure pulse as it was the case in the tests we did for pipes.

- To which extent can we benefit from the value of the dynamic load factor?
  Note: In vessels having dimensions as used in the process industry the width of the detonative peaks hitting the wall will be much less than half of the cycle time of the fundamental oscillation modes of the vessel. This will reduce the effective displacement of the wall, i.e. the dynamic load factor can become $<< 1$.

- How to cope with the massive net forces acting on the vessels, which cause the vessels to be displaced?

- Only academic: are there fundamental differences in the processes causing the DDT when comparing pipe- and vessel-geometry?
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Typical applications of vessels filled with dry packings

- Vessels acting as demisters
- Vessel acting as flame arrestors
  (e.g. for self decomposable gases like Acetylene or Ethylene Oxide)
- Vessels acting as static mixers
Typical packings used in the process industry

Raschig Rings, L/D = 1, typical: $15 \text{ mm} \leq L \leq 50 \text{ mm}$

Pall Rings, L/D = 1, typical: $15 \text{ mm} \leq L \leq 50 \text{ mm}$

Sulzer Mellapak (e.g. 250.Y, 250 m²/m³)
Typical packings used in small-scale equipment

- Steatite granules, $2.5 \leq \phi \leq 3.2$ mm
- Raschig rings, 5 mm x 5 mm x 0.3 mm, 1.4541
- Raschig rings, 8 mm x 8 mm x 0.3 mm, 1.4541
- Raschig rings, 10 mm x 10 mm x 0.5 mm, 1.4541
Fundamental questions pertaining to the course of explosions in vessels with dry packings

- Can mixtures, which explode in deflagrative manner in empty vessels, transition to detonation in packed vessels?
  
  Yes! Example: hydrocarbon/air mixtures do not transition to detonation in empty vessels, but will do in a packing, if the packing diameter is larger than 1/3 of the detonation cell size of the mixture.

- If a DDT occurs:

  - Can we specify a **predetonation distance** as function of the dimensions of the packing elements?
    
    Yes! Example: stoichiometric hydrocarbon/air mixtures at 20 °C and 1 bar abs < \( p_{\text{initial}} < 5 \) bar abs have a predetonation distance of about 100 \( \cdot \phi_i \) in straight pipes (\( \phi_i \) is the inner pipe diameter). In packings this distance is only about 25 \( \cdot \phi_i \).
    
    (\( \phi_i \) denotes the packing diameter).

  - How large is the maximum **precompression factor** relative to the maximum precompression factor in the empty vessel?
    
    (specific BASF know how)

  - How large is the **static equivalent pressure** acting on the wall of the vessel compared to a detonation in an empty vessel?
    
    (specific BASF know how)
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Typical applications of vessels filled with irrigated packings

- Distillation columns

- Scrubbers
  (Cleaning of a gas stream by washing out entrained dust particles and/or unwanted gaseous components)

- Vessels used for pressure swing absorption
  - Absorbing one gaseous component of a multi component gas stream in a solvent under high pressure
  - Desorbing the dissolved gaseous component from the liquid solvent by flashing the solvent at low pressure
Schematic sketch of a vessel with an irrigated packing

Demister

Feed of liquid

Collector and Redistributor of Liquid

Packing

Packing

Feed of strip gas or gas to be washed

Drain of Liquid

1 m

2 m

5 m

2 m

5 m

2 m

3 m

Fundamental questions pertaining to the course of explosions in vessels with irrigated packings

- Can a DDT, which would happen inside the dry packing, be suppressed by the irrigation?

- If the DDT can be suppressed:
  - What is the required irrigation rate as function of $p_{\text{initial}}$?
  - What is the required irrigation rate as function of the diameter of the packing elements?

**Answers**

- Answers do very much depend on the process conditions of the system under investigation
- Number of investigated systems is still too small to generalize the results
Vessel geometry used by BASF for experiments

Typical irrigation rates: 20 – 75 m³/(m²*h) = 5.5 – 20.8 l/(m²*s)

Packing, e.g.:
- Pall Rings
  (15x15 up to 50 x 50)
- Raschig Rings
  (15x15 up to 25x25)
- Sulzer Mellapak
  (example: M250 Y)

Ignition in free gas space below packing

cyan:
explosive mixture

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Typical applications with explosive bubbles rising upwards in a liquid

- Partial oxidation reactions of organic liquids with air, oxygen enriched air, pure O₂ or N₂O
- Vinylation reactions of organic liquids
Schematic sketch of a gas-liquid partial oxidation or vinylation process (injection from bottom)

Characteristics of process:

- Large hold-up of organic liquid
- Injection of a gaseous oxidant or gas mixture containing the oxidant
- 5 to 20% of the liquid are taken by gas bubbles
- Large fraction of the bubbles can be in the **explosive range** due to vapour of the organic liquid (in case of reaction breakdown all bubbles can become explosive)
- Gas space in reactor dome is usually in **explosive range** due to organic vapour and/or organic mist
- Ignition sources can not be excluded (mostly: chemical ignitors)

**Note:**
Explosive range encompasses the purely deflagrative regime and the potentially detonative regime

**Upper reactor dome:**
- Often with detonable gas phase (oxidant, vapours, mists, inert gases)

**Black:**
- Reactor,
  - $20^\circ C \leq T \leq 300^\circ C$,
  - $6 \text{ barg} \leq p_{\text{design}} \leq 325 \text{ barg}$

**Blue:**
- Liquid to be partially oxidized or vinylated,
  - $20^\circ C \leq T \leq 300^\circ C$,
  - $0 \text{ barg} \leq p_{\text{operation}} \leq 30 \text{ barg}$
  - $5 \text{ m}^3 \leq V \leq 500 \text{ m}^3$

**Feed gas pipe for oxidant containing gas mixture or acetylene:**
- $O_2/N_2/CO_2/CO/H_2O/C_2H_2$
- $0 \text{ barg} \leq p_{\text{operation}} \leq 30 \text{ barg}$
- $1000 \text{ Nm}^3/\text{h} \leq V \leq 50000 \text{ Nm}^3/\text{h}$
Schematic sketch of a gas-liquid partial oxidation or vinylation process (injection from top with motive fluid)

*Note:* Gas to be injected is entrained by the motive fluid of the jet loop reactor („Schlaufenreaktor“)

- **Injected gas can be detonable**
- **Upper reactor dome:** Often with detonable gas phase (oxidant, vapours, mists, inert gases)

**Dimensions:**
- \(5 \text{ m} \leq \text{height} \leq 30 \text{ m}\)
- \(1 \text{ m} \leq f \leq 5 \text{ m}\)

**Legend:**
- Gas injection
- Motive fluid
- Guide tube
- Drain of product
- Off gas
Example for ignition of explosive bubbles by a propagating shock wave

**Liquid:** cyclohexane

**Bubbles:** cyclohexane/O₂

**Shock wave:** caused by detonation in C₂H₂/O₂ mixture in head space of reactor

Courtesy of Dr.-Ing. Konstantinos Mitropetos, Safety Expert, Process Safety, Merck KGaA, 64293 Darmstadt, Germany

https://depositonce.tu-berlin.de/handle/11303/1376
Fundamental questions pertaining to the course of bubble swarm explosions triggered by a detonation in the head space of the reactor

- Can the bubbles be ignited by adiabatic compression caused by the shockwave propagating in the liquid? (Assumption: shock wave is triggered by gas phase detonation in head space)

- If ignition occurs:
  - Can there be a DDT inside the bubbles?
  - How large is the static equivalent pressure acting on the wall?
  - Will all conceivable courses of the explosion in the bubbles (homogeneous runaway reaction, deflagration, detonation) lead to the same static equivalent pressure acting on the wall?

- If no ignition occurs:
  - Can we specify threshold values for the operating conditions (volumetric bubble load, $p_{\text{initial}}$, $T_{\text{initial}}$) by which an ignition of the bubbles can be avoided in general?
Research data not suited to assess bubble swarm detonation triggered by detonation in head space

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameter</th>
<th>Reactors used in published research</th>
<th>Reactors used in process industry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>L ≤ 1 m; $\phi_i \leq 0.2$ m</td>
<td>L ≤ 15 m; $\phi_i \leq 6$ m</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(lab scale)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>dimensions of reactors</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>volumetric gas fraction in liquid</td>
<td>very small</td>
<td>1 to 20 vol.-%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(mostly single bubbles)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>bubble diameter</td>
<td>≤ 20 mm</td>
<td>≤ 200 mm</td>
</tr>
</tbody>
</table>

### geometric data

### experimental results

| 4   | ignitability of bubbles containing explosive mixture | yes | (still unknown) |
| 5   | pressure at wall caused by exploding bubbles        | negligible | (still unknown) |
| 6   | water hammer                                       | negligible | (conceivable) |

Due to large differences in (1), (2) and (3), the results from lab scale tests are not suited to assess real scale scenarios!!

(e.g. liquid in real reactors has much higher compressibility (due to higher gas fraction) and will be accelerated to much higher speeds (combined effect of higher gas fraction and larger length of reactor)
Experimental setup of BASF to investigate bubble swarm detonation

Results to be expected by the end of 2019
Overview

- Brief background info: deflagrative and detonative explosions in gaseous mixtures
- Motivation for research on gas phase detonations
- Detonations in pipes
- Detonations in empty vessels (i.e. no turbulence enhancing elements inside)
- Detonations in vessels filled with dry packings
- Detonations in vessels filled with irrigated packing
- Detonations in bubble swarms rising upwards in a liquid

- Particularly dangerous geometries in context with detonations
  - Short pipe connected to large vessel
  - Long pipe connected to large vessel
- Detonation-like reactions by adiabatic compression in Block-and-Bleed units and replaced pipe sections
- Present status of adopting the pipe results in regulation, guidelines, standards etc.
Problem with short pipe connected to large vessel

- Many gas mixtures only deflagrate in vessel-geometry but undergo transition to detonation in pipe geometry
- Usually: volume of vessel >>> volume of short pipe

At the moment when the deflagrative flame front reaches the point where the pipe is tied in, the unburned mixture in the pipe is precompressed by a factor equal to the deflagration pressure ratio (typically 4 to 25). When, upon further propagation, the flame transitions to detonation, the resulting pressures are extremely large.
Example 1: 20 l sphere with 45 cm pipe ($\phi_i = 6$ mm)

20 l sphere used for explosion experiments

10x2 pipe to vacuum pump (foto of new pipe)

Valve

10x2 pipe ruptured at location of DDT, thereafter the curved part molt.

(hydraulic burst pressure of pipe is about 3480 bar; pipe material: 1.4541; deflagration pressure ratio of the mixture was only ca. 5 at $T_{initial} = 250$ C)

Mixture in sphere:
- 0.5 vol.-% Tetradecane,
- 99.5 vol.-% $N_2O$,
- 25 bar abs, 250 C
Example 2: Reactor with 1 m³ headspace and a DN80 pipe

pressure retention valve

filter (optional)

ball valve (open)

decomposable gas
80°C, 20 bar abs
1 m³

Reaktor, PN160

Liquid

Question:
What is the maximum permissible length L of the DN80 pipe such that a deflagrative decomposition starting in the headspace of the reactor does not transition to detonation in the pipe?
Example 2: result of a real-scale test

Example 2: result of a real-scale test

- This pipe is open to atmosphere
- Location of DDT
- Filter
- 100 l vessel
- Location of ignition
- DN80 pipe
- Blind lens with 10 mm bore to simulate partially open pressure retention valve, 30 bar rupture disk directly behind the lens

After test
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Problem with long pipe connected to a large vessel

- Explosive mixture present in vessel and pipe explodes in deflagrative or detonative manner. The resulting pressures are sustained by the equipment.

- Usually: volume of vessel >>>>> volume of long pipe

The cooling rates in the pipe are much faster than in the vessel.
⇒ Hot reaction gases (2400 K to 3000 K) flow from the vessel into the pipe.
⇒ Excessive heating of pipe at point where connected to vessel
⇒ Rupture of pipe at that point because yield strength $R_{p0.2}$ drops to very low values

**Note:** Let $n$ denote the number of moles in the pipe directly after the explosion has terminated. Then the pipe will typically receive $9*n$ hot moles from the vessel within a short time span after completion of the explosion.
Example 1: vessel with long pipe

4.5 l vessel, \( \phi_i = 90 \text{ mm}, L = 700 \text{ mm} \)

pipe 10x2 (\( \phi_o = 10 \text{ mm}, \phi_i = 6 \text{ mm}, s = 2 \text{ mm} \))

decomposition products of acetylene, \( p_{\text{initial}} = 28 \text{ bar abs}, T_{\text{initial}} = 20 ^\circ \text{C} \)

Case 1: pipe length is 1.5 m: no rupture

Case 2: pipe length is 4.3 m: rupture
Example 2: 275 l vessel with 82.5x14.2 pipe

- Ignition occurred in vessel (decomposition reaction is slow)
- About 60 s after ignition: pipe ruptured at flange where it was connected to the vessel due to excessive heating

Pipe 82.5x14.2 ($\phi_o = 82.5 \text{ mm}, \phi_i = 54.1, s = 14.26 \text{ mm}$)

Decomposition products of ethylene, $p_{\text{initial}} = 220 \text{ bar abs}, T_{\text{initial}} = 300 \degree \text{C}$
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Pipe rupture in a petrochemical plant in Lybia, 2004

**Sequence of events:**
1. V1 and V2 closed
2. pipe section between V1 and V2 was replaced, new pipe contained ambient air at ambient pressure
3. V1 was opened
4. replaced pipe section ruptured ahead of V2

**Interpretation:**
1. when re-pressurized by \( \text{CH}_4 \) a narrow zone with an explosive \( \text{CH}_4/\text{air} \) mixture is formed. Temperature rises from 50 °C to 895 °C (\( \kappa = 1.4 \)) or 764 °C (\( \kappa = 1.35 \))
2. autoignition in compressed zone comparable to the autoignition of precompressed gas at DDT-location in a pipe => reaction completed such fast that pressure relief by expansion of reaction gases into the infinitely long upstream pipe can not occur within the time span it takes for the oxidation reaction => rupture.
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State of adopting the pipe results in regulation, guidelines, standards etc

- **Germany:** TRGS 407, Anhang 4
  - long pipe scenarios for $C_2H_2$-Detonations included
  - a pipe is considered as detonation pressure resistant only on basis of the wall thickness, not on basis of its official design pressure.

- **ASME:** In 2015 a working group was established to develop a new ASME code case on detonation pressure resistant pipe design. Work has been postponed so far due to work overload.

- **NFPA:** NFPA 67 “Guide on Explosion Protection for Gaseous Mixtures in Pipe Systems” is going to be revised shortly, in particular chapters 5 to 8 dealing with principles of detonations in pipes. Members of BASF Corporation take part.

- Still much work to be done to make the pipe results “penetrate” the existing guidelines.

- **Possibly:** Extra chapter to be included in DIN EN 13480 **Metallic industrial piping – Part 3: Design and calculation**