Experimental Research on Gas Phase Detonations

Hans-Peter Schildberg
BASF SE
RCP/CH - L511
D-67056 Ludwigshafen
Germany
Email: hans-peter.schildberg@basf.com
Tel: +49 621 60-56049

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Location: Van der Valk Hotel, Laan van Europa 1600, 3317 DB Dordrecht, NL; +31 78 8700 800; www.vandervalkhoteldordrecht.nl

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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
1989 – 1993	Research on novel magnetic tapes (evaporated CO-Ni - layers, sputtered Co-Cr layers) in the Research Department of BASF in Ludwigshafen, Germany.
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)

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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.

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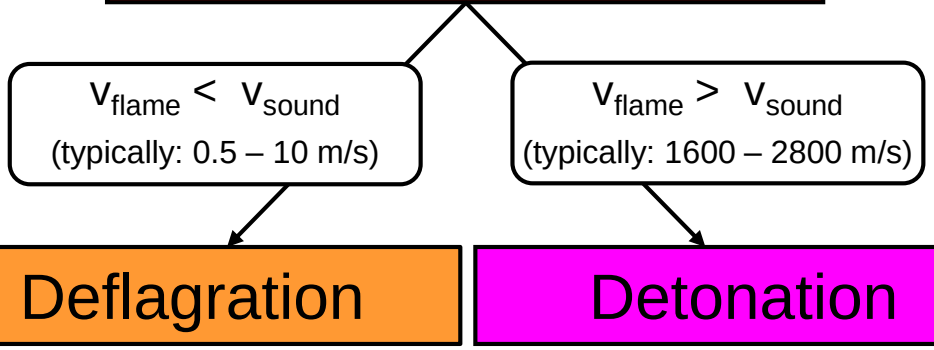
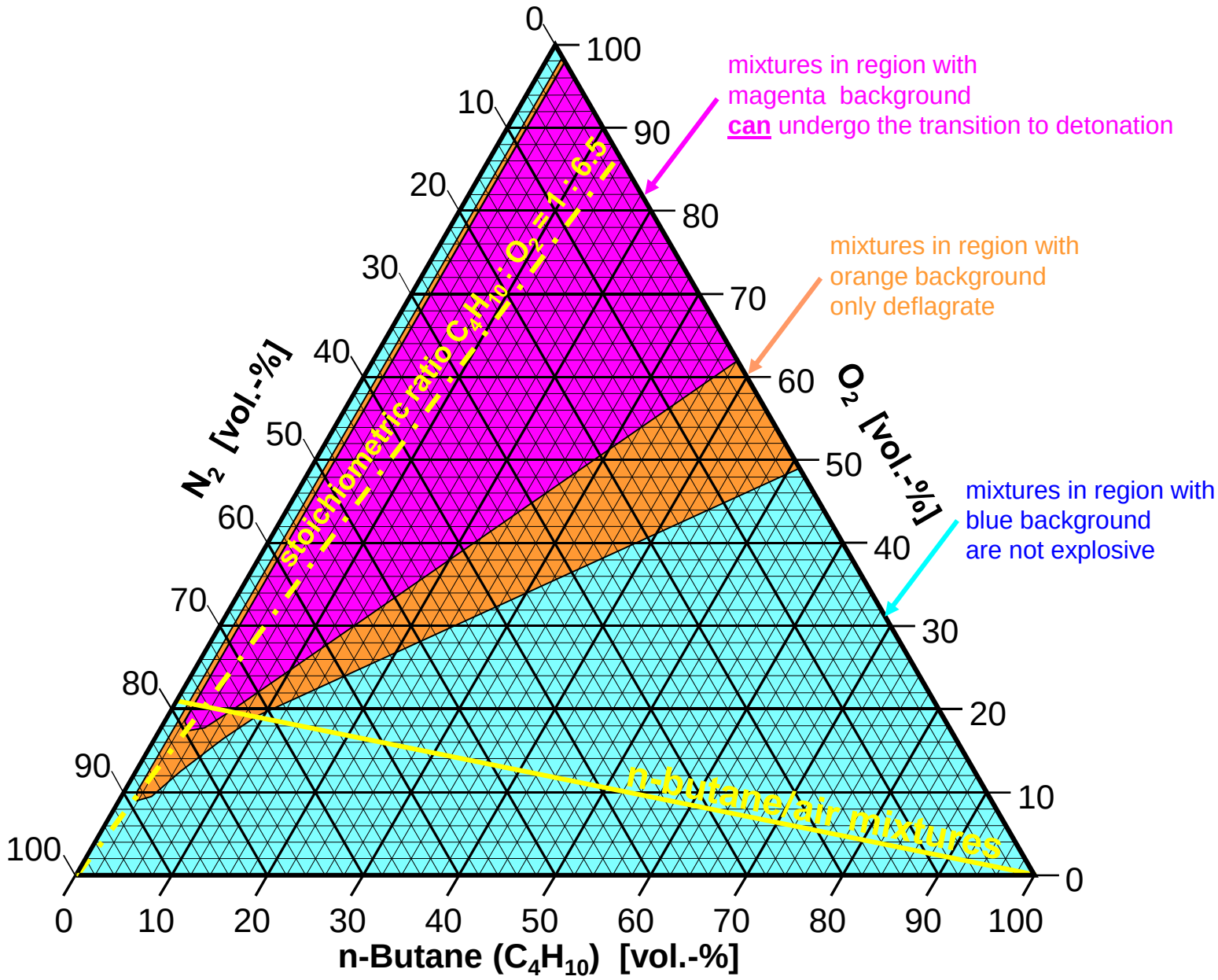
Gas Phase Explosion

(Self-sustaining flame front)



	Deflagration	Detonation
occurrence of shock wave:	no	yes
mechanisms for triggering the reaction in the unburnt mixture	• transfer of heat from flame front to unburnt mixture • diffusion of radicals from flamefront into unburnt mixture	adiabatic compression by shock wave heats up gas mixture to $T >> T_{autoignition}$ (flame front is coupled to shock front)
propagation speed of pressure $v_{pressure}$:	$v_{pressure} = v_{sound}$	$v_{pressure} = v_{flame} > v_{sound}$
pressure venting:	possible	not possible ($v_{flame} > v_{sound}$!!)
explosion pressure ratio $r = p_{ex}/p_{initial}$:	$r \leq 25$	much larger than for deflagrations
influence of geometry of enclosure on $r = p_{ex}/p_{initial}$:	no	yes, substantial
spatial pressure distribution:	same pressure at any location ($\Rightarrow$ no net force on containment)	substantial differences between pressures at different locations (huge net forces on containment)

Example: Deflagrative and potentially detonative explosion regime of n-Butane/O_2/N_2 at 1 bar abs, 20 °C



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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*ϕ_i distance to point of ignition (=1.8 m), 3 bar abs, 15°C, pipelength = 4 m, ϕ_i = 20 mm

4.9 vol.-% C_3H_8, Versuch 9, slow motion

Versuch9 Propan 4.9 O2 95.1, 3 bar abs,-84000-FPS.wmv

4.9 vol.-% C_3H_8, Versuch 9, real time

Versuch9 Propan 4.9 O2 95.1, 3 bar abs,-Echtzeit.wmv

4.03 vol.-% C_3H_8, Versuch 7, slow motion

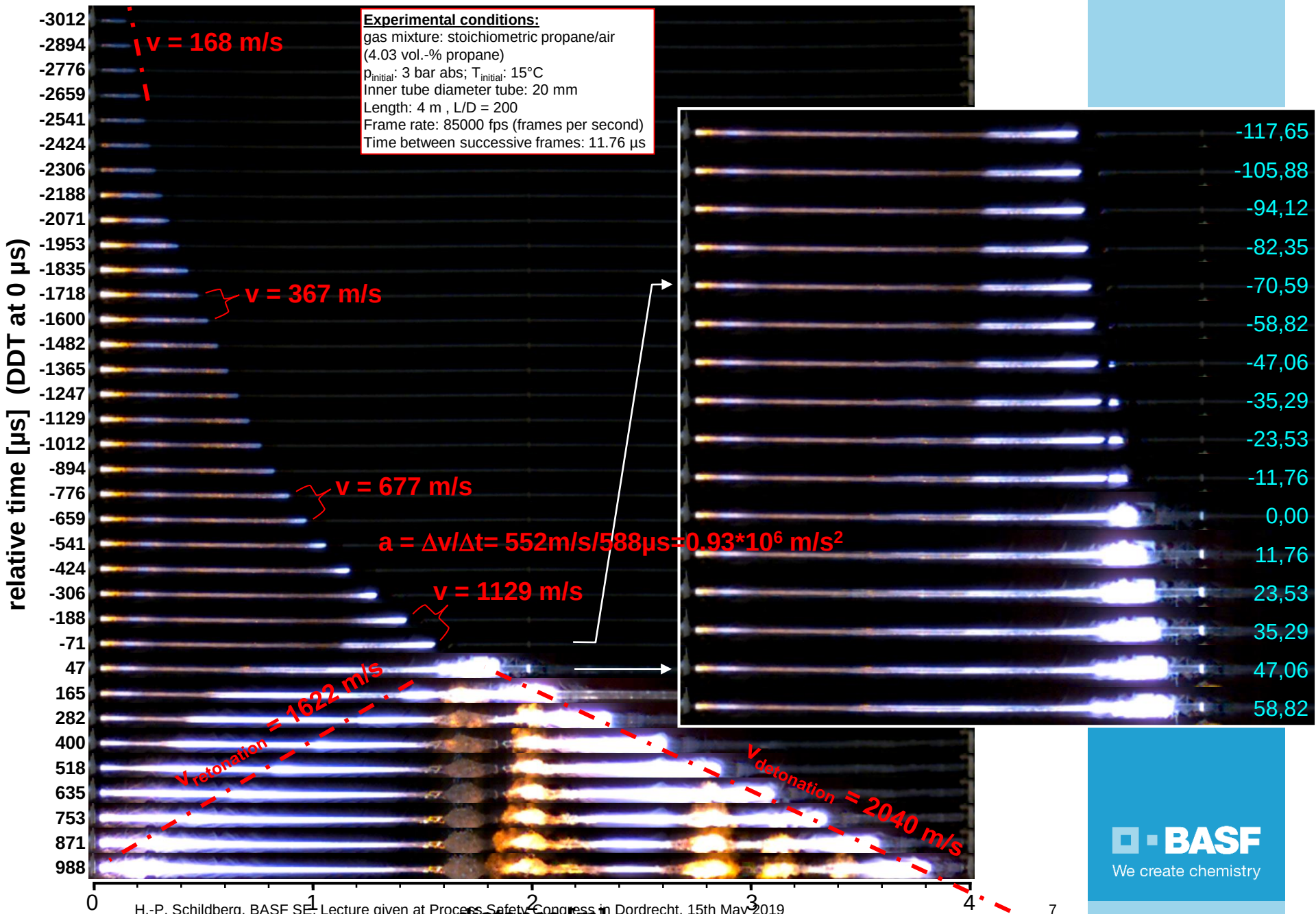
Versuch7 Propan 4 O2 96, 3 bar abs,100000-FPS.wmv

4.03 vol.-% C_3H_8, Versuch 7, real time

Versuch7 Propan 4 O2 96, 3 bar abs,-Echtzeit.wmv

Note: stoichiometric concentration of propane in air is 4.03 vol.-%

DDT in propane/air at 3 bar abs, 15 °C (Versuch 9)



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Parameter important to assess probability of DDT: the detonation cell size λ

- λ characterizes the microstructure of the detonation front with respect to pressure distribution

- Values of λ of stoichiometric combustible/air- and combustible/O_2-mixtures at $p_{initial}$ = 1 bar abs and $T_{initial}$ = 20 °C:

combustible	detonation cell size λ [mm]	
	oxidant = air	oxidant = O_2
H_2	16	1.5
CH_4	305	2
C_2H_2	4	0.1
C_2H_4	28	0.8
C_2H_6	40	1.0
C_3H_6	52	
C_3H_8	55	
n-C_4H_{10}	50-62	
C_6H_{14}	51	

Note:

a) λ is proportional to the inverse of $p_{initial}$

b) λ is in good approximation proportional to T [K]

References:

1) M.A. Nettleton in *Gaseous Detonations*, Chapman and Hall Ltd, London (1987), ISBN 0 412 27040 4 (pages 59, 63)
2) I.O. Moen, Journal of Hazardous Materials 33, p. 159-192 (1993)
3) F.R. Schauer, C. L. Miser, K.C. Tucker, R. P. Bradley and J.L. Hoke, Proceedings of 43rd AIAA Aerospace Sciences Meeting, January 10-13, 2005, Reno, NV, USA
4) Y. Auret, D. Desbordes, H.N. Presles, Detonation structure of C_2H_4/O_2/Ar mixtures at elevated initial temperature, Shock Waves **9**, 107 -111 (1999)

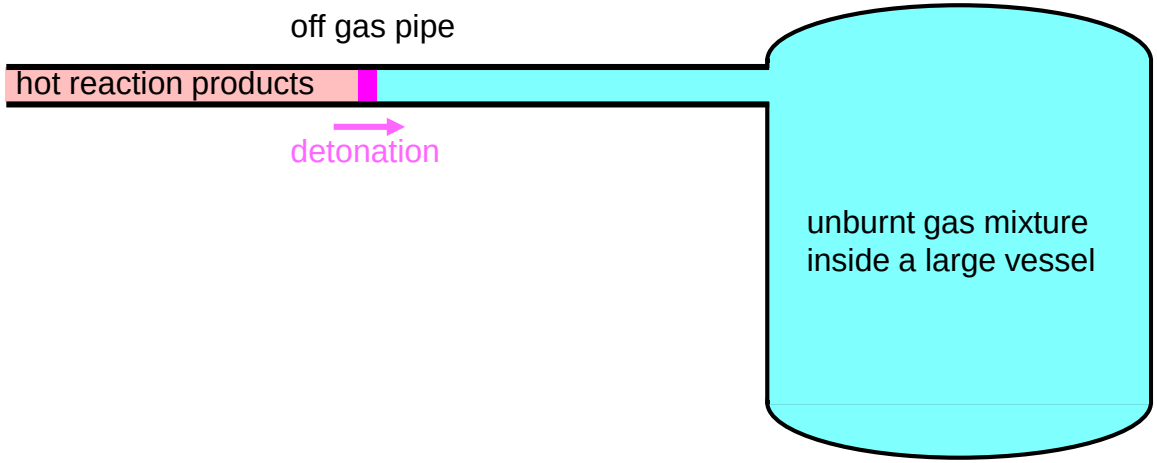
Meaning of the detonation cell size λ

- **Theoretical contemplation [1]:**
  In a pipe with an internal diameter $\phi_i < \lambda/3 \cong \lambda/\pi$ 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 $\phi_i < \lambda/3 \cong \lambda/\pi$ 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·λ, the detonation coming in from the pipe will revert to a deflagration upon entering the vessel („13·λ rule“).
  Otherwise the detonation coming in from the pipe continues as detonation inside the vessel.



References:
[1] M.A. Nettleton in *Gaseous Detonations*, Chapman and Hall Ltd, London (1987), ISBN 0 412 27040 4 (pages 59, 63)
[2] John H. S. Lee, The Detonation Phenomenon, Cambridge University Press, ISBN 978-0-521-89723-5 , pages 286 ff (2008)
[3] Experience of BASF Safety Engineering Group, tests with Propene/Air in Raschig-ring packing, unpublished (2006).

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

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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:
  - **Focussed** 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

[1] H.P. Schildberg, J. Smeulers, G. Pape, *Experimental determination of the static equivalent pressure of gas phase detonations in pipes and comparison with numerical models*,
Proceedings of ASME **2013** Pressure Vessels and Piping Conference, *Proc. ASME.* 55690, Volume 5: High-Pressure Technology, ISBN: 978-0-7918-5569-0; doi: 10.1115/PVP2013-97677
(Paper No. PVP2013-97677, pp. V005T05A020; 15 pages; conference from July 14-18, 2013, Paris, France)

[2] H.P. Schildberg, *Experimental determination of the static equivalent pressure of detonative decompositions of acetylene in long pipes and Chapman-Jouguet pressure ratio*,
Proceedings of ASME **2014** Pressure Vessels and Piping Conference, Proc. ASME. 46025, Volume 5: High-Pressure Technology, ISBN: 978-0-7918-4602-5; doi: 10.1115/PVP2014-28197
(Paper No. PVP2014-28197, pp. V005T05A018; 13 pages; conference from July 20-24, 2014, Anaheim, California, USA

[3] H.P. Schildberg, *Experimental Determination of the Static Equivalent Pressures of detonative Explosions of Stoichiometric $H_2/O_2/N_2$-Mixtures in Long and Short pipes,*
Proceedings of the ASME **2015** Pressure Vessels and Piping Conference, *Proc. ASME.* 56987; Volume 5: High-Pressure Technology; Rudy Scavuzzo Student Paper Competition and 23rd Annual Student Paper Competition; ASME NDE Division, V005T05A015.July 19, 2015, PVP2015-45286, doi: 10.1115/PVP2015-45286
(Paper No. PVP2015-45286, 13 pages, conference from July 19-23, 2015, Boston, Massachusetts, USA)

[4] H.P. Schildberg, *Experimental Determination of the Static Equivalent Pressures of Detonative Explosions of Stoichiometric $CH_4/O_2/N_2$-Mixtures and of CH_4/O_2-Mixtures in Long Pipes*,
Proceedings of the ASME **2016** Pressure Vessels and Piping Conference, *Proc. ASME.* 50404; Volume 4: Fluid-Structure Interaction, V004T04A020.July 17, 2016, PVP2016-63223, doi: 10.1115/PVP2016-63223
(Paper No. PVP2016-63223, 13 pages, conference from July 17 - 21, 2016, Vancouver, BC, Canada)

[5] H.P. Schildberg, *Experimental Determination of the Static Equivalent Pressures of Detonative Explosions of Stoichiometric $C_2H_4/O_2/N_2$-Mixtures and of C_2H_4/O_2-Mixtures in Long Pipes and of stoichiometric $C_6H_{12}/O_2/N_2$ Mixtures in long and short pipes,*
Proceedings of the ASME **2018** Pressure Vessels and Piping Conference, Proc. ASME. 51661; Volume 5: High-Pressure Technology, V005T05A015.July 15, 2018, PVP2018-84493, doi: 10.1115/PVP2018-84493
(Paper No. PVP2018-84493, 14 pages, conference from July 16 - 20, 2018, Prague, Czech Republic)

[6] H.P. Schildberg, J. Eble, *Experimental Determination of the Static Equivalent Pressures of Detonative Explosions of Cyclohexane/O2/N2-Mixtures in Long and Short Pipes (parts 1, 2,3),* Proceedings of the *16th International Symposium on Loss Prevention and Safety Promotion in the Process Industries*, 17.6.-19.6.**2019**, Delft, Netherlands. Guest Editors: Genserik Reniers, Bruno Fabiano; Copyright © 2019, AIDIC Servizi S.r.l.; ISBN 978-88-95608-72-3; ISSN 2283-9216

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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
(Proceedings of the 15th International Symposium on Loss Prevention and Safety Promotion in the Process Industries, 5.6.-8.6.2016, Freiburg, Germany. Guest Editors: Eddy de Rademaeker, Peter Schmelzer, Copyright © 2016, AIDIC Servizi S.r.l., ISBN 978-88-95608-39-6; ISSN 2283-9216)

[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
(Proceedings of the 15th International Symposium on Loss Prevention and Safety Promotion in the Process Industries, 5.6.-8.6.2016, Freiburg, Germany. Guest Editors: Eddy de Rademaeker, Peter Schmelzer Copyright © 2016, AIDIC Servizi S.r.l., ISBN 978-88-95608-39-6; ISSN 2283-9216)

[9] Technische Regel für Gefahrstoffe 407 (TRGS 407), Tätigkeiten mit Gasen – Gefährdungsbeurteilung, Gemeinsames Ministerialblatt Nr. 12-17 (26.04.2016), p. 328 – 364, ISSN 0939-4729
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).
Note 3: Das Gemeinsame Ministerialblatt (GMBl) ist das amtliche Publikationsorgan der Bundesregierung und wird vom Bundesministerium des Innern seit 1950 herausgegeben. Hier veröffentlichen nahezu alle Bundesministerien die von ihnen erlassenen oder ergänzten Allgemeinen Verwaltungsvorschriften, Verordnungen, Richtlinien, Erlasse, Anordnungen, Rundschreiben und Bekanntmachungen von allgemeiner Bedeutung sowie Stellenausschreibungen einschließlich ihres nachgeordneten Bereichs.

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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

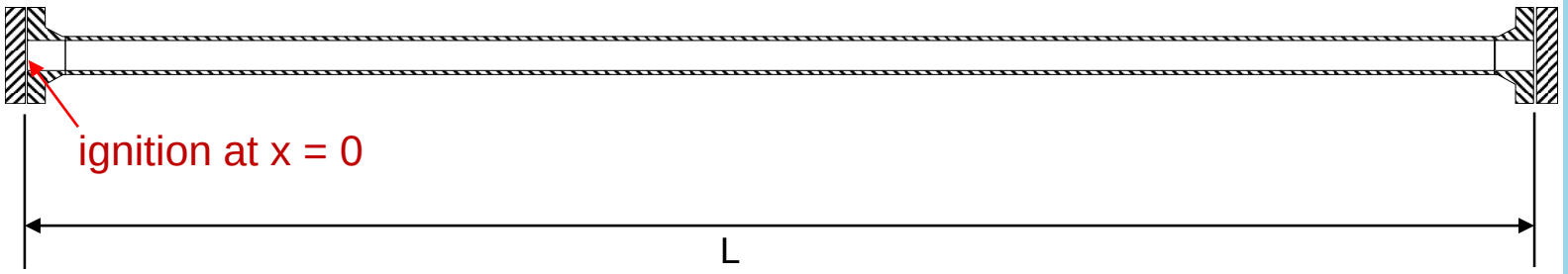
- 6 scenarios are design-relevant

- An experimental method ("*pipe wall deformation method*") was established to determine the "*static equivalent pressures (p_{stat})*" of each detonative scenario
  - **Direct** correlation between input parameters (mixture composition) and the desired result (p_{stat}).
    There are no complex intermediate steps and apprioximation 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.

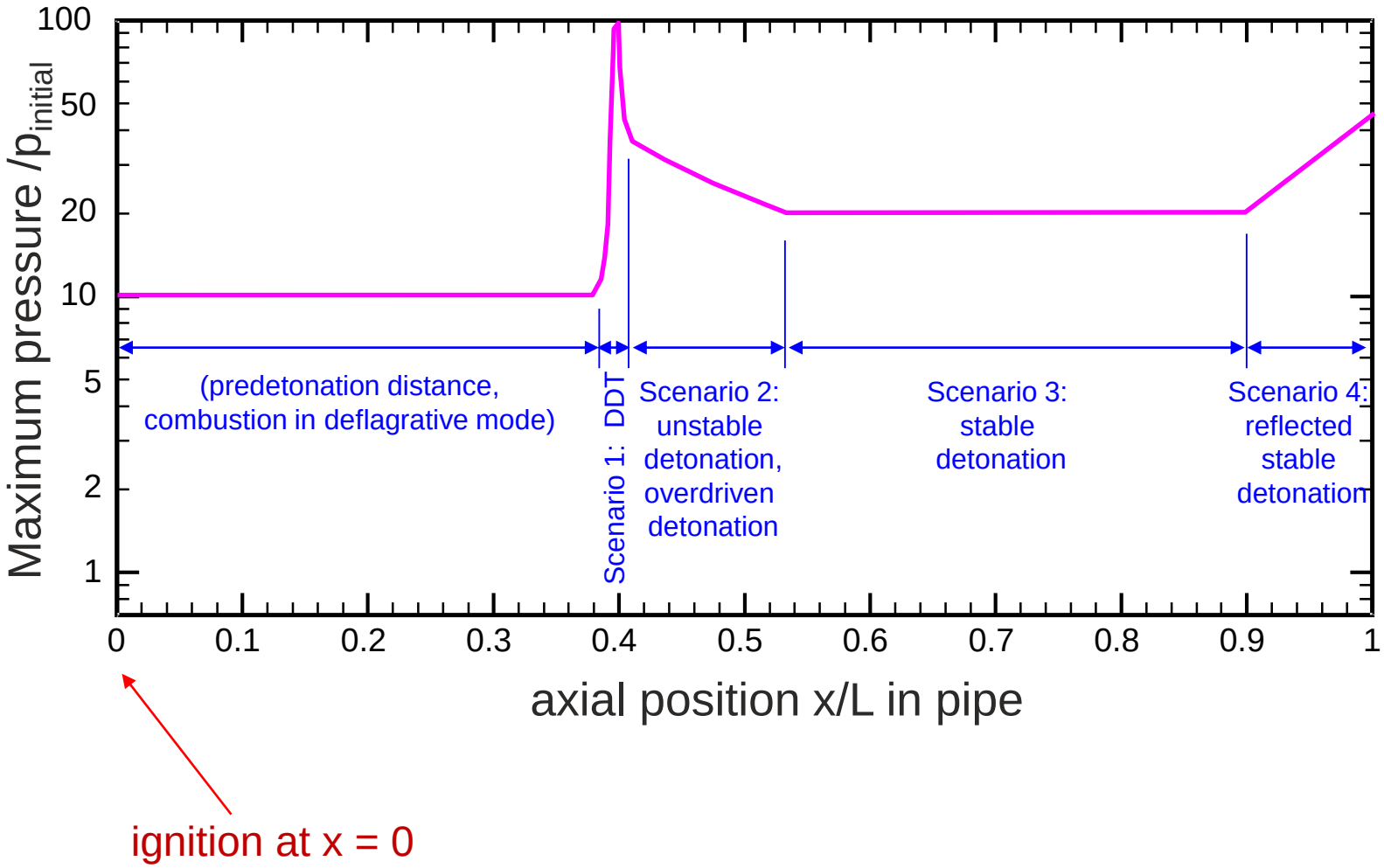
Help to visualize the different detonative pressure scenarios



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

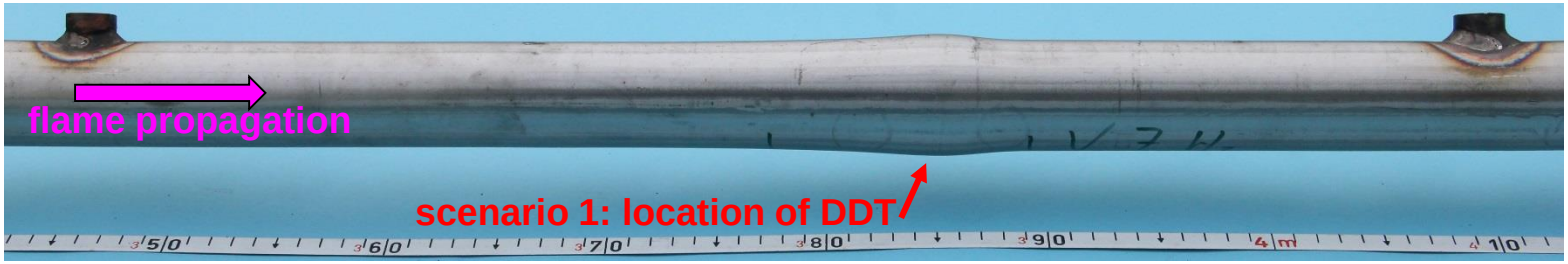
2nd step: record the maximum pressure ratios found in the pipe at any axial position during the course of the explosion

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)

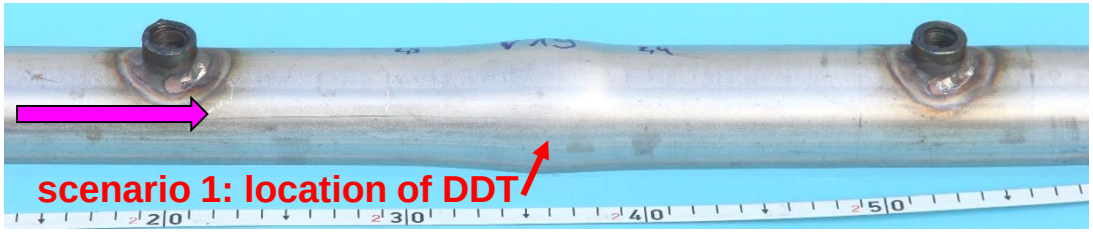


Example: local pressures of scenarios 1 and 4 made visible by residual plastic deformation in wall of long pipe

Test 7: 12.2 bar abs, 20 °C, stoichiometric H_2/air (H_2:O_2:N_2=29.56:14.78:55.66 [vol.-%])
48.3 x 2.6 pipe, material: 1.4541

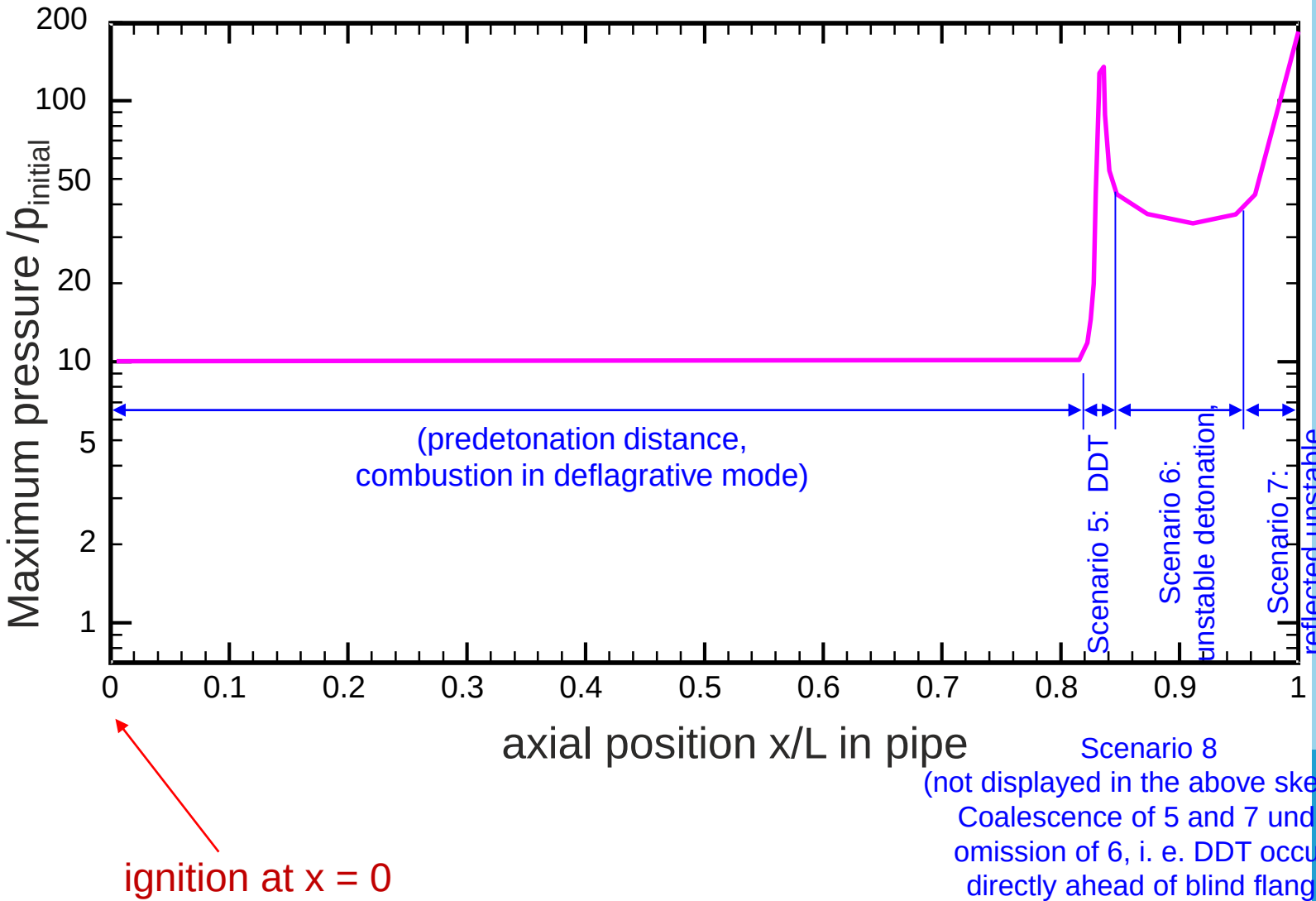


Test 19: 10 bar abs, 20 °C, CH_4 : O_2 = 11.25 : 88.75 [vol.-%], 48.3 x 2.6 pipe, material: 1.4541



Test 19: 35 bar abs, 20 °C, H_2:O_2:N_2=50:25:25 [vol.-%], 48.3x2.6-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)



ignition at x = 0

Scenario 8
(not displayed in the above sketch):
Coalescence of 5 and 7 under
omission of 6, i. e. DDT occurs
directly ahead of blind flange

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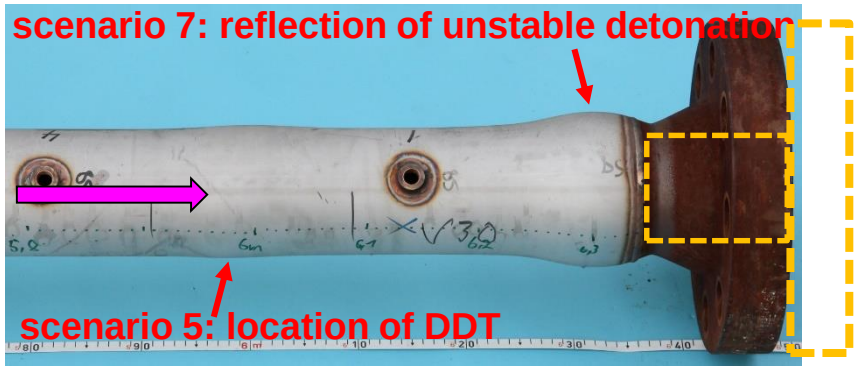
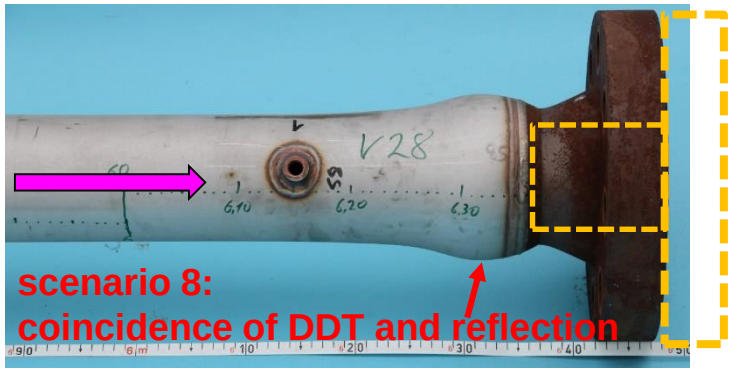
Example: local pressures of scenarios 5, 7, 8 made visible by residual plastic deformation in wall of short pipe

Test 26: 4.5 bar abs, 20 °C, H_2:O_2:N_2=28.6:14.3:57.1 [vol.-%]

Test 30:
4.0 bar abs, 20 °C,
H_2:O_2:N_2=28.6:14.3:57.1 [vol.-%]



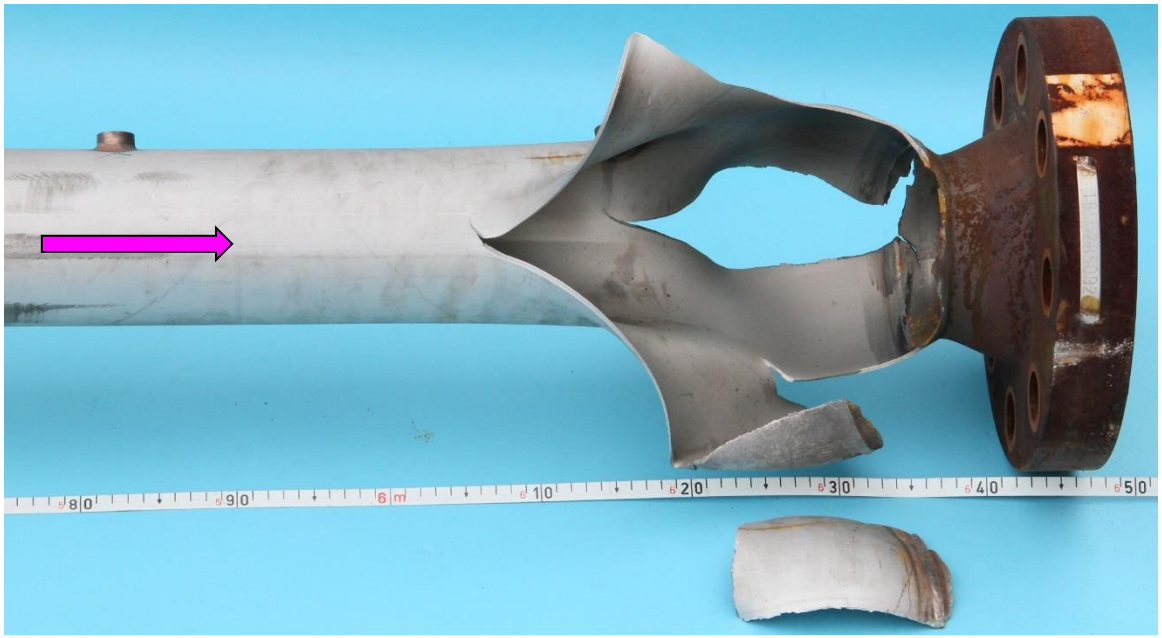
Test 28:
4.5 bar abs, 20 °C
H_2:O_2:N_2= 28.1:14.05:57.85 [vol.-%]



Example: bulging in short pipes (scenario 8)

Test no. 28:
4.5 bar abs,
14.05 vol.-% O_2
in stoichiometric
$H_2/O_2/N_2$

Test no. 29:
4.63 bar abs,
14.175 vol.-% O_2
in stoichiometric
$H_2/O_2/N_2$



Static equivalent pressures for the 8 detonative pressure scenarios in pipes

Type of pressure scenario			Static equivalent pressures for any detonable gas mixture
no.	pipe	name	
1	long pipe	DDT	$p_{stat\_DDT\_long} = \boldsymbol{R} \cdot p_{stat\_stable}$
2		unstable detonation	(irrelevant for pipe design)
3		stable detonation	$p_{stat\_stable} = \alpha \cdot p_{CJ\_r} \cdot p_{initial}$
4		reflected stable detonation	$p_{stat\_reflected\_stable} = 2.4 \cdot p_{stat\_stable}$
5	short pipe	DDT	$p_{stat\_DDT\_short} = 1.5 \cdot p_{stat\_DDT\_long} = 1.5 \cdot \boldsymbol{R} \cdot p_{stat\_stable}$
6		unstable detonation	(irrelevant for pipe design)
7		reflected unstable detonation	$p_{stat\_reflected\_instable} = 1.5 \cdot 2 \cdot p_{stat\_reflected\_stable} = 1.5 \cdot 2 \cdot 2.4 \cdot p_{stat\_stable}$
8		coincidence of DDT and reflection	$p_{stat\_coincidence\_DDT\_reflection} = 2.4 \cdot p_{stat\_DDT\_short} = 2.4 \cdot 1.5 \cdot p_{stat\_DDT\_long} = 2.4 \cdot 1.5 \cdot \boldsymbol{R} \cdot p_{stat\_stable}$

Factor ***R*** depends on reactivity of gas mixture

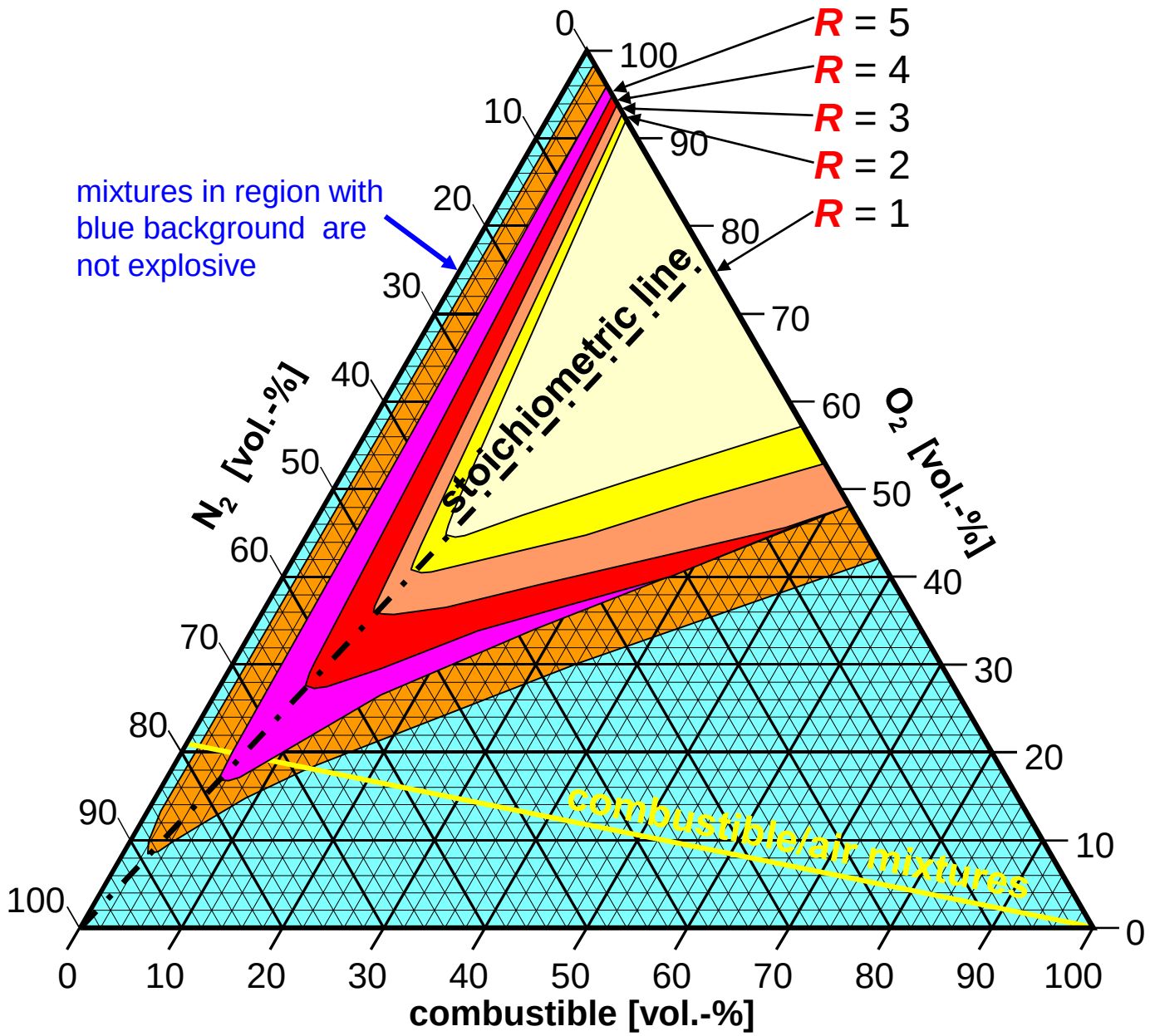
Formulae for p_{stat} are valid for any other explosive gas mixture at any $p_{initial}$ and $T_{initial}$.

Short pipe scenario can be predicted based on long pipe scenarios 1 and 3

Note:

- α = 0.7 (valid in general)
- p_{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 -> backup slides to this lecture

Variation of R over the explosive range of a ternary mixture of type combustible/O_2/N_2 (tentative)



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

Type of pressure scenario			p_{stat} (expressed as multiple of $p_{initial}$)
no.	**pipe**	**name**	
1	long pipe	DDT	*64.6*
2		unstable detonation	-
3		stable detonation	*13.2*
4		reflected stable detonation	*33*
5	short pipe	DDT	*81.8*
6		unstable detonation	-
7		reflected unstable detonation	*128*
8		coincidence of DDT and reflection	*232*

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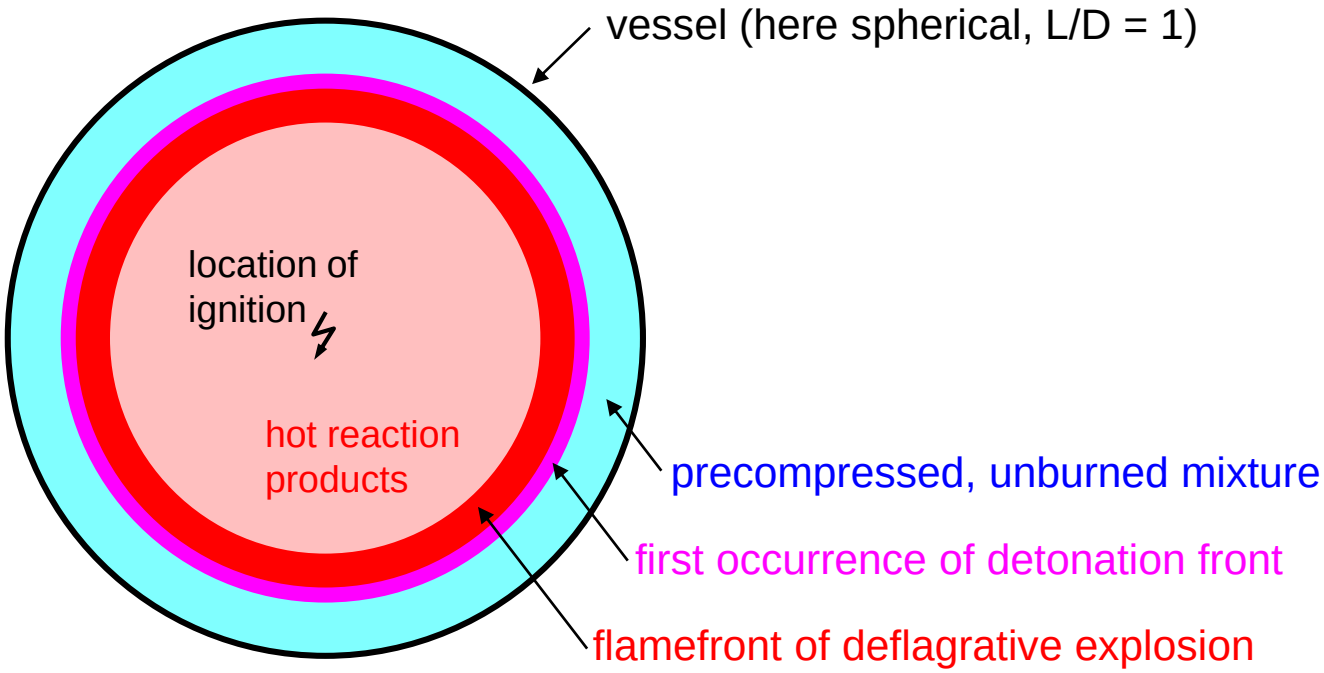
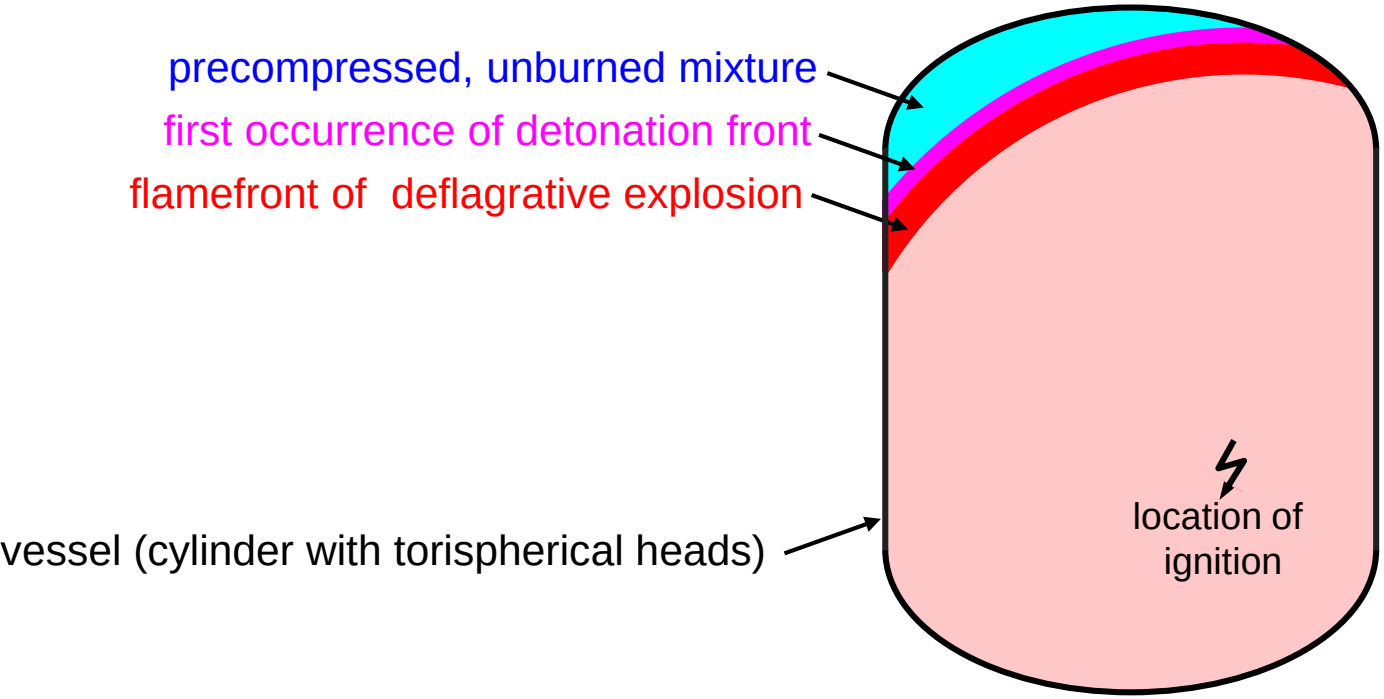
Fundamental problem when deflagration to detonation transitions occur in empty vessels



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

Schematic sketch of an explosion with DDT inside a vessel



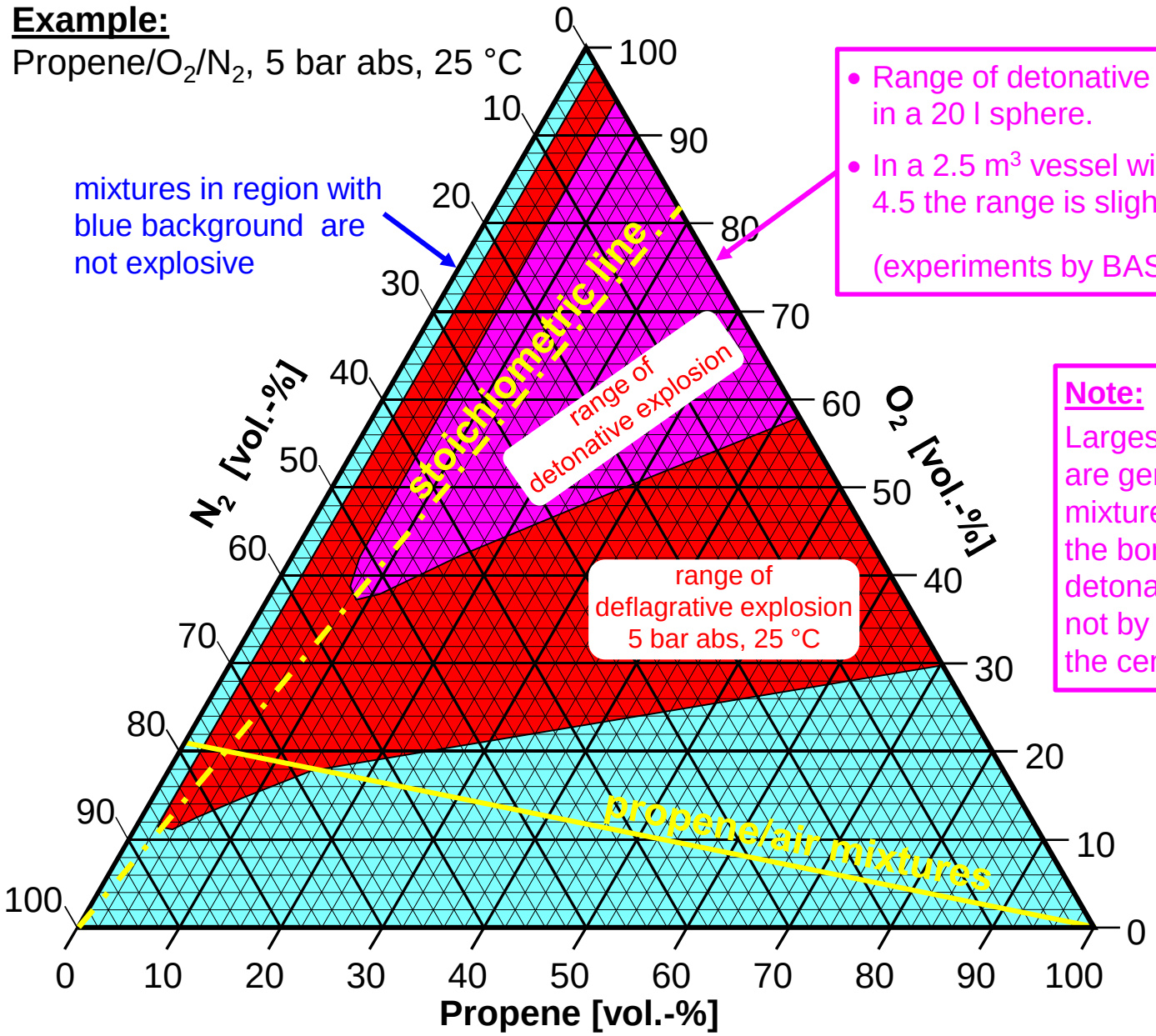
If a DDT occurs at this time instant, maximum pressure loads can be expected, because the unreacted mixture is almost precompressed to $r \cdot p_{initial}$

(r denotes the deflagration pressure ratio, p_{intial} 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/O_2/N_2, 5 bar abs, 25 °C



- Range of detonative explosions in a 20 l sphere.
- In a 2.5 m^3 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 !!!!!

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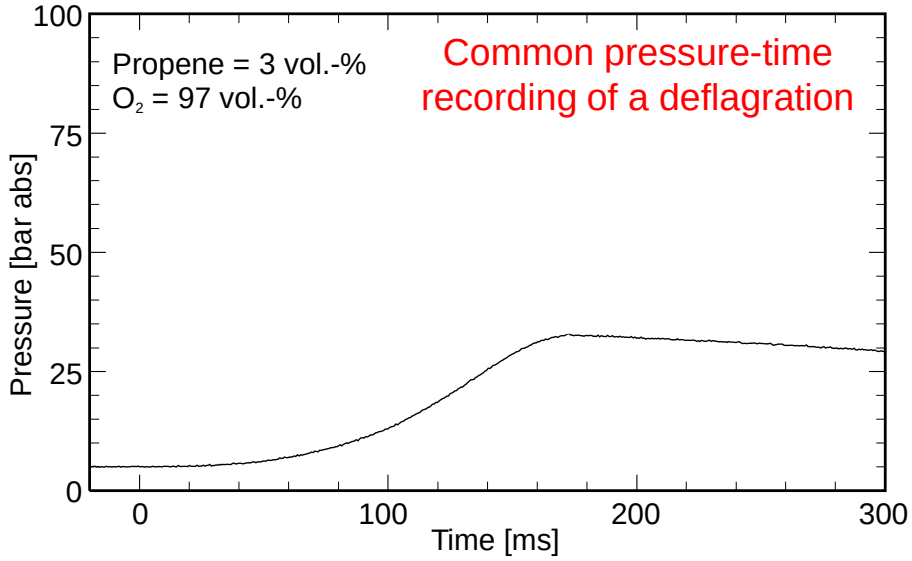
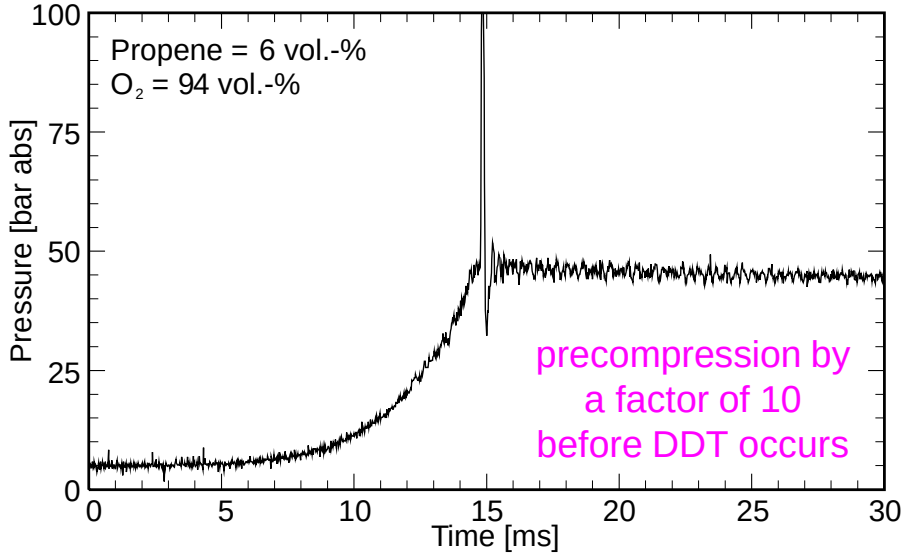
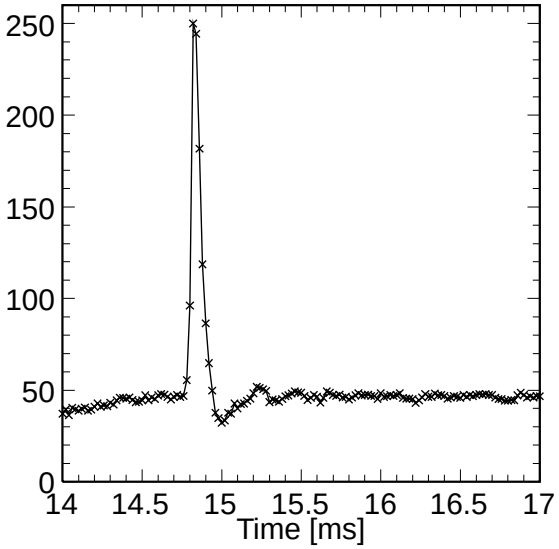
Pressure/Time recordings of explosions of Propene/O_2-mixtures at 5 bar abs, 20°C in a 20 l sphere (1/2)

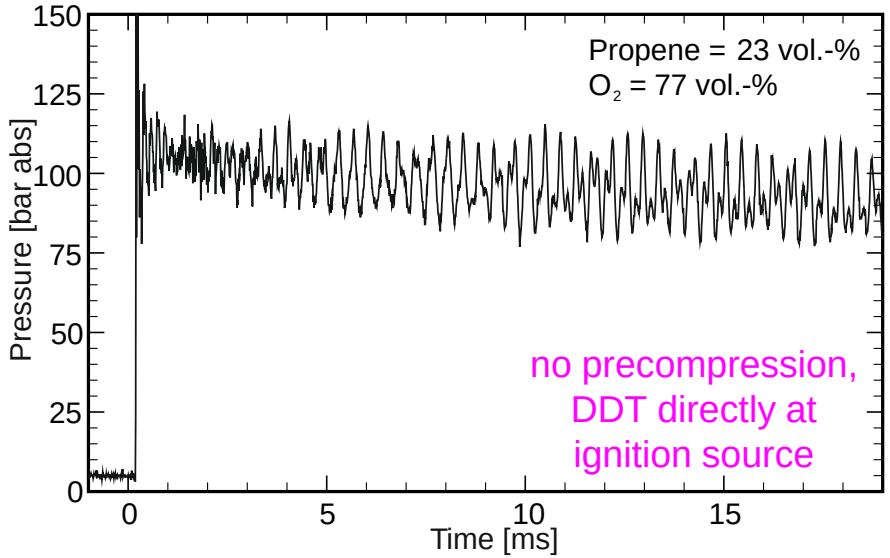


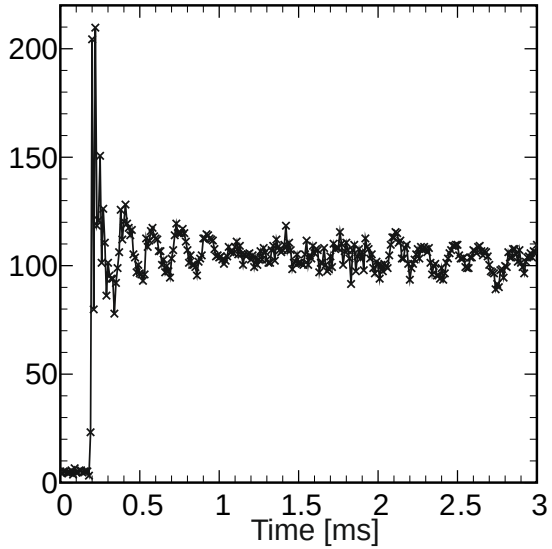


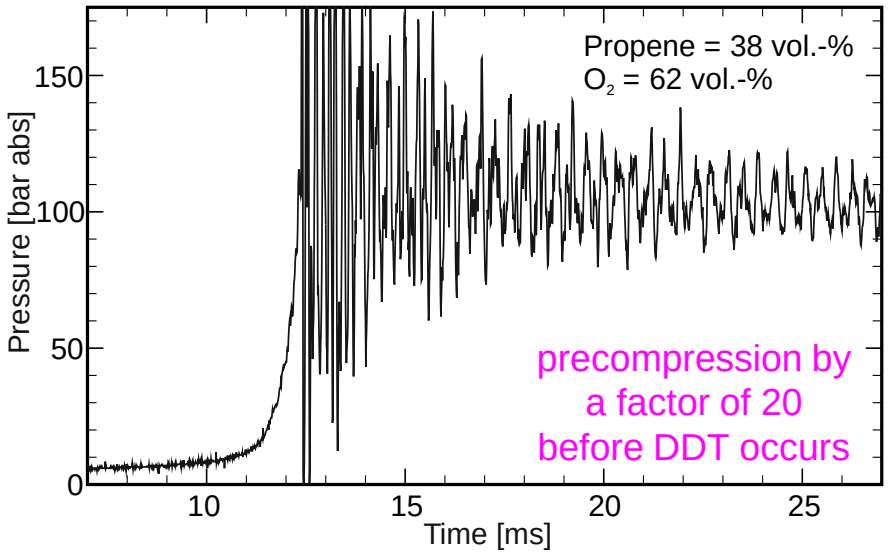


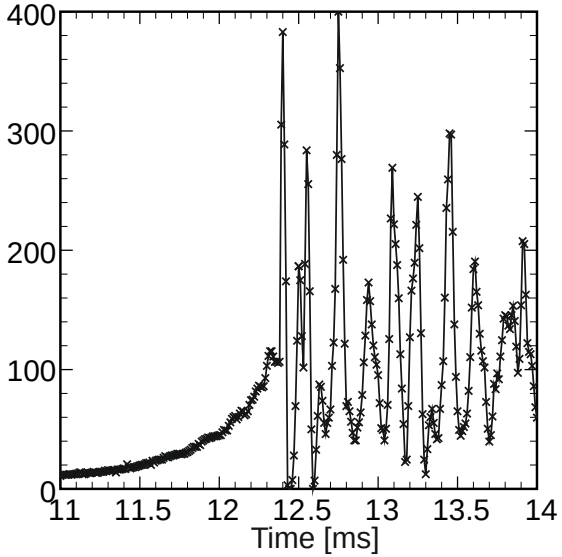
Reference: "The course of the explosions of combustible/O_2/N_2 mixtures in vessel-like geometry", H.-P. Schildberg, Forschung im Ingenieurwesen (2009) 73, 33-65, DOI 10.1007/s10010-009-0091-6

Pressure/Time recordings of explosions of Propene/O_2-mixtures at 5 bar abs, 20°C in a 20 l sphere (2/2)









Fundamental questions when quantifying hazards associated with potential detonations in vessels

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

- What is the largest conceivable value of the static equivalent pressure p_{stat} in comparision to p_{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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- Detonations in vessels filled with irrigated packing
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Typical applications of vessels filled with dry packings

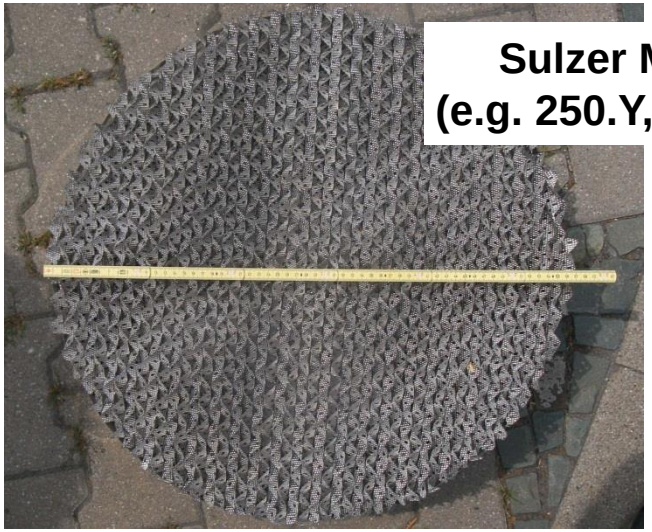
- Vessels acting as demisters
- Vessel acting as flame arrestors
  (e.g. for self decomposable gases like Acetylene or Ethylene Oxide)
- Vessels acting as static mixers

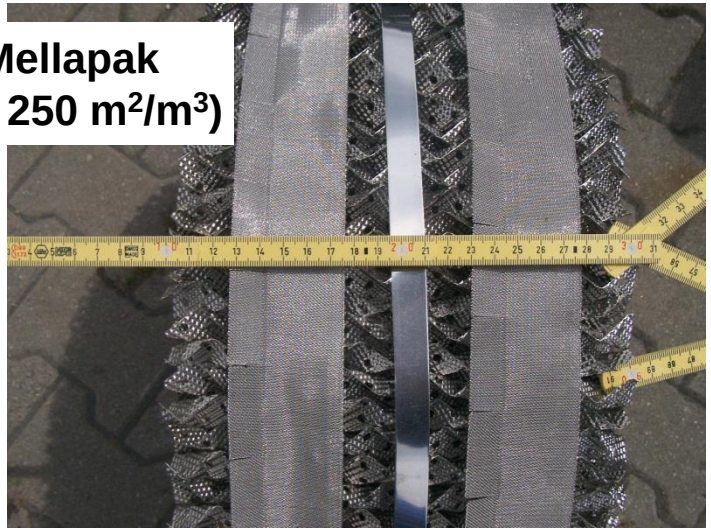
Typical packings used in the process industry

Raschig Rings, L/D = 1,
typical: 15 mm ≤ L ≤ 50 mm

Pall Rings, L/D = 1,
typical: 15 mm ≤ L ≤ 50 mm

Sulzer Mellapak
(e.g. 250.Y, 250 m^2/m^3)





Typical packings used in small-scale equipment

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 < $p_{initial}$ < 5 bar abs have a predetonation distance of about 100 · ϕ_i in straight pipes (ϕ_i is the inner pipe diameter). In packings this distance is only about 25 · ϕ_i . (ϕ_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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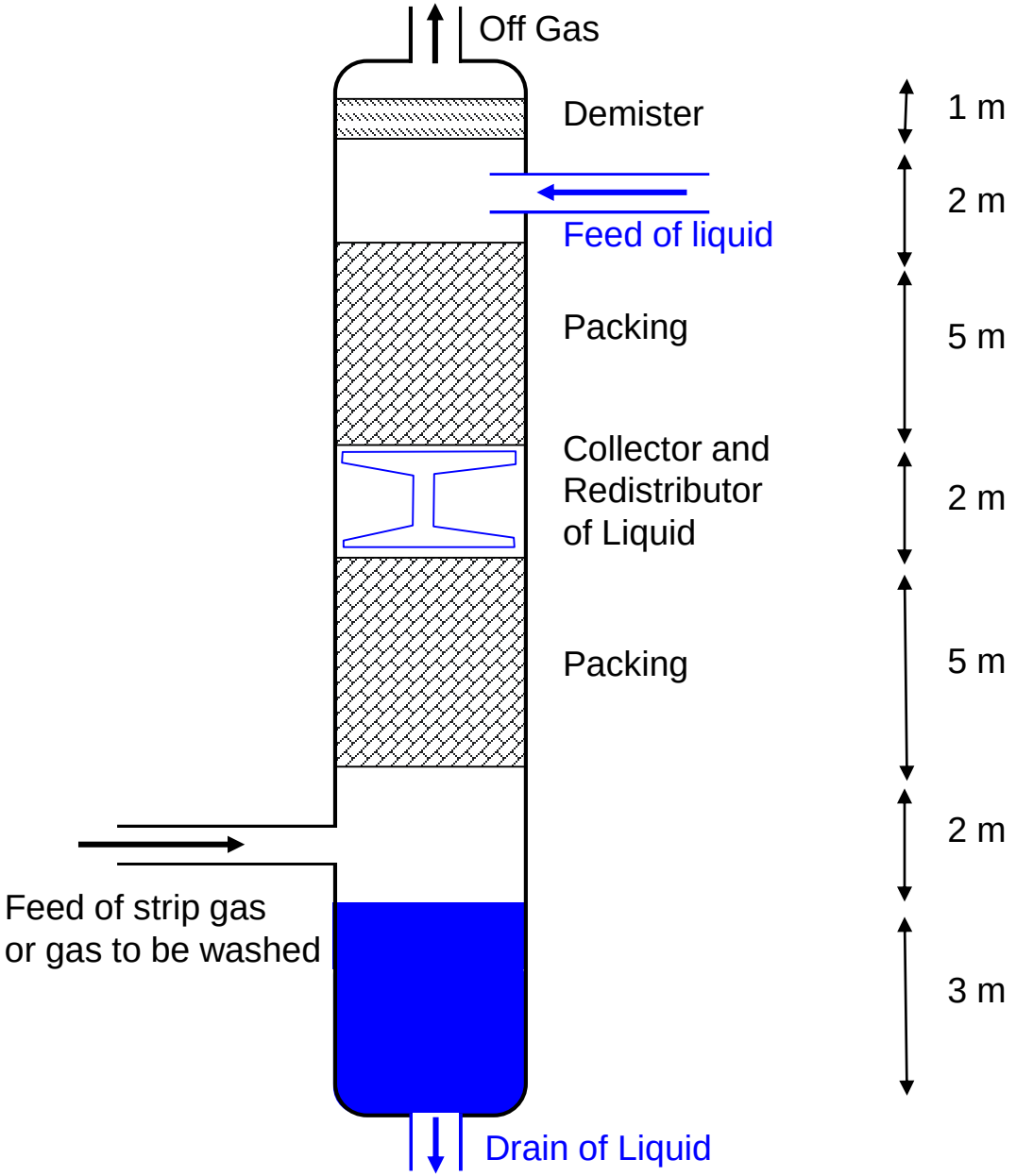
Typical applications of vessels filled with irrigated packings

- 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



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

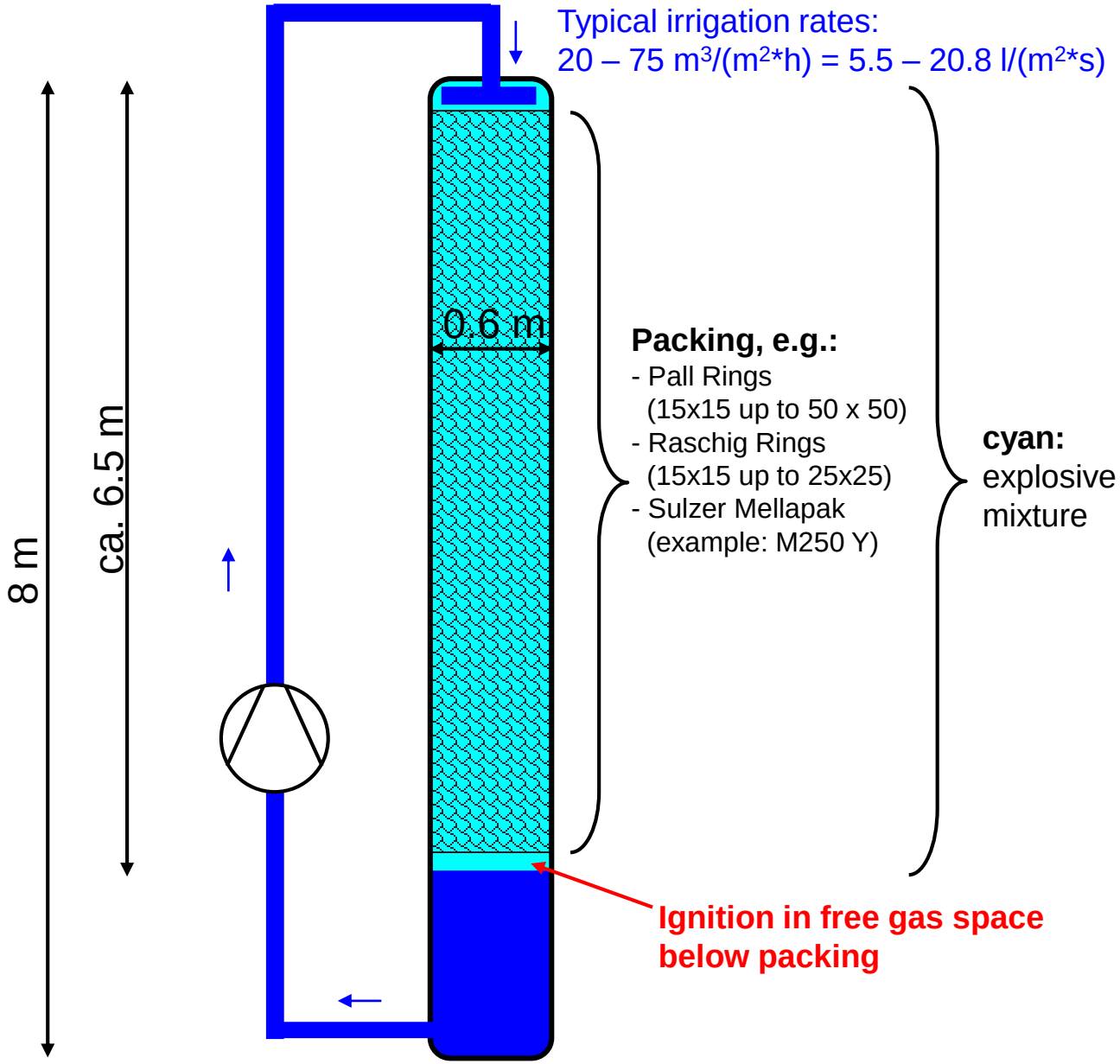
- Can a DDT, which would happen inside the dry packing, be suppressed by the irrigation?

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



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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 O_2 or N_2O
- Vinylation reactions of organic liquids

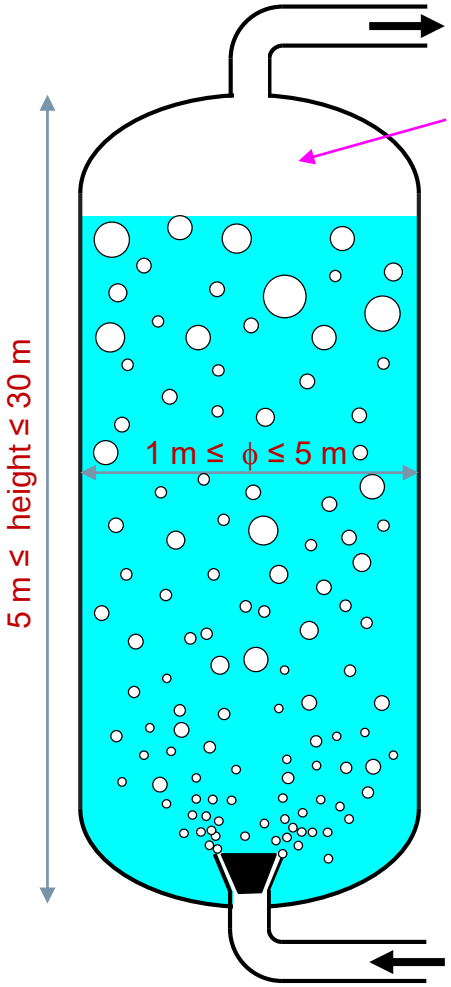
Schematic sketch of a gas-liquid partial oxidation or vinylation process (injection from bottom)

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



off gas pipe

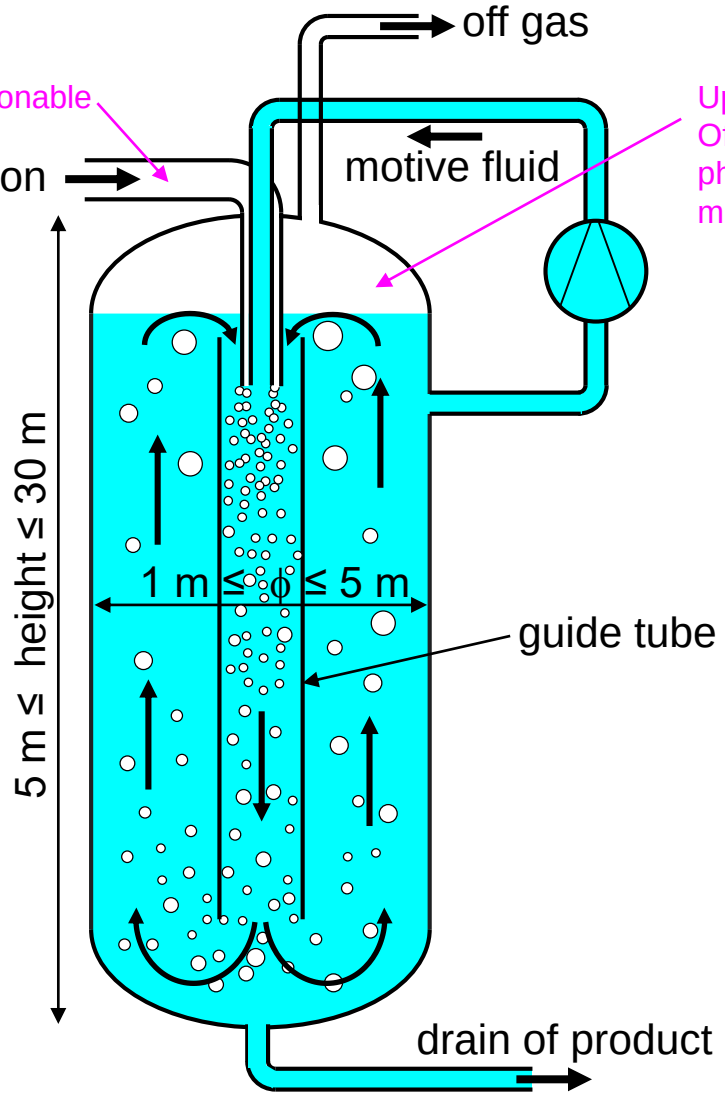
Upper reactor dome:
Often with detonable gas phase
(oxidant, vapours, mists, inert gases)

Black:
Reactor,
20°C ≤ T ≤ 300 °C,
6 barg ≤ p_{design} ≤ 325 barg

Blue:
Liquid to be partially oxidized or vinylated,
20°C ≤ T ≤ 300 °C,
0 barg ≤ $p_{operation}$ ≤ 30 barg
5 m^3 ≤ V ≤ 500 m^3

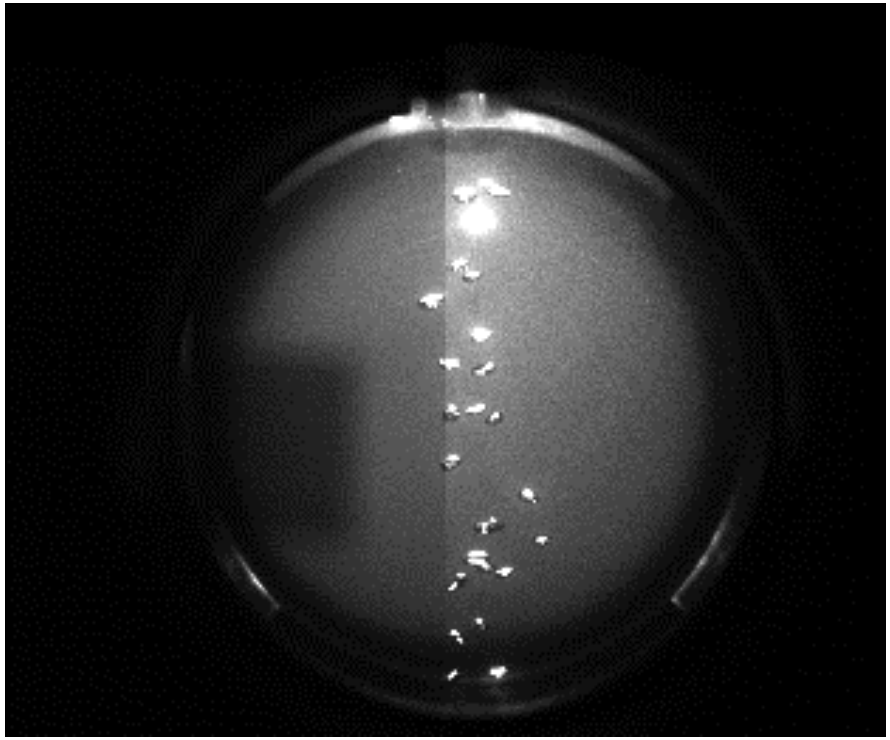
Feed gas pipe for oxidant containing gas mixture or acetylene:
$O_2/N_2/CO_2/CO/H_2O,C_2H_2$
0 barg ≤ $p_{operation}$ ≤ 30 barg
1000 Nm^3/h ≤ V ≤ 50000 Nm^3/h

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“)

Example for ignition of explosive bubbles by a propagating shock wave



Liquid: cyclohexane
Bubbles: cyclohexane/O_2
Shock wave: caused by detonation in C_2H_2/O_2 mixture in head space of reactor

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

Reference: K. Mitropetros, *Shock induced bubble explosions in liquid cyclohexane*, PhD thesis, Technical University Berlin (2005) 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, $p_{initial}$, $T_{initial}$) 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

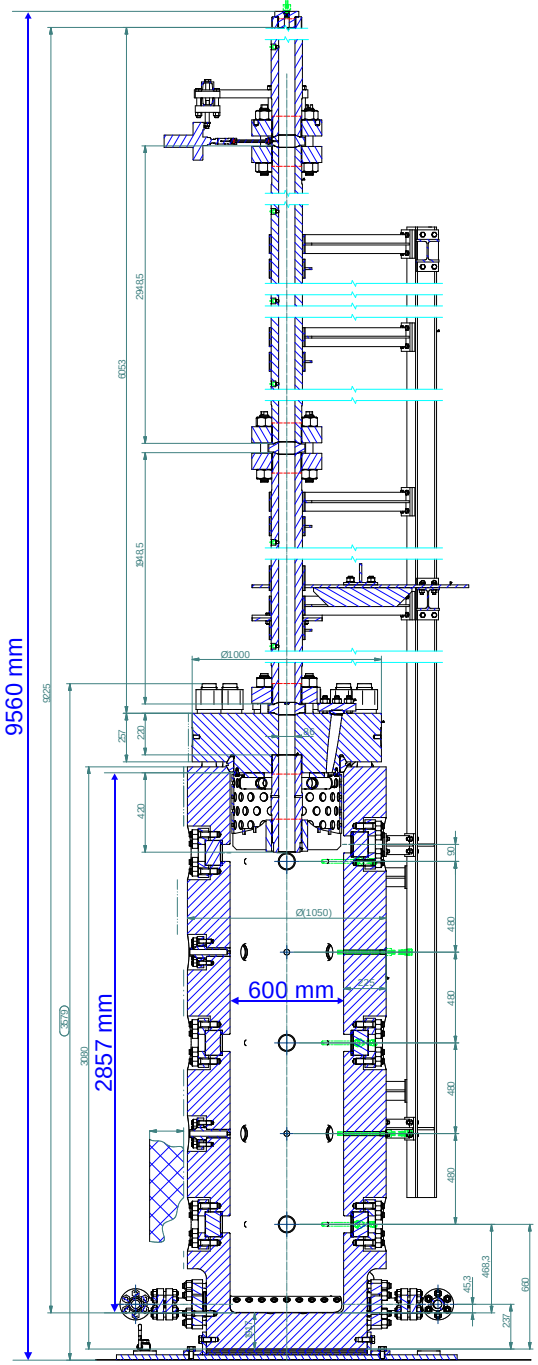
No.	Parameter	Reactors used in	
		published research	process industry
geometric data			
1	dimensions of reactors	L ≤ 1 m; ϕ_i ≤ 0.2 m (lab scale)	L ≤ 15 m; ϕ_i ≤ 6 m
2	volumetric gas fraction in liquid	very small (mostly single bubbles)	1 to 20 vol.-%
3	bubble diameter	≤ 20 mm	≤ 200 mm
experimental results			
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



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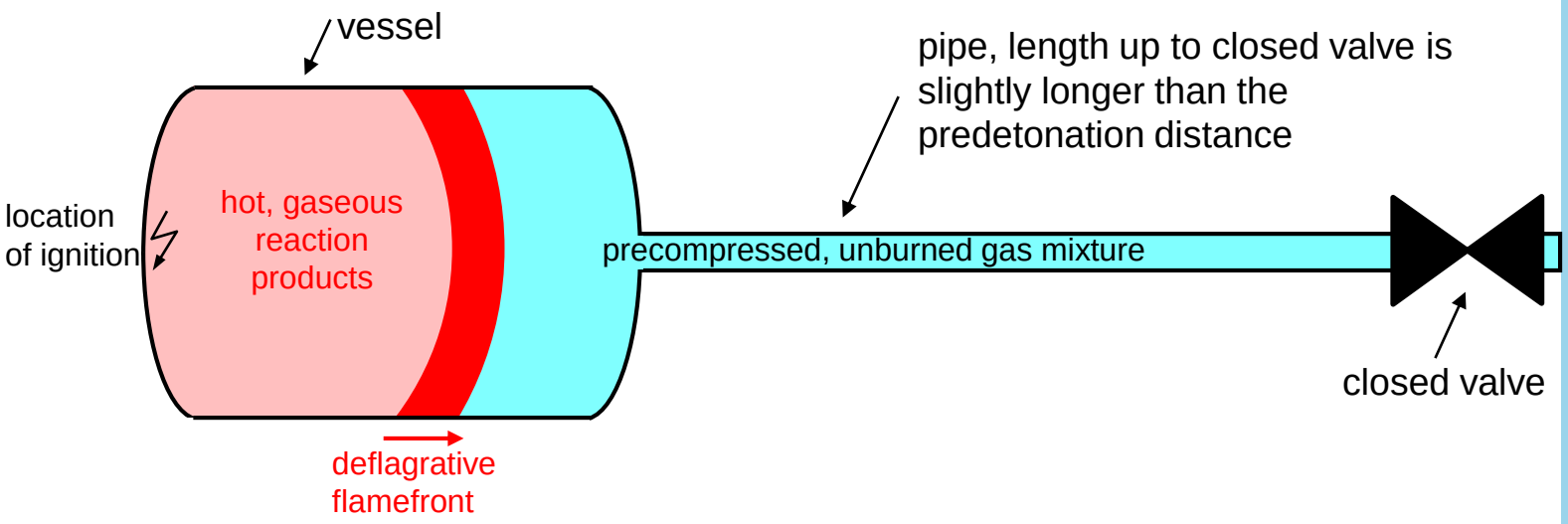
Problem with short pipe connected to large vessel



- 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).

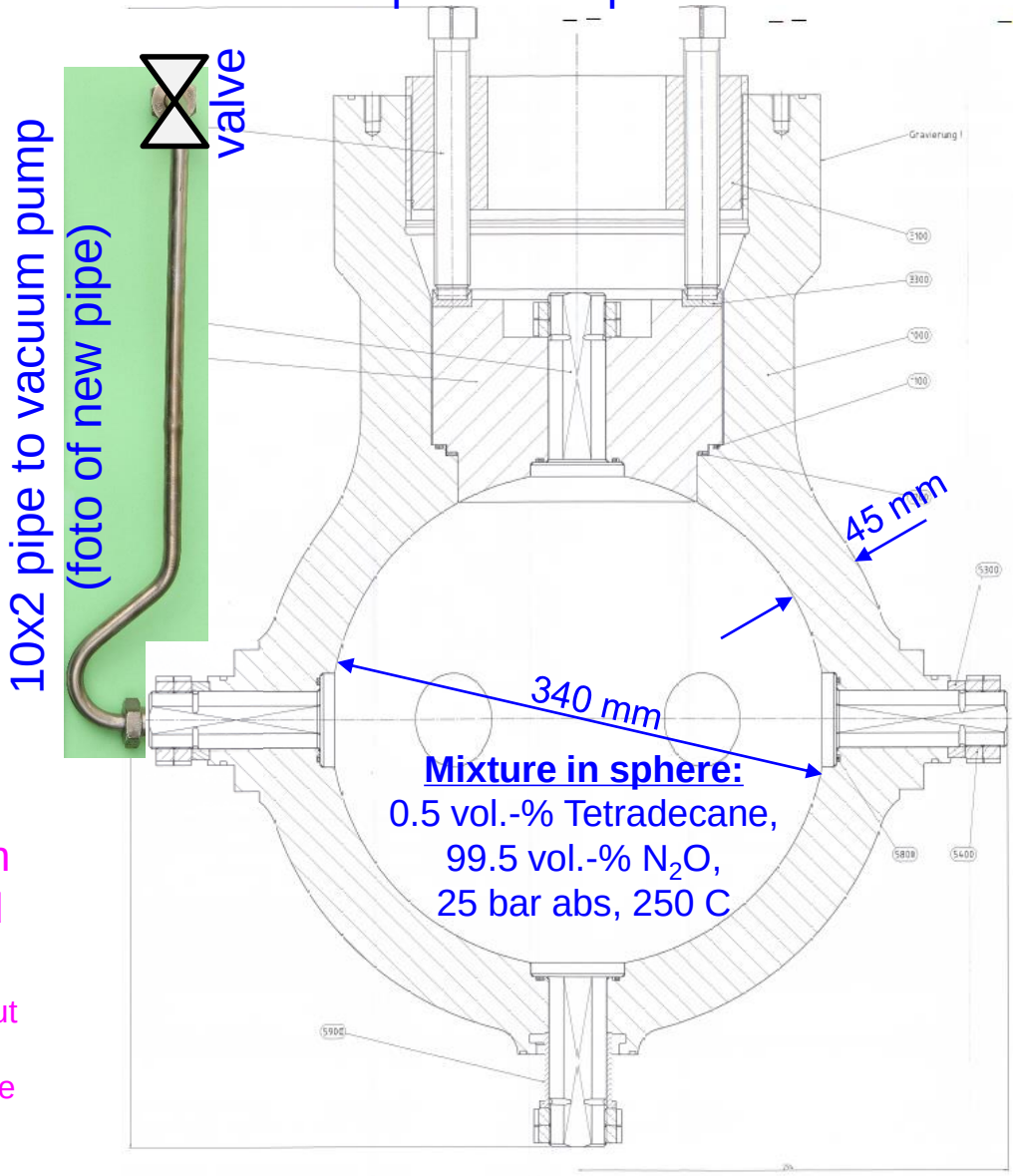
When, upon further propagation, the flame transitions to detonation, the **resulting pressures are extremely large**

Example 1: 20 l sphere with 45 cm pipe (ϕ_i = 6 mm)

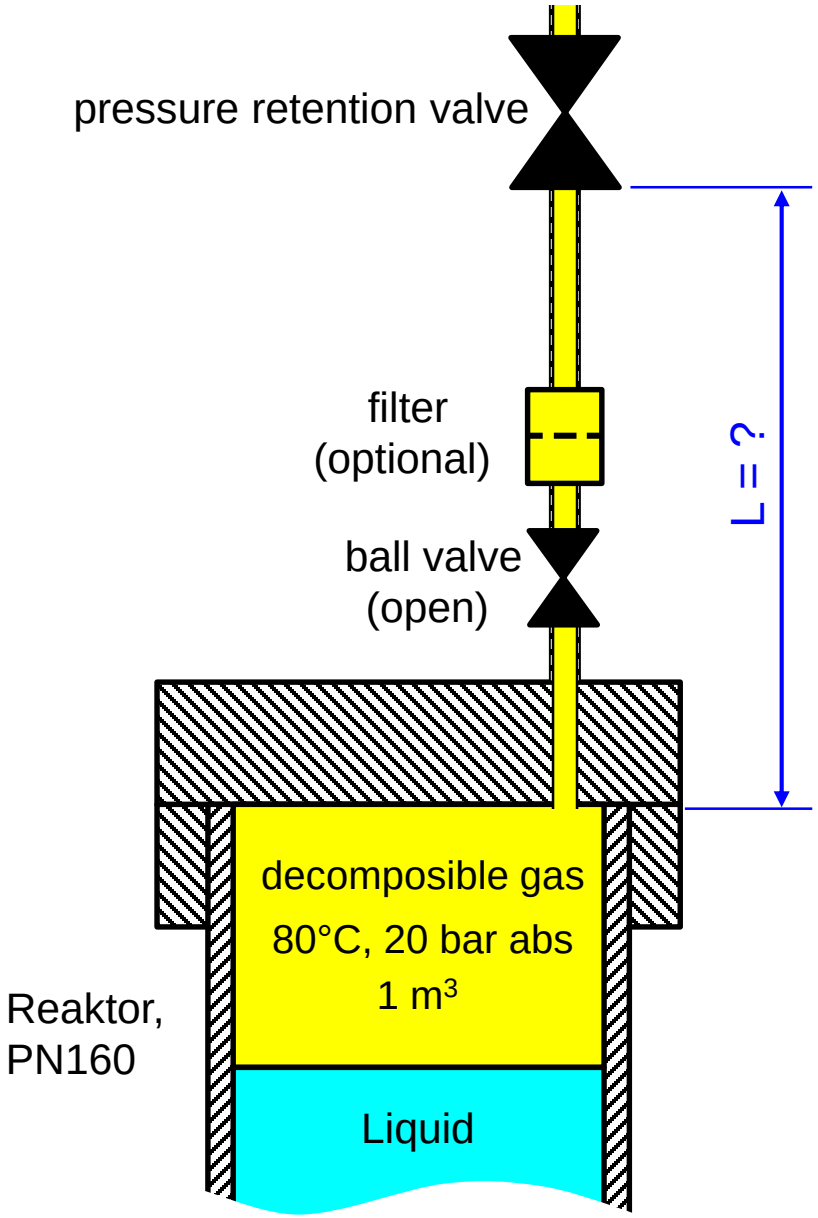
10x2 pipe ruptured at location of DDT, thereafter the curved part molt.

(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)

20 l sphere used for explosion experiments



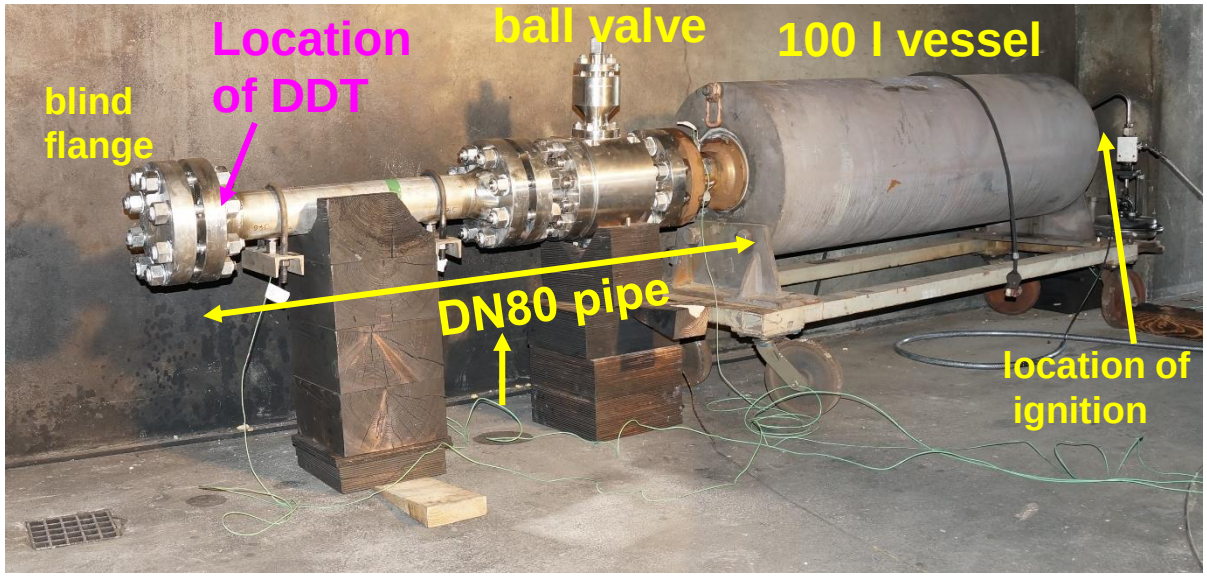
Example 2: Reactor with 1 m³ headspace and a DN80 pipe

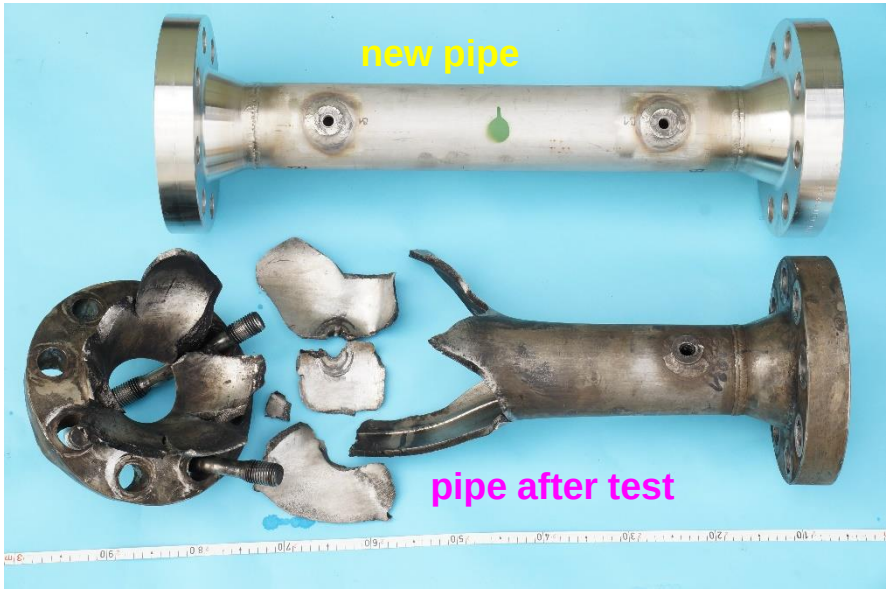


Question:

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





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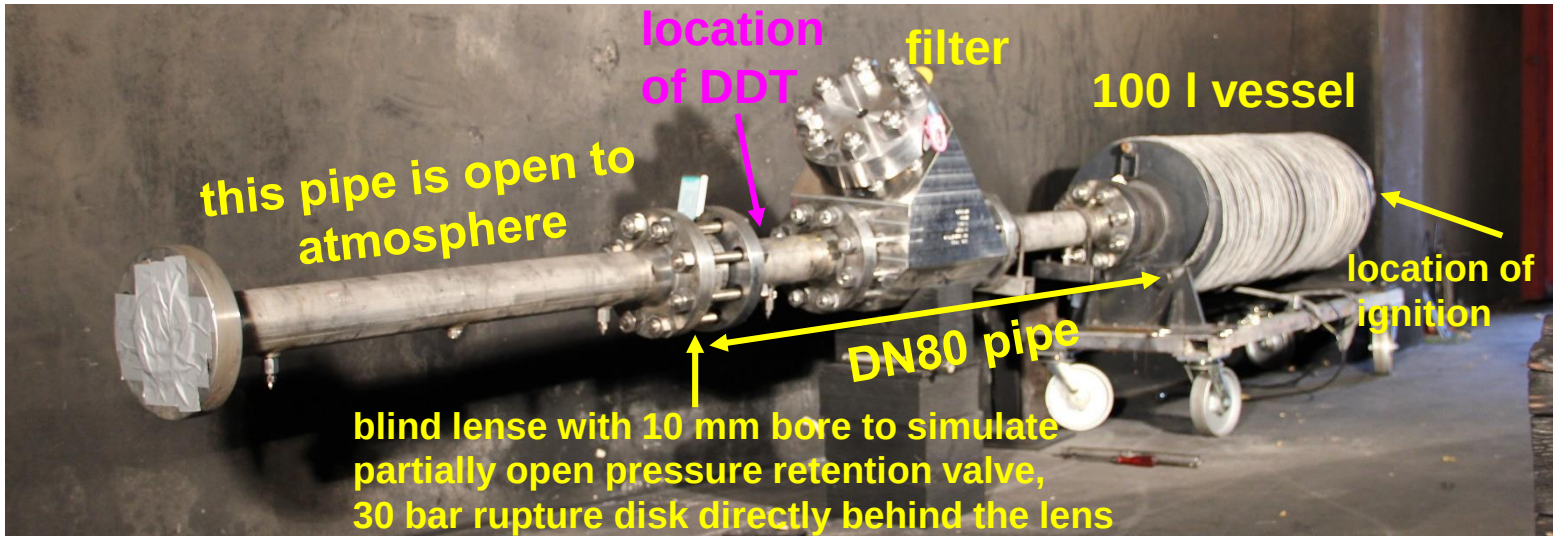

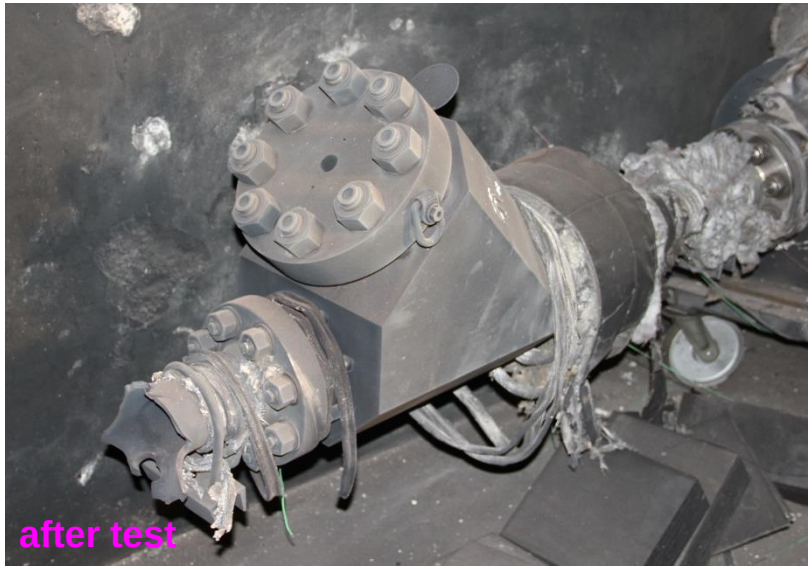

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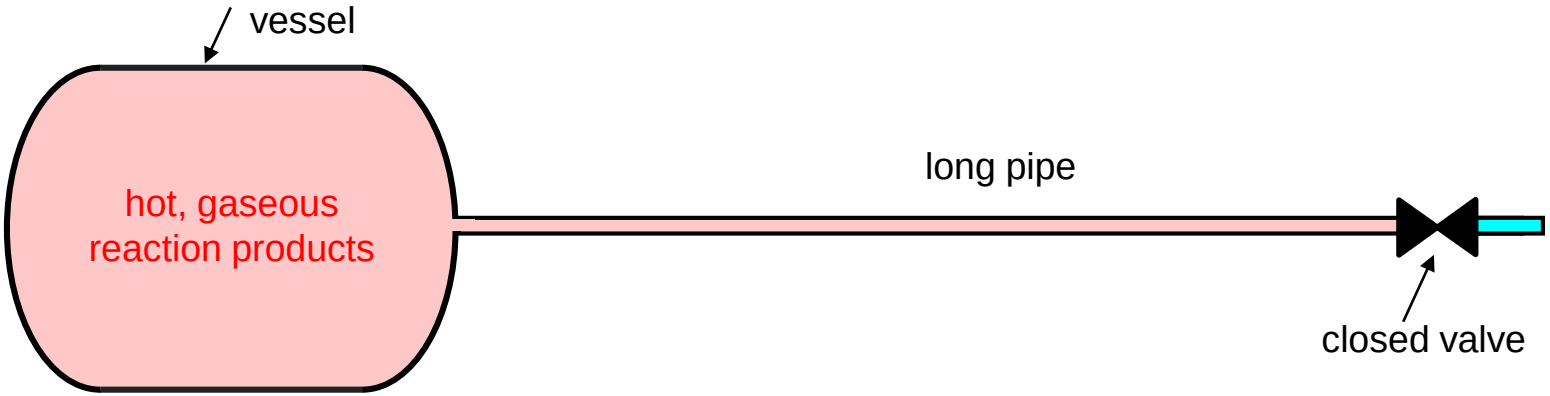
Problem with long pipe connected to a large vessel

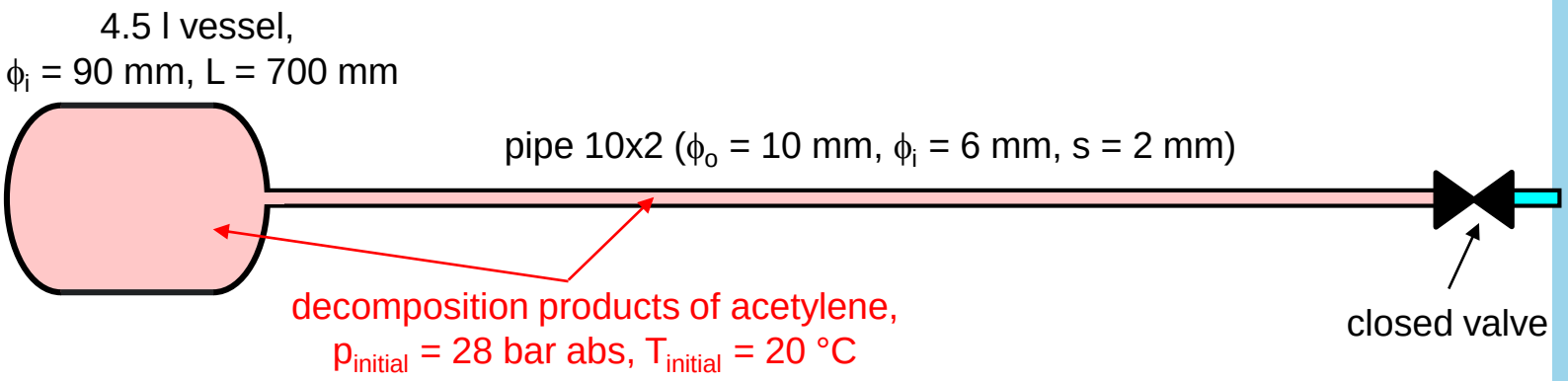


- Explosive mixture present in vessel and pipe explodes in deflagrative or detonative manner. The resulting pressures are sustained by the equipment.
- Usually: volume of vessel >>> volume of long pipe

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

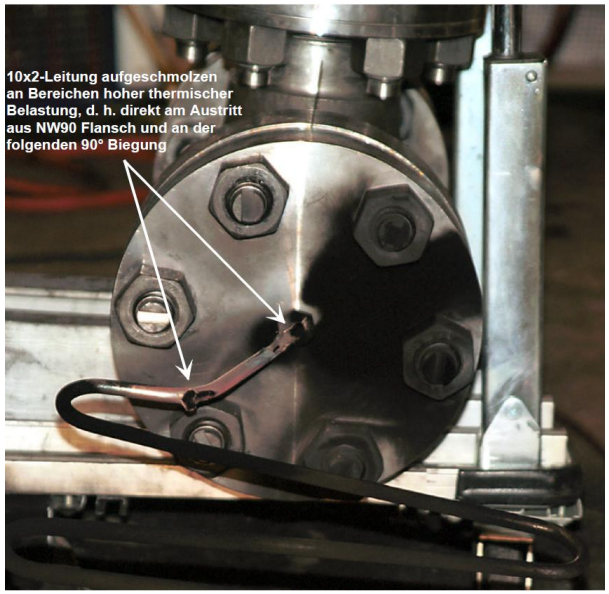
Note: Let n denote the number of moles in the pipe directly after the explosion has terminated. Then the pipe will typically receive 9*n hot moles from the vessel within a short time span after completion of the explosion.

Example 1: vessel with long pipe

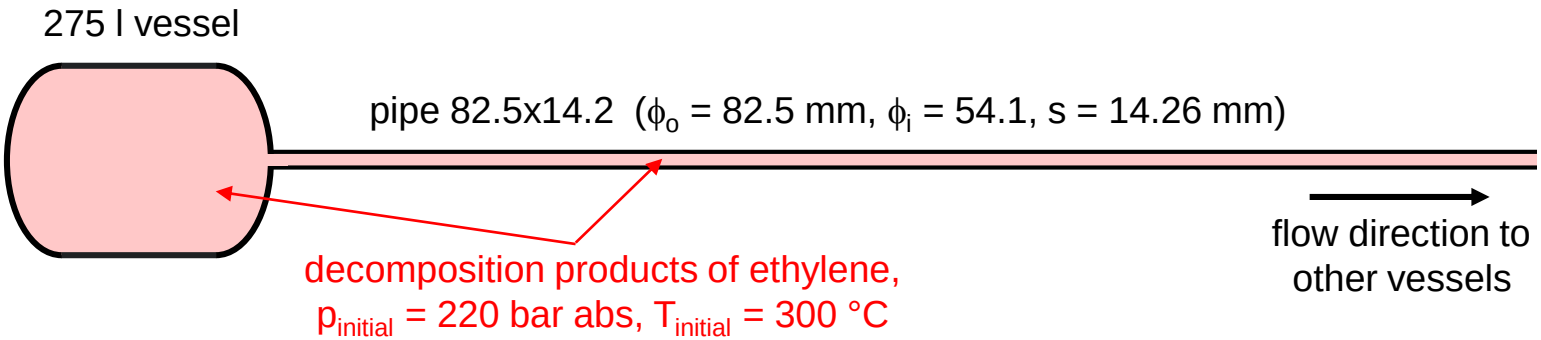


Case 1: pipe length is 1.5 m: no rupture

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

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

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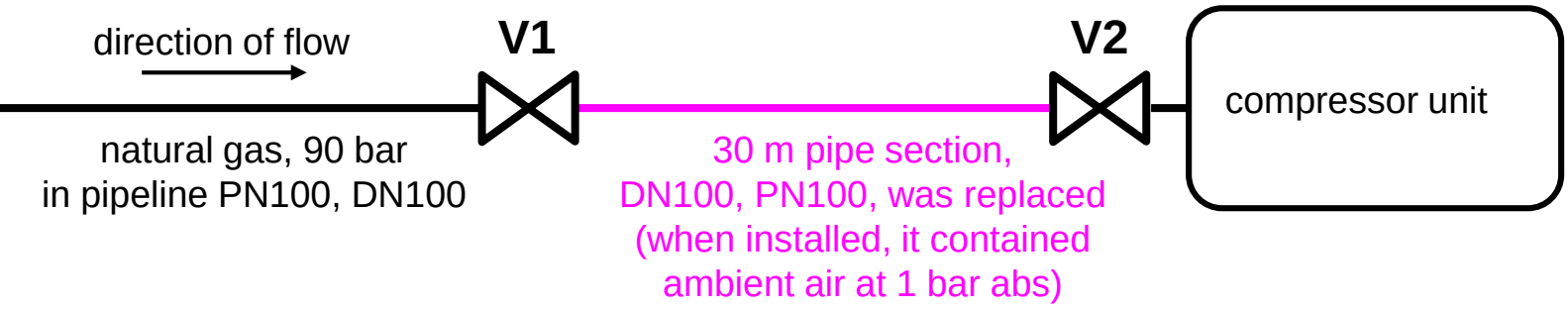
Pipe rupture in a petrochemical plant in Lybia, 2004



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 CH_4 a narrow zone with an explosive CH_4/air mixture is formed. Temperature rises from 50 °C to 895 °C (κ = 1.4) or 764 °C (κ = 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.

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
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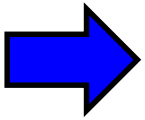
State of adopting the pipe results in regulation, guidelines, standards etc

- **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***

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