Course of explosions in Propene/O_2/N_2 and Methane/O_2/N_2 mixtures in vessels of 20 l to 2500 l and load on the walls

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Outline of talk

- **Introduction**
- **Explosion characteristics**
- **Course of explosion in 20 l sphere**
- **Pressure load P_{det} on the wall of the vessel**
  - quantification of P_{det} for four scenarios occuring in a pipe (no precompression)
  - quantification of P_{det} for four scenarios occuring in a pipe (with precompression)
  - quantification of P_{det} for Propene/O_2/N_2 in vessel at $P_{initial}$ = 5 bar abs, $T_{initial}$ = 20 °C
- **Comparison: detonative regimes**
  in 20 l vessels ↔ 100, 500, 2500 l vessels
- **Predetonation distances of Propene/O_2 in tubes**
- **Did ignition source directly trigger a spherical detonation?**

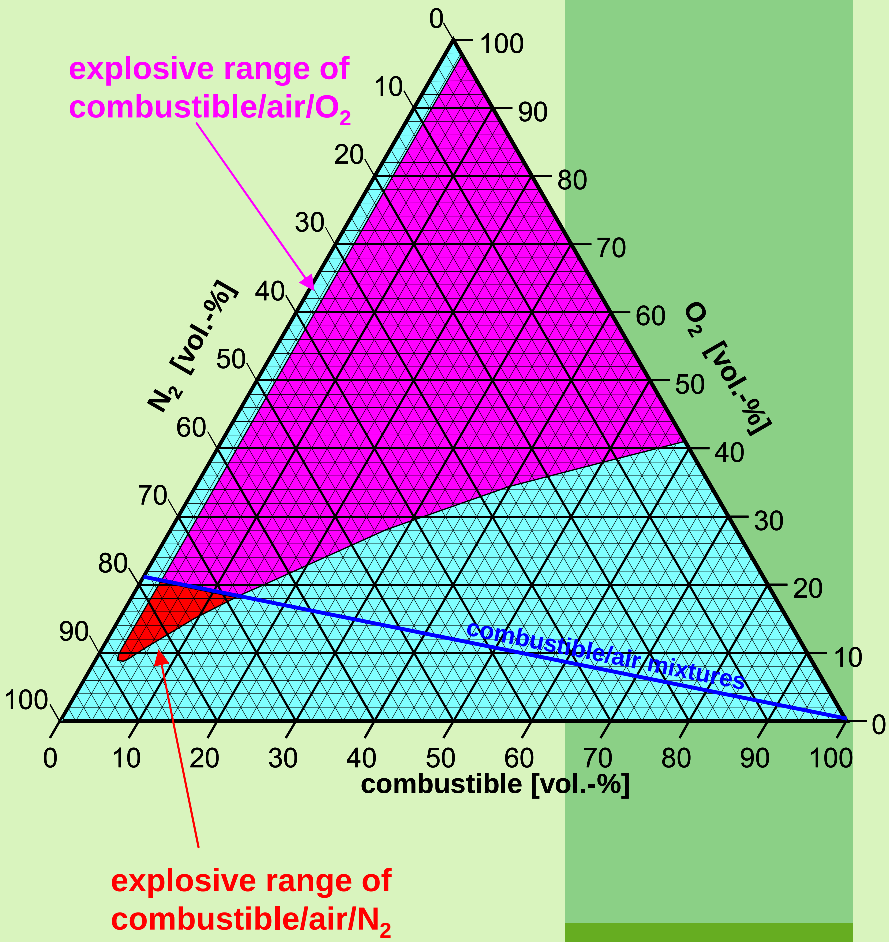
Information available in literature on explosive gas mixtures of type combustible/O_2/N_2

- **Explosion characteristics (explosion limits, p_{ex}, $(dp/dt)_{ex}$)**

		$p_{initial} \leq 1\ bar_a$	$p_{initial} > 1\ bar_a$
combustible / air /N_2	explosion limits	+ +	o
	p_{ex}, $(dp/dt)_{ex}$	+	-
combustible / air /O_2	explosion limits	o	- -
	p_{ex}, $(dp/dt)_{ex}$	- -	- -

- **Course of explosion (deflagrative, detonative, heat explosion)**

		$p_{initial} \leq 1\ bar_a$	$p_{initial} > 1\ bar_a$
combustible / air /N_2	pipe (L/D > 100)	+ +	+
	vessel (L/D ≅ 1)	+	- -
combustible / air /O_2	pipe (L/D > 100)	-	- -
	vessel (L/D ≅ 1)	- -	- -



=> Much work needed to better understand combustible/air/O_2 mixtures

Motivation for this work

Trend in partial oxidation reactions:

- replacing air or diluted air as oxidant by oxygen enriched air or by pure oxygen

Advantages:

- increase of yield in space and time
- lower operating pressures

Critical Issue when dealing with combustible/air/O_2-mixtures: Process Safety

- vessel-like geometry
  - explosion characteristics
  - course of explosion (deflagration, detonation)

Focus of this work

- bubble column geometry (explosive gaseous bubbles dispersed in liquid)
  - mechanisms of flame propagation
  - course of explosion (deflagration, detonation)

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Gaseous mixtures investigated

Propene / O_2 / N_2,

Methane / O_2 / N_2

} very detailed exp. investigations

Hydrogen / O_2

Cyclohexane / NO

Cyclohexane / N_2O

Cyclohexane / NO_2

} only for one value of $P_{initial}$ and $T_{initial}$

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Experimental setup

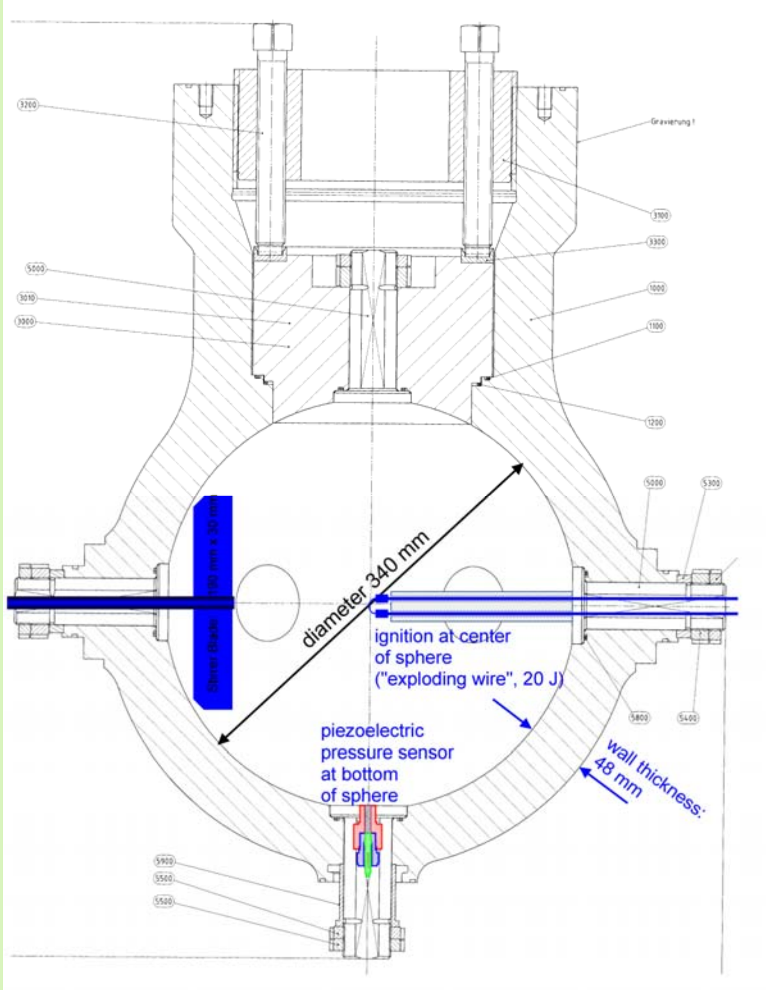
Test vessel:
20 l sphere

Ignition source:
exploding wire according to EN1839,
Bomb method, section 4.2.3.3.3
(arc discharge, ca. 200 A over ca. 3 ms)

Ignition energy:
ca. 20 J

Mixture preparation:
partial pressure method,
ideal gas characteristics assumed

20 l sphere, P_{max}=600 bar, T_{max}=500°C



References for complete documentation of explosion characteristics

H.P. Schildberg in deliverables no. 8 and no. 13 of EU-Research Project SAFEKINEX, Contract No. EVG1-CT-2002-00072; download possible from *www.safekinex.org*

“Explosion characteristics of Propene/O2/N2 at 1, 5, 10 and 30 bar abs, 25 °C and 200 °C”,
Hans-Peter Schildberg in *„Process Safety and Industrial Explosion Protection“*,
editor: ESMG – European Safety Management Group e. V. , Hamm, Germany (2005), ISBN 3-9807567-4-2
(proceedings of the International ESMG Symposium 2005 in Nürnberg, Germany, 32 pages)

“Determination of the Explosion Behaviour of Methane and Propene in Air or Oxygen at Standard and Elevated Conditions”,
A.A. Pekalski, H.-P. Schildberg, P.S.D. Smallegange, S.M. Lemkowitz, J.F. Zevenbergen, M. Braithwaite, H.J. Pasman, 11th International Symposium Loss Prevention and Safety Promotion in the Process Industries (2004), Praha Congress Centre 31st May-3rd June 2004;
Thematic Section B, page 2118-2138 (ISBN 80-02-01574-6)

“Determination of the Explosion Behaviour of Methane and Propene in Air or Oxygen at Standard and Elevated Conditions”,
A.A. Pekalski, H.-P. Schildberg, P.S.D. Smallegange, S.M. Lemkowitz, J.F. Zevenbergen, M. Braithwaite, H.J. Pasman, Process Safety and Environmental Protection, Volume **83,** issue B5, 421-429 (2005)

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Questions to be raised when considering explosions of combustible/air/O_2 mixtures in vessel-like geometry

- What compositions will undergo a transition from Deflagration to Detonation (DDT) after ignition with a thermal ignition source?
- What is the largest conceivable pressure load on the vessel wall?
- How does the volume of the vessel affect the detonative range?
- How about the „obscure“ effects reported mostly only in non-public communication?

  (Vessels believed to be explosion pressure proof did sometimes rupture, but when repeating the experiment at same initial pressure with even the worst case mixture (i.e. what one believed to be worst case), a mechanically identical vessel did withstand the load).
- Will combustible/air mixtures remain deflagrative for higher values of $T_{initial}$ and $P_{initial}$?

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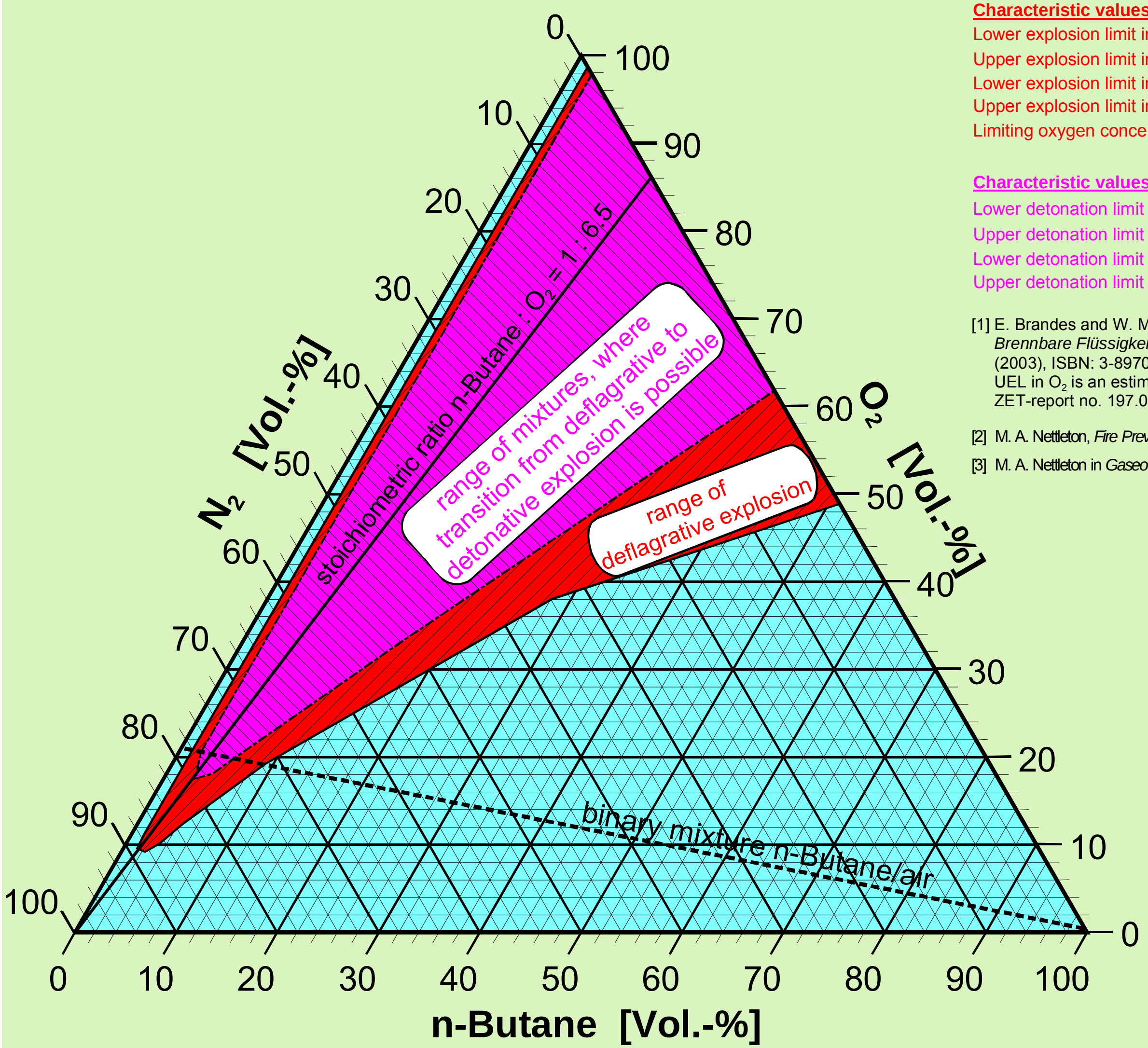
Literature data on deflagrative and potentially detonative explosion regime of n-Butane/O_2/N_2 at 1 bar abs, 20 °C



Characteristic values of the explosive range [1]:

Lower explosion limit in O_2: 1.4 vol.-%
Upper explosion limit in O_2: 51 vol.-%
Lower explosion limit in air: 1.4 vol.-%
Upper explosion limit in air: 9.4 vol.-%
Limiting oxygen concentration: 9.4 vol.-%

Characteristic values of the potentially detonative range [2,3]:

Lower detonation limit in O_2: 2.05 vol.-%
Upper detonation limit in O_2: 38 vol.-%
Lower detonation limit in air: 1.98 vol.-%
Upper detonation limit in air: 6.18 vol.-%

[1] E. Brandes and W. Möller, *Sicherheitstechnische Kenngrößen - Band 1: Brennbare Flüssigkeiten und Gase*, Wirtschaftsverlag NW, Bremerhaven (2003), ISBN: 3-89701-745-8;
UEL in O_2 is an estimate, basis is measured value of 56 Vol-% at 200 °C, ZET-report no. 197.0390.3N

[2] M. A. Nettleton, *Fire Prev. Sci. and Tech.* No **23**, p.29 (1980)

[3] M. A. Nettleton in *Gaseous Detonations*, p. 76, Chapman and Hall Ltd, New York (1987)

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What does „potentially detonative regime“ mean?

- If a mixture lies **outside the potentially detonative regime**, an explosion will under all circumstances (e.g. type of ignition source, geometry) only be deflagrative

- If the mixture lies **inside the potentially detonative regime** and a **detonative ignition source** triggers an explosion, the flame front will propagate as detonation right from the beginning

- If the mixture lies **inside the potentially detonative regime** and a **thermal*** **ignition source** triggers an explosion, the flame front will initially propagate as deflagration and the transition to detonation (DDT) will not necessarily occur!

  There are further conditions that have to be fullfilled to enable the DDT (e. g. geometry of the containment must support flame acceleration).
  However, in practical applications it is mostly hard to assess to which degree these conditions are satisfied.
  There are absolutely no simulation tools (e.g. reactive CFD codes) available which could predict the DDT in vessels at least to some rudimentary extent.

***:** in process plants almost all ignition sources are thermal. The initial stage of the explosion they can trigger is always deflagrative

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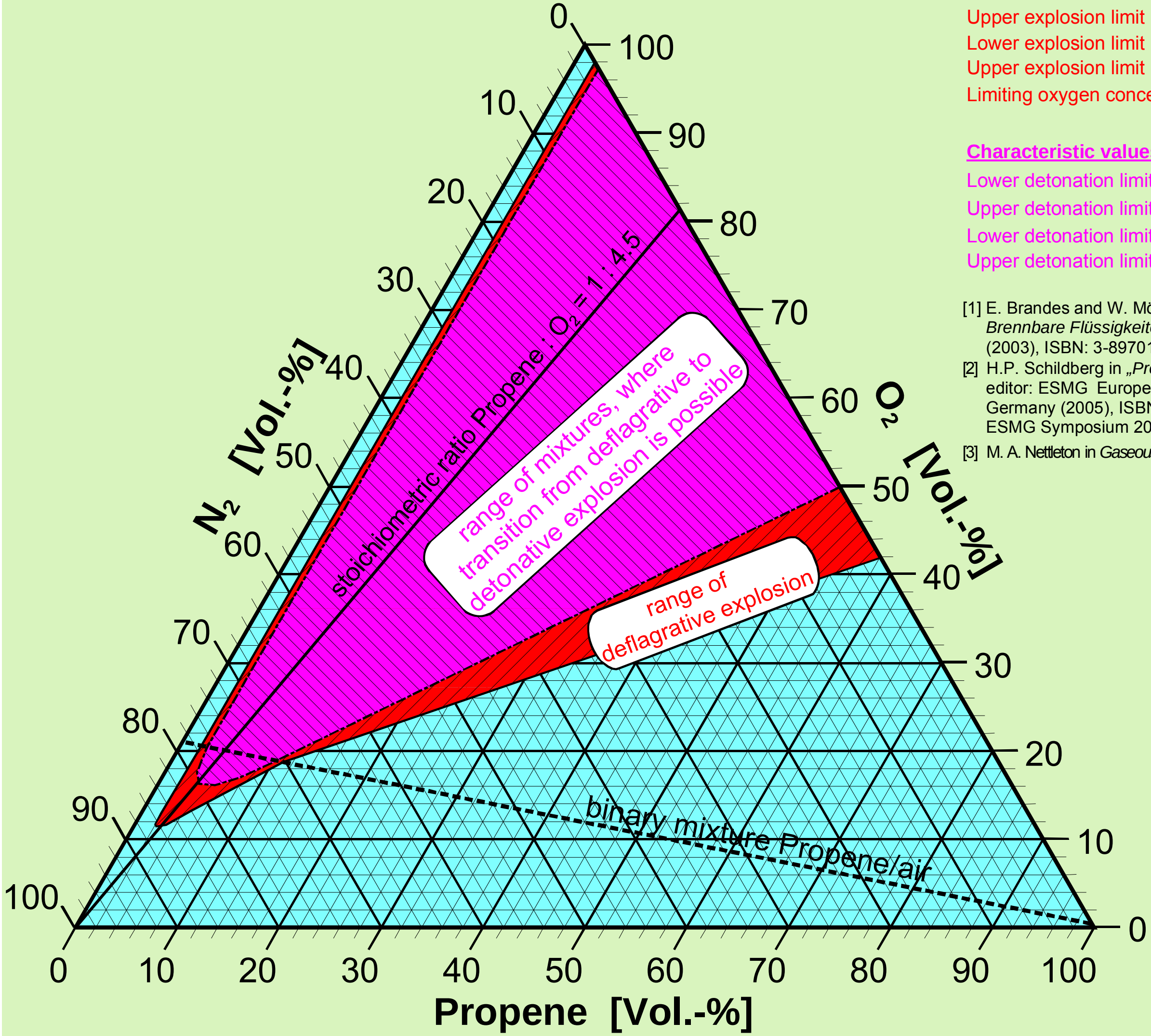
Literature data on deflagrative and potentially detonative explosion regime of Propen/O_2/N_2 at 1 bar abs, 20 °C



Characteristic values of the explosive range [1,2]:

Lower explosion limit in O_2: 2 vol.-%

Upper explosion limit in O_2: 58 vol.-%

Lower explosion limit in air: 2 vol.-%

Upper explosion limit in air: 11 vol.-%

Limiting oxygen concentration: 11.5 vol.-%

Characteristic values of the potentially detonative range [3]:

Lower detonation limit in O_2: 2.50 vol.-%

Upper detonation limit in O_2: 50 vol.-%

Lower detonation limit in air: 3.55 vol.-%

Upper detonation limit in air: 10.4 vol.-%

[1] E. Brandes and W. Möller, *Sicherheitstechnische Kenngrößen - Band 1: Brennbare Flüssigkeiten und Gase*, Wirtschaftsverlag NW, Bremerhaven (2003), ISBN: 3-89701-745-8;

[2] H.P. Schildberg in *„Process Safety and Industrial Explosion Protection“*, editor: ESMG European Safety Management Group e. V. , Hamm, Germany (2005), ISBN 3-9807567-4-2 (proceedings of the International ESMG Symposium 2005 in Nürnberg, Germany, 32 pages)

[3] M. A. Nettleton in *Gaseous Detonations*, p. 76, Chapman and Hall Ltd, New York (1987)

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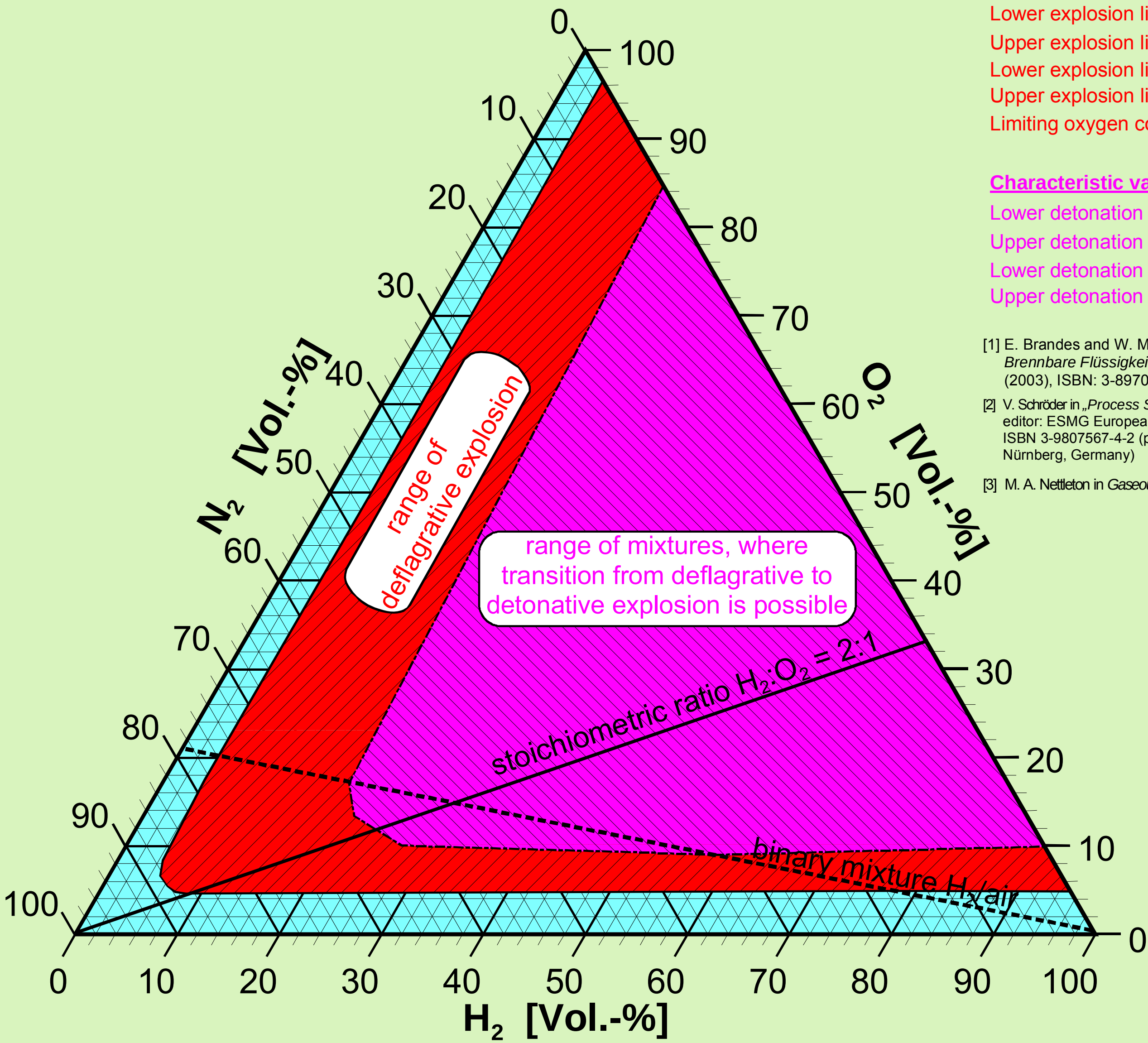
Literature data on deflagrative and potentially detonative explosion regime of $H_2/O_2/N_2$ at 1 bar abs, 20 °C



Characteristic values of the explosive range [1,2]:

Lower explosion limit in O_2: 4 vol.-%
Upper explosion limit in O_2: 95.2 vol.-%
Lower explosion limit in air: 4 vol.-%
Upper explosion limit in air: 77 vol.-%
Limiting oxygen concentration: 4.3 vol.-%

Characteristic values of the potentially detonative range [3]:

Lower detonation limit in O_2: 15 vol.-%
Upper detonation limit in O_2: 90 vol.-%
Lower detonation limit in air: 18.3 vol.-%
Upper detonation limit in air: 58.9 vol.-%

[1] E. Brandes and W. Möller, *Sicherheitstechnische Kenngrößen - Band 1: Brennbare Flüssigkeiten und Gase*, Wirtschaftsverlag NW, Bremerhaven (2003), ISBN: 3-89701-745-8

[2] V. Schröder in „*Process Safety and Industrial Explosion Protection*“, editor: ESMG European Safety Management Group e. V. , Hamm, Germany (2005), ISBN 3-9807567-4-2 (proceedings of the International ESMG Symposium 2005 in Nürnberg, Germany)

[3] M. A. Nettleton in *Gaseous Detonations*, p. 76, Chapman and Hall Ltd, New York (1987)

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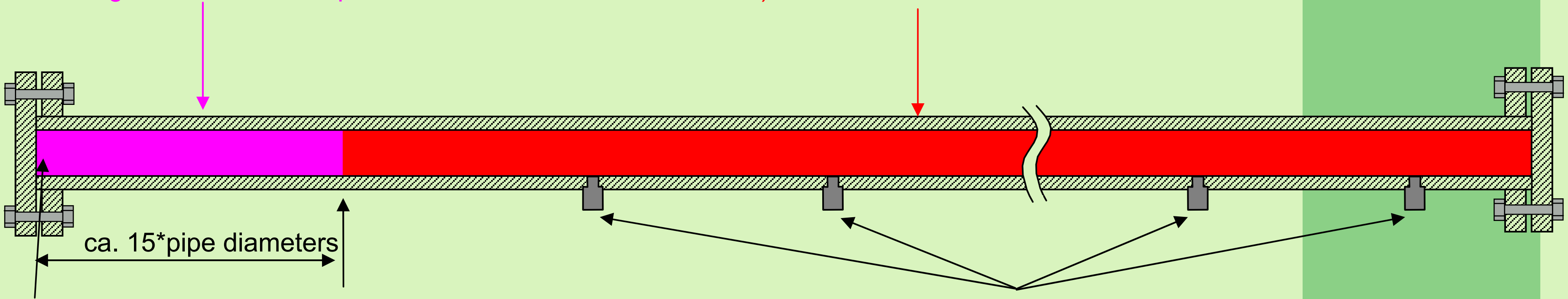
Experimental setup to determine the potentially detonative range of explosive gas mixtures

„Booster-mixture“, Acetylene/O_2, stoichiometric with respect to formation of CO and H_2O. It transits to detonation after a few millimeters and acts upon the mixture to be tested with a stronger detonation front than the one that occurs in the mixture when it undergoes a detontive explosion

mixture to be tested for potential detonability (i.e. ability to propagate a detonation which was once initiated either by an external source or by an initially deflagrative explosion in the mixture to be tested, which succeeded in running up to a detonation)



location of thermal ignition source for booster mixture

thin membrane or nothing (after injecting the mixture to be tested the booster mixture is injected close to the ignition source and propagates almost as plug flow into the pipe)

Signals of pressure and/or flame sensors give evidence whether a stable detonation could be triggered in the mixture

Note:

Pipe must be long enough for to allow that the initial state of the overdriven detonation can pass over to a stable final state, which can be either a stable detonation or a deflagration in the mixture to be tested.

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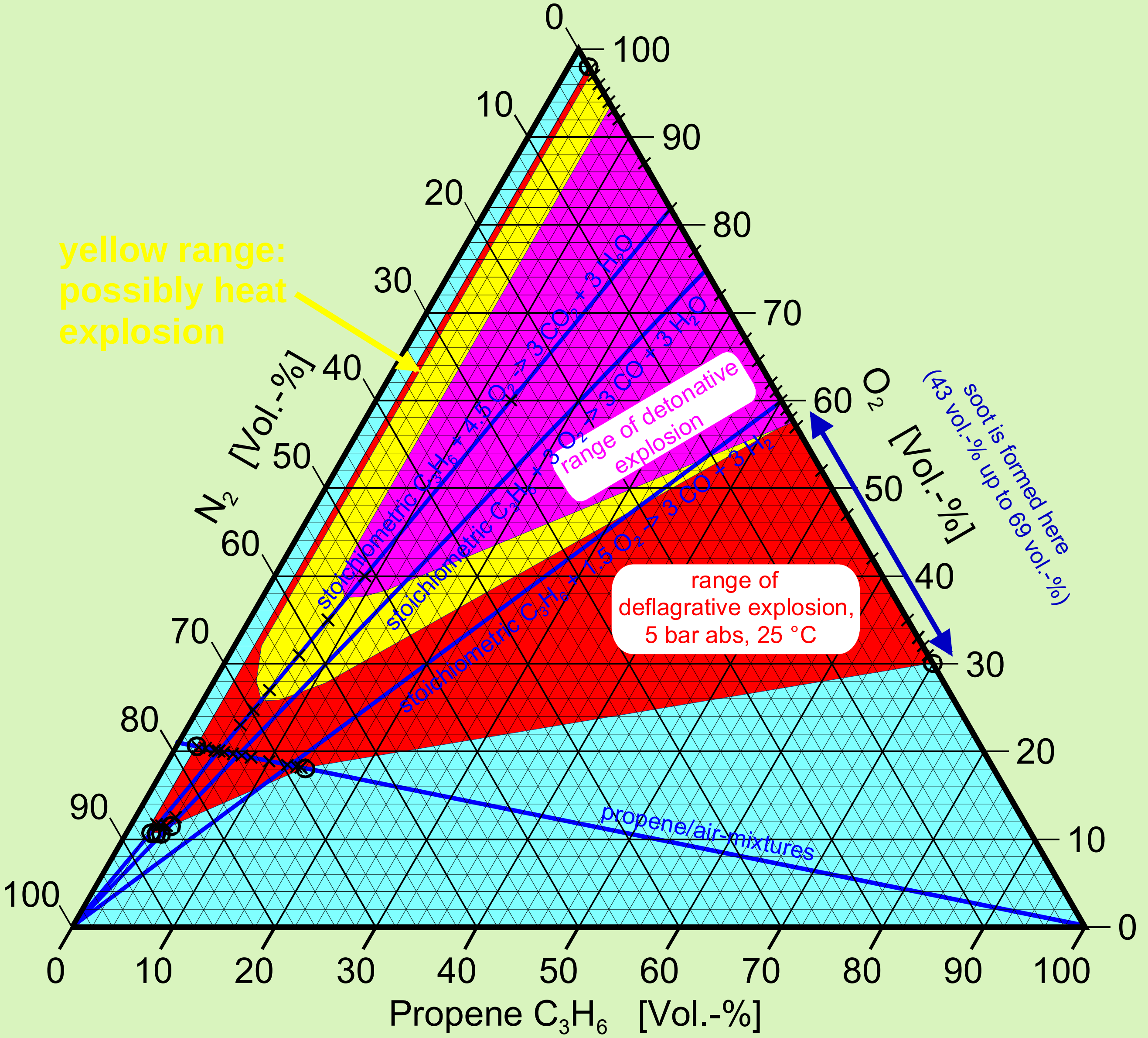
Different explosion regimes (deflagration, heat explosion, detonation) found for Propene/O_2/N_2 in a 20 l sphere at 5 bar abs, 25 °C



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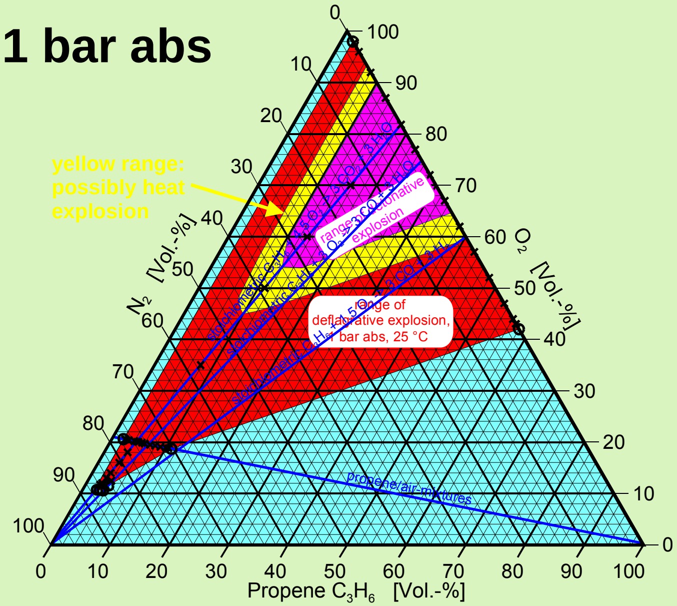
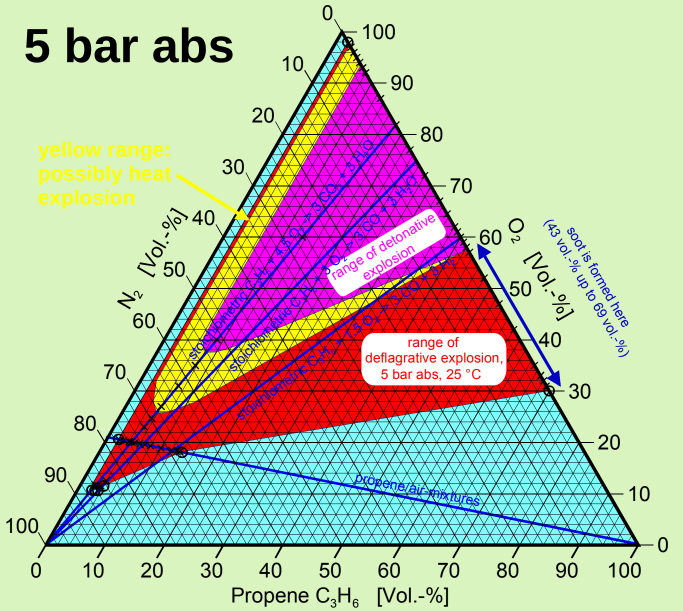
Different explosion regimes (deflagration, heat explosion, detonation) of Propene/O_2/N_2 in a 20 l sphere at $P_{initial}$ = 1, 5 and 10 bar abs, 25 °C

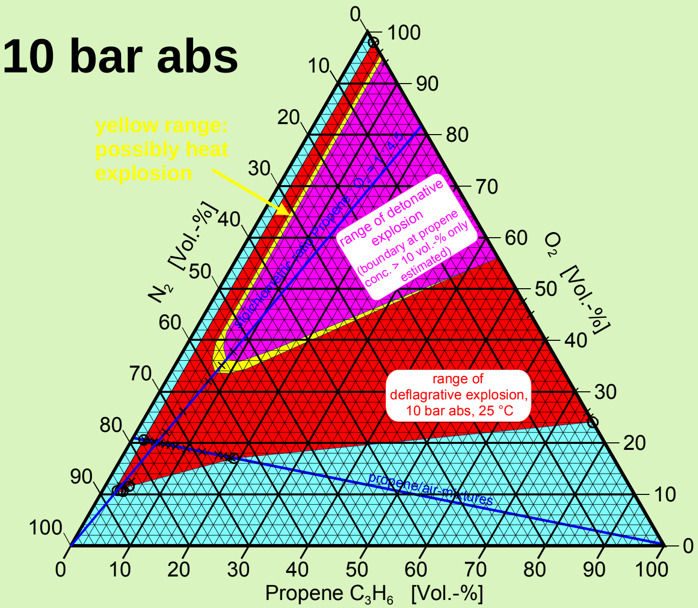
1 bar abs



5 bar abs



10 bar abs



30 bar abs

(Heat explosion range and detonative range were not determined. It might be that the detonative range even extends down to the air line)

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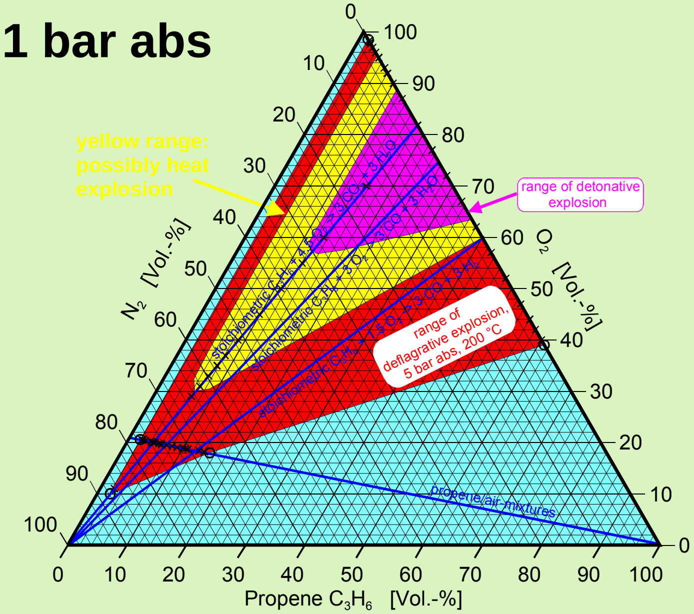
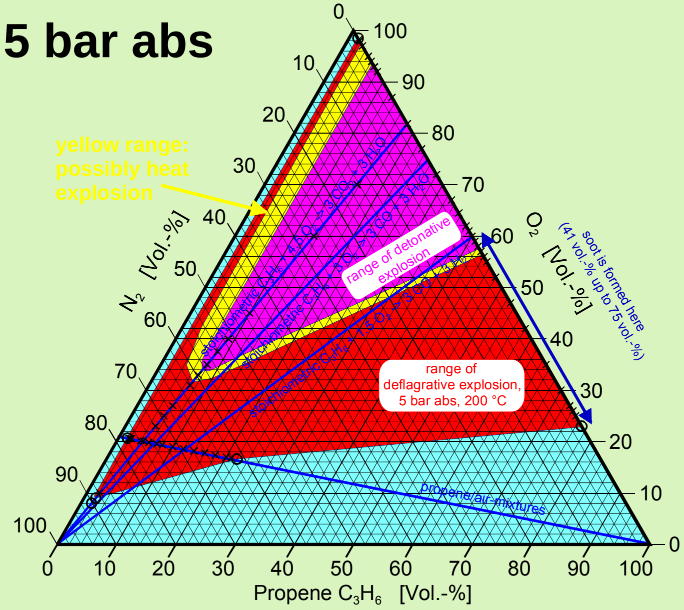
Different explosion regimes (deflagration, heat explosion, detonation) of Propene/O_2/N_2 in a 20 l sphere at 1, 5 and 10 bar abs, 200 °C

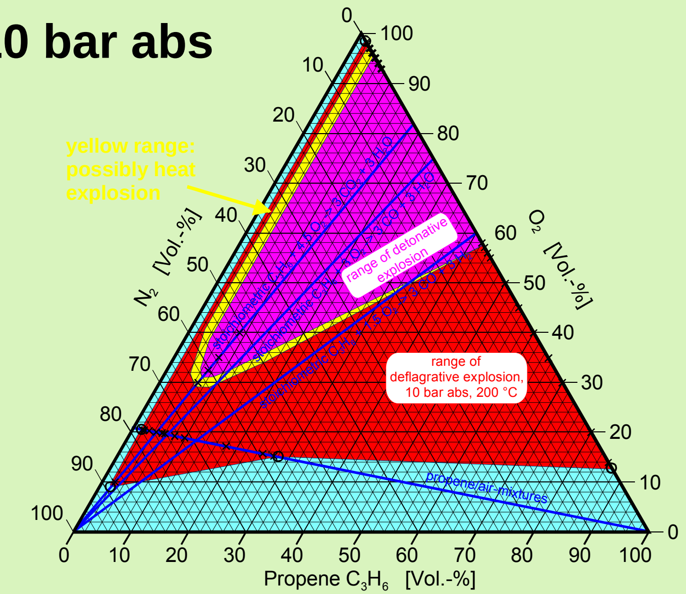
1 bar abs



5 bar abs



10 bar abs



30 bar abs

(Heat explosion range and detonative range were not determined. It might be that the detonative range even extends down to the air line)

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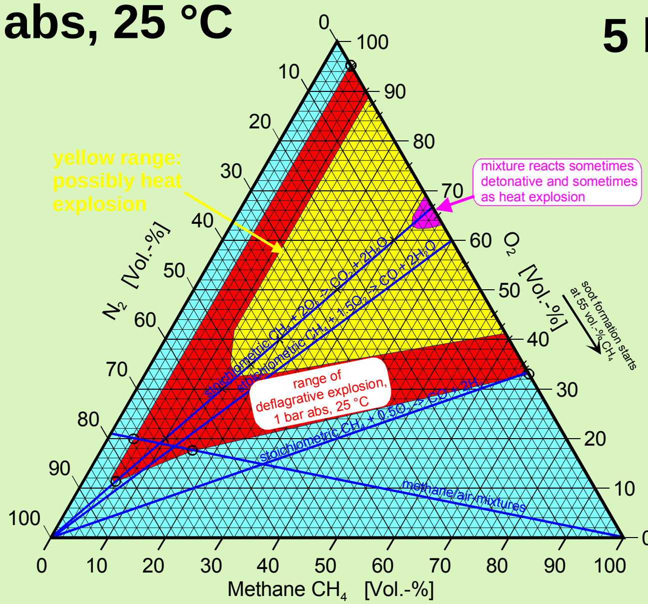
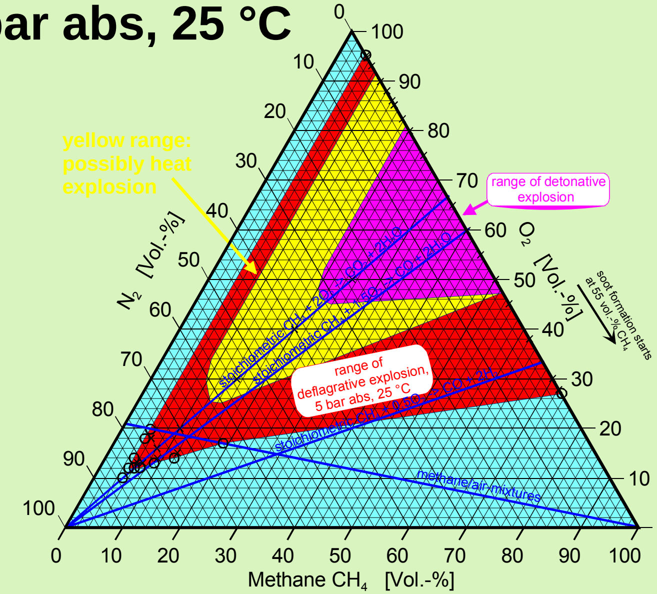
Different explosion regimes (deflagration, heat explosion, detonation) of Methane/O_2/N_2 in a 20 l sphere at 1 and 5 bar abs, 25 °C and 200 °C

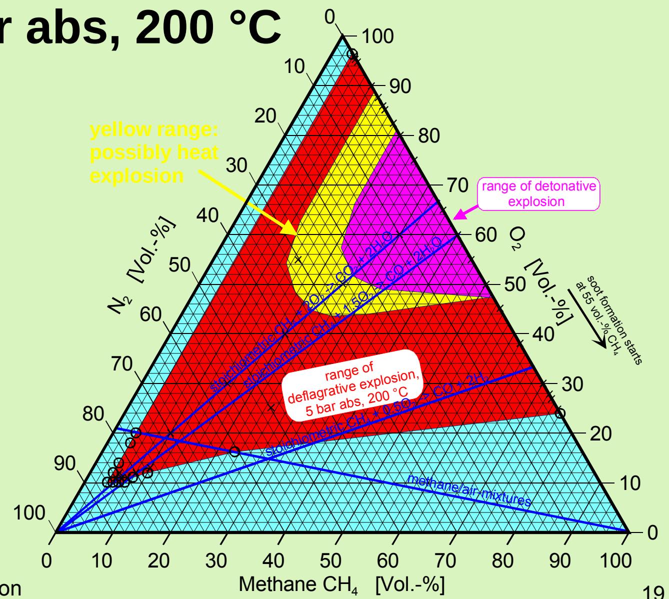
1 bar abs, 25 °C



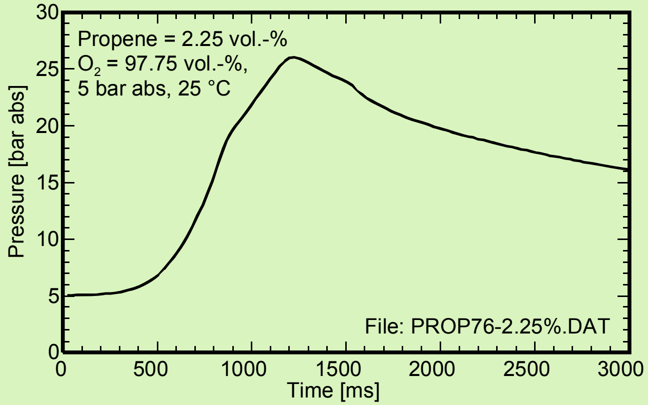
5 bar abs, 25 °C

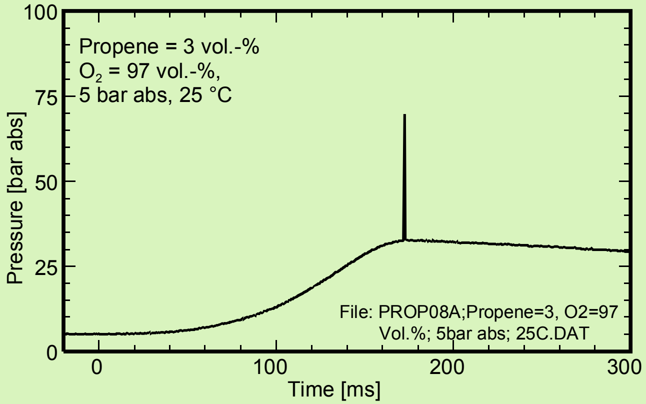


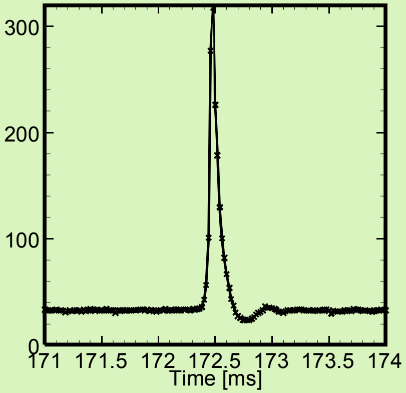
5 bar abs, 200 °C

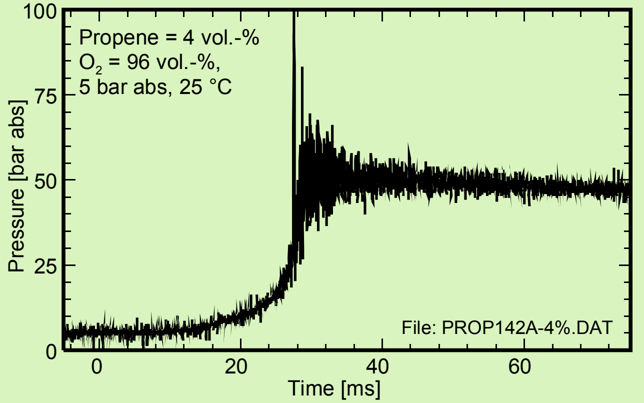


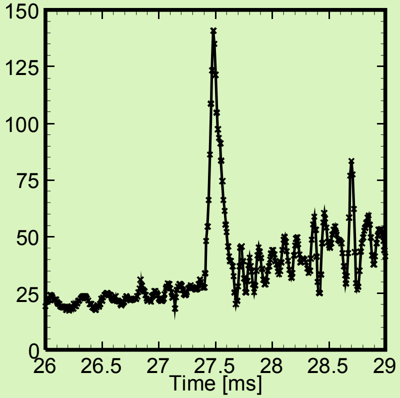
Pressure-time traces of Propene/O_2 at 5 bar, 25 °C (1)

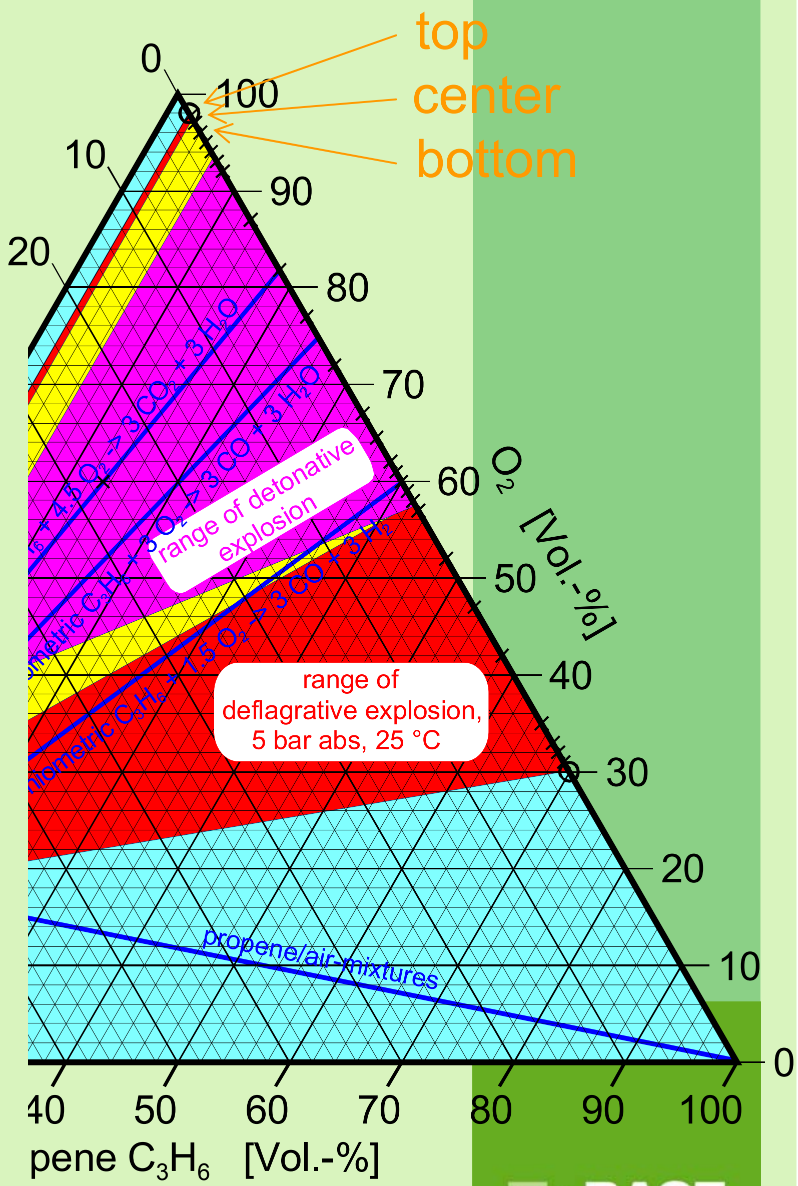












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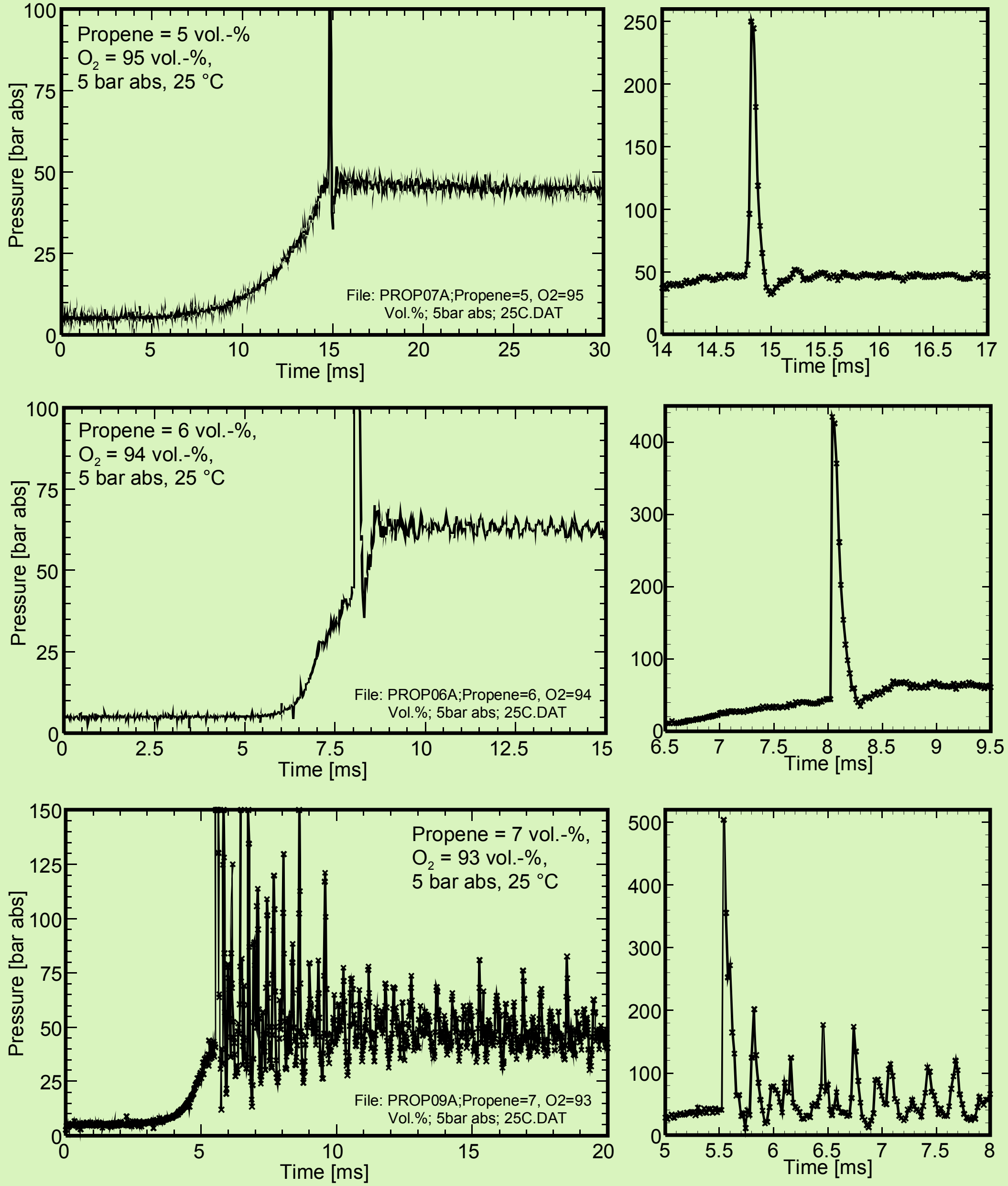
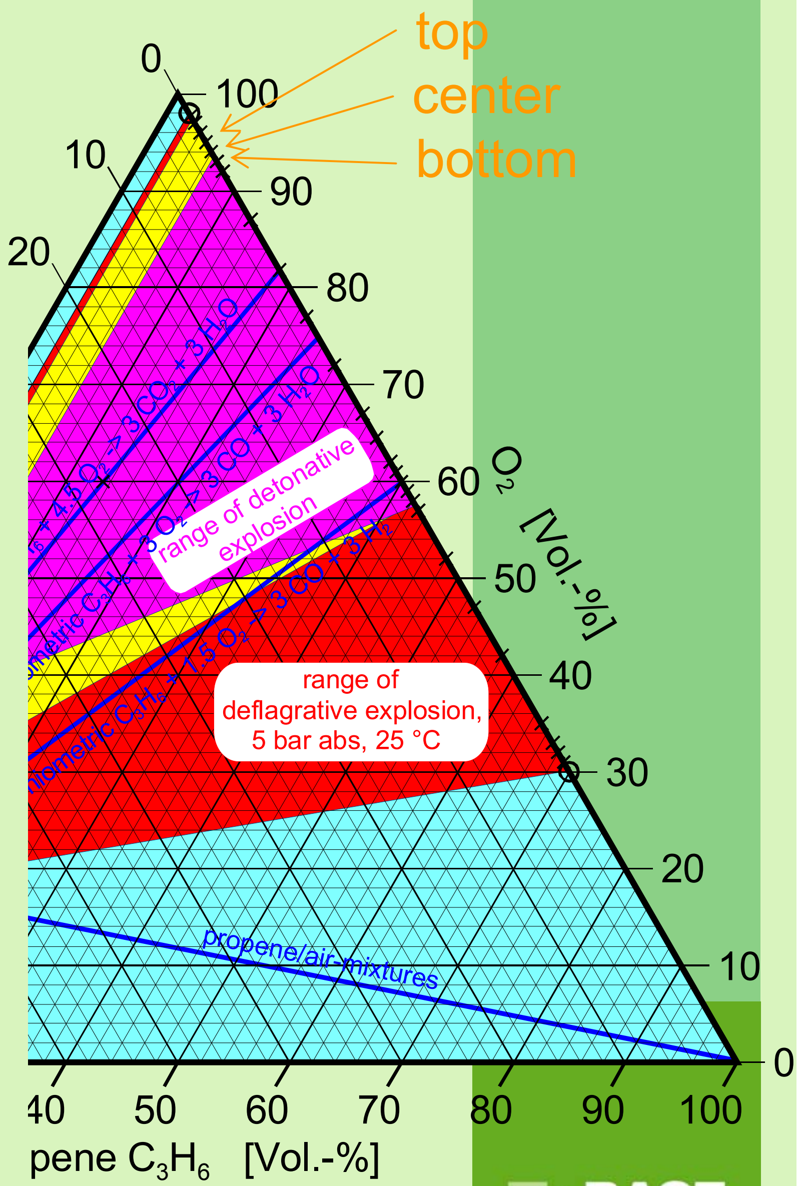
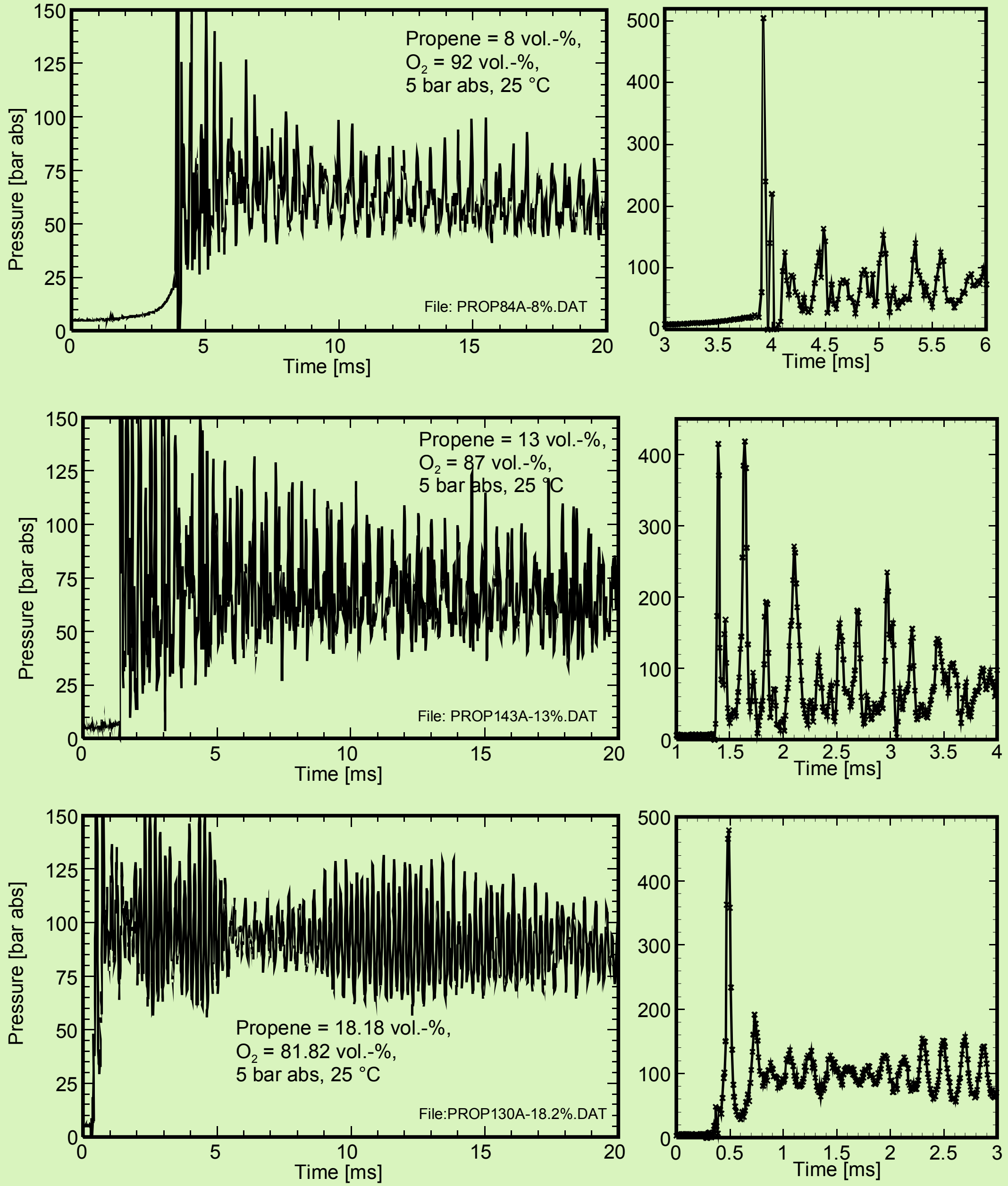
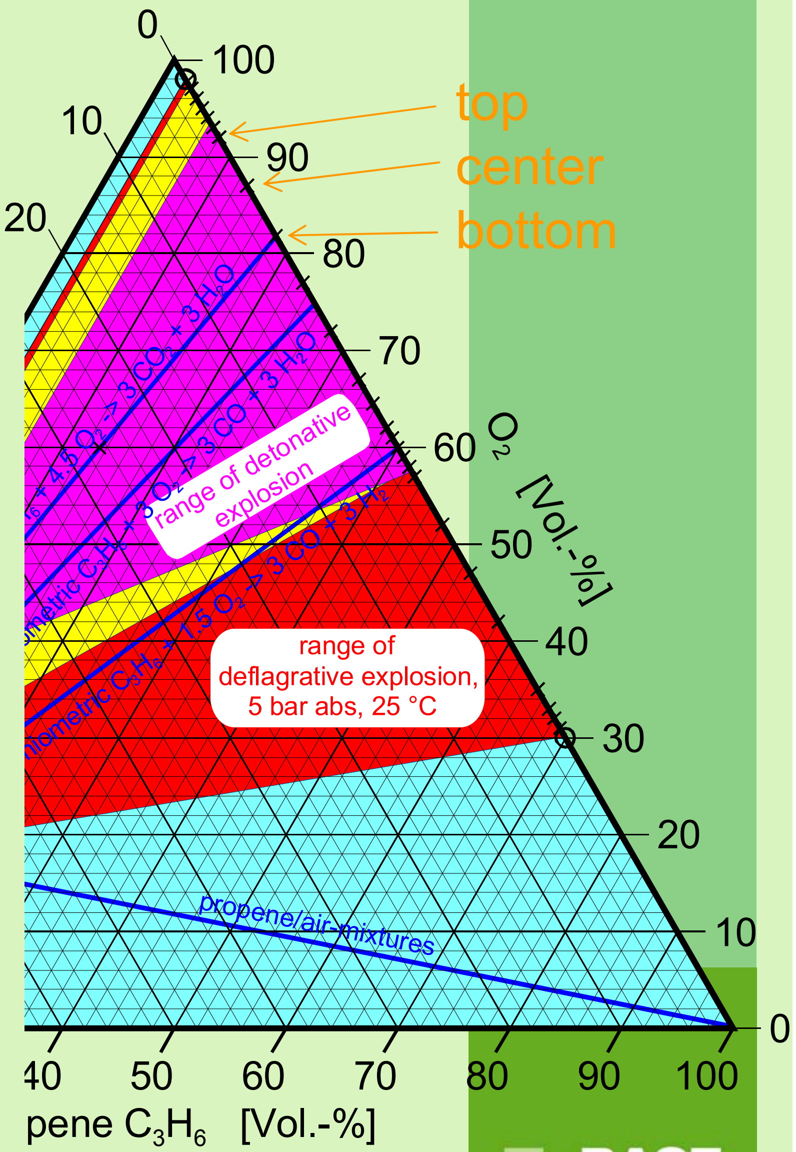
Pressure-time traces of Propene/O_2 at 5 bar, 25 °C (2)





Pressure-time traces of Propene/O_2 at 5 bar, 25 °C (3)





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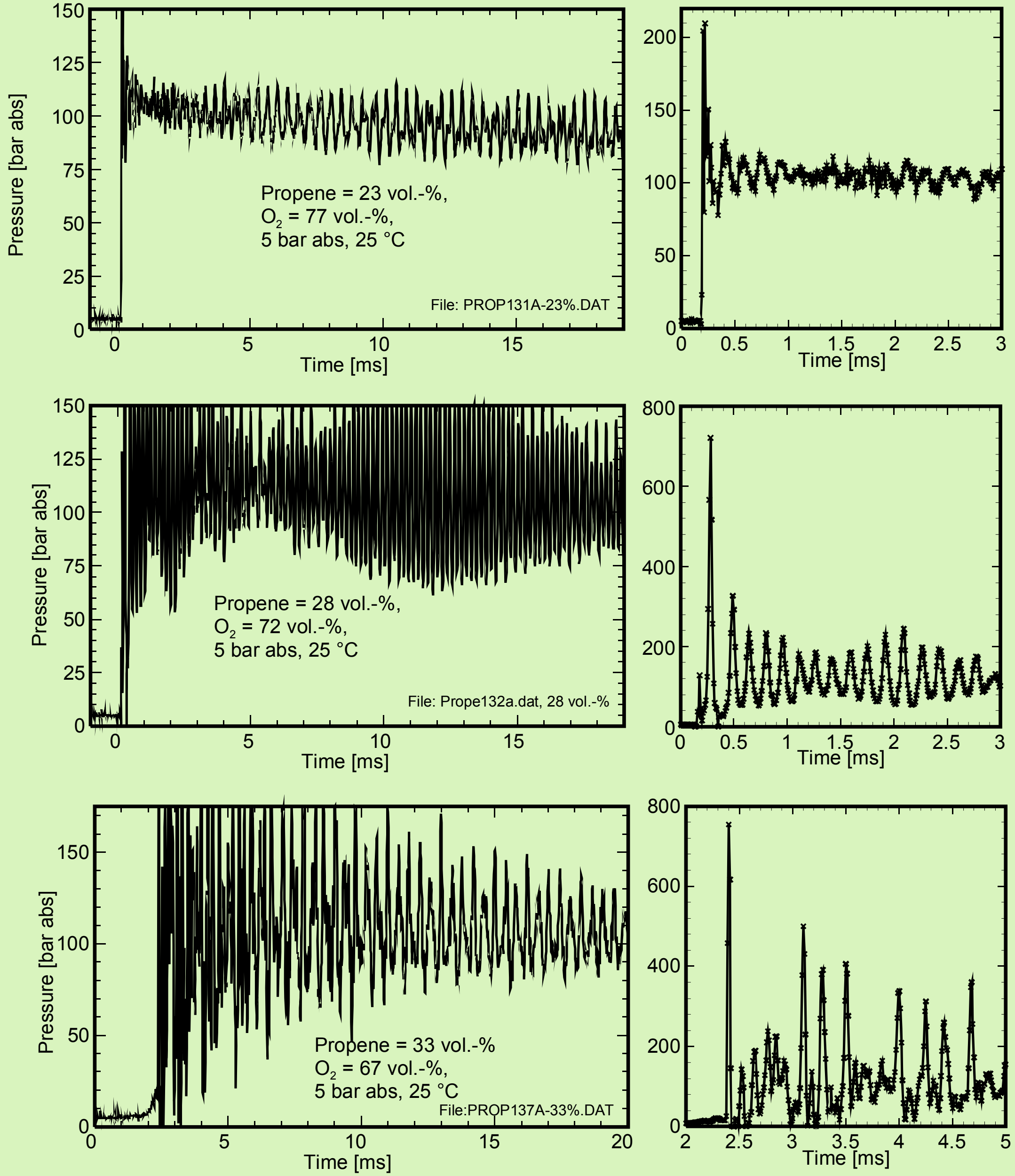
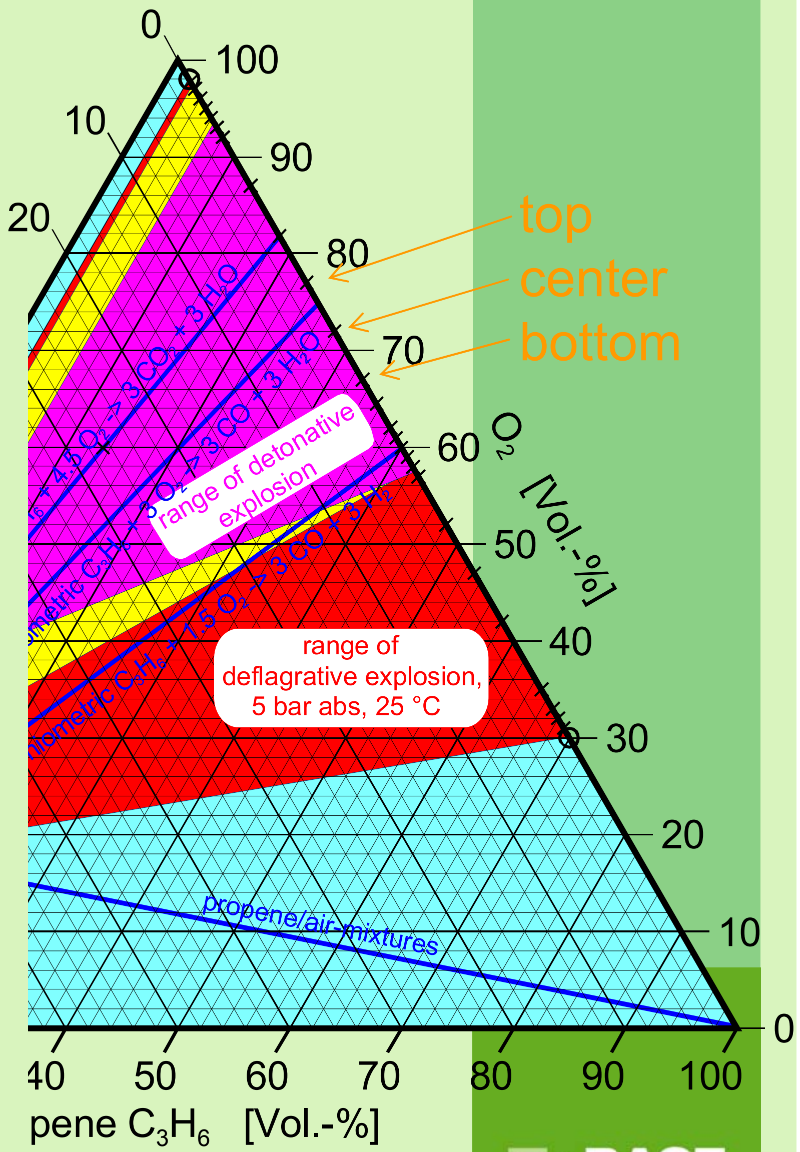
Pressure-time traces of Propene/O_2 at 5 bar, 25 °C (4)





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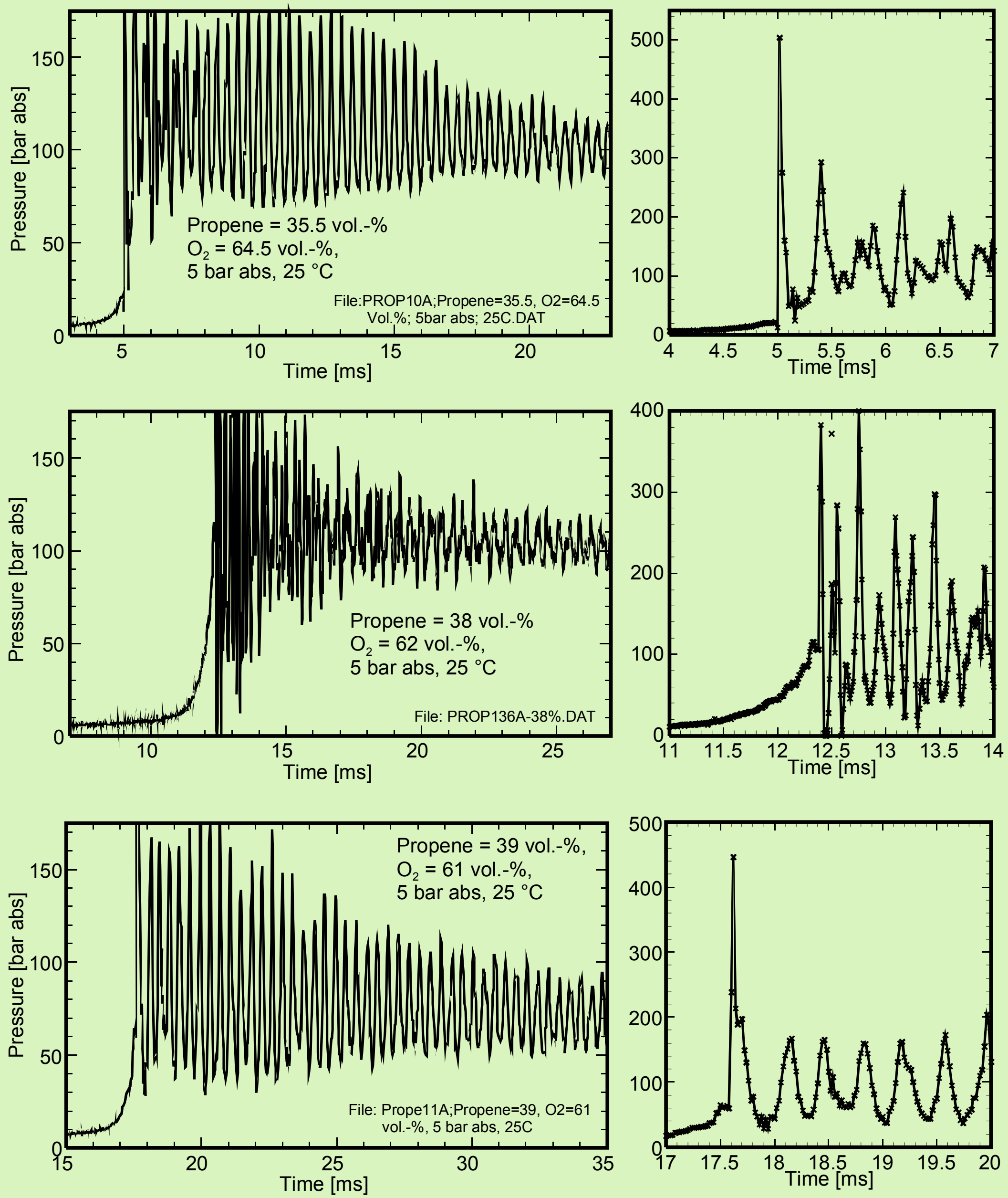
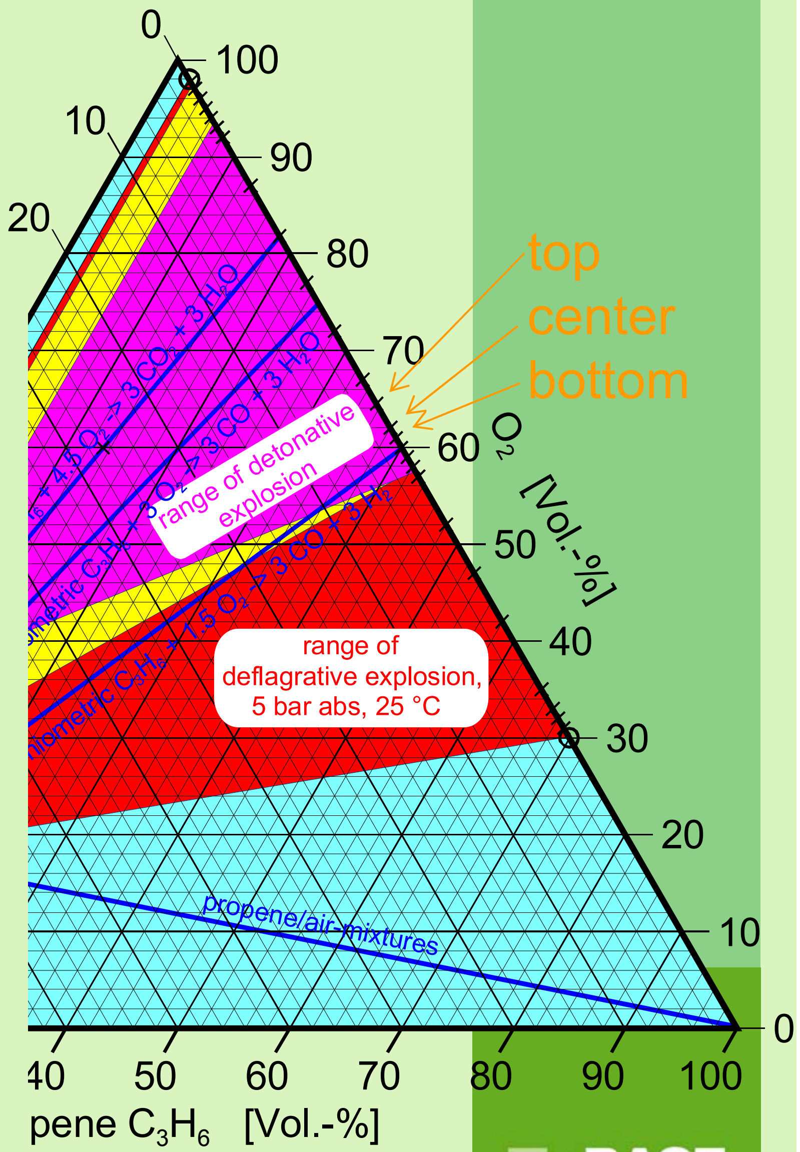
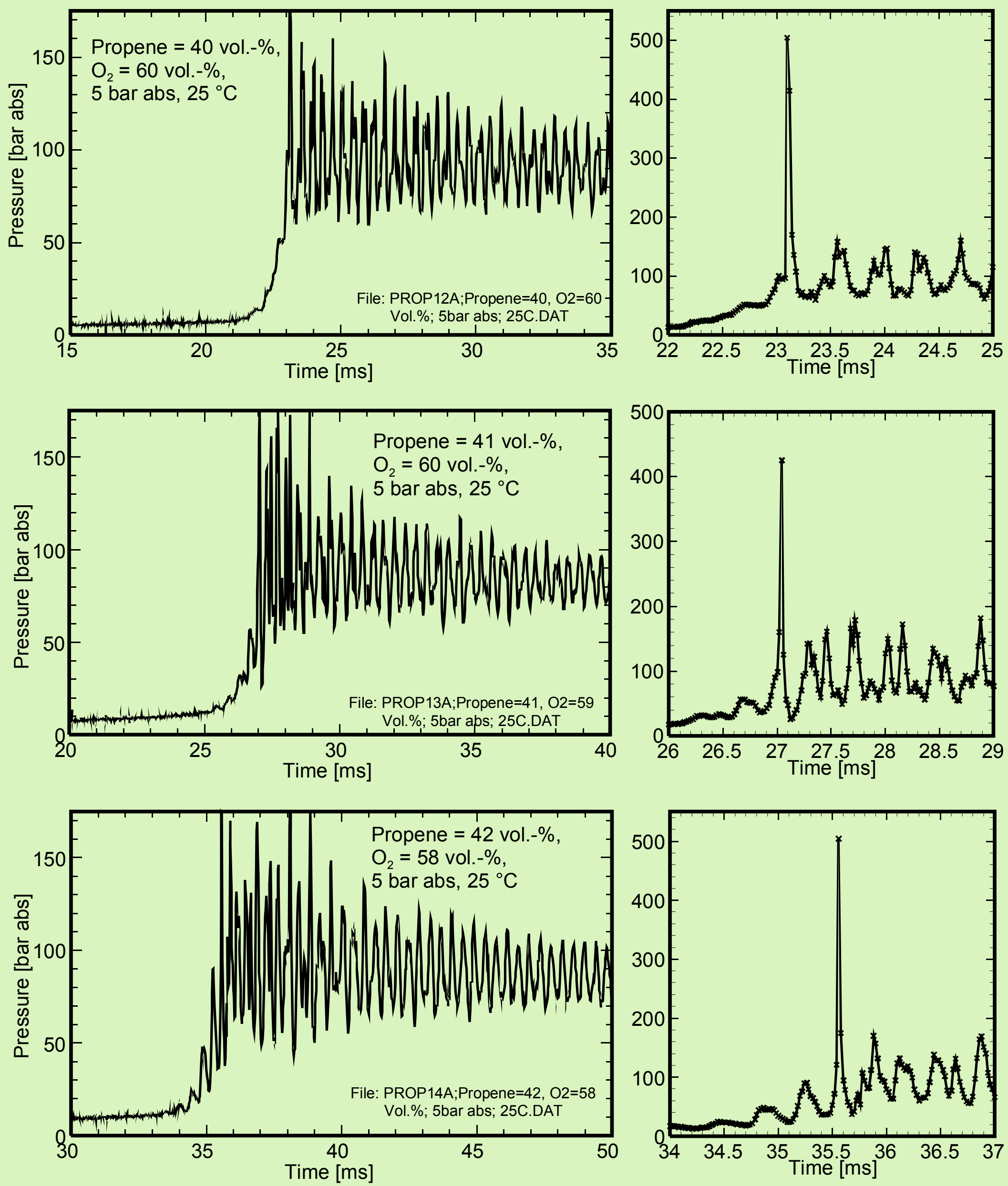
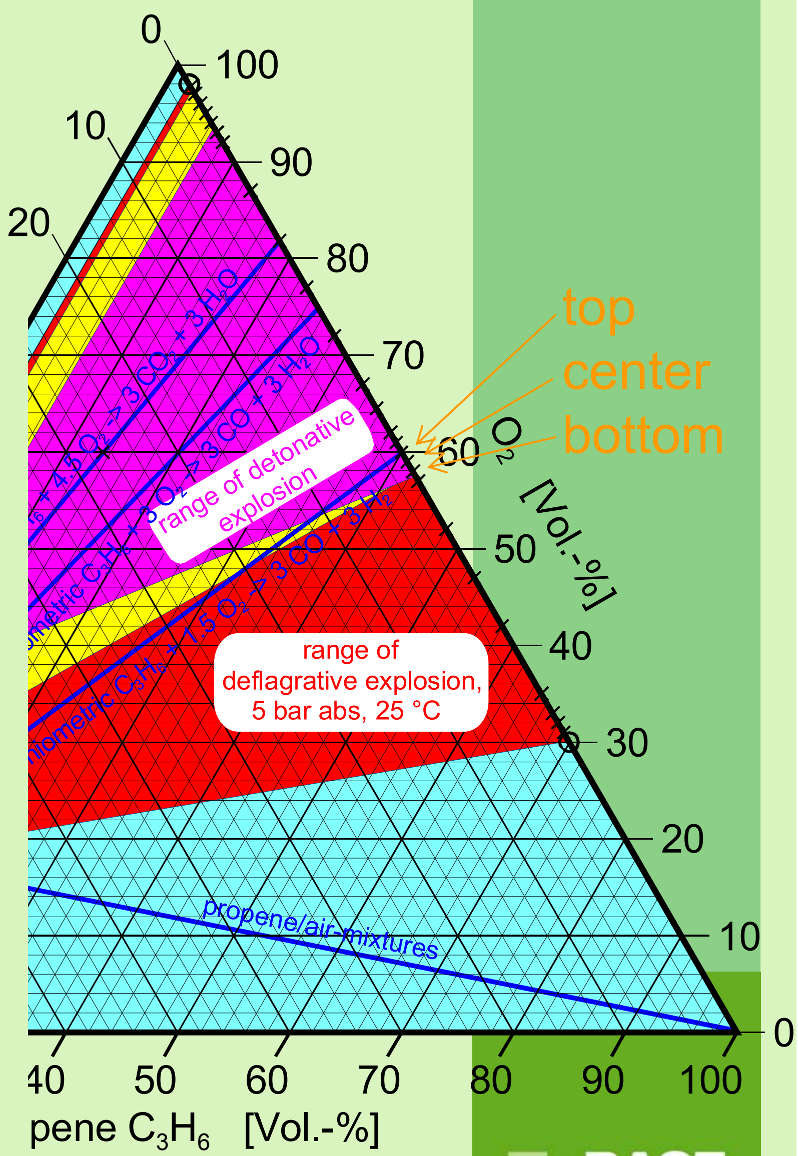
Pressure-time traces of Propene/O_2 at 5 bar, 25 °C (5)





Pressure-time traces of Propene/O_2 at 5 bar, 25 °C (6)





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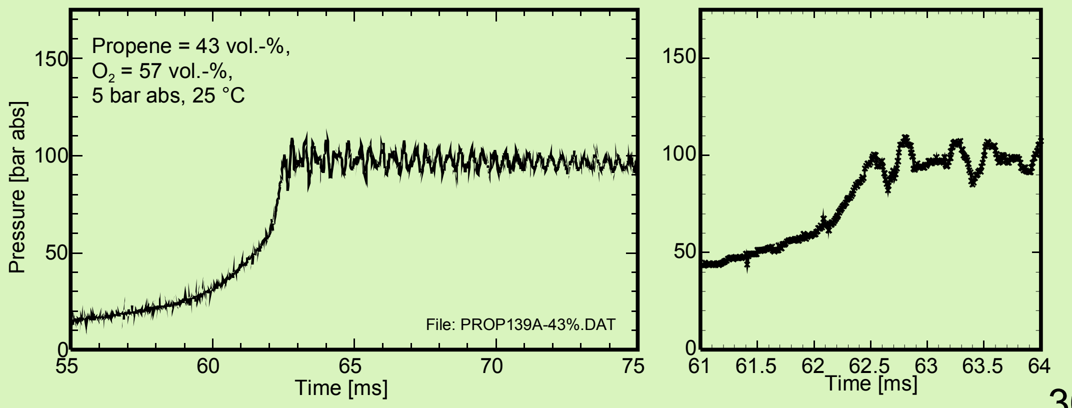
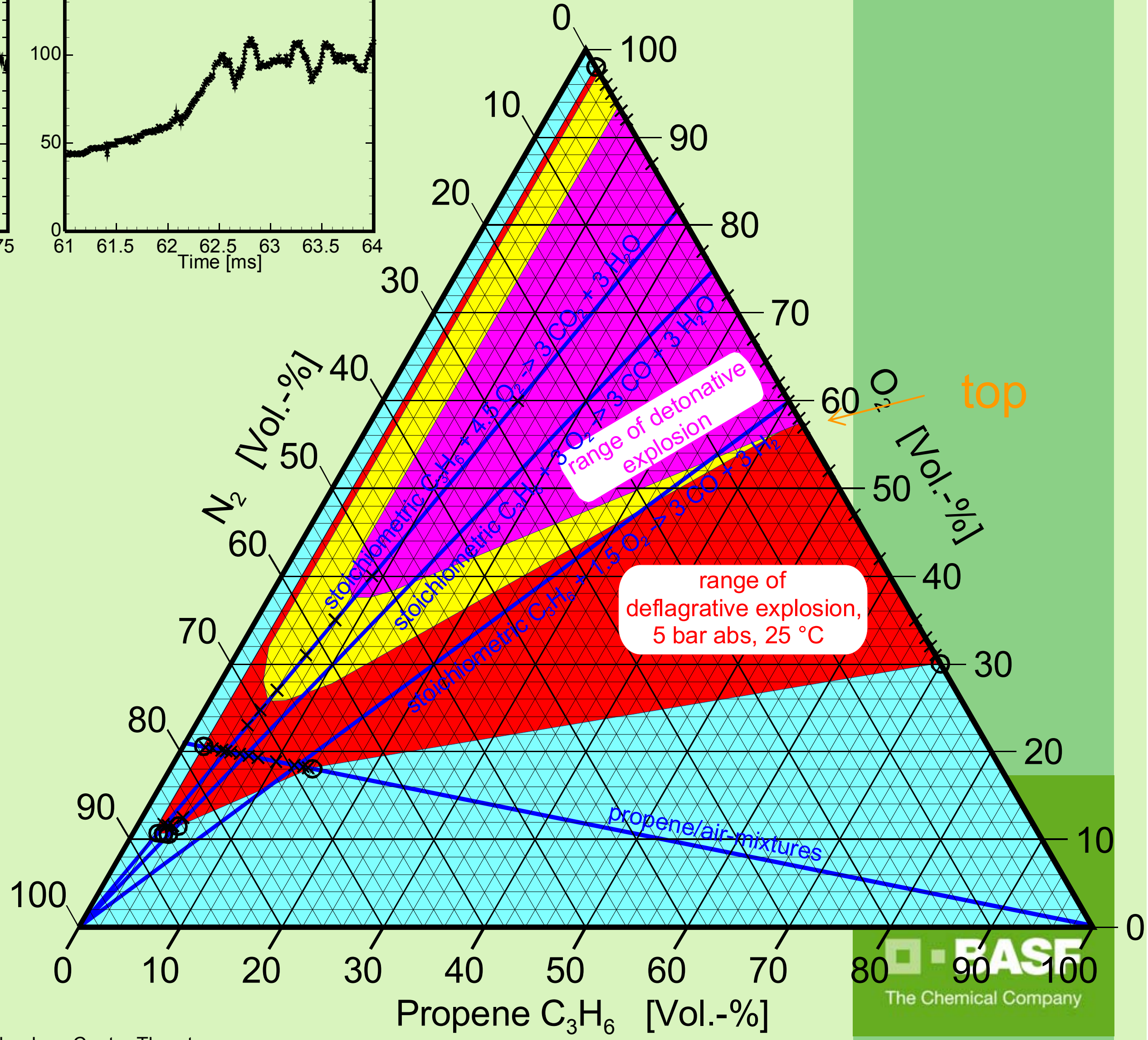
Pressure-time traces of Propene/O_2 at 5 bar, 25 °C (7)





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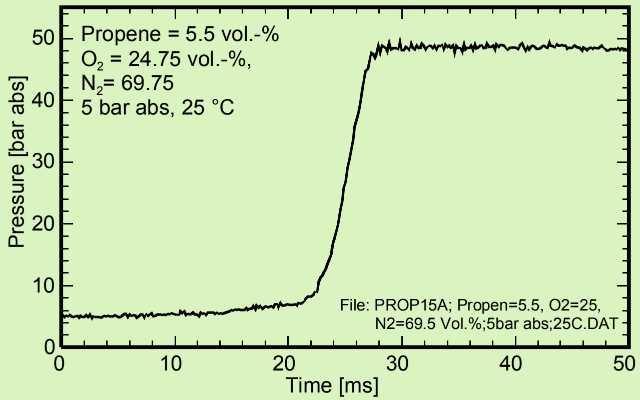
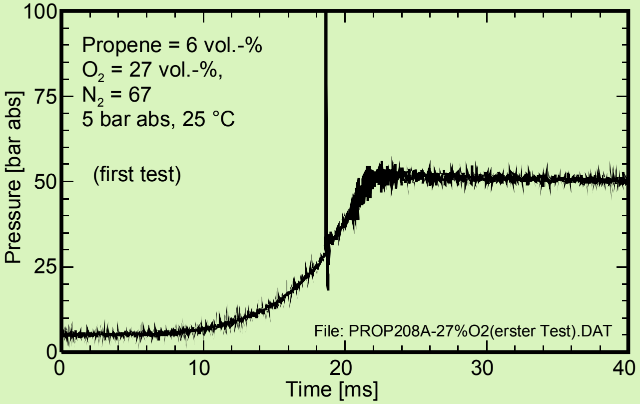
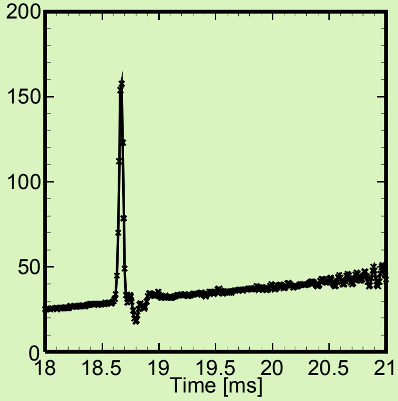
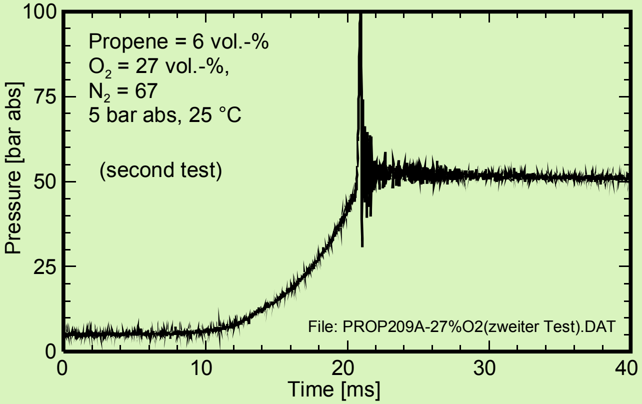
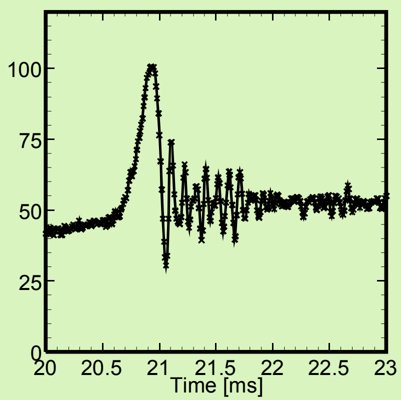
Pressure-time traces of stoich. Propene/O_2/N_2 at 5 bar, 25 °C (1)

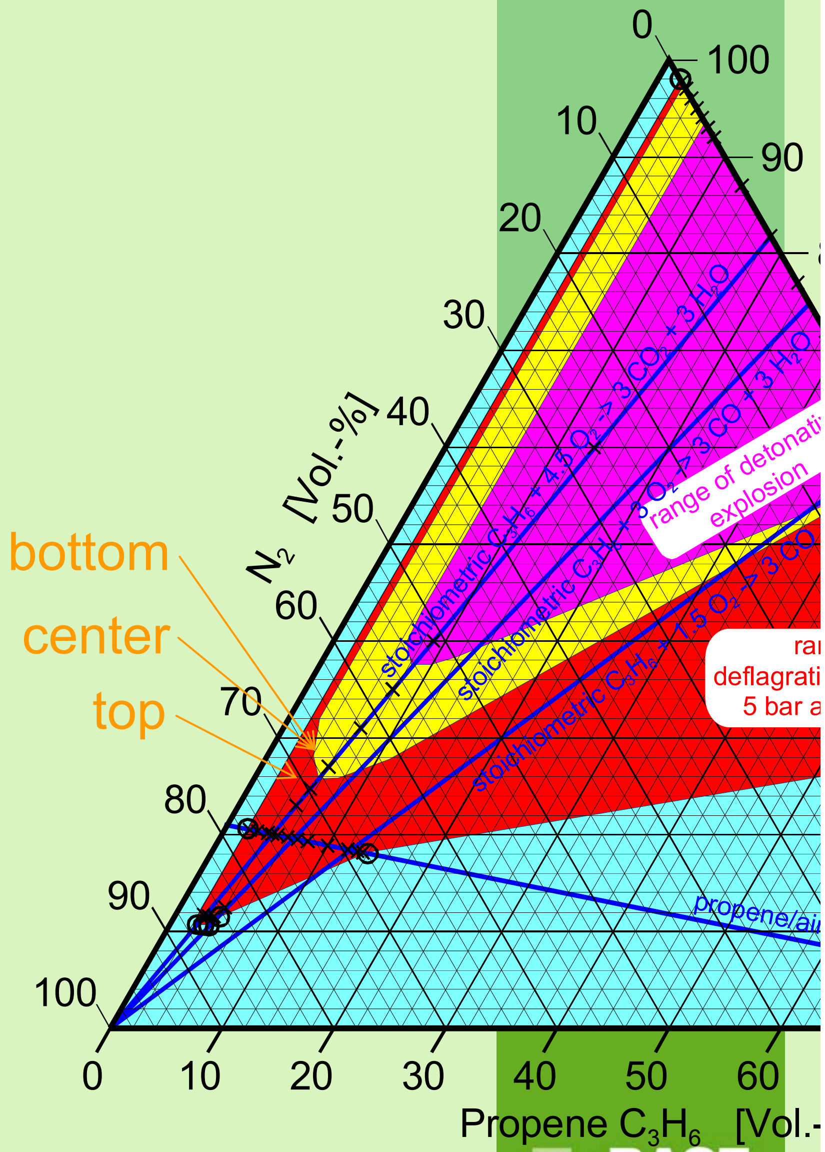




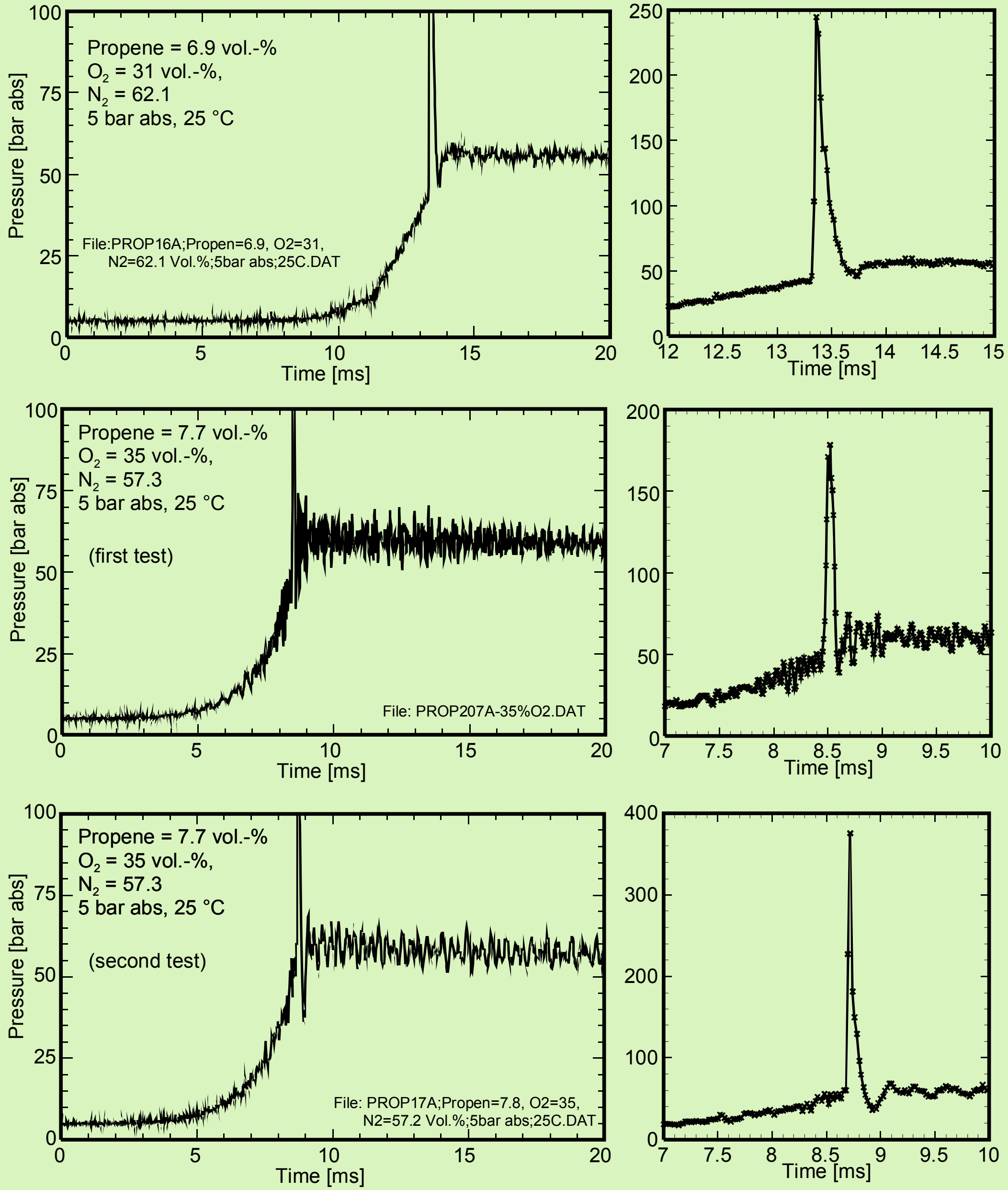


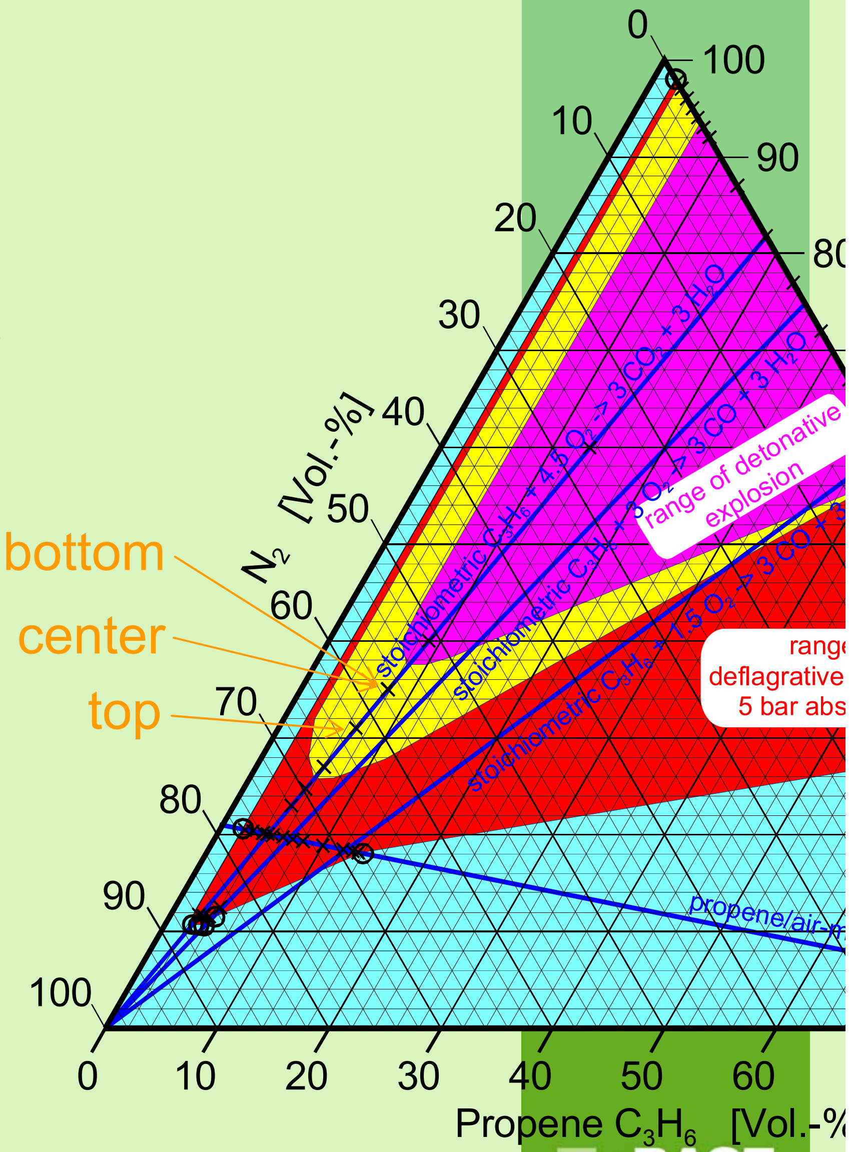






Pressure-time traces of stoich. Propene/O_2/N_2 at 5 bar, 25 °C (2)





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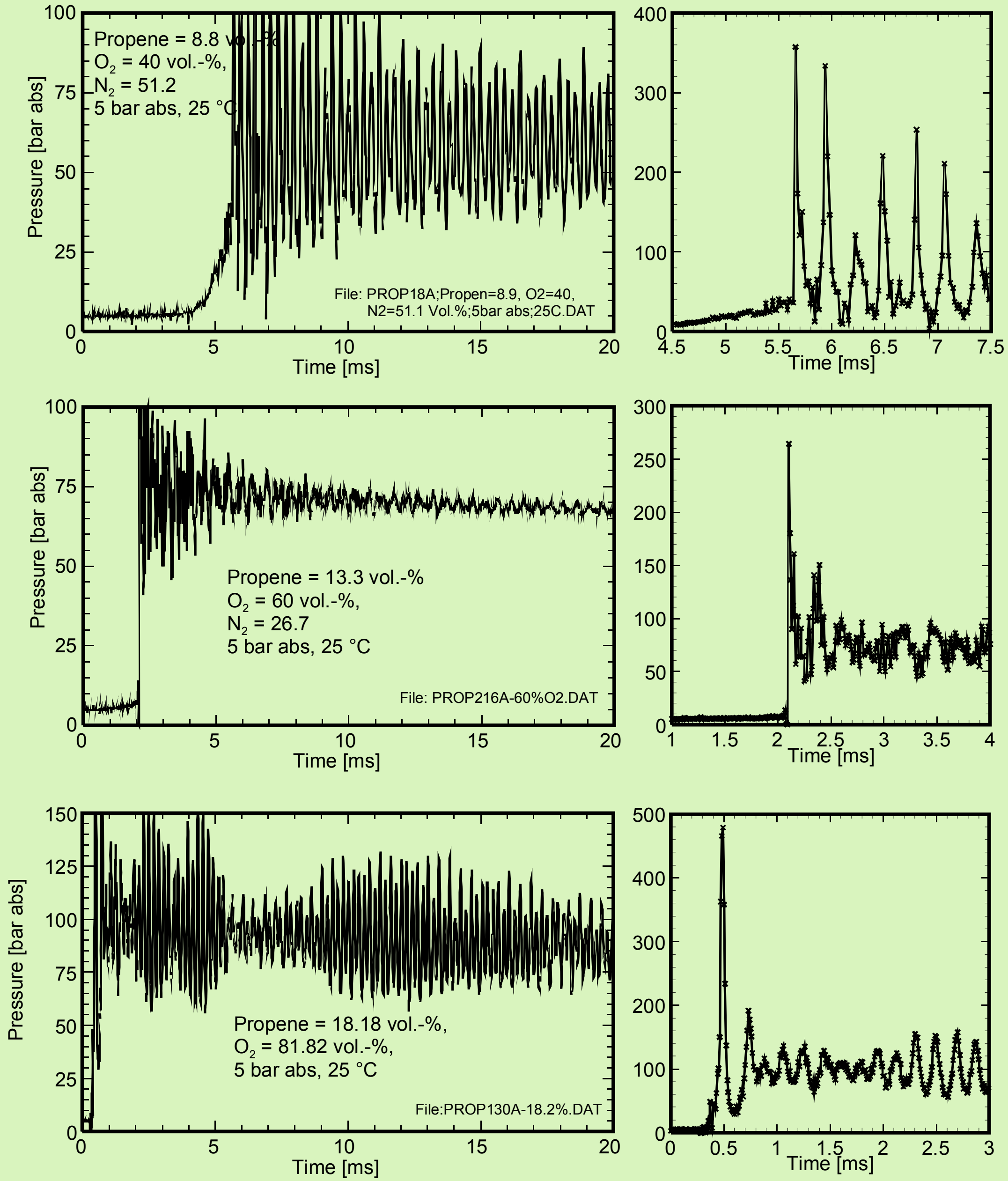
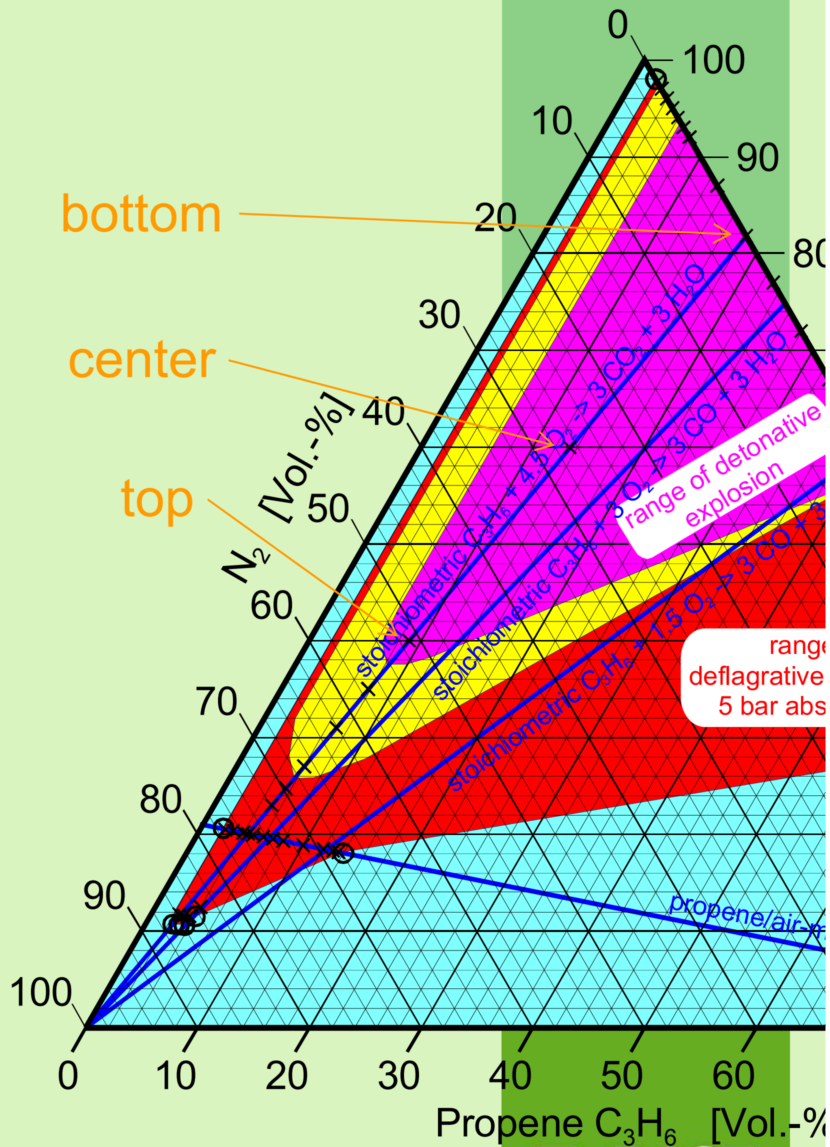
Pressure-time traces of stoich. Propene/O_2/N_2 at 5 bar, 25 °C (3)





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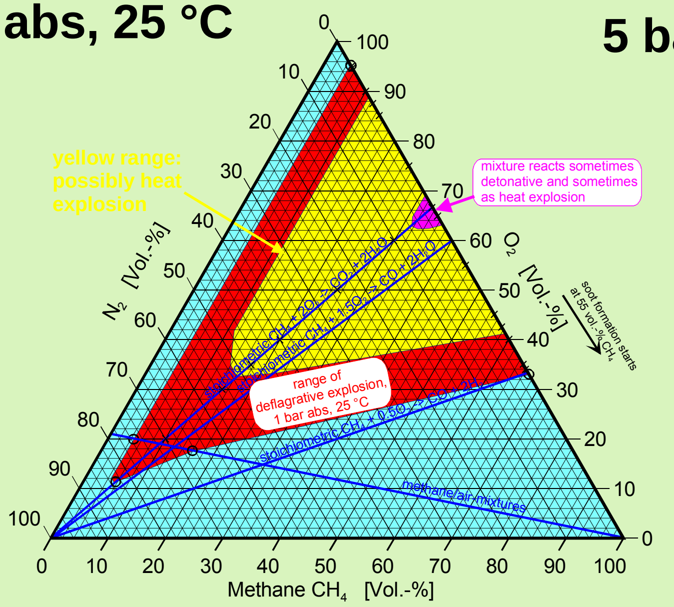
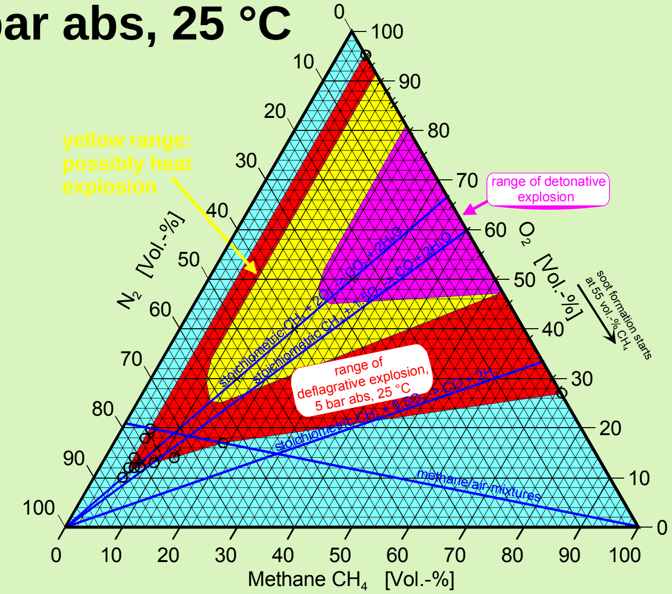
Different explosion regimes (deflagration, heat explosion, detonation) of Methane/O_2/N_2 in a 20 l sphere at 1 and 5 bar abs, 25 °C and 200 °C

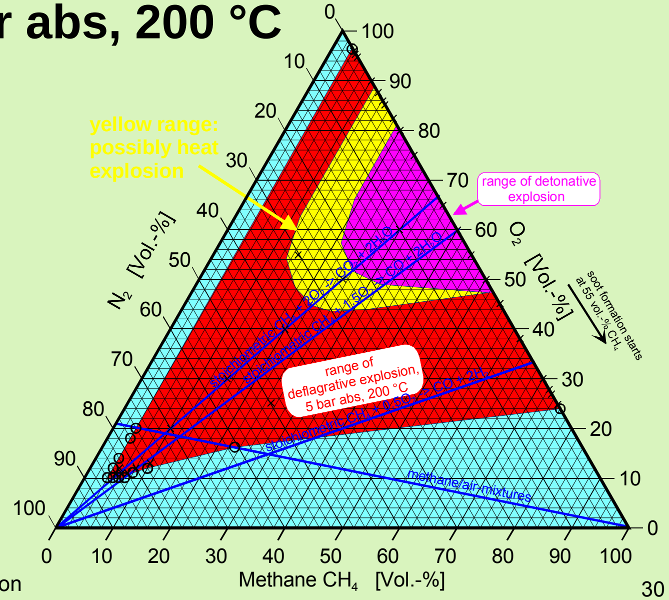
1 bar abs, 25 °C



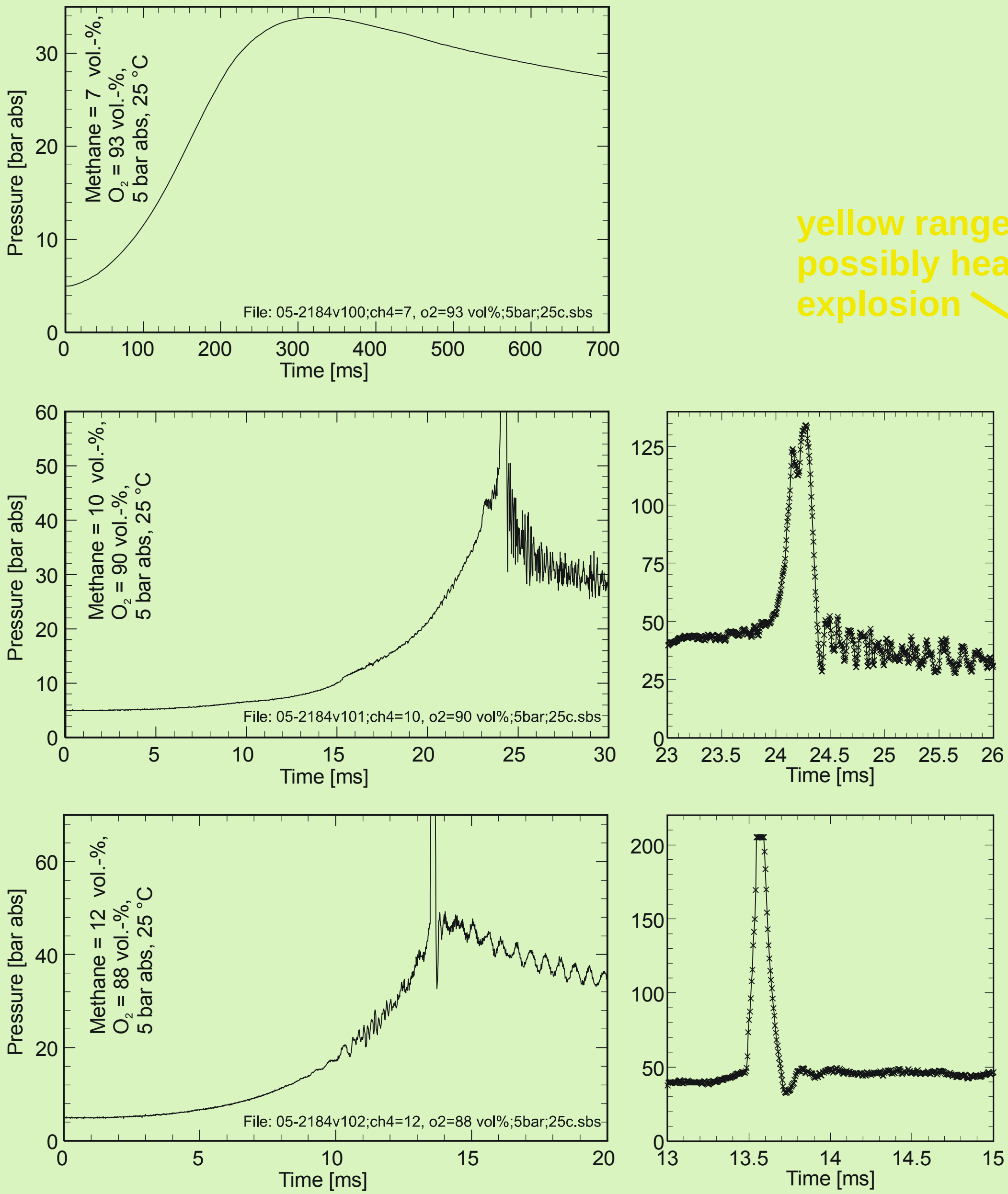
5 bar abs, 25 °C

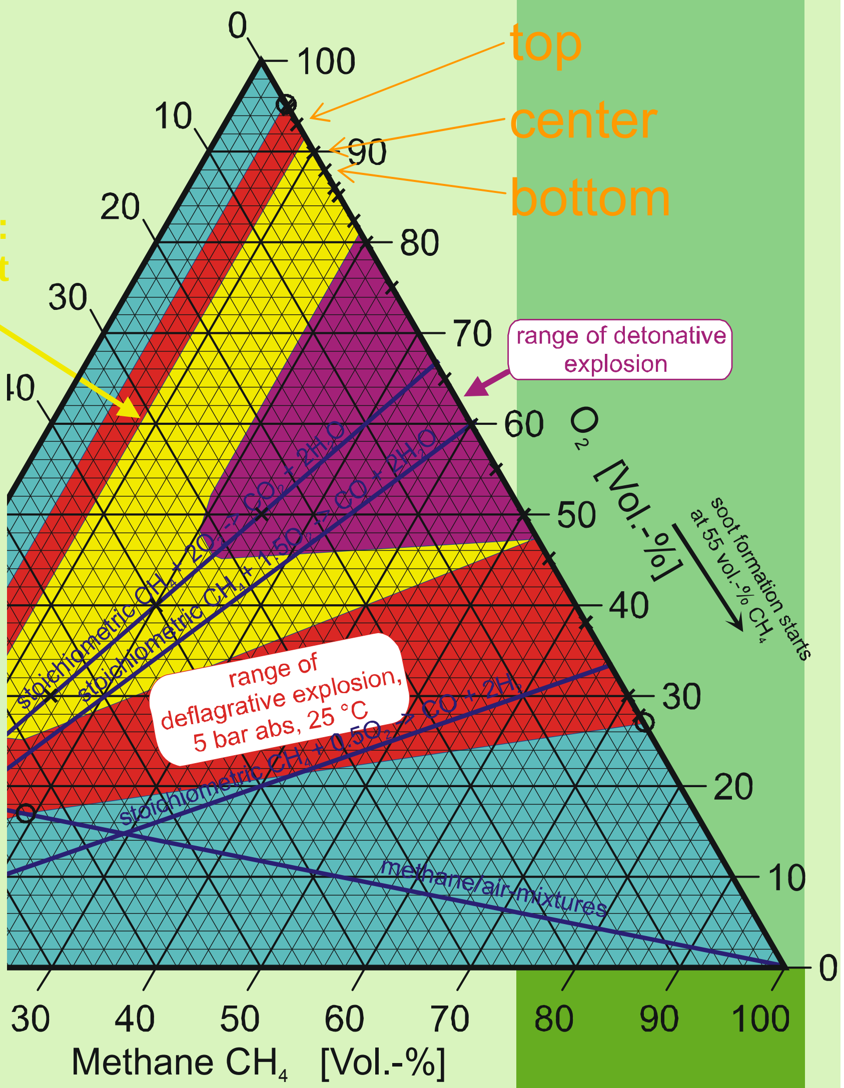


5 bar abs, 200 °C



Pressure-time traces of Methane/O_2 at 5 bar, 25 °C (1)





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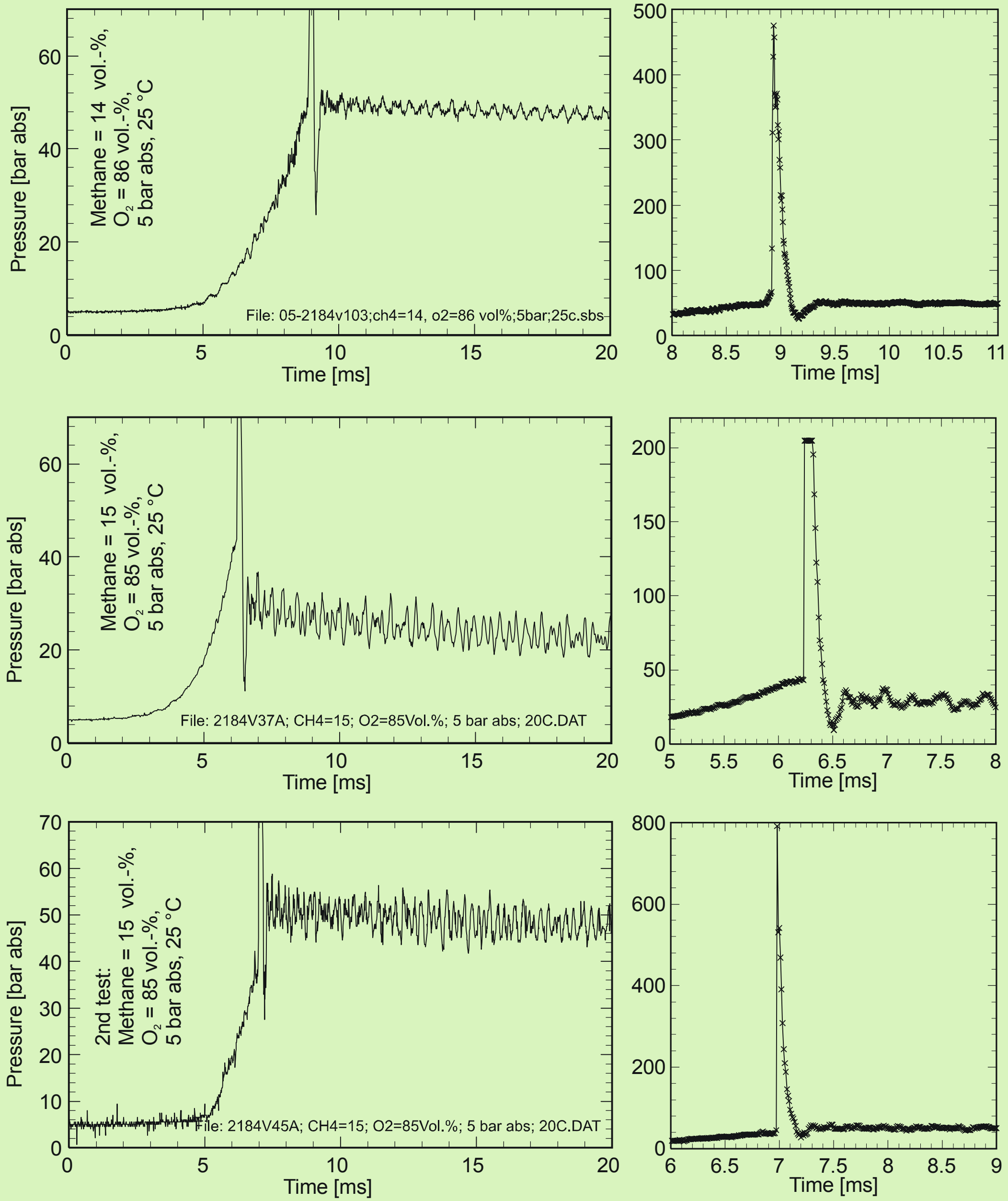
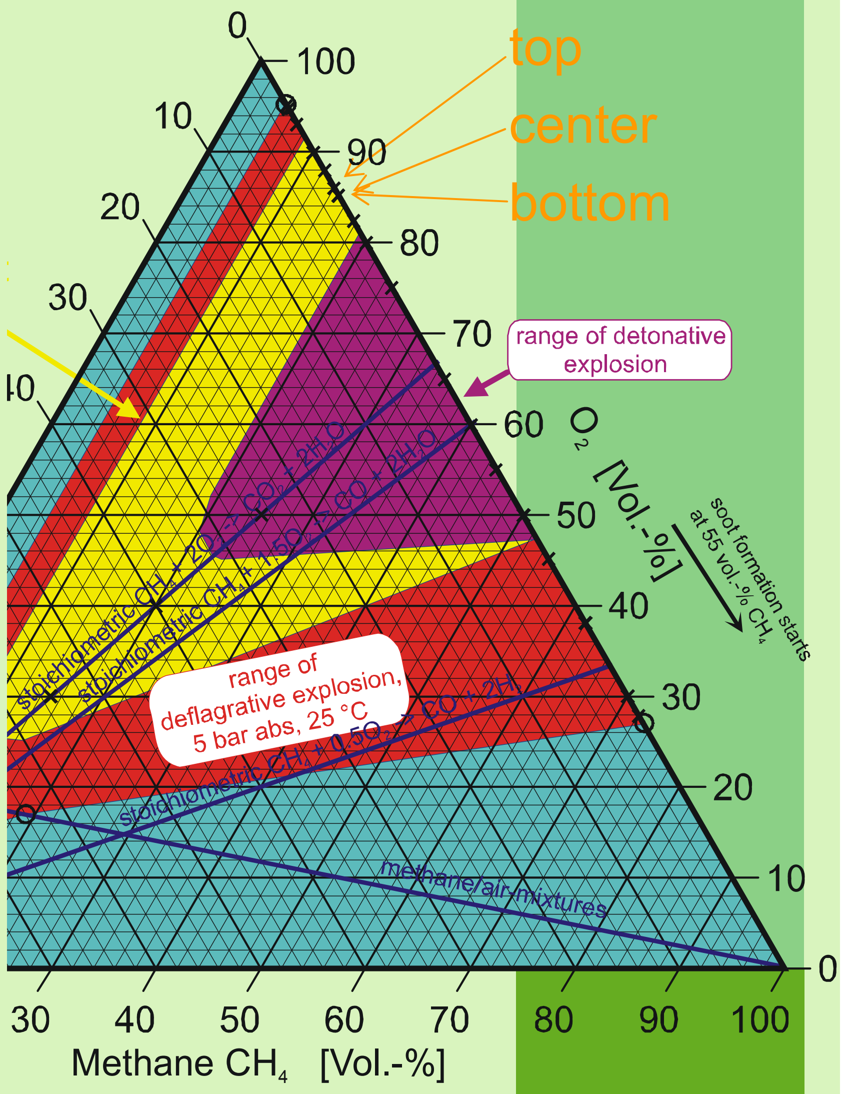
H.-P. Schildberg, 41st UKELG meeting, 13 May 2008, Shell Technology Centre Thornton

Pressure-time traces of Methane/O_2 at 5 bar, 25 °C (2)





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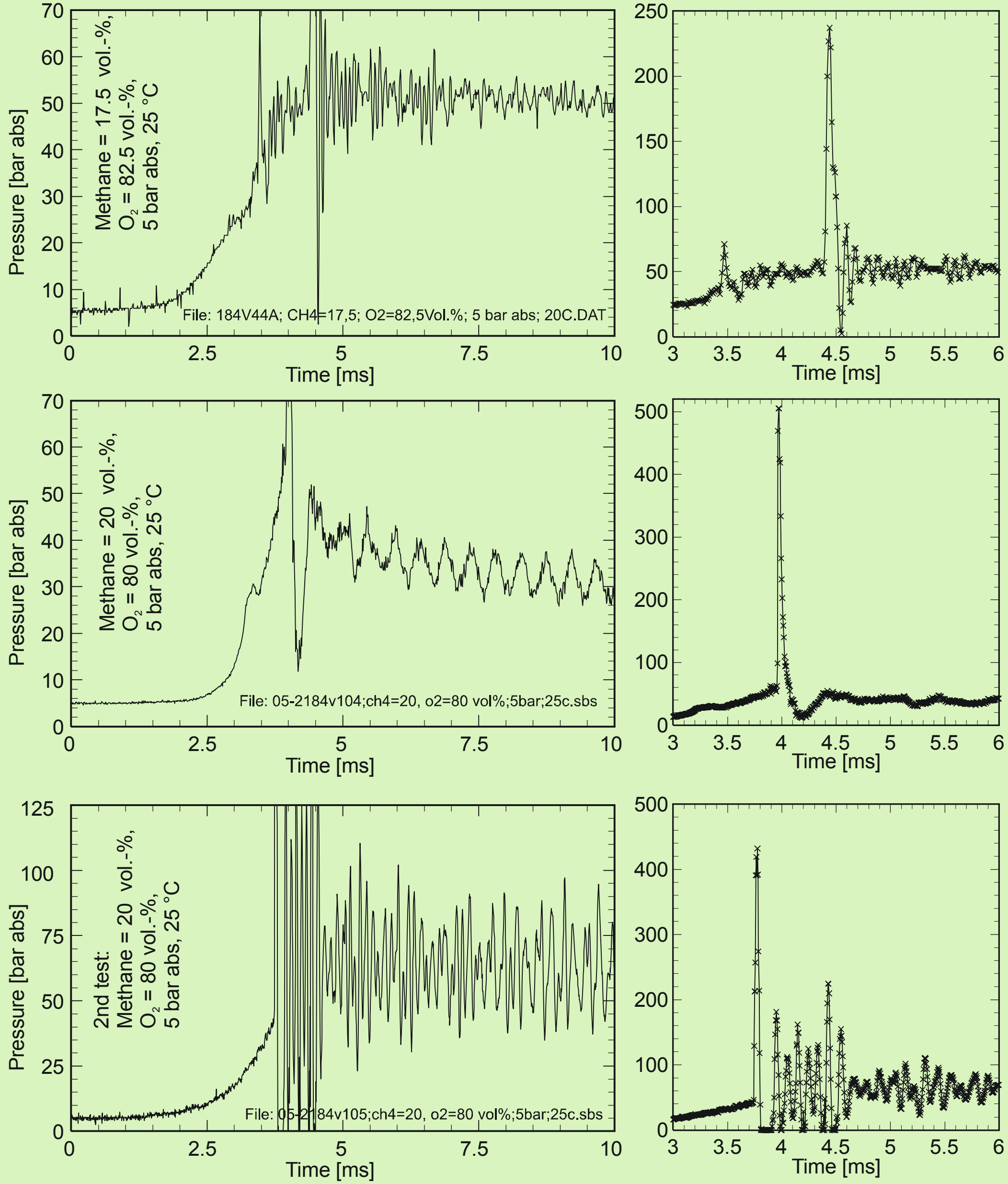
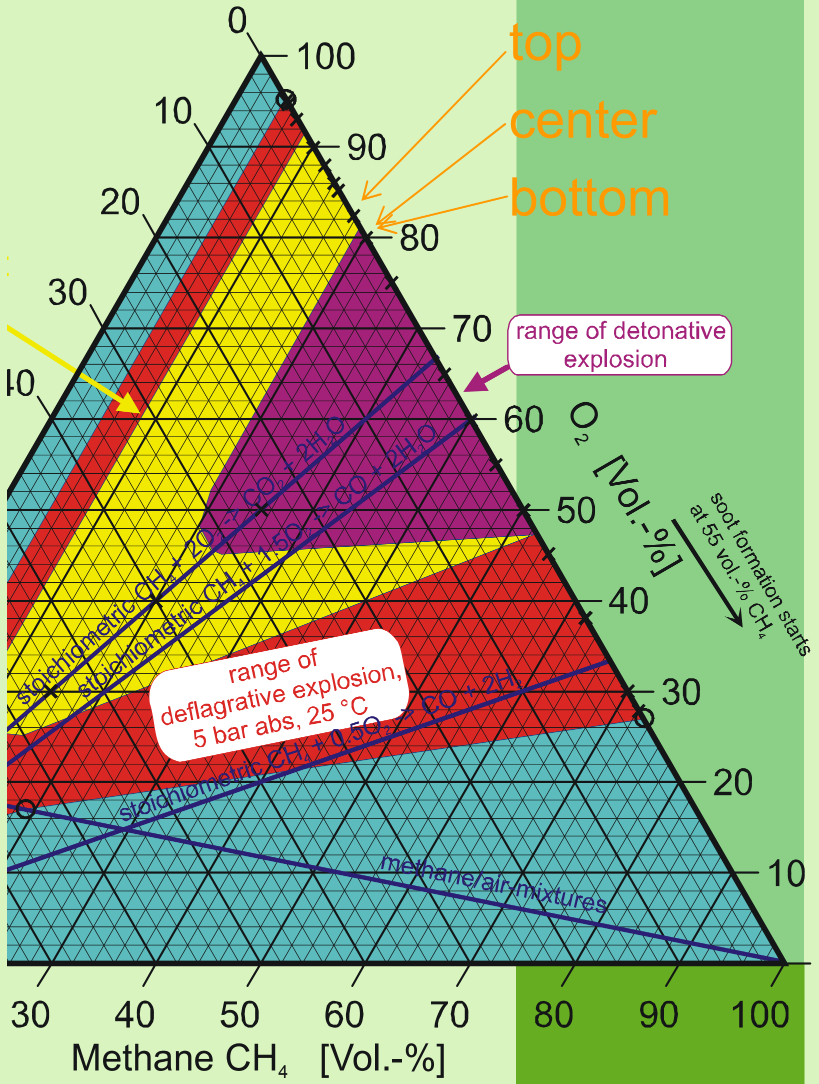
Pressure-time traces of Methane/O_2 at 5 bar, 25 °C (3)





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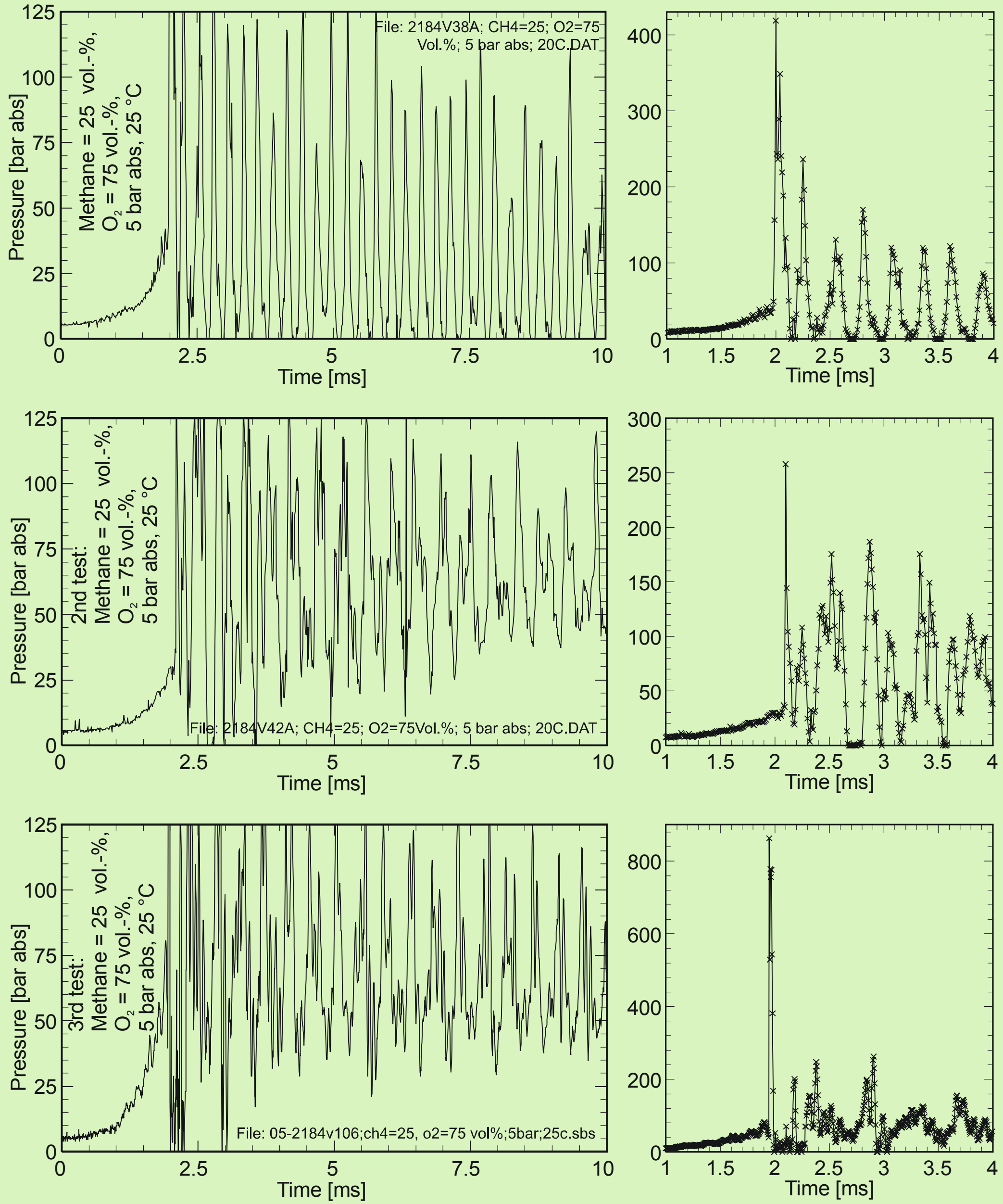
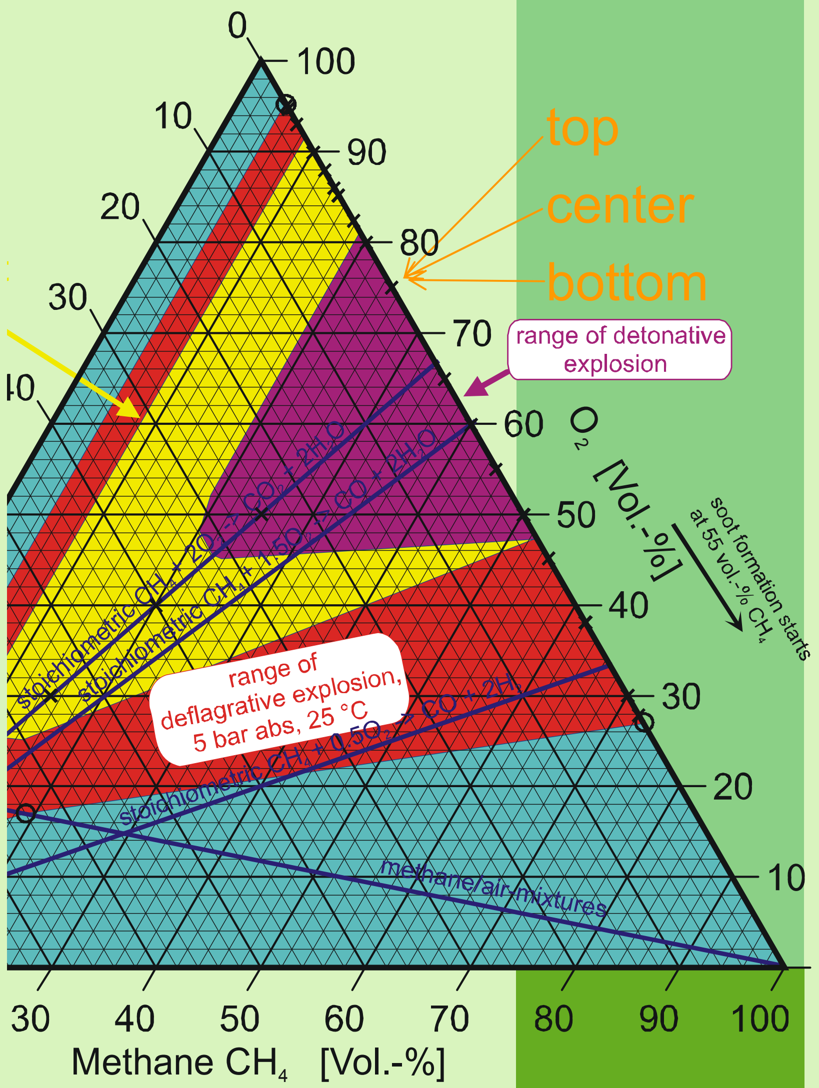
Pressure-time traces of Methane/O_2 at 5 bar, 25 °C (4)





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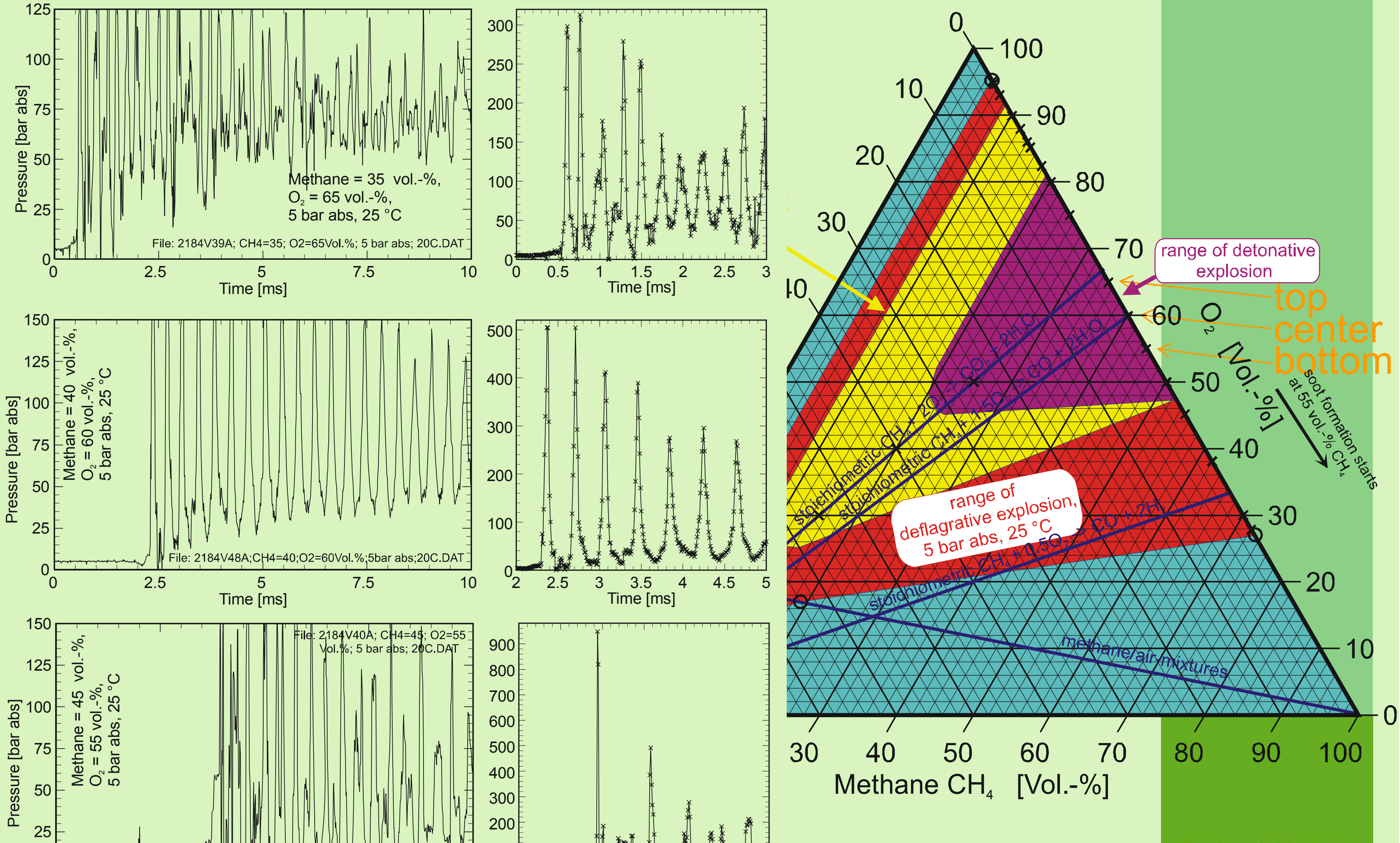
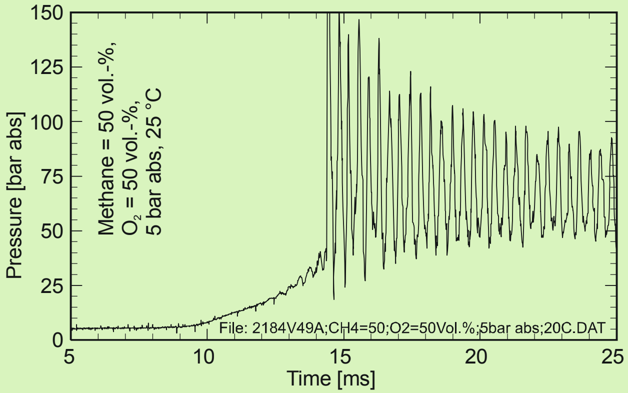
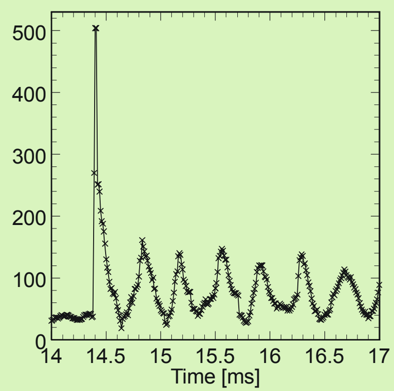
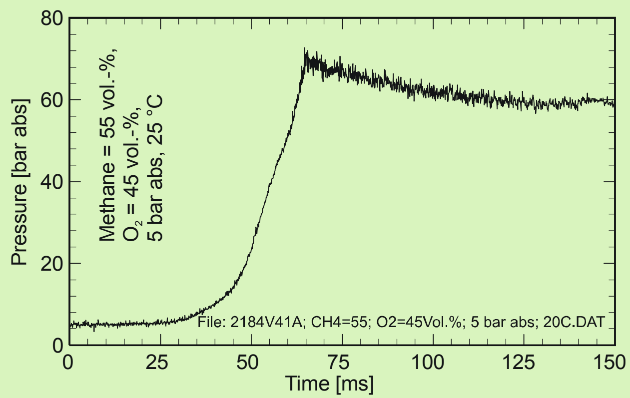
Pressure-time traces of Methane/O_2 at 5 bar, 25 °C (5)

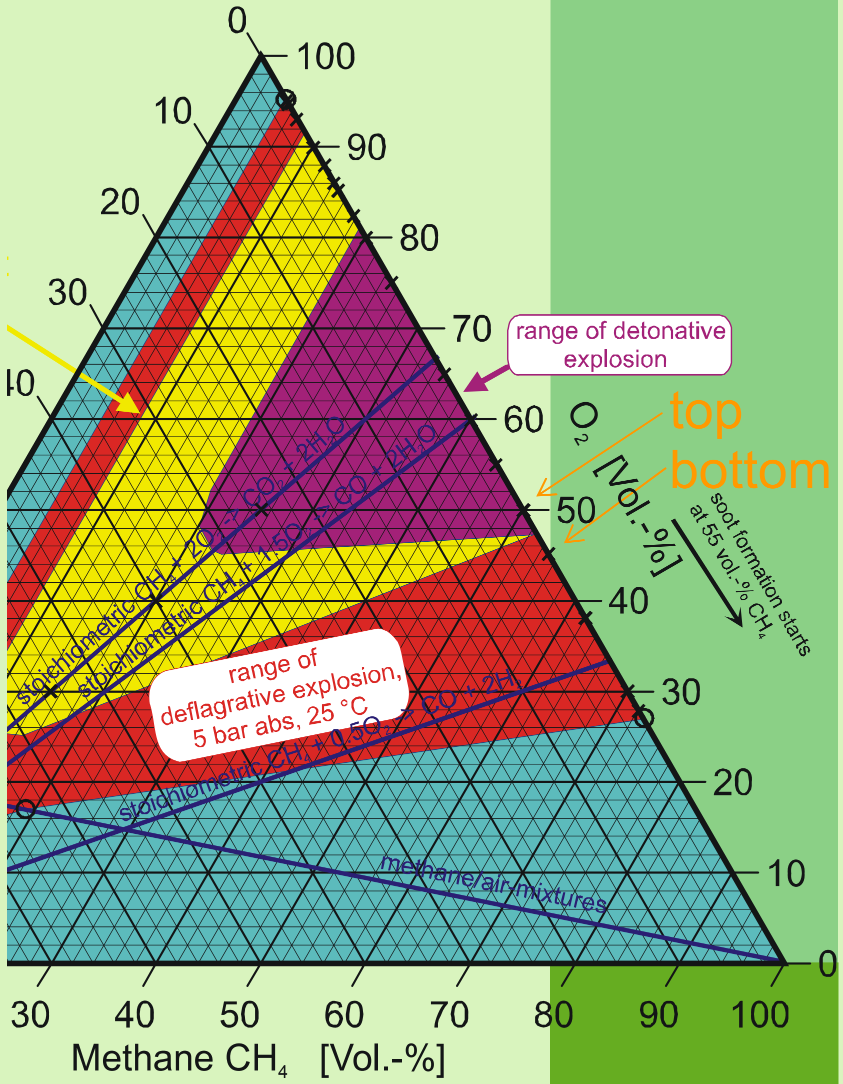


Pressure-time traces of Methane/O_2 at 5 bar, 25 °C (6)









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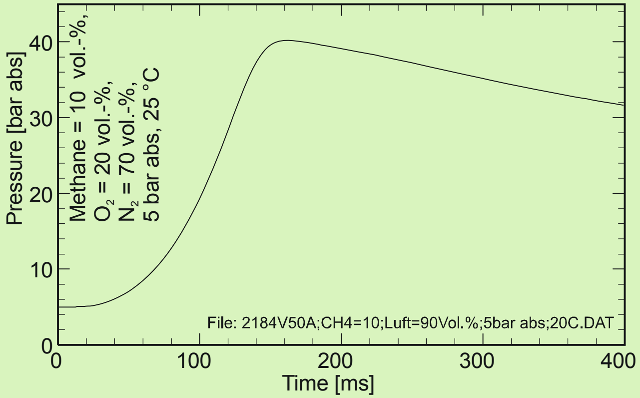
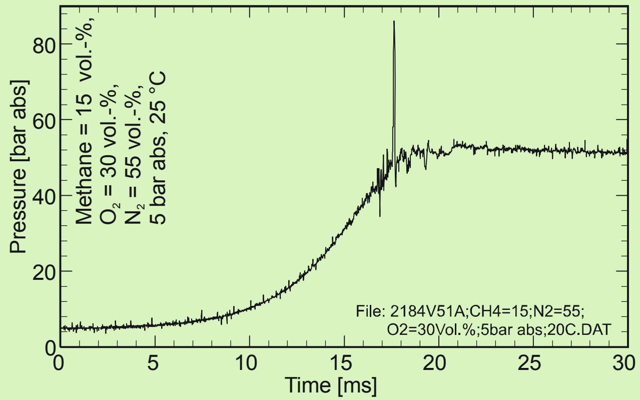
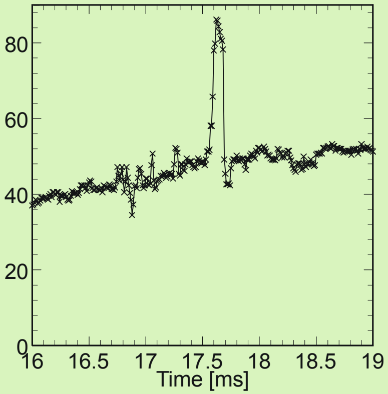
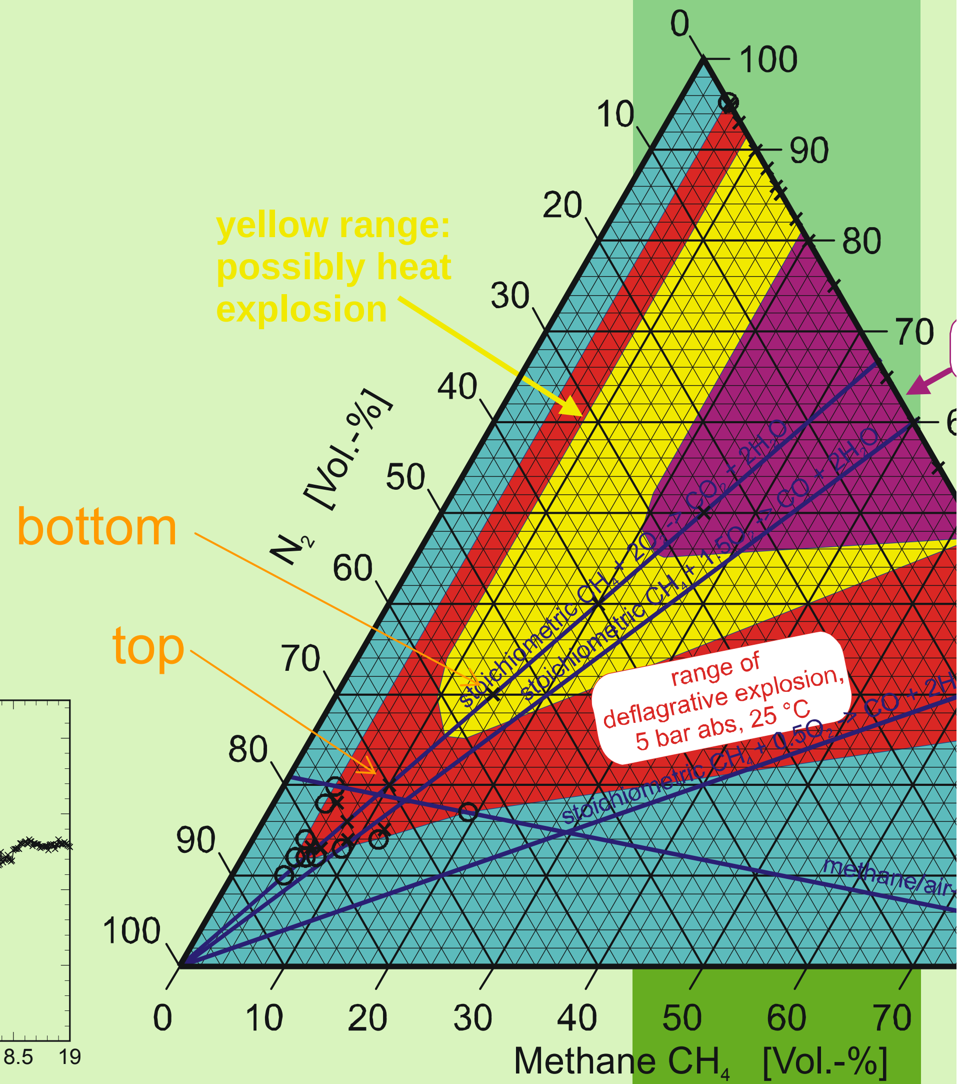
Pressure-time traces of stoich. Methane/O_2/N_2 at 5 bar, 25 °C (1)









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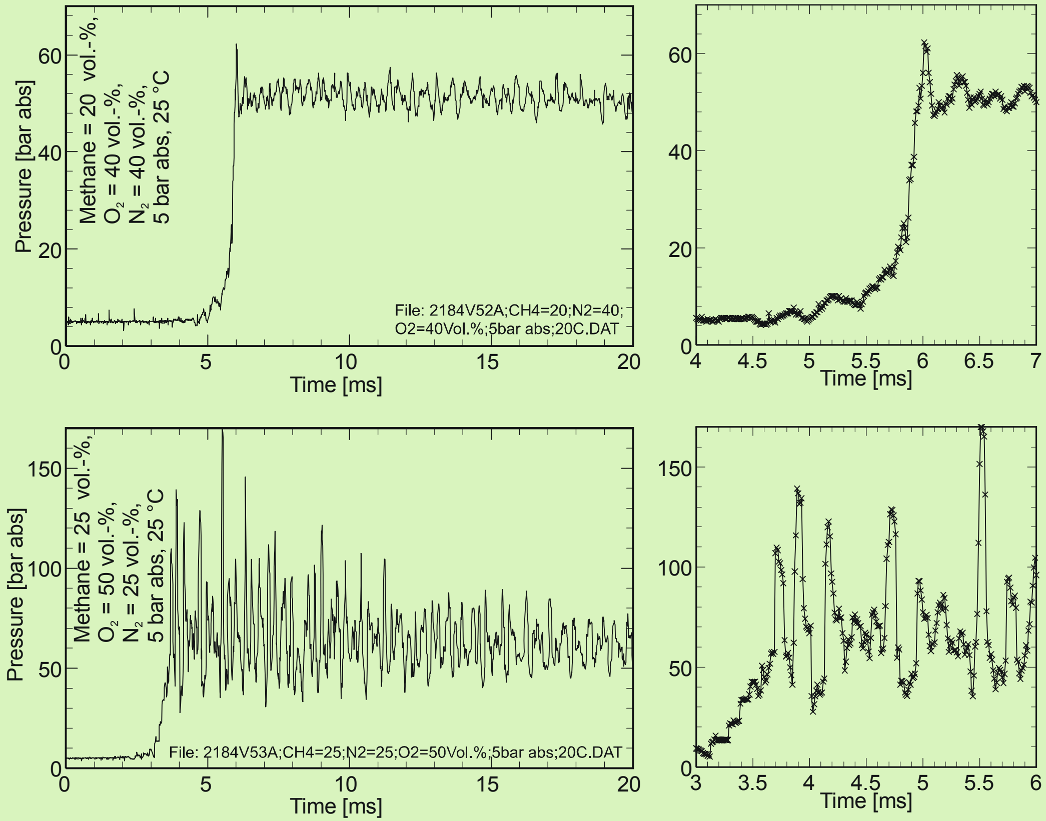
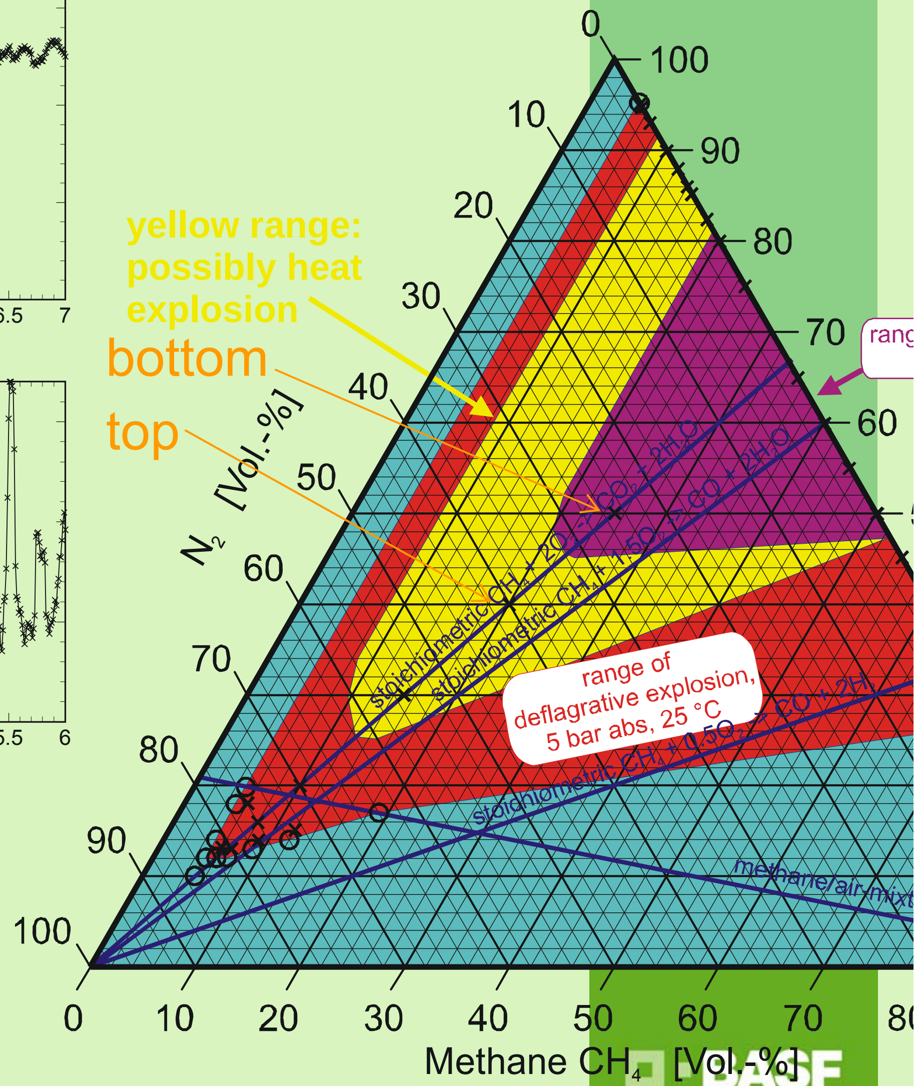
Pressure-time traces of stoich. Methane/O_2/N_2 at 5 bar, 25 °C (2)





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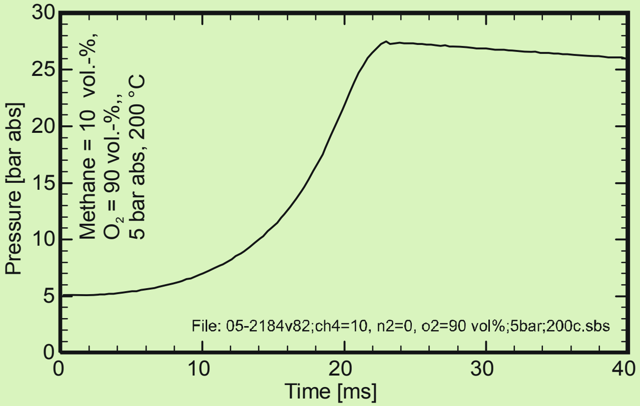
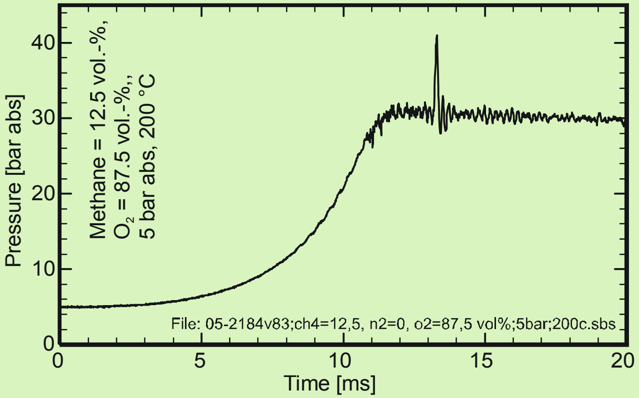
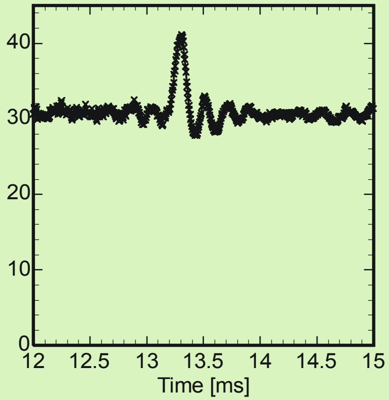
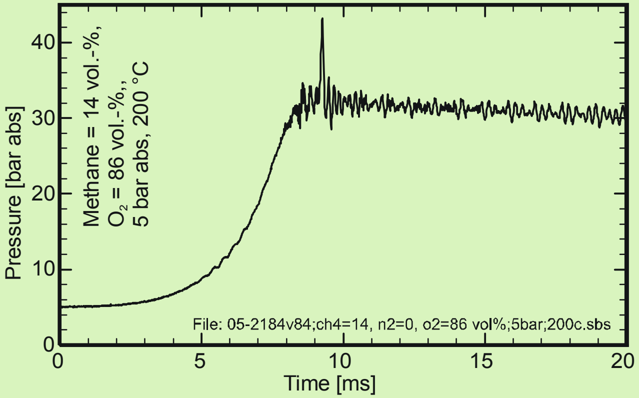
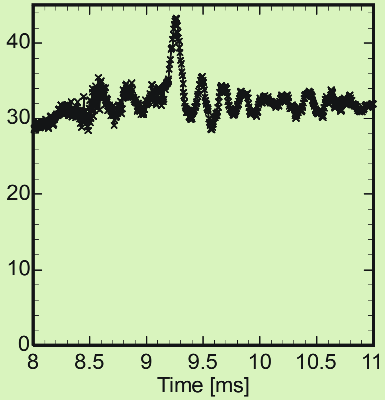
Pressure-time traces of Methane/O_2 at 5 bar, 200 °C (1)

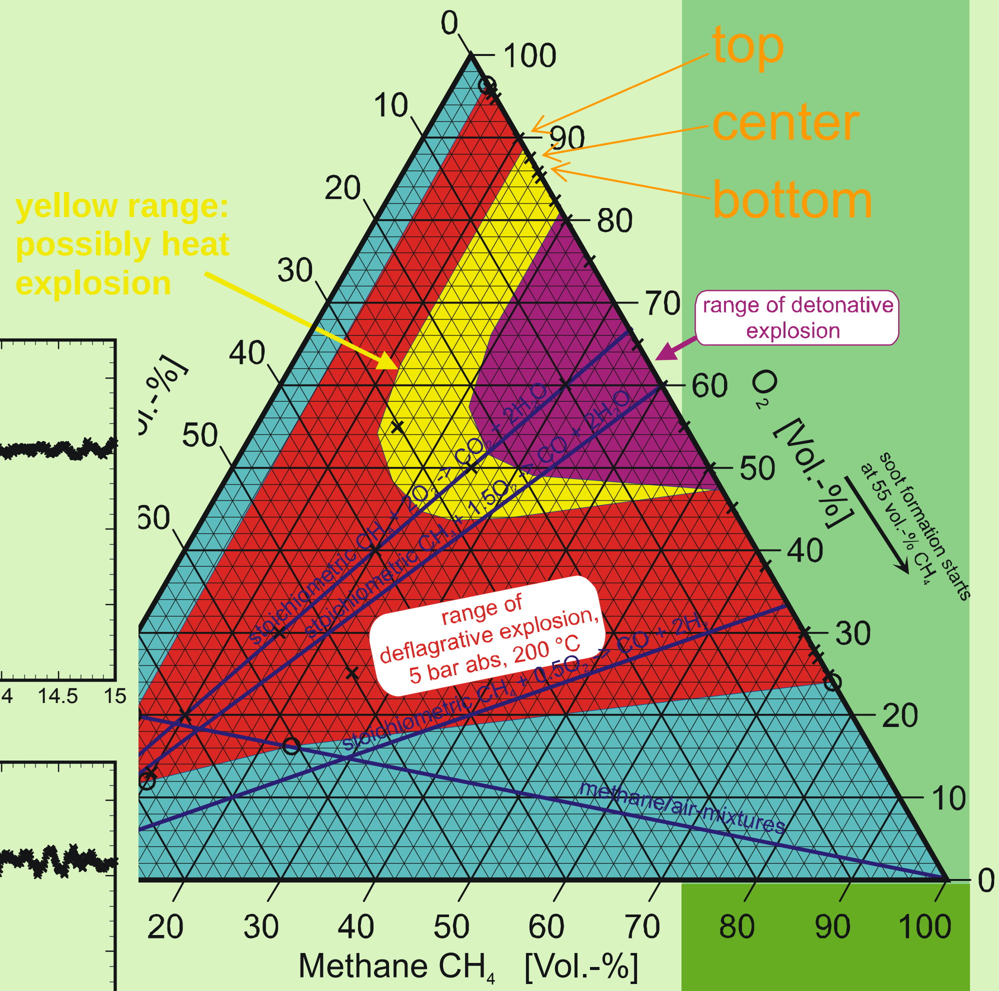




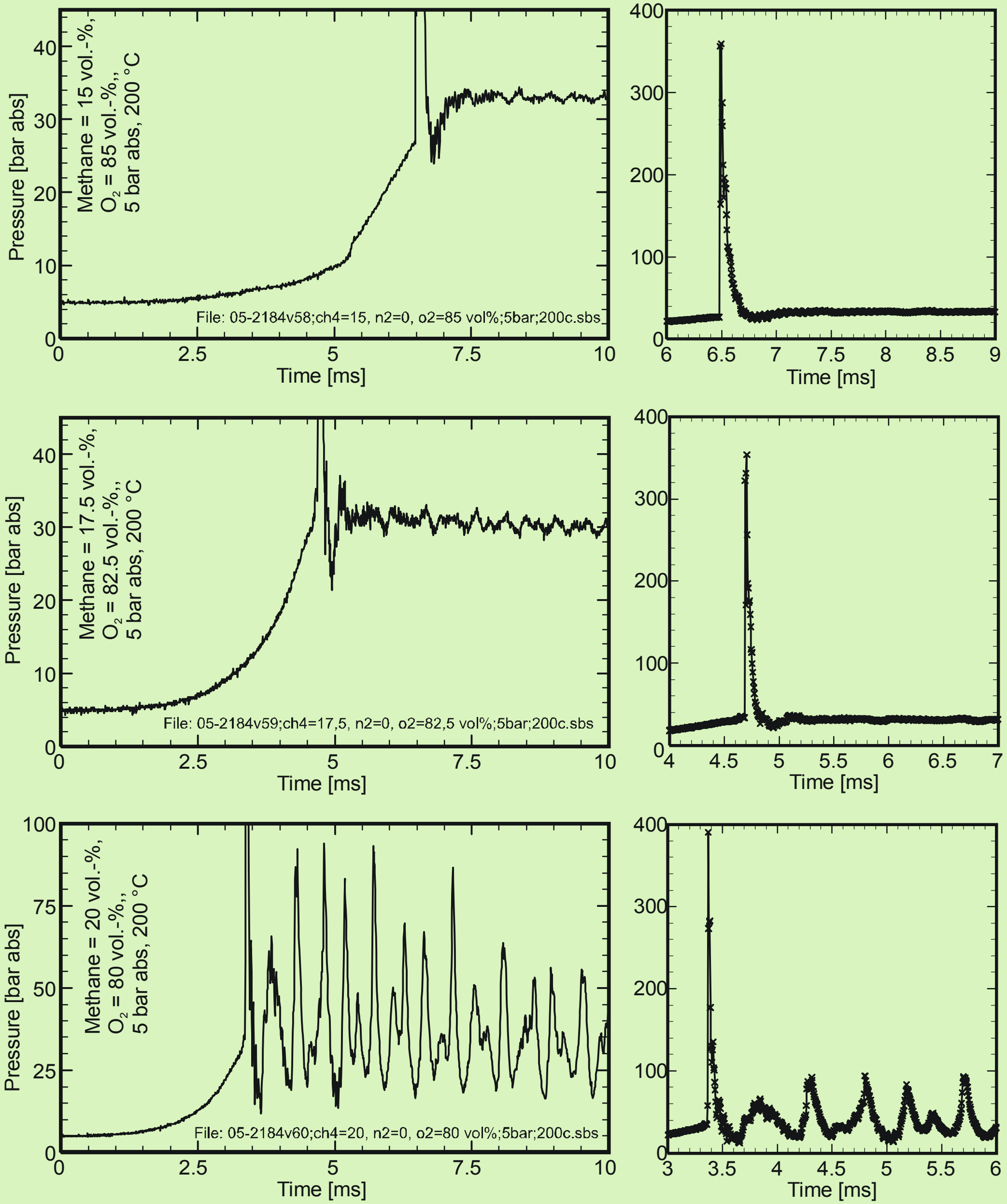


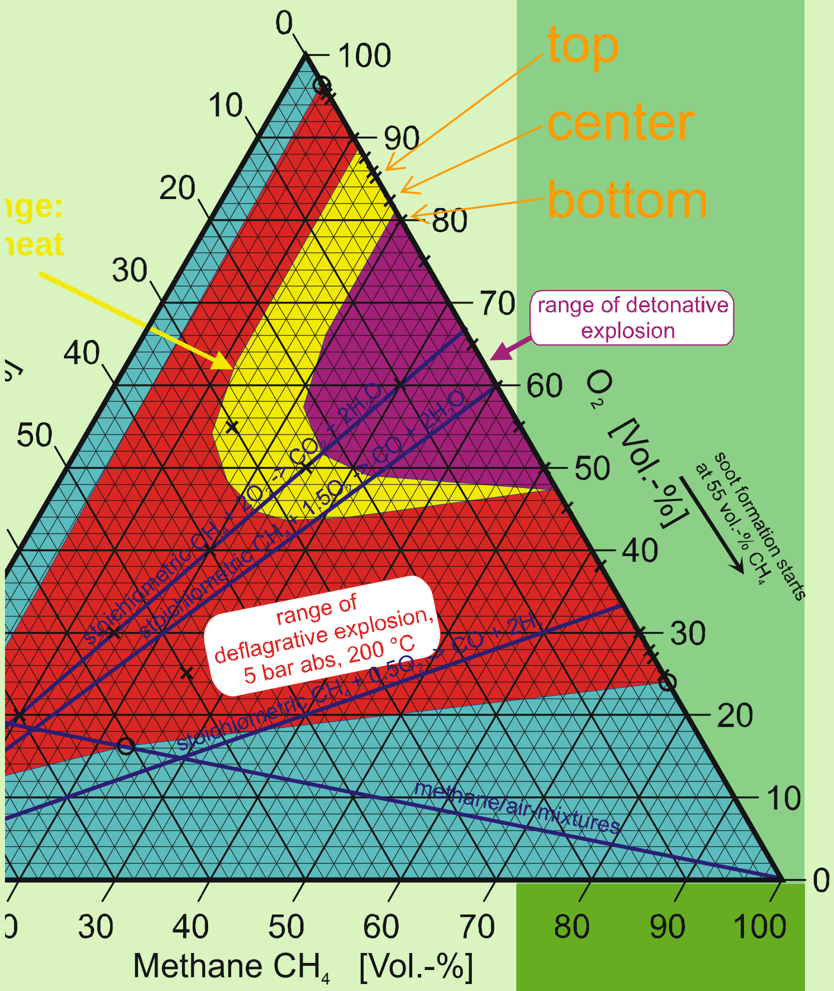






Pressure-time traces of Methane/O_2 at 5 bar, 200 °C (2)





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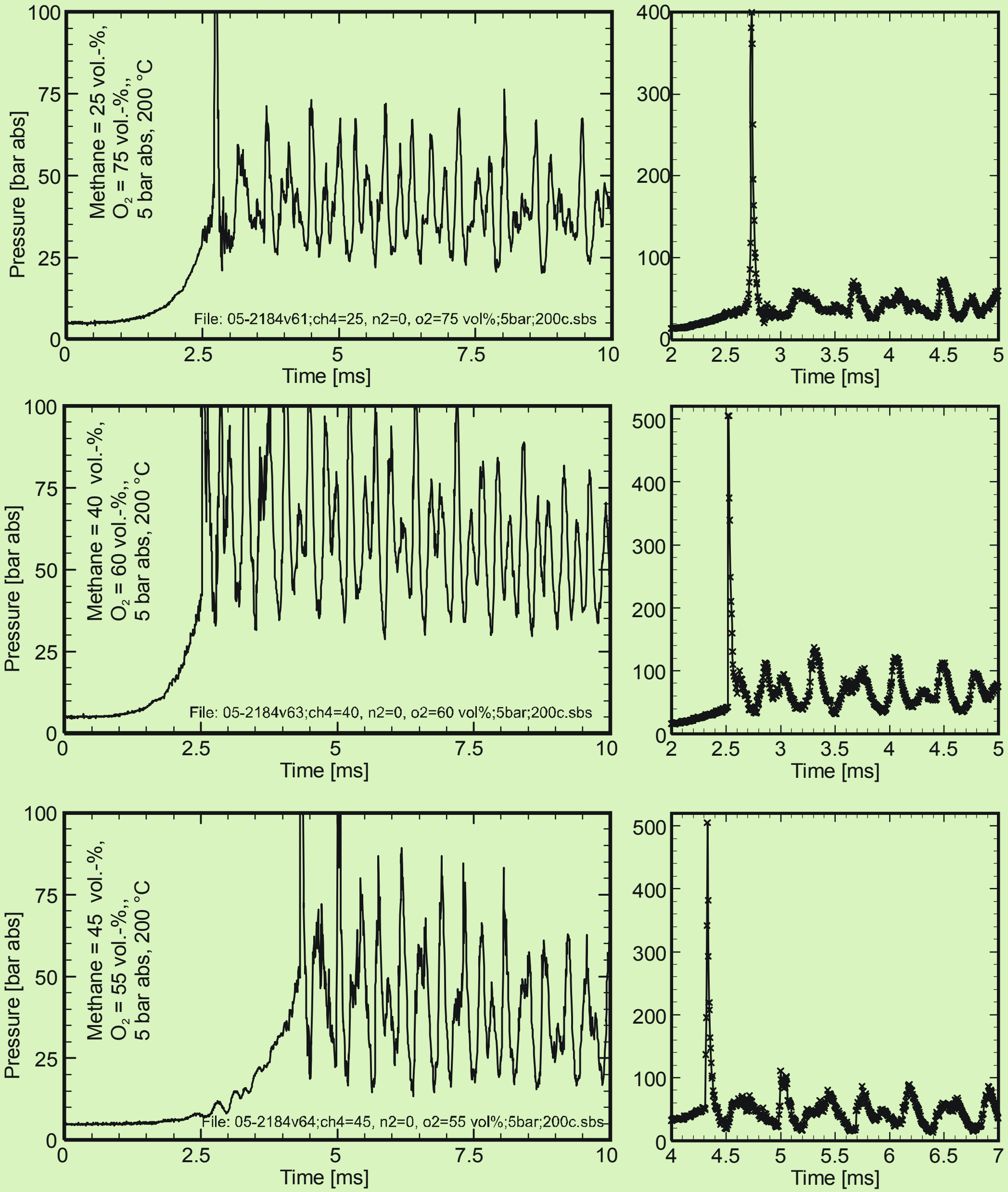
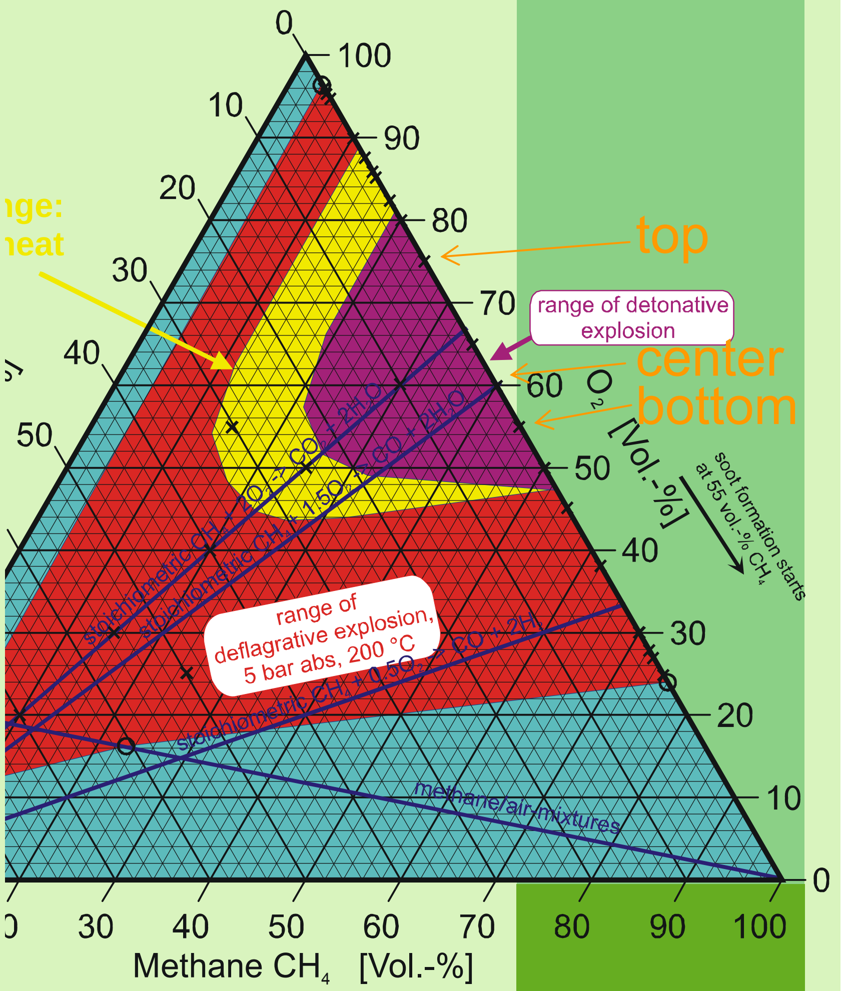
Pressure-time traces of Methane/O_2 at 5 bar, 200 °C (3)





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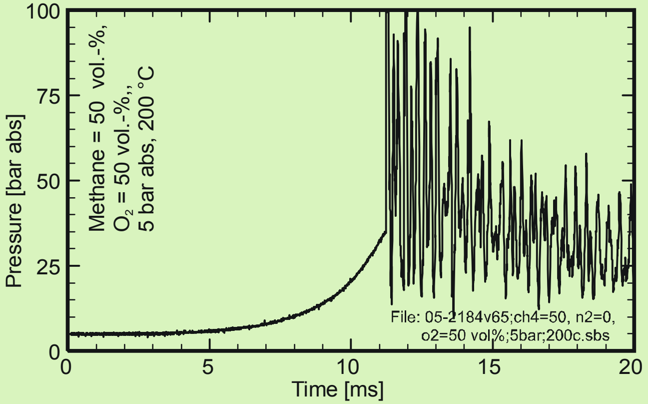
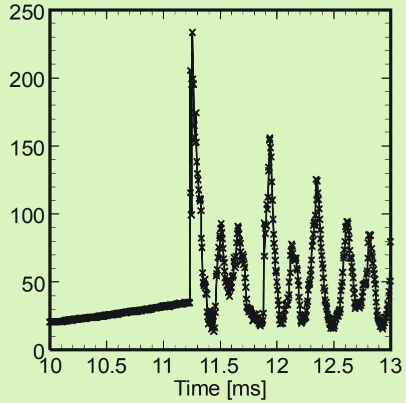
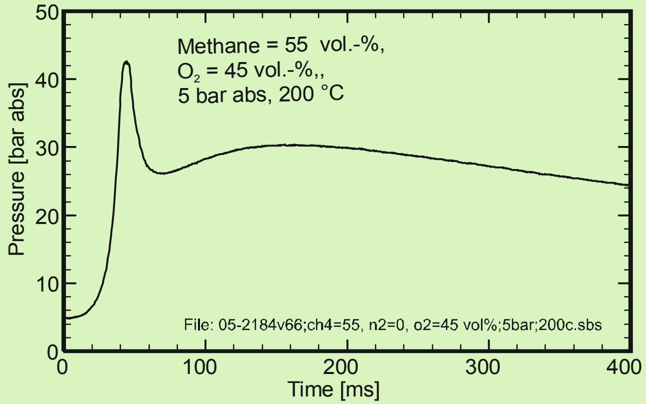
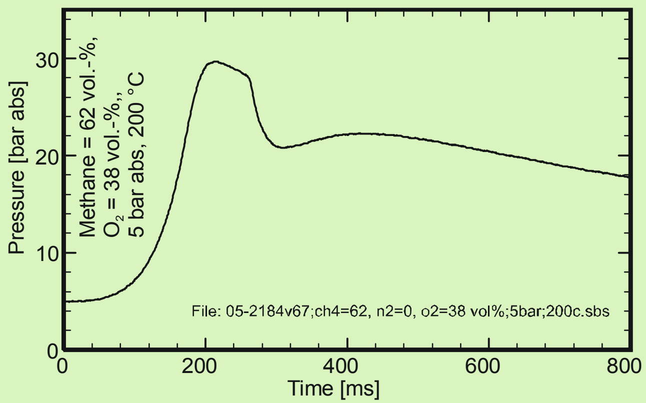
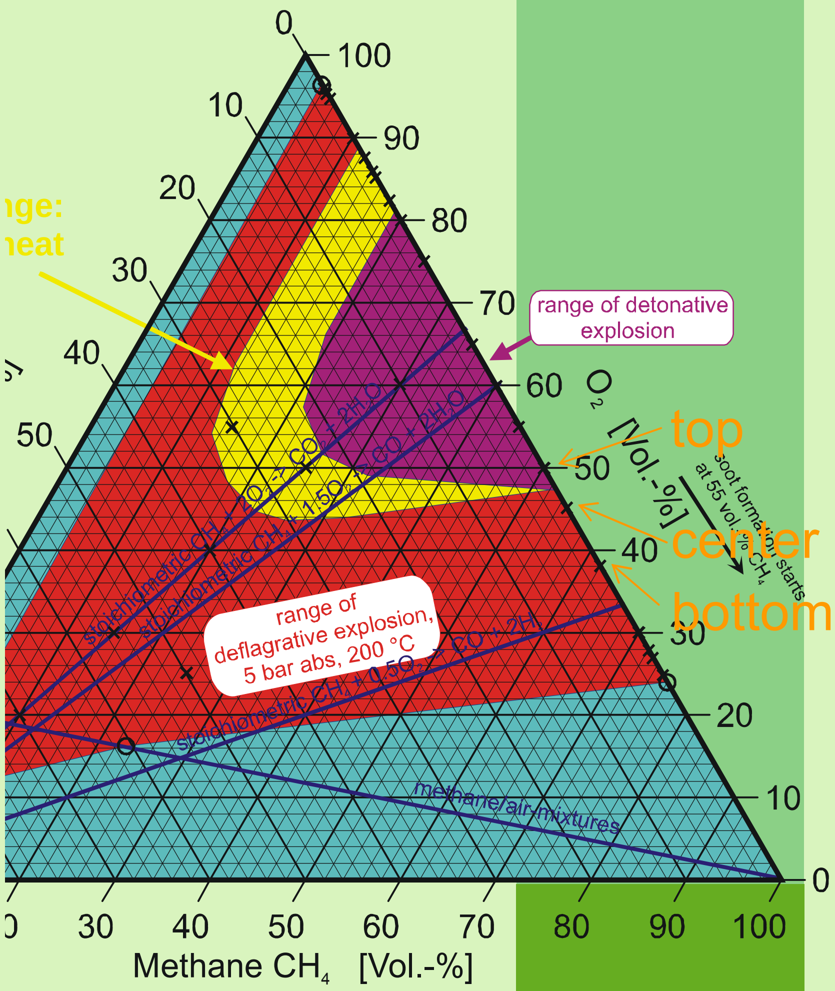
Pressure-time traces of Methane/O_2 at 5 bar, 200 °C (4)











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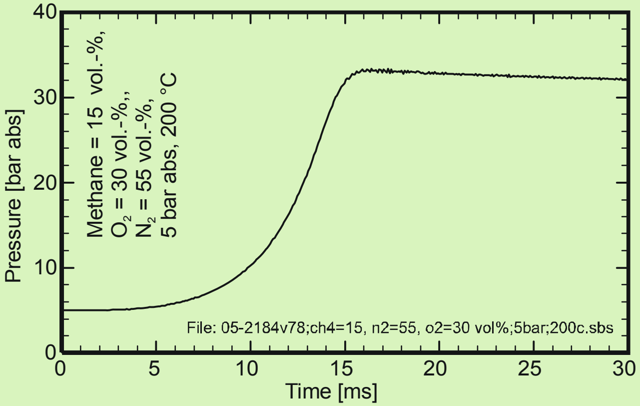
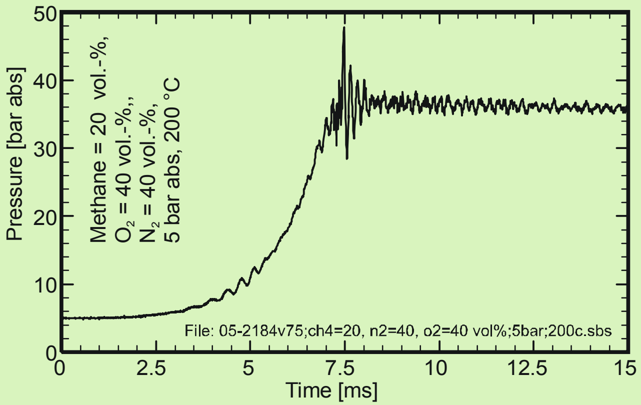
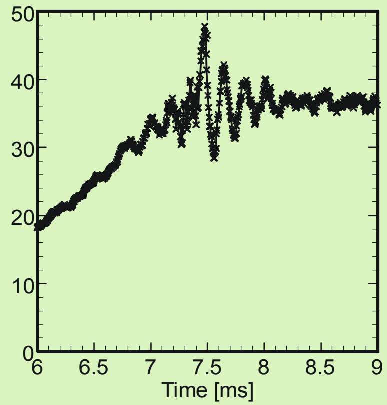
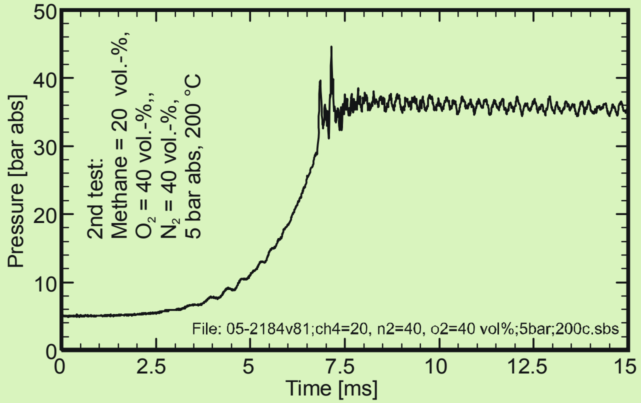
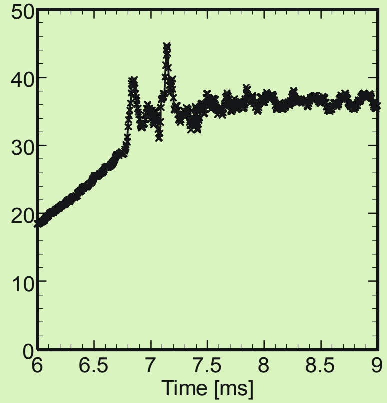
Pressure-time traces of stoich. Methane/O_2/N_2 at 5 bar, 200 °C (1)

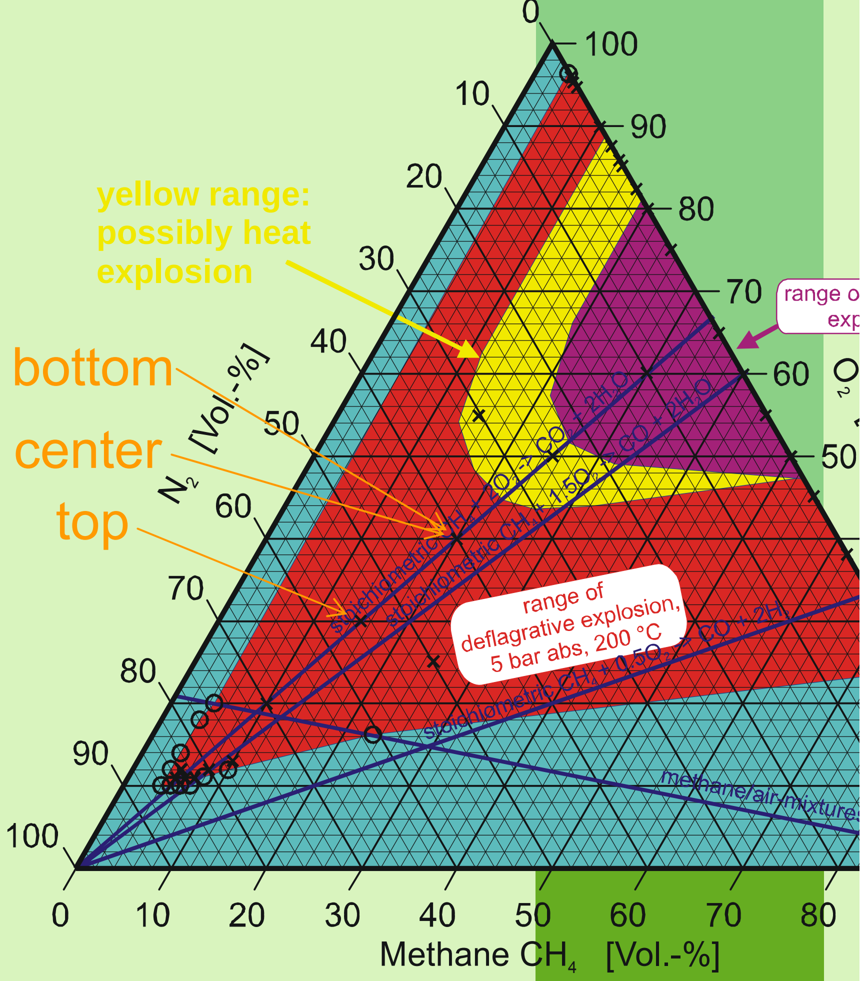












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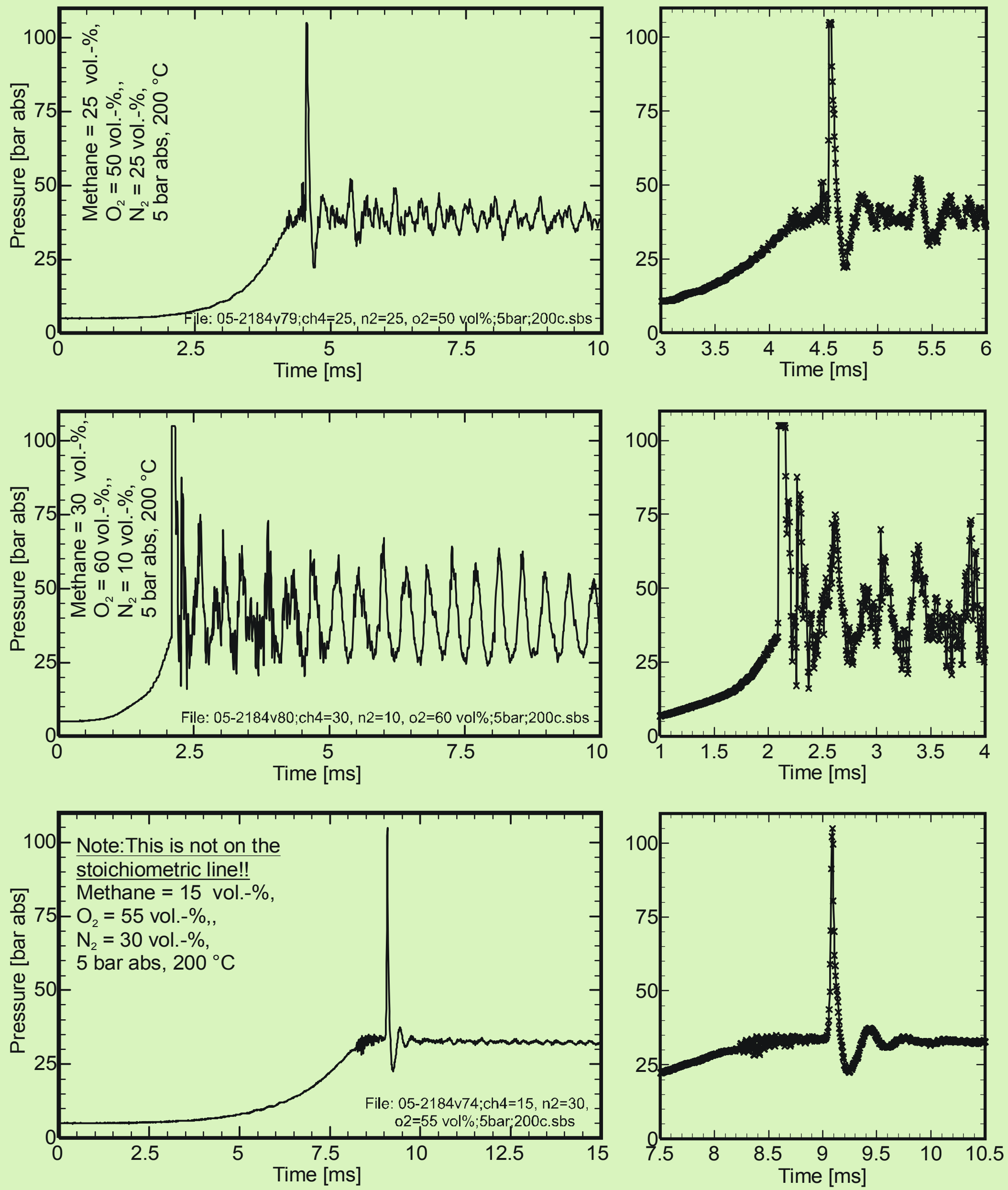
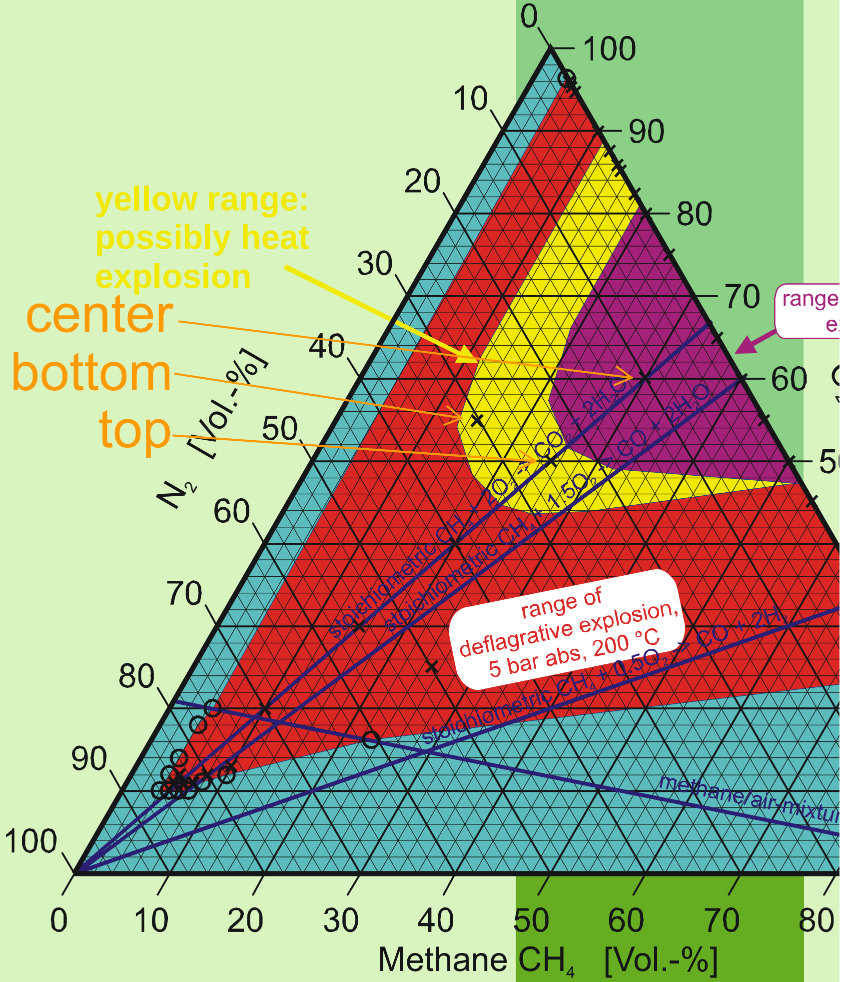
Pressure-time traces of stoich. Methane/O_2/N_2 at 5 bar, 200 °C (2)





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Summary of the differences in the pressure time diagrams between explosions in vessels that were triggered by a thermal ignition and ended up as deflagration, “heat explosion” or detonation

	course of explosion		
	deflagration	heat explosion	detonation
presence of pressure pulse	no	yes	yes
width of pressure pulse at half height [µs]	(not applicable)	100 - 200	< 50
height of pressure pulse divided by pressure in mixture just before its occurrence	(not applicable)	typically 4 to 7 (equals deflagration pressure ratio of the precompressed unreacted mixture)	typically 15 to 50 (due to too small sampling rate the true maximum was presumably mostly missed)
precompression ratio at the moment when pressure pulse occurs	(not applicable)	5 – 10 (largest value equals $p_{ex}/p_{initial}$ of the corresponding gas mixture)	1 – 20 (largest value equals $p_{ex}/p_{initial}$ of the corresponding gas mixture)
"oscillations" in reaction gases after occurrence of pressure pulse	no oscillations anyway	no oscillations	massive oscillations (due to shock front bouncing backwards and for-wards in reaction gases)
acoustic sound heard outside the vessel	nothing	“click”	prolonged whistle

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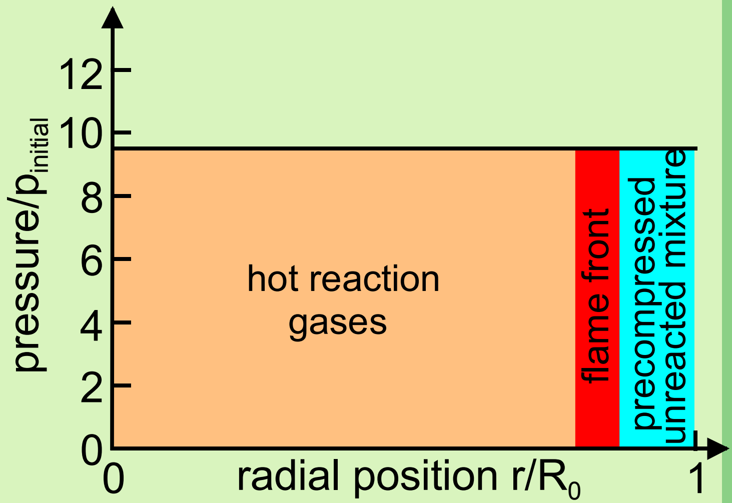
Heat explosion – tentative explanation of the course of events

Before heat explosion:

Reaction rate sufficiently slow to allow for pressure equilibrium over entire sphere

Pressure as function of radial position in 20 l sphere ($p_{initial}$ = 1 bar abs) just before heat explosion occurs in the precompressed, unreacted mixture (R_0 = 17 cm)



At heat explosion:

Immediate temperature rise and hence also pressure rise in the shell so far unreacted, but heated by adiabatic compression. The induction time must be of the order of 0.1 ms or even less, otherwise the flame front of the initial deflagration would have run through the thin shell of unreacted mixture before the heat explosion could develop.

After heat explosion:

reaction gases flow to the central part of the sphere and pressure equilibrium is attained

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Temperatures obtainable by adiabatic compression

$p_{final}/p_{initial}$	T_{final} [°C] resulting for different values of γ in case that $T_{initial}$ = 35 °C = 308 K				T_{final} [°C] resulting for differrent values of γ in case that $T_{initial}$ = 200 °C = 473 K			
	γ = 1,4	γ = 1,3	γ = 1,2	γ = 1,1	γ = 1,4	γ = 1,3	γ = 1,2	γ = 1,1
1,5	72,8	65,2	56,5	46,6	258,1	246,4	233,1	217,8
2	102,5	88,4	72,7	55,0	303,6	282,0	257,9	230,8
3	148,6	123,9	96,9	67,3	374,4	336,5	295,0	249,7
4	184,7	151,1	115,1	76,4	429,9	378,3	322,9	263,5
5	214,8	173,5	129,8	83,5	476,1	412,7	345,5	274,5
6	240,9	192,7	142,2	89,5	516,2	442,2	364,6	283,7
7	264,0	209,6	153,0	94,6	551,7	468,1	381,2	291,5
8	284,9	224,7	162,6	99,1	583,8	491,3	395,9	298,4
9	304,0	238,4	171,2	103,1	613,1	512,4	409,2	304,6
10	321,7	251,0	179,1	106,7	640,2	531,7	421,3	310,1
12	353,5	273,5	193,0	113,1	689,1	566,3	442,7	319,9
14	381,7	293,3	205,2	118,5	732,4	596,7	461,3	328,2
16	407,1	311,0	215,9	123,3	771,5	623,9	477,8	335,6
18	430,4	327,1	225,6	127,6	807,2	648,6	492,7	342,1
20	451,9	341,9	234,4	131,4	840,2	671,3	506,3	348,1

Temperatures may well lie above the ignition temperatures the mixtures presumably have in the precompressed state!

Formula for temperature increase due to adiabatic compression: $T_{final} = T_{initial} \cdot \left(p_{final} / p_{initial} \right)^{(\gamma - 1)/\gamma}$

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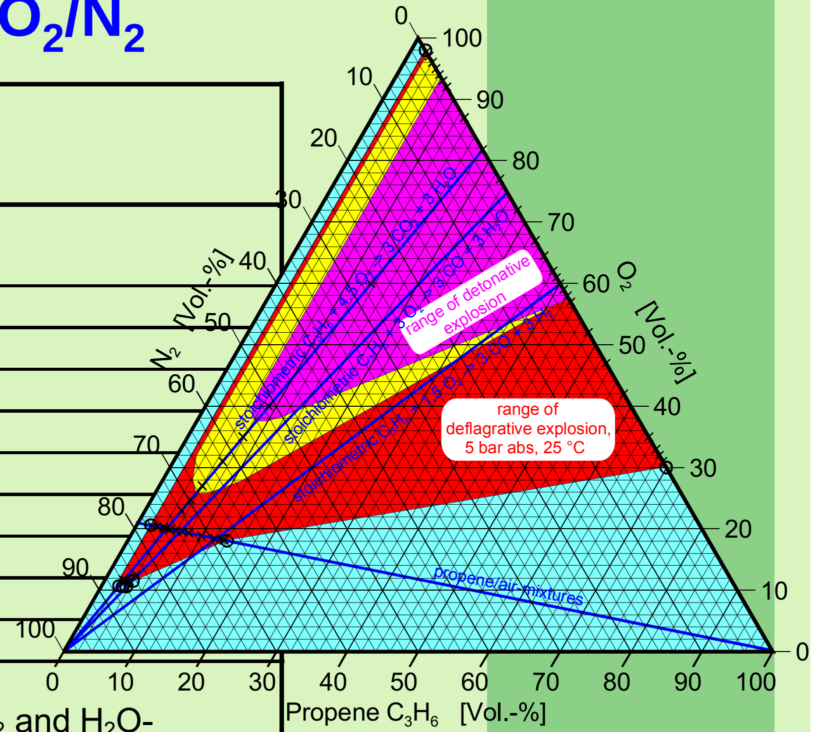
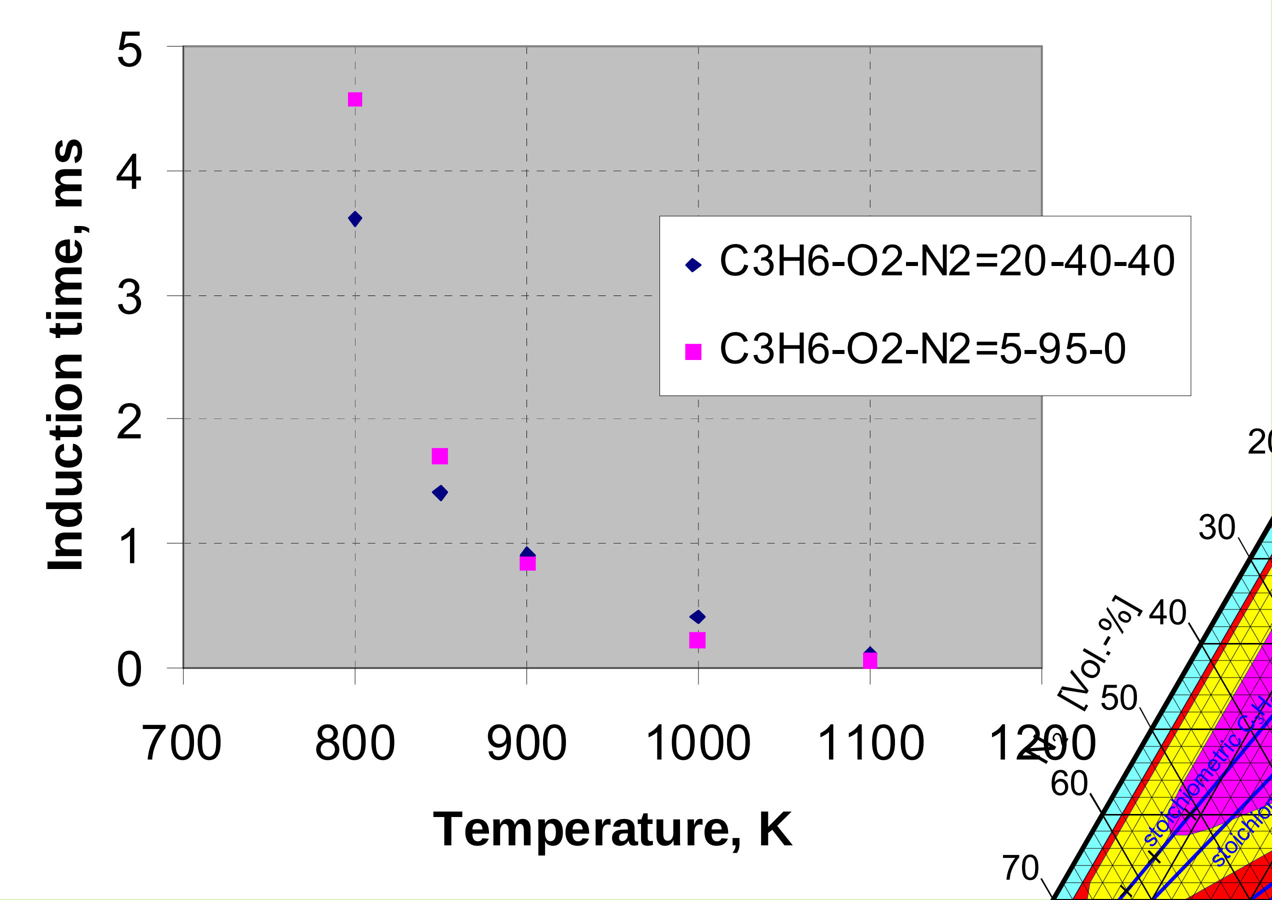
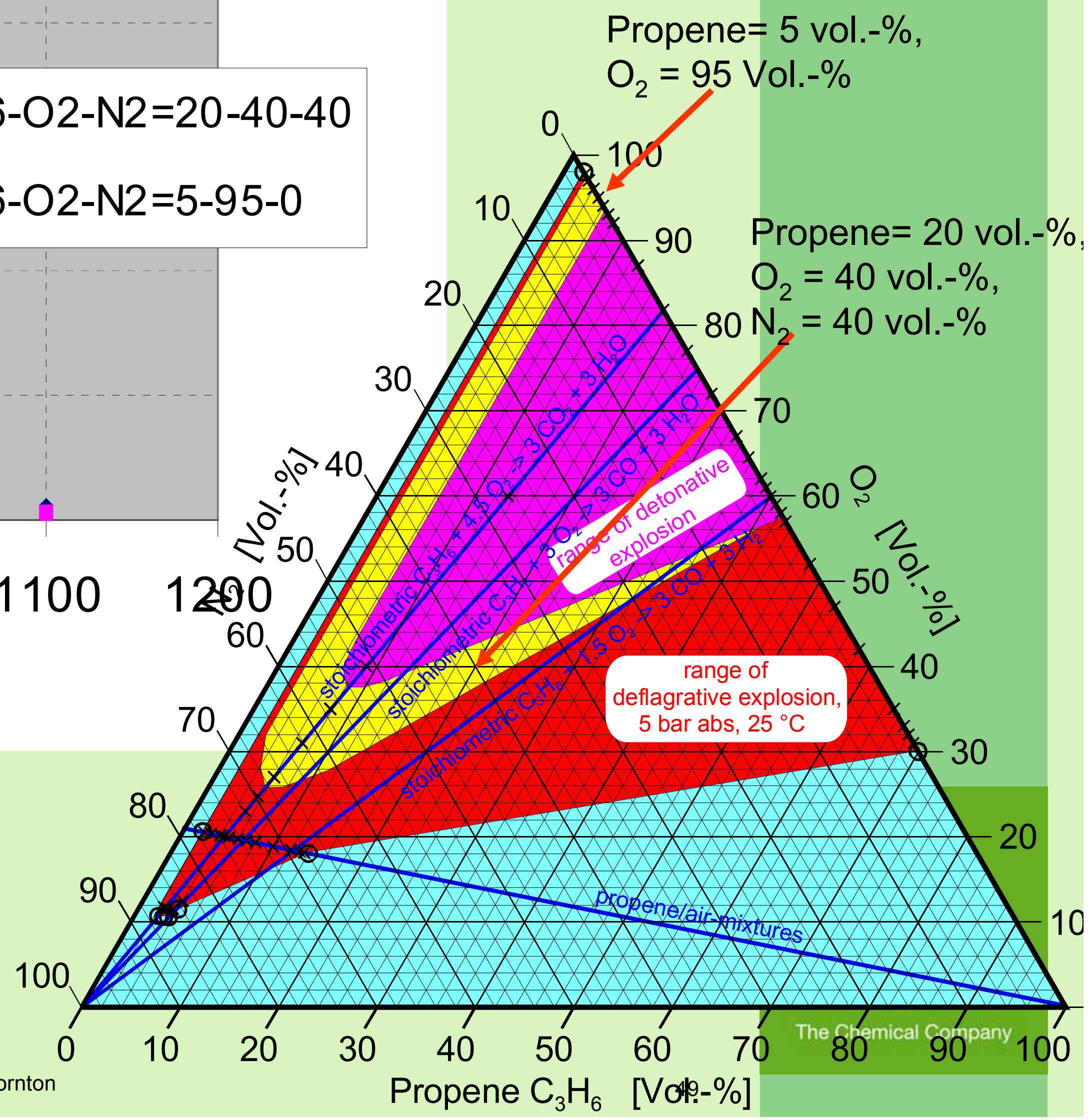
Autoignition temperatures of Propene/O_2/N_2

Propene [Vol.-%]	O_2 [Vol.-%]	N_2 [Vol.-%]	Autoignition Temperature (AIT) [°C]
AIT [°C] at $P_{initial}$ = 5 bar abs for Propene/O_2 mixtures			
4.46	95.54	0	280
7	93	0	270
10	90	0	270
20	80	0	260
30	70	0	260
40	60	0	250
50	50	0	250
60	40	0	250
AIT [°C] at $P_{initial}$ = 5 bar abs for stoichiometric (with respect to CO_2 and H_2O-formation) Propene/O_2 mixtures, i.e. Propene:O_2 = 1 : 4.5			
4.46	20.07	75.47	280
7	31.5	61.5	270
10	45	45.0	270
AIT [°C] at $P_{initial}$ = 1 bar abs for stoichiometric (with respect to CO_2 and H_2O-formation) Propene/O_2 mixtures, i.e. Propene:O_2 = 1 : 4.5			
4.46	20.07	75.47	485 (CHEMSAFE, DIN-method in open Erlenmeyer flask)
7.0	31.5	61.5	410
10.0	45.0	45.0	310
15.5	70.0	14.5	290



Induction times of two mixture compositions lying in the yellow range of the explosion diagram at 5 bar abs





Calculation by A.A. Konnov,
Department of Mechanical Engineering
Vrije Universiteit Brussel (VUB),
based on the rate coefficients for all elementary reactions

Is “heat explosion” a realistic assumption for what happens in yellow range of the explosion triangle ?

- temperatures achieved by adiabatic compression lie well above the autoignition temperature, i. e. heat explosion is possible in principle

- **but:** induction times calculated on the basis of the rate coefficients of the elementary reactions are still far too long (The induction time would have to be of the order of 0.1 ms or even less, otherwise the flame front of the initial deflagration would have run already through the thin shell of unreacted mixture before the heat explosion can develop).

- including the influence of thermal radiation from the cental part of the sphere does not give a substancial reduction in induction times either (calculation of Hans Pasman)

⇒ Not really clear what happens in the yellow range of the explosion triangle

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Summary on explosion regimes of combustible/air/O_2 mixtures ignited with a thermal ignition source in vessel-like geometry

- There are three explosion regimes: deflagration, „heat explosion", detonation

- The detonative range in the 20 l sphere is discernibly smaller than the potentially detonative range

- What really happens in the „heat explosion" regime is not yet really understood, maybe the pressure time curves are just due to failed DDT's

- The „heat explosion" regime becomes much smaller with increasing initial pressure

- Mixtures of type combustible/air seem to remain deflagrative even at elevated pressures and temperatures.
  However, the data collected so far do not allow to exclude that the detonative regime will expand down to the air line when going to extremely high initial pressures and large vessel volumes.

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- Introduction
- Explosion characteristics
- Course of explosion in 20 l sphere
- **Pressure load P_{det} on the wall of the vessel**
  - quantification of P_{det} for four scenarios occuring in a pipe (no precompression)
  - quantification of P_{det} for four scenarios occuring in a pipe (with precompression)
  - quantification of P_{det} for Propene/O_2/N_2 in vessel at $P_{initial}$ = 5 bar abs, $T_{initial}$ = 20 °C
- Comparison: detonative regimes in 20 l vessels ↔ 100, 500, 2500 l vessels
- Predetonation distances of Propene/O_2 in tubes
- Did ignition source directly trigger a spherical detonation?

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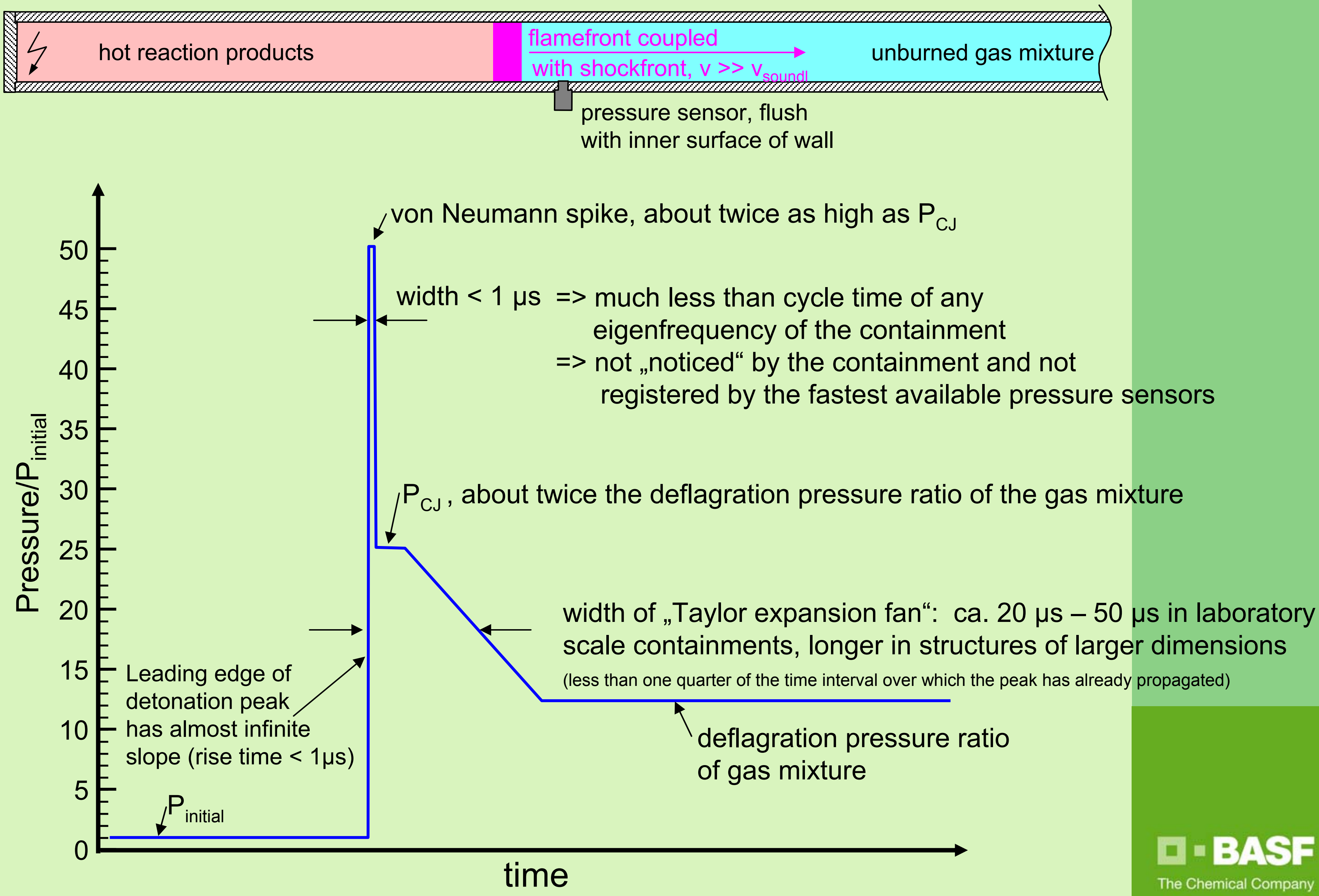
Schematic pressure-time trace of a detonative pressure pulse



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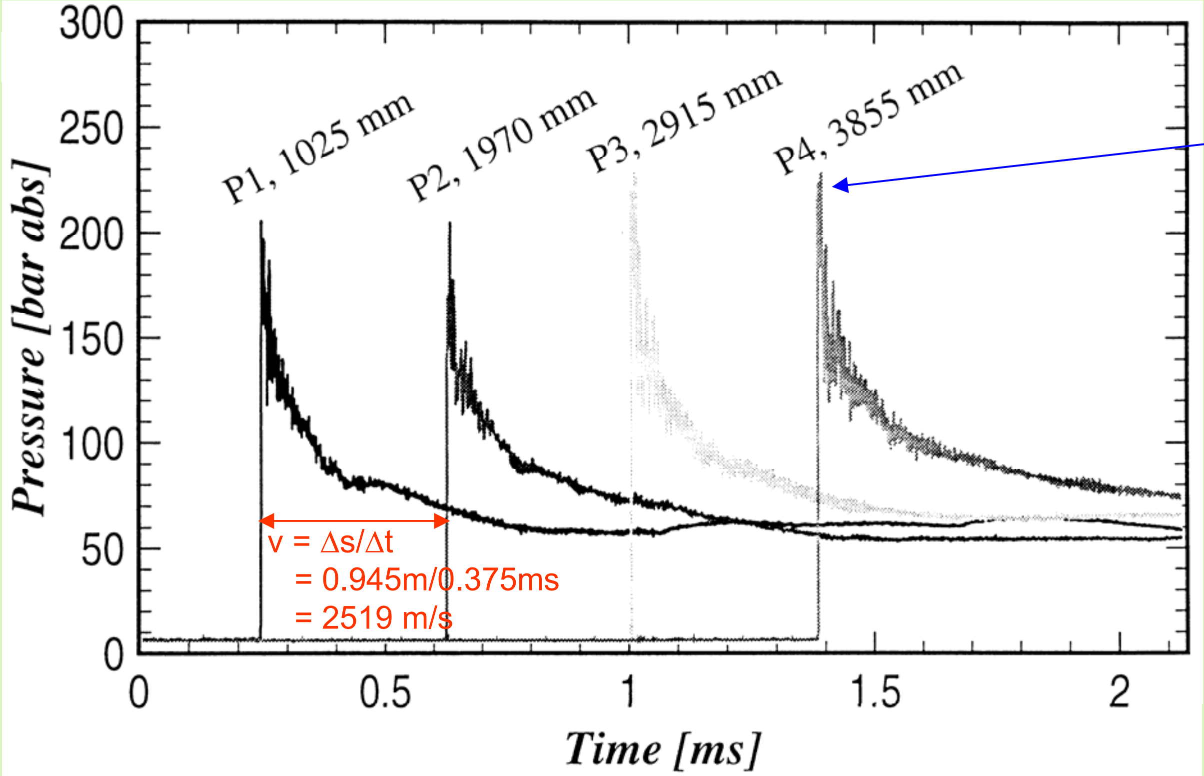
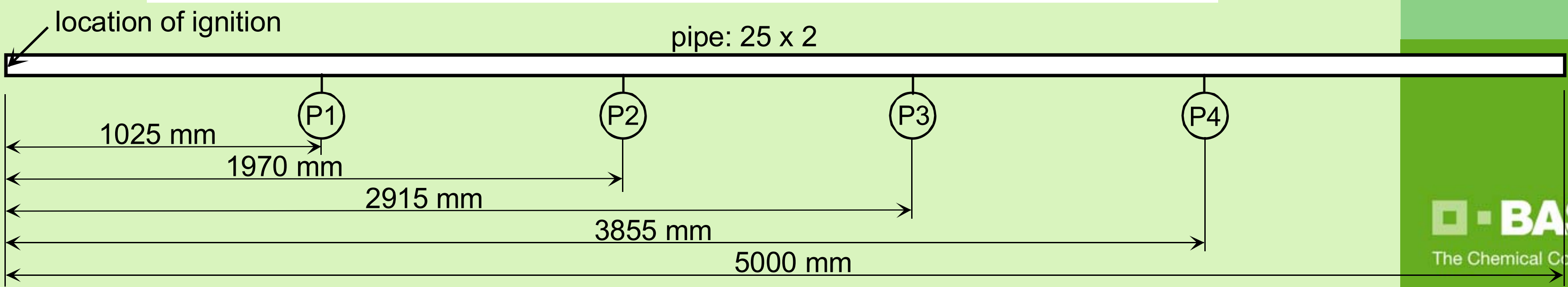
Pressure-time diagrams recorded during a detonation in a long pipe at different locations (1/2)

<u>Example:</u> Propane/O_2, stoichiometric, $P_{initial}$ = 6 bar abs, $T_{initial}$ = 20 °C, pipe 25x2, L = 5 m, side-on pressure



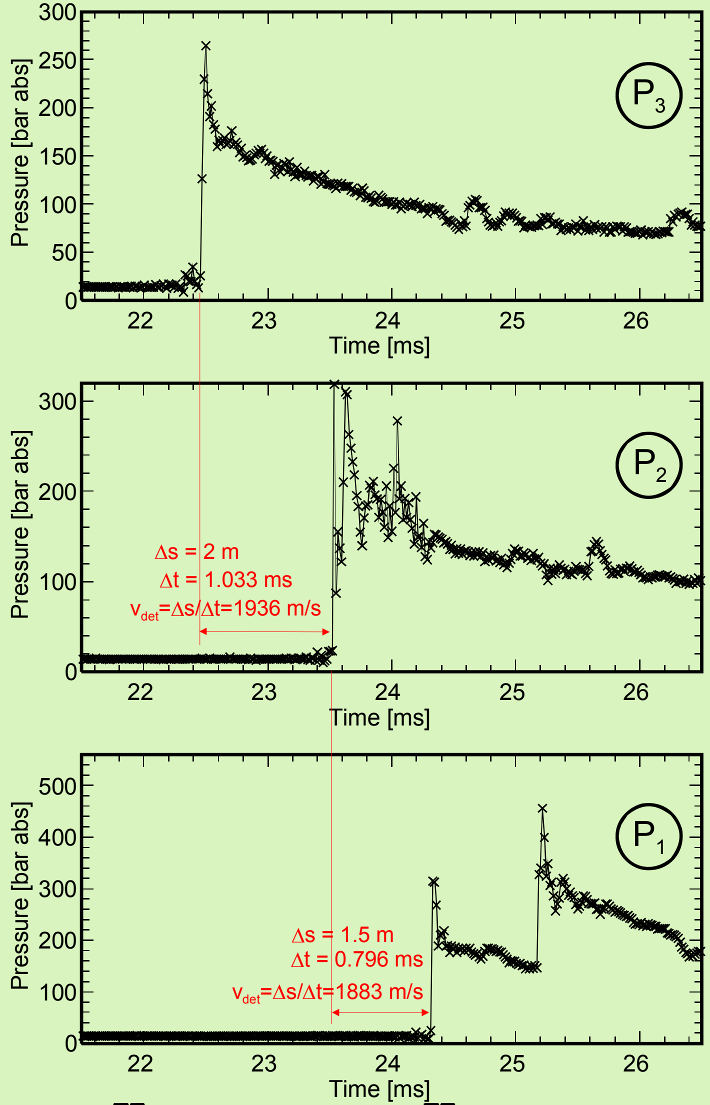
$P_{det} \cong 35*P_{initial}$

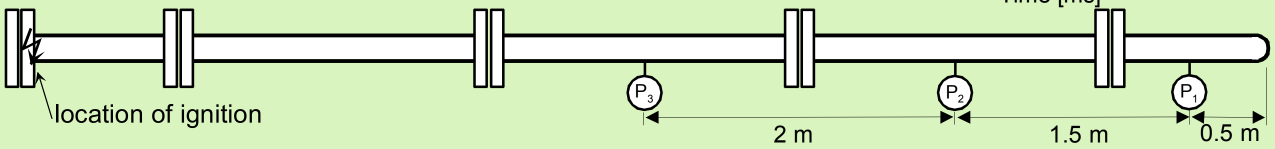
(same value at all sensors)



Pressure-time diagrams recorded during a detonation in a long pipe at different locations (2/2)

<u>Experiment:</u>
Ethylene/air stoichiometric, 14 bar abs, 20 °C, side-on pressure,
pipe: ϕ_i = 44.3 mm, ϕ_o = 48.3 mm,
L = 8 m,
turbulence enhancer in front of ignition source to reduce run-up distance





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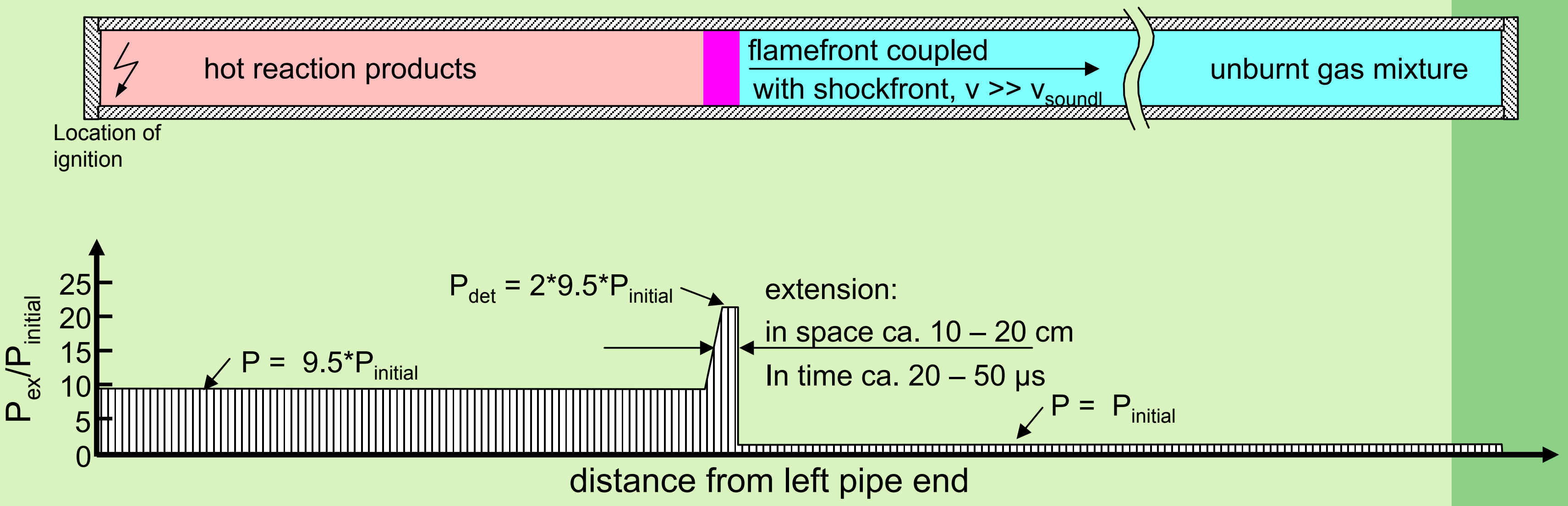
Qualitative consideration: differences between the pressures produced in a long pipe by a deflagration and by a detonation (2/2)

Example: Propane/air, stoichiometric, $T_{initial}$ = 20 °C, explosion pressure ratio: 9.5 (simplification: no heat loss to wall)

Detonative Explosion (predetonation stage necglected)

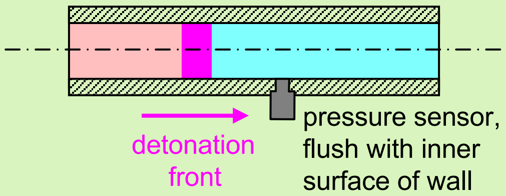


P is different at different locations in the pipe:

- behind shockfront: $P = 9.5*P_{initial}$ (9.5 is explosion pressure ratio of mixture)
- at shockfront: $P = 2*9.5*P_{initial}$ (i.e. about twice as high as behind shockfront)
- in front of shockfront: $P = P_{initial}$
  (reason: reaction gases would like to expand into region ahead of shockfront, but speed of sound in hot reaction gases only about 1000 m/s whereas shockfront propagates with about 1700 m/s)

Detonation pressures P_{det} in long pipes ($L \gg L_{predet}$, no precompression)

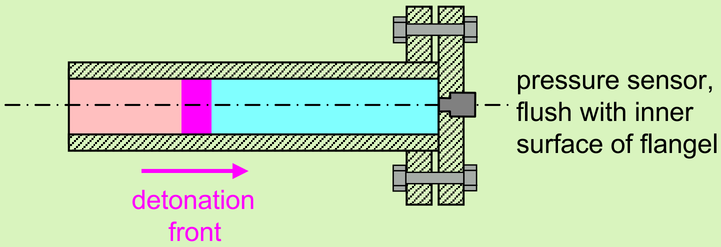
- **Stable Detonation, side-on pressure (i. e. in plane perpendicular to shockfront)**



$$P_{det} = P_{initial} * P_{CJ}$$

P_{CJ} is the so-called
Chapman-Jouguet-pressure ratio
of the explosive gas mixture

- **Stable Detonation, reflected pressure (i. e. in plane parallel to shockfront, e. g. blind flange)**



$$P_{det} = P_{initial} * P_{CJ} * F_{reflec}$$

$$2 \leq F_{reflec} \leq 2.5$$

Important:
The pipe directly ahead of the blind flange experiences the reflected pressure as well. The length of this section corresponds to the axial extension of the taylor expansion fan.
(In lab-scale equipment of up to 5 m length a section of about 3 pipe diameters from the blind flange back into the pipe is affected, in longer pipes this section increases).

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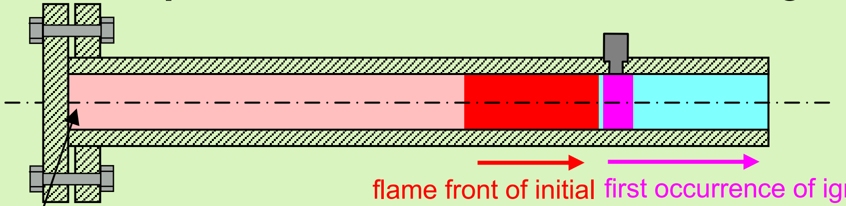
Detonation pressures P_{det} in long pipes ($L >> L_{predet}$, no precompression) (continued)

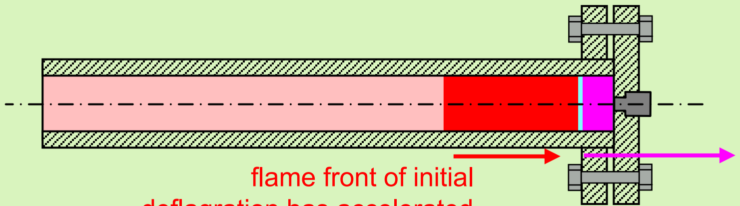
- **Side-on pressure at location where Deflagration-to-Detonation transition (DDT) occurs**



$$P_{det} = P_{initial} * P_{CJ} * F_{DDT}$$

$$1.5 \leq F_{DDT} \leq 2$$

- **Reflected pressure, if DDT occurs directly in front of blind flange (a very rare case!)**



$$P_{det} = P_{initial} * P_{CJ} * F_{DDT} * F_{reflec}$$

$$1.5 \leq F_{DDT} \leq 2$$

$$2 \leq F_{reflec} \leq 2.5$$

Important:
The pipe directly ahead of the blind flange experiences the reflected pressure as well. The length of this section corresponds to the axial extension of the taylor expansion fan.
(In lab-scale equipment of up to 5 m length a section of about 3 pipe diameters from the blind flange back into the pipe is affected, in longer pipes this section increases).

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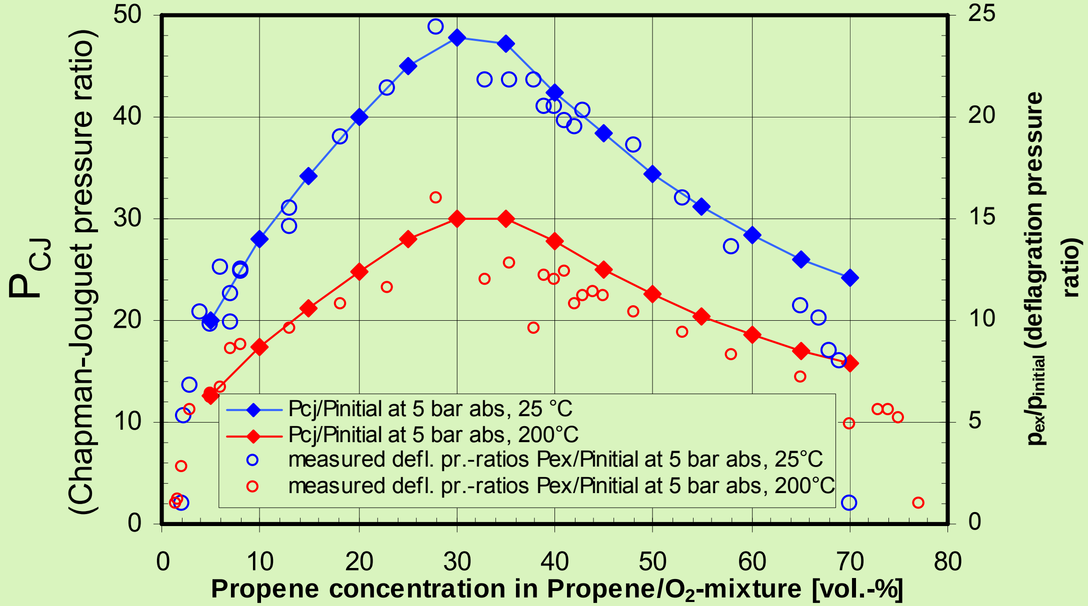
Chapman-Jouguet pressure ratios P_{CJ} calculated by STANJAN

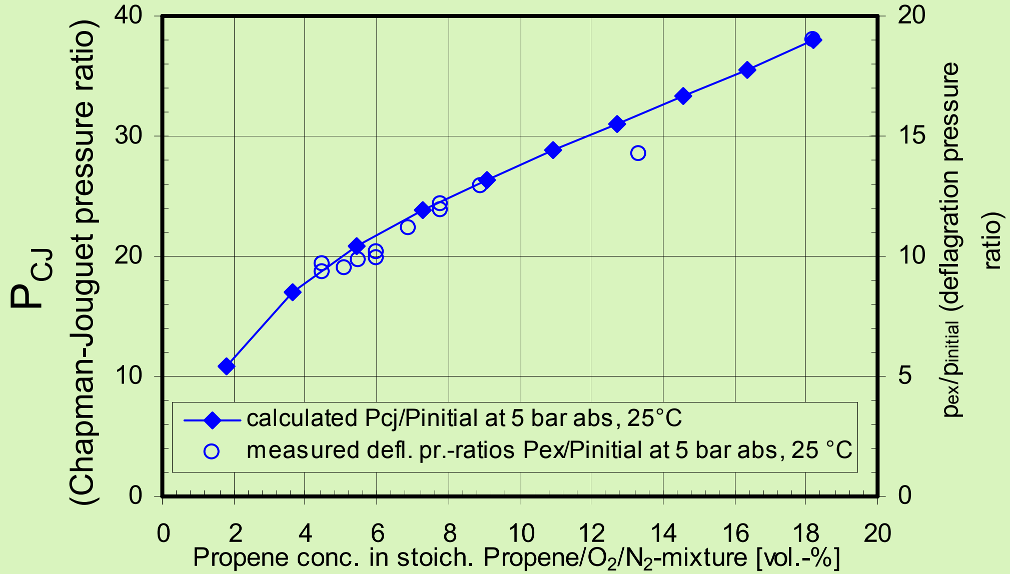
<u>Example:</u> Propene/O_2/N_2



<u>Solid lines:</u>
Calculated Chapman-Jouguet pressure ratios for $p_{initial}$ = 5 bar abs (by Prof. M. Braithwaite with software package STANJAN)

<u>Symbols:</u>
Measured deflagration pressure ratios (scale on right side of plots)

The values are just about half of the Chapman-Jouguet pressure ratios!!



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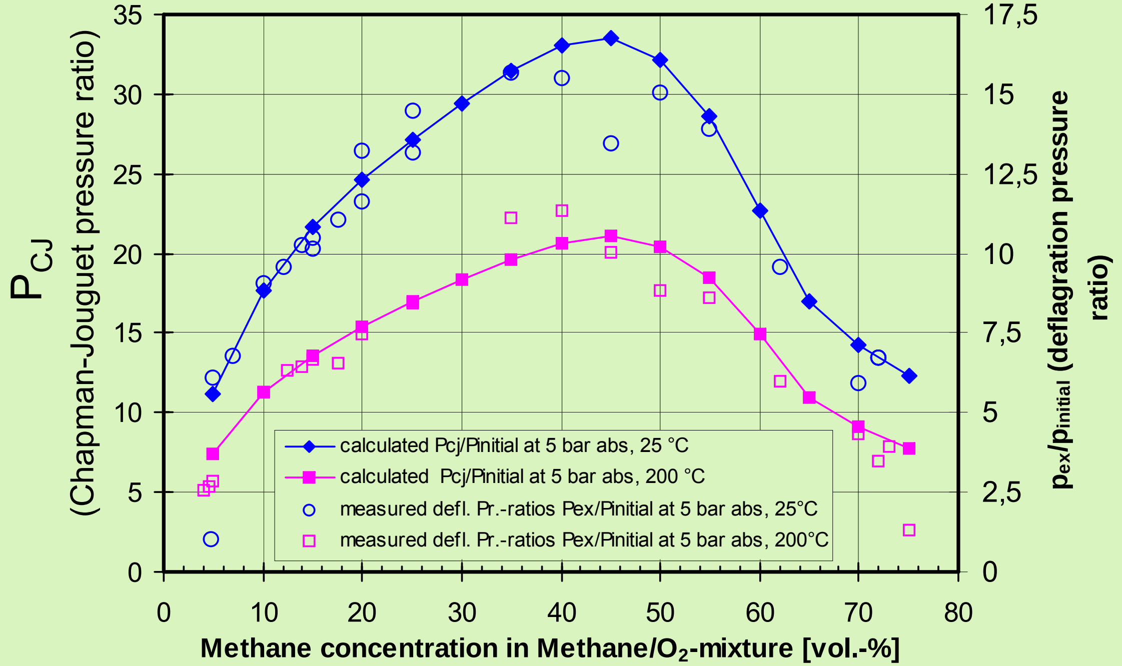
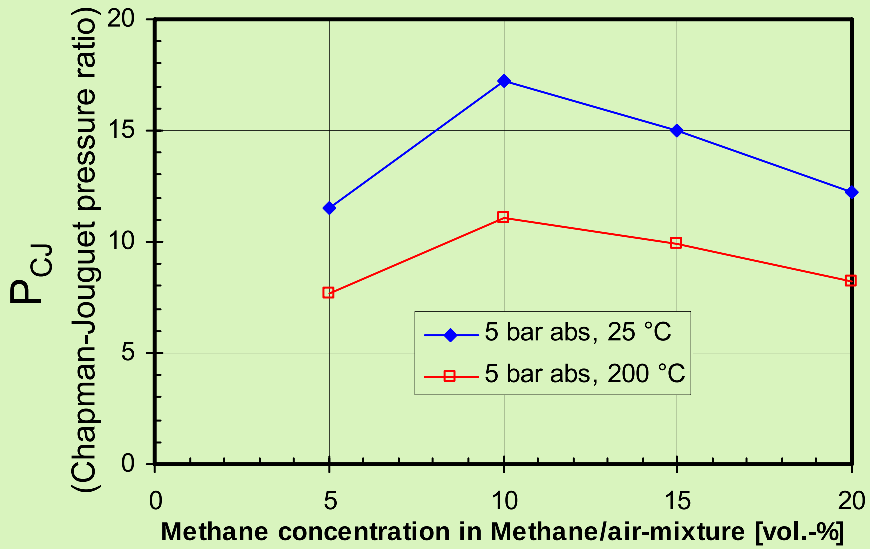
Chapman-Jouguet pressure ratios P_{CJ} calculated by STANJAN

Example: Methane/O_2/N_2





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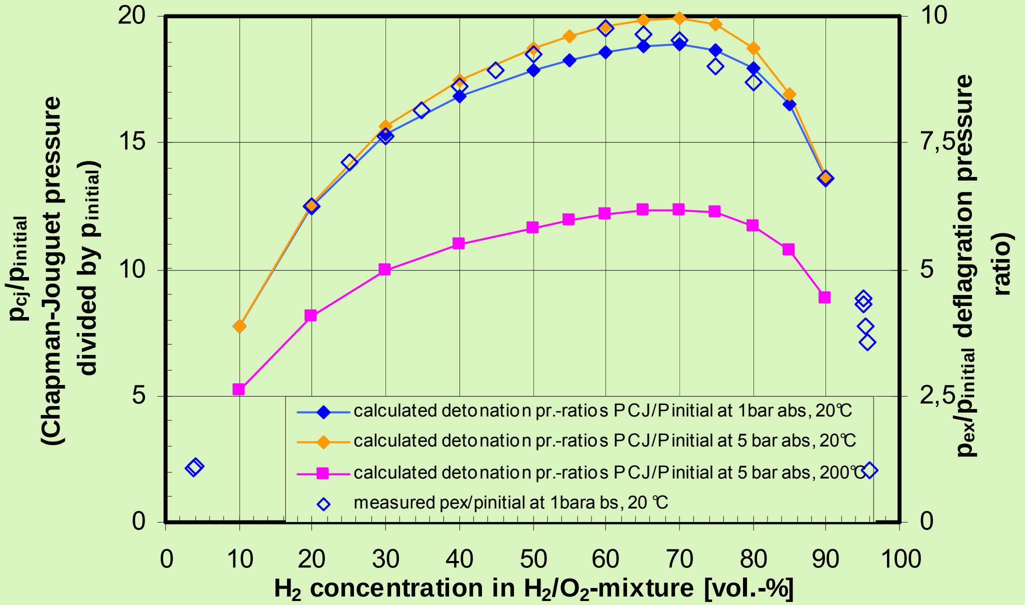
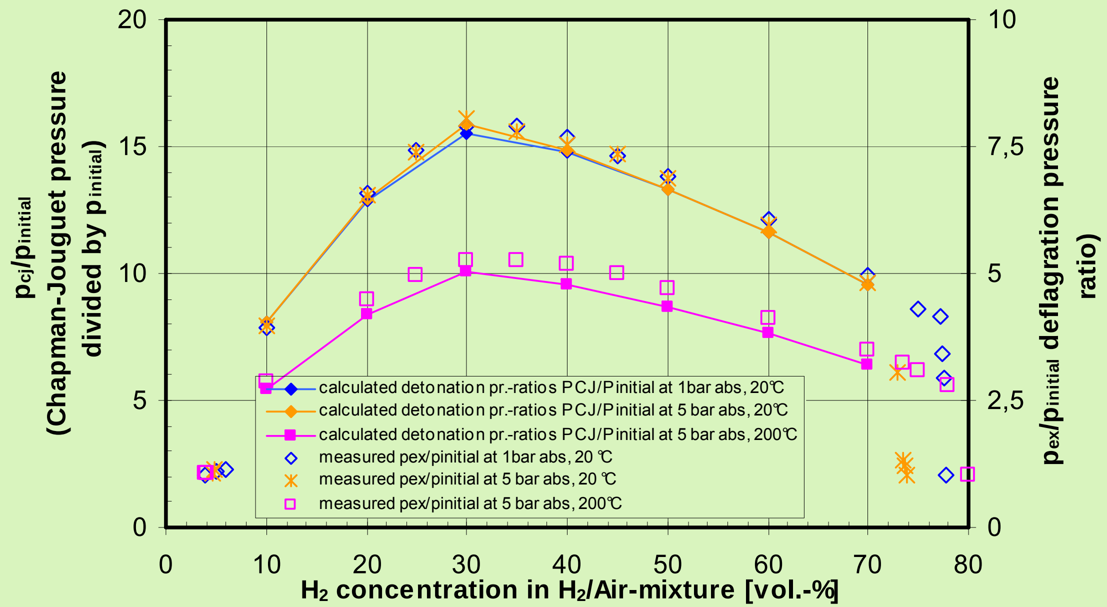
Chapman-Jouguet pressure ratios P_{CJ} calculated by STANJAN

Example: $H_2/O_2/N_2$





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Chapman-Jouguet pressure ratios P_{CJ} calculated on basis of detonation velocity

$$P_{CJ} = p_{det} / p_{initial} = (\gamma * M^2 + 1)/(\gamma + 1)$$

$$\approx (\gamma * M^2)/(\gamma + 1)$$

$$= (D^2 * MW)/(R * T_{initial} * (\gamma + 1))$$

$$= \rho / p_{initial} * D^2/(\gamma + 1)$$

meaning of symbols:

$M = D/c$	Mach number
D	propagation speed of detonation [m/s]
$c = (\gamma * p_{initial} / \rho)^{0.5}$	speed of sound in the unreacted gas mixture [m/s]
ρ	density of unreacted gas mixture [kg/m^3]
MW	mean molar mass of unreacted gas mixture [kg/mol]
R=8.314	universal gas constant [J/(mol*K)]
γ	c_p/c_v, for diatomic gases γ = 1.4
$T_{initial}$, $p_{initial}$	initial temperature [K], initial pressure [Pa] of gas mixture
p_{det}	side on pressure of stable detonation

Remarks:

For using STANJAN various thermodynamic parameters of the reaction components must be known. If these are not available, the detonation velocity is experimentally easily aminable with high precision by recording the side-on pressure of the propagating detonation at different axial locations in the pipe with piezoelectric pressure sensors. Since the absolute signal value, which is actually the quantity one is looking for, is often prone to errors, one has to use the „bypass“ over the speed.

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General remarks on Chapman-Jouguet pressure ratios P_{CJ}

- Chapman-Jouguet pressure ratios can be calculated by e.g. STANJAN (freeware, STANJAN Chemical Equilibrium Solver v4.01, Stanford University 2003)

- If thermodynamic quantities required by STANJAN are not available for all components of the considered explosive gas mixture, P_{CJ} can be calculated on the basis of the experimentally determined detonation speed.

- **Chapman-Jouguet pressure ratios are with good precision twice as high as the explosion pressure ratio found for deflagrative explosion:**
  - stoichiometric combustible/air- mixtures at 20°C: $16 \leq P_{CJ} \leq 20$
  - stoichiometric combustible/O_2-mixtures at 20 °C: $30 \leq P_{CJ} \leq 50$

- Chapman-Jouguet pressure ratio is inversely proportional to the absolute initial temperature. (Propagation speed of detonation is almost independent of $T_{initial}$!)

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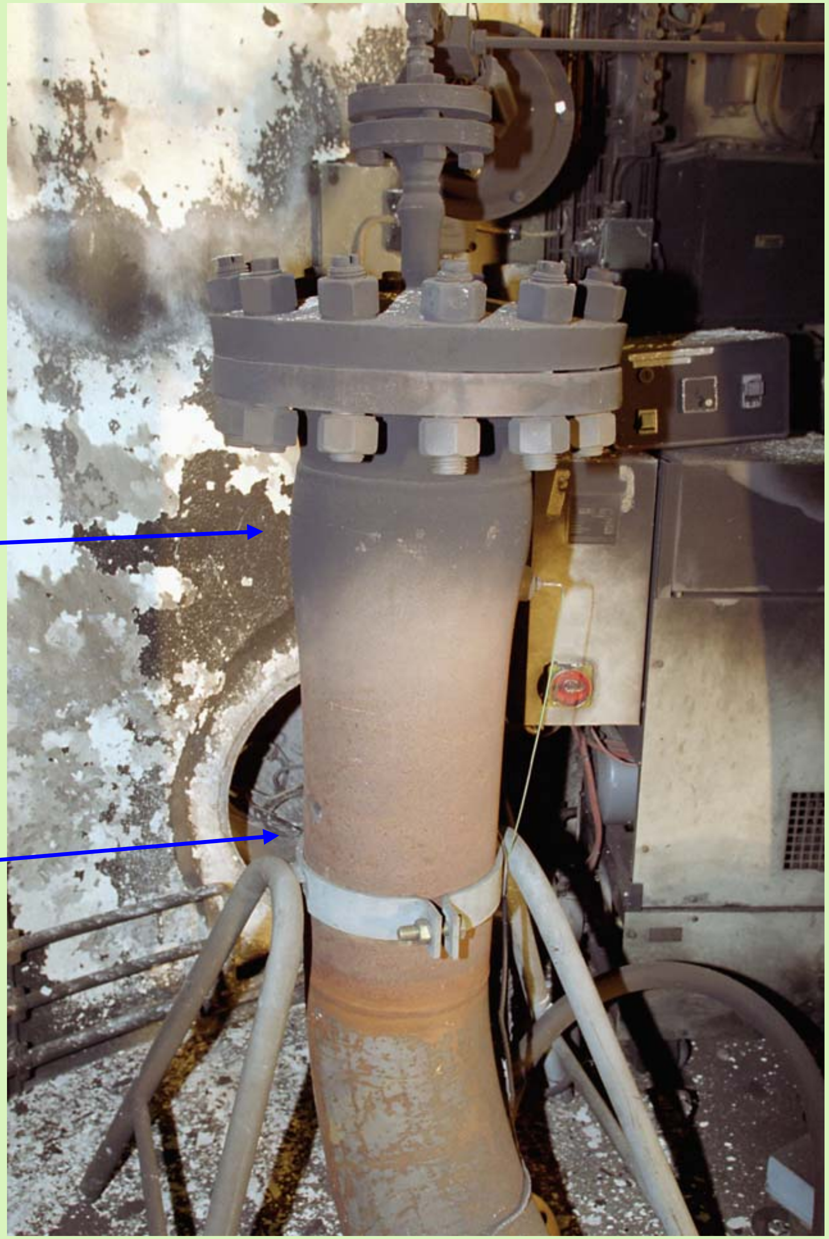
Example: bulging out of a pipe end due to reflected pressure

<u>Experiment:</u>
Acetylene, 8 bar abs, 20 °C, pipe 220.9 x 8.2, i.e. ϕ_i = 204.5 mm, material: St35.8, $R_{p0.2}$ = 230 N/mm^2, $P_{Rp0.2}$=184 bar, L = 8 m, detonative ignition source to reduce run-up distance;
side-on pressure ca. 400 bar,
reflected pressure ca. 800 bar

Increase of tube diameter directly in front of blind flange to 117 % of original value

no increase in diameter in the section that has only been exposed to the side-on pressure



Example: Rupture of pipe end due to reflected pressure

Experiment:
Ethylene/air stoichiometric, 17 bar abs, 20 °C, pipe 76.1 x 2.6, i.e. ϕ_i = 70.9, material: 1.4541, $R_{p0.2}$ = 210 N/mm^2, $P_{Rp0.2}$=154 bar, L = 8 m; side-on pressure ca. 340 bar, reflected pressure ca. 765 bar

increase in diameter to 105 % of original value in the section that has only been exposed to the side-on pressure

end of tube, which was exposed to the reflected pressure, is fragmented

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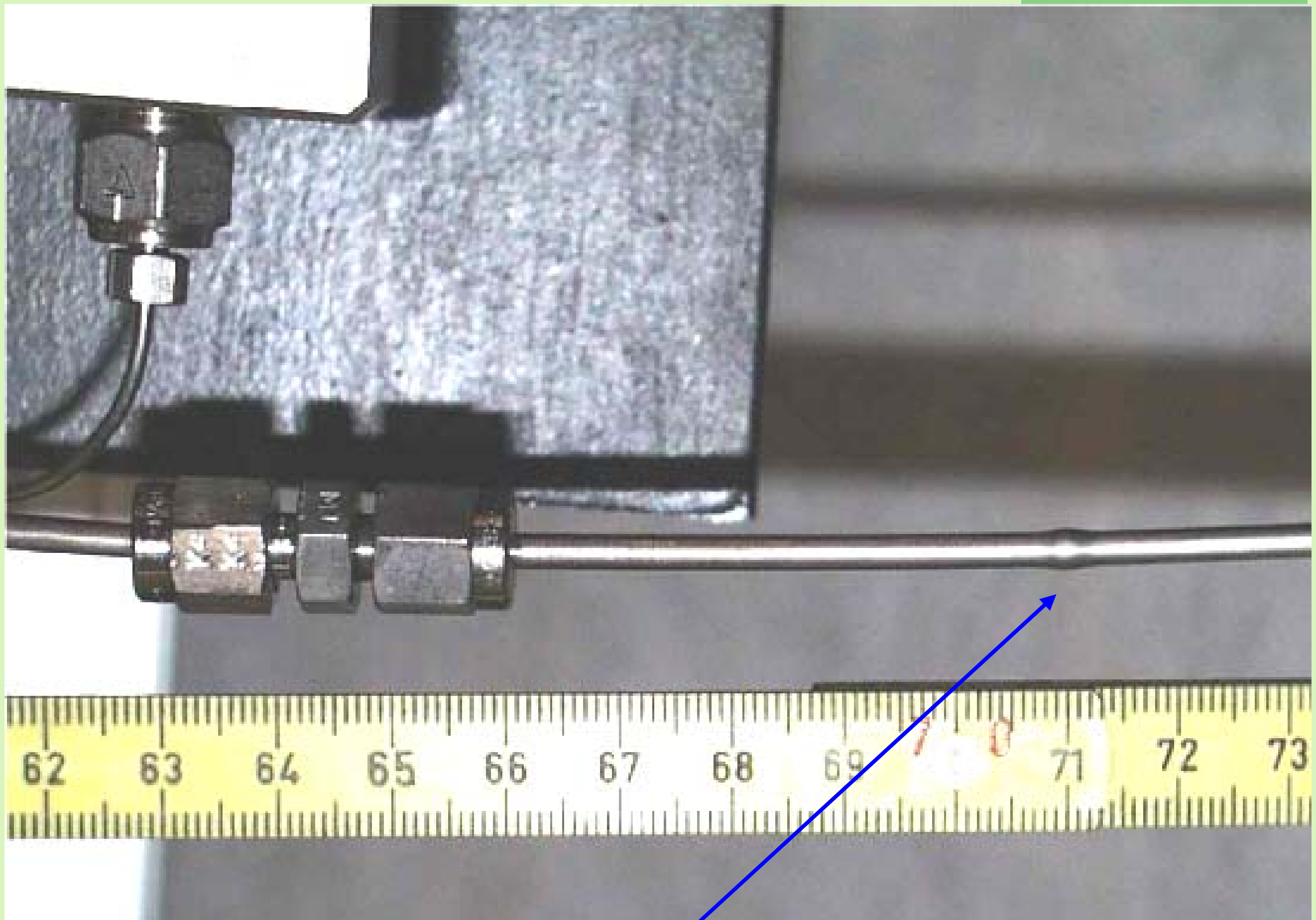
Example: bulging out of a pipe wall due to the extra pressure at the point where the DDT occurs

<u>Experiment:</u>
Acetylene, 24 bar abs, 20 °C, pipe 3.17 x 0.5, ϕ_i = 2.17 mm, material: 1.4541, $R_{p0.2} \geq 250$ N/mm^2, $P_{Rp0.2} \geq 1152$ bar, kaltgezogen, L = 10 m



Localized bulging of tube is attributed to the location of the deflagration to detonation transition

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  - quantification of P_{det} for four scenarios occuring in a pipe (with precompression)
  - quantification of P_{det} for Propene/O_2/N_2 in vessel at $P_{initial}$ = 5 bar abs, $T_{initial}$ = 20 °C
- **Comparison: detonative regimes**
  in 20 l vessels ↔ 100, 500, 2500 l vessels
- **Predetonation distances of Propene/O_2 in tubes**

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How does precompression („pressure piling“) come into existence?

During the initial deflagrative stage of the explosion each volume element that reacts through expands by a factor equal to the explosion pressure ratio at the expense of the volume available for the yet unreacted mixture.

If this volume is large compared to the volume occupied by the reaction gases formed during initial deflagrative stage, the pressure in the yet unreacted mixture will almost stay the same as at the moment of ignition ($P = P_{initial}$).

However, if this volume is small, the yet unreacted mixture will be precompressed. When the deflagration to detonation transition then occurs, the detonation will not propagate in a mixture at pressure $P = P_{initial}$, but at $P = F_{precomp} * P_{initial}$

$F_{precomp}$ may attain any value between 1 and the explosion pressure ratio of the gas mixture (up to 10 for combustible/air-mixtures, up to 24 for combustible/O_2-mixtures).

The temperature rise that comes along with the fast and hence adiabatic compression will slightly alleviate the detonative pressure P_{det}. This is accounted for by the Factor F_{temp} (details see next slide)

In the formulae given beforehand for P_{det}, $F_{precomp}$ and F_{temp} will appear as additional factors

Temperature factor F_{temp}

The temperature factor F_{temp} accounts for the reduction of the Chapman-Jouguet pressure ratio due to the rise in temperature of the unburned mixture brought about by the precompression during the initial deflagrative stage of the explosion.

I: Temperature T_{final} of unburned mixture attained by adiabatic compression:

$$T_{final} = T_{initial} \cdot \left(p_{final} \big/ p_{initial} \right)^{(\gamma-1)/\gamma} = T_{initial} \cdot F_{precomp}^{\;(\gamma-1)/\gamma}$$

with: $\gamma = c_p/c_v$ (γ = 1.4 for ideal gases)

$T_{initial}$ = temperature at moment of ignition

II: Chapman-Jouguet pressure ratio is inversely proportional to the temperature the gas mixture exhibits at the moment of detonation (here denoted by T_{final}).

F_{temp} results from the combined effect of **I:** and **II:**

$$F_{temp} = \frac{T_{initial}}{T_{final}} = \left(\frac{1}{F_{precomp}} \right)^{(\gamma-1)/\gamma}$$

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Temperatures obtainable by adiabatic compression

$P_{final}/P_{initial}$	$T_{initial}$ = 25 °C = 298 K: T_{final} [°C] for different values of $\gamma = c_p/c_v$			
	γ = 1,4	γ = 1,3	γ = 1,2	γ = 1,1
1,2	40,9	37,8	34,2	30,0
1,5	61,6	54,2	45,8	36,2
2	90,3	76,7	61,5	44,4
4	169,8	137,3	102,5	65,0
6	224,2	177,6	128,7	77,7
8	266,8	208,5	148,4	87,0
10	302,3	234,0	164,4	94,4
12	333,1	255,8	177,9	100,5
14	360,4	274,9	189,6	105,8
16	385,0	292,1	200,0	110,4
18	407,6	307,6	209,4	114,6
20	428,4	321,9	218,0	118,3
25	474,5	353,4	236,6	126,3
30	514,5	380,3	252,3	133,0
35	550,0	403,9	266,0	138,7
40	582,0	425,1	278,1	143,7
45	611,2	444,3	289,0	148,2
50	638,2	462,0	299,0	152,3

$P_{final}/P_{initial}$	$T_{initial}$ = 200 °C = 473 K: T_{final} [°C] for different values of $\gamma = c_p/c_v$			
	γ = 1,4	γ = 1,3	γ = 1,2	γ = 1,1
1,2	225,3	220,3	214,6	207,9
1,5	258,1	246,4	233,1	217,8
2	303,6	282,0	257,9	230,8
4	429,9	378,3	322,9	263,5
6	516,2	442,2	364,6	283,7
8	583,8	491,3	395,9	298,4
10	640,2	531,7	421,3	310,1
12	689,1	566,3	442,7	319,9
14	732,4	596,7	461,3	328,2
16	771,5	623,9	477,8	335,6
18	807,2	648,6	492,7	342,1
20	840,2	671,3	506,3	348,1
25	913,5	721,2	535,8	360,8
30	977,0	763,9	560,8	371,4
35	1033,2	801,4	582,5	380,5
40	1084,0	835,1	601,7	388,5
45	1130,5	865,6	619,1	395,6
50	1173,4	893,6	634,9	402,0

Formula for temperature increase due to adiabatic compression: $T_{final} = T_{initial} \cdot \left(p_{final} / p_{initial} \right)^{(\gamma-1)/\gamma}$

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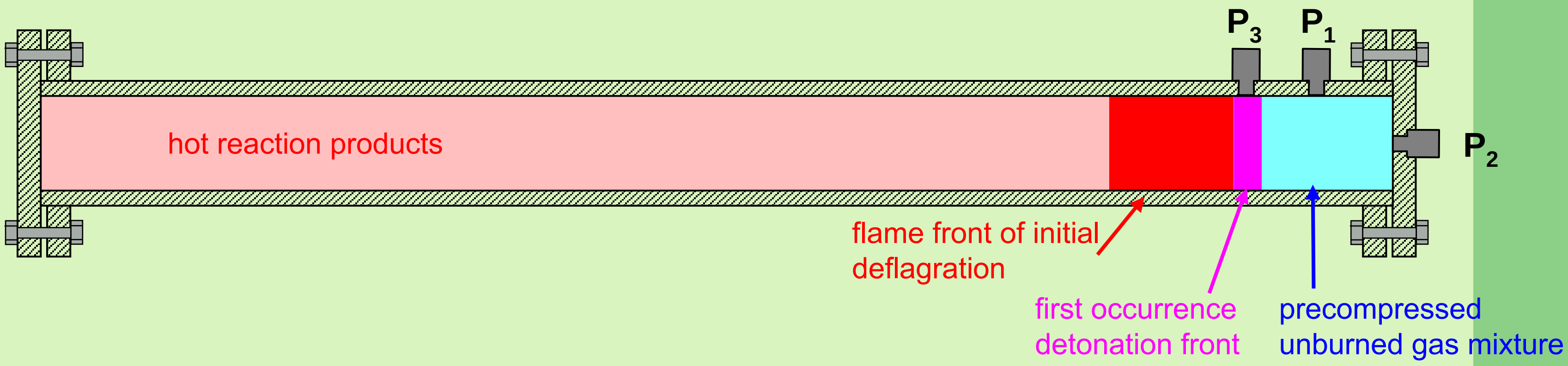
Example 1: precompression in a pipe

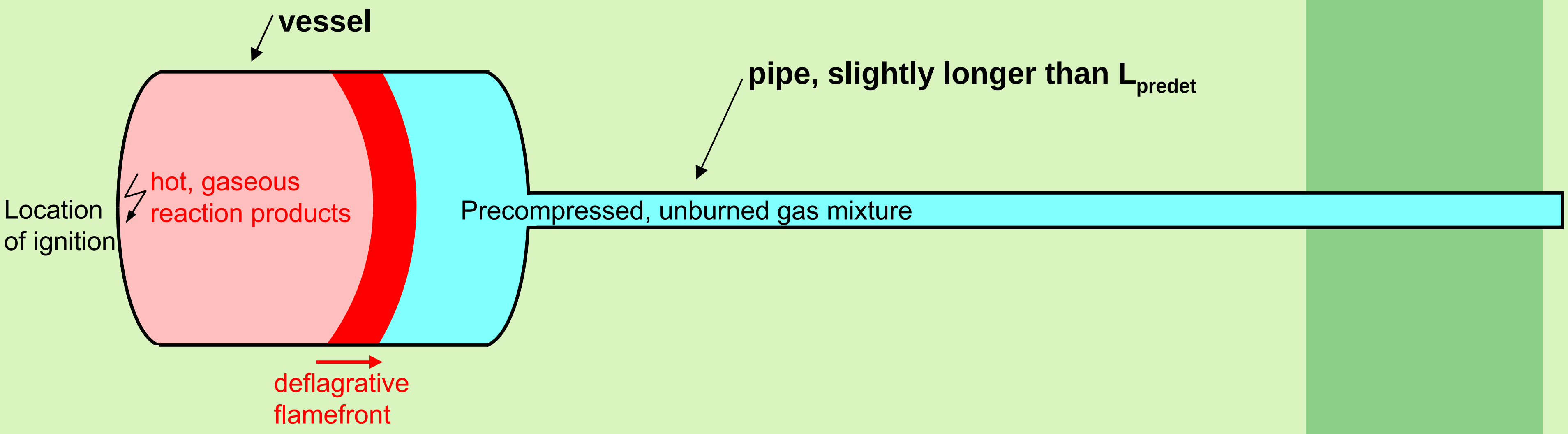


If the pipe is only slightly longer than the predetonation distance, the unburned gas which is remaining at the moment when the DDT occurs may have been precompressed by a factor $F_{precomp}$ by the initial deflagrative stage of the combustion.

$F_{precomp}$ may attain any value between 1 and the explosion pressure ratio of the gas mixture (up to 10 for combustible/air-mixtures, up to 24 for combustible/O_2-mixtures).

The temperature rise that comes along with the fast and hence adiabatic compression will slightly alleviate the detonative pressure P_{det}. This is accounted for by the Factor F_{temp}

Example 2: precompression in the vessel-pipe configuration



If in the vessel the DDT does not happen because of the unfavourable L/D-ratio and if the volume of the pipe is small compared to the volume of the vessel, the precompression factor may come close to the highest possible value, i. e. the explosion pressure ratio.
The highest possible value is usually not attained, because the available time is too short to pressurize the pipe up to the same pressure as in the vessel.

This configuration occurs frequently in practical applications, because vessels often have nozzles onto which short pipe segments with a block valve are welded.

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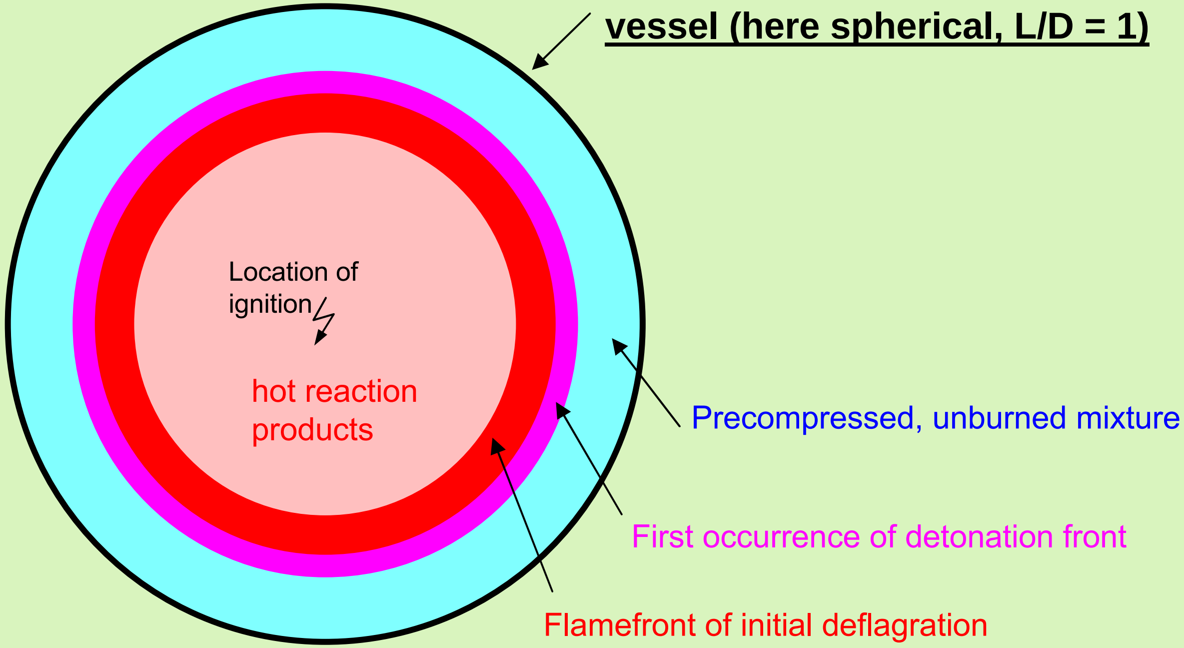
Example 3: precompression in empty vessels (i.e. without packing inside)

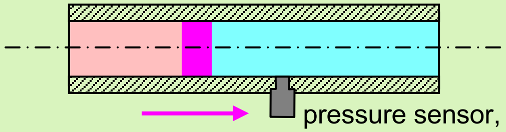


If there is a transition from deflagration to detonation in the vessel, precompression will almost always occur, because the diameter is usually not much larger than the predetonation distance. **The precompression factor may attain the highest possible value, i. e. the explosion pressure ratio.**

Reference: GCT report 105.0428.3N, 106.0104.3I

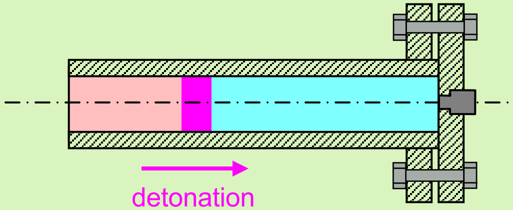
Detonation pressures P_{det} in pipes with precompression (1/2)

- **Side-on pressure (i. e. in plane perpendicular to shockfront)**



$$P_{det} = P_{initial} * P_{CJ} * F_{precomp} * F_{temp}$$

- **Reflected pressure (i. e. in plane parallel to shockfront, e. g. blind flange)**



$$P_{det} = P_{initial} * P_{CJ} * F_{reflec} * F_{precomp} * F_{temp}$$

Important:
about 3 pipe diameters from the blind flange back into the pipe this higher pressure also acts on the wall of the pipe!

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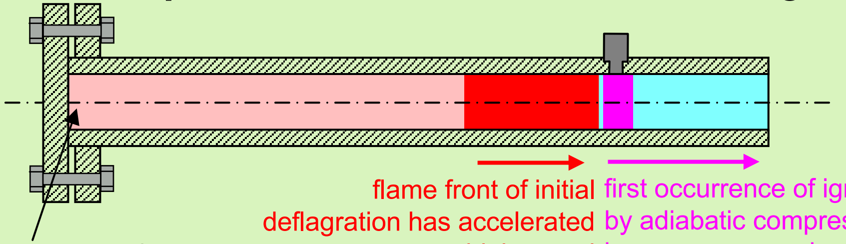
Detonation pressures P_{det} in pipes with precompression (2/2)

- **Side-on pressure at location where Deflagration-to-Detonation transition (DDT) occurs**



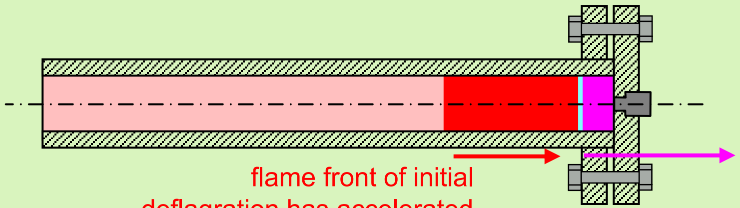
flame front of initial deflagration has accelerated to a very high speed

first occurrence of ignition by adiabatic compression in precompressed mixture; generation of shock front coupled with flame front, propagating leftwards

location of ignition

$$P_{det} = P_{initial} * P_{CJ} * F_{DDT} * F_{precomp} * F_{temp}$$

- **Reflected pressure, if DDT occurs directly in front of blind flange (a very rare case!)**



flame front of initial deflagration has accelerated to a very high speed

first occurrence of ignition by adiabatic compression in precompressed mixture; generation of shock front coupled with flame front, propagating leftwards

$$P_{det} = P_{initial} * P_{CJ} * F_{DDT} * F_{reflec} * F_{precomp} * F_{temp}$$

Important:
about 3 pipe diameters from the blind flange back into the pipe this higher pressure also acts on the wall of the pipe!

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Detonation pressure P_{det} acting on the wall of a vessel (almost always with precompression)

P_{det} = Initial pressure in vessel at moment of ignition ($P_{initial}$)

x Chapman-Jouguet pressure ratio of the mixture at the temperature the mixture exhibits at the moment of ignition (P_{CJ})

x Precompression factor ($F_{Precomp}$)

x Temperature factor (F_{Temp})

x Factor accounting for reflection of stable detonation at wall (F_{reflec})

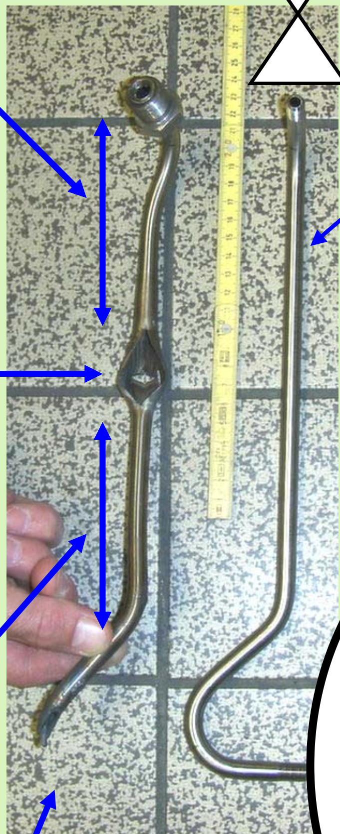
x Factor accounting for extra pressure if DDT happens directly before wall (F_{DDT}), otherwise factor is 1

$P_{det} = P_{initial} * P_{CJ} * F_{precomp} * F_{temp} * F_{reflec} * (F_{DDT}$ or 1, depending on where DDT happened**)**

Example: Rupture of the wall of a pipe installed in the vessel-pipe configuration due to precompression

closed Valve
(to vacuum pump)

detonation in this section,
outer diameter is 102 % to 110 % of original value



10x2 pipe (1.4541)
rupture pressure in hydraulic test: 3480 bar

rupture at location of DDT in precompressed mixture

only deflagration in this section,
outer diameter is not increased

Rest of the bend has been burned off by outflowing hot reaction gases

20 l sphere

$P_{initial}$ = 25 bar abs,
$T_{initial}$ = 250 °C

99.5 vol.-% N_2O
0.5 vol.-% Tetradecane

Ignition in center of sphere

- **Introduction**
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  - quantification of P_{det} for four scenarios occuring in a pipe (with precompression)
  - quantification of P_{det} for Propene/O_2/N_2 in vessel at $P_{initial}$ = 5 bar abs, $T_{initial}$ = 20 °C
- **Comparison: detonative regimes**
  in 20 l vessels ↔ 100, 500, 2500 l vessels
- **Predetonation distances of Propene/O_2 in tubes**

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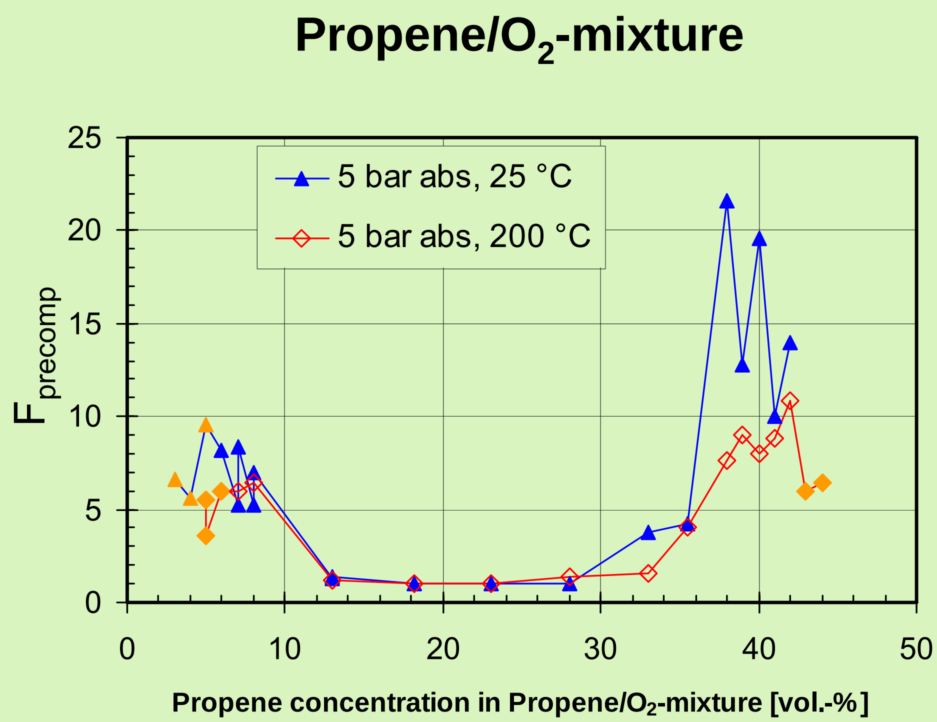
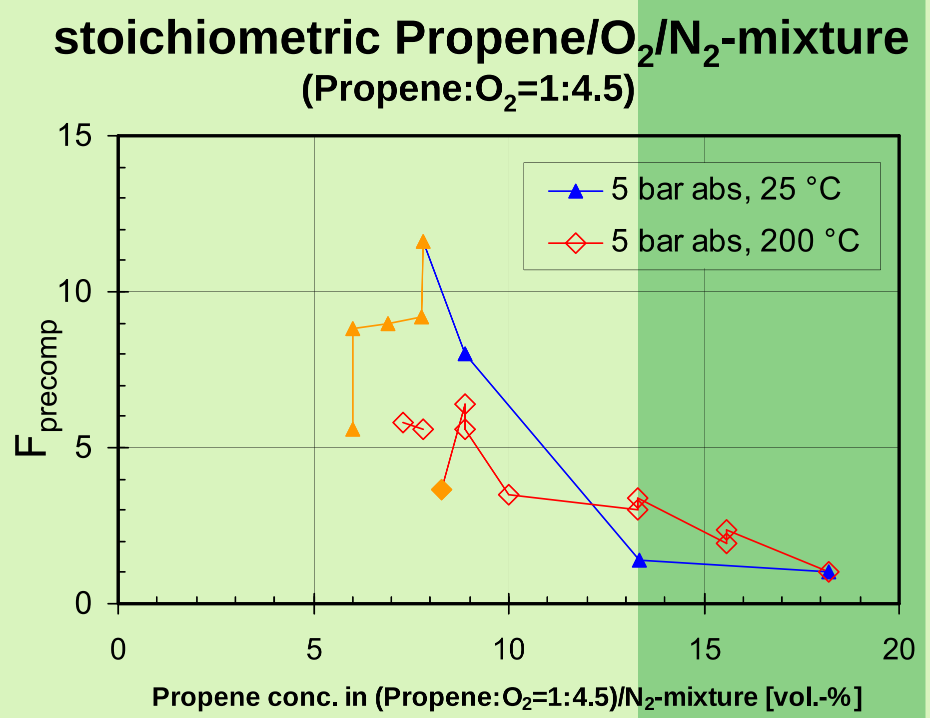
Precompression factors $F_{precomp}$ in the heat explosion and detonative range of explosion diagrams of Propene/O_2/N_2 at 5 bar abs, 25 °C and 200 °C





orange filled symbols: heat explosion
blue and red symbols: detonation

Note: on stoichiometric line at 200 °C only deflagration for one test with 7.8 vol.-% Propene

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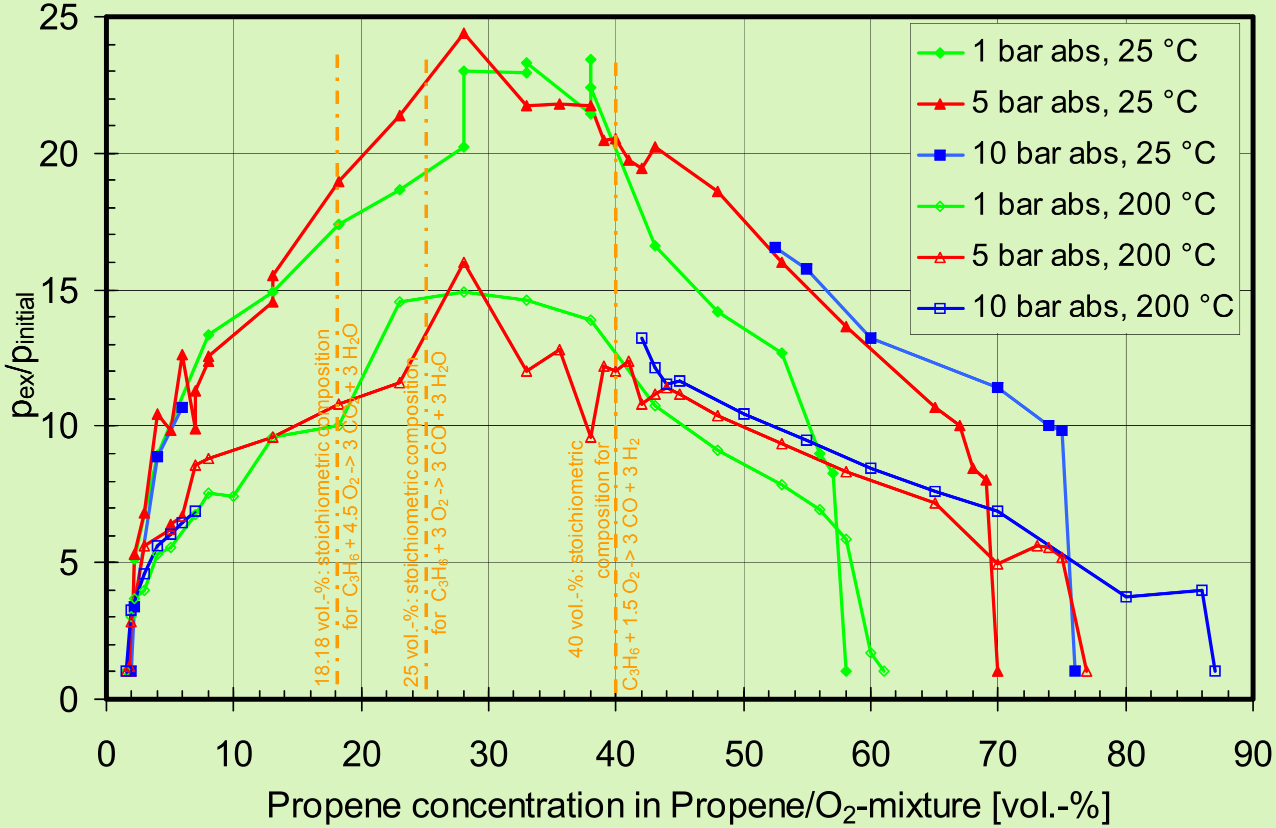
Upper limit for precompression factors

The precompression factors attain at maximum the deflagration pressure ratio!

Example for Propene/O_2-mixtures:



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Example: Detonative pressure pulses P_{det} acting on the wall of a 20 l sphere in case of Propene/O_2/N_2, $P_{initial}$ = 5 bar abs, $T_{initial}$ = 25°C

$$P_{\det} = 5 barabs \cdot 20 \cdot 10 \cdot \left(\frac{1}{10}\right)^{(1.4-1)/1.4} \cdot 2.25 \cdot 1.75 = 2039 barabs$$

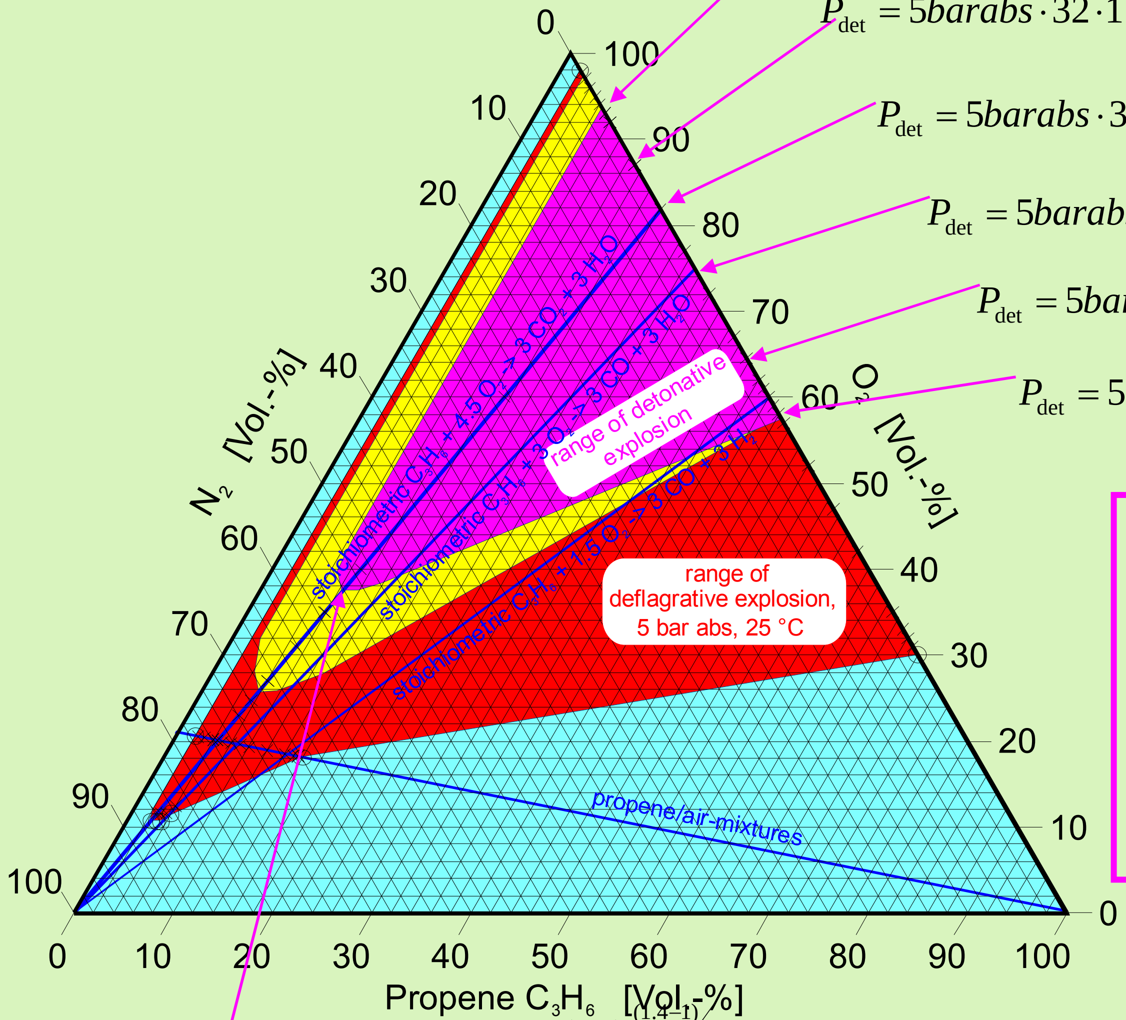
$$P_{\det} = 5 barabs \cdot 32 \cdot 1.1 \cdot \left(\frac{1}{1.1}\right)^{(1.4-1)/1.4} \cdot 2.25 \cdot 1 = 385 barabs$$

$$P_{\det} = 5 barabs \cdot 37 \cdot 1 \cdot \left(\frac{1}{1}\right)^{(1.4-1)/1.4} \cdot 2.25 \cdot 1 = 416 barabs$$

$$P_{\det} = 5 barabs \cdot 44 \cdot 1 \cdot \left(\frac{1}{1}\right)^{(1.4-1)/1.4} \cdot 2.25 \cdot 1 = 495 barabs$$

$$P_{\det} = 5 barabs \cdot 47 \cdot 4 \cdot \left(\frac{1}{4}\right)^{(1.4-1)/1.4} \cdot 2.25 \cdot 1 = 1627 barabs$$

$$P_{\det} = 5 barabs \cdot 40 \cdot 20 \cdot \left(\frac{1}{20}\right)^{(1.4-1)/1.4} \cdot 2.25 \cdot 1.75 = 6692 bara$$



$$P_{\det} = 5 barabs \cdot 27 \cdot 13 \cdot \left(\frac{1}{13}\right)^{(1.4-1)/1.4} \cdot 2.25 \cdot 1.75 = 3320 barabs$$

Pressure at border line of detonative range about factor 6 to 17 larger than in center because of precompression.

The highest value attainable by $P_{det}/P_{initial}$ is about 1300 !!

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Summary concerning pressure load

- Pressures acting on the wall may be a factor 1300 higher than the initial pressure in the mixture. The main reason is that in vessels the highest theoretically possible precompression factors (=deflagration pressure ratios) actually do occur !!

- Pressure at the border line of detonative range about factor 6 to 17 larger than in center because of precompression!
(I.e. in the detonative regime the lowest pressure load on the wall is generated by mixtures in the vicinitiy of the stoichiometric combustible/O_2-mixtures)

- The „obscure“ effects talked about in non-public communication seem to be explainable with precompression

- Since in the empty vessel the static equivalent pressure P_{stat} of the detonative pressure pulse P_{det} is at least $0.5*P_{det}$, the lower limit for the required pressure resistance of a detonation pressure proof empty vessel is known.
Since this lower limit is extremely high,it is questionable whether the design of a detonation pressure proof empty vessel is economically justifiable.

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  - quantification of P_{det} for four scenarios occuring in a pipe (with precompression)
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- **Comparison: detonative regimes in 20 l vessels ↔ 100, 500, 2500 l vessels**
- **Predetonation distances of Propene/O_2 in tubes**
- **Did ignition source directly trigger a spherical detonation?**

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Vessels used for the experiments

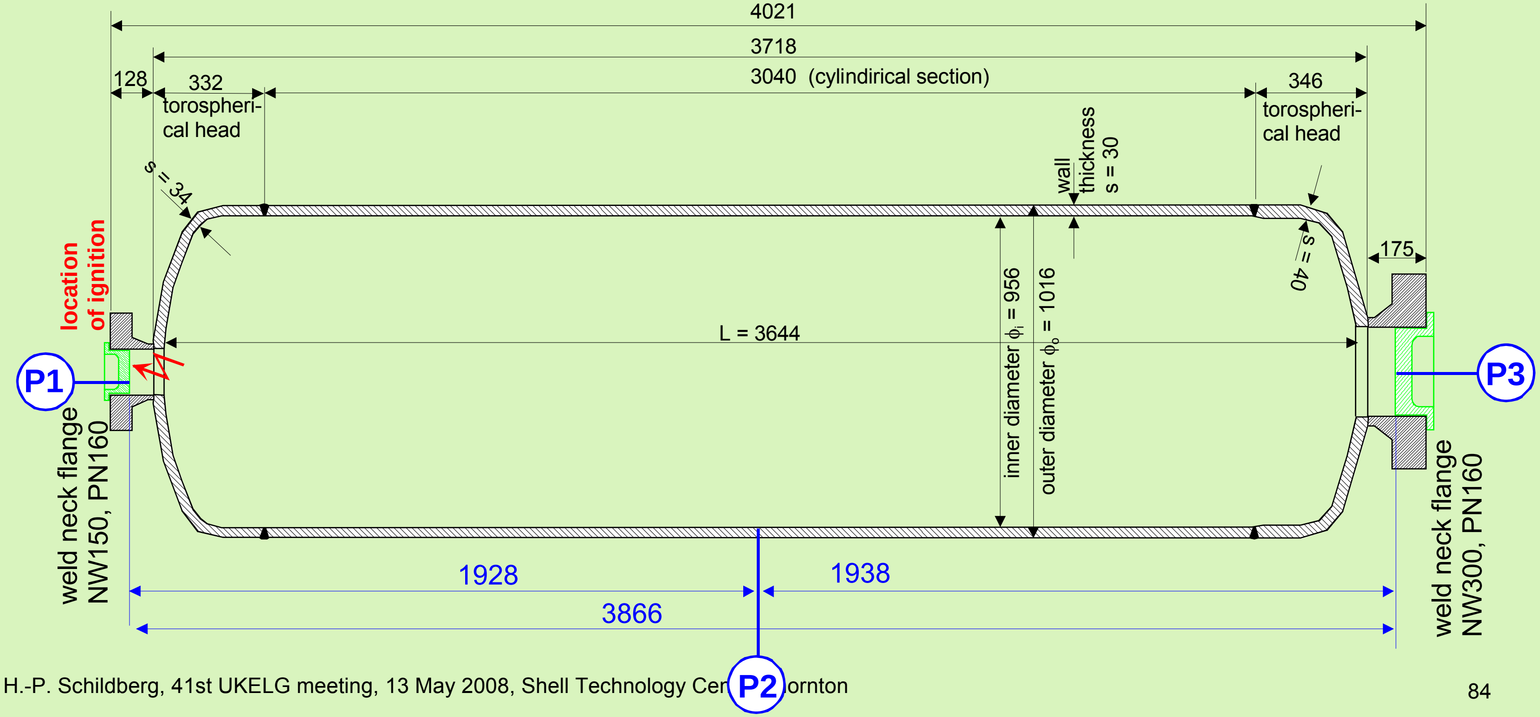
Characteristic parameters of all vessels:

100 l vessel: L = 1309 mm; ϕ_i = 327.2 mm; L/ ϕ_i =4.0; distance P1-P3 = 1343 mm

500 l vessel: L = 2146 mm; ϕ_i = 570 mm; L/ ϕ_i =3.76; distance P1-P3 = 2309 mm

2500 l vessel: L = 3644 mm; ϕ_i = 956 mm; L/ ϕ_i =3.8; distance P1-P3 = 3866 mm

Sketch of 2500 l vessel (the others are alike, only smaller):



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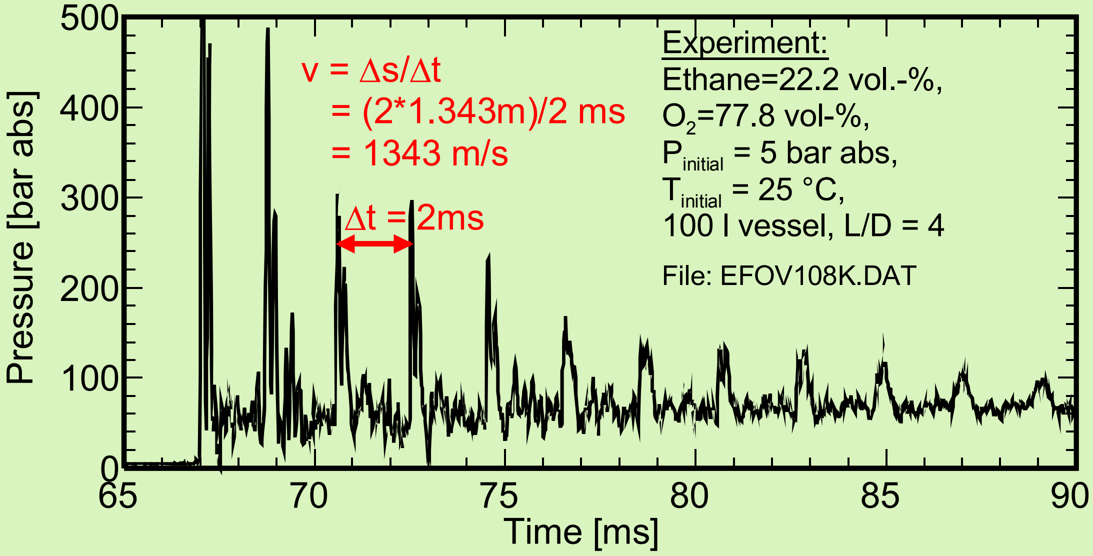
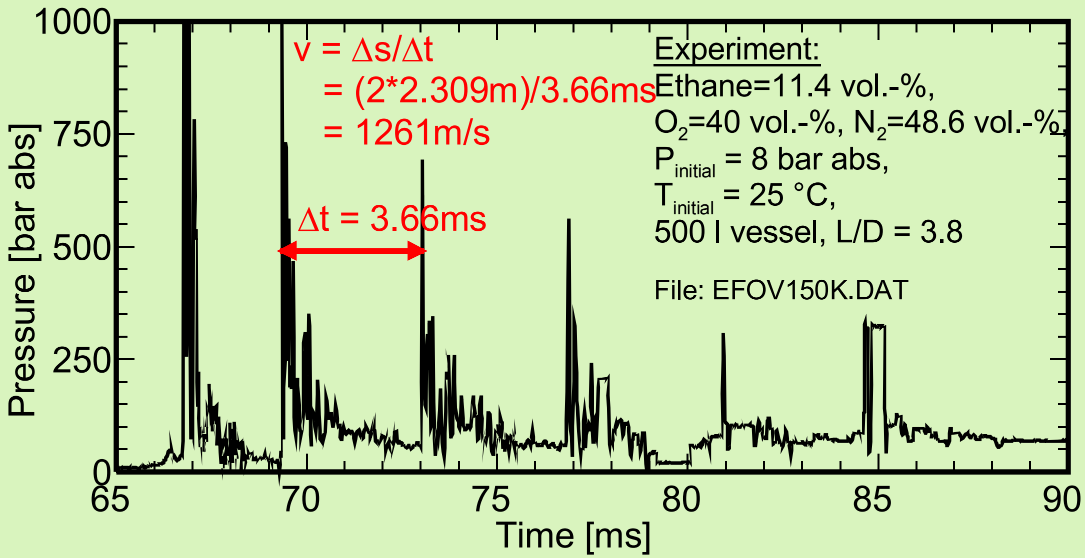
Examples for pressure/time recordings by sensor P3 in 100 l and 500 l vessel





The peaks are due to the shockwave of the detonation which after having reached the one end of the vessel is reflected backwards into the hot reaction gas, travels until reaching the opposite torospherical head of the vessel, is again reflected and so on

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Results of tests with stoichiometric Ethane/O_2/N_2-mixtures in vessels ranging from 20 l to 2500 l

Tests with $P_{initial}$ = 4 bar abs

O_2-conc. in stoichiometric mixture [vol.-%]	course of explosion	
	20 l sphere	2500 l cylinder, L/D=3.8
30	deflagrative	deflagrative
35	heat explosion	
40	detonative	detonative

Tests with $P_{initial}$ = 8 bar abs

O_2-conc. in stoichiometric mixture [vol.-%]	course of explosion		
	20 l sphere	100 l cylinder, L/D=4	500 l cylinder, L/D=3.76
30	deflagrative	deflagrative	deflagrative
35	detonative		
40	detonative	detonative	detonative

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Summary of comparison of explosive regimes of combustible/O_2/N_2 mixtures in vessels of different volume

- For stoichiometric mixtures there is - within experimental accuracy - no change in the critical composition (transition from deflagrative to detonative combustion) when varying the vessel volume over two orders of magnitude !!!

- For combustible/O_2 mixtures the potential change of the critical compositions with vessel volume could not yet be studied.

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- **Introduction**

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- **Course of explosion in 20 l sphere**

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  - quantification of P_{det} for four scenarios occuring in a pipe (with precompression)
  - quantification of P_{det} for Propene/O_2/N_2 in vessel at $P_{initial}$ = 5 bar abs, $T_{initial}$ = 20 °C

- **Comparison: detonative regimes in 20 l vessels ↔ 100, 500, 2500 l vessels**

- **Predetonation distances of Propene/O_2 in tubes**

- **Did ignition source directly trigger a spherical detonation?**

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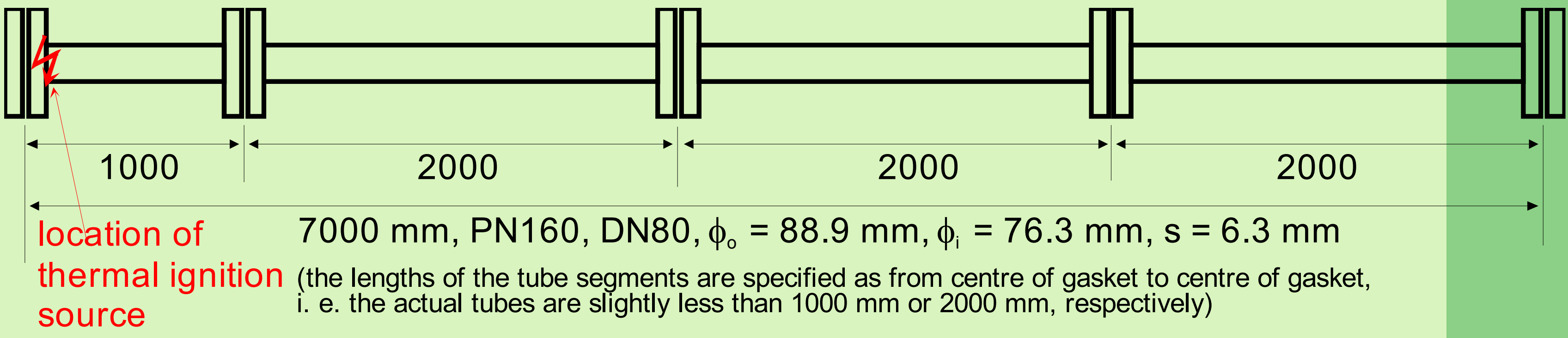
Experimental setup to determine predetonation distances of Propene/O_2-mixtures in a ϕ_i = 76.3 mm pipe at $p_{initial}$ = 5 bar abs, 25°C



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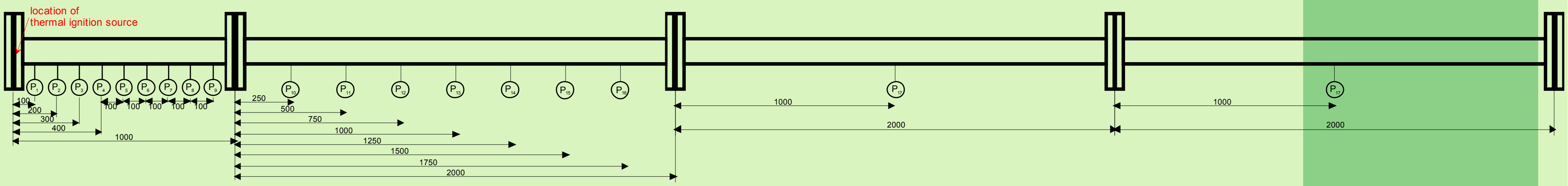
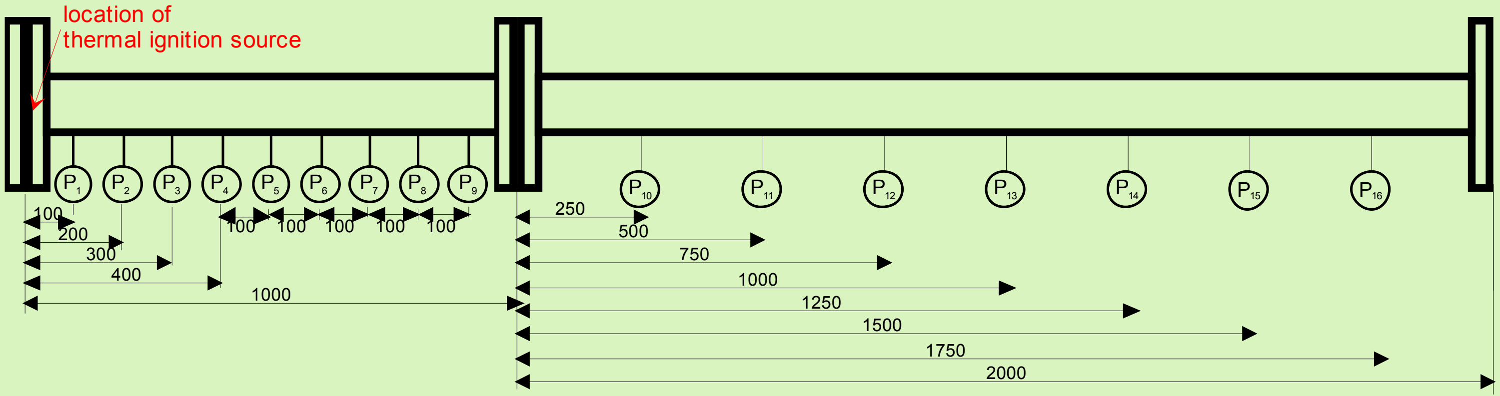
Position of pressure sensors in the ϕ_i = 76.3 mm pipe



Enlarged section of first two pipe segments:



Pressure sensors used (all piezoelectric, supplied by PCB):

PCB M112A05, 0 - 345 bar, ca. 16 pC/bar
PCB M113A03, 0 - 1034 bar, ca. 5 pC/bar
PCB M119A11, 0 - 5520 bar, ca. 3.6 pC/bar

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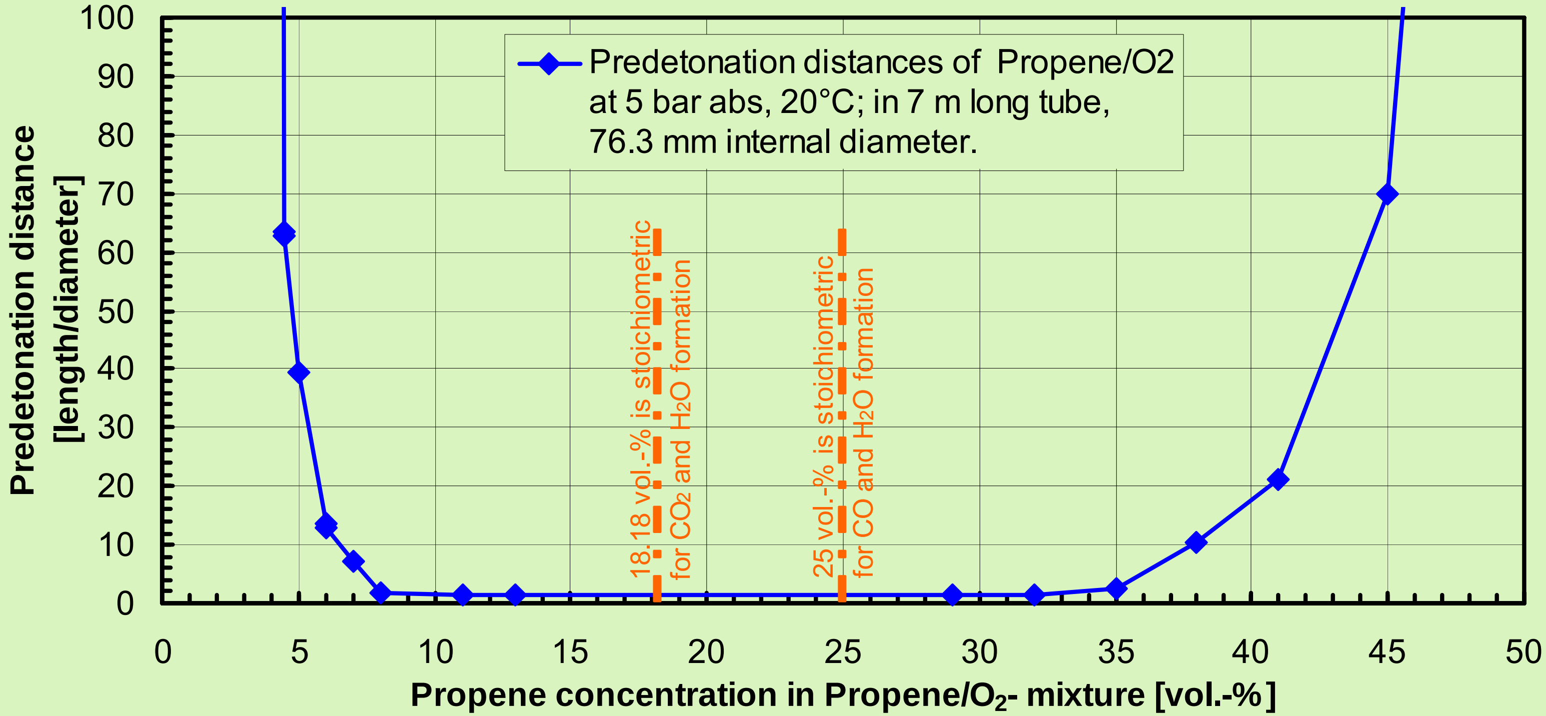
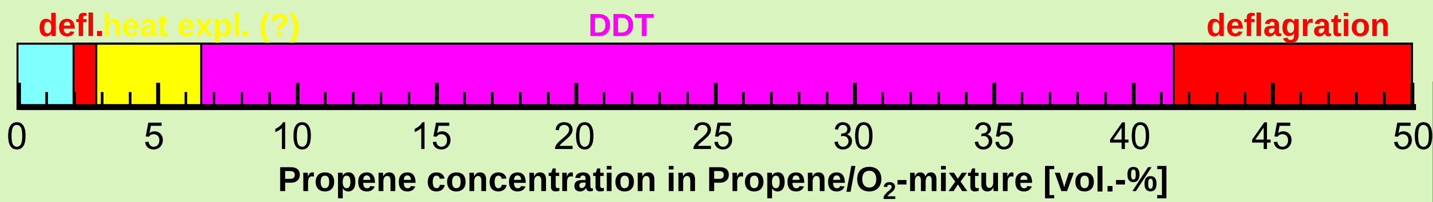
Predetonation distances of Propene/O_2 in a ϕ_i = 76.3 mm pipe at 5 bar abs, 20 °C

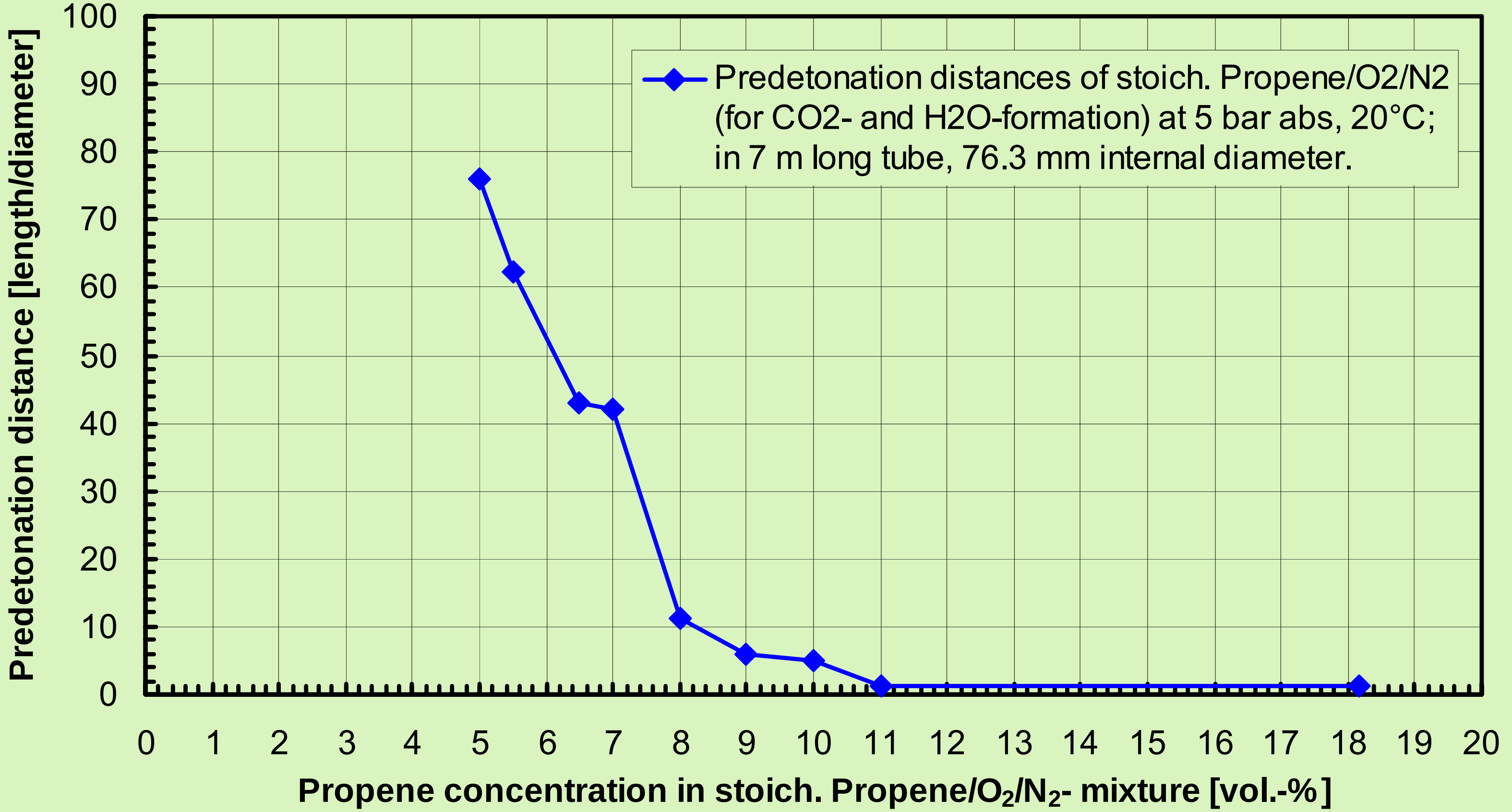


Course of explosion in 20 l sphere, ϕ_i = 340 mm:

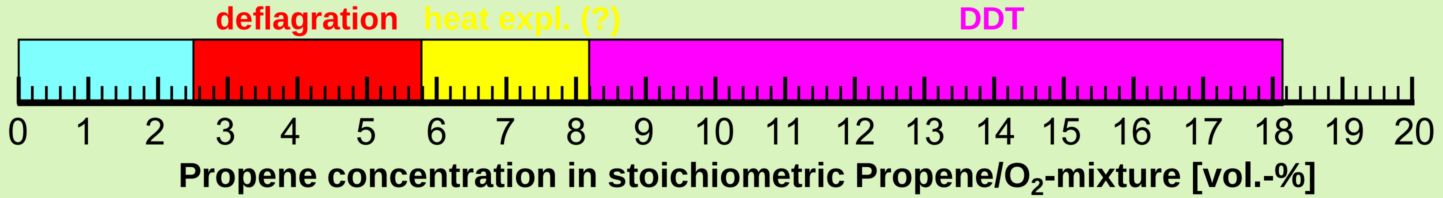


Note: in 7 m long pipe with ϕ_i = 76.3 mm no DDT for Propene conc. ≤4 vol.-% (i.e. predet.distance > L/D=92)
in 11 m long pipe with ϕ_i = 86 mm no DDT for Propene conc. ≥50 vol.-% (i.e. predet.distance > L/D=127)

Predetonation distances of stoichiometric Propene/O_2/N_2 in a ϕ_i = 76.3 mm pipe at 5 bar abs, 20 °C



Course of explosion in 20 l sphere, ϕ_i = 340 mm:



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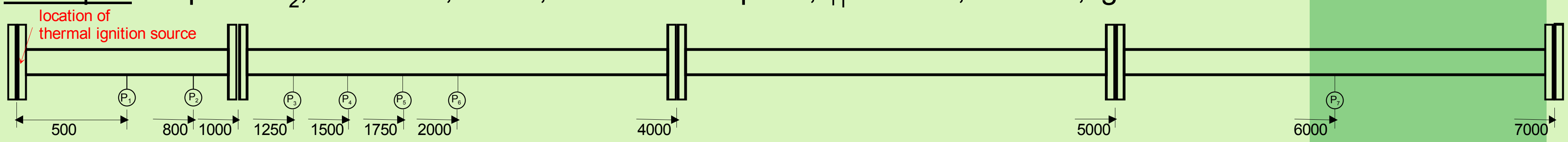
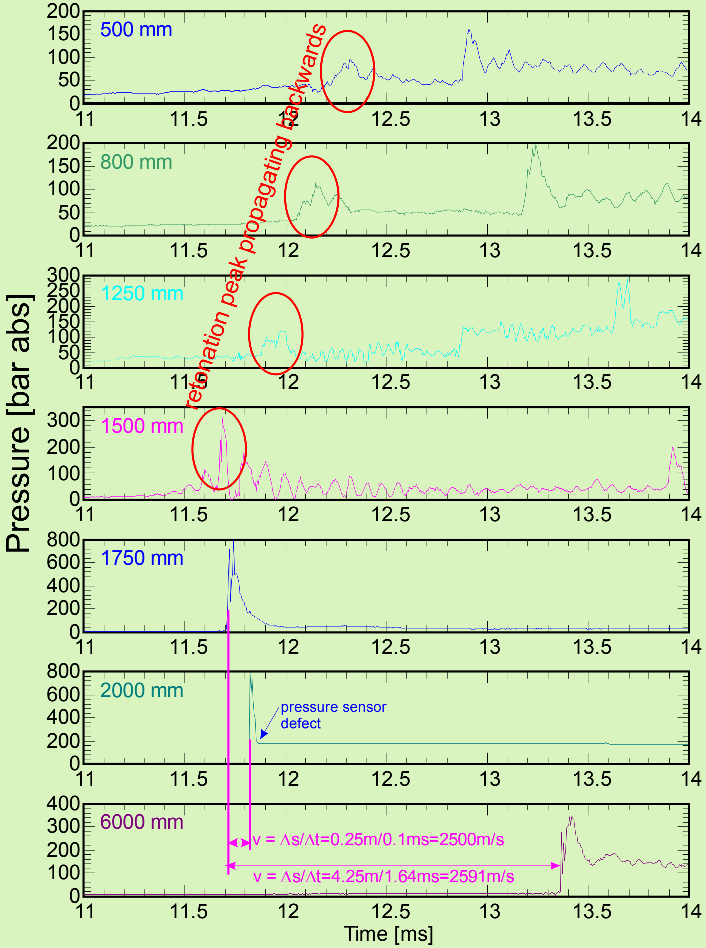
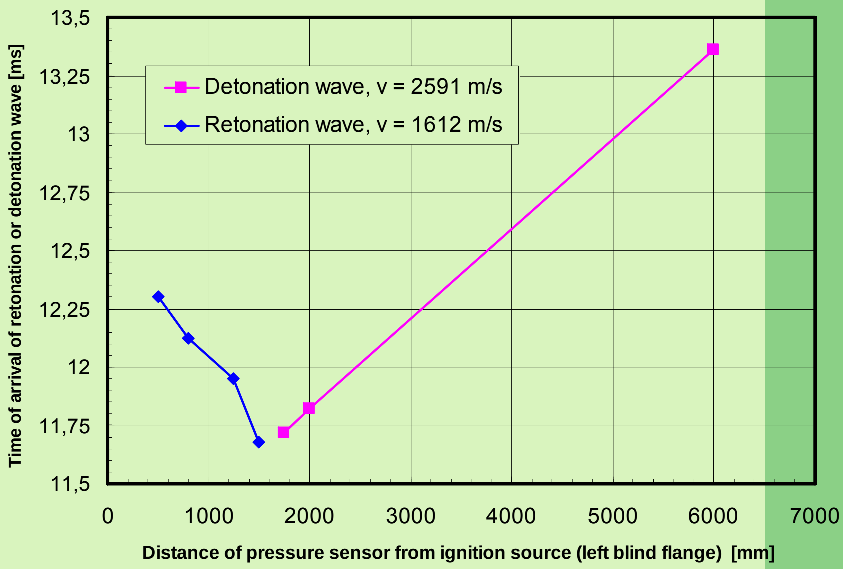
Example for how to determine the predetonation distance in pipes from pressure/time diagrams

Example: Propene/O_2, 5 bar abs, 20 °C, 41 vol.-% Propene, ϕ_i=76 mm, L = 7 m, ignition at t = 0 ms







Predetonation distance is given by intersection of distance-time curve of retonation and detonation wave.
(in this example: L_{predet} = 1560±50 mm)

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Clarification of an apparent contradiction with respect to predetonation distances

Lean mixtures that require up to 760 mm (L/D ≅ 10) predetonation distance in a pipe and
rich mixtures that require up to 1500 mm (L/D ≅ 20) predetonation distance in a pipe
manage to run up to detonation in a sphere with radius 170 mm !!!

At first glance this is an unexpected result:

In the pipe the unburnt gas is made stream turbulent between rigid walls by expansion of the reaction products. This should encourage flame acceleration.
Hence, if for some mixture the predetonation distance in a pipe is larger than the radius of the sphere, one would not expect this mixture to run up to detonation in the sphere.

Possible reasons that mixture detonates in sphere although in pipe l_{predet} >> radius of sphere:

- In the sphere there is massive precompression (up to factor of 12 on lean side and up to a factor of 20 on rich side of detonative range) which is absent in long pipes. Predetonation distances reduce with increasing pressure (see next slide).
- Based on the precompression difference between lean and rich side it qualitatively makes sense that on the rich side mixtures which exhibit about twice the predetonation distance in a pipe as mixtures on the lean side, still run up to detonation in the sphere
- Because precompression in the sphere is adiabatic, the temperature of the mixture rises substantially (see next slide). Possibly this also contributes to reducing the predetonation distance (????)
- In sphere sonic pressure waves of initial deflagration are reflected backwards and interfere with combustion zone, which might accelerate the flame. In long pipes this effect should almost be absent.

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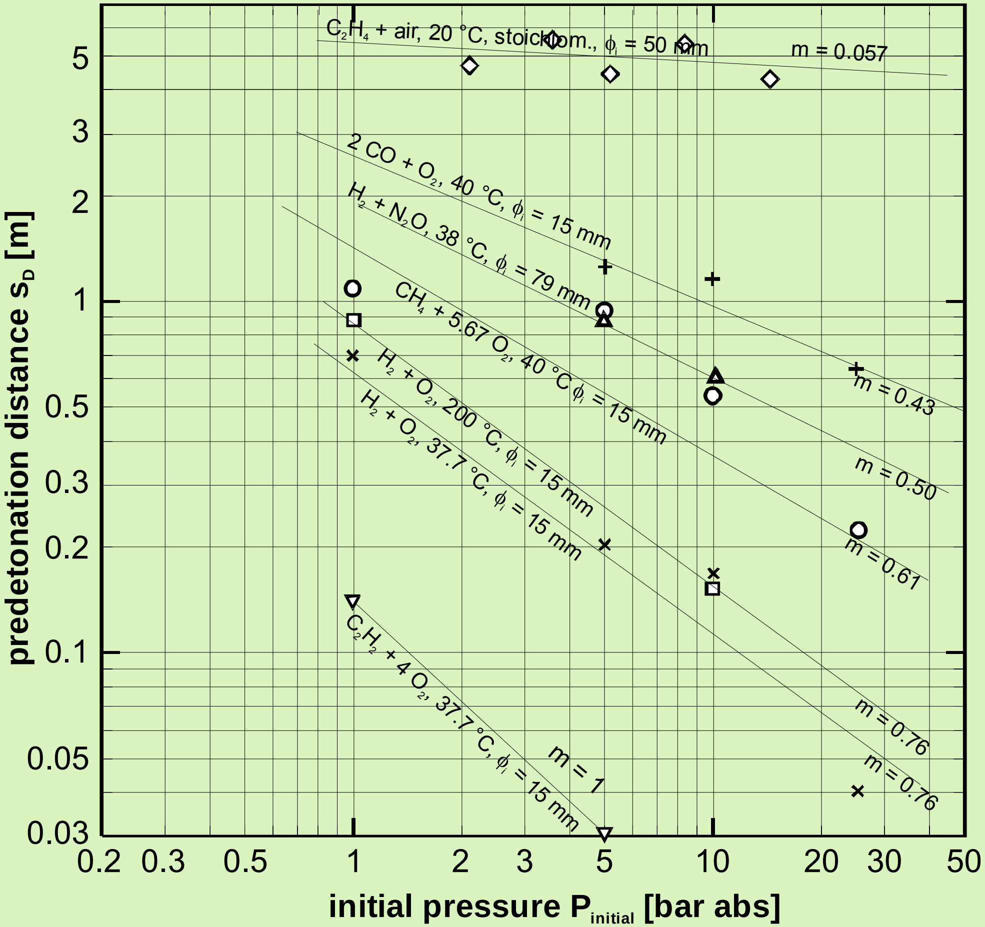
Predetonation distances as function of initial pressure



Empirical law for the pressure dependence of the predetonation distance:

$$s_D = \frac{\text{const.}}{(P_{ini})^m}$$

◇ C_2H_4 + air, 20 °C, stoichiom., ϕ_i = 50 mm, L = 22 m (I. Ginsburg and W. L. Bulkley, Chemical Engineenig Progress, Vol. 59, no. 2, p. 82 - 86 (1963)

+ 2 CO + O_2, 40 °C, ϕ_i = 15 mm, L = 2.94 m
○ CH_4 + 5.67 O_2, 40 °C ϕ_i = 15 mm, L = 2.94 m
□ H_2 + O_2, 200 °C, ϕ_i = 15 mm, L = 2.94 m
× H_2 + O_2, 37.7 °C, ϕ_i = 15 mm, L = 2.94 m
▽ C_2H_2 + 4 O_2, 37.7 °C, ϕ_i = 15 mm, L = 2.94 m

} L.E. Bollinger, M. C. Fong and R. Edse, American Rocket Society: ARS Journal (Easton, Pa) 31, p. 588 - 595 (1961)

△ H_2 + N_2O, 37.7 °C, ϕ_i = 79 mm , L = 2.94 m (L.E. Bollinger, J. A. Laughrey and R. Edse, American Rocket Society: ARS Journal (Easton, Pa) 32, p. 81 - 82 (1962)

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Temperatures obtainable by adiabatic compression

$P_{final}/P_{initial}$	$T_{initial}$ = 25 °C = 298 K — T_{final} [°C] for different values of $\gamma = c_p/c_v$: γ = 1,4	γ = 1,3	γ = 1,2	γ = 1,1
1,2	40,9	37,8	34,2	30,0
1,5	61,6	54,2	45,8	36,2
2	90,3	76,7	61,5	44,4
4	169,8	137,3	102,5	65,0
6	224,2	177,6	128,7	77,7
8	266,8	208,5	148,4	87,0
10	302,3	234,0	164,4	94,4
12	333,1	255,8	177,9	100,5
14	360,4	274,9	189,6	105,8
16	385,0	292,1	200,0	110,4
18	407,6	307,6	209,4	114,6
20	428,4	321,9	218,0	118,3
25	474,5	353,4	236,6	126,3
30	514,5	380,3	252,3	133,0
35	550,0	403,9	266,0	138,7
40	582,0	425,1	278,1	143,7
45	611,2	444,3	289,0	148,2
50	638,2	462,0	299,0	152,3

$P_{final}/P_{initial}$	$T_{initial}$ = 200 °C = 473 K — T_{final} [°C] for different values of $\gamma = c_p/c_v$: γ = 1,4	γ = 1,3	γ = 1,2	γ = 1,1
1,2	225,3	220,3	214,6	207,9
1,5	258,1	246,4	233,1	217,8
2	303,6	282,0	257,9	230,8
4	429,9	378,3	322,9	263,5
6	516,2	442,2	364,6	283,7
8	583,8	491,3	395,9	298,4
10	640,2	531,7	421,3	310,1
12	689,1	566,3	442,7	319,9
14	732,4	596,7	461,3	328,2
16	771,5	623,9	477,8	335,6
18	807,2	648,6	492,7	342,1
20	840,2	671,3	506,3	348,1
25	913,5	721,2	535,8	360,8
30	977,0	763,9	560,8	371,4
35	1033,2	801,4	582,5	380,5
40	1084,0	835,1	601,7	388,5
45	1130,5	865,6	619,1	395,6
50	1173,4	893,6	634,9	402,0

Formula for temperature increase due to adiabatic compression: $T_{final} = T_{initial} \cdot \left(p_{final} / p_{initial} \right)^{(\gamma - 1)/\gamma}$

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Summary on predetonation distances of Propene/O_2

- Predetonation distances change drastically (about 2 orders of magnitude) over a relatively narrow range of compositions
- Above result corroborates the so far preliminary conclusion drawn from the comparisons of the detonative regimes found in 20, 100, 500 and 2500 l vessels (detonative range in 20 l sphere about the same as in 2500 l vessel)
- Above statements are compatible with the well established observation that combustible/air mixtures do not run up to detonation in empty vessels ->>>> see next slide ->>>>>

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Tentative generalisation of the results found for the course of the explosion of Propene/O_2/N_2 in the 20 l sphere and in tubes (thermal ignition presumed!)

Combustible/air-mixtures do not detonate in vessels of any practical size.

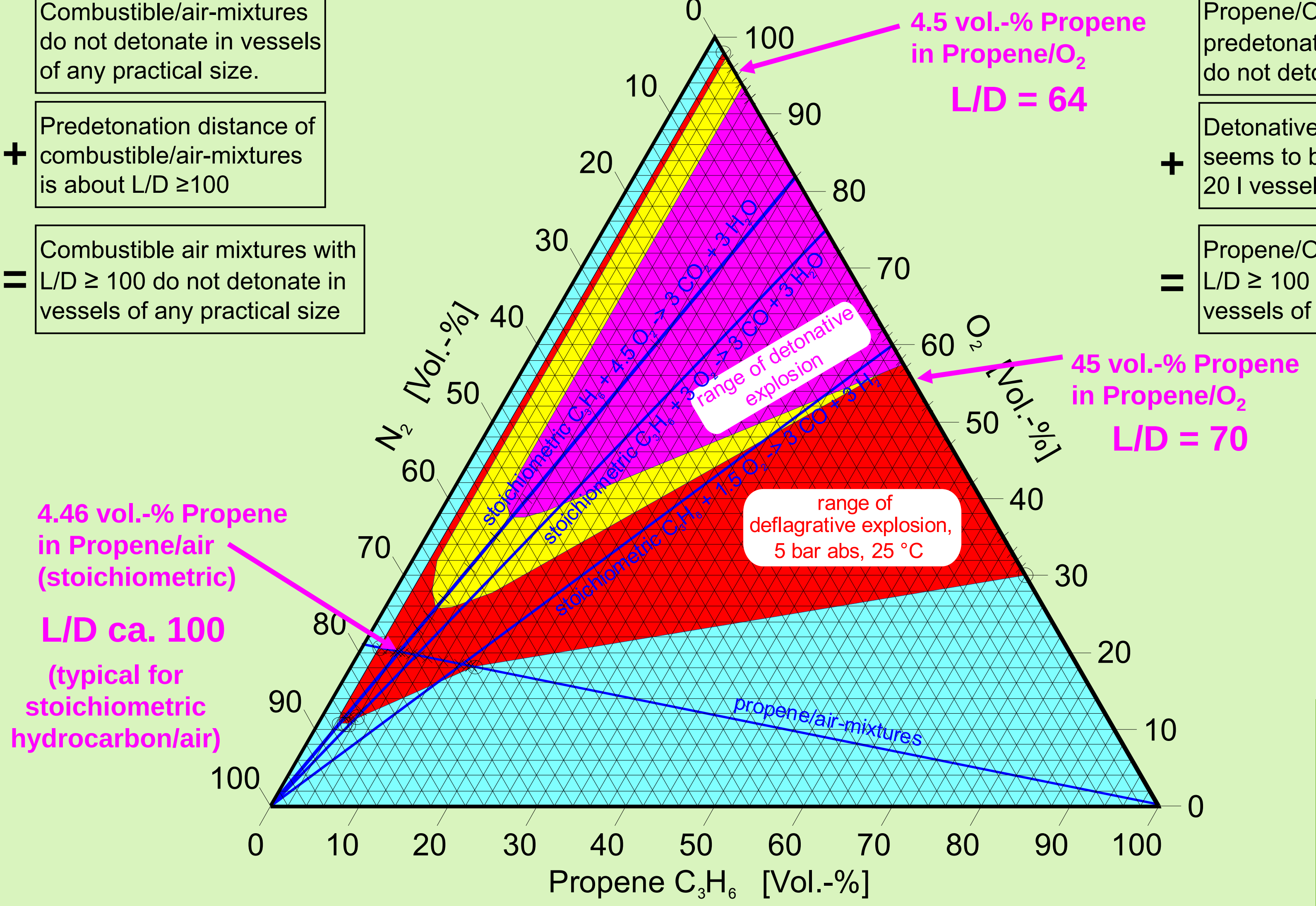
\+ Predetonation distance of combustible/air-mixtures is about L/D ≥100

= Combustible air mixtures with L/D ≥ 100 do not detonate in vessels of any practical size

Propene/O_2 mixtures with predetonation distances L/D ≥ 100 do not detonate in 20 l vessel

\+ Detonative range in larger vessels seems to be about the same as in 20 l vessel

= Propene/O_2-mixtures with L/D ≥ 100 do not detonate in vessels of any practical size



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  - quantification of P_{det} for four scenarios occuring in a pipe (no precompression)
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  - quantification of P_{det} for Propene/O_2/N_2 in vessel at $P_{initial}$ = 5 bar abs, $T_{initial}$ = 20 °C
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  in 20 l vessels ↔ 100, 500, 2500 l vessels
- **Predetonation distances of Propene/O_2 in tubes**
- **Did ignition source directly trigger a spherical detonation?**

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Did our the ignition source directly trigger a spherical detonation?

Ignition source used is fusing wire according to EN 1839, section 4.2.3.3.3 :

- wire of 0.2 mm diameter, ca. 5 mm long, clamped between two electrodes

- by a thyristor the wire is connected for a fraction of a half wave with the secondary coil of an insulation transformer (thyristor typically opens between 0° and 150° and closes at 180°)

- wire melts in about first millisecond

- just when first contact breaks apart between the electrodes by the melting of the wire an arc discharge emerges and keeps on burning until the voltage between the pole tips falls back to 0.

This ignition source must be rated as purely thermal, since the shock wave associated with the first occurrence of the arc discharge is negligible (see next slides)

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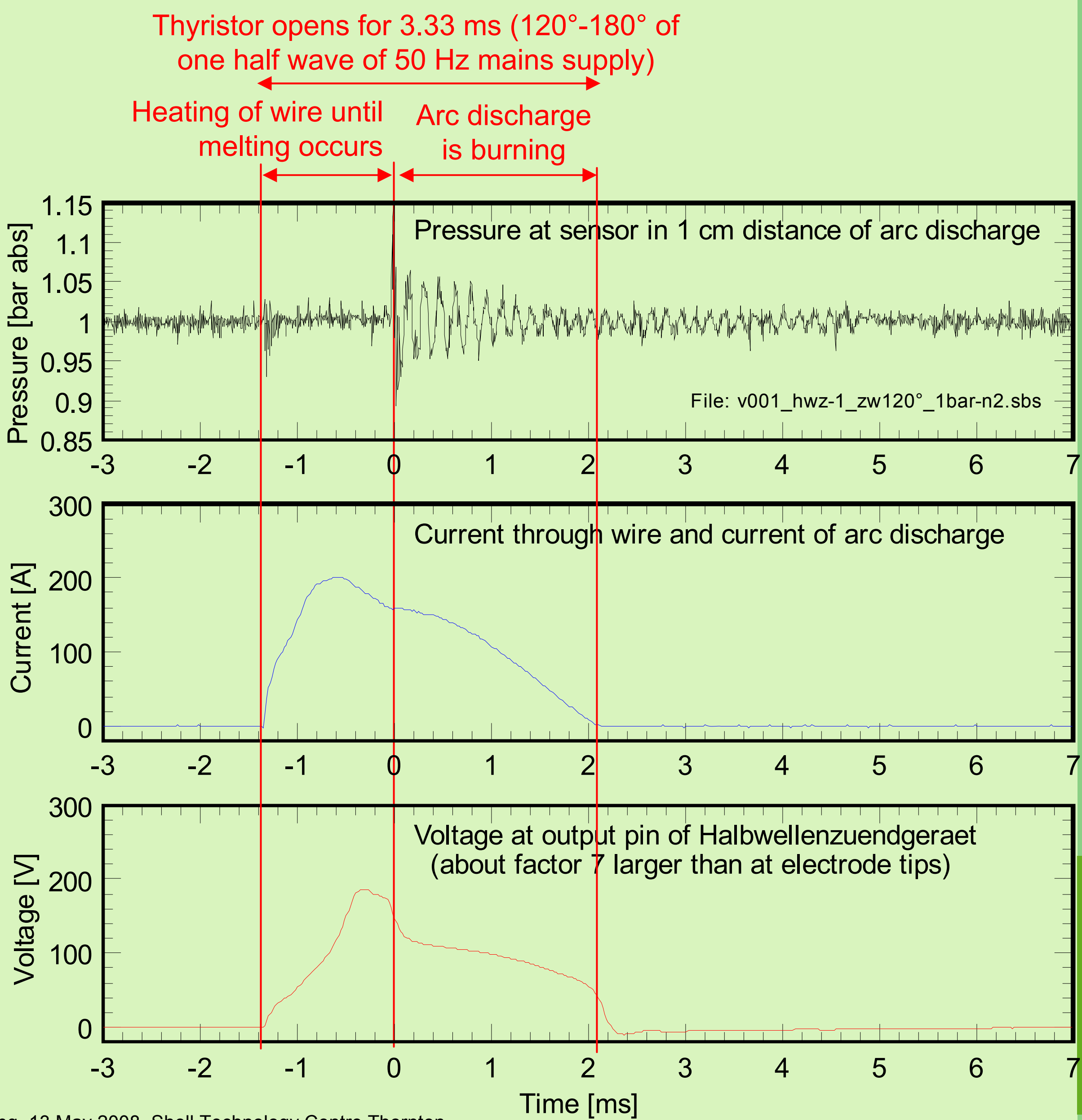
Current/time, Voltage/time and Pressure/time diagrams of ignition source *„melting wire with subsequent arc discharge“* (1/5)

Example:
ignited in 1 bar N_2
at 20°C,
thyristor switched on
from 120° to 180°
of one half cycle
of mains supply



In about 50% of all ignitions conducted 1 bar N_2 at 20°C there was not at all any pressure detected by the piezoelectric sensor (irrespective of the duration the thyristor was switched on)

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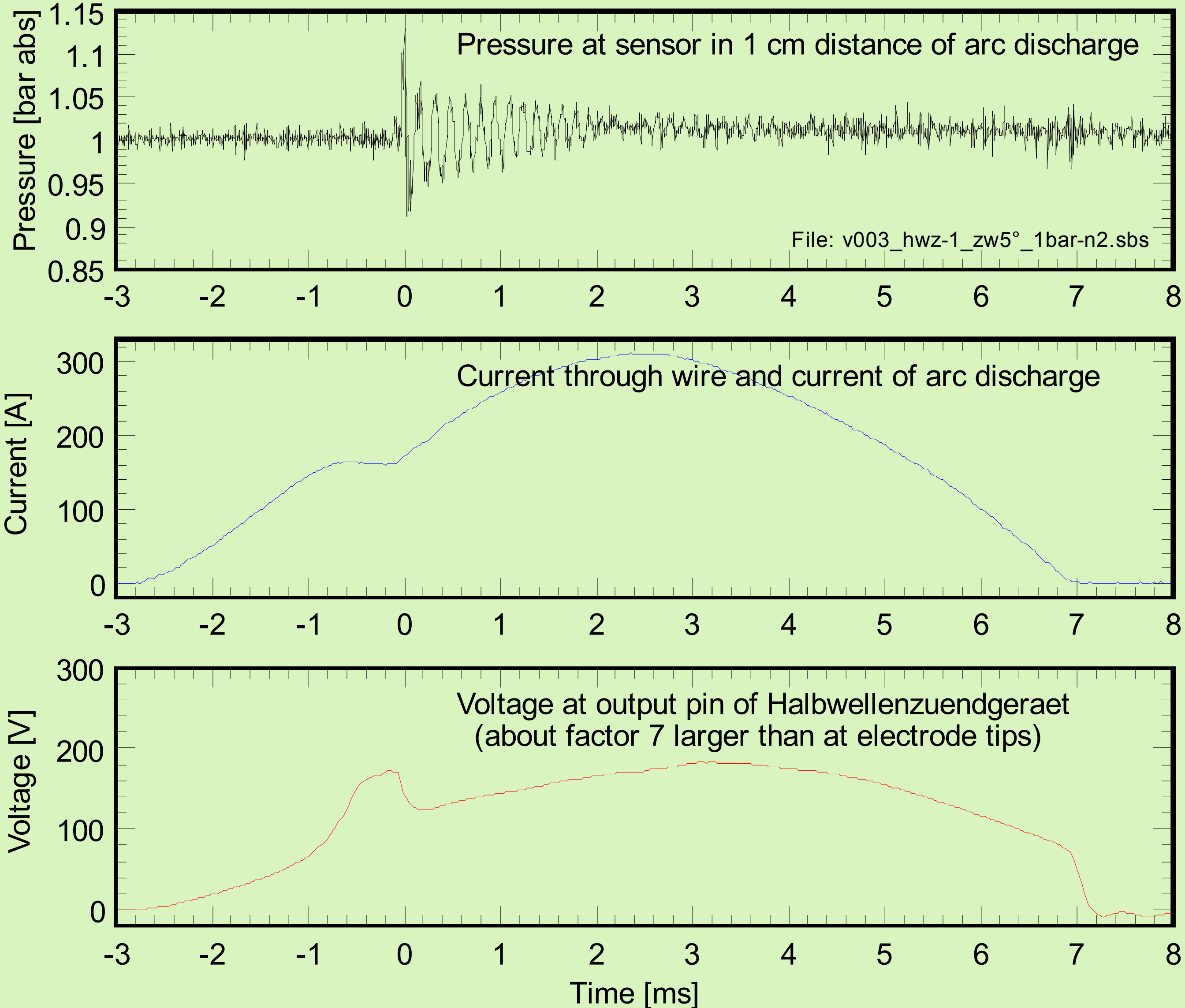
Current/time, Voltage/time and Pressure/time diagrams of ignition source *„melting wire with subsequent arc discharge“* (2/5)

Example: ignited in 1 bar N_2 at 20°C, thyristor switched on from 5° to 180° of one half cycle of mains supply



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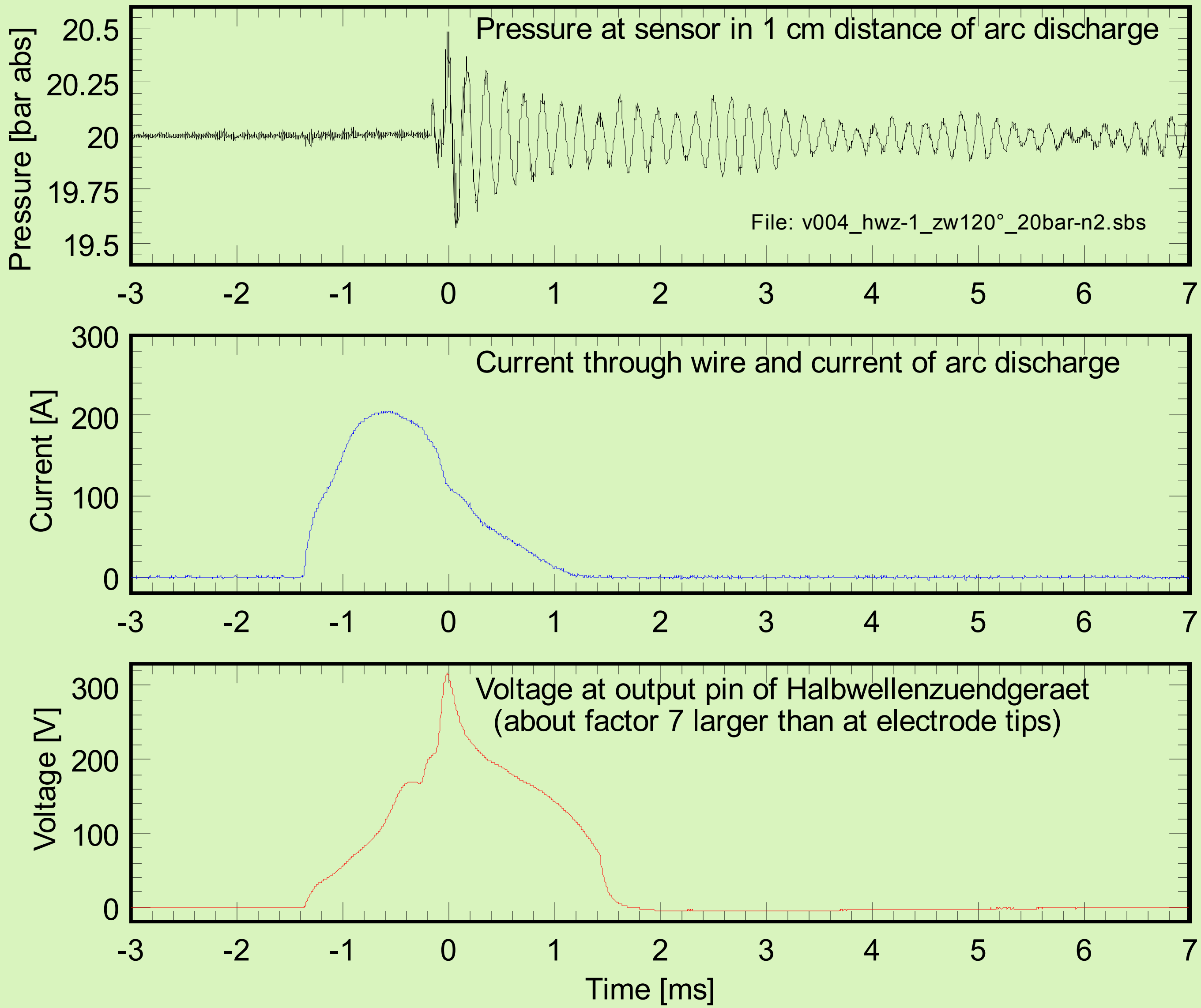
Current/time, Voltage/time and Pressure/time diagrams of ignition source *„melting wire with subsequent arc discharge“* (3/5)

Example: ignited in 20 bar N_2 at 20°C, thyristor switched on from 120° to 180° of one half cycle of mains supply



For all ignitions conducted at 20 bar N_2 and at 20°C there was a pressure signal detected by the piezoelectric sensor of the order of $\Delta p = \pm 0.4$ to ± 0.7 bar

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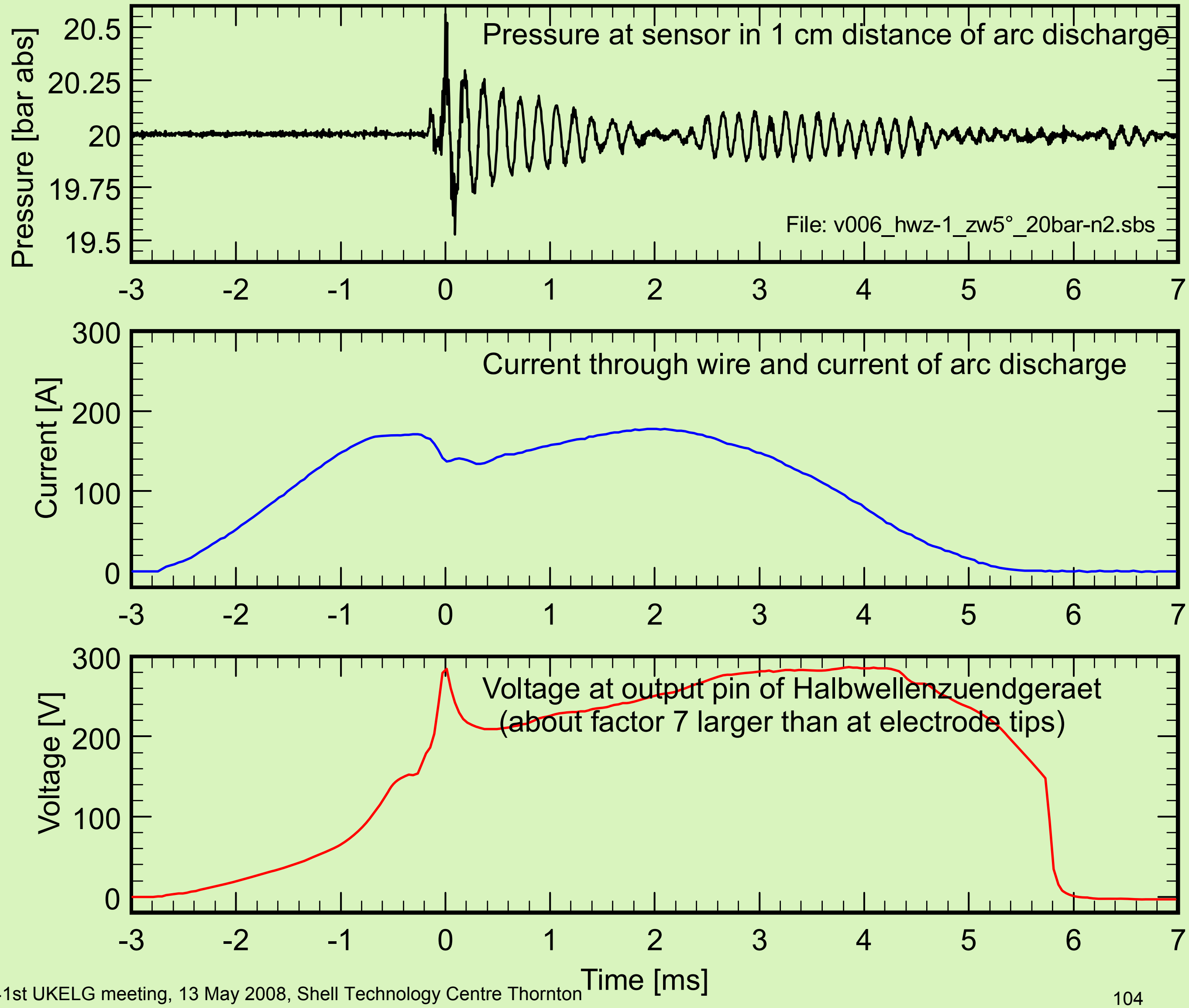
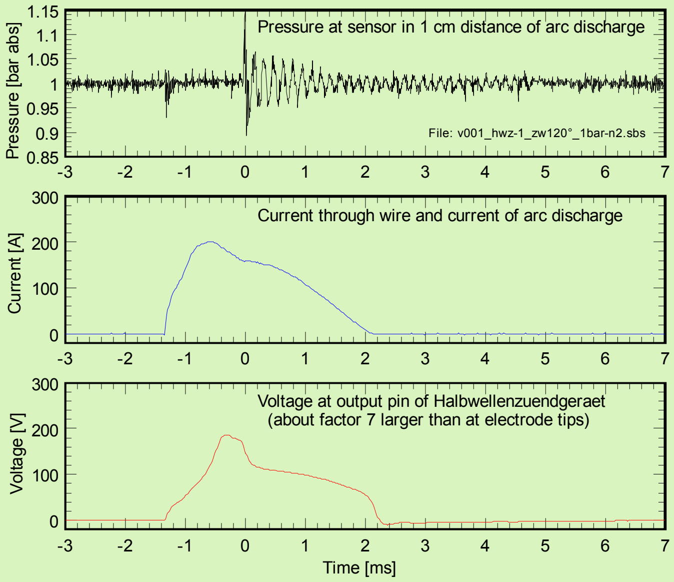
Current/time, Voltage/time and Pressure/time diagrams of ignition source *„melting wire with subsequent arc discharge“* (4/5)

Example: ignited in 20 bar N_2 at 20°C, thyristor switched on from 5° to 180° of one half cycle of mains supply

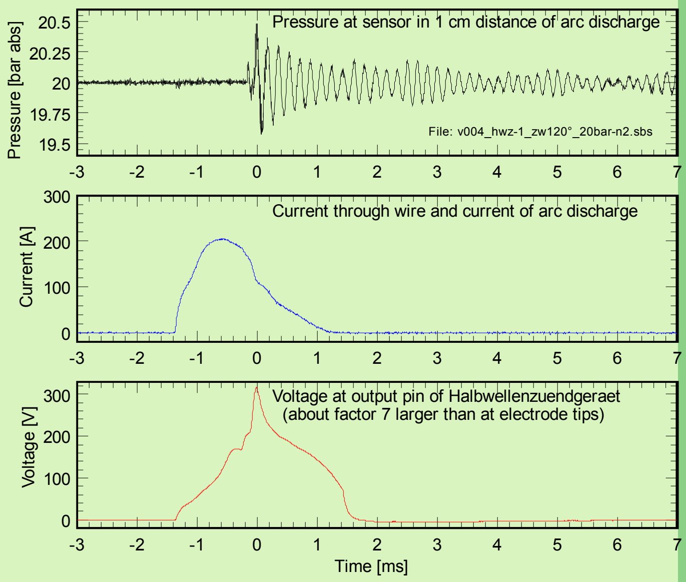


Current/time, Voltage/time and Pressure/time diagrams of ignition source *„melting wire with subsequent arc discharge“* (5/5)

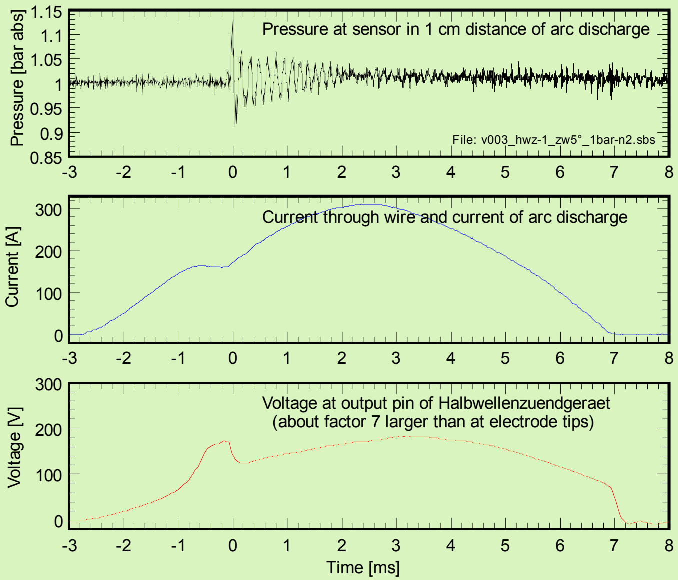
1 bar N_2, 120° - 180°



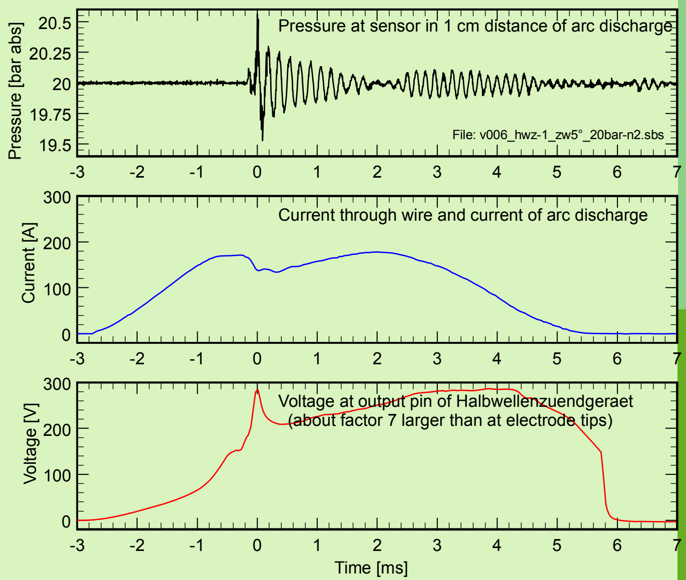
20 bar N_2, 120° - 180°



1 bar N_2, 5° - 180°



20 bar N_2, 5° - 180°



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Summary of talk

- **Abundant set of explosion characteristics in the important but so far mostly unexplored combustible/air/O_2 region of the explosive range**
- **Detonative range in empty vessels is determined**
- **Pressure load on the wall is understood quantitatively**
- **The link between detonation in pipes and in vessels is established**

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