

# Fundamentals of Combustion

## Lec 4: Ignition

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## Ignition Processes

Ignition is an instationary process. We divide into:

### Spatially homogeneous -->

#### 'Explosion'

##### 'Thermal Explosion'

- fast heat release (instantaneous)
- strong increase of pressure

##### 'Radical Chain Reaction'

- Heat release is delayed
- 'Ignition delay time' ( $\mu\text{s} - \text{s}$ )
- Radical chain reactions are dominating the process

### With flame wave

#### 'Detonation'

- Flame propagation with pressure wave
- Pressure wave induces ignition
- with speed of sound  
(typ.  $v \approx 1000 \text{ m/s}$  !)

#### 'Deflagration'

- Flame propagation dominated by diffusive-reactive processes (--> laminar premixed flame)
- Pressure change low
- $v \approx 0,5 \text{ m/s}$  ('slow' !!!)

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## Semenov's Analysis of Thermal Explosion (1935, simplified)

Balance of heat:

- One-step reaction Fuel + Air  $\rightarrow$  Products
- Reaction rate  $\sim \exp(-E_A/RT)$ , thus heat production rate  $P$  exponentially dependant on  $T$
- Heat loss (to surrounding)  $L \sim (T - T_s)$

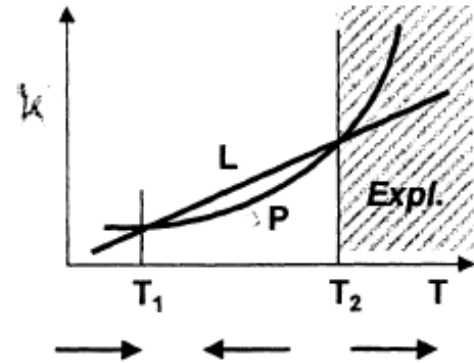
If  $P > L \rightarrow T$  increases

$T_1$  stable fix point

$T_2$  unstable fix point

$T > T_2 \rightarrow$  Reaction increases (explosion)

$T < T_1 \rightarrow T$  increases to  $T_1$



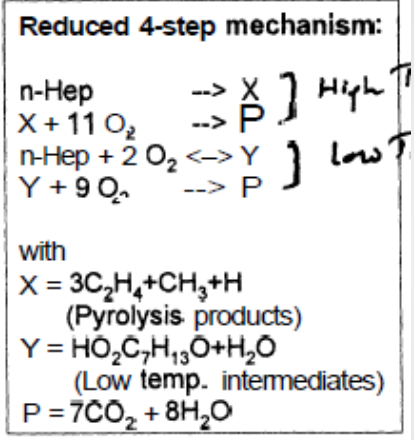
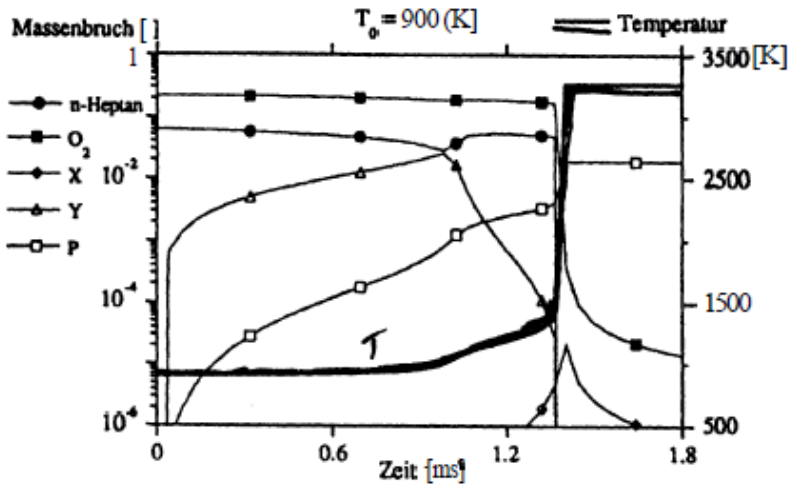
(For adiabatic system: no loss, system explodes)

## 'Radical Chain Explosion' / 'Autoignition'

- Can happen for  $H_2/O_2$  and for  $H_1C_j$  / Air mixtures
- Typical: "Ignition-delay time" (range us - ms - s - h)
- Comes from complex reaction processes:
  - Radical chain-branching steps are starting first without (noticeable) heat release,
  - Number of radicals (H, OH, O, ...) increases esponentially (e.g. within some ms from 1 ppb to 1 ppm). Temperature remains (nearly) constant.
  - Finally the radical pool becomes large enough to consume significant fraction of fuel, and rapid ignition starts.

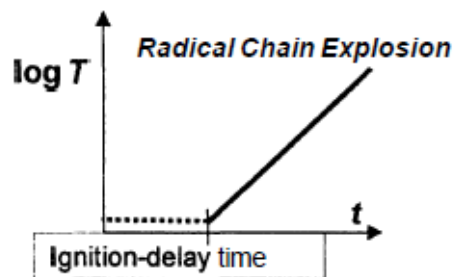
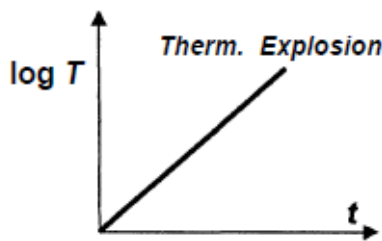
# Self ignition process

Calculation example of self-ignition process (n-heptane/air, 40 bar, 900 K)



## 'Radical Chain Explosion' / 'Autoignition'

- Is dominant e.g. in diesel engines (based on self ignition).
- Important in safety considerations (e.g. mixing of fuel into air for premixed combustion - gas turbine)
- Residence time must be below ignition-delay time. *critical time for liquid fuels*

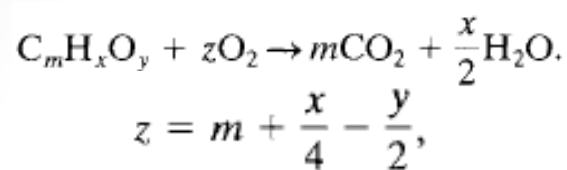


## Flammability limits:

- Vapor-air mixtures will ignite and burn only over a well-specified range of compositions.
- The mixture will not burn when the composition is lower than the lower flammable limit (LFL); the mixture is too lean for combustion.
- The mixture is also not combustible when the composition is too rich; that is, when it is above the upper flammable limit (UFL).
- A mixture is flammable only when the composition is between the LFL and the UFL.
- Commonly used units are volume percent fuel (percentage of fuel plus air).
- Lower explosion limit (LEL) and upper explosion limit (UEL) are used interchangeably with LFL and UFL.

## Limiting Oxygen Concentration and Inerting

For general combustion reaction



where  $z$  has units of moles  $O_2$ /mole fuel.

$$LFL = \frac{0.55(100)}{4.76m + 1.19x - 2.38y + 1},$$

$$UFL = \frac{3.50(100)}{4.76m + 1.19x - 2.38y + 1}.$$

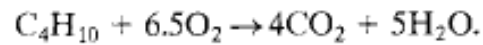
OR

$$LFL = \frac{-3.42}{\Delta H_c} + 0.569\Delta H_c + 0.0538\Delta H_c^2 + 1.80,$$

$$UFL = 6.30\Delta H_c + 0.567\Delta H_c^2 + 23.5,$$

$$\text{LOC} = \text{LFL} \left( \frac{\text{moles O}_2}{\text{moles fuel}} \right)$$

for butane (C<sub>4</sub>H<sub>10</sub>).



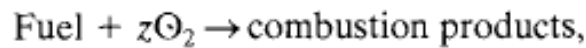
$$\begin{aligned} \text{LOC} &= \left( 1.9 \frac{\text{moles fuel}}{\text{total moles}} \right) \left( \frac{6.5 \text{ moles O}_2}{1.0 \text{ moles fuel}} \right) \\ &= 12.4 \text{ vol. \% O}_2. \end{aligned}$$

Below the limiting oxygen concentration (LOC) the reaction cannot generate enough energy to heat the entire mixture of gases (including the inert gases) to the extent required for the self-propagation of the flame.

## Flammability Diagram

- A general way to represent the flammability of a gas or vapor is by the triangle diagram
- Concentrations of fuel, oxygen, and inert material (in volume or mole %) are plotted on the three axes.
- Each apex of the triangle represents either 100% fuel, oxygen, or nitrogen.
- The tick marks on the scales show the direction in which the scale moves across the figure.
- Thus point A represents a mixture composed of 60% methane, 20% oxygen, and 20% nitrogen.
- The zone enclosed by the dashed line represents all mixtures that are flammable.
- Because point A lies outside the flammable zone, a mixture of this composition is not flammable.

- The air line represents all possible combinations of fuel plus air.
- The air line intersects the nitrogen axis at 79% nitrogen (and 21 % oxygen), which is the composition of pure air.
- The UFL and the LFL are shown as the intersection of the flammability zone boundary with the air line.
- Any gas mixture containing oxygen below the LOC is not flammable

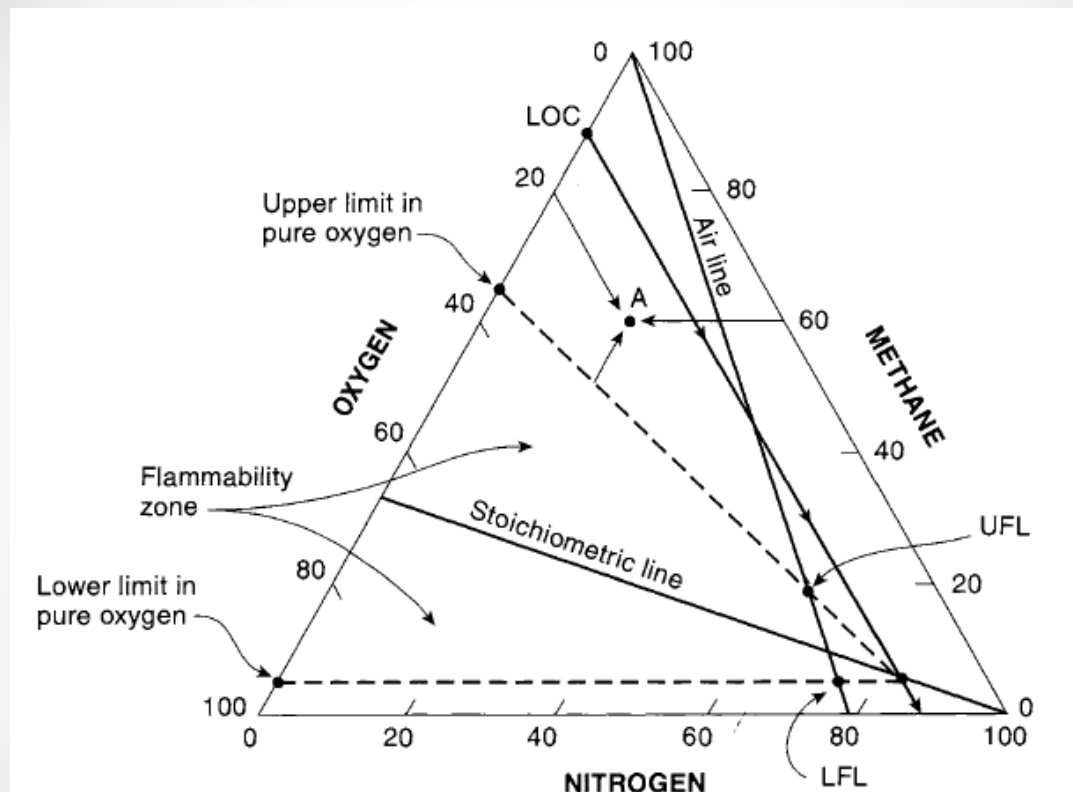


where  $z$  is the stoichiometric coefficient for oxygen.

- The intersection of the stoichiometric line with the oxygen axis (in volume % oxygen) is given by

$$100\left(\frac{z}{1+z}\right)$$

The stoichiometric line is drawn from this point to the pure nitrogen apex.



## Ignitions Limits

(for safety considerations !)

No ignition possible if low O<sub>2</sub> or low fuel.

Mixture	Lower Ign.Limit (Vol% Fuel-Gas)	Upper Ign.Lim. (Vol%Fuel-Gas)
H <sub>2</sub> /Air	4	75
CH <sub>4</sub> /Air	5	15
C <sub>3</sub> H <sub>8</sub> /Air	2,1	9,5
CH <sub>4</sub> /Air, 50 bar	<b>4,8</b>	48
CH <sub>4</sub> /Air, 100 bar	4,6	57
CH <sub>4</sub> /O <sub>2</sub>	5	60
Gasoline/Air	<b>0,6 - 1</b>	<b>6 - 8</b>
Diesel/Air	ca. 0,6	ca. 6,5

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## Ignition temperature, Flash point

### Ignition Temperature

Lower Limit for possible self ignition  
(DIN 51794)

(Real ignition temperature depends on  
several parameters)

$\lambda=1, 1\text{bar}$	Ignition temp.
H <sub>2</sub> /Air	560°C
CH <sub>4</sub> /Air	610°C
C <sub>3</sub> H <sub>8</sub> /Air	470°C
C <sub>8</sub> H <sub>18</sub> /Air	<b>210°C</b>
C <sub>6</sub> H <sub>6</sub> /Air	555°C
Gasoline	430-550°C

### Fiammpunkt (Flash point)

Temp. of a liquid fuel, above which  
the evaporated gas can be ignited

Gefahren- klasse	Fiammpunkt
I	<21°C
II	21-55°C
III	55-100°C
Gasoline	-16 ... +10°C
Diesel	+55 ... +120°C

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## Ignition limit for fuel-mixtures (foll. Le Chatelier)

$$Z = \frac{a+b+\dots}{\frac{a}{A} + \frac{b}{B} + \dots}$$

with  $a, b$  mole fraction of diff. fuel components,  
with  $A, B$  their lower (resp. upper) ignition limit

lower ignition limit  $\rightarrow A, B$  are lower ignition limit of C  
higher ignition limit  $\rightarrow A, B$  are higher ignition limit of C

## Temperature dependence of ignition limits (foll. Zabeidakis)

$$Z_u(t) = Z_{u,25^\circ\text{C}} \cdot (1 - c \cdot (t - 25^\circ\text{C}))$$

$$Z_o(t) = Z_{o,25^\circ\text{C}} \cdot (1 + c \cdot (t - 25^\circ\text{C}))$$

$c = 0,000721$  for many hydrocarbons  
for  $\text{H}_2$  (and other fuels)  $c$  can differ

**Note:**  
Range of ignitable mixture  
increases for higher temperature

## Ignition Energy

- The minimum ignition energy (MIE) is the minimum energy input required to initiate combustion.
- All flammable materials (including dusts) have MIEs.
- The MIE depends on the specific chemical or mixture, the concentration, pressure, and temperature

Experimental data indicate that

- the MIE decreases with an increase in pressure,
- the MIE of dusts is, in general, at energy levels somewhat higher than combustible gases, and
- an increase in the nitrogen concentration increases the MIE.



Chemical	Minimum ignition energy (mJ)
Acetylene	0.020
Benzene	0.225
1,3-Butadiene	0.125
<i>n</i> -Butane	0.260
Cyclohexane	0.223
Cyclopropane	0.180
Ethane	0.240
Ethene	0.124
Ethylacetate	0.480
Ethylene oxide	0.062
<i>n</i> -Heptane	0.240
Hexane	0.248
Hydrogen	0.018
Methane	0.280
Methanol	0.140
Methyl acetylene	0.120
Methyl ethyl ketone	0.280
<i>n</i> -Pentane	0.220
2-Pentane	0.180
Propane	0.250

<sup>1</sup>Data from I. Glassman, *Combustion*, 3d ed. (New York: Academic Press, 1996).

## Octane number

**Knock:** Mixture ignites by itself (not desired)

Measure of resistance to knock of gasoline fuel.

Measure chosen between 0 and 100 from comparison with mixture of non-knocking **Isooctane** (OZ 100) and strongly knocking ***n*-Heptane** (OZ 0).

Determination with comparative test (Single cylinder-CFR-testing method)

**ROZ** (Research OZ): at 600 rpm, air preheated to 52 °C

**MOZ** (Motor OZ): at 900 rpm, mixture preheated to 149 °C:      MOZ < ROZ

Gasoline grades (in Germany):

Normal:      min. 91,0 ROZ / 82,5 MOZ

Super:      min. 95,0 ROZ / 85,0 MOZ

SuperPlus: min. 98,0 ROZ / 88,0 MOZ

## Cetane number

Diesel engine: based on self-ignition of mixture

Measure of **ignitability** of diesel fuel.

The cetane number is the content of cetane (volume percent) in a **mixture of cetane and alpha-methyl-naphthalene**, where the ignition delay is equal to the diesel fuel probe. Tested under defined conditions in a test engine.

The cetane number is of strong importance for the quality of the combustion process in the diesel engine.

If cetane number too low: tendency to more soot emission.

Typical cetane number of diesel is 50 .. 55.

*EU norm max CN 51*

## Quenching Distance

Near cold walls combustion is quenched (inhibited) due to heat loss (and eventually due to changed surface reaction steps)

→ **'Quenching Distance'**

Applications:

- Grid above flame
- Flame safety lamps, 1815 (Davy'sche Sicherheitslampe)
- Device to prevent flashback
- Explosion protected electro motor

Problems:

- Unburnt hydrocarbons due to flame quench near wall of IC-engine.

Quenching Distance ( $t=25^{\circ}\text{C}$ )	
H <sub>2</sub> /Air	0,7 mm
CH <sub>4</sub> /Air	2 mm
C <sub>3</sub> H <sub>8</sub> /Air	1,8 mm

*Internal Co. limits*