

Theoretical bases for fire 2



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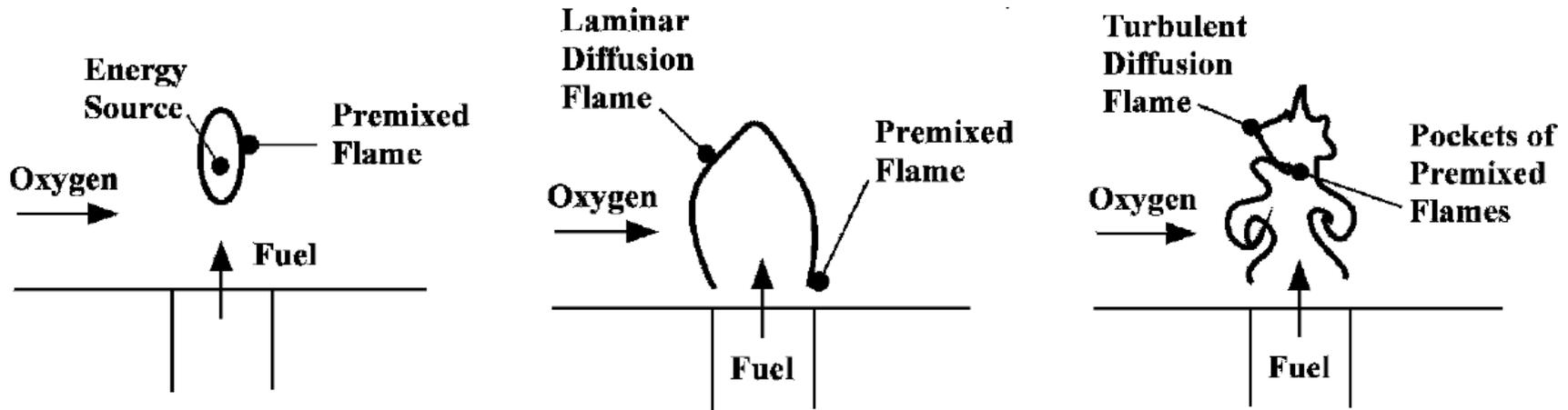


From diffusion to premixed flames

In order to initiate a diffusion flame, we must first have premixed flame.

In regions where a diffusion flame is near a cold wall, we are likely to have an intermediary premixed flame.

Even in a turbulent diffusion flame, some state of a premixed flame must exist.



An example :



Basics of combustion: combustion modes

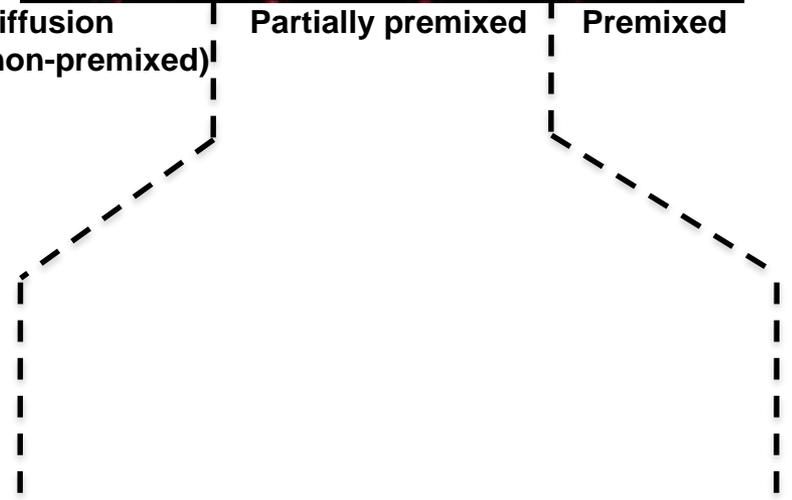
From diffusion to premixed flames



Diffusion
(non-premixed)

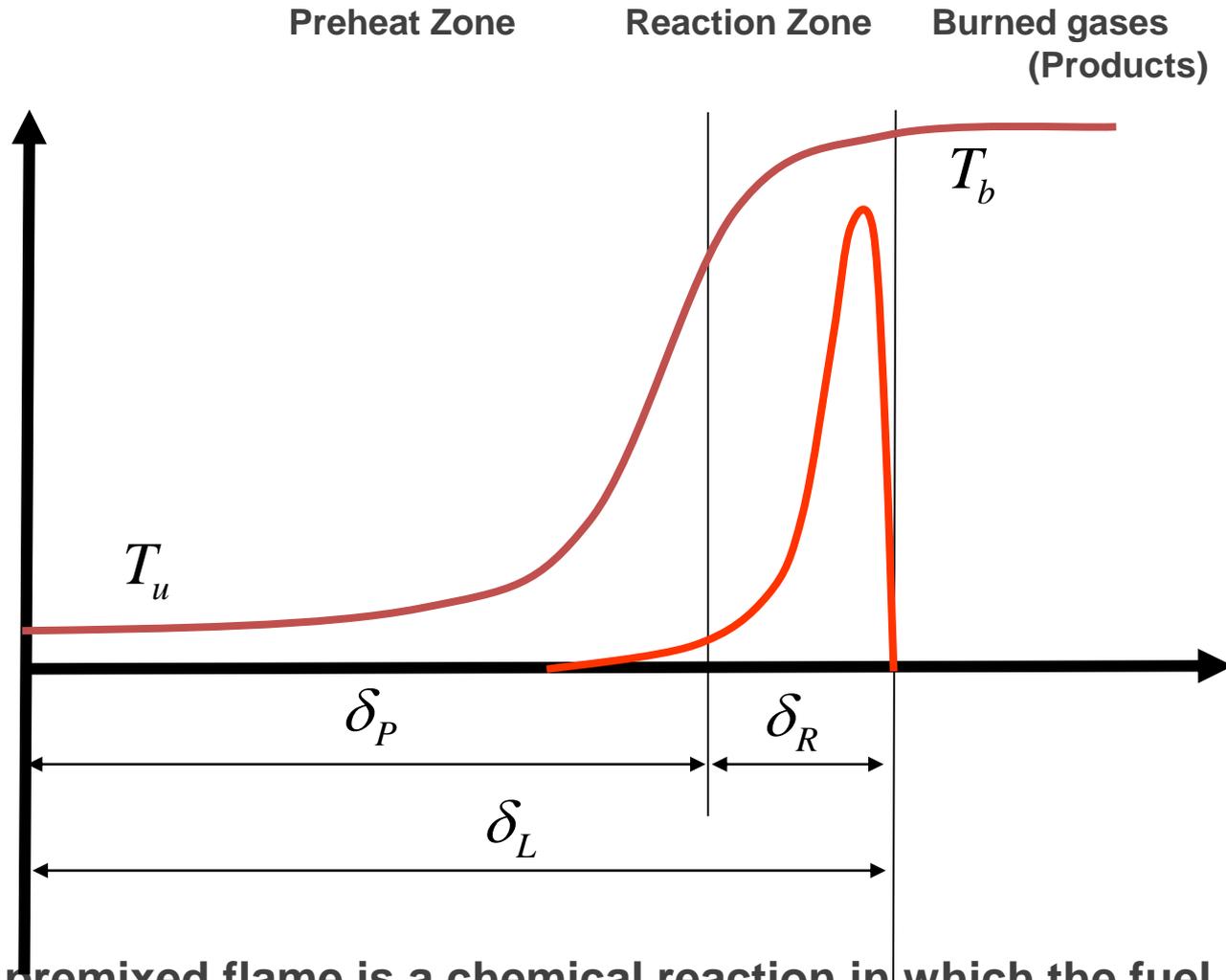
Partially premixed

Premixed



Basics of combustion: combustion modes

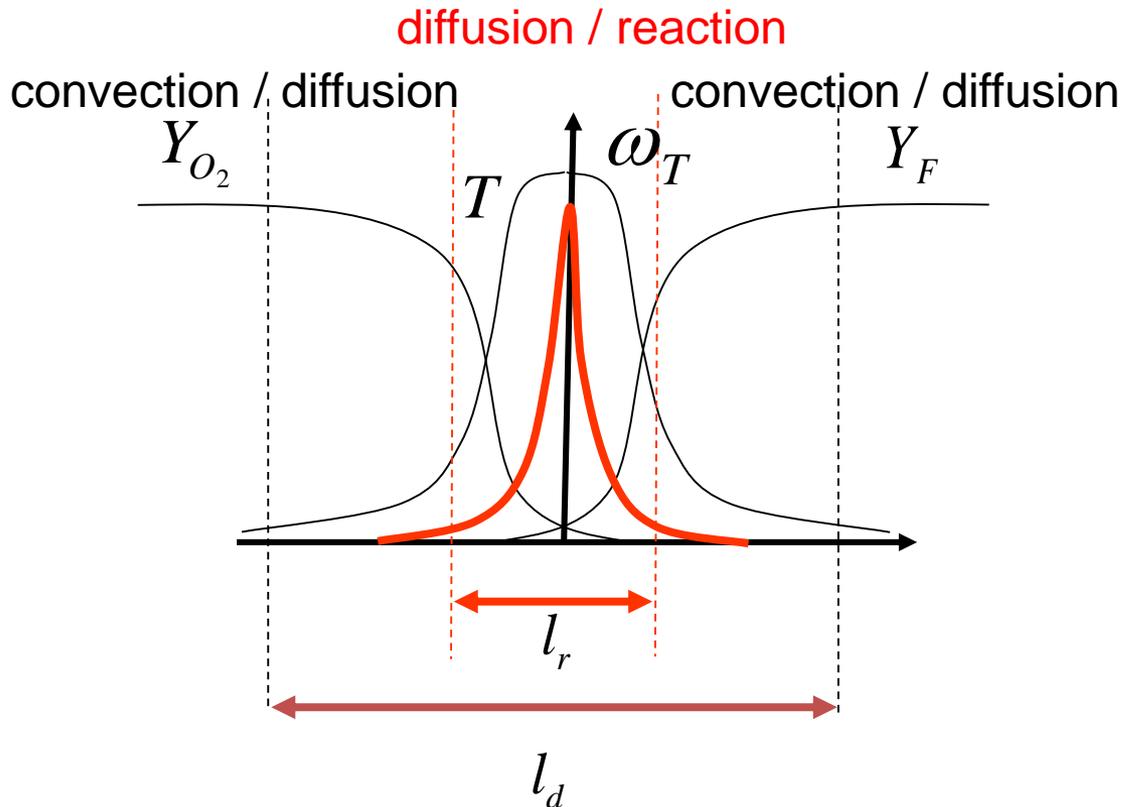
Premixed flame



A premixed flame is a chemical reaction in which the fuel and the oxygen (oxidizer) are mixed before they burn.

Basics of combustion: combustion modes

Diffusion Flames (non premixed flame)
Non premixed injection of reactants



In a diffusion flame the fuel and oxygen are separated and must come together before they burn.

Basics of combustion: combustion modes

We shall examine several aspects of premixed flames :

- What determines whether a reaction occurs ?**
- What is the speed of the reaction in the fuel-oxidizer mixture ?**
- What determines extinction of the reaction ?**
- What determines inflammability ?**

Contents

- 1. Basics of combustion : combustion modes**
- 2. Ignition phenomena**
- 3. MIE (Minimum Ignition Energy)**
- 4. Flame speed**
- 5. Flammability limits**

Ignition phenomena

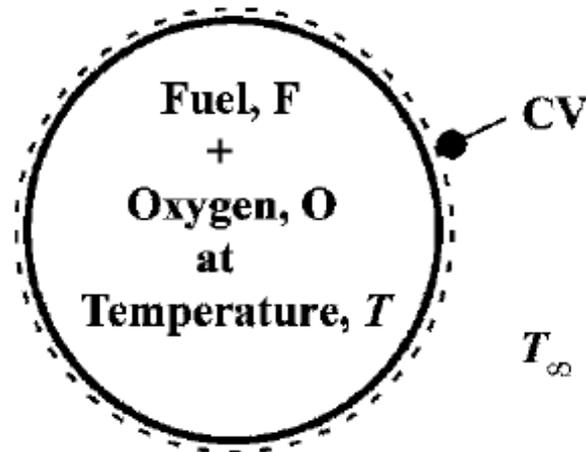
Ignition is the mechanism leading to the onset of a vigorous combustion reaction and is characterized by a rapid increase of the species temperature.

An understanding of ignition is important in a wide range of combustion processes, from designing practical combustion devices to preventing unwanted fires.

Spontaneous combustion

- **T = ambient:** metastable state, reaction rate is almost null
- **When T increases:**
 - **If $T > T_i$** Beginning of exothermic oxidation reaction:
production of enough radicals to ignite
 - **If $T < T_i$** Heat released is not sufficient to increase the temperature, because endothermic reactions absorb the heat to crack the fuel:
not enough radicals are produced to ignite

A gaseous mixture of fuel and oxidizer is placed in a closed vessel of fixed volume. Regard the vessel as a perfect conductor of heat with negligible thickness. The properties of the gaseous mixture are uniform in the vessel.



Actually, we expect $T > T_{\infty}$ due to the release of chemical energy, so this is a heat loss.

We write this loss as :

$$\dot{Q}_L = hS(T - T_{\infty})$$

Let us ignore the effect of concentration, i.e. we will take a zeroth-order reaction, and examine the concept of a “critical” temperature for combustion. We follow an approach due to Semenov.

The chemical energy release rate is written as :

$$\dot{Q}_R = \dot{m}_{F,r}''' V \Delta h_c$$

$$\dot{m}_{F,r}''' = \rho A_0 Y_F^n Y_{O_2}^m e^{-E/(RT)} \quad \dot{m}_{F,r}''' = A e^{-E/(RT)}$$

Then we can write

$$mc_v \frac{dT}{dt} = \dot{Q}_R - \dot{Q}_L$$

Semenov theory

Auto-ignition conditions

$$dT/dt > 0$$



Production > *Heat loss*

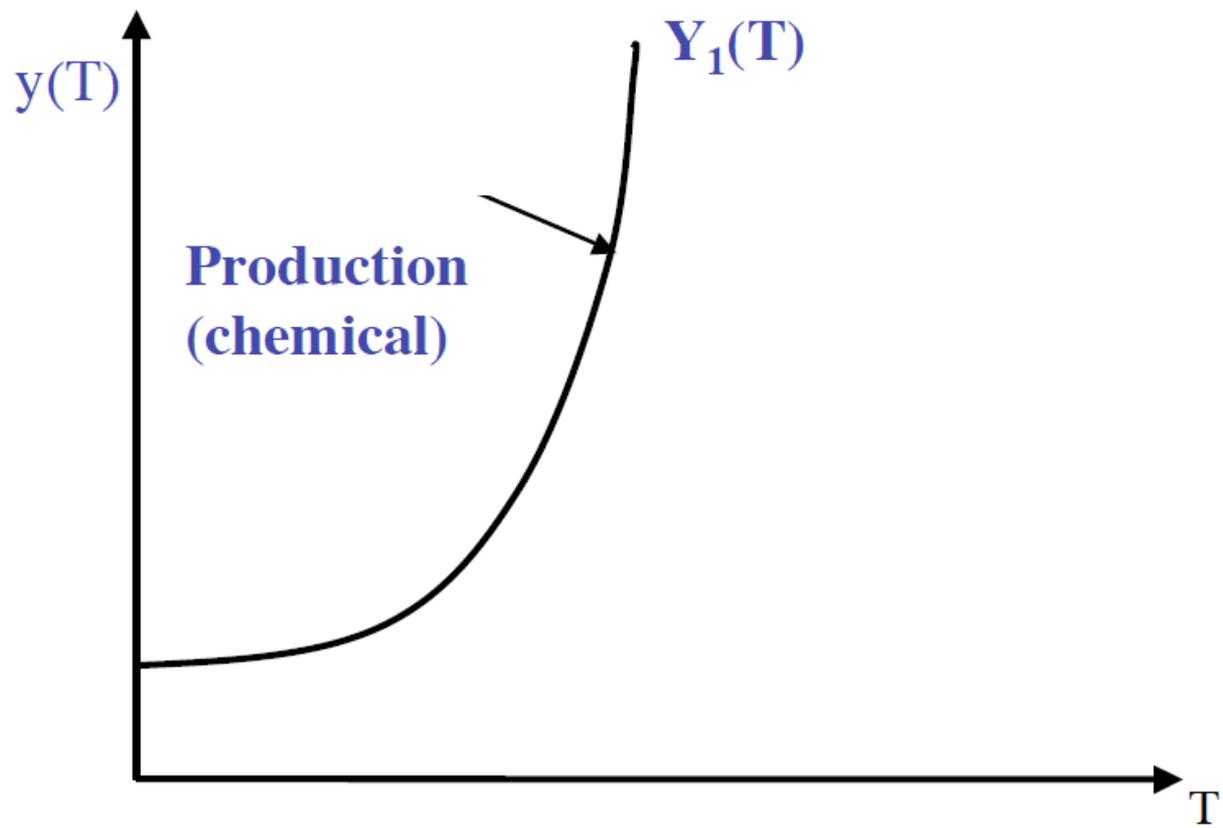
$$\dot{m}''' \Delta h_c > h \frac{S}{V} (T - T_\infty)$$

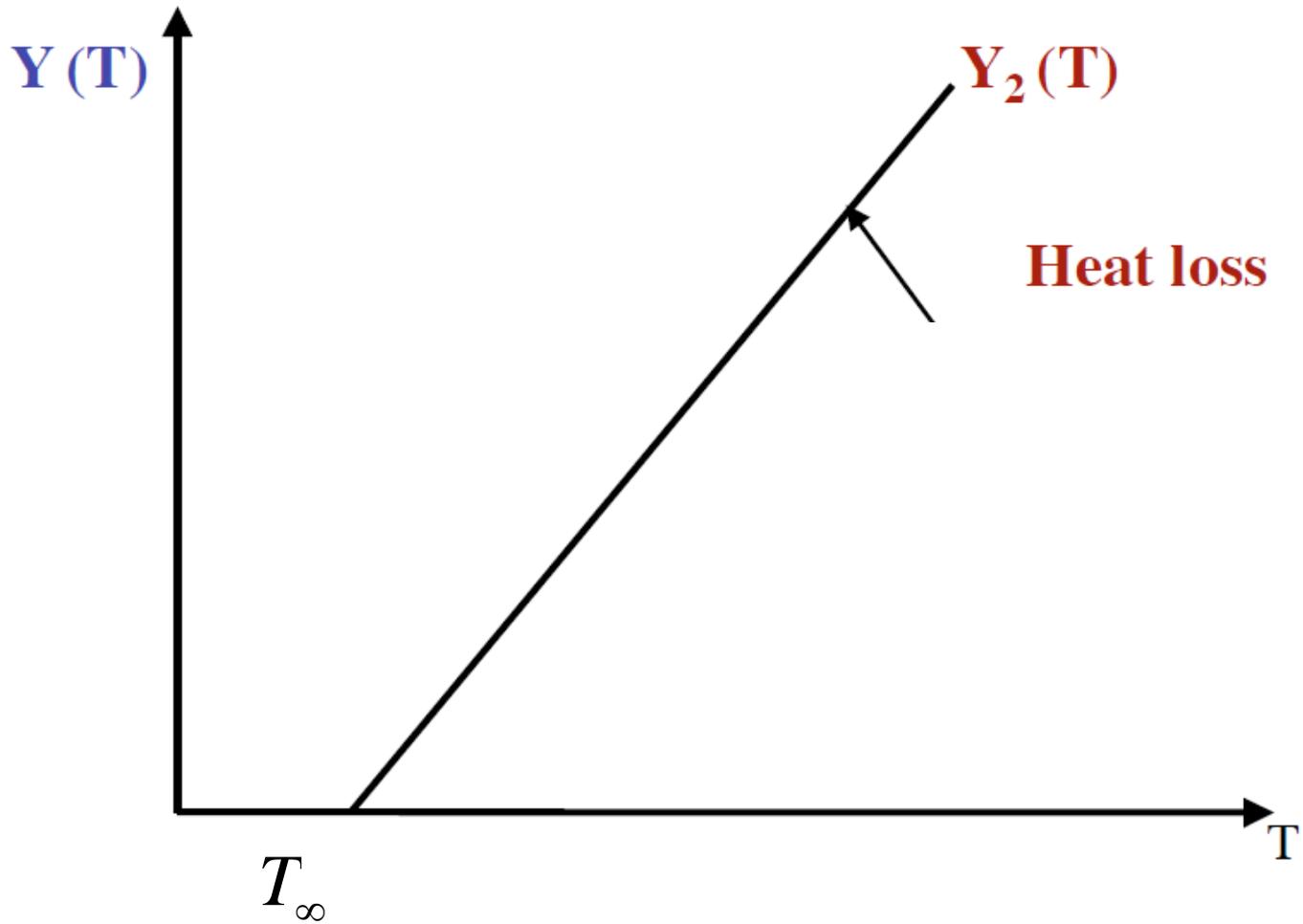


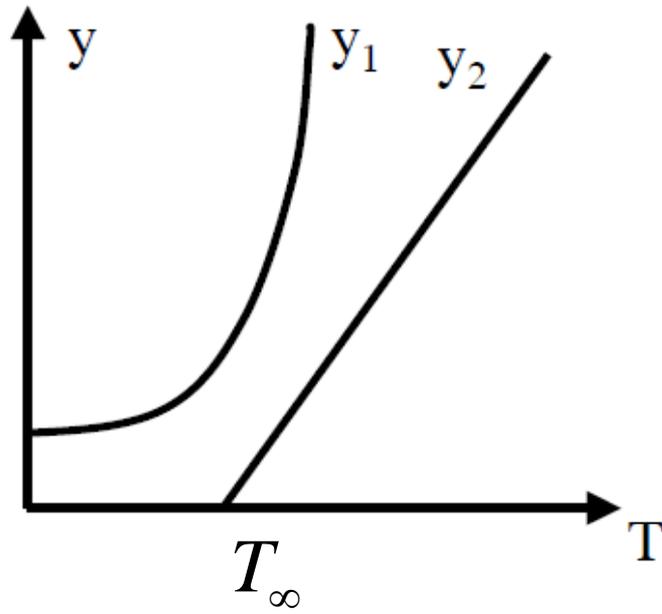
$$y_1(T)$$



$$y_2(T)$$

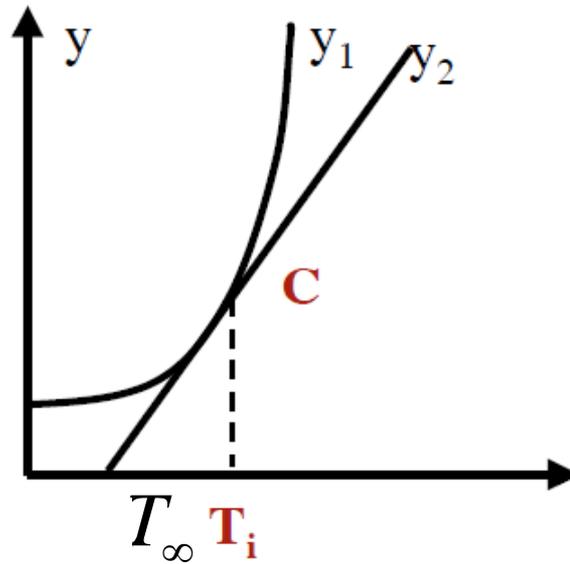






Auto-ignition

Termination of ignition limits (P_i , T_i)



$$\dot{m}''' \Delta h_c = h \frac{S}{V} (T - T_\infty)$$

At the critical point C:

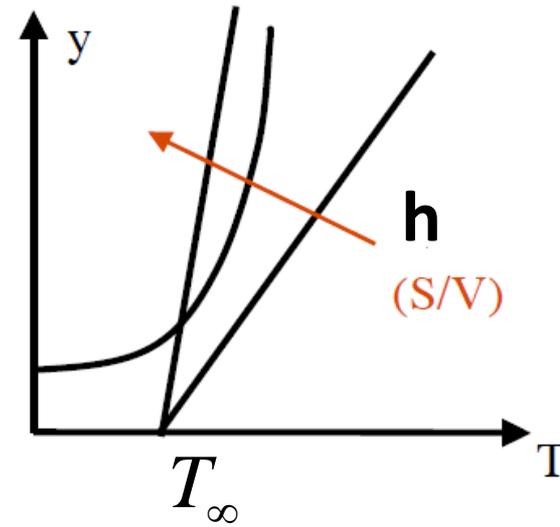
$$\left\{ \begin{array}{l} (y_1)_C = (y_2)_C \\ \left(\frac{dy_1}{dT} \right)_C = \left(\frac{dy_2}{dT} \right)_C \end{array} \right.$$

Competition of heat loss and chemical energy release

Varying h or (S/V)

The critical temperature T_c is not an intrinsic mixture property.

Indeed, it is function of h and (S/V)



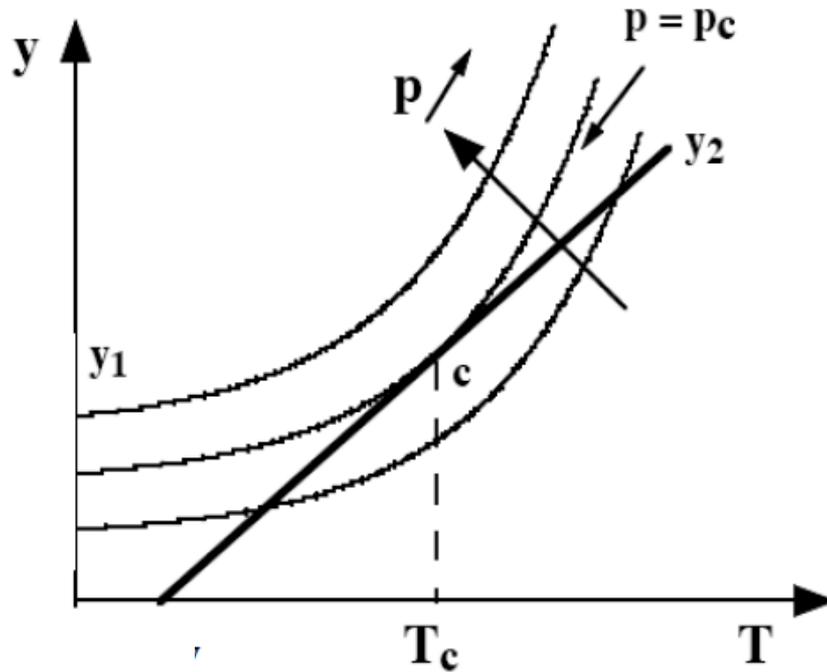
If the system is **well insulated**, h **decreases**, and it **increases the risk of auto-ignition**

$$S / V = 1 / L$$

If L goes up, S/V decreases and it **Increases the risk of auto-ignition**

--

Varying P



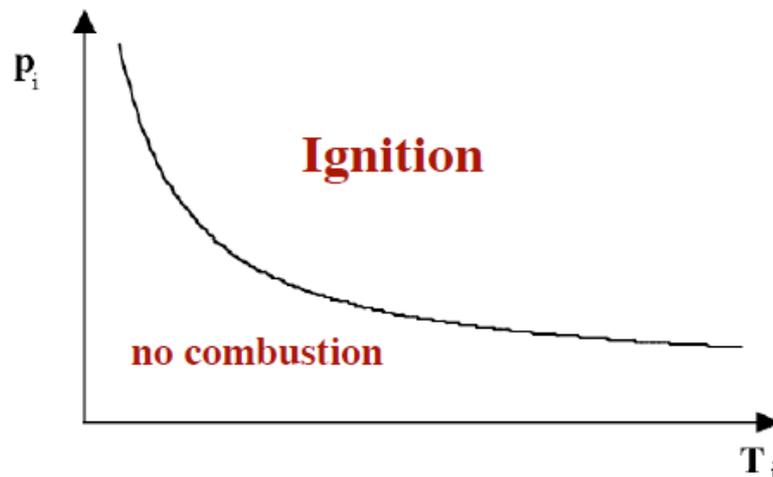
There exists a **critical pressure P_c** above which there is always mixture auto-ignition.

Effect of pressure on the Autoignition Temperature

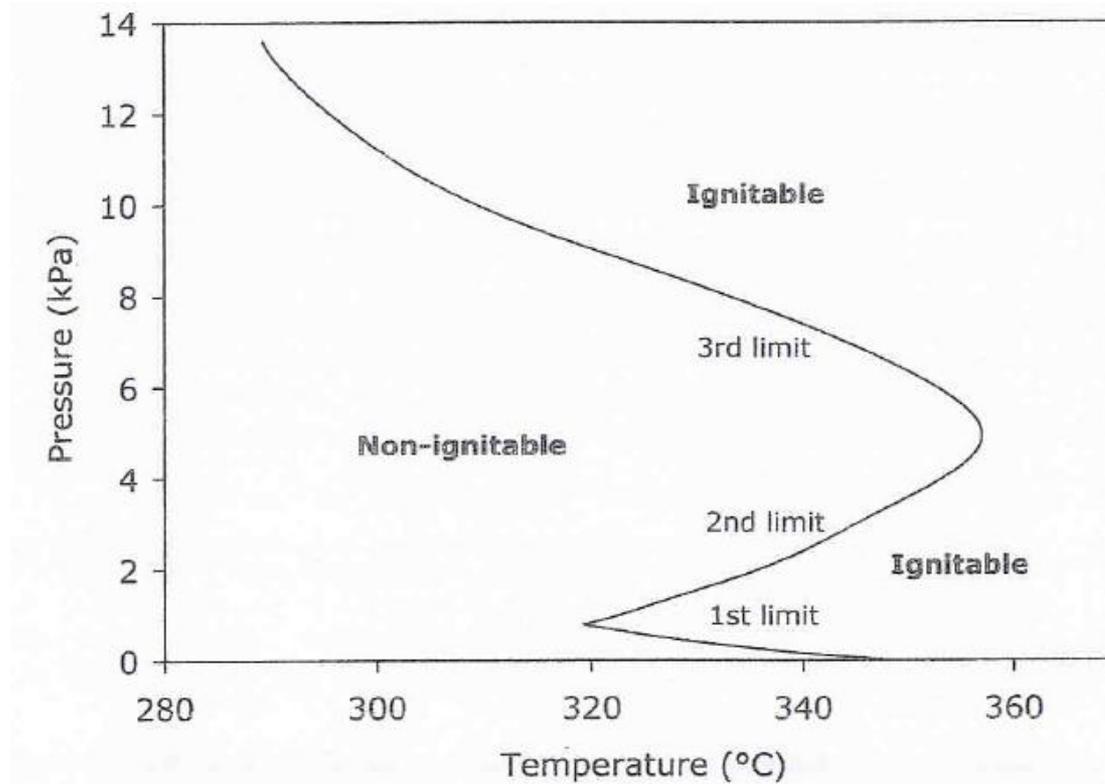
Raising the pressure generally lowers the AIT. The theory discussed above indicates that :

$$\ln \frac{P}{T^2} = \frac{A}{T} + B$$

Determination of ignition limits (P_i , T_i)



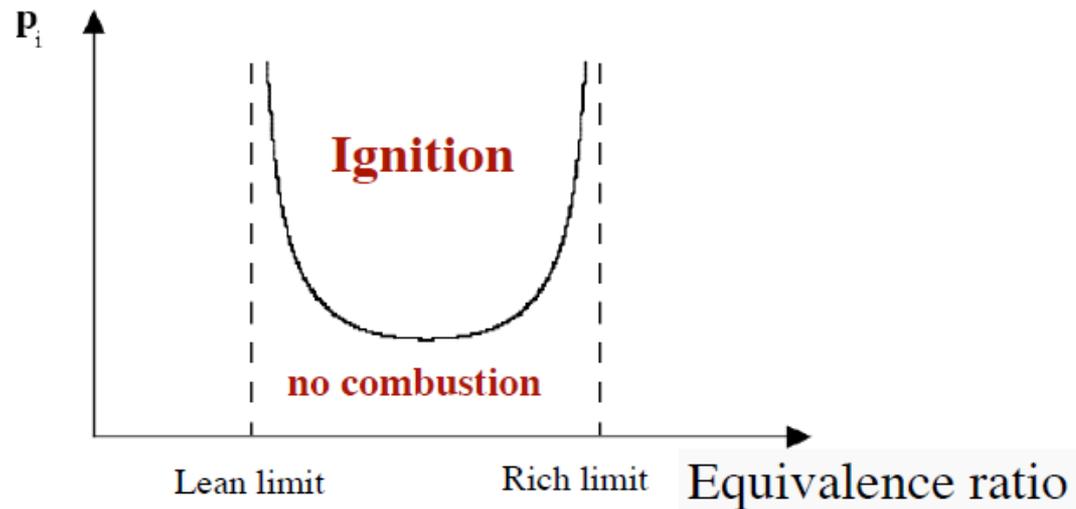
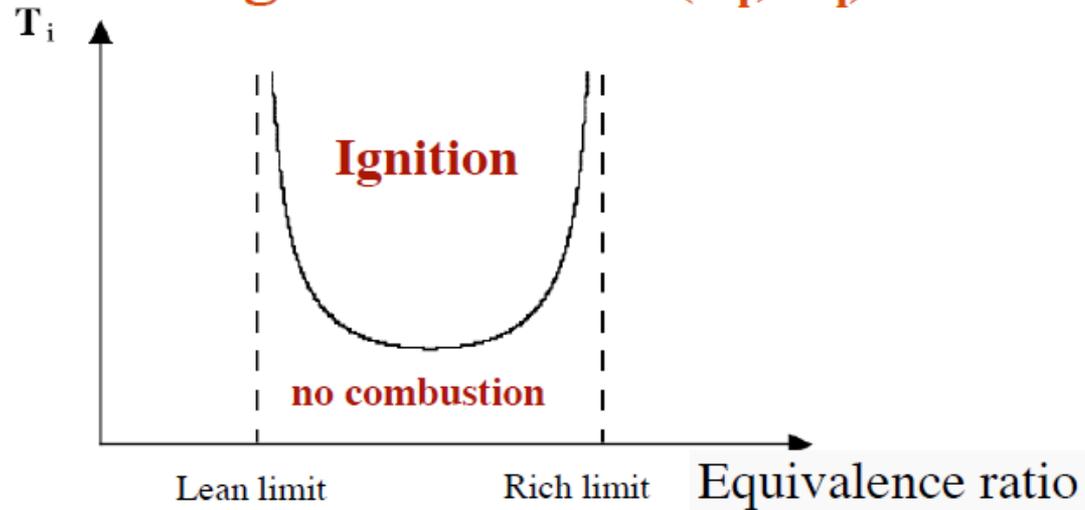
Effect of pressure on the Autoignition Temperature



The ignition regions for a stoichiometric mixture of H₂S

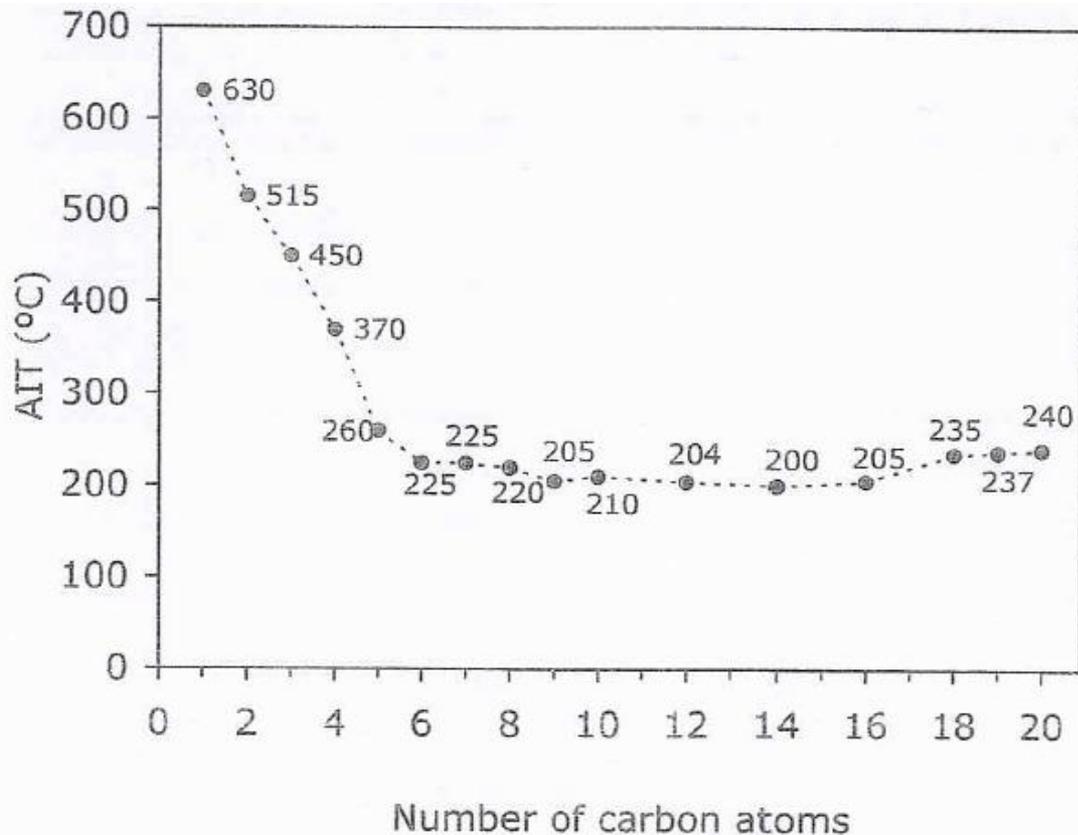
[Babrauskas]

Determination of ignition limits (P_i , T_i)

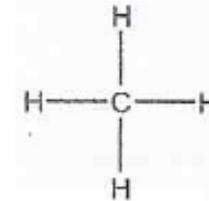


Fuel	AIT (°C)
Methane, CH ₄	540
Ethane, C ₂ H ₆	515
Propane, C ₃ H ₈	450
<i>n</i> -Hexane, C ₆ H ₁₄	225
<i>n</i> -Heptane, C ₇ H ₁₆	215
Methanol, CH ₃ OH	385
Ethanol, C ₂ H ₅ OH	365
Kerosene	210
Gasoline	~450
JP-4	240
Hydrogen, H ₂	400

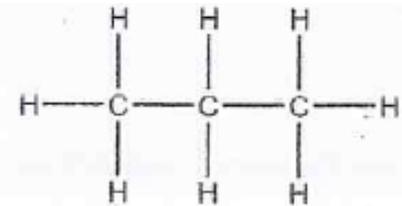
Autoignition temperatures (at 25°C and 1 atm) [Zabetakis]



The AIT of n-alkane hydrocarbons in air, as a function of the number of carbon atoms [Babrauskas]



Methane



Propane

Hydrocarbons molecules of higher molar mass have carbon-carbon and carbon-hydrogen bonds. Methane has no C-C bond.

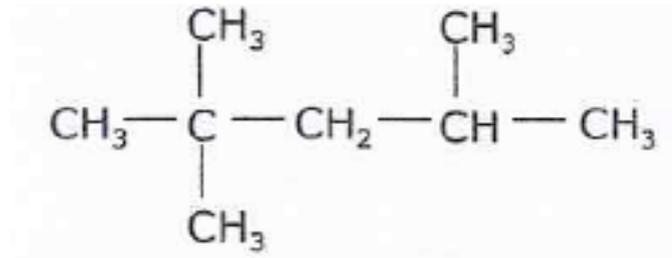
439 $\text{kJ}\cdot\text{mol}^{-1}$ must be supplied to break a C-H in methane, but only 356 $\text{kJ}\cdot\text{mol}^{-1}$ to break the C-C bond in propane and 305 to 320 $\text{kJ}\cdot\text{mol}^{-1}$ in larger hydrocarbon molecules.

Branched molecules typically have higher AIT values than straight-chain molecules.

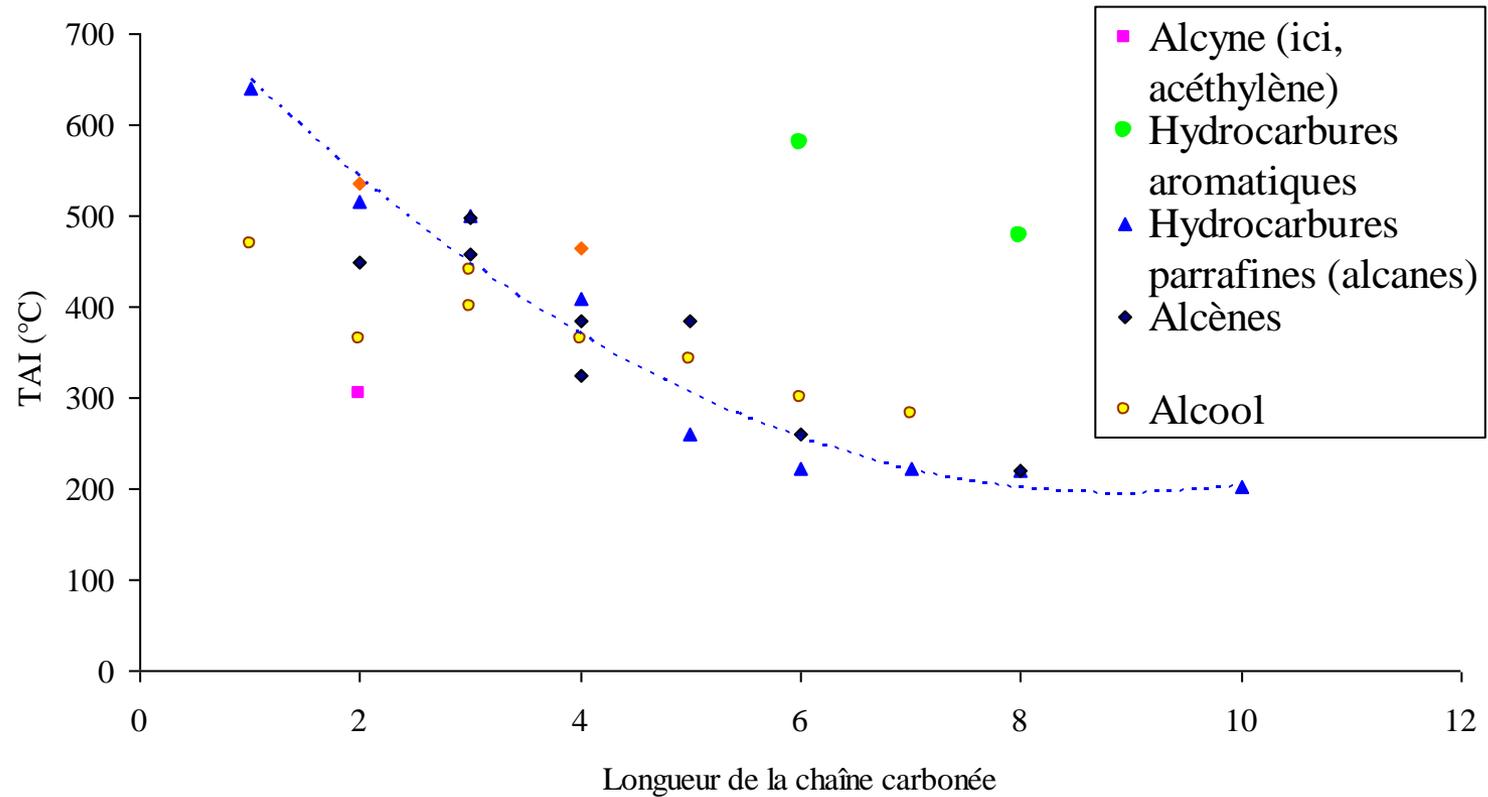
Ex : Knock in engine

n-octane has an AIT of 220 °C

Iso-octane has an AIT of 415°C



Variable affecting the AIT : Molecular structure

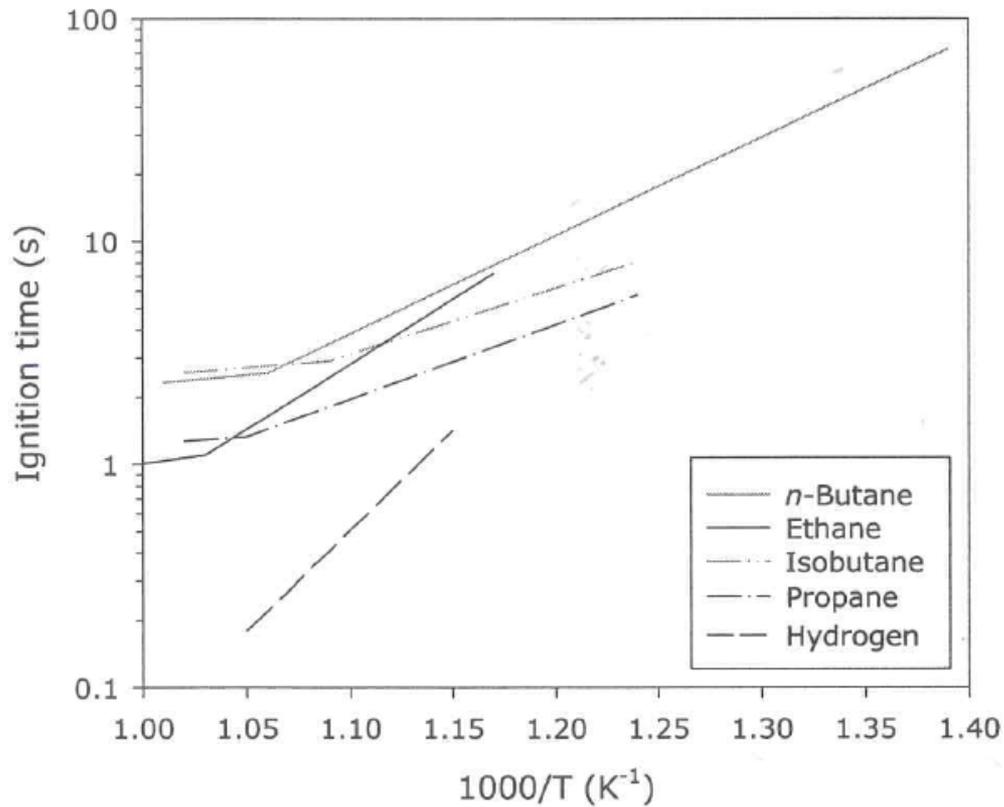


Ignition time

The time needed for a gas mixture ignite, when exposed to an elevated temperature environment, can range from about 0,01 ms to hundreds of seconds.

If simple Arrhenius kinetics is used and Semenov's theory is adopted, then a relation of form is expected.

$$\ln t_{ig} = \left(\frac{E}{R} \right) \frac{1}{T} + a$$



Ignition times for several fuel gases (stoichiometric concentration of the fuel in air), as measured by Anagnostou et al.

Oxygene concentration

The AIT in oxygen for such substances (below 400°C) can be greatly below its air value.

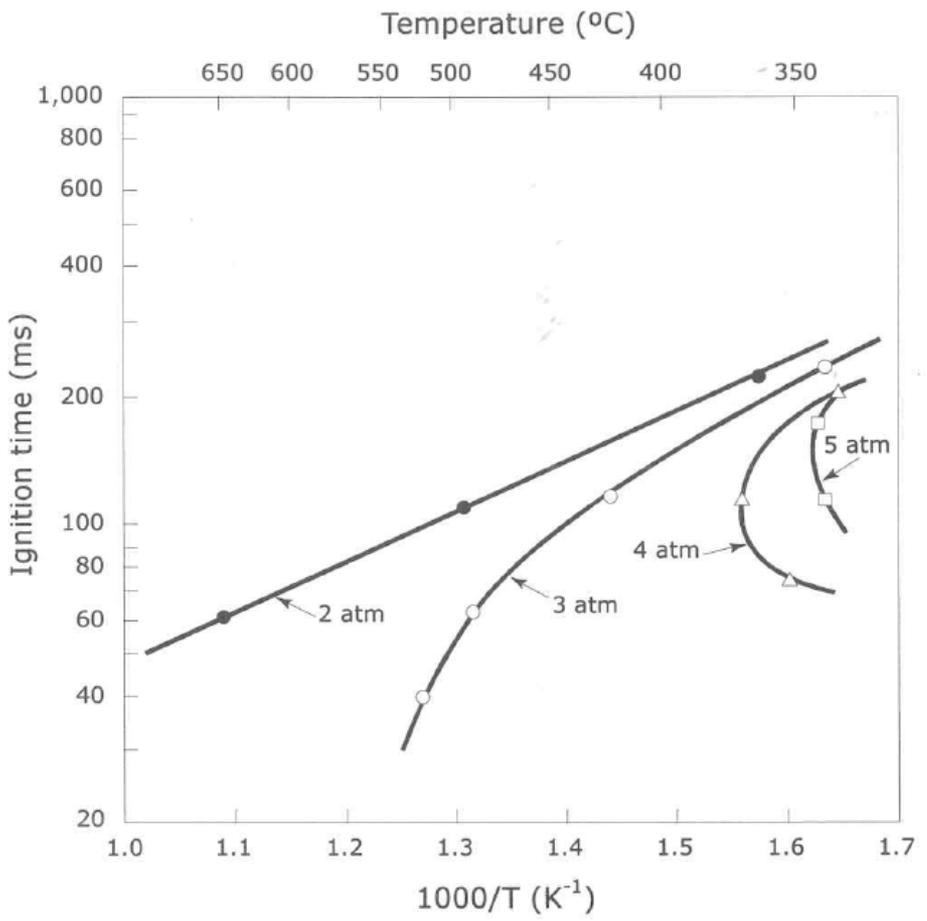
Increasing the oxygen concentration generally decreases the ignition time.

Experiments show that the oxygen concentration effect is :

$$t_{ig} = \frac{b}{[O_2]^n} e^{\frac{E}{RT}}$$

Effect of pressure

Effect of pressure on the ignition time of pentane (as measured by the Bureau of Mines)



Increasing the mixture pressure generally shortens the ignition time.

It has been proposed that the pressure-dependence has the form : $t_{ig} \propto P^{-n} e^{\frac{E}{RT}}$

Or, alternatively, as : $\ln t_{ig} = \left(\frac{E}{R}\right) \frac{1}{T} - n \ln P + a'$ $0,4 \leq n \leq 2,5$

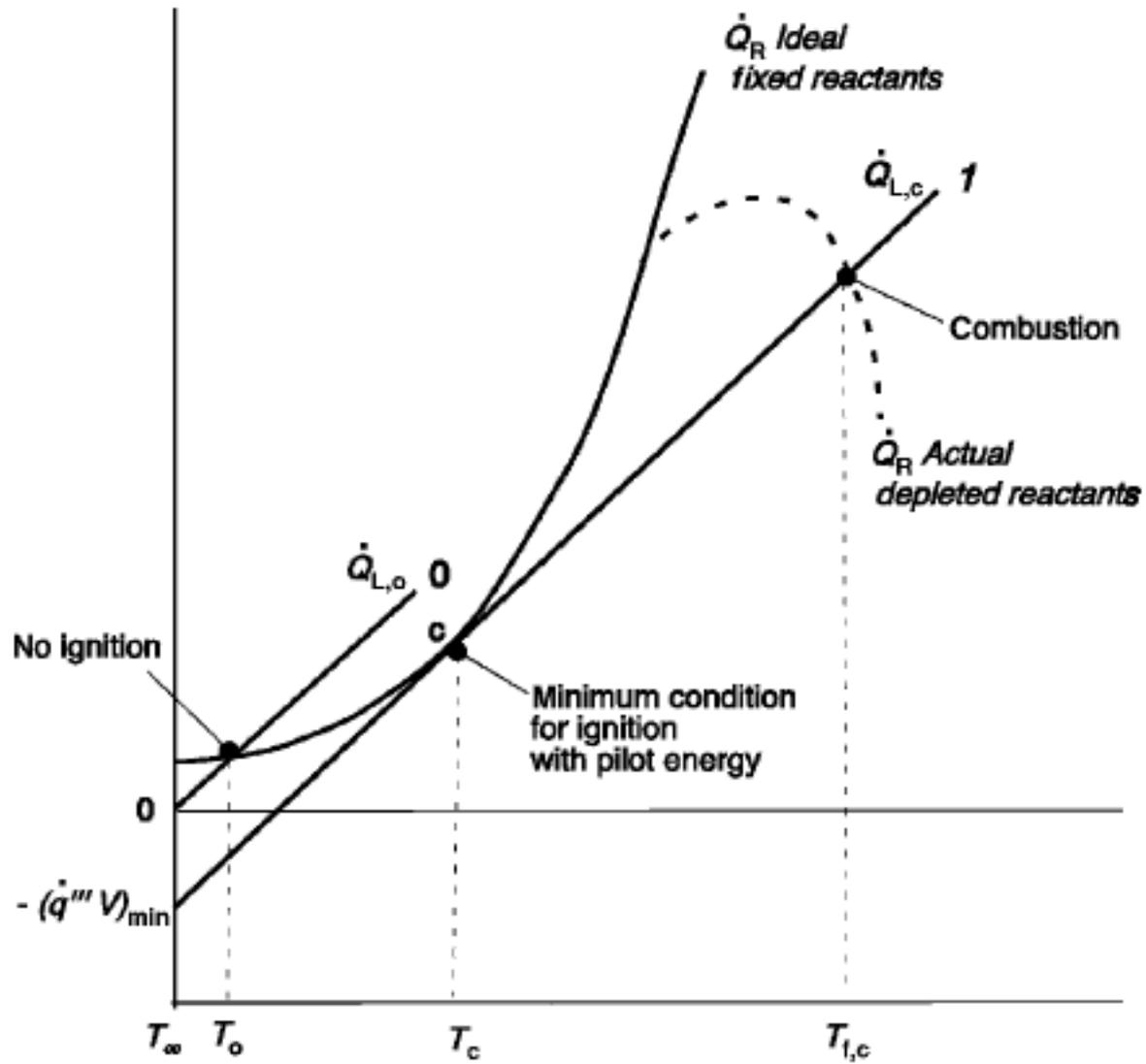
Piloted ignition or MIE (Minimum Ignition Energy)

$$\rho V c_p \frac{dT}{dt} = \dot{m}_F''' \Delta h_c V + \dot{q}''' V - hS(T - T_\infty)$$

$$\dot{Q}_R = \dot{m}_F''' \Delta h_c V$$

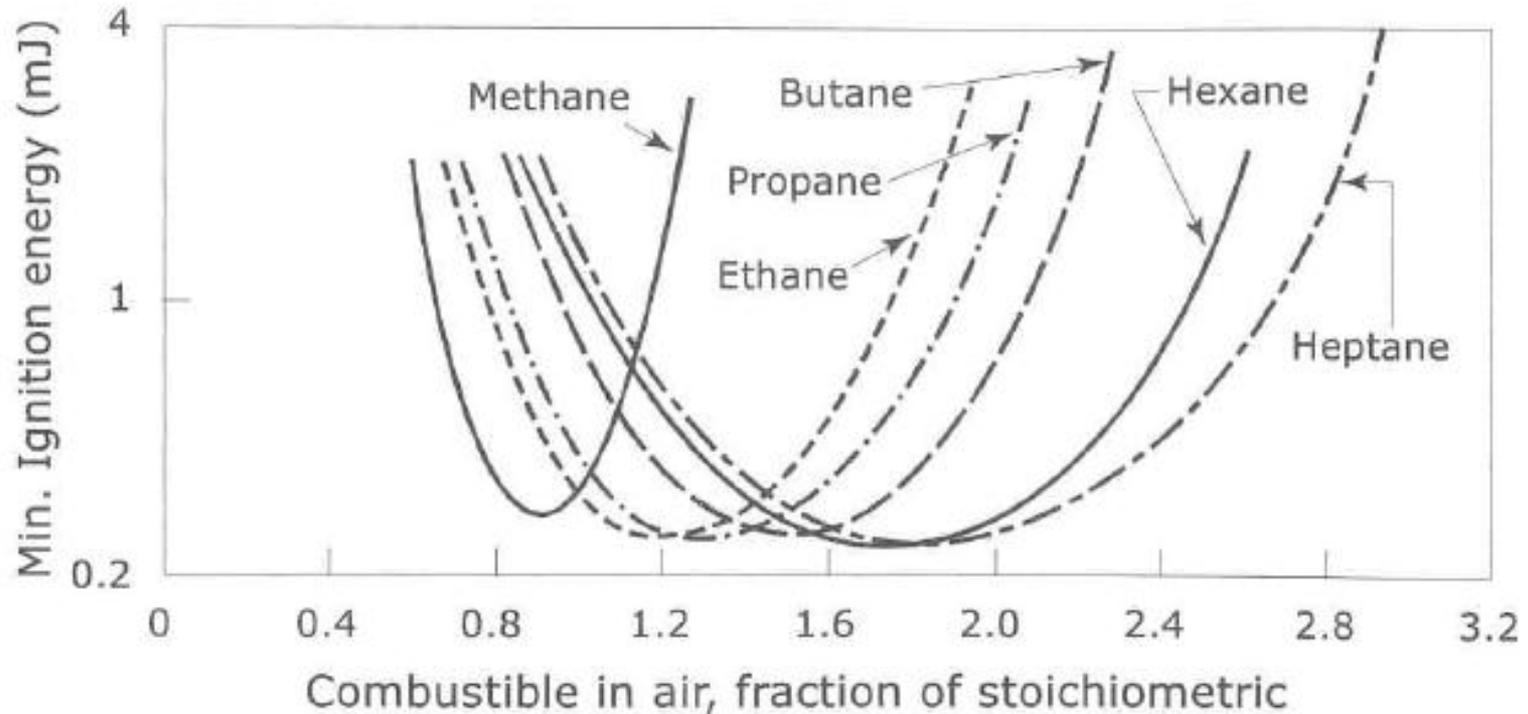
and the net loss term as

$$\dot{Q}_L = hS(T - T_\infty) - \dot{q}''' V$$



[Quintiere]

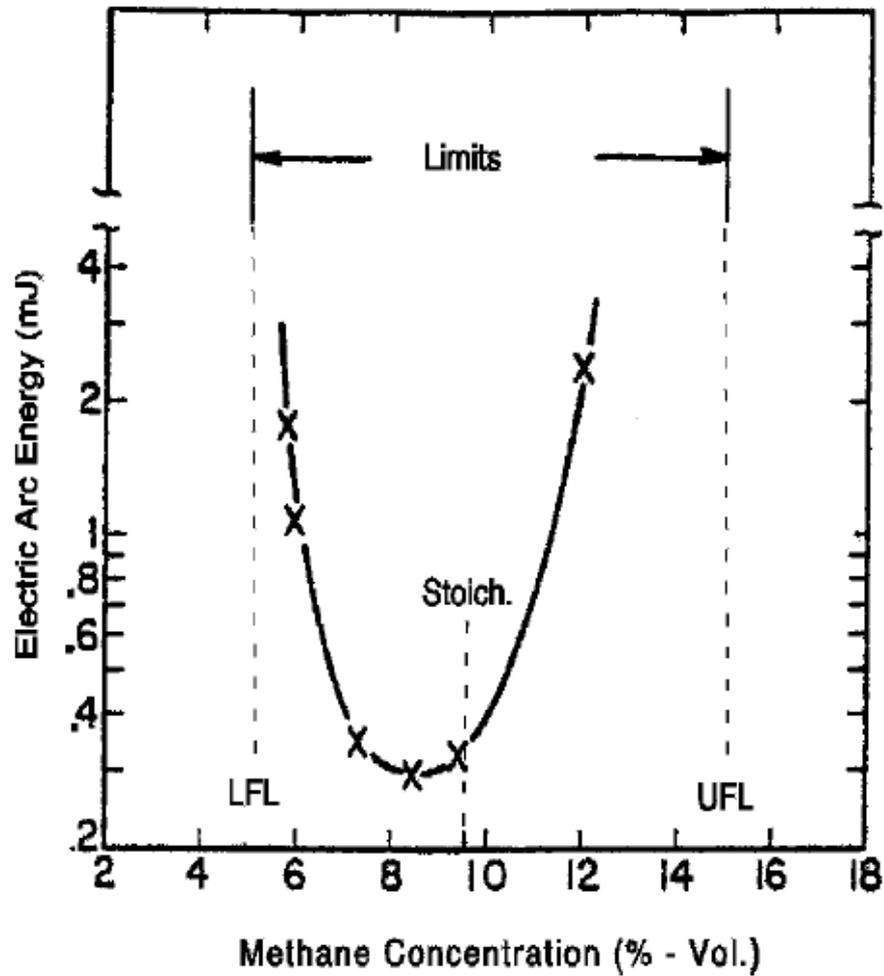
Fuel concentration



The effect of fuel/air mixture on the MIE for alkane-series hydrocarbons [Babrauskas]

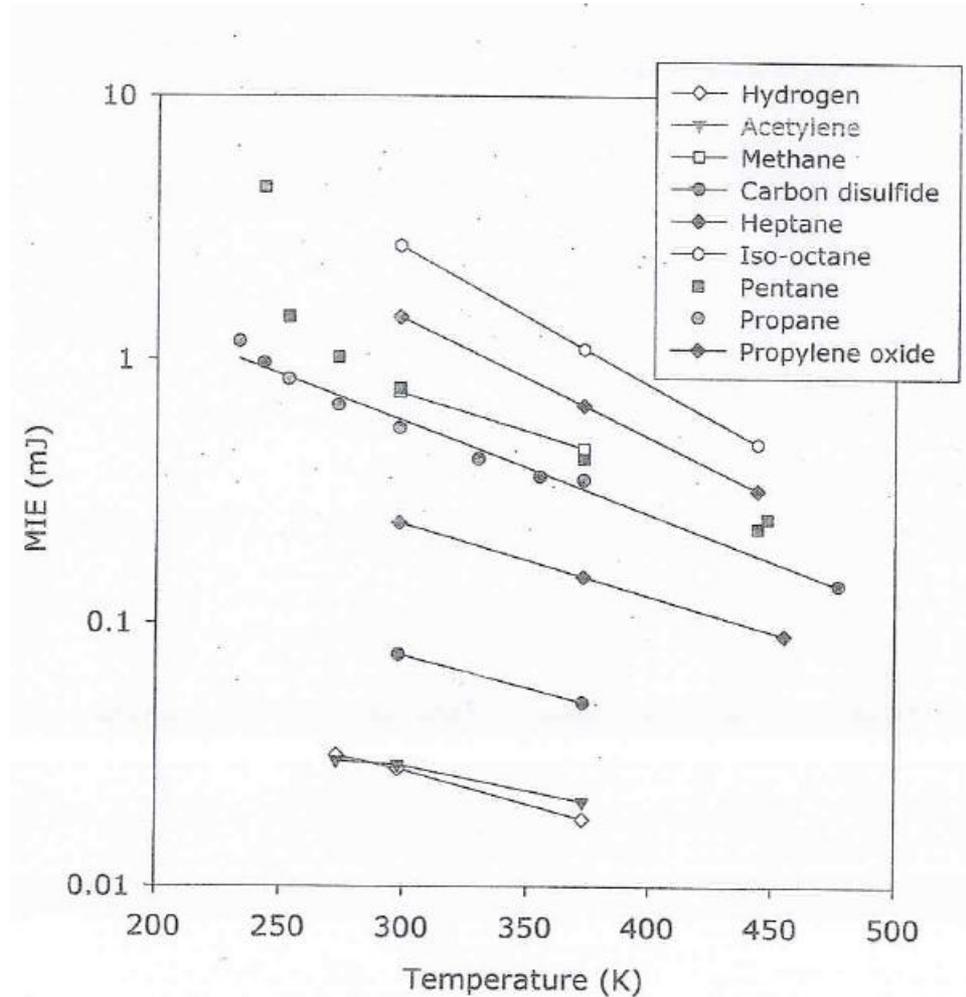
**If the fuel and the oxidizer had identical diffusivities mixture condition ($\Phi = 1$)
Molecular lighter than air (hydrogen, methane) have higher diffusivities and the MIE for those occurs at $\Phi < 1$.**

Most other fuel molecules are heavier than air, and for them the MIE occurs at $\Phi > 1$.



Ignitability curve and limits of flammability for methane-air mixtures at atmospheric pressure at 26°C [Zabetakis]

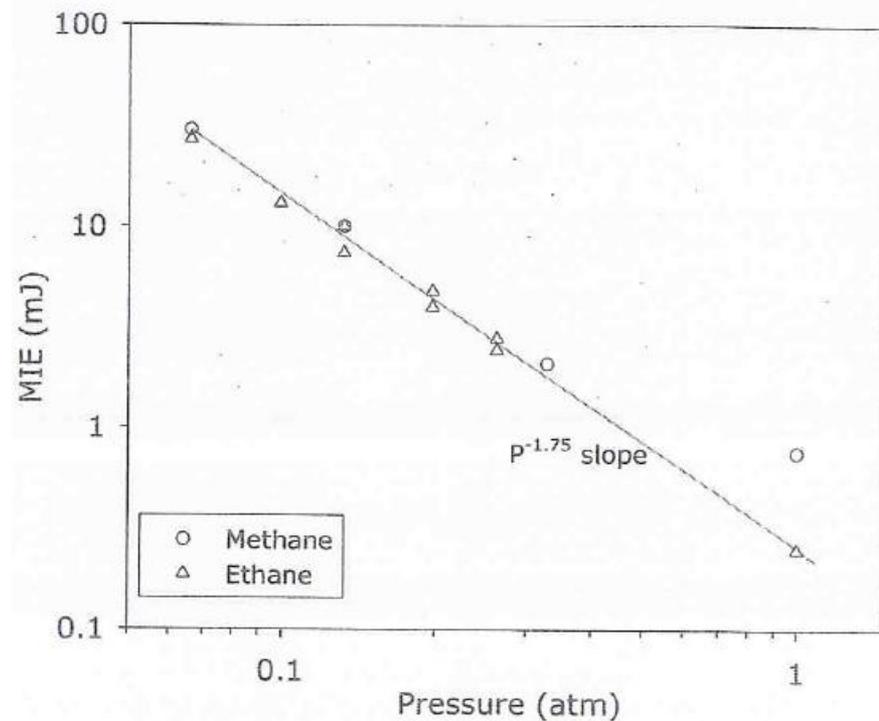
Effect of temperature



Increasing temperature lowers the MIE . The straight-line relationship indicates

$$\text{that : } \ln(MIE) \propto \frac{1}{T}$$

Effect of pressure



Pressure effect on MIE [Babrauskas]

Increasing pressure lowers the MIE. The relationship is generally considered to go

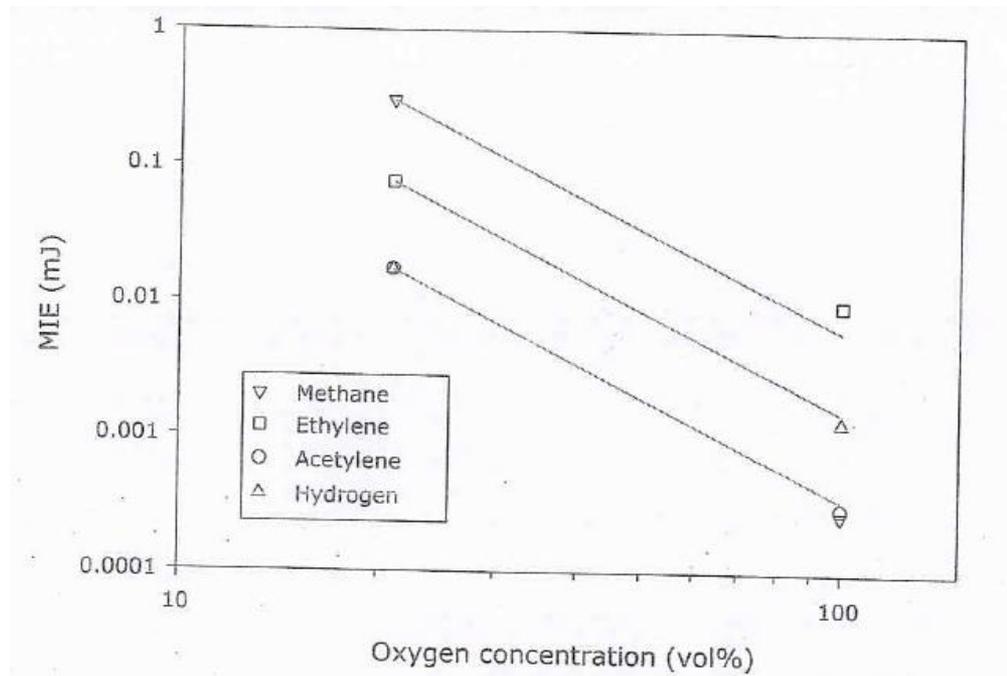
as : $MIE \propto P^{-n}$, where n is the range 1,72 to 2,1. Example data for ethane

and methane are shown in this Figure.

Oxygene concentration

$MIE \propto (OI)^{-2,5}$, where OI = oxygen index, $O_2/(O_2+N_2)$

$$MIE_{propane} = 0,0034P^{-2,1}(OI)^{-2,5}$$



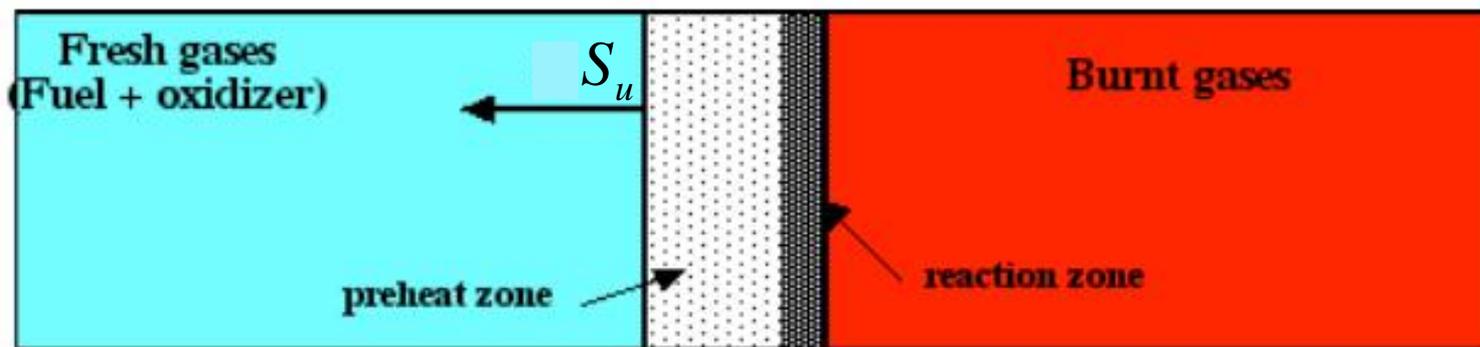
Flame speed

Flammability is defined for a mixture of fuel and oxidizer when a sustained propagation occurs after ignition. The results for a given mixture depends on temperature, pressure, heat losses and flow effects.

The speed of this propagation also depends on whether the flow remains laminar or becomes turbulent, and whether it exceeds the speed of sound (Detonation). The pressure rise across the burning region is relatively low for a deflagration.

The ideal flame speed is called the burning velocity and is defined as the normal speed of an adiabatic plane (laminar) combustion region measured with respect to the unburned gas mixture.

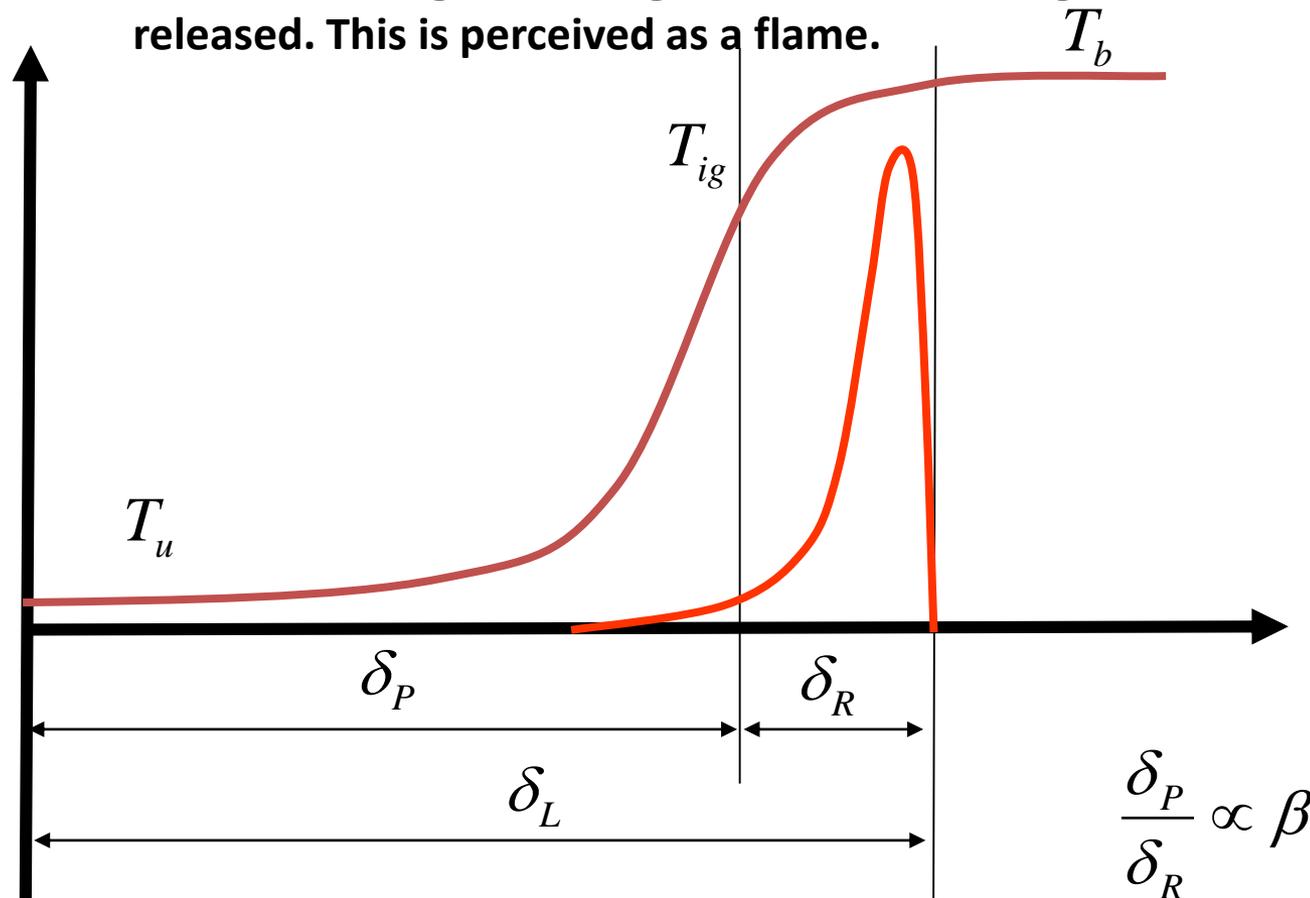
The ability to predict flame speed is limited by the same factors used to predict the autoignition or flammability limits. However, an approximate analysis first considered by Mallard and Le Chatelier can be useful for quantitative estimates.



$$\rho_u S_u = \rho_b v_b = \dot{m}'' \quad \text{or the mass flux, where } \dot{m}'' \text{ is constant.}$$

Consider a planar combustion region in an adiabatic duct that is fixed in space and is steadily supplied with a mixture of fuel (F), oxidizer (O) and diluent (D) at the velocity S_u . The process is divided into two stages :

- I. A preheat region in which the heat transfer from the flame brings the unburned mixture to its critical temperature for ignition, T_{ig} .
- II. The second stage is the region zone where a significant chemical energy is released. This is perceived as a flame.



Structure d'une flamme de pré-mélange (en propagation libre, non étirée)

Burning velocity theory

The conservation of energy applied to the preheat zone requires a knowledge of the 'ignition' temperature, T_{ig} and the heat transferred to the preheat region. We assume that radiation effects are negligible and approximate this heat flux as :

$$\dot{q}'' = -k \frac{dT}{dx} \approx k \left(\frac{T_b - T_{ig}}{\delta_R} \right)$$

We only seek an order of magnitude estimation and insight into the important variables. With this approximation the energy equation is :

$$\rho_u S_u c_p (T_{ig} - T_u) \approx k \left(\frac{T_b - T_{ig}}{\delta_R} \right)$$

$$S_u \approx \left(\frac{T_b - T_{ig}}{T_{ig} - T_u} \right) \frac{\alpha}{\delta_R}$$

Typical value of the flame thickness

From the previous order of magnitude analysis

$$S_U \propto \frac{\lambda}{\rho_u C_P \delta_R} \propto \frac{\alpha}{\delta_R} \qquad \delta_R \propto \frac{\alpha}{S_U}$$

Using representative values for thermal diffusivity and 1 m/s for the velocity of propagation, it gives 0.1 mm ...

and such a value is OK with experiments

The gain further insight into the effect of kinetics on the flame speed, we write the energy equation for the control volume (Reaction zone) as :

$$\rho_u S_u c_p (T_b - T_{ig}) = \dot{m}_F''' \Delta h_c \delta_R - \dot{q}''$$

We can make the same approximation, $\dot{q}'' = -k \frac{dT}{dx} \approx k \left(\frac{T_b - T_{ig}}{\delta_R} \right)$

and substitute for δ_R using equation

$$S_u \approx \left(\frac{T_b - T_{ig}}{T_{ig} - T_u} \right) \frac{\alpha}{\delta_R}$$

It can be shown that

$$S_u = \left\{ \frac{[(T_b - T_{ig}) / (T_{ig} - T_u)] \alpha \dot{m}_F''' \Delta h_c}{\rho_u c_p (T_b - T_u)} \right\}^{1/2}$$

We approximate $\frac{T_b - T_{ig}}{T_{ig} - T_u} \approx \frac{1500}{500} = 3$

$$S_u \approx \left[\frac{3 \alpha \Delta h_c \dot{m}_F'''}{\rho_u c_p (T_b - T_u)} \right]^{1/2}$$

And substitute to estimate the flame speed as :

With the Arrhenius law for RR (Reaction rate), the temperature dependence can be expressed :

$$S_U \propto \sqrt{e^{-E_a/RT}} = e^{-E_a/2RT}$$

This results is one of the most important relationship in laminar-flame theories.

And the effect of pressure, this equation implies that for second-order chemical reactions, the laminar-flame speed should be independent of pressure.

$$S_U \propto \sqrt{\frac{1}{\rho} P^{n-1}} \propto \sqrt{P^{n-2}}$$

Fuel lean results

For our estimations and the adiabatic control volume, T_b should be the adiabatic flame temperature.

Consider a fuel-lean case in which no excess fuel leaves the control volume.

All the fuel is burned. Then by the conservation of species,

$$\rho_u S_u Y_{F,u} = \dot{m}_F''' \delta_R$$

In addition, conservation of energy for the entire control volume gives (preheat and reactions zones)

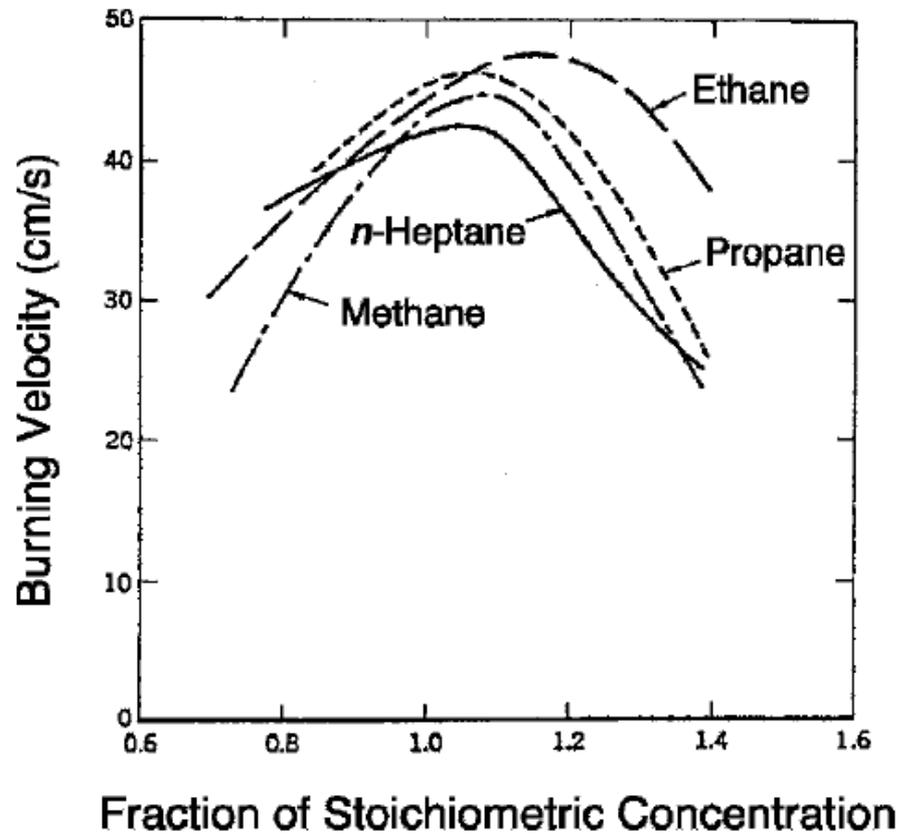
$$\rho_u S_u c_p (T_b - T_u) = \dot{m}_F''' \delta_R \Delta h_c$$

Combining these equations gives $c_p (T_b - T_u) = Y_{F,u} \Delta h_c$

for the fuel-lean adiabatic case. Then equation can be written as :

$$S_u \approx \left[\frac{3\alpha \Delta h_c \dot{m}_F'''}{\rho_u c_p (T_b - T_u)} \right]^{1/2}$$

$$S_u = \left(\frac{3\alpha \dot{m}_F'''}{\rho_u Y_{F,u}} \right)^{1/2}$$



Typical burning velocities (Zabetakis)

Typical values of laminar flame propagation velocity

Flame propagation velocity in normal conditions (pressure and temperature)

CH₄-air, stoichiometric: 0.43 m/s

C₂H₂-air, stoichiometric: 1.44 m/s

H₂-air, stoichiometric: 1.70 m/s

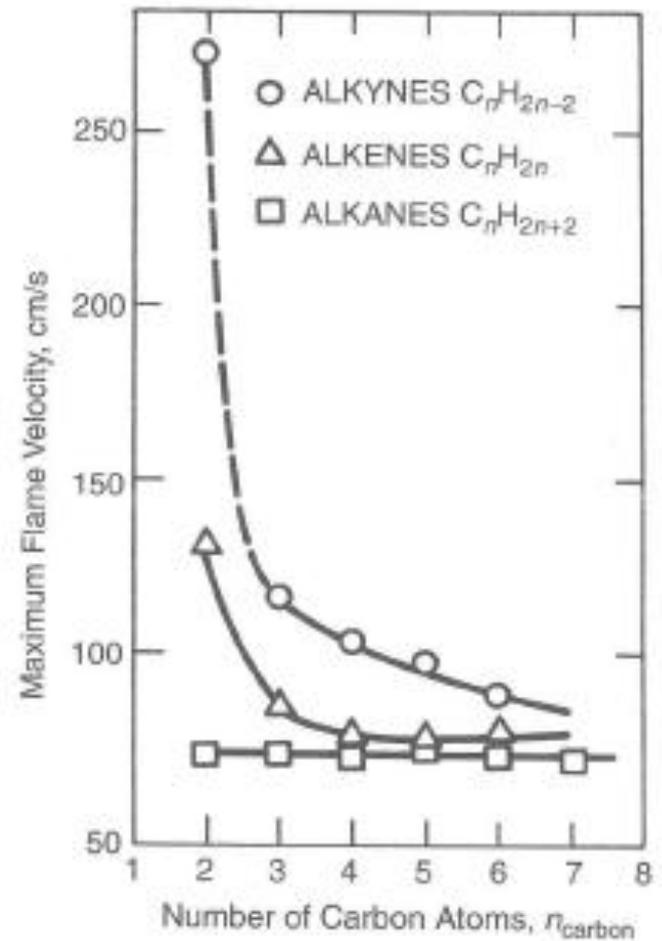
H₂-air, lean mixture 0.8: 1.20 m/s

It is generally acceptable to assume that a mixture with maximum flame temperature is also a mixture with maximum flame speed.

In very lean or very rich mixtures, it is impossible to propagate a flame because there is too little fuel or oxidant to maintain a steady deflagration wave. Thus, there exist upper and lower flammability limits.

Effect of fuel molecular structure

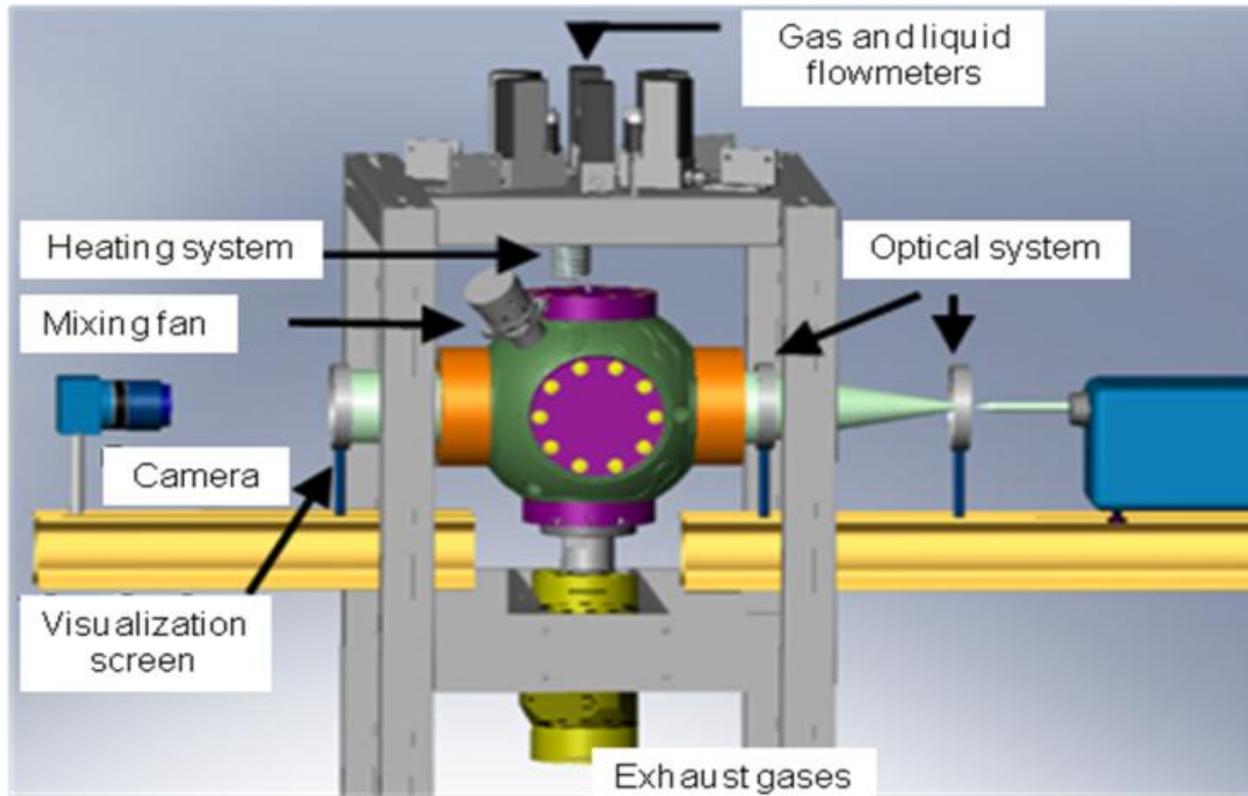
Effect of the number of carbon atoms in the chain on maximum flame velocity (Reynolds and Gerstein)



For saturated hydrocarbons [alkanes : also know as paraffins], the maximum flame speed (70 cm/s) is nearly independent of the number of carbons in the molecule for unsaturated hydrocarbons [either alkenes (also known as olefins) such C_2H_4 (ethylene)], or alkynes (such acetylene C_2H_2), the laminar-flame speed is higher for fuels with a smaller number of carbons atoms.

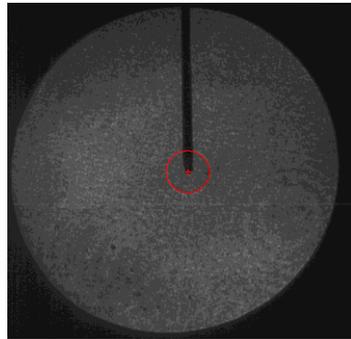
EXPERIMENTAL SETUP

➤ Spherical expanding flame method



- Equivalence ratios of pinene/air mixtures: 0.7 to 1.4
- Temperatures: 85 to 180 °C

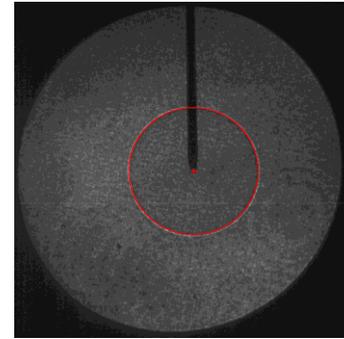
EXPERIMENTAL SETUP



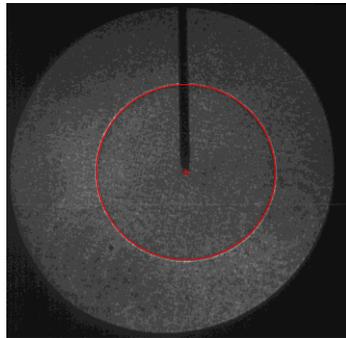
$t = 1.5$ ms



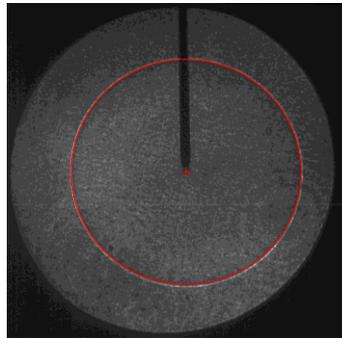
$t = 3.0$ ms



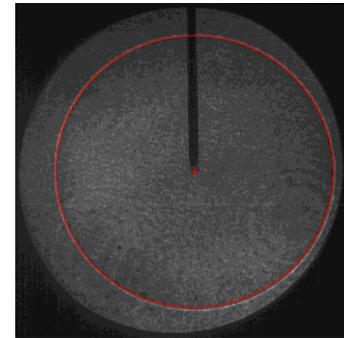
$t = 4.5$ ms



$t = 6.0$ ms



$t = 7.5$ ms



$t = 9.0$ ms

✓ Temporal evolution of a **stoichiometric *pinene*/air mixture** flame front

The results show that the flame speed depends on kinetics and thermal diffusion.

Any heat losses will decrease the temperature and therefore the burning rate and flame speed as well.

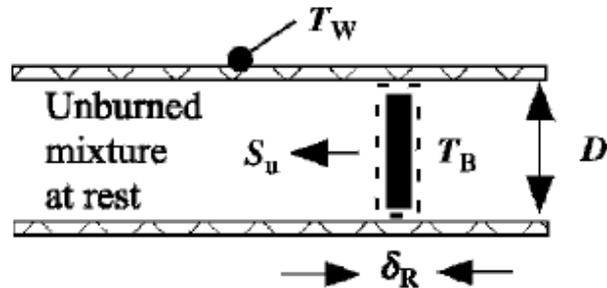
Indeed, if the heat losses are sufficient, no solution to equations may not be possible. Let us investigate this possibility.

Quenching Diameter

In the previous analysis, the heat loss was taken to be from the flame to the surrounding gas. If a solid is present, it will introduce some heat loss.

This will be examined in terms of flame propagation in a duct. For a large-diameter duct, a moving flame may only be affected at its edges where heat loss can occur to the duct wall. For a small-diameter duct, the diameter that will not allow a flame to propagate is called the quenching diameter, D_Q

$$\dot{Q}_L = h\pi D\delta_R(T_b - T_w)$$



$$\dot{m}''' \Delta h_c < h \frac{S}{V} (T - T_\infty)$$

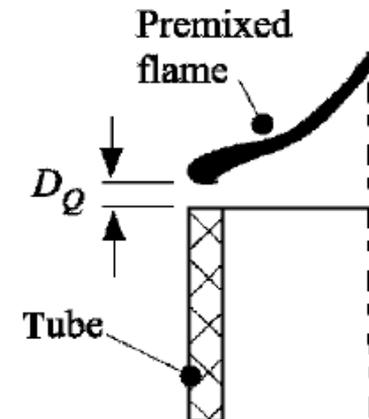
Quenching distance analysis

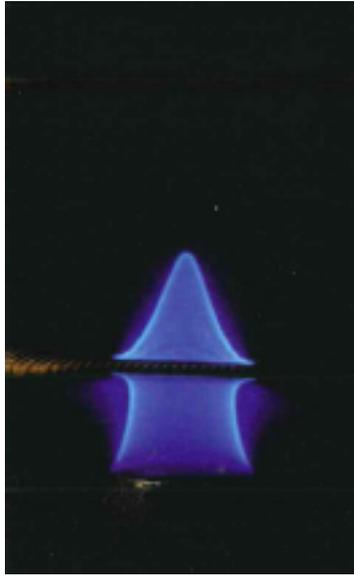
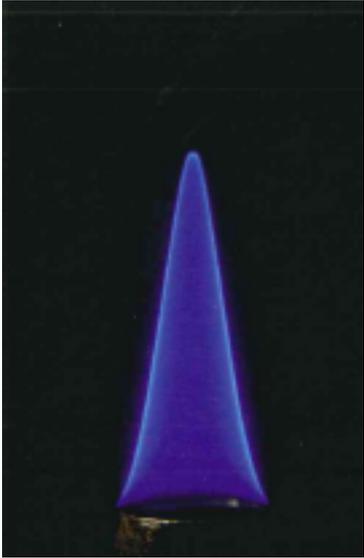
$$D_Q \propto \frac{\alpha}{S_U}$$

Fuel	S_u , Maximum (in air) (m/s)	D_Q , Stoichiometric (in air) (mm)
Hydrogen	2.9	0.64
Acetylene	1.5	2.3
Methane	0.52	2.5

The quenching distance is of practical importance in preventing flashback by means of a flame arrestor. This safety device is simply a porous matrix whose pores are below the quenching distance in size.

Even in a diffusion flame the region near a surface becomes a premixed flame since fuel and oxygen can come together in this 'quenched' region.





Heat loss effects and extinction

Consider the entire control volume in figure, but now heat is lost to the surroundings at the temperature of the unburned mixture, T_u . Such an analysis was described by Meyer. The conservation of energy for the entire control volume is :

$$\rho_u S_u c_p (T_b - T_u) = \dot{m}_F''' \delta_R \Delta h_c - \dot{q}''$$

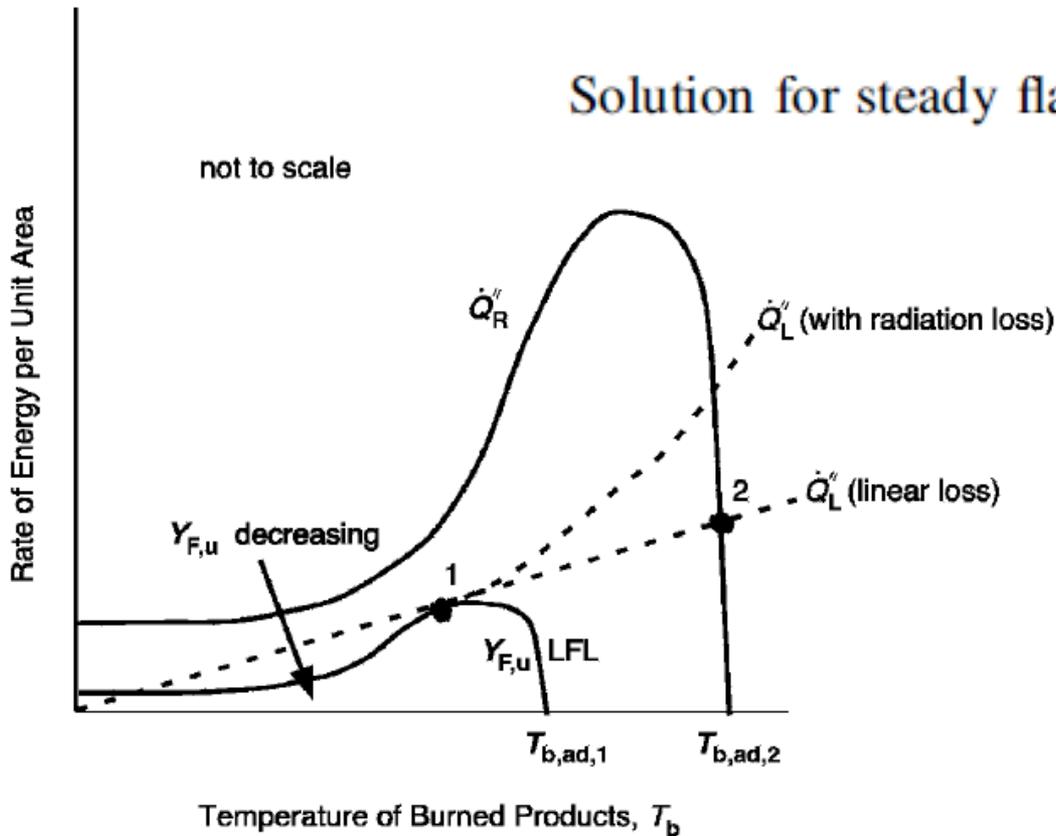
Consider the fuel-lean case, in which equation applies. Substituting gives :

$$\rho_u S_u Y_{F,u} = \dot{m}_F''' \delta_R$$
$$\dot{m}_F''' \delta_R \left[\Delta h_c - \frac{c_p (T_b - T_u)}{Y_{F,u}} \right] = \dot{q}''$$

Note that when $\dot{q}'' = 0$, T_b is the adiabatic flame temperature. We can regard this equation as a balance between the net energy released and energy lost :

$$\dot{Q}_R'' = \dot{m}_F''' \delta_R \left[\Delta h_c - \frac{c_p (T_b - T_u)}{Y_{F,u}} \right]$$

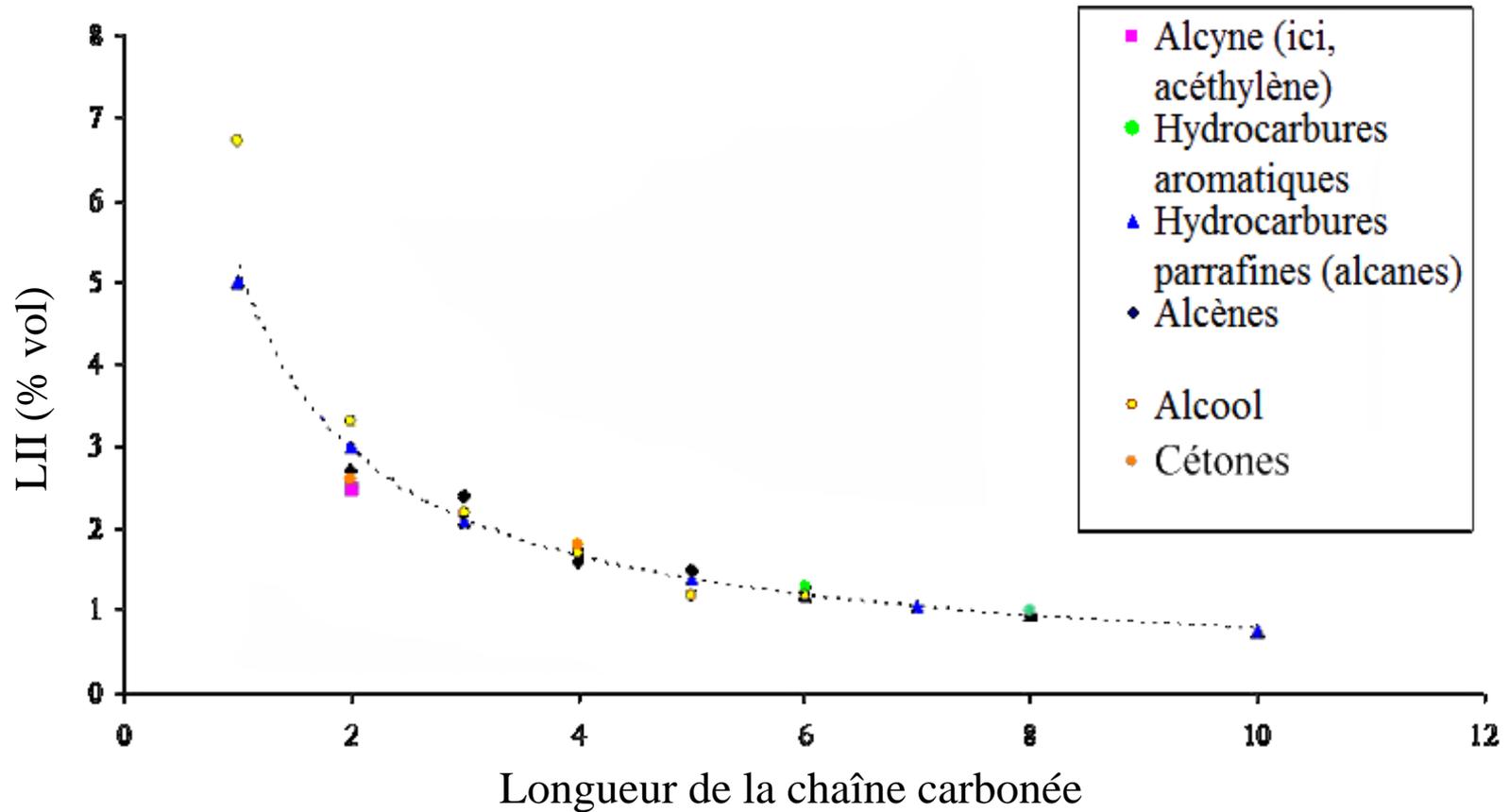
Solution for steady flame speed

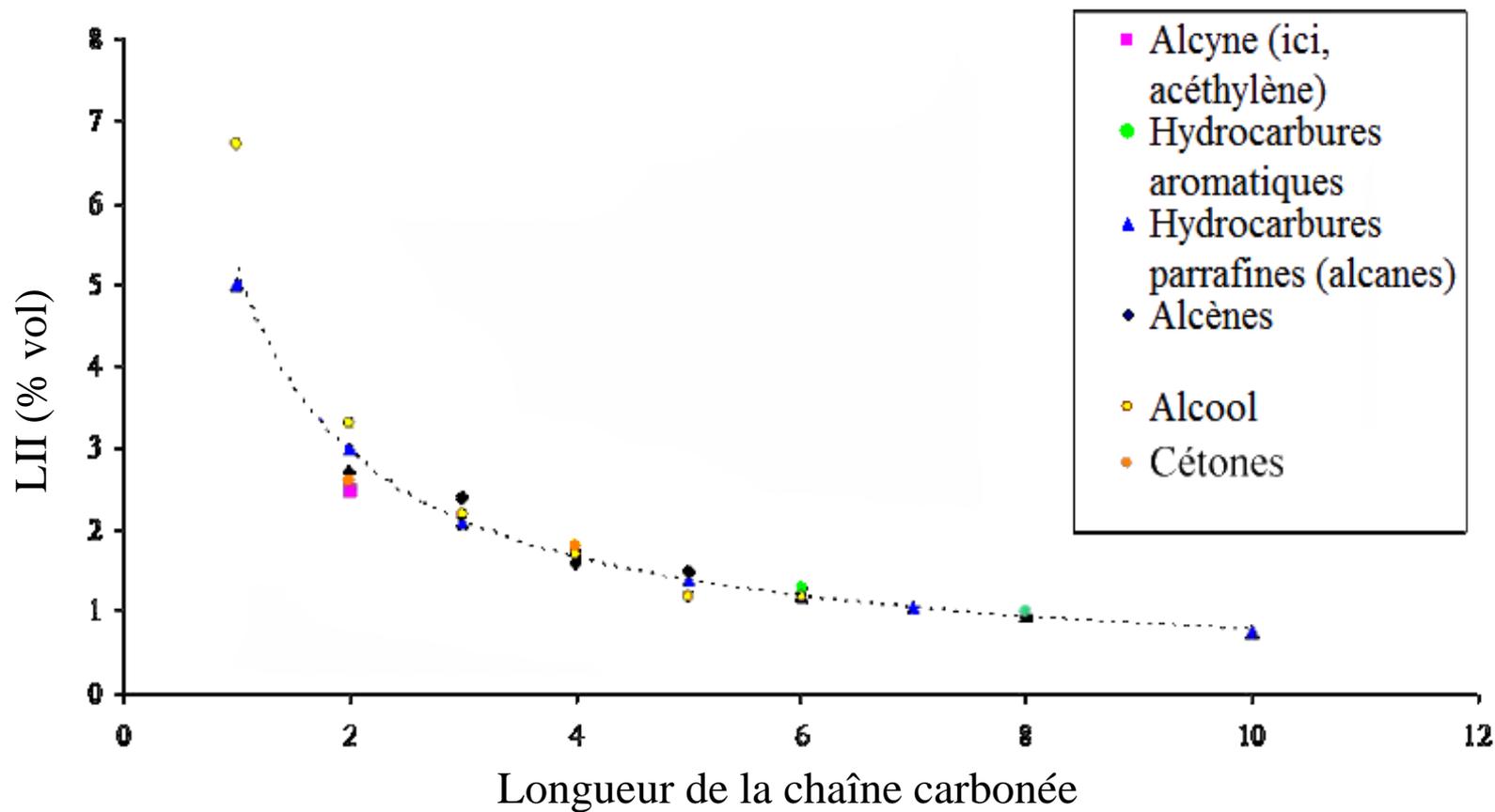


As $Y_{F,u}$ is decreased, a point of tangency will occur for some value. This is the lowest fuel concentration for which a steady propagation is possible. Any further decrease in $Y_{F,u}$ will not allow propagation even if ignition is achieved. The critical tangency condition value for this fuel concentration is called the lower flammable limit (LFL).

As the fuel concentration is increased above stoichiometric on the rich side, the incompleteness of combustion will reduce ΔH_c . Hence, this will decrease T and the burning rate, causing a similar effect and leading to extinction. This critical fuel-rich concentration is called upper flammable limit (UFL)

Flammability Limits





With this value in hand, if the LFL is known at a temperature T_1 (normally this will be 25°C), then it can be evaluated at another temperature T_2 according to :

$$LFL_{T_2} = LFL_{T_1} \left(1 - \frac{T_2 - T_1}{1300 - T_1} \right)$$

If T_1 is, in fact, 25°C, then the expression becomes :

$$\frac{LFL_{T_2}}{LFL_{25}} = 1 - 0,000784(T_2 - 25)$$

The general relationship above will also not hold if the substance starts to decompose at elevated temperatures.

The general relation above does not hold for hydrogen, and for hydrogen the expression is :

$$\frac{LFL_{T_2}}{LFL_{25}} = 1 - 0,00129(T_2 - 25)$$

The UFL increases with temperature be computed according to :

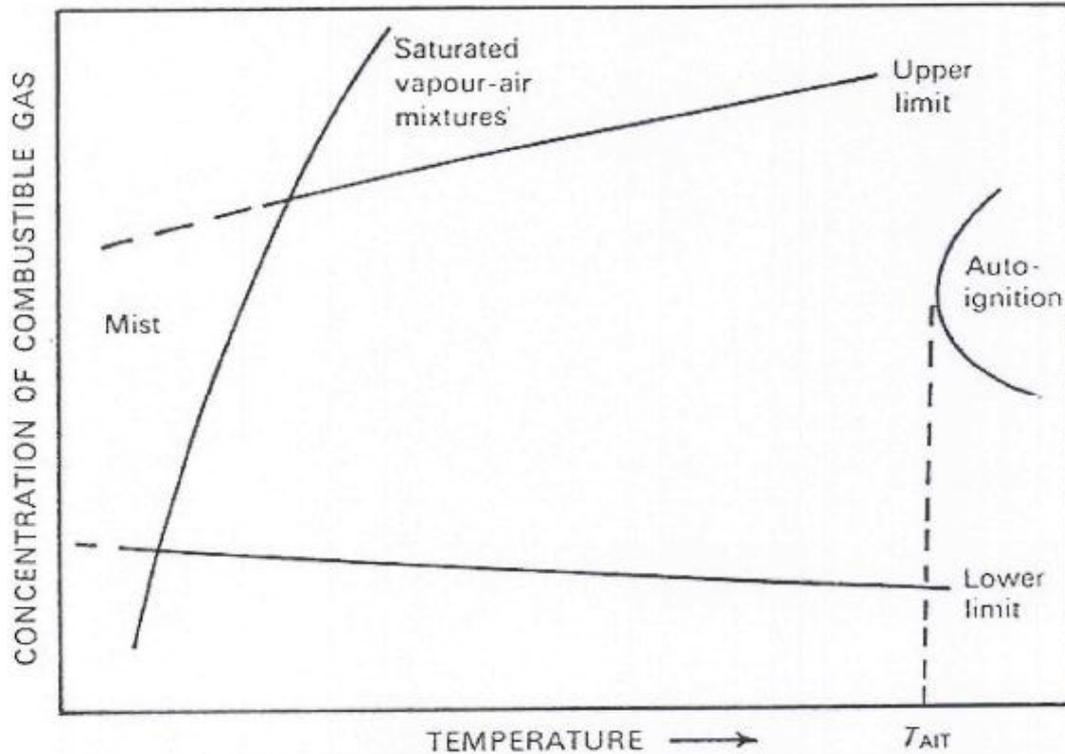
$$UFL_{T_2} = UFL_{T_1} \left(1 - \frac{T_2 - T_1}{1412 - T_1} \right)$$

If T_1 is 25°C, then the expression becomes :

$$\frac{UFL_{T_2}}{UFL_{25}} = 1 + 0,000721(T_2 - 25)$$

Flammability Limits

Effect of temperature on flammability for a given pressure



Limits of flammability in standard air (% by volume)

Fuel vapor	Stoichiometric	Lean limit	Rich limit
Methane	9.47	5.0	15.0
Ethane	5.64	2.9	13.0
Propane	4.02	2.0	9.5
Isooctane	1.65	0.95	6.0
Carbon monoxide	29.50	12.5	74
Acetylene	7.72	2.5	80
Hydrogen	29.50	4.0	75
Methanol	12.24	6.7	36

The region of autoignition is characterized as a combustion reaction throughout the mixture at those temperatures and concentrations indicated. Outside that temperature domain only piloted ignition is possible, and flammability is manifested by a propagating combustion reaction through the mixture.

Flammability limits

Stable flame propagation : combustible mixture composition between lower and higher flammability limits LFL and UFL.

Mixtures :

Le Chatelier mixing rule for combustible volume fractions x_i :

$$LFL_{mix} = \frac{100}{\sum_j \frac{X_j}{LFL_j}}$$

and similar for UFL_{mix}

- CO : 4,3 (34,4%) LFL = 12,5 , UFL = 74
- Methane : 3,3 (26,4 %) LFL = 8 , UFL = 12
- Hydrogen : 4,9 (39,2 %) LFL = 4 , UFL = 75
- Air : 87,5
- **C fuel = 12,5% > LFLmix risk**

LFL mix = 6,3% UFLmix = 31,4%

Effect of pressure

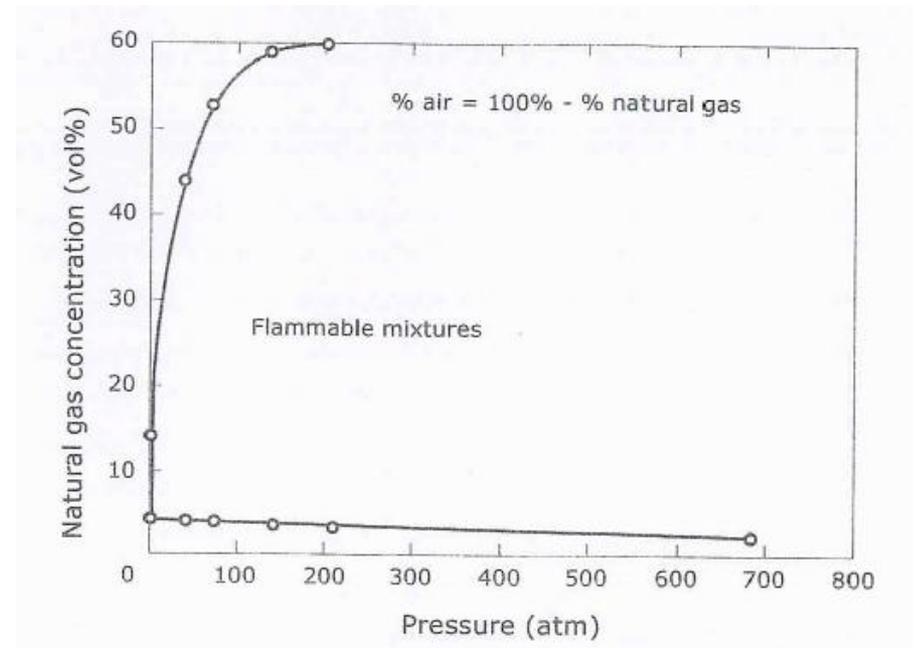
Increasing the initial pressure of the gas mixture generally increases both the LFL and UFL, as illustrated in Figure and Table for natural gas. The relations can be represented by the formulas :

$$LFL = LFL_a - 0,31 \ln P$$

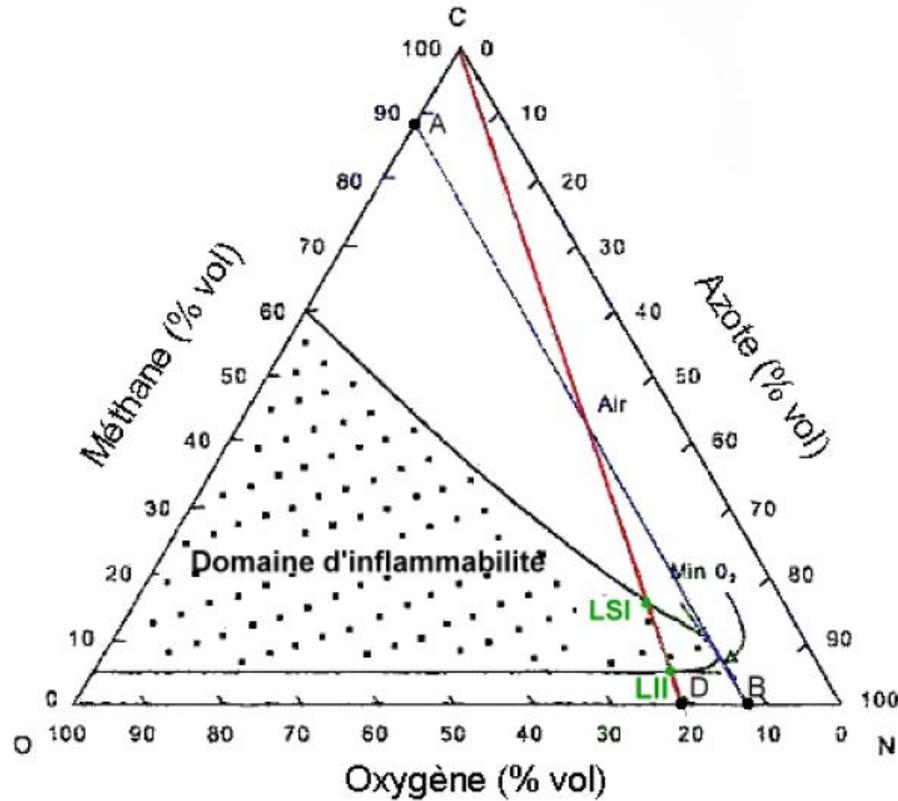
$$UFL = UFL_a + 8,9 \ln P$$

Limits of flammability of natural gas in 20°C dry air versus pressure (% by volume)
[Jones et al.]

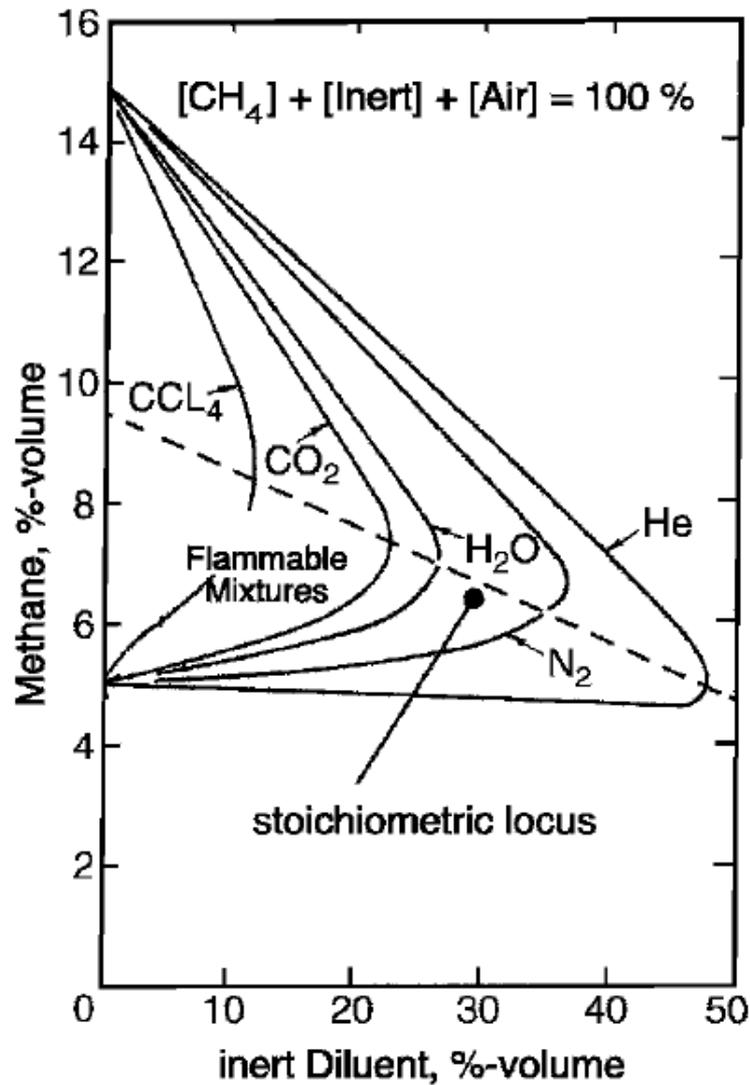
Pressure (atm)	Lean limit	Rich limit
1	4.50	14.2
35	4.45	44.2
69	4.00	52.9
137	3.60	59.0
205	3.15	60 (est.)



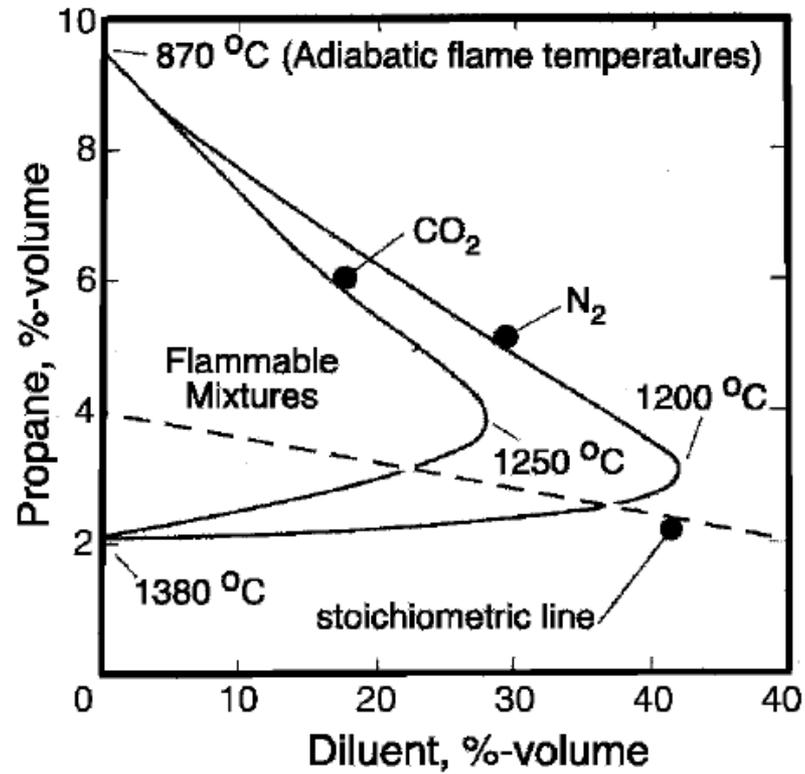
Flammability diagram



Flammability diagram for three-component systems at 26 °C and 1 atm



Limits of flammability of various methane-inert gas-air mixtures at 25°C and atmospheric pressure (from Zabetakis)



Adiabatic flame temperature and mixture concentration for propane

Oxygen concentration

The LFL does not vary with an increase in oxygen concentration, and its value in pure oxygen is generally identical to the value in atmospheres of 21% oxygen.

The UFL, however, greatly increases with oxygen concentration.

$$UFL(oxygen) = 120 - \frac{216}{\sqrt{UFL(air)}}$$

If oxygen concentration decreased below 21%, then eventually a minimum oxygen concentration is reached.

$$MOC = LFL \cdot \gamma$$

Where γ = stoichiometric oxygen/fuel mole ratio

It can also be seen that the prediction can be made as :

$$MOC = LFL \cdot \frac{1}{4,77} \left(\frac{100}{C_{st}} - 1 \right)$$

Where C_{st} = stoichiometric fuel concentration (%).

For n-hexane, LFL = 1,2% and C_{st} = 2,16%

At the LFL, $(100-1,2) \cdot 0,21 = 20,7\%$ O₂ and N₂ = 78,1%

$\gamma = 9,5$ MOC = $1,2 \cdot 9,5 = 11,4\%$. The experimentally determined value is 11,9%.

H₂ MOC = $4 \cdot 0,5 = 2\%$





Merci de votre attention

Feu d'un tonneau de 350 L de Cognac, 2007.