



Dedicated to the memory of
Professor Victor-Emanuel Sahini (1927–2017)

OVERALL KINETICS OF GAS-PHASE IGNITION OF n-PENTANE – AIR MIXTURES USING AN ISOTHERMALLY HEATED PLATINUM FILAMENT

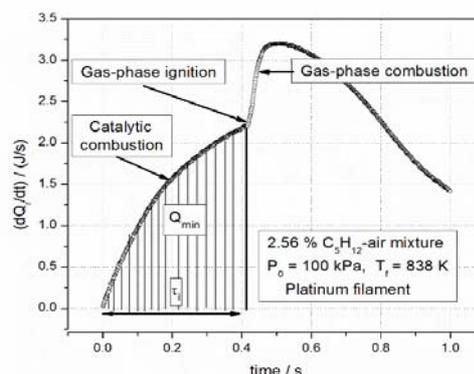
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Overall kinetic parameters – activation energy and reaction order – of gas-phase ignition of the stoichiometric (2.56%) and a lean (2.22%) n-pentane – air mixtures induced by an isothermally heated platinum filament were reported and compared with those previously published for catalytic ignition on a stretched platinum wire. The isothermal heating circuitry allows the detection of ignition and development of both surface and gas-phase reactions. The results were obtained from the analysis of the measured gas-phase induction periods (delays) and of the corresponding minimum (critical) energy for different temperatures between 633 and 1075 K and pressures between 27 and 100 kPa. The configuration of the ignition source as filament constitutes a more favorable geometry for a stronger interaction between heterogeneous and homogeneous reactions, promoting the gas phase ignition.



INTRODUCTION

Risk analysis in connection with ignition of flammable mixtures by hot surfaces was a topic of great interest since the beginning of the industrial age. A critical examination of early studies was carried out by Laurendeau¹ for methane-air mixtures, frequently involved in uncontrolled explosions. The simplest critical condition for ignition arises from the examination of conductive heat transfer leading to a temperature gradient within the boundary layer which surrounds the hot solid surface. The corresponding runaway

condition in the form $(dT/dx)_{wall} = 0$, where x is the distance from surface, is known as the Van't Hoff criterion. Its applicability has been verified by numerous researchers.¹ Several more realistic criteria have been subsequently proposed, taking into account the contribution of transient processes as well as of chain reactions and catalytic effects. A special interest has been shown for the catalytic combustion reactions². Starting from the simple finding that the ignition temperature for a catalytic surface is higher than for a noncatalytic one, the effect has been exploited for developing a new combustion technology – catalytic combustion –

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able to use the combustion heat at much lower temperatures, reducing significantly the NO_x formation.³⁻⁶ The overall catalytic ignition process implies a strong dynamic coupling (through heat and mass transfer) between the catalytic surface and the early stages of gas-phase reactions, generally known as heterogeneous-homogeneous (H-H) combustion which find applications in some new combustion technologies.⁷⁻¹¹ The ignition of flammable mixtures by hot catalytic or non-catalytic surfaces was investigated using numerous experimental configurations from wires, filaments, foils, plates, strips to metal gauzes and microchannel reactors. A particular methodology, used also in the present investigation, preserves a constant temperature during ignition and subsequent combustion, reducing the number of system variables.¹²⁻¹⁶ The previously reported kinetic analysis of isothermal catalytic ignition on a stretched platinum wire of n-pentane-air mixtures¹⁷ suggested a further insight into the role of ignition source configuration on the

interaction between heterogeneous and homogeneous combustion.

EXPERIMENTAL

The experimental measurements use a previously reported technique consisting in an isothermal heating of the ignition source - a catalytic wire or a filament.¹²⁻¹⁷ The ignition source having the resistance R_f is connected in series with a standard resistor with the resistance R_{std} , constituting together an arm of a Wheatstone bridge fed from a power supply with a voltage adjustable to maintain a constant filament resistance (and hence a constant temperature). The voltage across the standard resistor, U_{std} , is related with the input power P_f on the filament with resistance R_f :

$$P_f = R_f \cdot U_{std}^2 / R_{std}^2 \quad (1)$$

when the filament is immersed in a fuel-air gaseous mixture, an exothermic reaction occurs on its surface and/or its neighborhood. The corresponding input power is consequently lower than in air for the same filament temperature and gas pressure. The difference gives approximately¹³ the chemical heat release rate, dQ_r/dt :

$$dQ_r/dt = (R_f / R_{std}^2) \cdot [(U_{std}^2)_{air} \cdot (U_{std}^2)_{mixture}] \quad (2)$$

All experiments were performed in a cylindrical stainless steel cell with internal diameter and height of 60 and 62 mm, respectively, equipped with two thick brass wires for filament connection, an upper transparent window used for visual observation of gas phase ignition/combustion and a gas feed/evacuation stopcock. The filament is made from a platinum wire of 0.1 mm diameter and 126 mm length processed as a coil with 10 turns unevenly spaced to ensure a uniform heating. The coil has a diameter of 4 mm and a length of 22 mm and is located in central position. The gaseous mixtures were prepared in metallic cylinders by partial pressure method with n-pentane component obtained through liquid n-pentane (Sigma-Aldrich) vaporization, which has a vapor pressure of 53.3 kPa at 20°C. Two n-pentane-air mixtures were prepared: the stoichiometric mixture with 2.56% ($\varphi = 1.0$) and the lean mixture with 2.22% ($\varphi = 0.86$). The experiments were carried out in stagnant mixtures where significant natural convection occurs, for initial pressures between 27 and 100 kPa and filament temperature between 633 and 1075 K. The variation in time of U_{std} was recorded using a Tektronix TDS 210 oscilloscope. The average filament temperature was calculated using a resistance-temperature calibration equation taken from literature.¹³

RESULTS AND DISCUSSION

The mixtures containing 2.22 and 2.56% n-pentane in air were chosen for the simplicity of their stoichiometry, assuming that only CO_2 and H_2O are the significant products. A typical result showing the variation of U_{std} in time is illustrated in Figure 1.

The decrease of U_{std} in time at the beginning represents the exothermic surface (catalytic) process up to the ignition period τ_i , when the gas phase ignition occurs, releasing a supplementary heat which is transferred to the filament. If two experiments are performed in the same conditions, in air and in reactive mixture, one can assume that the thermal conductivities of the two gases are practically the same and the chemical heat release rate, dQ_r/dt can be evaluated using the equation (2), as illustrated in Figure 2.

Significant differences can be observed between filament and stretched wire effect: the catalytic combustion is followed by a sudden increase of dQ_r/dt marking the gas phase ignition in the first case, while it reaches a quasi-steady-state in the second one. Later, when the fuel and oxygen concentrations decrease significantly, the quasi-steady-state level decreases progressively. Two important properties can be evaluated easily on a dQ_r/dt versus time diagram for platinum filament ignition: the gas phase ignition time or ignition delay τ_i and the minimum (or critical) energy Q_{min} , representing the total heat liberated by surface reactions until the gas phase ignition time is reached, both being related with the kinetic properties of the process. Q_{min} can be evaluated numerically from measured R_f , R_{std} and U_{std} or from calculated dQ_r/dt as:

$$Q_{min} = \int_0^{\tau_i} (dQ_r/dt) dt = (R_f / R_{std}^2) \cdot \int_0^{\tau_i} [(U_{std}^2)_{air} - (U_{std}^2)_{mixture}] dt \quad (3)$$

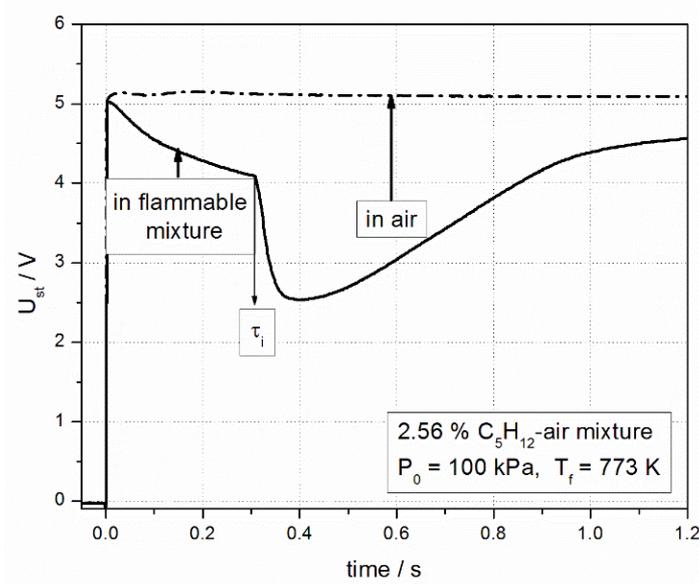


Fig. 1 – U_{std} versus time diagram for the stoichiometric mixture showing the gas phase ignition time.

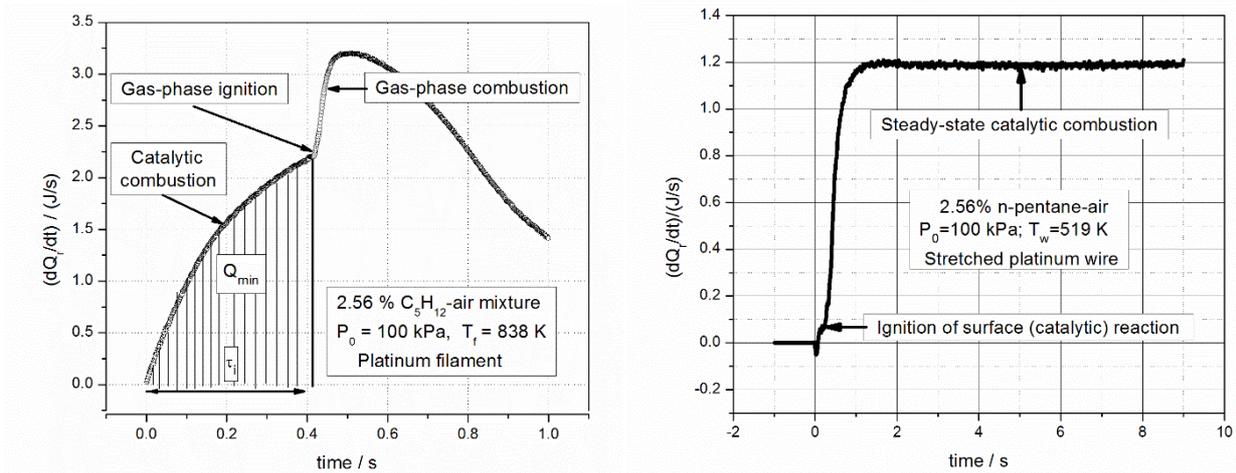


Fig. 2 – The variation of the chemical heat release rate, dQ_c/dt , for the stoichiometric n-pentane-air mixture at $P_0 = 100$ kPa on platinum filament at $T_f = 838$ K (left) and on stretched platinum wire at $T_w = 519$ K (right).

The ignition period dependence on the operational variables is given approximately as the reciprocal of the reaction rate of a single

$$r_R = a_0 \cdot P_F^{n_F} \cdot P_{ox}^{n_{ox}} \cdot \exp(-E_a / RT_f) = a_0 \cdot P_0^n \cdot X_F^{n_F} \cdot X_{ox}^{n_{ox}} \cdot \exp(-E_a / RT_f) \quad (4)$$

where a_0 is a constant, P partial pressures of fuel or oxygen, P_0 total pressure, n partial and overall reaction orders and E_a overall activation energy, X

$$\tau_i \propto 1/r_R = a_1 \cdot P_0^{-n} \cdot X_F^{-n_F} \cdot X_{ox}^{-n_{ox}} \cdot \exp(E_a / RT_f) = a_2 \cdot P_0^{-n} \cdot \exp(E_a / RT_f) \quad (5)$$

where a_1 , a_2 are constants, the last expression being valid for a constant composition.

A linear regression of $\ln(\tau_i/s)$ versus $1/T_f$ at constant pressure or of $\ln(\tau_i/s)$ versus $\ln(P_0/kPa)$ at

reaction.^{12, 14, 16} Using an empirical, Arrhenius type, kinetic equation of the form:

the molar fraction, then the ignition period is given by:

constant temperature yields a straight line allowing the evaluation of the overall gas phase ignition parameters, as shown in Figure 3. Within the limits of experimental errors, similar results were

obtained for both 2.22% and 2.56% n-pentane-air mixtures between 27 and 100 kPa, without a significant trend. The activation energies are very close to diffusion limit of gas phase reactions. Such a result is in agreement with the accepted mechanism of free radicals' implication in the gas phase ignition near catalytic surfaces.^{2,3} For filament configuration the heterogeneous-homogeneous interaction is favored as compared to a stretched wire, approaching the conditions encountered in micro-combustion devices.⁹

Slightly close results were obtained from a 3D regression analysis which gave $E_a = 51$ kJ/mol and $n = 2.4$ (Fig. 4). These results are significantly different from those reported for catalytic ignition

of similar mixtures on stretched platinum wire¹⁷ ($E_a = 100$ kJ/mol and $n = 0.1 - 0.2$). The high dispersion of the experimental results, reflected in a small value of the coefficient of determination, is due to the inherent changes of filament geometry and of the structural changes of the platinum wire reported in literature.¹⁸

The chemical heat release rate, dQ_r/dt is proportional to the reaction rate of the heterogeneous catalytic reaction r_R , surface of the whole platinum wire of the filament S_f and the standard molar heat of combustion $\Delta_r H_T^0$:

$$dQ_r/dt = S_f \cdot \Delta_r H_T^0 \cdot r_R \quad (6)$$

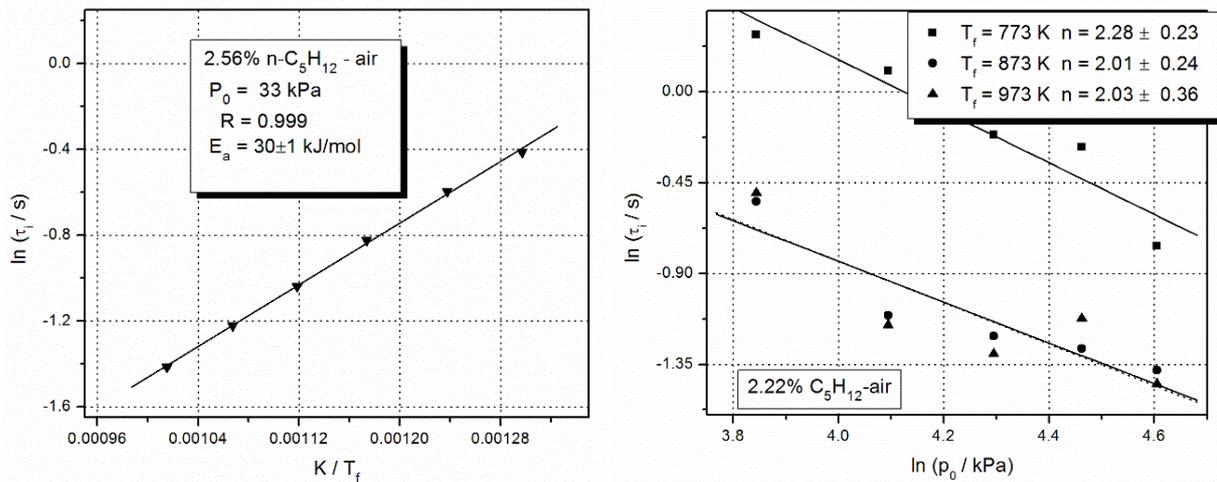


Fig. 3 – Isobaric and isothermal variations of the gas phase ignition delay.

2.56% C₅H₁₂-air mixture
 $\tau_i = a(P_0)^b \exp(c/T_f)$
 $r^2 = 0.7318704$ DF Adj $r^2 = 0.69356617$ FitStdErr = 0.2154032 Fstat = 30.024937
 $a = 6.038182$ $b = -2.3917725$
 $c = 6107.4585$

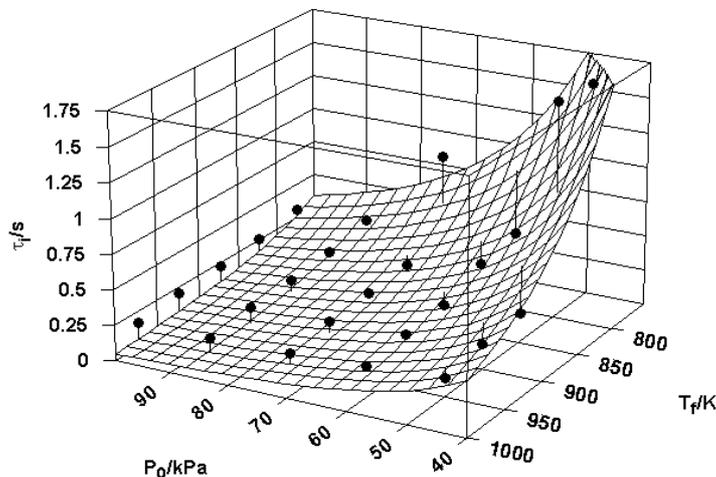


Fig. 4 – A 3D regression of the ignition delay on gas pressure and filament temperature.

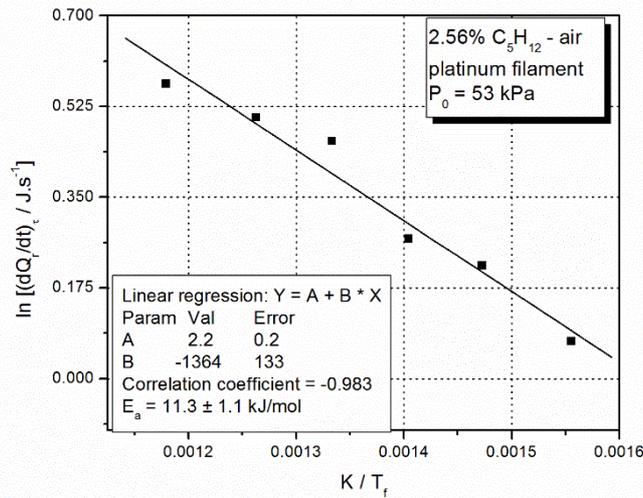


Fig. 5 – Variation with temperature of the chemical heat release rate.

A particular value of dQ_r/dt is that at the ignition time, $(dQ_r/dt)_\tau$. From equations (6) and (4) one obtains:

$$(dQ/dt)_\tau = a_3 \cdot P_0^n \cdot \exp(-E_a / RT_f) \quad (7)$$

where a_3 is a constant for a certain composition. An example at constant pressure is illustrated in

Figure 5, showing that the resulted activation energy is well in the range of diffusion controlled processes, in accord with the results obtained from ignition delay variation.

The definition of the minimum energy Q_{min} given by equation (3) can be detailed as a function of the operational and kinetic parameters as:

$$Q_{min} = a_4 \cdot P_0^n \cdot \exp(-E_a / RT_f) \cdot \int_0^{\tau_i} (X_F^{n_F} \cdot X_{ox}^{n_{ox}}) dt \quad (8)$$

If the natural convection arising from the high temperature gradient between heated filament and surrounding gas succeeds to refresh the gas

composition around filament, then a simpler relationship is obtained:

$$Q_{min} = a_3 \cdot P_0^n \cdot (X_{F,0}^{n_F} \cdot X_{ox,0}^{n_{ox}}) \cdot \exp(-E_a / RT_f) \cdot \tau_i \quad (9)$$

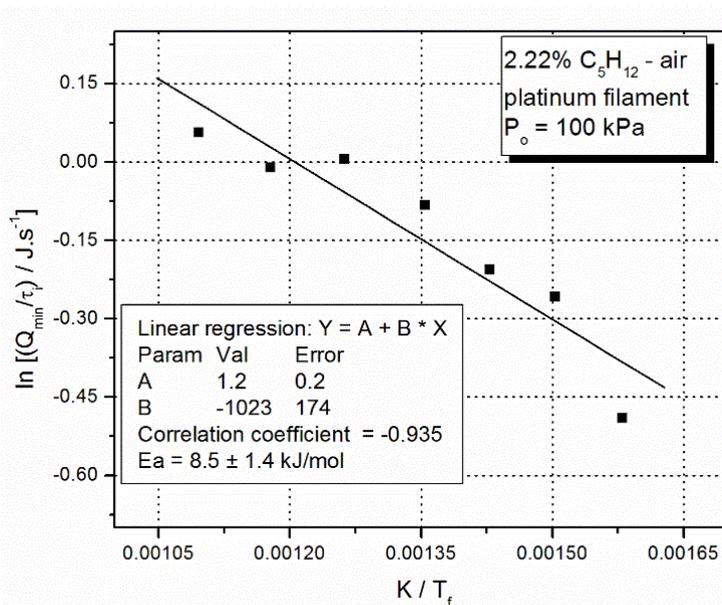


Fig. 6 – Variation with temperature of the composite function Q_{min}/τ_i

The analysis of the temperature dependence of $\ln(Q_{\min} / \tau_i)$ versus $1/T_f$ can indicate if the above assumption is fulfilled within the limits of experimental error.

The corresponding activation energy is very close to the value obtained from the regression of $(dQ_r/dt)_\tau$ versus $1/T_f$, proving that, even if the measurements were carried out in stagnant mixtures, during the short time of surface combustion, the natural convection ensured a quasi-constant gas composition around the filament.

Several studies dedicated to catalytic combustion of alkanes (n-butane and isobutane)^{13, 19, 20} and of complex mixture from liquefied petroleum gas²¹ on stretched platinum wires of 0.1 mm diameter in isothermal conditions have shown that, for temperatures up to 1,000 K and atmospheric and sub-atmospheric pressures, the gas phase ignition was not possible. On the other hand, when filaments are used (e. g. for propylene-air mixtures^{12, 22, 23}), the gas phase ignition was obtained even at lower temperatures. Consequently, one can say that the gas phase ignition is promoted on the filament where the active species produced on the inside platinum surface diffuse towards the center, while on a stretched wire, in similar conditions, the active species flux is divergent.

CONCLUSIONS

The overall kinetic parameters of the gas phase ignition of n-pentane-air mixtures at atmospheric and sub-atmospheric pressures using platinum filaments having temperatures between 633 and 1075 K were calculated from the temperature and pressure dependence of the induction delay, of the chemical heat release rate and of the minimum (critical) energy. The obtained activation energies vary between 8 and 51 kJ/mol and are close to the diffusion controlled processes in the gas phase, in contrast with the activation energies previously reported for catalytic ignition ($E_a = 100$ kJ/mol). The overall reaction order for the gas phase

ignition ($n = 2.0-2.4$) is within the range of gas phase combustion reactions, different from catalytic combustion reactions with much lower values ($n = 0.1-0.2$).

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