

Heterogeneous catalytic ignition of n-butane/air mixtures on platinum

Research Article

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Abstract: The heterogeneous catalytic ignition of lean to stoichiometric n-butane/air mixtures were studied at various total pressures between 10 and 100 kPa and at temperatures equal to or larger than the critical ignition temperatures. The induction periods, ignition and extinction temperatures were measured under strict isothermal conditions. The discussion presented in this paper is based on several literature models. The data analysis allowed for the determination of the overall kinetic parameters. The rigorous isothermal conditions indicated that the extinction temperatures are lower than the ignition, a behavior different from the results obtained in stagnation-point flow reactors.

Keywords: Catalytic ignition • n-Butane • Platinum wire • Ignition delay • Bifurcation

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1. Introduction

The catalytic ignition of fuel/air mixtures has received renewed interest due to its role in the early stages of the process, and in the stability of practical combustion devices. Catalytic ignition is connected to two important processes: the ignition of the heterogeneous catalytic reaction occurring only on the catalyst surface [1-4] and the ignition of the gas-phase homogeneous combustion induced or facilitated by catalytic reactions [5-7]. In this paper we present several aspects connected with the ignition of heterogeneous catalytic combustion on a thin platinum wire working under a strict isothermal environment. This severe restriction offers new insight into the complex physical and chemical processes occurring at a gas/solid interface. This subject also has significant relevance for understanding and adjusting the safe and optimal operation of gauze reactors [8-10]. Previous studies have shown that the catalytic combustion is associated with bifurcation phenomena whose basic characteristics consist of ignitions,

extinctions and autothermal points, and sometimes accompanied by a more complex behavior [4,11-13]. Unlike the most widespread experimental technique used to study the ignition-extinction behavior on noble metal catalysts that is based on the stagnation-point flow reactors at ambient pressure [4,13-15], the isothermally heated platinum wire technique used in this investigation [16,17] allows for the measurements of ignition, extinction, autothermal points, and the induction periods in stagnant mixtures at various total pressures, over a wide range of operating conditions. From a theoretical point of view [11], the catalytic combustion has been studied either by a large activation energy asymptotic analysis using a one-step overall reaction mechanism [18], or by numerical simulations using networks of elementary reactions [19]. Many attempts have been made to explain the significance of the ignition and extinction temperatures [13,20]. According to the results obtained for the hydrocarbon combustion on platinum foils in stagnation-point flow reactors (e.g. [14,15,18]), the extinction temperature is always higher than the

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ignition one. This finding is in disagreement with several mechanistic studies, which predict an opposite order [13]. Our measurements indicate that under isothermal conditions the extinction temperatures are indeed lower than the ignition ones. It should be also mentioned that most of studies referring to ignition criteria are based on steady-state models which predict only the critical wall temperature, without taking into consideration the occurrence of an ignition delay [21]. However it was occasionally measured and used to evaluate the overall activation energy [5,16] and was recently analyzed by adopting a transient approach to the ignition problem. This analysis has raised a legitimate question concerning the discrimination between the adiabaticity criterion and the thermal runaway criteria [21].

The aim of the present paper is to measure the ignition and extinction temperatures and the induction periods for a heterogeneous catalytic ignition of lean to stoichiometric *n*-butane/air mixtures, indicating a restricted range of experimental conditions for these measurements. Assuming that the induction period is proportional to the inverse of the overall reaction rate, by analogy with the gas-phase auto-ignition process [22], the overall activation parameters are evaluated and compared with the results obtained for the total oxidation on platinum foils of lower alkanes in a recirculating batch reactor [23]. The obtained analytical expression of the induction period is also compared with the more detailed models referring to ignition by heated surfaces [24,25].

2. Experimental Procedures

The experimental details referring to the reaction heat flow rate measurements on the isothermally heated platinum wires and the sample preparation were

given elsewhere [16,17]. Briefly, samples of air or fuel/air mixtures are alternatively introduced into an evacuated test cell at the same initial pressures. The test cell is a cylinder of 9 cm diameter and height. For the measurements in a flow regime, a stainless steel wire mesh disc was placed at the bottom of the cell to ensure a uniform gas flow. The input and output ducts were provided with flame arresters. The platinum wire, of 45 mm length and 0.1 mm diameter (99.99%, from Aldrich), soldered on the top of the brass feeding conductors, located in the centre of the cell, is rapidly heated following a quasi-rectangular profile using the discharge of a capacitor. It is subsequently maintained at a constant temperature using a power supply regulated by a feedback loop designed to maintain a constant resistance and temperature of the platinum wire. The feedback is supplied by a Wheatstone bridge containing the platinum wire, a standard resistor and a potentiometer. The nominal value of the wire resistance (and temperature) is adjusted from this potentiometer. In order to maintain a constant temperature, the input power on the wire decreases when an exothermal reaction occurs on it. It is calculated by measuring the voltage drop, U_{std} , across the standard resistor connected in series with the wire and knowing the wire and standard resistances R_w and R_{std} as:

$$P_{input} = \frac{R_w \times U_{std}^2}{R_{std}^2} \quad (1)$$

The alternative run performed in air under similar conditions with the reactive mixture is used to eliminate the heat losses associated with conduction, convection and radiation.

The measurement of R_w for a certain input power allows the calculation of the wire temperature using a calibration procedure [17]. The temperature

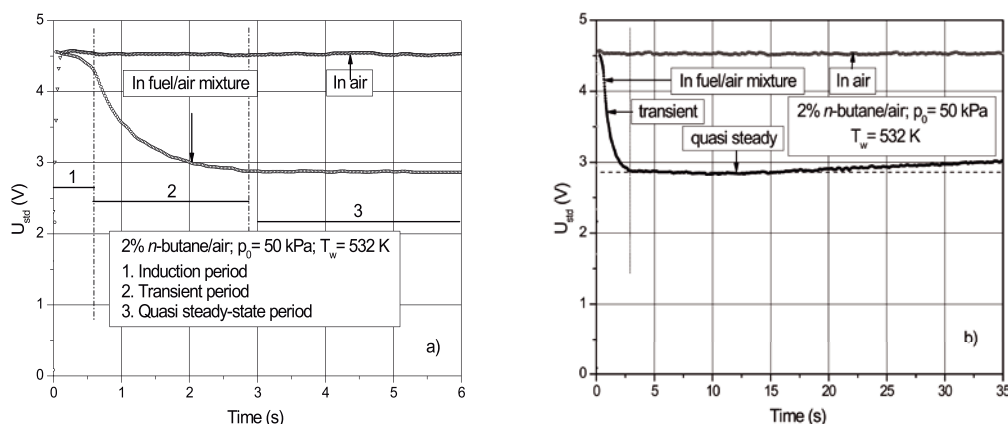


Figure 1. An illustrative diagram for the variation of U_{std} against time in air and in a reactive mixture: a) – the early interval (0 – 6 s) showing the induction, transient and quasi steady-state periods; b) – the extended recording (0 – 35 s) showing the ascending trend of U_{std} in time resulted from the progressive fuel consumption and associated increase of the input power.

measurement based on the resistance – temperature calibration curve was often utilized and validated for catalytic ignition studies on very thin platinum wires [1-3,7,26]. A drawback of this method arises from the existence of a temperature distribution along the wire due to heat losses to the colder feeding conductors. However the evaluation of the center point temperature according to a simple heat loss model proved to have an insignificant effect on the parameter estimation [7]. An average temperature was considered in this paper. From the above presentation it is obvious that the higher the input power, the larger the resistance R_w and, consequently, the wire temperature. To increase the measurement reproducibility, the platinum wire was systematically heated at $\approx 800^\circ\text{C}$ in air at ambient pressure, before each test.

A schematic showing U_{std} vs. time variation in air and in 2% *n*-butane/air mixture is given in Fig. 1. The diagram shows a combustion process exhibiting an induction period followed by a transient regime that is characterized by a continuous decrease of U_{std} to a quasi steady-state catalytic combustion.

Depending on the nature of the fuel and concentration, total pressure and wire temperature, the induction period can decrease until it becomes negligibly small (undetectable). On the other hand, for a certain mixture, the decrease of the wire temperature reaches an extreme value where the mixture no longer reacts. The critical ignition temperature is a value that is slightly higher (up to 2 K) than this extreme value when the mixture is ignited after a long induction period. As seen in Fig. 2, the ignition is detected by a sudden decrease in the input power required to maintain a constant temperature (The initial wire temperature T_w is larger than the ignition temperature T_{ign}). It should be specified that the quasi steady-state catalytic combustion lasts for a very long

time as compared to the first two periods, until the bulk concentration of the fuel decreases significantly. During this quasi steady-state catalytic combustion, the input power can be slowly decreased by readjusting the bridge potentiometer until extinction occurs (represented by a sudden increase of the input power). The peaks pointing downwards appear during the sudden adjustment of the bridge potentiometer (input power decrease). The imposed stepwise decrease of the input power, leading to a lower wire temperature, induces a corresponding decrease of the reaction rate. Consequently U_{std} remains approximately constant during this operation.

A heated wire embedded in a stagnant gaseous mixture induces a natural convection. When a chemical reaction occurs on the wire, leading to the reactant consumption, the natural convection, as well as the resulted concentration gradient, contributes to replenish the reactant supply to the wire surface. In order to verify whether or not the combustion in a stagnant mixture could be modified significantly through reactants consumption and products formation, several measurements were conducted in a flow regime at atmospheric pressure for flow rates which ensure sufficiently low Reynolds numbers ($Re \approx 1$) [3,7]. The example given in Fig. 2b illustrates the similarities between the flow and stagnant systems. The validity of this statement will be discussed later.

It can be observed that the extinction temperature, T_{ext} , is always lower than the ignition temperature, T_{ign} .

The difference between the input power on the wire in air and in a reactive mixture gives the reaction heat flow rate, dQ_r/dt [17]

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

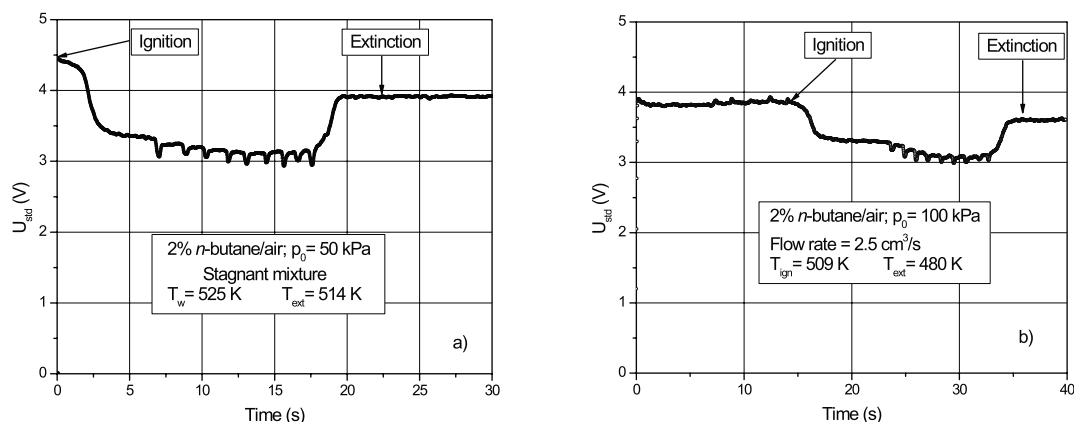


Figure 2. Two diagrams depicting the procedure to measure the ignition and extinction conditions: a) – in a stagnant mixture; b) – in a laminar flow system; the peaks pointing upwards on the left segment represent the step increase of the input power, up to ignition.

It is related to the reaction rate, r_R , of the heterogeneous catalytic process through:

$$r_R = \frac{1}{\Delta^c H_T^0 \cdot S_w} \times \frac{dQ}{dt} \quad (3)$$

where $\Delta^c H_T^0$ is the standard heat of combustion and S_w the wire surface. The reaction heat flow rate was calculated for the quasi steady-state regime and was utilized to evaluate the overall activation parameters of the catalytic reaction. The numerical value adopted for $\Delta^c H_T^0$ requires a well-defined stoichiometry for the combustion reaction. In a number of authoritative works [1,7,23,26-28] it has been established, using chromatography or mass spectrometry, that the combustion of a lean to stoichiometric lower alkanes/air mixtures on platinum wires or foils in similar conditions occurs with the conversion of hydrocarbon to only CO_2 and H_2O . Based on these arguments it was assumed that the same stoichiometry is valid in our working conditions and consequently, $\Delta^c H_T^0$, was taken for the complete combustion of *n*-butane.

3. Results and Discussion

Two types of measurements were carried out within the framework of this investigation:

1) Recording of U_{std} vs. time curves, which were used to measure the induction periods, τ_i , and the reaction heat flow rates, dQ/dt , during the quasi steady-state regime for lean and stoichiometric *n*-butane/air mixtures at various wire temperatures and total pressures.

2) Determination of ignition and extinction temperatures for the same mixtures at various total pressures.

3.1. Induction periods

The accessible ranges of the measured parameters are given in Table 1.

The overall reaction rate, r_R , of the catalytic combustion is described by an Arrhenius type kinetic equation of the form:

$$r_R = A \times (p_F/p^*)^{n_F} \times (p_{O_2}/p^*)^{n_{O_2}} \times e^{-E_a/RT_w} = A_0 \times (p_F/p^*)^n \times e^{-E_a/RT_w} \quad (4)$$

where A and A_0 are the pre-exponential factors, p_F , p_{O_2} and p^* are the fuel, oxygen and standard pressures, n_F , n_{O_2} and n are the partial and overall reaction orders, E_a is the overall activation energy, R is the ideal gas constant and T_w is the wire temperature.

Assuming that τ_i is proportional to the inverse of the overall reaction rate, by analogy with the gas-phase auto-ignition process [22], the overall activation parameters for the early stages of ignition can be evaluated according to:

$$\tau_i = \beta \times (p_0/p^*)^{-n} \times e^{E_a/RT_w} \quad (5)$$

where β is a proportionality constant including the pre-exponential factor and a critical amount, ΔC^* , of a reactant required to for ignition ($r_R = \Delta C^*/\Delta t = \Delta C^*/\tau_i$). The simple analytical form of Eq. (5) was used as early as in 1961 [5]. More elaborated treatments have been used since then to address the problem of transient ignition of fuel/air mixtures by heated surfaces without catalytic activity [24,25], to obtain explicit analytical equations similar to Eq. (5), but including a detailed physical significance of the involved parameters. As long as the overall process is not diffusion controlled, the combustion occurring within a thin gas layer around a solid surface should not be formally different from the catalytic combustion involving adsorbed species. Until more realistic numerical methods, already advanced for stagnation-point flow configuration [21], solve the problem of transient ignition for various experimental configurations, a rationalization of the experimental results referring to pressure and temperature effect on the induction period using the simple Eq. (5) seems to be a realistic approach.

The reaction heat flow rates, dQ/dt , and the corresponding reaction rates, r_R , during the quasi steady-state regime were evaluated according to Eqs. (2) and (3), where $\Delta^c H_T^0 \approx \Delta^c H_{298}^0 = 2658.5 \text{ kJ mol}^{-1}$ and the geometrical wire surface is $S_w = 1.41 \times 10^{-5} \text{ m}^2$ [17]. The corresponding turnover frequency was calculated as: $\text{TOF} = r_R/\Gamma_{\text{Pt}}$, where Γ_{Pt} is the atomic surface density of platinum exposed atoms, approximated to $2.49 \times 10^{-5} \text{ mol m}^{-2}$ [23].

An Arrhenius plot based on Eq. (5) at constant pressure is given in Fig. 3.

Table 1. The measured parameters for the accessible ranges of induction periods.

% n-butane	2.0		2.5		3.1	
$p_{\min, \max}/\text{kPa}$	30	100	30	100	30	100
$T_{\min}/T_{\max} \text{ (K)}$	564/625	487/549	546/564	496/552	493/543	475/534
$\tau_{\max}/\tau_{\min} \text{ (s)}$	1.10/0.28	1.84/0.12	0.73/0.53	2.15/0.15	2.50/0.20	2.38/0.15

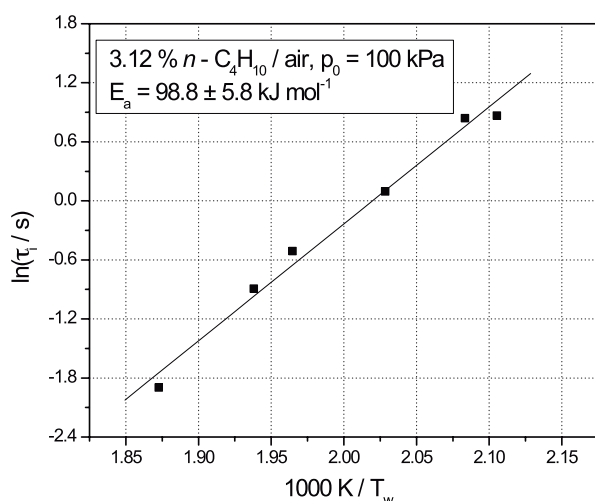


Figure 3. An Arrhenius plot for the temperature dependence of the induction period.

The analysis of the quasi steady-state regime was carried out using the following equation:

$$dQ_i/dt = A \times (p_0/p^*)^n \times e^{-E_a/RT_w} \quad (6)$$

The results for both the induction period and the quasi steady-state regime are given in Table 2.

It can be seen that the activation energy for the ignition process ($\ln \tau_i = f(1/T_w)$) has no significant variation with the fuel content or with the total pressure, except for with the lowest investigated pressure and leaner fuel mixtures. The derived activation energies are in good agreement with those obtained using other methods: $E_a = 71 \text{ kJ mol}^{-1}$ obtained in a recirculating batch reactor with analysis of reacting mixture composition [23], $E_a = 84 \text{ kJ mol}^{-1}$ obtained using the heated wire technique in a flow reactor [26], $E_a = 92 \text{ kJ mol}^{-1}$ obtained

using a heated gas technique in a flow reactor [27], $E_a = 71 \text{ kJ mol}^{-1}$ from ignition temperature measurements in a flow system [1], $E_a = 106 \text{ kJ mol}^{-1}$ obtained in a flow system with analysis of a reacting mixture composition [28]. After ignition, the activation energy has a sudden jump to typical diffusion controlled values, as can be seen from the analysis of quasi steady-state values using the regression $\ln(dQ_i/dt) = f(1/T_w)$. This is also in agreement with the model of the ignition process as a sudden transition from kinetic to mixed or diffusion control [2,29,30].

The pressure dependence of τ_i or of dQ_i/dt at constant temperature gives the overall reaction order, according to Eqs. (5) or (6). This reflects the sensitivity of the measured property to the change of total pressure. Typical values for ignition are $n = 1.43$ (2.5% *n*-butane/air, $T_w = 564 \text{ K}$) and for a quasi steady-state regime $n = 0.63$ (3.1% *n*-butane/air, $T_w = 493 \text{ K}$). Within the limits of experimental errors the results are similar for all other conditions. It is obvious that the ignition is more sensitive to a pressure change than quasi steady-state combustion.

Several typical figures of the involved parameters are given in Table 3. The measured reaction rates, r_R , can be compared with the fuel collision frequency, v_F , with the platinum surface covered preponderantly with oxygen, calculated according to $v_F = p_F/(2\pi M_F RT_w)^{1/2}$ with M_F the molar mass of the fuel [30]. The ratio r_R/v_F is of the order 2×10^{-4} , indicating the existence of significant controlling factors, characteristic for surface processes.

At these temperatures *TOF* has very large values, but significantly smaller than the previously reported one, $TOF = 5.3 \times 10^3 \text{ s}^{-1}$ at 840 K [17]. These relatively large figures suggest a further comparison with other reported results. To our knowledge there is no available

Table 2. Activation energies $E_a/(\text{kJ mol}^{-1})$ from $\ln \tau_i = f(1/T_w)$ and from $\ln(dQ_i/dt) = f(1/T_w)$

p_0 (kPa)	% <i>n</i> -butane					
	3.1		2.5		2.0	
	$E_a(\text{from } \tau_i)$	$E_a(\text{from } Q_i)$	$E_a(\text{from } \tau_i)$	$E_a(\text{from } Q_i)$	$E_a(\text{from } \tau_i)$	$E_a(\text{from } Q_i)$
100	98.8±5.8	9.43±0.30	109.6±9.1	7.23±0.28	92.9±7.4	11.3±0.77
70	75.0±9.1	7.71±0.49	105.4±9.9	7.71±1.29	105.7±12	12.1±1.37
50	74.8±8.8	7.94±0.76	99.0±11	13.2±2.63	93.0±13	23.1±2.00
30	79.1±1.4	12.7±0.32	49.8±4	—	63.9±6.5	—

Table 3. Selected ignition properties for the stoichiometric *n*-C₄H₁₀/air mixture at $p_0 = 30 \text{ kPa}$

T_w (K)	τ (s)	(dQ_i/dt) (J s ⁻¹)	r_R (mol m ⁻² s ⁻¹)	v_F (mol m ⁻² s ⁻¹)	$10^{-3} \times TOF$ (s ⁻¹)
493	2.50	0.53	0.0141	69.4	0.56
543	0.20	0.65	0.0173	66.0	0.69

data that has been measured and processed under the same conditions. Yao [28] reported a $TOF = 10.4 \text{ s}^{-1}$ for the catalytic combustion of *n*-butane on platinum wires at $T = 498 \text{ K}$ for a partial pressure of the fuel of 0.1 kPa . By extrapolating Yao's results, a stoichiometric mixture at 100 kPa results in a $TOF = 320 \text{ s}^{-1}$. Much lower values were measured for supported platinum on Al_2O_3 and on $\text{CeO}_2/\text{Al}_2\text{O}_3$ in similar conditions. Aryafar and Zaera [23] reported a $TOF = 27 \text{ s}^{-1}$ for the catalytic combustion of *n*-butane on nickel foils at $T = 948 \text{ K}$ and partial pressure of the fuel of 0.66 kPa and also found that the catalytic activity of the three metals is in the order $\text{Pt} > \text{Pd} > \text{Ni}$. Descorme, Jacobs and Somorjai [31] reported a TOF between 1 and 260 s^{-1} for the ethane combustion on palladium foil under similar conditions. The reported figures are of the same order of magnitude as our results, and the differences which can be attributed to the experimental technique. The supported catalysts, more efficient from the view point of dispersion, seem to be less reactive [28] and their catalytic activity is strongly dependent on the support structure and texture, catalyst dispersion, flow conditions, gas nature and composition [32–35]. A difference of one order of magnitude between our results given in Table 3 and our previously reported value [17] could be attributed primarily to the significant contribution of homogeneous reactions occurring near the catalyst surface which becomes important at higher temperatures. This contribution has been previously noted and discussed by numerous groups [36–39].

3.2. Ignition and extinction temperatures

The temperature hysteresis accompanying the catalytic combustion, with the extinction temperature lower than the ignition one, was recently referred to in [13], discussed in detail in [13,42] and measured in [43]. The measurements were carried out in a continuous fixed bed reactor with external recycling loop, working as a continuous stirred flow reactor, for the total oxidation of CO on Pd and toluene on Pt, with the catalysts supported on glass fibres. The results were obtained using a controlled isothermal regime and the order of the two critical temperatures was similar to our results. To validate our results obtained for stagnant

mixtures, several measurements were carried out in a flow system at normal pressure, as illustrated in Fig. 2. For low flow rates the results were in good agreement with those obtained in stagnant system. Moreover a simple calculation of the fuel consumption during the measurement of the extinction temperature indicates that the composition around the wire is changed by only several percents. For the stoichiometric mixture with a reaction heat flow rate $dQ_r/dt = 0.65 \text{ J s}^{-1}$ at $T = 543 \text{ K}$, (see Table 3), the reacted fuel mole number during the time t is $n_c = (dQ_r/dt) \times t / \Delta^c H_T^0 = 2.43 \times 10^{-7} \times t = 7.3 \times 10^{-6} \text{ mol}$ for $t = 30 \text{ s}$. At $p_0 = 30 \text{ kPa}$ and ambient temperature the test cell contains $2.1 \times 10^{-4} \text{ mol}$ fuel. It can be seen that only 3.5% of the fuel reacted in 30 s. This decrease of fuel and the corresponding formation of the combustion products can be detected on the diagram U_{std} vs. time (Fig. 1b). For this low conversion the effect of the combustion products can be also neglected. The results of critical ignition and extinction temperatures measurements are given in Table 4.

For a given total pressure, the ignition temperature increases when fuel content decreases, in agreement with earlier observations [1–4,7,14,15,18,26]. The measured ignition temperatures have been successfully used to evaluate the overall [1–4] or elementary [40,41] kinetic parameters of the ignition process. It has been shown that the ignition process depends on many parameters including the total pressure of the gas mixture. The data given in Table 4 indicate a systematic increase of the ignition temperature as the total pressure decreases. This correlation can be also used to evaluate the overall activation energy if an analytical relationship between these variables is assumed to describe adequately the heterogeneous ignition process.

The data given in Table 4 were analyzed using the results advanced by Hiam, Wise and Chaikin [1] for a first order surface reaction and developed by Schwartz, Holbrook and Wise [2] for surface reactions of various orders with respect to fuel. The relevant equation for a kinetically controlled heterogeneous catalytic ignition, with a large excess of oxygen, has the form [1]:

$$C_F / (T_{\text{ign}} - T_0)^2 = \alpha_1 \times e^{E_a / RT_{\text{ign}}} \quad (7)$$

Table 4. Ignition, T_{ign} , and extinction, T_{ext} , temperatures (in K) for *n*-butane/air mixtures

Fuel % (volume)	p_0/kPa									
	100		70		50		30		10	
	Ign	Ext	Ign	Ext	Ign	Ext	Ign	Ext	Ign	Ext
3.1	475	*	484	*	492	*	501	*	516	*
2.50	496	434	502	475	516	504	538	–	–	–
2.00	507	475	510	498	520	512	546	–	–	–
1.50	534	519	543	534	564	554	580	–	–	–

* autothermal; – not available

where α_1 is a constant and the fuel molar concentration C_F can be substituted by the linearly related molar fraction $X_F = C_F \times RT_0/p_0$, if the local composition is considered to be the same as the bulk value. If the composition is calculated around a thin layer near the heated wire, T_0 should be replaced by a higher temperature which can be at most equal to T_{ign} . As the differences in the evaluated activation energy between these two procedures are not significant, our results refer to the bulk fuel concentration. An improved Eq. was obtained by Schwartz, Holbrook and Wise [2] by replacing C_F by C_F^n , where n is the partial reaction order with respect to fuel. For $n > 1$ the activation energy evaluated from (7) is higher than for $n = 1$.

Since the presented experimental method allows for the measurements of the ignition (and extinction) temperatures at various total pressures, we extended the application of Eq. (7) to a series of measurements at constant x_F and different total pressures p_0 :

$$p_0/(T_{ign} - T_0)^2 = \alpha_2 \times e^{E_a/RT_{ign}} \quad (8)$$

Eq. (8) can also be improved for an overall reaction order where $n \neq 1$, when p_0 is replaced by p_0^n and can be used when x_F is kept constant.

From the regression analysis of the data in Table 4 using Eq. (7) the activation energies vary between 43 and 47 kJ mol⁻¹ (for lower and higher pressures, respectively). Within the limits of estimation precision these differences are not significant. However, the activation energy of 71 kJ mol⁻¹ reported in [1] for a more diluted *n*-butane/air mixture suggest that the ignition of more concentrated mixtures, up to the stoichiometric one, follows higher order kinetics.

From the regression analysis of the same data using Eq. (8) with a constant x_F , the average activation energy is 82 kJ mol⁻¹, except for the stoichiometric mixture for which the activation energy is 111 kJ mol⁻¹. All of these values are closer to those obtained from induction period with wire temperature discussed above and to those reported by other researchers, suggesting the proposed method as a complementary and useful one for the overall kinetic parameter estimation. Finally,

it should be pointed out that the measured extinction temperatures are lower than the ignition ones and, to our knowledge, this behaviour can be attributed to the isothermal regime, and is reported for the first time. Further work in this area will be done in the near future.

4. Conclusions

New kinetic data was determined and reported concerning the heterogeneous catalytic ignition of lean to stoichiometric *n*-butane/air mixtures on isothermally heated platinum wire. The experiments were designed to measure the induction periods for mixtures with different compositions at different total pressures and wire temperatures. A simple kinetic model derived assuming a single step combustion reaction was used in order to rationalize the experimental results. The measurements were performed between the ignition temperatures and those temperatures which still permitted the reliable measurement of the induction period. Within this interval, the activation energy could be evaluated and compared with the activation energy following the ignition process. The results confirm the sudden transition from kinetic to mixed or diffusion control during the ignition process. The use of a technique based on the measurements in strict isothermal conditions, a process difficult to be achieved with strongly exothermic reactions, allowed for the measurement of ignition and extinction temperatures in a new environment. It was found that under these conditions extinction occurs at lower temperatures than ignition. The measured ignition temperatures were used to evaluate the overall activation energy.

Acknowledgments

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