



## A FIRST-DERIVATIVE METHOD TO EVALUATE THE KINETIC PARAMETERS FROM TRANSIENTS OF CATALYTIC IGNITION ON PLATINUM WIRES

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**abstract** The transient period for the catalytic combustion on isothermally heated platinum wires at high temperatures, described by a three parameter kinetic equation, can be conveniently exploited for the evaluation of the activation parameters using the first-derivative with respect to time of the chemical heat flow rate, an experimentally accessible property. The first-derivative curve has only two parameters, containing the essential information regarding the diffusion and reaction steps. The results obtained by this method agree very well with those reported from a nonlinear regression analysis of the integral equation, for the catalytic combustion of n-butane/air stoichiometric mixture.

### 1. Introduction

The catalytic combustion of different fuels, especially saturated hydrocarbons, is a subject of renewed interest due to its potentiality to drastically reduce the pollutant emission [1]. Numerous aspects of this process have been analyzed by prestigious research groups and a number of practical applications are already in current use. Notwithstanding, the kinetics of the overall catalytic process in various experimental conditions remained a subject of broader complexity, requiring the knowledge of the component steps: surface reactions, adsorption and desorption, mass and heat transport of both reactants and products. Among numerous catalysts, platinum has a special position due to its increased activity for many reactions of practical interest. The use of platinum foils or wires in order to obtain details regarding the kinetics of the catalytic combustion revealed a number of characteristic features, specific to temperature, pressure and composition ranges. The analysis of the heat balance during catalytic combustion on isothermally heated platinum wires proved out to be a useful procedure to obtain reliable kinetic information on both overall and detailed steps. When the platinum surface has a relatively low temperature, but higher than the catalytic ignition temperature, the ignition process requires an ignition period which decreases when the temperature increases. At higher temperatures, the ignition period becomes negligible compared with the temperature rise time of the ignition source and the ignition can be adequately described as a transient period when the heat flow rate increases from zero to a steady state value. At temperatures closed to ignition, the overall activation energies for

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alkane catalytic combustion are typically between 43 and 134 kJ·mol<sup>-1</sup> [1]. At higher temperatures frequently encountered in many applications, the activation energy decreases significantly reaching ultimately the diffusion limit [2]. The method of isothermally heated platinum wire, discussed in several previous papers, indicated the possibility to obtain the activation energy within a large range of temperatures [2,3]. This method is used in the present paper to evaluate the activation energy for the catalytic combustion of a stoichiometric n-butane/air mixture at sub-atmospheric pressures, using the first-derivative of the time dependent chemical heat flow rate.

## 2. Experimental

All measurements were done using the equipment described in several previous papers [2,3]. The air or the fuel/air mixture is alternatively admitted into the test cell and a platinum wire, located in the centre of the cell, is heated suddenly to a chosen temperature and then maintained constant. Any exothermal reaction occurring on the platinum surface in the fuel/air mixture is compensated by a decrease of the input power, as compared to the case when only the air is present in the cell. The feeding circuit allows the measurements of the characteristic electrical properties necessary to calculate the chemical heat flow rate  $F_r = dQ_r/dt$ :

$$dQ_r/dt = (R_w/R_{std}^2) \cdot \left[ (U_{std}^2)_{air} - (U_{std}^2)_{mixture} \right] \quad (1)$$

where  $R_w$ ,  $R_{std}$ ,  $U_{std}$  are the resistances of platinum wire and of a standard resistor, and the voltage across the standard resistor, in air and in combustible mixture, respectively. The measurement of these quantities allows the calculation of the chemical heat flow rate, which is a function on fuel, composition, total pressure and temperature. The wire temperature can be evaluated conveniently using a resistance-temperature relationship found in literature. The best one is of the form:

$$T_w = 273.15 + D_0 + \sum_{i=1}^9 D_i \cdot \left[ \frac{x - 2.64}{1.64} \right]^i \quad (2)$$

where  $x$  is the ratio between the wire resistance at temperature  $T_w$  and at 273.15 K and  $D_0$ ,  $D_i$  are constants given in literature [4]. All the other details were given elsewhere [2,3].

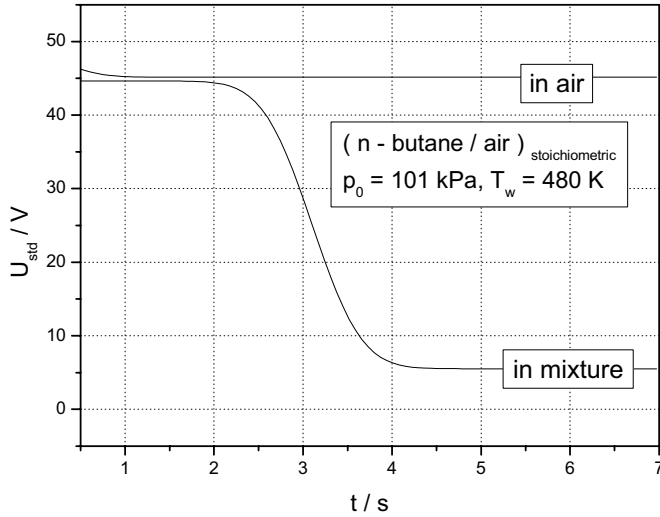
## 3. Results and discussion

At lower temperatures, when the overall catalytic process starts to change from kinetic to diffusion control, the typical experimental results are of the form given in Fig. 1.

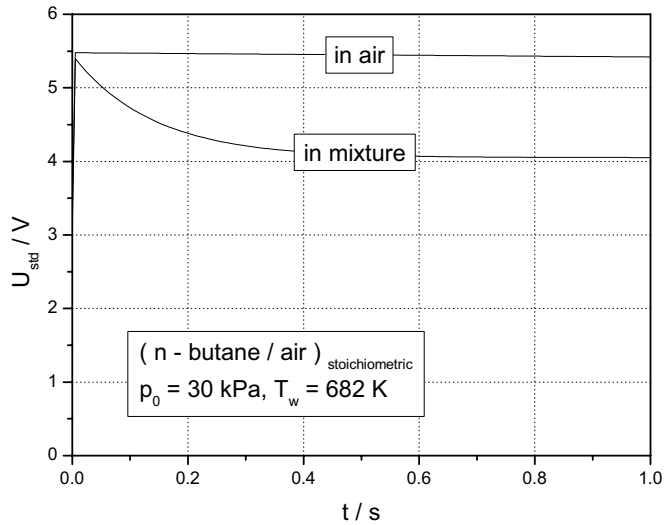
At higher temperatures, when the overall process is dominated by diffusion, the induction period becomes negligible small and the results are obtained in the form given in Fig. 2.

The subsequent analysis refers to experiments at higher temperatures, when the chemical heat flow rate obtained from the primary data can be expressed in the analytical form [2]:

$$\frac{dQ_r}{dt} = F_r = a + b \cdot (1 - \exp(-ct)) \quad (3)$$



**Fig. 1** Primary  $U_{std}$  versus time data, indicating the existence of an induction period



**Fig. 2** Primary  $U_{std}$  versus time data, apparently without the existence of an induction period

Here  $a$  is a characteristic constant dependent on the heat evolved at the beginning of the ignition process,  $b = \frac{\Delta^c H_T^0 \cdot S \cdot k_D \cdot k_r \cdot C_0}{k_D + k_r}$  and  $c = (k_D + k_r)/\phi$ , where  $\Delta^c H_T^0$  is the standard heat of combustion at temperature  $T$ ,  $S$  is the surface of the platinum wire,  $C_0$  is the molar concentration of fuel in the mixture,  $k_r$  and  $k_D$  are the rate constants for surface reaction and for diffusion, respectively and  $\phi$  is a characteristic length which can be taken equal to unity, used to obtain a physically correct dimension for the parameter  $c$ .

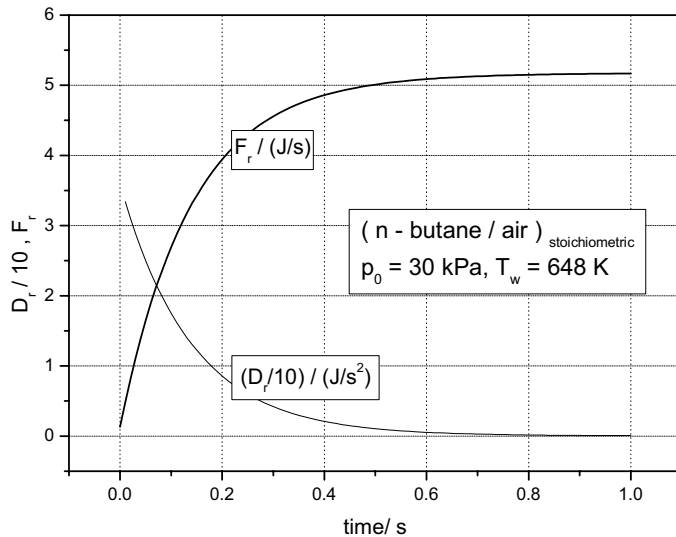
Under diffusion control, when  $k_r \gg k_D$ , the parameters  $b$  and  $c$  become:

$$b = \Delta^c H_T^0 \cdot S \cdot k_D \cdot C_0 \text{ and } c = k_r / \phi \quad (4)$$

The first-derivative of eqn. (3) takes the form:

$$D_r = \frac{dF_r}{dt} = b \cdot c \exp(-ct) \quad (5)$$

The time dependencies of  $F_r$  and  $D_r$  are illustrated in Fig. 3, for a stoichiometric n-butane/air mixture:



**Fig. 3** Heat flow rate,  $F_r$ , and its first derivative,  $D_r$ , for a stoichiometric n-butane/air mixture

The first-derivative contains only two parameters and can be used to evaluate the activation energy for both surface reaction and diffusion. The results can be compared with those obtained from the nonlinear regression analysis of equation (3). The required first-derivative with respect to time can be easily obtained from the original dependence  $F_r = f(t)$  using the available numerical methods.

The eqn. (5) can be subsequently used in two simple ways:

Method 1 is based on the linear regression of  $\ln(D_r)$  against time, at the same pressure and temperature:

$$\ln D_r = \ln(b \cdot c) - ct \tag{6}$$

It gives the parameters  $c$  and  $b$  at different pressures and temperatures, allowing the estimation of the corresponding activation energies using the regressions  $\ln(c)$  or  $\ln(b)$  versus  $1/T$ . On the basis of assumption (4), these can be associated with the activation energies of surface reaction (from  $c$ ) and of diffusion (from  $b$ ).

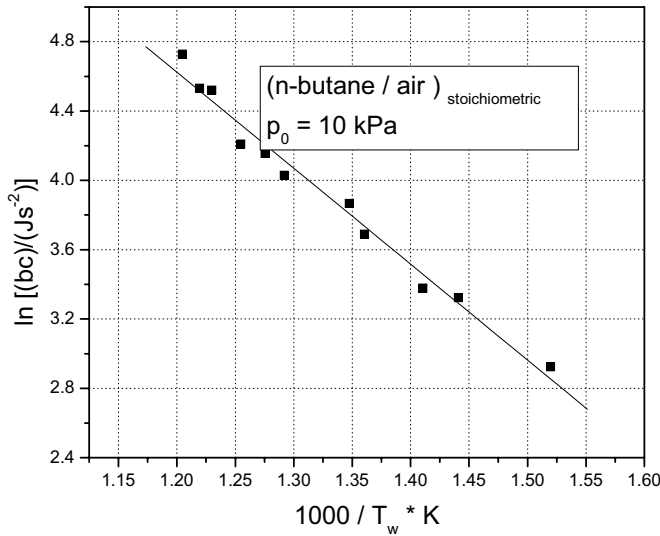
Method 2 is based on the extrapolation of  $D_r$  at  $t = 0$  at the same pressure and temperature, giving:

$$D_{r,0} = b \cdot c \tag{7}$$

The Arrhenius type plot  $\ln(D_{r,0})$  versus  $1/T$  and the corresponding regression give the sum of the activation energies for surface reaction and diffusion.

It should be noted that the interpretation of the obtained activation energies rely on the assumption that the overall process is diffusion controlled and consequently the parameters  $b$  and  $c$  have the approximate meaning given by (4).

The general trend and the quality of the obtained correlations are shown in Figs. 4 and 5.



**Fig. 4** Arrhenius type plot of the product  $(b \cdot c)$  resulted from the extrapolation method.

The results of this processing, compared with the reported data obtained from the nonlinear regression analysis, are given in Table 1. The activation energies resulted from parameter  $b$ , using either the original three parameter equation or its first-derivative, are within the range

of diffusion controlled processes in gas phase at high temperatures. Within the limits of experimental errors, they are pressure independent. The activation energies resulted from parameter  $c$ , associated with the surface reaction, are significantly larger and have practically the same values for both methods. The composite activation energies resulted from the extrapolation method, are practically equal to the sum of the activation energies for diffusion and for surface reaction, substantiating both the model and the compatibility of the proposed processing methods.

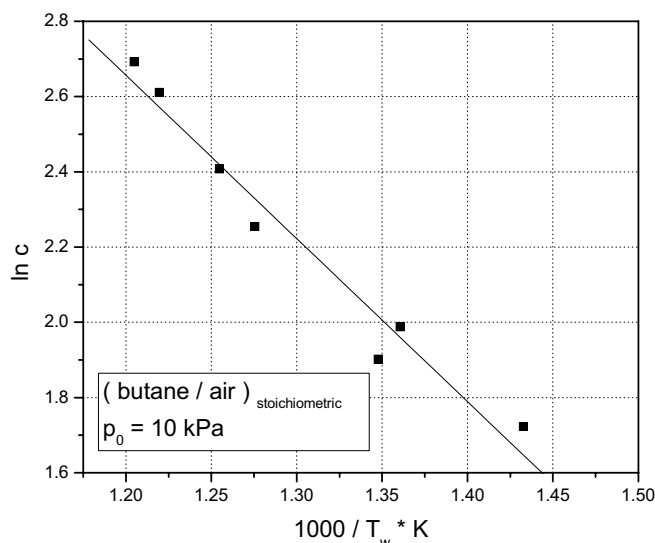


Fig. 5 Arrhenius type plot of parameter  $c$  resulted from the linear regression  $\ln D_r = \ln(b \cdot c) - ct$ .

Table 1 Activation energies (kJ/mol) obtained from the nonlinear regression (NLR) [2] and from the first-derivative method [present work] using the characteristic parameters  $b$  and  $c$

$p_0$ (kPa)	NLR $b$	NLR $c$	$\ln(D_r) - t$ $b$	$\ln(D_r) - t$ $c$	$D_{r,0}$ $bc$
10	$5.2 \pm 0.5$	$31.7 \pm 1.2$	$5.8 \pm 1.4$	$36.0 \pm 3.2$	$46.0 \pm 2.1$
20	$6.0 \pm 0.7$	$21.1 \pm 0.9$	$6.0 \pm 0.6$	$22.2 \pm 0.5$	$24.2 \pm 1.3$
30	$6.1 \pm 0.4$	$23.7 \pm 0.1$	$3.4 \pm 0.2$	$17.3 \pm 0.7$	$26.9 \pm 1.9$
40	$5.5 \pm 0.4$	$16.9 \pm 0.6$	$4.6 \pm 0.3$	$16.5 \pm 0.6$	$18.0 \pm 0.6$
50	$5.0 \pm 0.2$	$14.9 \pm 0.5$	$5.1 \pm 0.4$	$14.5 \pm 0.8$	$27.3 \pm 0.6$
60	$6.5 \pm 0.4$	$17.9 \pm 0.7$	$6.7 \pm 0.4$	$17.1 \pm 0.6$	$24.3 \pm 1.2$
70	$8.7 \pm 0.7$	$17.3 \pm 0.7$	$5.0 \pm 0.4$	$17.9 \pm 0.5$	$23.0 \pm 0.6$

## Conclusions

The first-derivative of the experimentally available chemical heat flow rate as a function of time offers the possibility to evaluate the activation energies of both diffusion and surface

reaction for catalytic combustion reactions of fuels at high temperatures, on isothermally heated platinum wires. The comparison of the obtained results with those reported using a nonlinear regression analysis of the primary curve indicates a very good agreement. Additionally, the direct evaluation of the composite activation energy, representing the sum of the diffusion and surface reaction activation energies, is a reliable proof for the kinetic model validation.

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