Coupled Catalytic/Gas Phase Ignition of Propane-Oxygen-Inert Mixtures on an Isothermally Heated Platinum Filament Supported on Quartz Bar

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The ignition of gaseous flammable mixtures on catalytically active hot solid surfaces is an intricate process implying the tight interaction between surface and gas phase reactions. The paper presents the results obtained from the study of coupled catalytic-gas phase ignition of propane-oxygen-inert mixtures on an isothermally heated platinum filament stabilized on a thin quartz bar, measuring the induction periods, τ_i, rates of heat release, $(dQ_i/dt)_\tau$ and minimum ignition energies, Q_{min}. The experiments were conducted at different initial pressures between 73 and 101 kPa and filament temperatures between 1080 and 1184 K for 2.68% propane-air mixture and 4.02% propane-air mixture diluted with Ar or N_2 in ratio 2:1. For any total pressure, the fuel concentration is the same in each mixture, the complementary composition containing the necessary oxygen for complete combustion and inerts or/and excess oxygen. The measured properties were rationalized using Arrhenius-type kinetic equations.

Keywords: propane, gas phase ignition, platinum filament, overall activation energy, overall reaction order

The ignition of gaseous explosive mixture using heated solid surfaces has numerous applications in many industrial processes [1-3]. Beside the interest of the catalytic ignition application of flammable mixture on hot solid surfaces, the risk analysis and the assessment of potential hazard during production, transportation and storing of different fuels are also important [4-8]. The catalytic ignition is dependent on both solid surface and gas composition. The added inert component (nitrogen, argon, carbon dioxide) can be used as a modulator able to restrict or even to suppress the ignition. A practical method to control a combustion reaction can be diluting reactants with an inert. Inerts can affect the overall reaction due to the change of transport and thermo-physical properties (e.g. specific heat, diffusivities etc), partial removal of combustion heat, change of reaction rates as a result of partial pressures changes, and change due to the deactivation of active species through third-body collisions encountered in gas phase reactions [9]. The reactions on a catalytic surface leading to the surface ignition, which can be followed by a gas phase ignition, are also strongly dependent on the inert nature and concentration. At present, these issues are not well understood and are of increasing interest [7-9].

There are some critical conditions necessary for ignition occurrence. A very specific property characterizing the system is the induction period of the ignition and its dependence on the mixture pressure and composition as well as on the surface temperature [2,10-11].

Two distinct ignition stages are recognized within the overall process: surface ignition and gas phase ignition. The necessary information regarding these coupled processes can be obtained using an electric circuit designed to produce a quasi-rectangular temperature jump of a platinum filament and to keep it constant during the ignition process. The exothermal reactions occurring on or near platinum surface produce a chemical heat flux, which lowers the necessary input power, indicating the extent of the exothermal process. The output of this circuit allows the visualization of both surface ignition and gas phase ignition occurring after characteristic induction periods.

The simple models which give the pressure and composition dependencies of the induction period refer to initial gas composition, before the ignition. Depending on the relative value of the induction period as well as on the relative contribution of chemical reactions and transport processes, this composition can be significantly changed.

In this paper, the measured induction periods for gas phase ignition on a heated platinum wire supported on a quartz bar were reported for 2.68% propane-air mixture and 4.02% propane-air diluted in ration 2:1 with nitrogen or argon at various initial pressures and filament temperatures.

From their temperature and pressure dependence, the overall activation energy and reaction order were calculated. The chemical heat flux and minimum ignition energy variation during the surface reaction allow also the evaluation of possible changes of the activation energy and reaction order.

The stoichiometric propane-air mixture was thoroughly examined in many laboratories and there are reliable reference data in literature for comparison [12-15].

A review of the most important features of explosion initiation by hot bodies with the characteristic parameters of the initiation source was presented by [16] and the most important notions and definitions used in research are given in e.g. [17, 18].

Dilution of gaseous flammable mixtures with inerts for safety reasons, from explosion mitigation to total suppression, is a common practice. This type of modulation has many consequences on the ignition and subsequent flame development. The most important seems to be the decrease of the available energy density due to the partial removal of fuel and oxygen as heat generator and the presence of inerts as supplementary heat sink. The present study aims at estimating the comparative inerting efficiency of N_2 and Ar when all other operational properties of propane-oxygen-inert mixtures are kept constant.

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Experimental part

The experimental setup with an electronic circuit designed to obtain a quasi-rectangular temperature profile of a platinum filament was previously described in detail [19-25] and given in figure 1.
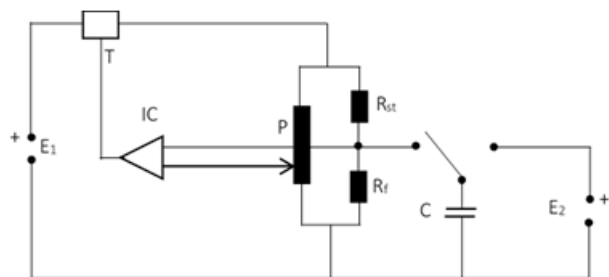

Fig. 1. Electric circuitry for quasi-rectangular temperature jump and isothermal heating

Mixture	Composition (vol%)				φ^*
	C_3H_8	O_2	N_2	Ar	
(2.68% C_3H_8-air)	2.68	20.44	76.88	-	0.66
(4.02% C_3H_8-air) + N_2, ratio 2:1	2.68	13.45	83.88	-	1.00
(4.02% C_3H_8-air) + Ar, ratio 2:1	2.68	13.45	50.47	33.40	1.00

* the equivalence ratio $\varphi = ([C_3H_8]/[O_2])/([C_3H_8]/[O2])_{stoich}$ is the actual fuel to oxidizer ratio divided by the fuel to oxidizer ratio of the stoichiometric mixture, i.e. a composition where the fuel and the oxidizer are completely converted to CO_2 and H_2O (assuming no dissociation in the flame).

A platinum wire coiled as filament, supported on a thin quartz bar, with resistance R_f a standard resistor with resistance R_{st} and a potentiometer P form a Wheatstone bridge. The discharge of a condenser C previously charged at a suitable voltage (established by trial and error) across the filament in less than 1 ms insures the temperature jump, while an integrated circuit IC senses the bridge unbalance and adjusts the feed voltage through a transistor T, allowing a continuous monitoring of R_f. The initial setting of potentiometer adjusts the value of R_f and consequently the wire temperature. The transient or stationary voltages U_{st} across R_{st} are recorded using a Tektronix TDS 210 oscilloscope for digital recording of transient processes.

The platinum filament is assembled in the center of a cylindrical test vessel. To maintain the symmetry of the platinum filament, it was supported on a thin quartz bar (ϕ=1 mm, l = 50 mm) useful in preserving the filament geometry especially at higher temperatures when it tends to bend.

The test vessel is evacuated and filled with air or with gaseous fuel/air mixture of known composition at initial experimental pressures. The gaseous mixtures containing propane in air with/without inert were prepared in a stainless-steel cylinder at maximum 500 kPa total pressure by partial pressure method and used 24 h after mixing.

Experiments were made at various filament temperatures (within the range 1080-1184 K), at variable initial pressure (within the range 73-101 kPa) for 2.68% *n*-propane-O_2-inert mixtures (inerts: argon and nitrogen). The composition and the equivalence ratio of the studied inflammable mixtures are given in table 1.

The corresponding thermal $U_{st}= f(t)$ diagrams are used to calculate the critical parameters of ignition and to establish the overall kinetics of the process.

The induction period τ_i depends on gas composition and total initial pressure p_0, as well as on filament temperature T_f. The induction periods are related to the overall kinetic parameters of the combustion reaction and can be used for their evaluation. The thermal ignition theory indicates that the induction period can be expressed as a function of p_0 and T_f by the following relationship [4]:

$$\tau_i = a_0 \cdot p_0^{-n} \cdot e^{E_a/RT_f} \tag{1}$$

where a_0 is a constant, n is the overall reaction order, E_a is the apparent activation energy, and R is the universal gas constant. Due to the complexity of the overall process, parameters n and E_a/RT have no mechanistic significances but can be useful as normalized sensitivity coefficients of reaction rate r_R [15] with respect to total pressure:

$$n = \partial \ln(r_R)/\partial \ln(P_0) \tag{2}$$

and to temperature:

$$E_a/RT = \partial \ln(r_R)/\partial \ln(T) \tag{3}$$

The differences between the rates of the heat transfer from filament to air and to the flammable mixture originate essentially in the exothermic combustion reaction on the platinum surface and in the surrounding gas [19]:

$$(dQ_r/dt) = \frac{R_f}{R_{st}^2}\left[(U_{st}^2)_{air} - (U_{st}^2)_{mixture}\right] \tag{4}$$

If dQ_r/dt is related to the rate of the overall combustion reaction, the following relationship is obtained:

$$(dQ_r/dt) = \alpha \cdot p_0^n \cdot \left(X_{ox}^{n1} \cdot X_f^{n2}\right) \cdot e^{-(E_a/RT_w)} \tag{5}$$

where, as a first approximation, α is a constant. X_{ox} and X_f are the molar fractions of oxygen and fuel, respectively, and n_1 and n_2 are the corresponding reaction orders with respect to oxygen and fuel.

The thermal diagrams U_{st} = f(t) can be also used to calculated the minimum ignition energy. Q_{min}, for this type of ignition as [19-20]:

$$Q_{min} = \int_0^\tau (dQ_r/dt) = \frac{R_w}{R_{st}^2}\int_0^\tau \left[(U_{st}^2)_{air} - (U_{st}^2)_{mixture}\right] \cdot dt \tag{6}$$

Similarly, its kinetic significance for an overall process of Arrhenius type is given by [21]:

$$Q_{min} = \int_0^\tau \alpha \cdot p_0^n \cdot \left(X_{ox}^{n1} \cdot X_f^{n2}\right) \cdot e^{-(E_a/RT_f)} \tag{7}$$

Results and discussions

The exothermal process of the combustion reaction in the adsorbed layer or in the adjacent gas phase can be identified on the experimental diagrams (thermograms) giving the voltage U_{st} across the standard resistor in time. The output of the acquisition system for a typical run with the platinum filament in air and in the test mixtures are
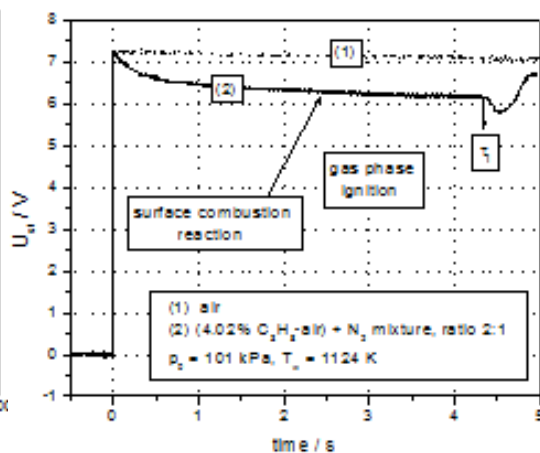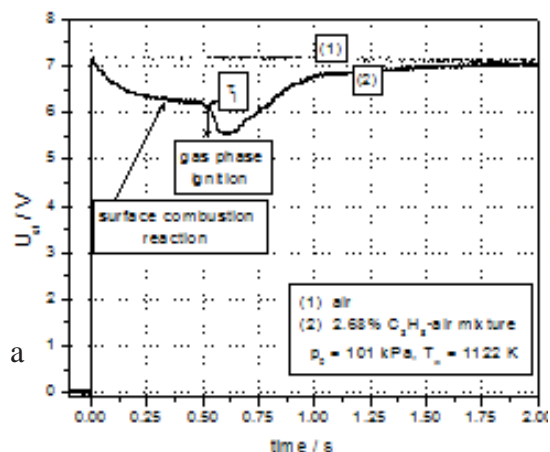
Fig. 2. Typical thermal diagrams for: (a) air and lean (2.68% propane-air) mixture (2.68% C_3H_8, 20.44% O_2, 76.88% N_2) and (b) air and stoichiometric 4.02% propane-air diluted with N_2 in ratio 2:1 (2.68% C_3H_8, 13.45% O_2, 83.88% N_2)

given in figures 2a and 2b, at the same initial pressure and temperature. The exothermal reaction can be detected by the lowering of the input voltage necessary to maintain a constant wire temperature. The initial decreasing represents the surface reaction, while the subsequent sudden decrease represents the ignition of the gaseous mixture.

The rate of heat release, dQ_r / dt, and the minimum ignition energy, Q_{min}, can be calculated according to equation (4) as illustrated in figure 3.

The rate of heat release, 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 $\Delta_r H_T^0$:

$$(dQ_r/dt) = S_f \cdot \Delta_r H_T^0 \cdot r_R \qquad (8)$$

A particular value of dQ_r/dt is that at the ignition time, $(dQ_r / dt)_\tau$. From equations (8) and (5) one obtains the compact form [21]:

$$(dQ_r/dt)_\tau = a_2 \cdot p_0^n \cdot \exp(-E_a/RT_f) \quad (9)$$

On the other hand, 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 [21]:

$$Q_{min} = a_3 \cdot p_0^n \cdot (X_{f,0}^{n_1} \cdot X_{ox}^{n_2}) \cdot \exp(-E_a/RT_f) \cdot \tau_i \quad (10)$$

where a_2, a_3 are composite parameters.

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 errors.

The measured (τ_i) or calculated properties (dQ_r/dt and Q_{min}) dependent on gas composition and initial pressure p_0, as well as on filament temperature T_f are related to the overall kinetic parameters of the combustion reaction and can be used for their evaluation.

The results were analyzed using both a 2D nonlinear regression analysis, either at quasi-constant pressures or at quasi-constant temperatures, and a more statistically relevant 3D nonlinear regression analysis. From 2D nonlinear analysis, the results given in table 2 are obtained.

According to its significance as the reciprocal of the reaction rate, the temperature dependence of the induction period should follow an Arrhenius type behaviour, with positive values of activation energy as shown by the results given in table 2. For the imposed restrictive conditions, with the same fuel molar concentration, there are significant differences between the examinend mixtures brought about by the differences between inerts, both of them producing a lowering of the activation energy, the most efficient being N_2.
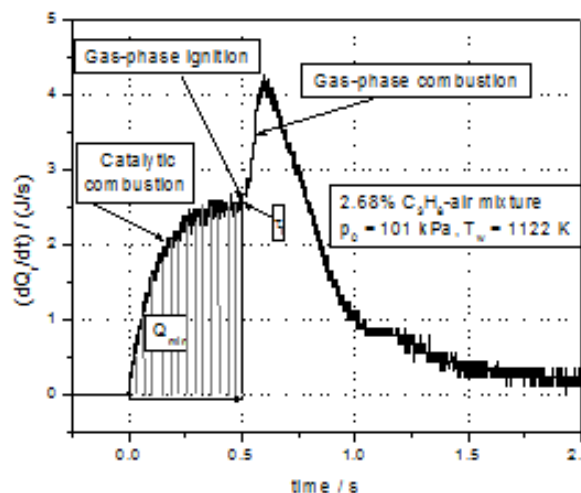

Fig. 3. Illustration for the rate of heat release and minimum energy calculation

The negative values of the pressure coefficient indicate a decrease of the induction period when the pressure rises.

Different results were obtained from the analysis of the same data using either equation (9) or (10) as regression $\ln(dQ_r/dt)_\tau$ or $\ln(Q_{min}/\tau_i)$ vs. $1/T_f$ illustrated in figure 4 and table 3.

An examination of the results given in table 3 indicates an anti–Arrhenius dependence of $\ln(dQ/dt)_\tau$ with respect to $1/T_f$ which, according to equation (9), should give a negative slope. The same anti–Arrhenius dependence of $\ln(Q_{min})$ with respect to $1/T_f$ according to equation (10), should give also a negative slope. A similar trend was also reported for iso-butane-air mixtures [25] and for n-butane/air mixtures [26], using the same experimental technique and was explained on the basis of uncompensated reactant depletion within the layer adjacent to the catalytic surface [27].

Similar results were obtained from the 3D nonlinear regression analysis, as illustrated in figure 5 and detailed in table 4.

Within the limits of experimental and model errors, the general trend is n < 0, which indicates a significant decrease of all measured and calculated properties, τ, $(dQ_r / dt)_\tau$, Q_{min} when pressure increases. From safety point of view, the consequence is the weakening of the system stability. The temperature sensitivity is however different: Arrhenius type dependence for τ and anti-Arrhenius type dependence for $(dQ_r/dt)_\tau$ and Q_{min}.

All these properties characteristic for ignition, together with flame propagation properties [28, 29] and ignition temperature [30, 31] are essential to establish the safety regulation in gaseous flammable mixtures.
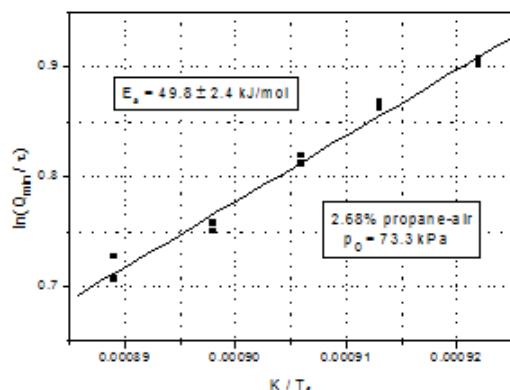
Fig. 4. Illustration of the anti-Arrhenius dependence of $\ln[(Q_{min}/\tau_i)/(J/s)]$ on the reciprocal of filament temperature
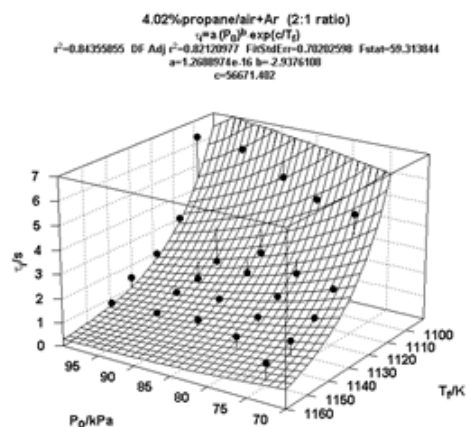

Fig. 5. Illustration of 3D regression analysis for the mixture 4.02% propane/air+Ar (2:1 ratio)

Table 2
OVERALL RESULTS FROM THE 2D NONLINEAR REGRESSION ANALYSIS

System	Restrictions	Model	R^2	n	$E_a/(kJ/mol)$
2.68% C_3H_8-air	p_0=101 kPa	$\ln(\tau/s)=a+b/T_f$	0.962	-	483±32
	p_0=94.0 kPa	$\ln(\tau/s)=a+b/T_f$	0.992	-	508±16
	p_0=86.7 kPa	$\ln(\tau/s)=a+b/T_f$	0.978	-	365±19
	p_0=80.0 kPa	$\ln(\tau/s)=a+b/T_f$	0.990	-	415±15
	p_0=73.3 kPa	$\ln(\tau/s)=a+b/T_f$	0.988	-	406±16
	T_f=1163 K	$\ln(\tau/s)=m+n\ln(P_0/kPa)$	0.996	-1.78±0.04	-
	T_f=1166 K	$\ln(\tau/s)=m+n\ln(P_0/kPa)$	0.996	-1.78±0.04	-
2.68% C_3H_8-air+Ar	p_0=101 kPa	$\ln(\tau/s)=a+b/T_f$	0.962	-	276±18
	p_0=94.0 kPa	$\ln(\tau/s)=a+b/T_f$	0.859	-	283±38
	p_0=86.7 kPa	$\ln(\tau/s)=a+b/T_f$	0.927	-	201±20
	p_0=80.0 kPa	$\ln(\tau/s)=a+b/T_f$	0.921	-	205±21
	p_0=73.3 kPa	$\ln(\tau/s)=a+b/T_f$	0.908	-	187±21
	T_f=1163 K	$\ln(\tau/s)=m+n\ln(p_0/kPa)$	0.954	-3.23±0.24	-
	T_f=1094 K	$\ln(\tau/s)=m+n\ln(p_0/kPa)$	0.895	-3.83±0.66	-
2.68% C_3H_8-air+N_2	p_0=101 kPa	$\ln(\tau/s)=a+b/T_f$	0.860	-	194±28
	p_0=94.0 kPa	$\ln(\tau/s)=a+b/T_f$	0.923	-	118±11
	p_0=86.7 kPa	$\ln(\tau/s)=a+b/T_f$	0.961	-	117±8
	p_0=80.0 kPa	$\ln(\tau/s)=a+b/T_f$	0.964	-	121±8
	p_0=73.3 kPa	$\ln(\tau/s)=a+b/T_f$	0.995	-	100±3
	T_f=1162 K	$\ln(\tau/s)=m+n\ln(p_0/kPa)$	0.964	-2.64±0.18	-

Table 3
RESULTS FOR APPARENT ACTIVATION ENERGY FROM $\ln(dQr/dt)_\tau$ AND $\ln(Q_{min}/\tau)$ vs. $1/T_f$ REGRESSION AT p_0=101.3 kPa

System	$E_a/(kJ/mol)$	
	From $\ln(dQr/dt)_\tau$	From $\ln(Q_{min}/\tau_i)$
2.68% C_3H_8-air	259±22	73.1±4.6
2.68% C_3H_8-air+Ar	196±15	56.4±9.2
2.68% C_3H_8-air+N_2	-	50.1±19

System	Model	Method	R^2	n	E_a/(kJ/mol)
2.68% C_3H_8-air	$ap^b exp(+c/T)$	τ/s	0.865	-4.52±0.62	343±34
	$ap^b exp(+c/T)$	$(dQ_r/dt)_\tau$/(J/s)	0.714	-0.93±0.33	132±19
	$ap^b exp(+c/T)$	Q_{min}/J	0.852	-4.38±0.70	371±39
2.68% C_3H_8-air+Ar	$ap^b exp(+c/T)$	τ/s	0.844	-2.94±0.57	471±50
	$ap^b exp(+c/T)$	$(dQ_r/dt)_\tau$/(J/s)	0.854	-0.80±0.19	151±14
	$ap^b exp(+c/T)$	Q_{min}/J	0.743	-2.72±0.81	480±71
2.68% C_3H_8-air+N_2	$ap^b exp(+c/T)$	τ/s	0.849	-2.19±0.30	211±23
	$ap^b exp(+c/T)$	$(dQ_r/dt)_\tau$/(J/s)	0.728	-1.31±0.71	80±52
	$ap^b exp(+c/T)$	Q_{min}/J	0.714	-2.12±0.48	224±36

Table 4
OVERALL RESULTS FROM
THE 3D NONLINEAR
REGRESSION ANALYSIS

Conclusions

The ignition of a 2.68% propane-air mixture and 4.02% propane-air mixtures diluted with N_2 or Ar in ration 2:1 was studied at different initial pressures and filament temperatures using an isothermally heated platinum filament supported on a thin quartz bar to maintain a stable configuration.

The study followed the comparative inerting efficiency of N_2 and Ar when all other operational properties of propane-oxygen-inert mixtures were kept constant. To reduce the number of variables, the fuel molar concentration was the same for any total pressure.

The recorded thermal diagrams in air and in the test mixture allowed the measurement of the induction periods (τ_i), of the corresponding chemical heat fluxes (dQ_r/dt)$_\tau$ and minimum ignition energy (Q_{min}) at the end of this period, before the gas phase ignition.

The temperature and pressure dependence of the induction periods, of the chemical heat fluxes and minimum ignition energy, gave the overall activation energies and reaction orders. The anti-Arrhenius behavior can be attributed to the depletion of the reactants within the diffusion film around the catalytic surface, which cannot be longer compensated from the bulk due to very fast catalytic reaction.

References

1.COHN, J.G., Fuel, **76**, no. 5, 1997, p. 407.
2.BOLK, J.K., SICCAMA, N.B., WESTERTERP, K.R., Chem. Eng. Sci., **51**, 1996, p. 2231.
3.SHEINTUCH, M., LUSS, D., J. Catal., **68**, 1981, p. 245.
4.LEWIS, B., VON ELBE, G., Combustion, Flames an Explosion of Gases, Academic Press Inc, New York, 1987, Chap. V.
5.VAN TIGGELEN, A., BALACEANU, J., BURGER, J., DE SOETE, G., SAJUS, L., SALE, B., VAN TIGGELEN, P., Oxidations et Combustions, Ed. Technip, Paris, 1968, Chap. VI.3.
6.POWEL, F., Proc. 9-th Intern. Symp. Prev. Occup. Accidents Diseases Chem. Ind. Lucerna, 1984, p. 267.
7.GRIFFIN, T.A., PFEFFERLE, L.D., AIChE J., **36**, 1990, p. 861.
8.PARK, Y.K., FERNANDES, N.E., VLACHOS, D.G., Chem. Eng. Sci., **54**, 1999, p. 3635.
9.DUPONT, V., ZHANG, S.H., WILLIAMS, A., Chem. Eng. Sci., **56**, 2001, p. 2659.
10.ASHMAN, L.E., BUCHLER, A., Comb. Flame, **5**, 1961, p. 113.
11.CHO, P., LAW, C.K., Comb. Flame, **66**, 1986, p. 159.
12.HIAM, L., WISE, H., CHAIKIN, S., J. Catal., **9-10**, 1968, p. 272.
13.VESER, G., ZIAUDDIN, M., SCHMIDT, L.D., Catal. Today, **47**, 1999, p. 219.
14.VESER, G., SCHMIDT, L.D., AIChE J., **42**, 1996, p. 1077.
15.MITU, M., RAZUS, D. OANCEA, D., J. Therm. Analysis Calorim, 131, 2018, p. 175
16.RAZUS, D., OANCEA, D., IONESCU, N.I., Rev. Chim. (Bucharest), **51**, no. 8, 2000, p. 590.
17.RAZUS, D., OANCEA, D., IONESCU, N.I., GOSA, V., Rev. Chim. (Bucharest), **45**, no. 12, 1994, p. 1097.
18.STEEN, H., GOEDDE, M., BOTHE, H., Handbook of explosion prevention and protection, Ed. M. Hattwig. H. Steen. Wiley-VCH, Ignition by hot surfaces, (2004) Chap. 2.3.
19.OANCEA, D., RAZUS, D., MITU, M., CONSTANTINESCU, S., Rev. Roum. Chim., **47**, no. (1-2), 2002, p. 91.
20.OANCEA, D., MITU, M., PINCU, E., RAZUS, D., Rev. Roum. Chim., **49**, no. (3-4), 2004, p. 391.
21.MITU, M., RAZUS, D., OANCEA, D., Rev. Roum. Chim., **62**, no. (8-9), 2017, p. 613.
22.OANCEA, D., RAZUS, D., MITU, M., Rev. Roum. Chim., **50**, no. (11-12), 2005, p. 991.
23.OANCEA, D., MUNTEANU, V., RAZUS, D., MITU, M., Rev. Roum. Chim., **56**, no. 3, 2011, p. 255.
24.MITU, M., MUNTEANU, V., RAZUS, D., OANCEA, D., Rev. Roum. Chim., **59**, no. 9, 2014, p. 727.
25.STAICU, O., MUNTEANU, V., RAZUS, D., OANCEA, D., Rev. Roum. Chim., **53**, no. 4, 2008, p. 277.
26.OANCEA, D., STAICU, O., MUNTEANU, V., RAZUS, D., Catal. Lett., **121**, 2008, p. 247.
27.LAW, C.K., CHUNG, S.H., Combust. Sci. Technol., **32**, 1983, p. 307
28. BRINZEA, V., MITU, M., MOVILEANU, C., RAZUS, D., OANCEA, D., Rev. Chim. (Bucharest), **62**, no. 2, 2011, p. 201
29. GIURCANU, V., MITU, M., RAZUS, D., OANCEA, A.D., Rev. Chim. (Bucharest), **67**, no. 6, 2016, p. 1984
30.BRANDES, E., FROBESE, D.H., MITU, M., Oil Gas European Magazine, 4, 2006, p. 199
31. MITU, M., BRANDES, E., Rev. Chim. (Bucharest), **68**, no. 5, 2017, p. 1035