



KINETICS OF ISOTHERMAL CATALYTIC IGNITION AND COMBUSTION OF LPG-AIR MIXTURES ON PLATINUM WIRE

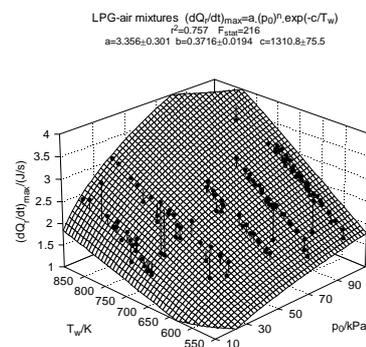
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The catalytic ignition and flameless steady combustion of lean to stoichiometric gaseous fuel-air mixtures, with equivalence ratios $\phi = 0.62, 0.71, 0.81, 0.90$ and 1.00 , resulted from liquefied petroleum gas (LPG) produced in Romania, containing 12 vol % propane, 87 vol % butane, and 1 vol % C5 fraction, were studied on heated platinum wire in isothermal regimes. The critical ignition temperatures at pressures between 20 and 101 kPa and maximum heat release rates, proportional to the rate of the catalytic combustion, within the same pressure range, and temperatures between 570 and 890 K were measured and discussed. The ignition temperature increases with LPG concentration and decreases with total gas pressure. The maximum heat release rate increases with both catalyst temperature and total gas pressure but is apparently independent of LPG content. At 20 kPa pressure the induction delays were measured at several catalyst temperatures. The technique of isothermal combustion allows the evaluation of the overall kinetic parameters on the basis of literature models.



INTRODUCTION

The liquefied petroleum gas (LPG) represents an increasingly used fuel in both domestic and automotive applications due to the present availability, lower pressure requirements for storage tanks, and associated reduced NO_x , CO and unburned hydrocarbon emissions resulted from its combustion. Its main components – propane and butanes – are present in different proportions in many blends according to the country of origin and processing technology. The presence in small amounts of other saturated hydrocarbons, especially pentanes, seems to play no significant role for most applications and consequently the combustion properties of LPG are frequently discussed in connection with those of propane and butanes. The research associated with LPG

combustion in various applications is directed to its ignition, propagation and thermal or/and mechanical efficiency on the one hand, and to safety requirements and environment protection on the other. The most important measured properties are the flammability limits,¹ laminar burning velocities and explosion index,^{2, 3} quenching distances, minimum ignition currents and minimum ignition energies,⁴ maximum explosion pressures and maximum rates of pressure rise,⁵ inerting effect of the combustion products,⁶ initial pressure and mixture composition influence on the explosivity parameters,⁷ effect of the exhaust gas on the laminar burning velocities.⁸ Another area of interest is the catalytic combustion of LPG, important for lower temperatures and cleaner operation of micro-combustors,^{9, 10} as well as for the development of high performance gas

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detectors.^{11, 12} Among the available experimental techniques, the isothermal flameless combustion on platinum wire represents a simple way to study both the kinetically controlled ignition and subsequent diffusion controlled steady process for different alkanes.¹³⁻²⁰ The present work investigated the effect of operational conditions – fuel content, total pressure and catalyst temperature – on the critical ignition temperature, ignition delay and rate of heat release.

RESULTS

The experimental results consist in diagrams representing the variation in time of the rate of heat release, a property directly proportional to the combustion rate on the catalytic surface of a platinum wire, for various values of wire temperature, T_w , gas composition and total pressure, p_0 . The diagram is obtained for stagnant mixtures in a closed vessel after a quasi-rectangular jump of wire temperature followed by an isothermal regime of the wire. When the catalyst temperature is decreased, a critical value, T_* , is found when the ignition no longer occurs. Typical results are shown in Fig. 1.

The curve 1 represents the case when the ignition delay is under the detection limit of the analytical method, its value being of the same order of magnitude with the rise time of the temperature jump from ambient to working temperature. From these experiments, typical for

most investigated systems, only the critical ignition temperatures, T_* , corresponding to $dQ_r/dt \cong 0$, and the maximum heat release rates, $(dQ_r/dt)_{\max}$, can be measured. After the maximum value, dQ_r/dt slightly decreases due to the progressive consumption of the reactants in the test vessel. The curve 2, obtained only at lower pressures, starts with a measurable induction delay dependent on LPG content and catalyst temperature. For intermediate pressures the results are not reproducible, probably due to significant structural changes of the platinum surface during combustion process.

The measured critical ignition temperatures are given in Fig. 2. It can be observed that T_* increases when LPG content increases, a behavior which is in opposite direction to that reported for different single alkane-air mixtures using either the same isothermal combustion technique,^{16, 18} a flow technique over a heated wire^{21, 22} or a stagnation point flow configuration on a platinum foil.^{23, 24}

From 141 recorded diagrams, only few presented measurable induction delays exhibiting an obvious trend with respect to temperature for mixtures containing 2.00, 2.30, and 2.90 % LPG, at $p_0=20$ kPa. The data could be analyzed on the basis of Arrhenius law.

The maximum heat release rate dQ_r/dt increases monotonically with respect to both gas pressure and catalyst temperature, but is apparently independent of fuel content, as illustrated in Table 1.

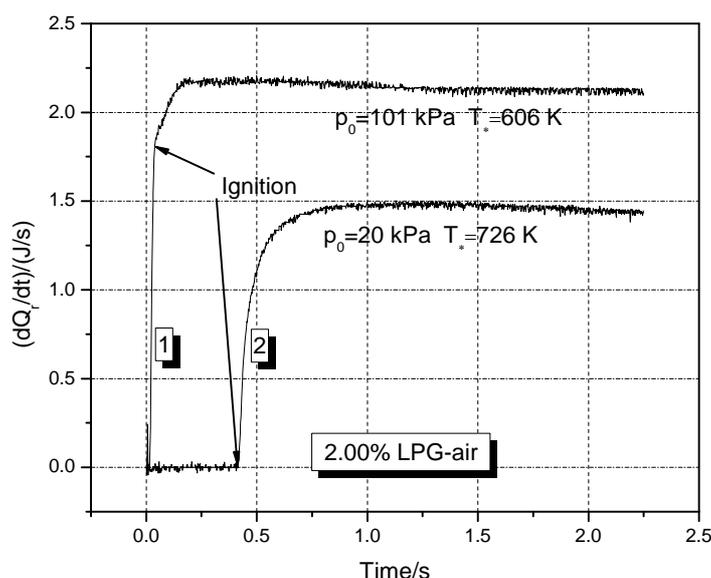


Fig. 1 – Representative diagram showing the variation in time of the heat release rate, dQ_r/dt , for 2.00 % LPG-air mixture at different total pressures and platinum wire temperatures.

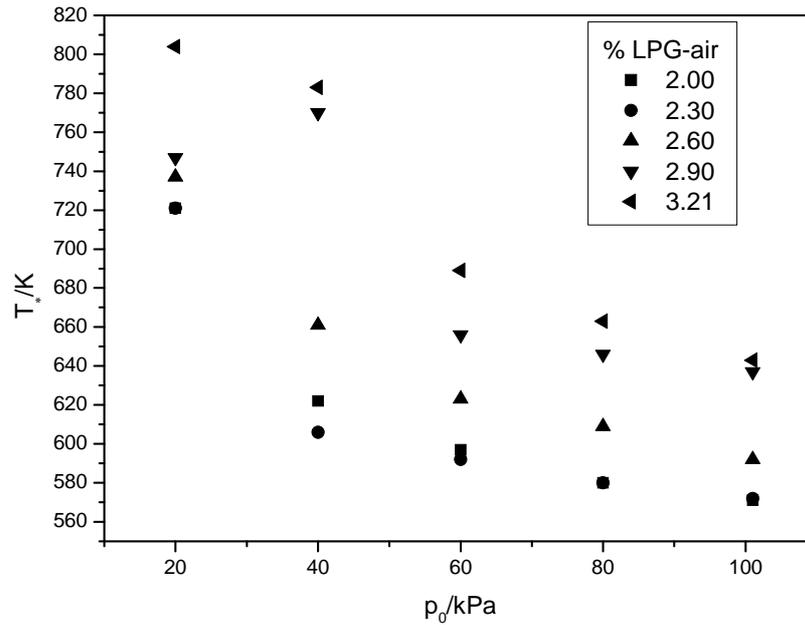


Fig. 2 – Critical ignition temperatures of different LPG-air mixtures.

Table 1

Variation of the maximum heat release rate with wire temperature, total gas pressure and fuel content

2.00 % LPG $p_0=101$ kPa		2.30 % LPG $T_w=620$ K		$p_0=101$ kPa $T_w=620$ K	
$(dQ_r/dt)_{\max}/(\text{J/s})$	T_w/K	$(dQ_r/dt)_{\max}/(\text{J/s})$	p_0/kPa	$(dQ_r/dt)_{\max}/(\text{J/s})$	% Fuel
2.20	605	0.80	20	2.30	2.00
2.30	625	1.50	40	2.20	2.30
2.40	640	1.90	60	2.22	2.60
2.60	656	2.10	80	2.10	2.90
2.70	672	2.20	101	2.20	3.21

DISCUSSION

The variation of the critical ignition temperature was analyzed using two literature models, adapted for the present work where the measurements at different total pressures are accessible. Hiam, Wise and Chaikin²¹ developed a model (H-W-C) for the flow combustion of alkanes on a platinum filament in large excess of oxygen at normal pressure and obtained the following equation for a first order reaction with respect to fuel:

$$\kappa_0 \cdot \frac{C_F}{(T^* - T_0)^2} = e^{+E_a/RT^*} \quad (1)$$

where κ_0 includes various constants, C_F is the bulk fuel concentration, T^* and T_0 are critical

ignition and ambient temperatures, E_a is the overall activation energy of the ignition process, and R is the gas constant. Since $C_F = x_F \cdot p_0 / RT_0$, where x_F is the fuel molar fraction, equation (1) takes the form:

$$\kappa_1 \cdot \frac{p_0}{(T^* - T_0)^2} = e^{+E_a/RT^*} \quad (2)$$

for a constant x_F , where the response variable is now the total pressure instead C_F . The activation energy can be evaluated fitting Equation (2) on experimental data, considering that the first order assumption is still valid. The results are given in Table 2. Schwartz, Holbrook and Wise²⁵ proposed a more flexible model (S-H-W) where the reaction order n with respect to fuel can take different values:

$$K_0 \cdot \frac{C_F^n}{(T_*)^2} = e^{+E_a/RT_*} \quad (3)$$

Similarly, for a constant x_F , the equation takes the form:

$$K_1 \cdot \frac{p_0^n}{(T_*)^2} = e^{+E_a/RT_*} \quad (4)$$

which is valid when n is either the partial reaction order with respect to fuel or the overall reaction order. The literature offers examples with $n=1$ for both cases.²¹⁻²⁷ The results for $n = 1$ and $n = 2$ are also given in Table 2.

There are no significant variations of the activation energy within the explored range of fuel concentrations, for all discussed models. This represents indirect evidence that the assumption of first order is acceptable. It can be seen that the

S-H-W model is strongly dependent on the assumed reaction order (1 or 2). In the absence of a reference value determined in similar experimental conditions, a safe choice is not possible taking also into account the complex nature of this parameter which includes reactants adsorption, complex surface reactions, and products desorption. For lean to stoichiometric n -butane-air mixtures,¹⁶ the activation energy measured with the same technique and evaluated with H-W-C model, varies between 43 and 47 kJ/mol, closer to the above reported values (H-W-C, $n = 1$ model).

The results indicate also that the ignition of LPG-air mixtures at normal pressure occurs faster than for the corresponding propane-air mixtures,^{17, 19} and n -butane-air mixtures.¹⁶ Measurable induction delays were obtained only for lower pressures. The results are given in Fig. 3.

Table 2

Activation energies (kJ/mol) from two models using total pressure/ignition temperature data

Model	% LPG				
	2.00	2.30	2.60	2.90	3.21
H-W-C ($n=1$)	35.7±4.0	34.5±6.5	40.3±1.8	35.8±12.4	36.2±6.8
S-H-W ($n=1$)	25.0±4.2	23.8±6.7	29.3±2.0	24.2±6.7	24.2±6.7
S-H-W ($n=2$)	60.6±8.2	58.3±13.2	69.5±3.8	60.0±24.8	60.4±13.5

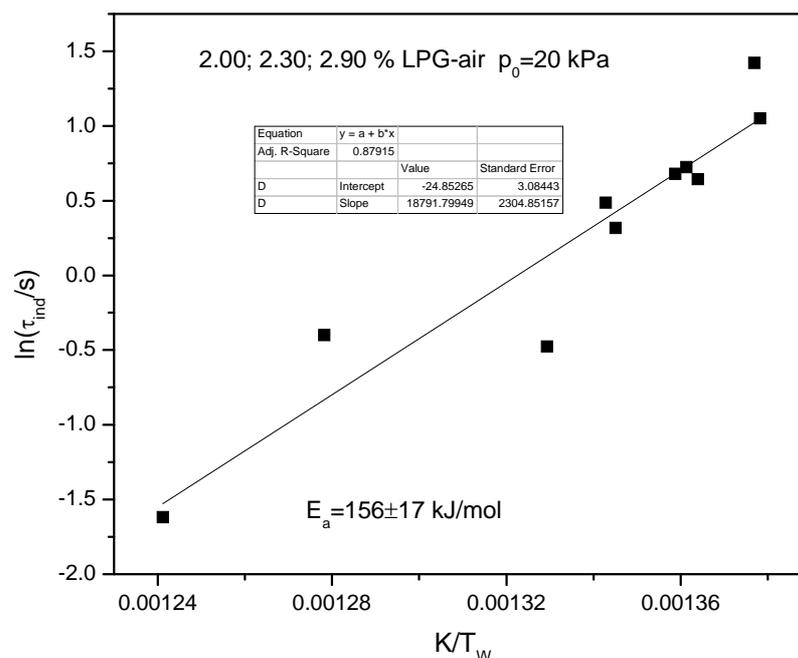


Fig. 3 – Ignition delays variation with catalyst temperature.

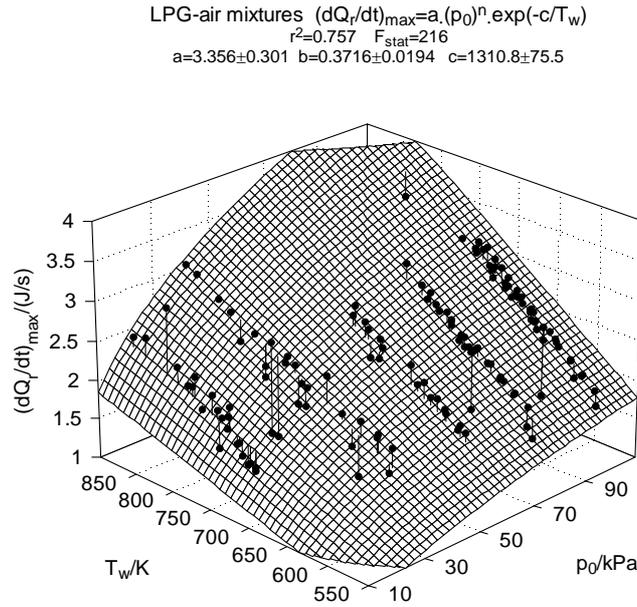


Fig. 4 – Nonlinear regression analysis for the maximum heat release rate.

The overall activation energy, evaluated from the empirical equation:^{16, 17, 19}

$$\tau_{\text{ind}} = a \cdot p_0^{-n} \cdot e^{+E_a/RT_w} \quad (5)$$

is higher than 91 to 100 kJ/mol for propane-air mixtures,^{17, 19} and than 93 to 110 kJ/mol for *n*-butane-air mixtures,¹⁶ showing a higher temperature sensitivity of the kinetically controlled ignition step for LPG-air mixtures.

The overall kinetic parameters of the maximum heat release rate, characterizing the steady flameless combustion, can be determined according to equation¹³ $dQ_r/dt = \Delta_c H_T^0 \cdot S \cdot r_R$ where $\Delta_c H_T^0$ is the heat of combustion, S the catalyst surface and r_R the catalytic reaction rate. Using a power law for r_R one obtains:

$$dQ_r/dt = k_0 \cdot p_0^n \cdot e^{-E_a/RT_w} \quad (6)$$

The nonlinear regression analysis of this equation on 141 experimental points is illustrated in Fig. 4.

The overall kinetic parameters $n = 0.372 \pm 0.019$ and $E_a = 10.89 \pm 0.63$ kJ/mol are characteristic for a diffusion controlled process and have practically the same values with those obtained for propane-air,¹⁷ *n*-butane-air,¹⁵ and *i*-butane-air mixtures.¹⁴ The steady flameless combustion of LPG-air mixtures has similar characteristics with those of its component-air mixtures.

EXPERIMENTAL

The diagrams giving the variation in time of the heat release rate, dQ_r/dt , were calculated according to a procedure described earlier.¹³⁻²⁰ A platinum wire from Aldrich (99.99 %), 45 mm long and 0.1 mm diameter, placed in the center of the test cell, is an arm of a Wheatstone bridge, fed from a specially designed power supply which ensures a quasi-rectangular jump of the wire temperature, followed by isothermal heating. The rise time of temperature jump is approximately 2 ms. The wire is connected in series with a standard resistor which allows the recording of the voltage drop across it. From the measured resistances R_w and R_{std} and the recorded voltage drops in air and in test fuel-air mixture, $(E_{\text{std}})_{\text{air}}$ and $(E_{\text{std}})_{\text{mixture}}$, the heat release rate can be calculated as:

$$dQ_r/dt = (R_w/R_{\text{std}}^2) \cdot [(E_{\text{std}}^2)_{\text{air}} - (E_{\text{std}}^2)_{\text{mixture}}] \quad (7)$$

The LPG-air mixtures were prepared from commercial blend containing 12 vol % propane, 87 vol % butane, and 1 vol % C5 fraction in stainless steel cylinders at a total pressure of 400 kPa by partial pressure method and used 24 h after mixing the components. For the mixtures containing 2.00, 2.30, 2.60, 2.90, and 3.21 % LPG in air, the equivalence ratios φ were 0.62, 0.71, 0.81, 0.90, and 1.00, calculated according to the fuel composition and the corresponding stoichiometric equations for complete combustion to CO_2 and H_2O . Before the combustion tests the platinum wire was activated by heating for at least five minutes at temperatures higher than 1000 K.

CONCLUSIONS

All studied LPG-air mixtures can be ignited on platinum wire within the temperature range 571 – 804 K for pressures from 20 to 101 kPa. The

critical ignition temperature increases with the fuel content, an opposite trend compared to single alkane-air mixtures. This behavior can be attributed to changes in the components adsorption on platinum surface which implies a complex competition between oxygen and alkanes. Except for lower pressures, the induction delays are much shorter (< 2 ms) as compared to single alkane-air mixtures. The steady flameless combustion is diffusion controlled with overall reaction order $n = 0.372 \pm 0.019$ and activation energy $E_a = 10.89 \pm 0.63$ kJ/mol, similar to those of component alkane-air mixtures.

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