

# ADDITIVE EFFECTS ON THE EXPLOSIVITY PARAMETERS OF GASEOUS MIXTURES

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The effect of additives on the explosivity parameters for ignition and propagation of gaseous deflagrations are reported and discussed. Being independent on a specific model of the combustion process, these parameters are very useful for a quick selection of the most adequate additive necessary to ensure safe operating conditions.

## Introduction

The influence of various additives acting as diluents, inhibitors, suppressants, or sensitizers on the explosivity parameters of gaseous mixtures is a subject of both theoretical and practical relevance. While the refined fundamental studies try to offer a rational explanation of the complex combustion phenomena at molecular level, at least for simplified limiting cases, the simpler technical tests represent the basic source necessary to establish the safety standards. The results reported up to now in the pertinent literature indicate that additives can operate either as inert diluents, decreasing the amount and the rate of the heat release, or as molecular modulators for the detailed chemistry of branched chain reactions [1-5]. The modulators can act either as inhibitors (and even as suppressants), representing potential sources of free radical scavenging agents, or as promoters having an accelerating effect through a fast decomposition with the formation of active radicals. While the dilution effect can be accounted for in terms of heat capacity and thermal conductivity changes, the inhibition and sensitization by small amounts of additives represent specific chemical effects, which appear to be effective especially during the initiation stages of an explosion. Specific effects have been reported for autoignition, deflagration, and detonation, showing the complexity of the implied mechanisms.

In the present paper some illustrative results are presented and discussed regarding the effects of additives on the explosivity parameters characterizing the gas-phase deflagrations.

## Experimental

All measurements were done using the equipment described in several previous papers [6÷17]. The minimum explosion pressures were measured in closed vessels using either inductive-capacitive sparks or isothermally heated filaments [6,7]. The ignition delay for initiation with inductive-capacitive sparks was evaluated from the pressure-time curves

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during the early stage of deflagrations in a closed vessel [14]. The quenching distances were measured using flanged electrodes and inductive-capacitive sparks [11,13]. The corresponding minimum ignition energies were calculated from the measured quenching distances according to a previously reported model [10]. The minimum ignition current was measured using a procedure proposed by the US Bureau of Mines [18]. The minimum temperature of ignition using a heated filament and the corresponding induction periods were measured using an electronically controlled system [16,17]. The propagation parameters (space velocities, normal burning velocities, the time necessary to reach the peak pressure, the peak pressure and the maximum rate of pressure rise) were calculated from the transient pressure-time records during the deflagration in a spherical cell with central ignition [8,9,12,15].

## Results and Discussion

The effect of additives on the laminar deflagration of a premixed explosive gaseous mixture can be analysed and discussed separately for ignition and for propagation.

### Ignition Parameters

The most relevant parameters characterising the ignition process are: the concentration explosion limits, minimum explosion pressure, ignition delay for capacitive-inductive spark ignition, quenching distance, minimum ignition energy, minimum ignition current for break sparks, minimum ignition temperature of a heated body, and induction period for ignition by a heated body.

The concentration explosion limits and minimum explosion pressures are strongly dependent on the presence of inert components [1,2]. However when  $N_2$  is substituted with  $CO_2$  in a stoichiometric  $C_3H_6$ -air mixture, the minimum explosion pressures seem to be practically independent of the inert nature as illustrated in Fig. 1 for a stoichiometric  $C_3H_6$ -air mixtures ignited by a heated platinum wire.

The ignition delay for inductive-capacitive sparks was observed and analysed for different  $C_3H_6$ -air mixtures at different initial pressures. The induction periods following the spark ignition were determined from the pressure-time curves for a stoichiometric  $C_3H_6$ -air mixture [14]. It was found that the presence of the end products (containing  $CO_2$ ) caused an increase of the induction period. The effect of increasing quantities of  $CO_2$  on the induction period of the same system is presented in Fig. 2. It can be seen that the induction period (ignition delay) increases up to an order of magnitude when the partial pressure of  $CO_2$  is 200 torr.

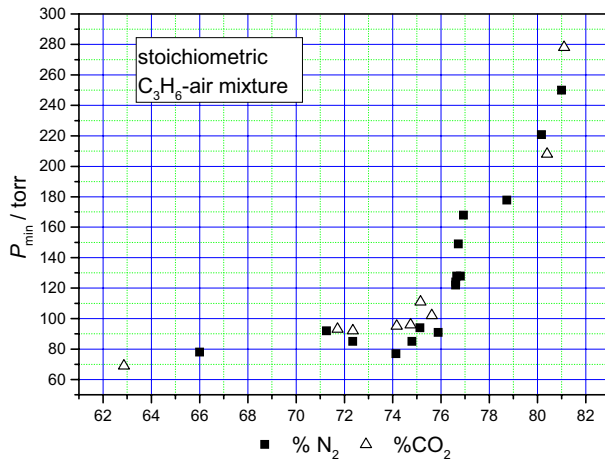


Fig. 1. Effect of N<sub>2</sub> and CO<sub>2</sub> on the minimum explosion pressure of a stoichiometric C<sub>3</sub>H<sub>6</sub>-air mixture.

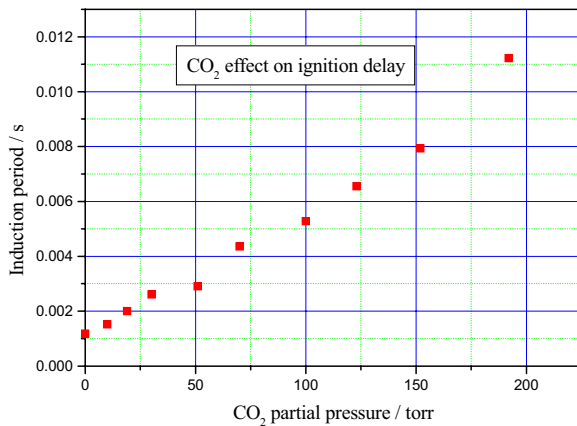


Fig. 2. The effect of CO<sub>2</sub> addition on the ignition periods for spark ignition of a stoichiometric propylene-air mixture.

The quenching distance,  $d_q$ , representing the minimum distance allowing the propagation of a deflagration, is a very sensitive parameter to the small changes of explosive mixture composition, including the presence of additives. An illustrative example is given in Fig. 3, for a stoichiometric propylene-oxygen mixture containing different amounts of nitrogen and argon. An increased quantity of argon, having a lower heat capacity and a lower thermal conductivity leads to an increase of the quenching distances, irrespective of the initial pressure of the mixture.

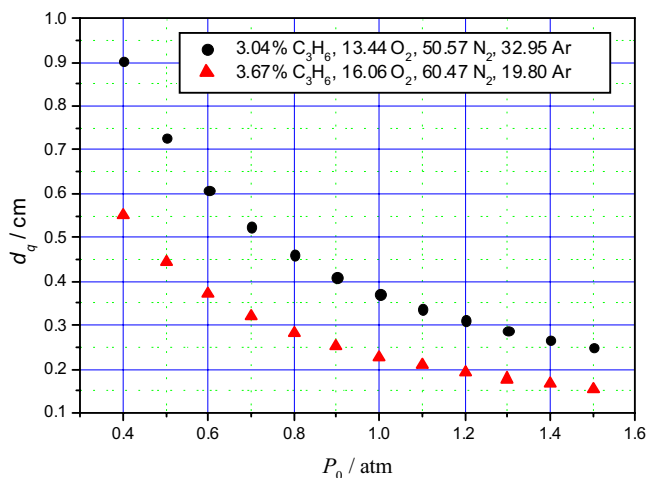


Fig. 3: The effect of inert gases on the quenching distance.

The minimum ignition energy exhibits the same trend like the quenching distance, as expected from the theoretical relationship proposed in a previous paper [10]:

$$H_{\min} = k \cdot P_i \cdot d_q^3 \quad (1)$$

where  $H_{\min}$  is the minimum ignition energy,  $P_i$  the initial pressure, and  $k$  a proportionality constant. This trend is shown in Fig. 4 for the same mixtures.

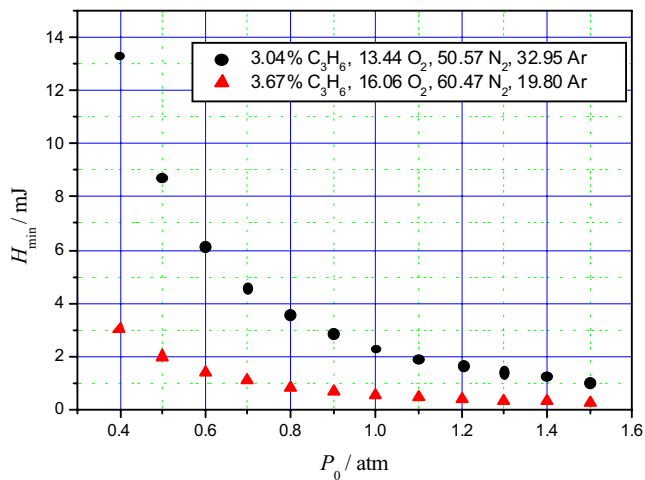


Fig. 4: The effect of inert gases on the minimum ignition energy.

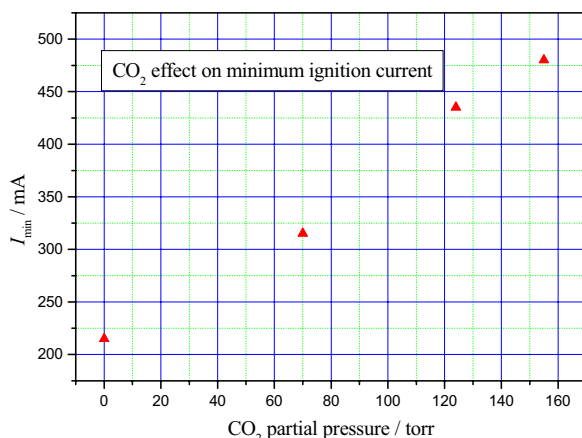


Fig. 5: The effect of CO<sub>2</sub> on the minimum ignition current for a stoichiometric propylene-air mixture.

The minimum ignition current characterises the ignition with a break spark produced when an electrical circuit containing an inductance is interrupted [18]. The minimum ignition current is a measure of the minimum ignition energy necessary in this case. When CO<sub>2</sub> is added to a propylene-air mixture, the minimum ignition current, and consequently the minimum ignition energy increases as shown in Fig. 5.

The minimum temperature of a heated body represents another ignition parameter sensitive to the mixture composition. Only few results regarding the effect of additives on the minimum ignition temperature have been reported in literature up to now. These results have been obtained in continuously flowing systems, when the filament temperature has been increased until the mixture has been ignited. Recently we have reported a new method devised to obtain the minimum ignition temperature by a sudden jump (< 2ms) of filament temperature, followed by an isothermal heating [16,17]. The preliminary results indicate a significant change of the minimum ignition temperature when nitrogen from air is partially substituted with argon (Table 1). The induction periods for a heated body can be measured with the same technique and are also very sensitive to the changes in composition of the explosive mixture, as can be seen in Table 1.

**Table 1**

Effect of Ar on the minimum ignition temperature of a platinum filament				
%Ar	%N <sub>2</sub>	<i>P</i> (torr)	<i>T</i> (°C)	
-	76	760	860	
16	60	760	680	
Effect of Ar on the ignition period				
%Ar	%N <sub>2</sub>	<i>T</i> (°C)	<i>P</i> (torr)	<i>τ</i> (ms)
-	76	960	406	1600
16	60	960	402	1.6

### Propagation Parameters

The pressure-time curves recorded in cylindrical or spherical vessels with central ignition can be used to characterize the effect of different variables on the propagation of laminar deflagrations. This can be done either by using the whole curve to calculate, according to some model, the space velocities,  $V_s$  and the normal burning velocities,  $S_u$ , or by using several characteristic points like the maximum pressure rise,  $P_{\max}$ , the corresponding maximum time,  $t_{\max}$ , and the maximum rate of pressure rise,  $(dP/dt)_{\max}$  [8,9,12,15].

The existing models reported in literature, recently improved by extending their validity range, were used to calculate the normal burning velocities for propylene-air mixtures with various amounts of inert additives. A comparison of the normal burning velocities, when nitrogen or carbon dioxide were added to the mixture, is shown in Fig. 6, indicating the higher efficiency of  $\text{CO}_2$  as flame retardant.

A more accessible parameter measuring the propagation rate in a closed vessel is the time necessary to attain the maximum pressure,  $t_{\max}$ . This overall parameter can be obtained much easier, directly from the pressure-time curve, being independent on a particular model of the combustion process. Moreover, it is very important for the design of the safety devices used for venting of large vessels containing explosive mixtures. It exhibits a monotonous increase with the inert content added to a stoichiometric propylene-air mixture.

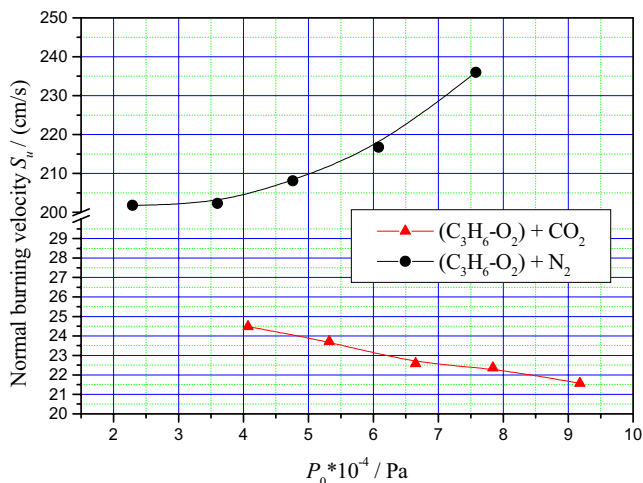


Fig. 6: Efficiency of  $\text{N}_2$  and  $\text{CO}_2$  as flame-retardants.

The maximum pressure rise,  $P_{\max}$ , is also an overall parameter measuring the available energy of the system, which can be given off as a result of the explosive combustion. Its physical significance was found from the modelling of the linear correlation between  $P_{\max}$  and  $P_0$ :

$$P_{\max} = a \cdot P_0 - b \quad (2)$$

where:

$$\underline{a} = \xi + \left( \frac{r_1}{\nu_1} \right) \cdot \frac{\Delta_c H_{298}^0}{C_e \cdot T_0} \quad (3)$$

with  $\xi$  - the ratio between the mole numbers of burnt and unburnt gases,  $r_1$  - the mole fraction of fuel in the mixture,  $\nu_1$  - its stoichiometric coefficient in the overall combustion reaction,  $\Delta_c H_{298}^0$  - the standard enthalpy of combustion,  $C_e$  - the average constant volume heat capacity of burnt gases, and  $T_0$  - the initial temperature of the mixture.

the inert gases are  $N_2$  and  $CO_2$  is shown in Fig. 7. The slope  $\underline{a}$  in equations (2) and (3) is given in Fig. 7 for increasing quantities of inert gases. To find out if the differences originate only in the heat capacities differences of the two inerts or can also reflect a possible dissociation of  $CO_2$ , the average heat capacities of burnt gases were calculated and the slopes  $\underline{a}$  were plotted against  $\left( 100 \cdot \frac{r_1}{\nu_1} \cdot \frac{1}{C_e} \right)$ . The results indicate that the significant factor responsible for the decrease of the maximum pressure when an inert gas is added is the heat capacity.

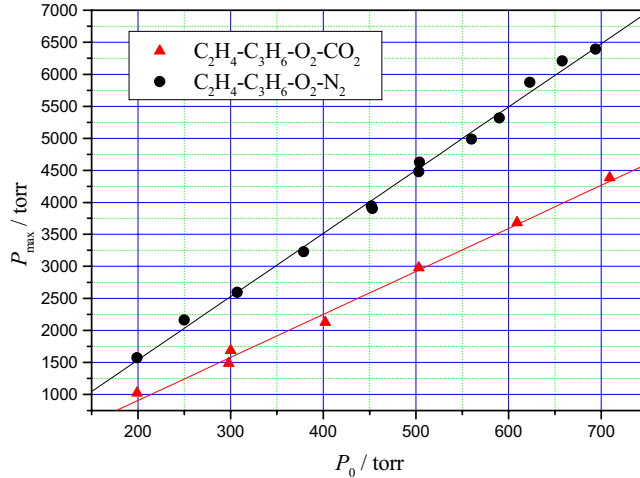


Fig. 7: Effect of  $CO_2$  and  $N_2$  on  $P_{max}$  for ethylene-propylene-air mixtures.

The rate of pressure rise,  $\left( \frac{dP}{dt} \right)$ , characterizes the dynamics of pressure evolution during an explosive combustion in closed vessels or confined areas. It represents an overall parameter summing up several properties like the flame speed, burning velocity, rate of energy release, and it is used to calculate a valuable characteristic called the severity factor:

$$K_G = \sqrt[3]{V} \cdot \left( \frac{dP}{dt} \right)_{max} \quad (4)$$

where  $V$  is the volume of the closed vessel and  $\left(\frac{dP}{dt}\right)_{\max}$  is the maximum rate of pressure rise. The severity factor is an important parameter for the design of a vessel exposed to an incidental explosion.

For a stagnant explosive mixture  $\left(\frac{dP}{dt}\right)_{\max}$  is dependent on the initial state of the system (pressure, temperature, composition), vessel volume and symmetry, and the location of the ignition source.

The presence of diluents decreases the severity factor according to their efficiencies, for a propylene-air mixture. For the same additive concentration,  $\text{CO}_2$  is more efficient as compared to  $\text{N}_2$ .

## Conclusions

The effects of additives and their relative efficiencies on the explosive combustion of gaseous mixtures can be established either by measuring several overall parameters characterising the ignition and propagation, or by a detailed modelling of these stages.

The first choice is simpler, independent on a specific model, and allows a rapid selection of the most adequate additive necessary to ensure safe operating condition, while the second one offers a deeper insight into the complex combustion mechanism, having a more predictive power.

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