

## QUENCHING DISTANCES OF STOICHIOMETRIC ETHYLENE-AIR MIXTURE WITH CO<sub>2</sub> ADDITION

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**abstract:** The effect of CO<sub>2</sub> addition between 4 and 16 vol.% on the ethylene-air mixture of stoichiometric composition has been studied over atmospheric and below atmospheric initial pressures. It was observed that CO<sub>2</sub> addition is more effective when initial pressure decreases, 16% CO<sub>2</sub> addition resulting in an increase of the quenching distance from 4.81 mm to 10.0 mm, at 21.3 kPa initial pressure. The apparent activation energy has been also evaluated and differences between CO<sub>2</sub>-added and CO<sub>2</sub>-free mixtures have been obtained and discussed.

**key words:** ethylene-air, quenching distance, flanged electrodes, CO<sub>2</sub> effect.

### Introduction

The effect of additives – diluents, inhibitors, and suppressants, respectively – on the ignition and propagation parameters of gaseous explosive mixtures has been previously explored [1]. It was found that the efficiency of the additives can be evaluated by measuring the overall parameters characterising the ignition and propagation; the method is simple and independent on a specific combustion model, and allows a rapid selection of the most adequate additive necessary to ensure safe operating condition.

Following these previous findings, the present study deals with the effect of carbon dioxide on quenching distance of stoichiometric ethylene-air.

### Experimental

The quenching distances have been measured using the flanged electrode technique similar to that first used by Lewis and von Elbe [2]; the experimental stand consists of two parts: the mixture preparation/admission/evacuation equipment and the test cell. Pressure has been monitored by digital gauges supplied by Cole Parmer; a custom made U-shaped Hg column has been used for calibration of digital gauges. Test cell [3], made of stainless steel, is equipped with a spark generator and a pressure transducer manufactured by Kistler; its signal is acquired by a Tektronics oscilloscope and a data acquisition card – PC Labcard PCL-818L. The ignition system is formed by two electrodes provided with 2.00 cm

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diameter flanges made of insulating material; the working electrode, is fitted with a vernier screw to allow variation of the spark gap.

In order to assess the effect of CO<sub>2</sub> addition to the flammability of stoichiometric ethylene/air mixture (stoichiometric concentration 6.54%), several mixtures with CO<sub>2</sub> concentration varying from 4% to 16% have been tested. CO<sub>2</sub> (99%) has been purchased from Linde Gas.

In all quenching distance measurements the initial pressure of the mixtures has been varied from 101.3 kPa to 21.3 kPa; the initial temperature is room temperature, 298 K.

## Results and Discussion

Table 1 shows the experimental quenching distances of stoichiometric ethylene/air mixture alone and with CO<sub>2</sub> addition ranging from 4% to 16%, at atmospheric and sub-atmospheric initial pressures and initial room temperature.

**Table 1: Quenching distances of stoichiometric ethylene/air mixtures with various CO<sub>2</sub>-added concentrations.**

initial pressure (kPa) \ quenching distance (mm)	CO <sub>2</sub> concentration (%)				
	0	4	8	12	16
101.3	1.13	1.25	1.47	1.74	2.11
81.3	1.37	1.63	1.78	2.07	2.50
71.3	1.55	1.79	2.02	2.29	2.75
61.3	1.77	2.09	2.34	2.64	3.24
51.3	2.06	2.44	2.71	3.10	4.51
41.3	2.47	3.07	3.38	4.95	5.50
31.3	3.32	3.99	5.11	6.61	7.80
21.3	4.81	6.48	7.48	8.69	10.00

One can observe that the increase in CO<sub>2</sub> concentration will result in an increase in the quenching distance. The effect is the same for all initial pressures taken into consideration. Moreover, at very low initial pressures, i.e. 21.3 kPa, 16% CO<sub>2</sub> addition to the stoichiometric ethylene/air mixture gives 10 mm for the value of the quenching distance: it almost reaches the fail-to-ignite domain.

It is worth mentioning that the effect of CO<sub>2</sub> addition on the initial pressure dependence of the quenching distance can be also assessed by observing the change in the slope of its

linearized dependence,  $\lg(d_q) = f(\lg(p_0))$ , whose physical significance is related to the overall reaction order:

$$m = 1 + \alpha - n \quad (1)$$

where,  $n$  is the overall reaction order,  $m$  is the baric exponent of the quenching distance, and  $\alpha$  represents the baric exponent of the normal burning velocity. Thus the overall reaction order can be evaluated according to [4] and the cited references therein:

$$n = 1 + \alpha - m \cong -2 \cdot m \quad (2)$$

Table 2 presents the results of the regression analysis with a straight line model applied to the linearized dependence of the quenching distance on initial pressure. Also, the last column of the table shows the calculated overall reaction orders calculated according to (2).

**Table 2. Results of the least squares regression analysis type  $Y = a + b \times X$  on the linearized dependence of the quenching distance on initial pressure,  $\lg(d_q) = f(\lg(p_0))$ , for stoichiometric ethylene-air mixture with various CO<sub>2</sub>-added concentrations**

CO <sub>2</sub> conc., %	regression parameters		correlation coef., $r$	SD*	Reaction order, $n$
	$a$	$b$			
0	1.90±0.02	-0.93±0.01	-0.9994	0.0080	1.85
4	2.15±0.04	-1.02±0.03	-0.9982	0.0150	2.04
8	2.27±0.06	-1.06±0.04	-0.9966	0.0212	2.11
12	2.45±0.12	-1.12±0.07	-0.9893	0.0401	2.23
16	2.46±0.09	-1.08±0.05	-0.9928	0.0316	2.15

\* - standard deviation

One can see a significant increase of the overall reaction order from 1.85 (0% CO<sub>2</sub>) to 2.23 (12% CO<sub>2</sub>), which is relevant as the effect of CO<sub>2</sub> to the overall process of combustion for stoichiometric ethylene/air mixture, and also can give information about a significant increase in contribution of the third body molecular collisions to the overall reaction mechanism.

Another important parameter from the kinetics point of view is the overall activation energy. One can express the Arrhenius type dependence of the quenching distance on the adiabatic flame temperature as in [3]:

$$d_q \cong f(T_f) \cdot e^{\frac{E_a}{2RT_f}} \quad (3)$$

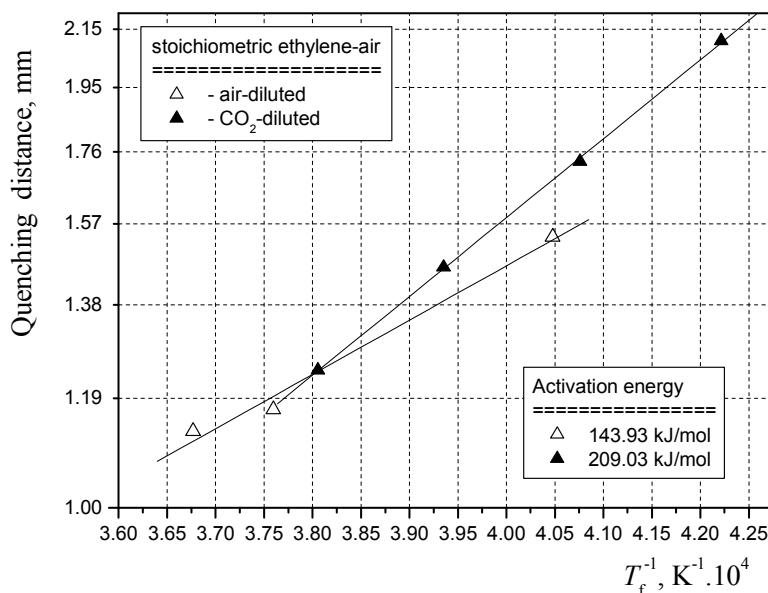
where  $E_a$  is the overall activation energy, in  $\text{J} \times \text{mol}^{-1}$ ,  $R$  is the gas law constant, in  $\text{J} \times \text{mol}^{-1} \times \text{K}^{-1}$ ,  $T_f$  is the adiabatic flame temperature, in K, and  $f(T_f)$  is an intricate function of  $T_f$ . One has to mention that the exponential expression is much more sensitive to small variations of the flame temperature than the pre-exponential function. The semi-logarithmic

dependence,  $\ln d_q = f(T_f^{-1})$ , at constant initial pressure, will give the evaluation of the activation energy of the overall combustion process.

One convenient method to obtain a flame temperature variation in the range between lean and stoichiometric fuel/air mixtures is based on the dilution with inert [5] or with air [6].

Fig. 1 shows the semi-logarithmic dependency of the quenching distance on adiabatic flame temperature, for stoichiometric ethylene/air mixture with “air” and CO<sub>2</sub> dilution. The adiabatic flame temperatures have been calculated from the thermodynamic properties of each mixture [7].

One can see that there is approximately 50 kJ difference in favour of the activation energy for CO<sub>2</sub>-diluted mixture. As compared to our previous findings, regarding the activation energy for stoichiometric propane/air [6], one can say that CO<sub>2</sub> addition is more effective in case of ethylene, at least for the initiation stage (whose characteristic is the quenching distance). Moreover, in a recent study [8], we reported 526 kJ×mol<sup>-1</sup> for the activation energy of the propagation stage (whose characteristic is the normal burning velocity) in stoichiometric ethylene/air.



**Fig. 1:** CO<sub>2</sub> effect on activation energy for ignition of stoichiometric ethylene/air mixture; semi-logarithmic scale.

This is a strong evidence of the inhibiting effect that CO<sub>2</sub> has on flammability of gaseous hydrocarbon/air mixtures, especially as propagation-proof additive. Also by comparing the CO<sub>2</sub>-effect to propane and to ethylene, respectively, one assumes that the higher the reactivity of the fuel the greater the inhibiting effect of CO<sub>2</sub> is, having as reference the characteristic values for stoichiometric mixtures.

## Conclusions

Quenching behaviour of stoichiometric ethylene-air mixture in presence of CO<sub>2</sub> has been investigated by measuring quenching distance at different initial pressures. It has been found that the increase of CO<sub>2</sub> concentration will increase the quenching distance; the effect is more significant at very low initial pressures, a 16% concentration of CO<sub>2</sub> added to the stoichiometric ethylene/air mixture gives 10 mm quenching distance at 21.3 kPa, which is very close to the non-ignition domain.

By observing the increase of the overall reaction order from 1.85 to 2.23 as an effect of CO<sub>2</sub> addition, it has been assumed that the third body molecular collisions is more and more significant to the overall reaction mechanism.

The evaluation of the overall activation energy allowed ones to find similar effect that CO<sub>2</sub> has to ethylene as to propane, with different magnitudes to the initiation and to the propagation process, respectively. It has been further assumed that CO<sub>2</sub> effect is higher if the reactivity of the fuel is higher.

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