

## THE INFLUENCE OF DIFFERENT DILUENTS ON THE FLAMMABILITY LIMITS OF ETHYLENE AT HIGH TEMPERATURES AND PRESSURES

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### Summary

For the safe design and operation of many chemical processes, it is necessary to know certain flammability limits at high temperatures and pressures. Despite the great importance of such safety problems, few data are available in the literature, and those available are unreliable. This is due to the experimental difficulties involved.

In this paper the different methods proposed for such measurements are critically discussed: the double-filling system appears to be the most suitable for avoiding the slow oxidation reactions before ignition. Flammability data up to 250°C and 20 atm for ethylene-oxygen mixtures with different diluents (nitrogen, carbon dioxide, methane) are presented.

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### Introduction

Recently a number of chemical processes have been developed for the direct oxidation of ethylene to ethylene oxide, acetaldehyde etc.

In the production of ethylene oxide a reactor may be fed with air diluted with nitrogen, or with oxygen diluted with carbon dioxide and/or hydrocarbons such as methane and ethane [1]. The layouts of the two processes are different mainly because in the plants using pure oxygen the recycling of unconverted ethylene is easily accomplished, while in the plants using air a second reactor must be used to convert the ethylene present in the large purge stream necessary to avoid the build-up of nitrogen concentration.

In both plants the ethylene oxidation is carried out over silver catalysts at a temperature of about 250°C and at a pressure up to 20 atm. It is then very important to control the oxygen concentration in the reacting mixture to avoid self-ignition phenomena and flame propagation from accidental ignition sources.

The knowledge of the upper flammability limits under the prevailing conditions of composition, temperature and pressure could be valuable in judging safe operation conditions in these processes.

Despite the relevance of such limits, few and unreliable data are available in the literature, mostly because of the experimental difficulties involved in

their measurement [2]. In particular, nearly all the available data refer to the ethylene-oxygen-nitrogen system, while no investigations have been made on the effect of diluents other than nitrogen.

In this paper, the techniques for the measurement of flammability limits at high pressure and temperature are discussed with the aim of selecting the most suitable one. Some results for these upper limits, obtained by the double-filling technique, are reported for mixtures of ethylene-oxygen with nitrogen, carbon dioxide and methane as diluents. The diluent effect is studied at 20 atm and 250°C with ethylene percentage ranging up to 20% and with a constant argon: oxygen ratio (1:1), because these are the conditions prevailing in many industrial processes.

### Experimental technique

In the determination of flammability limits at high pressure and/or temperature, many experimental problems arise. Experimental apparatus of different kind and size, and different techniques are used, often producing conflicting results, which show an anomalous dependence on pressure for many mixtures [2].

The high values of the pressure suggest the use of closed vessels for the measurements of these limits. In such apparatus various phenomena affect the experimental data: pressure and temperature of unburned gases increase so that the flame may vibrate and change its structure. The convective rise of the hot gases enhances the flame failure dependence on fluid dynamics [2-5]. Furthermore, the igniter characteristics (type, energy, position, etc.) have an influence on the flame kernel properties and then on its failure mechanism [6]. Moreover, only relatively small vessels can be used at higher pressures so that wall quenching also must be taken into account in explaining the spread of the results [2].

The occurrence of pre-flame reactions [2, 7] must be taken into account when the measurements are made both at high pressure and at high temperature. These reactions give random changes of the mixture composition before ignition and probably cause the differences in the data by Craven and Foster [8] and those by Brinkley and Van Dolah [9] for the upper limit values for the ethylene-air system at 300°C. The preoxidation and the wall quenching effects are not independent because the oxidation reactions may be inhibited by wall effects [7].

The above-mentioned problems must be taken into account when selecting the measurement technique for flammability limits at high pressure and temperature. The techniques used in the previous studies can be classified as follows:

(A) The mixture to be tested is prepared in a continuous flow vessel; the temperature can be raised to the final values either before [10] or after [11] the complete mixing of the reactants.

(B) The gases are mixed and heated directly in the explosion vessel; devices to speed up the mixing may [8, 12] or may not [9, 13] be used.

(C) The gases are well mixed in a separate closed vessel at ambient temperature and then fed to the explosion vessel at the test temperature [7, 14].

The first method gives rise to some problems for the preparation of the mixtures, in particular if many components are present. The consumption of reactants is very high and it is difficult to make many tests on the same mixture.

The second method removes the first two drawbacks but the preoxidation effects may be important because high residence times at high temperature are necessary.

The third method, which shortens the residence time at high temperature, appears to be the best one. Furthermore, it allows many runs to be carried out with the same mixture if the auxiliary vessel has sufficient volume and pressure, so that the reliability of the data can be tested. However, the smaller the vessel volume the better, provided wall quenching effects are not too prominent, in order to be effective in avoiding pre-oxidation effects. If a cylinder is used, the length of the vessel must not exceed a few diameters, to avoid the important fluid dynamic influence on the flame propagation [3]. Vessels of diameter between 4 and 15 cm and 10–30 cm long are sufficient in most cases, as also appears from the quenching diameter data [15]; the smallest vessels can be used at the higher pressures (above 10–15 atm) as the quenching diameter is inversely proportional to the pressure.

When considering the igniter energy, it must be taken into account that the smaller the diameter of the explosion vessel, the smaller the required ignition energy. The igniter could, in fact, notably change the temperature in the vessel and generate large flame kernels: in such a case an ignition phenomena could be mistaken for the flame propagation. For the smallest vessels (4–5 cm internal diameter), when using spark ignition, the electrode distance must not exceed 2 mm, while an igniter energy between 0.1 and 1 J should be used.

The flammability limits, as defined by Coward and Jones [16], should be independent of the power of the ignition source. Actually the flammability limits, unlike the adiabatic burning velocity, are not fundamental physico-chemical properties so that the ignition energy and many of the geometrical and fluid dynamic parameters can influence the results. However, the flammability limits are of value as guidelines for attaining safety conditions, providing that care is taken in evaluating the experimental technique used in their measurement. To ensure safe operation other parameters, such as burning velocity, should be known so that the explosion hazard may be evaluated and the relief devices to control the pressure rise can be designed [17, 18].

## Previous results

Flammability limits at high pressure and/or temperature for ethylene-containing mixtures are available for the ethylene-oxygen-nitrogen system. As different diluents are concerned, only some data up to 16 atm are reported for carbon dioxide [16].

Coward and Jones [16] and Miller [1] report the measurements published before 1966 and obtained using different techniques. For the sake of completeness, the more recent investigations are summarized in Tables 1 and 2. The different techniques used are compared in Table 1 while the temperature and pressure ranges investigated are reported in Table 2.

TABLE I

Different techniques used in flammability limit measurements

Authors	Ref.	Year	Explosion vessel*	Tech.	Igniter
De Soete	7	1975	Cylinder, ID=32, L = 90 mm	C	Spark, 25 J
Hofmann and Kappler	10	1975	Cylinder, ID=64, L = 1000 mm	A <sub>1</sub>	Spark, 20 J
Fiumara and Cardillo	11	1975	Cylinder, ID=70, L = 1500 mm	A <sub>2</sub>	Hot wire
Craven and Foster	8	1966	Sphere, ID=179 mm	B <sub>1</sub>	Exploding wire
Hashiguchi et al.	12	1966	Cylinder, ID=100, L = 1500 mm	B <sub>1</sub>	Exploding wire
Brinkley and Van Dolah	9	1962		B <sub>2</sub>	
Grewer and Lamprecht	13	1970	Cylinder, ID=100, L = 300 mm	B <sub>2</sub>	Exploding wire
Gaube et al.	14	1968	Cylinder, ID=60	C	Exploding wire

\*ID = internal diameter. L = length.

TABLE 2

Flammability data available for the ethylene/oxygen/nitrogen system (Numbers given are references, this paper)

Pressure (atm.)	1	3	5	7	9	10	15	26	30	50
Temp. (°C)										
20	8,10,11 12,14	8	11,12		8	11,12	11		11,12	12
50								14		
100			11	14		11				
200	10		11	14		11		14		
250	8	8	11		8					

Some of the authors listed in Table 1 discuss the effect of the pre-oxidation reactions on the flammability data. Pre-flame reactions were observed for temperatures higher than  $200^{\circ}\text{C}$  and pressures higher than 5 atm: at  $250^{\circ}\text{C}$  and 10 atm the autoignition phenomena prevented any measurement being carried out with the flow apparatus technique [11]. Craven and Foster did not observe pre-flame reaction up to  $250^{\circ}\text{C}$  and 9 atm with residence times in the explosion vessel lower than 2 min [8]. Gaube et al. [14] report fast pre-flame reactions at 26 atm and  $300^{\circ}\text{C}$ .

In conclusion, the available data suggest the relevance of pre-flame phenomena in ethylene-oxygen systems at pressures higher than 5 atm and temperature higher than  $200^{\circ}\text{C}$ .

### Experimental apparatus and procedure

The flammability limits reported here were measured with technique C by using a large auxiliary vessel at high pressure and room temperature to prepare the mixture to be tested.

Fig. 1 shows a schematical view of the apparatus. All the pressurized equip-

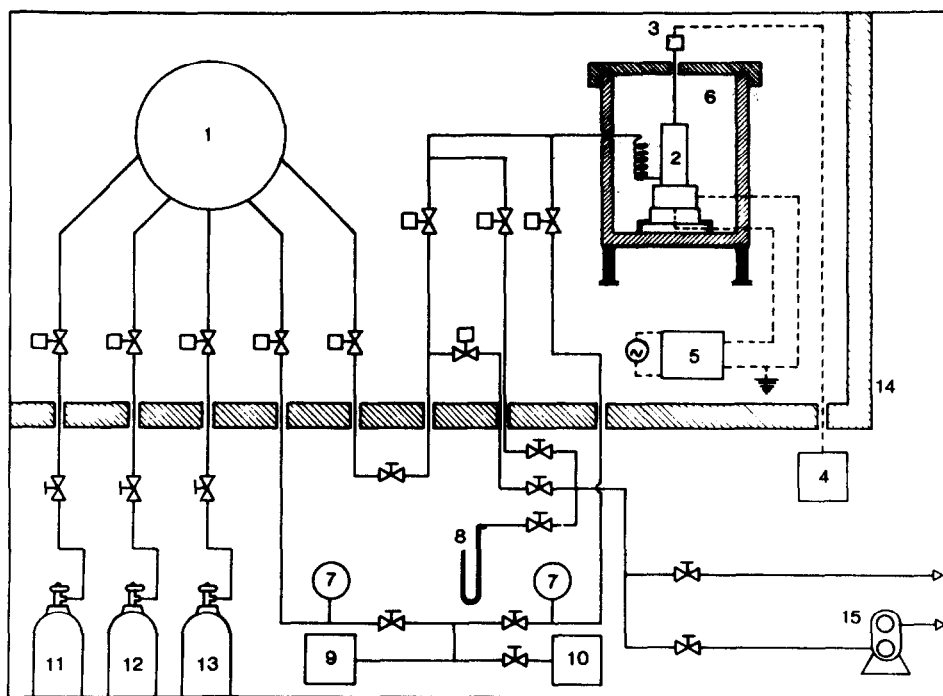


Fig. 1. Experimental apparatus. 1, Auxiliary vessel; 2, Test vessel; 3, Pressure transducer; 4, Recorder; 5, Igniter; 6, Furnace; 7-8, Manometers; 9, Oxygen analyzer; 10, Gas chromatograph; 11, Ethylene supply; 12, Oxygen-argon supply; 13, Diluent supply; 14, Safety wall; 15, Vacuum pump.

ment and the apparatus containing flammable mixtures are placed inside a blast cubicle, while the control and measurement devices are in the adjacent laboratory.

The explosion vessel is a cylinder of internal diameter 45 mm, 145 mm long, located in an electrically heated furnace. Hot air circulation gives uniform temperature in the vessel as tested by thermocouple measurement.

The mixture is prepared by the partial pressure method and stored in an auxiliary vessel, whose volume is about 13 l. In this vessel, the mixture is homogenized by a magnetic-coupled turbine impeller.

The composition of the mixture is determined exactly by using a paramagnetic oxygen analyzer (Taylor Servomex OA 137) and a gas-chromatograph (Carlo Erba Fractovap model C).

The auxiliary vessel, filled at 40 atm, is sufficiently large to allow many runs on the same mixture.

After the analysis, the mixture is fed through a coil into the explosion vessel previously evacuated by a vacuum pump; in such a way the temperature is rapidly raised to the desired value.

A spark plug is fixed at the bottom of the explosion vessel, so that the more conservative upward limits are determined. Sparks of 0.1 Joules can be produced by an inductive-capacitive power supply, which gives a voltage of up to about 40 kV, sufficient to generate the spark between two tungsten electrodes whose tips are 2 mm apart.

A DISA pressure measurement system, which includes the 51E01 reactance converter, the 51E02 oscillator and the 51F10 pressure transducer is used to follow the pressure pattern during the flame propagation.

For each mixture tested, three or more experiments were made for the case of non propagation: afterwards other reactants were fed into the auxiliary vessel to restore the pressure to 40 atm and to obtain a more reactive mixture for further tests.

Soot produced during flame propagation in rich mixtures can alter the result of successive experimental runs giving rise to sooty gaseous mixtures in the filling procedures and changing the characteristics of the ignition spark: it was therefore necessary to clean up the test vessel after each run had been carried out with a flammable mixture.

## Results and discussion

Preliminary experiments have been carried out to ensure that the technique used is not affected by pre-oxidation reactions, whose relevance have been discussed previously.

Fig. 2 shows the results of one such run, at 20 atm and 275°C. The initial mixture contains ethylene (17%), oxygen (16.1%), and nitrogen. Only for residence times longer than 10 min does the oxygen percentage show a detectable decrease. As the flammability test may be carried out at high temperature with residence times lower than 30 s, the reported data are free from pre-flame reaction effects.

The results of the experiments carried out at 250°C and 20 atm with different diluents are reported in Fig. 3, in which open symbols refer to mixtures which gave no detectable pressure rise. It appears that methane is the most efficient diluent and that carbon dioxide is more efficient than nitrogen. The different extinction powers of carbon dioxide and nitrogen may be attributed to their different heat capacities. On the contrary the great efficiency of methane cannot be explained by thermal arguments alone and its chemical reactivity must be taken into account.

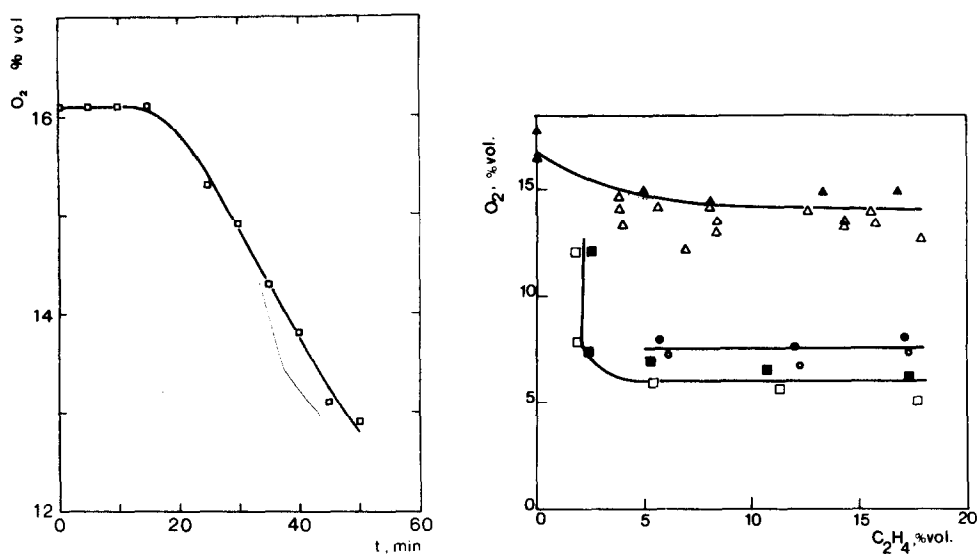


Fig. 2. Self ignition experiment: oxygen percentage decay as a function of residence time (initial conditions:  $T = 275^{\circ}\text{C}$ ,  $p = 20$  atm., ethylene = 17 vol %,  $\text{N}_2 = 50.8$  vol %).

Fig. 3. Limit oxygen percentage as a function of ethylene percentage at 250°C and 20 atm, for different diluents; oxygen-argon ratio 1:1 ( $\Delta$  = methane,  $\circ$  = carbon dioxide,  $\square$  = nitrogen).

Whatever diluent is used, the limit oxygen concentration is almost independent of the ethylene percentage in the range 5–20 vol %; for lower ethylene contents the carbon dioxide and nitrogen curves show a lower limit behaviour, while the methane curve ends with the methane-oxygen-argon upper limit.

The data for nitrogen are in good agreement with those by Gaube et al. [14], taking into account some minor differences in the experimental conditions; no comparison is available for the other two diluents.

Fig. 4 shows the temperature dependence of the upper flammability limit of ethylene in oxygen-argon mixtures at 10 atm.

Fig. 5 shows the upper flammability limit of ethylene in oxygen-argon mixtures as a function of the pressure at 250°C. The limit ethylene percentage

increases when increasing the pressure, with an asymptotic behaviour for pressures higher than about 10 atm.

Hashiguchi et al. [12] have determined the effect of the pressure on the upper flammability limit of ethylene in oxygen-nitrogen (1:1) mixtures at room temperature. Due to the different experimental conditions, their limit ethylene concentrations are not directly comparable with those presented here: however, they show an asymptotic pattern in the same pressure range.

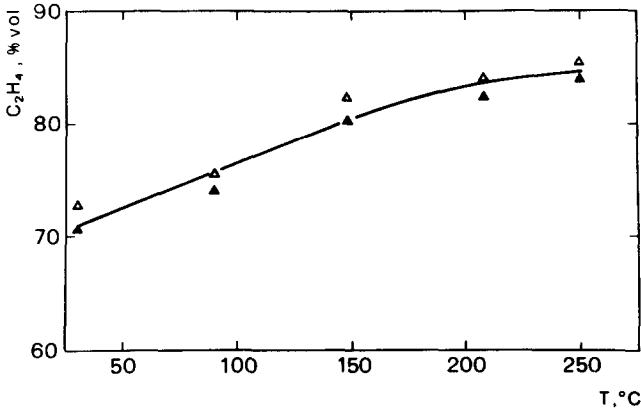


Fig. 4. Limit ethylene percentage as a function of temperature for ethylene-oxygen-argon mixtures at 10 atm; oxygen:argon ratio 1:1.

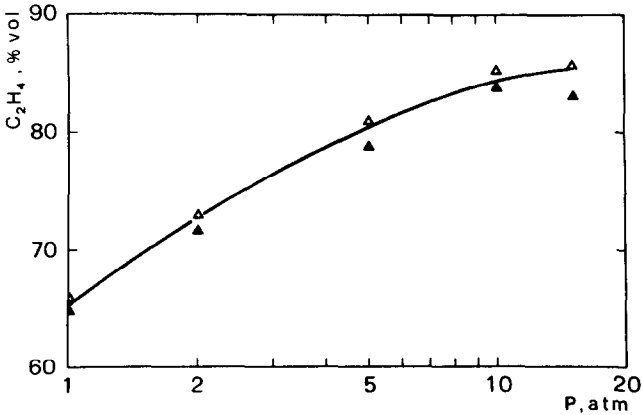


Fig. 5. Limit ethylene percentage as a function of pressure for ethylene-oxygen-argon mixtures at 250°C; oxygen:argon ratio 1:1.



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