Experimental study of CH4/O2/CO2 mixtures flammability

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Abstract

The oxy-combustion process uses $CH_4/O_2/CO_2/H_2O$ mixtures at various concentrations, according to the different operation phases. To analyze the risks associated to this process, the safety characteristics of these explosive mixtures have to be taken into account. A literature review showed that some safety features of methane in oxygen or in air were not available. Thus, the flammability ternary diagram of $CH_4/O_2/CO_2$ mixtures was determined at room temperature and 1 bar pressure. Furthermore, the influence of oxygen content on the explosion severity (Pmax; dP/dt) was investigated.

The ternary mixtures were prepared directly in a 20 L spherical test vessel. The concentrations of reactants were adjusted using the relationship between the partial pressure and the molar fraction of gas. The ignition source used was an alumel fusing wire.

The flammability limits of methane in oxygen were extrapolated at 5 and 68% vol., by using the established $CH_4/O_2/CO_2$ mixtures ternary diagram. It also confirmed that when the carbon dioxide concentration increases, the flammability range decreases: no ignition was observed when carbon dioxide content exceeded 73%.

A significant influence of the oxygen concentration on the explosion severity has been highlighted for $CH_4/O_2/CO_2$ mixtures containing respectively 10, 25, 45 and 65% vol. of carbon dioxide. The maximal explosion overpressure and the maximum pressure rise were both measured near the stœchiometry. Maximum values of Pmax and dP/dt measured for a 10% vol. carbon dioxide concentration were 11.2 bar rel. and 5904 bar/s respectively, while they were 3.6 bar rel. and 72 bar/s respectively in the case of a 65% vol. carbon dioxide content in the mixture.

1. Introduction

This study is part of a whole study intended to highlight the technological constraints and risks associated with the oxy-combustion process, to prevent incidents and accidents that could affect its technological development.
This process uses $CH_4/O_2/CO_2$ mixtures for varying concentrations, depending on different operation phases.
This paper aims to establish the explosion characteristics of these mixtures, since only a part of them are available in the literature [1] to [4]. In this study, the flammability diagram of $CH_4/O_2/CO_2$ mixtures is determined at room temperature and 1 bar pressure, in a 20 L spherical vessel. Furthermore, the influence of oxygen concentration on explosion characteristics Pmax and (dP/dt) is investigated.

2. Experimental

The ternary mixture is prepared directly into the test vessel. Its composition is calculated and measured by the relationship between partial pressure and molar fraction of gas. Indeed, the mole fraction of each component can be determined by measuring the pressure in the vessel after each addition of gas. Firstly, a partial vacuum below 40 mbar is obtained in the vessel, then CO_2, CH_4 and O_2 are successively added, up to 1 bar absolute. Before each test, the circuit and the chamber are purged with air. In addition, a control for absence of leakage is made once the partial vacuum is established in the vessel.
The test vessel used is a 20 L steel spherical vessel (fig. 1). It is equipped with gas inlets for introducing inert gas, fuel, oxygen and compressed air.

Figure 1: 20 L sphere

The ignition source used is a 0.1 mm diameter alumel fusing wire, disposed in the center of the vessel. The ignition is controlled electronically. This ignition source is consistent with that described in standard [5].
Measuring equipment implemented includes a piezoresistive static pressure sensor and two piezoelectric dynamic pressure sensors.

3. Results

3.1. flammability ternary diagram

The results obtained at 1 bar are shown on the ternary diagram (fig. 2). On this figure, the summit represents a pure component. The sides of the triangle represent mixtures reduced to two components.

Orange points label the compositions where an explosion was observed, whereas white points represent the compositions for which no explosion took place. The right straight indicates stœchiometric CH_4/O_2 mixtures. Gradually, the yellow area was determined, which represents the compositions of flammable $CO_2/CH_4/O_2$ mixtures.

The red crosses indicate the points on which the explosion characteristics of oxygen-enriched mixtures are measured.

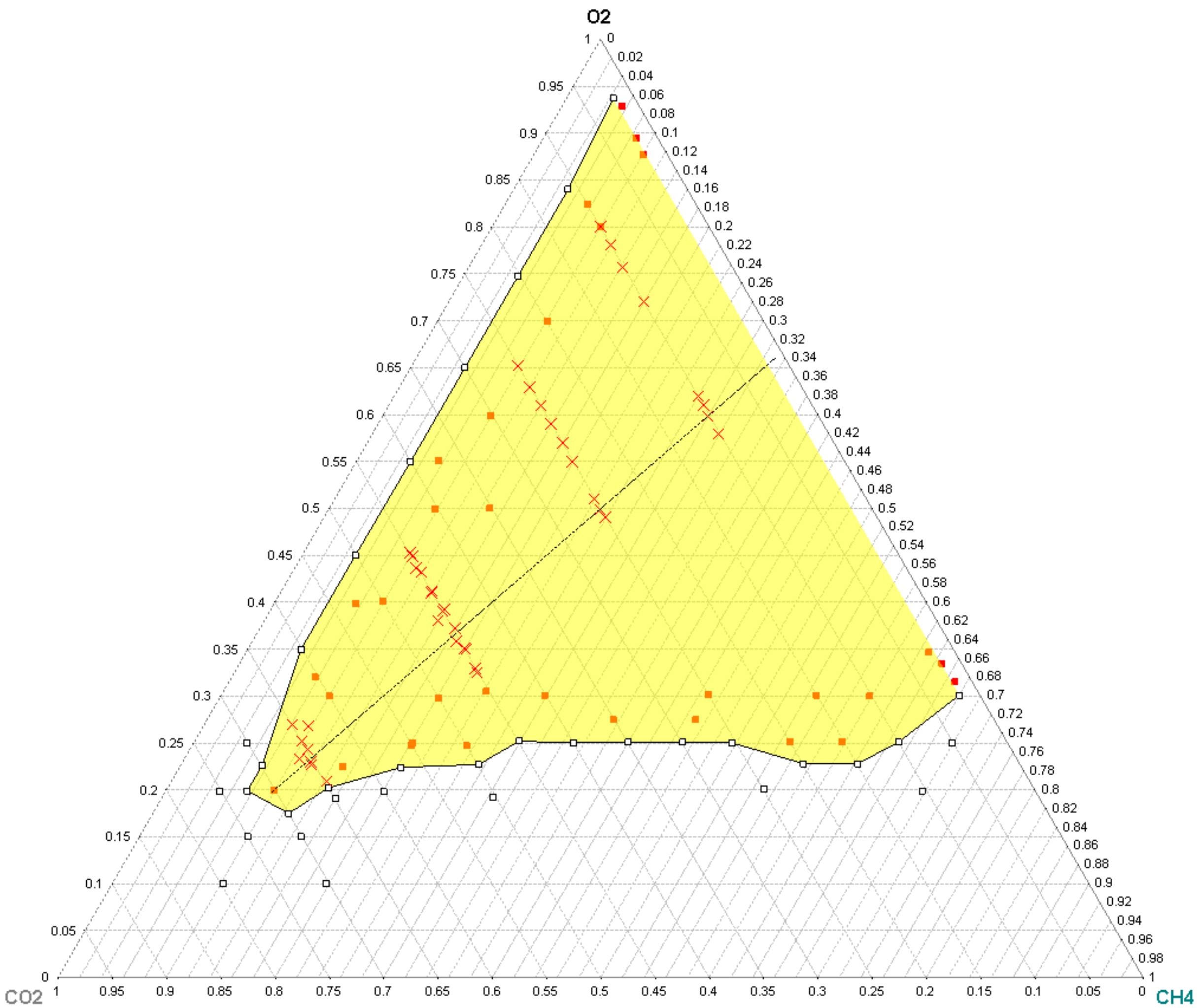

Figure 2: experimental flammability ternary diagram

3.2. flammability characteristics of O_2 enriched mixtures

The influence of oxygen concentration on the explosion severity was highlighted. The results of Pmax and (dP/dt) appear in Table 1 below.

Table 1 : Influence of oxygen concentration on the explosion severity

Molar Composition (%)			Results	
CO_2	CH_4	O_2	Pmax (bar rel.)	(dP/dt) (bar/s)
63.50	9.68	26.82	3.4	44
64.84	10.91	24.25	3.5	52
65.31	12.01	22.67	3.6	72
65.16	14.30	20.54	0	0
44.90	9.80	45.30	5.8	110
45.17	11.21	43.62	6.5	254
45.07	13.90	41.02	7	506
45.00	15.90	39.10	7.6	638
44.86	17.90	37.25	7.5	754
45.39	18.82	35.79	6.9	656
45.02	19.90	35.08	7.2	636
25.08	19.88	55.04	9.6	3080
25.07	23.92	51.01	10.1	2742
25.11	25.00	49.89	10.4	3918
25.04	25.85	49.11	9.3	2296
10.03	28.00	61.97	11.3	5904
10.01	28.97	61.02	11.1	5720
10.14	30.03	59.83	11.2	5692
10.14	31.93	57.93	10.5	5046

The two figures below (fig. 3 and 4) represent the evolution of the overpressure and the rate of pressure rise, for the different concentrations of inert gases tested.

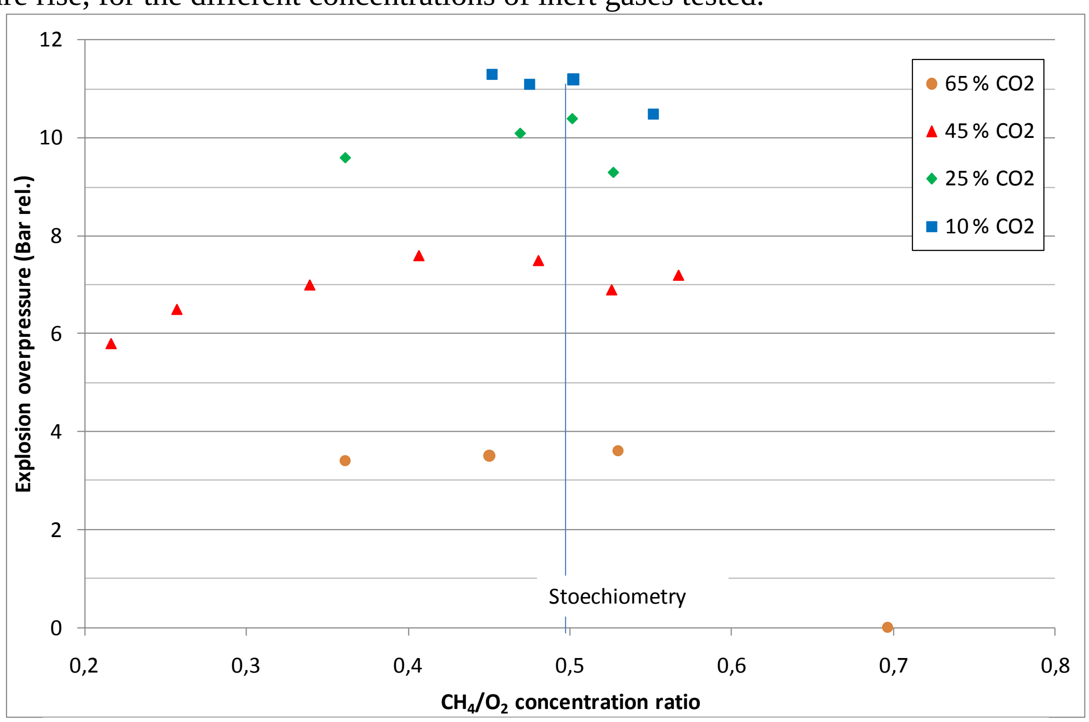

Figure 3: Evolution of the overpressure depending on the mixture composition

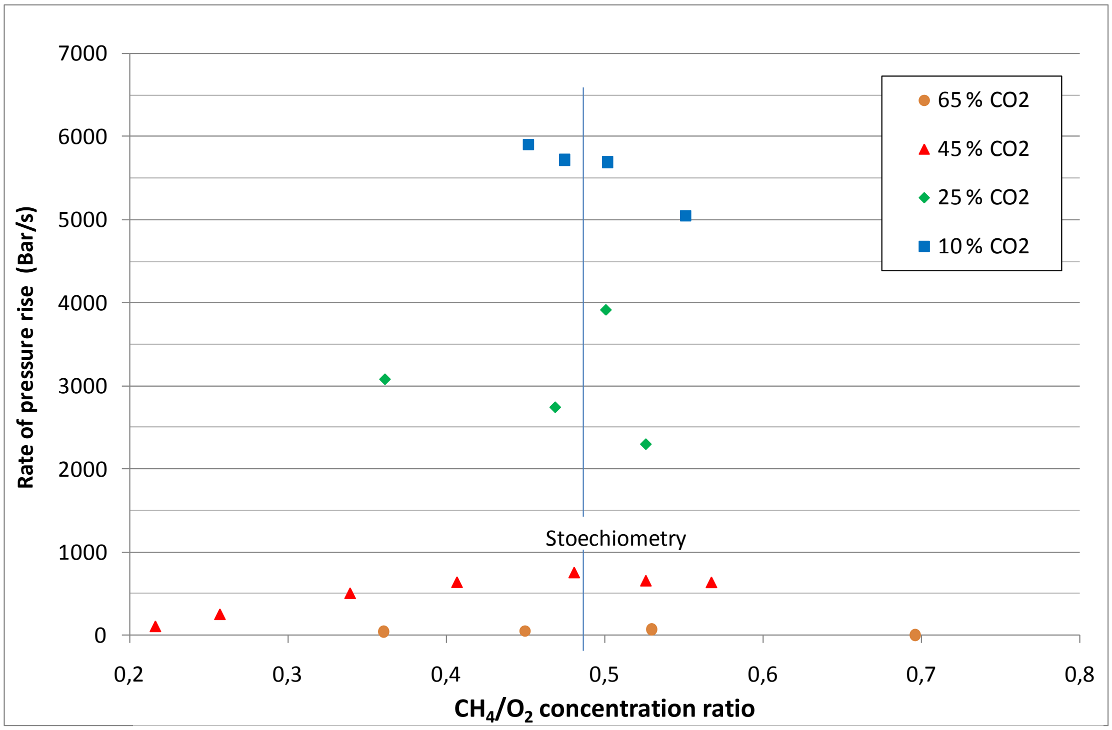

Figure 4: Evolution of the rate of pressure rise depending on the mixture composition

4. Discussion and conclusion

Determination of the flammability characteristics of binary CH_4/O_2 mixtures was not performed, since the vacuum obtained is partial and a minimal amount of N_2 is always present in the vessel. However, we can estimate by extrapolation LEL and UEL of methane in oxygen to be 5% and 68% respectively. In this diagram, we also noted that when the CO_2 concentration increases, the severity decreases. No ignition was observed when carbon dioxide content exceeded 73%.

The two graphs exposed highlight the significant influence of oxygen concentration on the violence of explosion. The explosion pressure and rate of pressure rise are highest near the stœchiometry. Elevated CO_2 concentration significantly reduced the explosion severity. Maximum values of Pmax and dP/dt measured for a 10% vol. carbon dioxide concentration were 11.2 bar rel. and 5904 bar/s respectively, while they were 3.6 bar rel. and 72 bar/s respectively in the case of a 65% vol. carbon dioxide content in the mixture.

5. References

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