

ON THE FLAMMABILITY LIMITS OF SATURATED VAPOURS OF HYDROCARBONS

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Summary

The upper flammability limits of saturated vapours of four hydrocarbons (cyclohexane, benzene, toluene and ethylbenzene) in oxygen–nitrogen and oxygen–carbon dioxide mixtures have been measured in the range 60–120°C and 1–10 atm by an experimental technique that avoids any extrapolation procedure.

The different reactivity of the four hydrocarbons is discussed, taking into account the pressure dependence of the flammability limits, which appeared particularly significant for cyclohexane–air mixtures.

Introduction

The liquid-phase oxidation processes of hydrocarbons with air or oxygen play an important role in the modern chemical industry. The definition of a new process or the revamping of an old one, for instance with the aim of using oxygen instead of air [1], requires the knowledge of the flammability regions of the relevant gaseous mixtures as a function of composition, pressure and temperature.

In spite of their practical importance, few data are available in the literature for pressures and temperatures of industrial interest. In particular, no data are available for mixtures containing the saturated vapours present in liquid-phase oxidation plants. Therefore these data must be obtained with tedious and not completely reliable extrapolation procedures.

In this paper we report the main features of a new technique that was recently developed for the direct measurement of the upper flammability limits of saturated vapours at high temperatures and pressures [2].

The flammability data relating to four hydrocarbons (cyclohexane, benzene, toluene and ethylbenzene) in oxygen–nitrogen and oxygen–carbon dioxide mixtures are also presented and discussed, pointing out the relationship between the flammability limits and the reactivity of the tested hydrocarbons.

Experimental apparatus and technique

The experimental apparatus (Fig. 1) is essentially that described in [2], the main modifications being the use of an adjustable-duration hot-wire igniter [3], and of an HP 5830 A gas-chromatograph to analyze the combustion products.

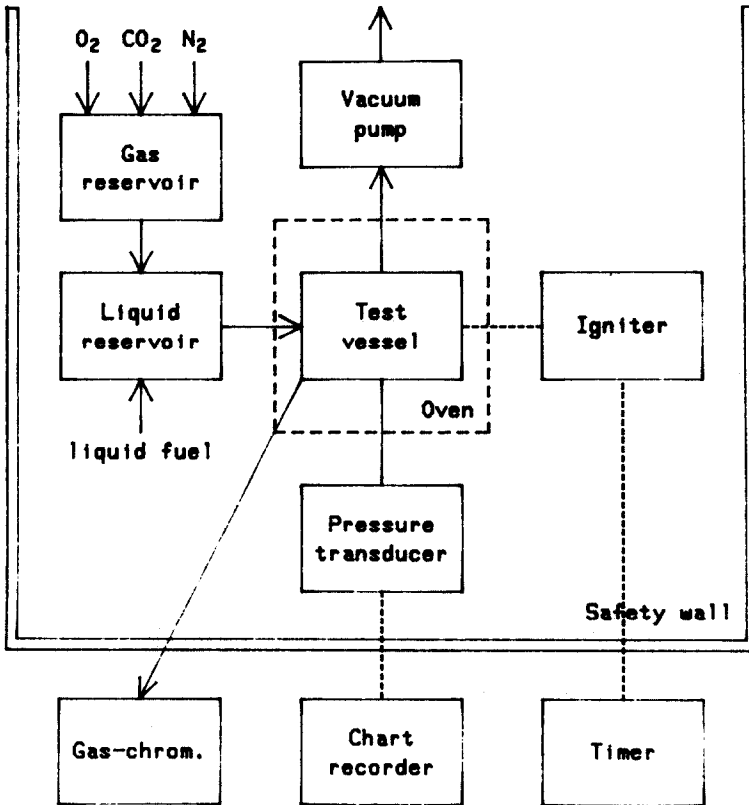


Fig. 1. Experimental apparatus.

The test vessel, a stainless steel cylinder 45 mm i.d. and 145 mm long, located in a temperature-controlled oven, is fed with liquid hydrocarbon by the pressurized oxygen-carbon dioxide or oxygen-nitrogen mixture. The amount of hydrocarbon used gives a saturated gaseous phase and a residual liquid phase in the test vessel.

The adjustable-duration hot-wire igniter consists of a thin, spiral shaped, nickel-chrome wire that is rapidly heated by means of a large current (about 20 A) from a low voltage generator (about 20 V). The heating current is switched off by a timer after about 0.4 s to obtain a rather high temperature

(about 1200°C) but to avoid the melting of the wire. The energy dissipated to the hot wire has been found to be 150 ± 10 J [3].

This apparatus and the experimental technique were designed to minimize the problems related to the correct measurement of the flammability limits at high temperatures and pressures [4].

Firstly, the residence time at high temperature and pressure before the ignition, i.e. the filling and heating time, must be as short as possible, so that pre-flame reactions do not affect the measured flammability limits. The gas-chromatographic analysis showed that, for residence times of about 20 min (more than 50 times the usual filling and heating time), all the hydrocarbons examined do not react even at the more severe conditions of pressure and temperature.

Moreover, a criterion must be found to define the boundary between "non-flammable" and "flammable" mixtures, that is the flammability limit. An easy-to-use, non-confusing and safe criterion must be used when a wide set of experimental data must be analyzed, even if any practical criterion is in some respects arbitrary. In fact, a smooth transition is observed, in particular at the upper limit, between the two regions and two different flammability limits (upward and downward) may be defined and their occurrence explained in terms of heat exchange from the flame to the surrounding environment [5].

Figures 2 and 3 show the smooth variation of the dimensionless pressure

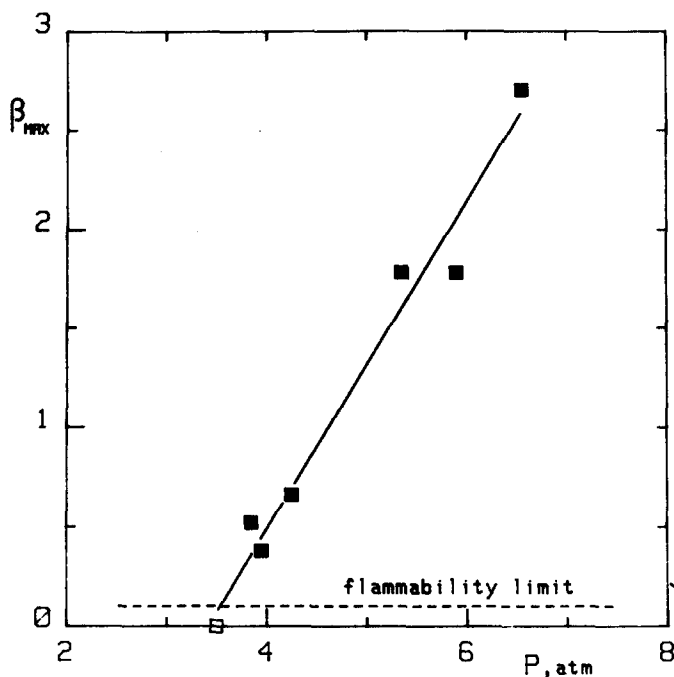


Fig. 2. Dimensionless pressure increases $\beta_{max} = (\bar{P}_{max} - P)/P$ versus the initial pressure P for saturated cyclohexane-oxygen mixtures at $T = 120^\circ\text{C}$, close to the upper flammability limit.

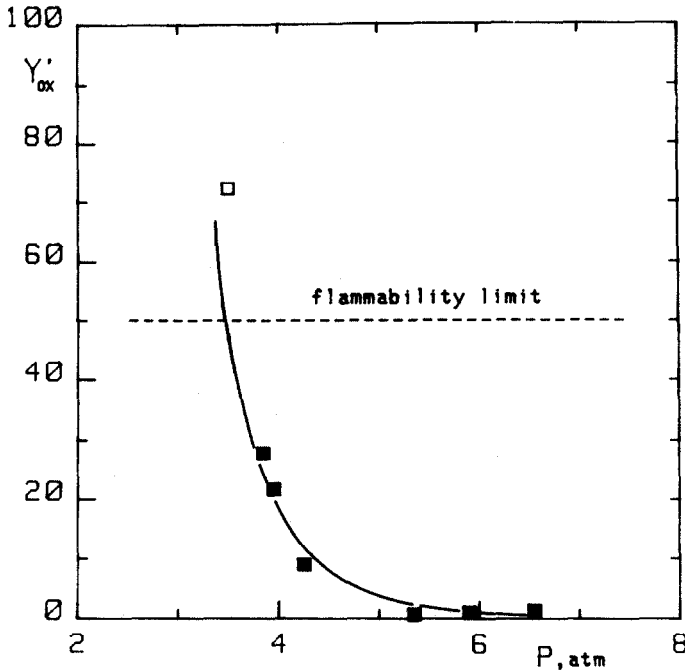


Fig. 3. Oxygen percentage Y'_{ox} in the burned gases versus the initial pressure P for saturated cyclohexane-oxygen mixtures at $T = 120^\circ\text{C}$, close to the upper flammability limit.

increase $\beta_{\max} = (P_{\max} - P)/P$ (normalized with respect to the initial pressure P) and of the oxygen percentage Y'_{ox} in the burned gases (measured on dry and fuel-free basis) as a function of the initial pressure P , in cyclohexane-oxygen mixtures at $T = 120^\circ\text{C}$. The initial pressure is the natural independent variable, because at constant temperature and oxygen/diluent ratio the upper flammability limit is reached by increasing P , that is the oxygen/fuel ratio. The two figures clearly show the continuous transition between non-flammable and flammable mixtures; while the β_{\max} vs. P plot is almost linear, the slope of the Y'_{ox} vs. P curve changes dramatically for values of Y'_{ox} corresponding to small values of β_{\max} . This behaviour may be used to define a mixture as non-flammable if Y'_{ox} is greater than 50 when it corresponds to β_{\max} smaller than 0.1. This criterion is rather conservative because the limit pressure increase is only about 1% of the theoretical maximum value.

Finally, the volume V of liquid fuel to be fed into the explosion vessel must be carefully considered. This amount must certainly be greater than the value V_0 which is theoretically sufficient to generate a two-phase saturated system (liquid and gaseous), but the effect of excess liquid must be determined. Figure 4 shows the behaviour of the limit pressure P as a function of V , for rich hydrocarbon-oxygen mixtures at 120°C . The limit pressure P obviously increases with increasing V , if the amount of fuel is not sufficient

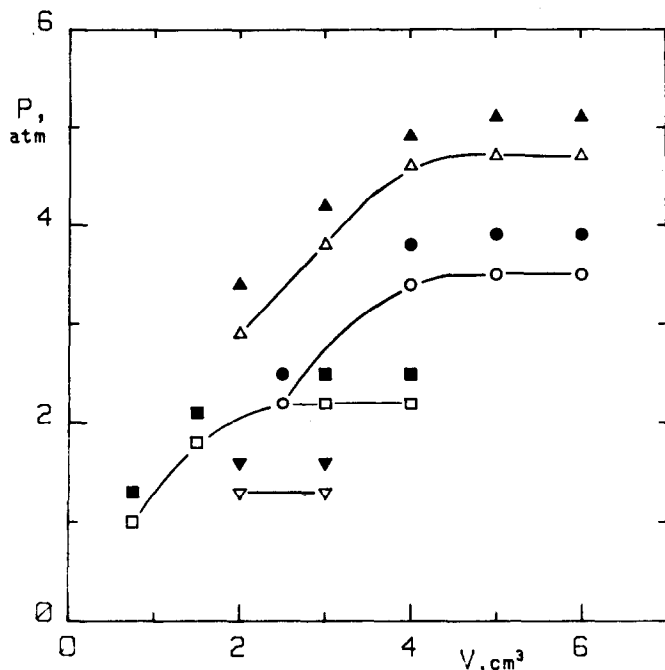


Fig. 4. Upper flammability pressure P versus the volume V of liquid fuel fed to the test vessel; saturated mixtures in pure oxygen at $T = 120^\circ\text{C}$. Hollow symbols: non-flammable mixtures; full symbols: flammable mixtures. ∇ , ethylbenzene $V_0 = 0.48 \text{ cm}^3$; \square , toluene $V_0 = 0.84 \text{ cm}^3$; \triangle , benzene $V_0 = 1.63 \text{ cm}^3$; \circ , cyclohexane $V_0 = 1.85 \text{ cm}^3$.

to saturate the gaseous phase, and a constant value is measured for V/V_0 greater than 3.

Different behaviour is observed at the lower limit, as shown in Fig. 5, for toluene—oxygen—carbon dioxide mixtures where the dimensionless pressure increase β_{\max} is plotted against the initial pressure P for different amounts of liquid toluene, all much larger than V_0 . On increasing V from 0.3 to 3 cm³ it appears that, while the upper limit remains constant, the lower limit widens greatly (from 7.5 to 11 atm).

Both these results can be explained by assuming that the combustible fog generated during the filling procedure increases the reactivity of the lean mixtures, while its effect is negligible when close to the upper limit. Recent and more detailed investigations of flame propagation in fuel droplet—vapour—air mixtures [6] seem to confirm these results, even though the experiments were carried out with near-stoichiometric mixtures.

These results show the validity of the proposed technique for the measurement of the upper flammability limits of saturated mixtures, while a correct measurement of the lower limits seems difficult. However, for liquid-phase hydrocarbons, oxidation-plant conditions close to the lower limit are never met, so that only the upper limits are of practical interest.

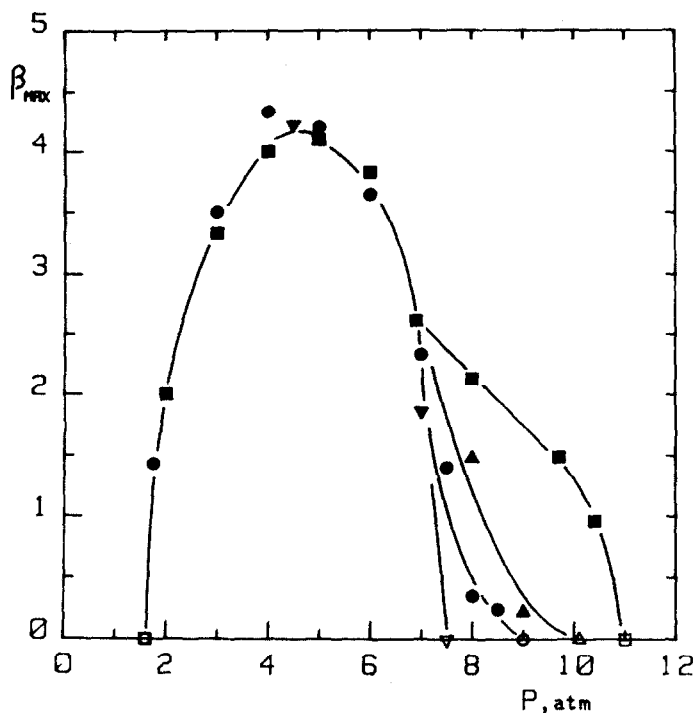


Fig. 5. Dimensionless pressure increases $\beta_{max} = (P_{max} - P)/P$ versus the initial pressure P for toluene-oxygen-carbon dioxide mixtures at $T = 50^\circ\text{C}$ and for different volumes V of liquid toluene fed to the test vessel; Y_{Ox} (oxygen percentage on toluene-free basis) = 24. ∇ , $V = 0.3 \text{ cm}^3$; \circ , $V = 0.5 \text{ cm}^3$; \triangle , $V = 1 \text{ cm}^3$; \square , $V = 3 \text{ cm}^3$. Hollow symbols: non-flammable mixtures; full symbols: flammable mixtures.

Experimental results

The upper flammability limits of three hydrocarbons (cyclohexane, benzene and ethylbenzene) have been measured in the temperature range 60 – 120°C and in the pressure range 1 – 10 atm , using both nitrogen and carbon dioxide as diluent. Also, some of the results obtained with toluene-oxygen-carbon dioxide mixtures [3] will be discussed here.

The flammability limits of cyclohexane-oxygen-nitrogen mixtures at 60 , 90 and 120°C are shown in Fig. 6 as Y_{Ox} , oxygen percentage on a hydrocarbon-free basis, versus the initial pressure P . Increasing the initial pressure causes a remarkable and regular decrease in Y_{Ox} which is observed for all temperatures investigated. At constant Y_{Ox} , the limit pressure increases with increasing temperature, but the widening of the flammable region on decreasing the temperature is only apparent, because the different vapour pressures must be taken into account. This can be done by expressing the experimental data as cyclohexane percentage Y_c and equivalence ratio $\Phi = (\text{fuel/oxygen})/(\text{fuel/oxygen})_{stoich}$ (Table 1). The values of Y_c and Φ increase with increasing temperature both in air and in oxygen, but irregular behaviour is

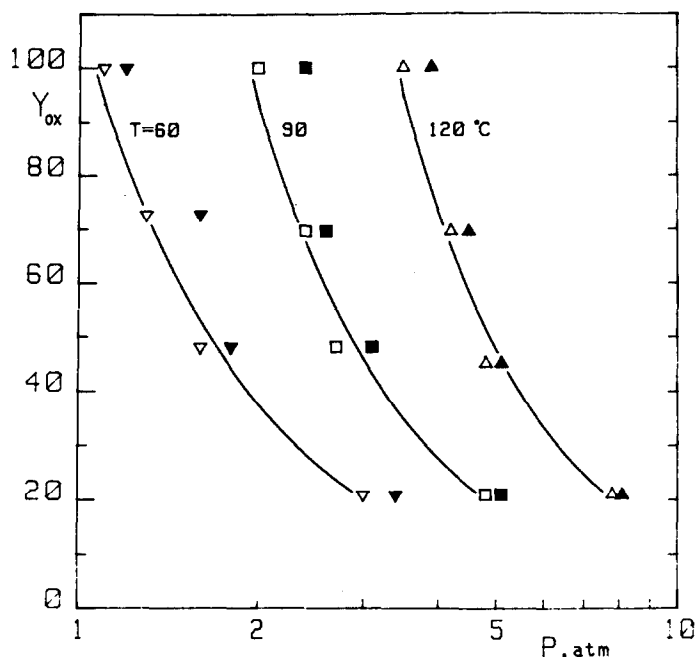


Fig. 6. Upper flammability limits of saturated cyclohexane-oxygen-nitrogen mixtures, expressed as Y_{ox} (oxygen percentage on fuel-free basis) versus the initial pressure P . Hollow symbols: non-flammable mixtures; full symbols: flammable mixtures.

TABLE I

Cyclohexane percentage Y_c and equivalence ratio ϕ at the upper flammability limit (saturated mixtures)

$T, ^\circ\text{C}$	Y_c			ϕ		
	60	90	120	60	90	120
cyclohexane— air	17.0	26.5	35.4	8.8	15.4	23.5
cyclohexane— oxygen	46.5	63.5	78.9	7.8	15.7	33.6

observed for the equivalence ratio: in fact the value in oxygen is slightly lower than that in air at the lowest temperature, while it is much higher at the highest temperature. If the pressure effect on the flammability limits is considered this result does not disagree with the general finding that the equivalence ratio at the upper flammability limit decreases on increasing the diluent percentage [2], irrespective of the temperature. Of course, it is not possible to measure independently the pressure and the temperature dependence of the flammability limits of saturated mixtures: the pressure depen-

dence may be evaluated only after correcting the data for the temperature, or vice versa. While no theoretical approach is available for the pressure dependence, the semi-empirical rule proposed for the temperature dependence of the lower flammability limit [7], expressed as fuel percentage Y_F , is:

$$\Delta Y_F = \frac{0.75 \cdot \Delta T}{(-\Delta H)} \quad (1)$$

This expression may also be used for the upper flammability limit if an appropriate value for the heat of combustion, ΔH , is used. This rule is based on the constancy of the flame temperature at the flammability limits and neglects the temperature dependence of the chemical equilibrium that may be assumed small if the temperature range considered is small.

For the present case the heat of combustion relative to carbon monoxide and hydrogen (i.e. $\Delta H = -120$ kcal/mol) has been used. This choice is supported by the gas-chromatographic analysis of the combustion products, and by the few experimental data available in literature for the temperature dependence of the upper flammability limits of cyclohexane-air mixtures [8]. When the experimental data of Fig. 6 are corrected for a temperature of 25°C in this way, the relevant pressure dependence is fairly well described by a power law, both for cyclohexane-oxygen and cyclohexane-air mixtures, as shown in Fig. 7. The exponent relative to cyclohexane-oxygen mixtures is

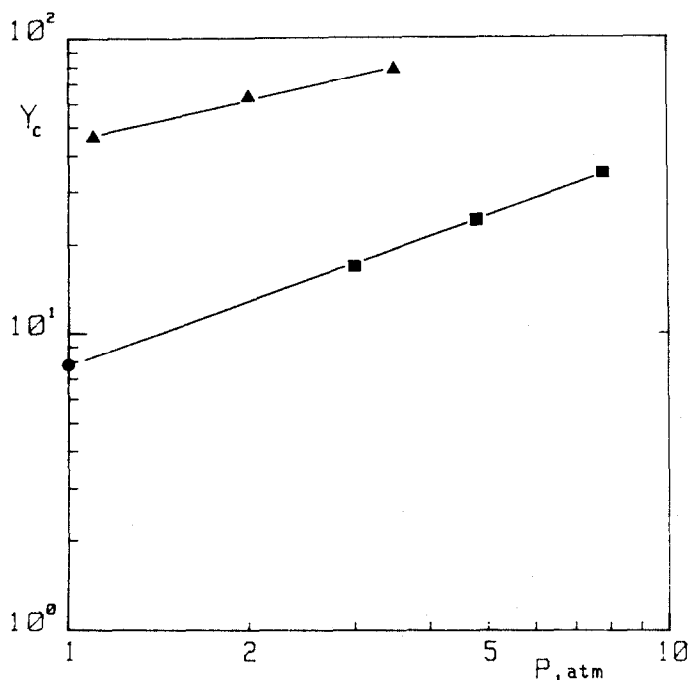


Fig. 7. Upper flammability limits Y_c of cyclohexane-oxygen (\blacktriangle) and cyclohexane-air (\blacksquare) mixtures, corrected to 25°C, versus the initial pressure P . \bullet : cyclohexane-air, ref. [7].

almost equal to that found for toluene—oxygen mixtures [3], while the rather strong pressure dependence for cyclohexane—air mixtures agrees with the few data available in the literature [8]. When the data presented in Table 1 are corrected for the pressure effect, a noticeable and regular variation of the equivalence ratio as a function of the diluent percentage is observed (Table 2). The data obtained in air agree with the literature data, when considering the temperature dependence.

TABLE 2

Cyclohexane percentage Y_c and equivalence ratio Φ at the upper flammability limit; values extrapolated to atmospheric pressure

$T, ^\circ\text{C}$	Y_c				Φ			
	Ref. [7]	This paper, saturated mixtures			Ref. [7]	This paper, saturated mixtures		
	25	60	90	120	25	60	90	120
cyclohexane—air	7.8	7.7	8.6	8.1	3.6	3.6	4.0	3.8
cyclohexane—oxygen	—	44.4	46.2	44.3	—	7.2	7.7	7.2

The flammability limits of the four hydrocarbons (cyclohexane, benzene, toluene, ethylbenzene) have been determined in oxygen—carbon dioxide mixtures, at $T = 120^\circ\text{C}$, and are presented in Fig. 8 as Y_{OX} , oxygen percentage on a hydrocarbon-free basis, versus the initial pressure P . The behaviour of the different hydrocarbons is similar to that observed for cyclohexane—oxygen—nitrogen mixtures at different temperatures. However, the curves have different slopes and the cyclohexane curve merges with the toluene one.

The comparison between the cyclohexane curves at 120°C (Figs. 6 and 8) shows that even though the dilution with nitrogen or carbon dioxide noticeably increases the limit flammability pressure, no significant difference is observed for the two diluents in the range of Y_{OX} investigated. This observation has been confirmed by other flammability tests carried out at different temperatures, both with cyclohexane and benzene.

Once again, these data must be corrected for the different vapour pressure by computing the hydrocarbon percentage Y_F and the equivalence ratio Φ . The values relative to hydrocarbon—oxygen mixtures are shown in Table 3. These data indicate a very high reactivity of cyclohexane as compared to the aromatic hydrocarbons, whose order of reactivity (benzene > toluene > ethylbenzene) is opposite to that reported in the literature at atmospheric pressure and 100°C [7]. However, these results are due to the different experimental pressure. In fact, the data relative to the aromatic hydrocarbons agree with the reactivity order reported in the literature when they are extrapolated to atmospheric pressure with the power law $Y_F \propto P^{0.46}$ found for toluene—oxy-

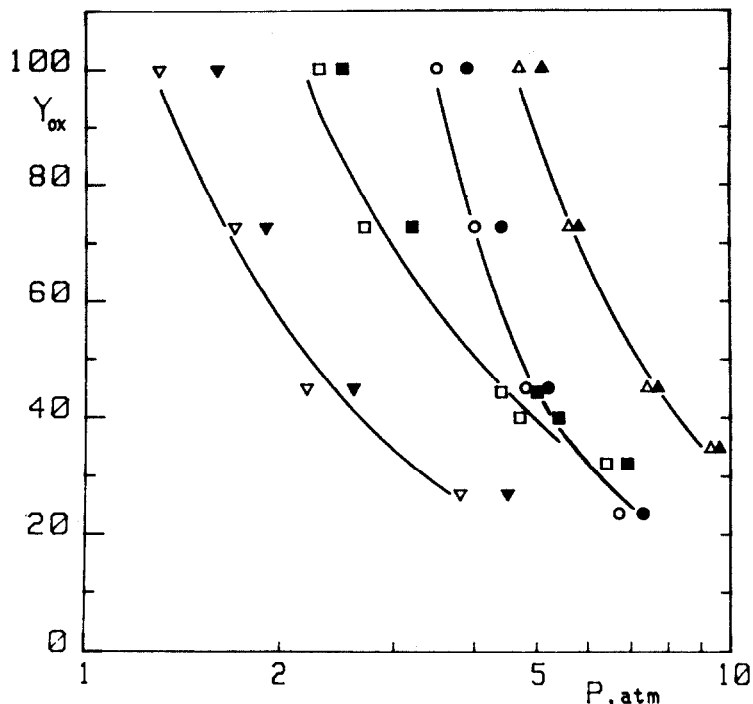


Fig. 8. Upper flammability limits of different hydrocarbons in oxygen-carbon dioxide mixtures, expressed as Y_{ox} (oxygen percentage on hydrocarbon-free basis) versus the initial pressure P , at $T = 120^\circ\text{C}$. Hollow symbols: non-flammable mixtures; full symbols: flammable mixtures. ∇ , ethylbenzene; \square , toluene; Δ , benzene; \circ , cyclohexane.

TABLE 3

Hydrocarbon percentage Y_F and equivalence ratio Φ at the upper flammability limit for different hydrocarbons

	Ref. [7], air 100°C , 1 atm		This paper, oxygen, 120°C saturated mixtures		This paper, oxygen, 120°C , $\Phi_{\text{oxygen}}/\Phi_{\text{air}}$ values ext. to 1 atm		
	Y_F	Φ	Y_F	Φ	Y_F	Φ	
cyclohexane	7.8*	3.6*	78.9	33.6	44.3	7.2	2
benzene	7.9	3.1	63.0	12.8	30.4	3.3	1.1
toluene	7.1	3.3	55.7	11.3	37.4	5.4	1.7
ethylbenzene	6.7	3.6	48.5	9.9	42.9	7.9	2.2

*At $T = 25^\circ\text{C}$.

gen and cyclohexane-oxygen mixtures (Table 3). Moreover, when the same correction is applied to cyclohexane, its reactivity appears to be comparable to that of ethylbenzene, as reported in the literature for hydrocarbon-air mixtures.

The effect of the diluent on the flammability limit may be evaluated through the ratio between the values of Φ in oxygen and those in air (Table 3). This ratio is only slightly larger than 1 for benzene, and increases with the length of the aliphatic chain added to the aromatic ring; moreover, the cyclohexane value is intermediate between those relative to toluene and ethylbenzene, in agreement with the expected reactivity of the cycloalkane ring.

Conclusions

The upper flammability limits of saturated vapours of different hydrocarbons and their dependence on pressure and temperature have been measured with a direct experimental technique, whose reliability has been confirmed by comparison with the few data available in the literature. A good correlation with the reactivity and the molecular structure of the different hydrocarbons tested has been observed.

The experimental technique here employed presents some limitations in measuring the lower flammability limits. Indeed, a remarkable dependence of the lower limits on the volume of liquid hydrocarbon fed in the test vessel has been observed, most likely due to the formation of hydrocarbon fogs during the filling procedure. This result restricts the use of the proposed technique to the measurement of the upper limits, which are the only ones of practical interest for the safe operation of the liquid-phase hydrocarbon oxidation plants.

Acknowledgements

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