The effect of oxygen concentration on CO yields in fires

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THE EFFECT OF OXYGEN CONCENTRATION ON CO YIELDS IN FIRES

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ABSTRACT

In addition to global ventilation effects on fires, vitiation of air is a ventilation related phenomenon that can also affect the generation of chemical species in a built environment. The paper is a contribution to the study on the subject. Experiments were performed at lab-scale with the Fire Propagation Apparatus in order to study the effect of air vitiation on the CO yield. Results are also presented for the fuel burning rate. Both carbon dioxide and nitrogen were used as diluents in the inlet air flows. The oxygen concentration was decreased stepwise until the extinction point was reached. A first set of experiments was performed in well-ventilatedfire conditions (equivalence ration between 0.1 and 0.25). A second set of experiments was carried out in under-ventilatedfire conditions (equivalence ratio equal to 1.1). The results revealed usefulfor improving the combustion sub-model predictions in a zone model under development.

1. INTRODUCTION

In a recent paper, Brohez et al have presented a zone model for the prediction of temperature and composition of fire gases in enclosures where fire scenarios with moderate forced ventilation are dealt with[1]. The combustion sub-model was based on the concept of the global equivalence ratio[2] in order to take into account the influence of the ventilation effect on the generation of species. This sub-model relies on the use of a database for chemical substances of interest as fuels which contains empirical relationships giving the combustion products yields as functions of the global equivalence ratio. These correlations were derived from fire test results obtained at lab-scale with the Fire Propagation Apparatus which was recently described in the ASTM E-2058[3].

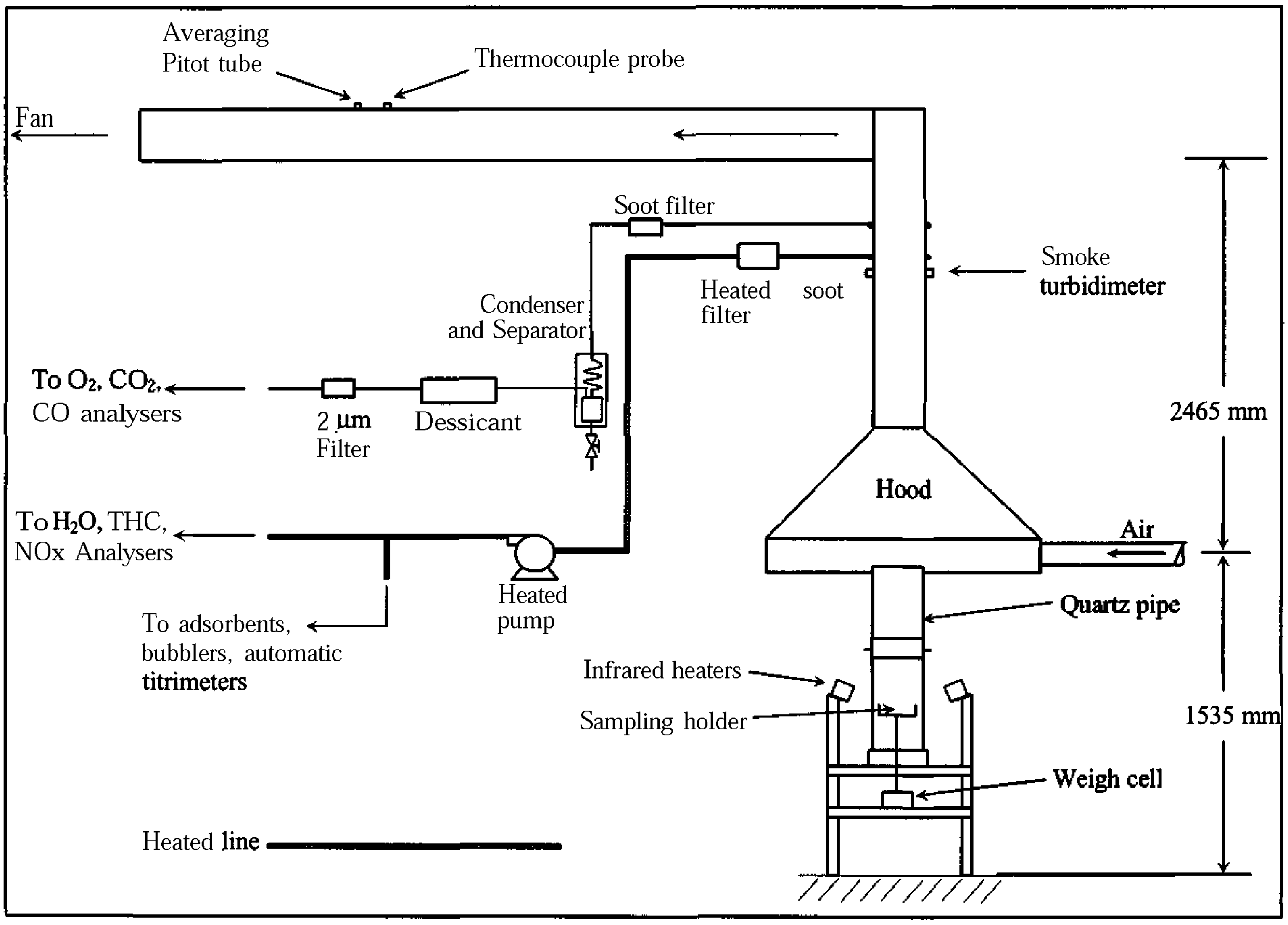
It has been shown that the predictions of the zone model were generally in good agreement with experimental results obtained at larger scale (room fire experiments) with pyridine pool fires. However, CO concentration was not so well predicted in the early stage of development of the model, especially for low oxygen concentrations in the compartment. The concentration of CO was underestimated by a factor of about 2. In addition to the fire ventilation effect, it could be pointed out that the molar fraction of oxygen at the flame base has an additional effect on the CO yield[2,4]. The mixing process of combustion products with ambient air due to the enclosure leads to a reduction in oxygen concentration and thus to air vitiation of the combustion air feeding the reactive (flaming) zone. The vitiation of air which can affect the CO yield was not primarily taken into account in the zone model.

This paper presents experiments which were carried out at lab-scale, in order to analyse the effect of air vitiation on the CO generation for pyridine as fuel. The effect of air vitiation on the burning rate of the fuel is also presented. In a first set of experiments, well-ventilated fire conditions were adjusted with both N_2 or CO_2 used as diluents in inlet flows in the Fire Propagation Apparatus. Experiments were carried out with oxygen concentrations which were decreased stepwise until the extinction point was reached. A second set of experiments was carried out with a value of about 1.1 for the equivalence ratio (with CO_2 used as diluent). The two set of experimental results were processed and plotted in a single graph illustrating the way they can be used in zone models for improving combustion sub-model predictions.

2. THE FIRE PROPAGATION APPARATUS - EXPERIMENTAL PROCEDURE

Experiments were carried out at bench-scale with the Fire Propagation Apparatus implemented in the INERIS Fire Laboratory[5]. A schematic view of the calorimeter is presented in figure 1. The combustion chamber consists of two cylindrical quartz pipes with a diameter of 160 mm which are placed on each other by means of a ring made of stainless steel. This combustion chamber allows to perform experiments in controlled atmosphere. The fuel sample is located inside the quartz tube in a sample holder put-on a weigh cell.

Figure 1 : Schematic of the Fire Propagation Apparatus



Two mass flow meters allow the operator to set the desired mass flow rate of air of up to 300 $Nl.min^{-1}$. Another mass flow meter allow the introduction of CO_2, N_2 or O_2 into the incoming air for non-ambient combustion conditions. The air may thus be enriched or depleted in oxygen. The composition of oxidising stream is measured by an oxygen analyser, the sampling probe is located below the specimen holder in the combustion chamber.

The upper part of the calorimeter is the exhaust system with the instrumentation section. Standard characterisation of the composition of fire gases and smoke relies on the routine use of the on-line gas measuring devices. The heat release rate is measured from both Oxygen Consumption and Carbon Dioxide Generation calorimetries[6,7].

3. EXPERIMENTAL RESULTS

3.1. Well-ventilated fire conditions

A first series of tests was performed with a constant inlet flow rate of ambient air of 250 **Nl/min,** under **well-ventilated** fire conditions (the values of global equivalence ratio were between 0.1 and 0.25). In order to reduce oxygen concentration in the oxidising stream, inlet flow rate of air was progressively diluted by addition of inlet flows of nitrogen or carbon dioxide. Experiments were carried out with oxygen concentrations which were decreased stepwise until the extinction point was reached.
During the whole experimental program using **pyridine** as fuel, an external heat flux of 15 kW/m^2 was applied only until ignition of fuel vapour occurred, then stopped. From these experiments, the yields of CO_2, CO, THC, NO, NO_2 and HCN were measured. In the present **paper,** results for CO yield and fuel burning rate are presented.

Vitiation of air clearly decreases the fuel burning rate. As the oxygen concentration is decreased from 21 % to a value near the extinction limit of the fire, the fuel mass loss rate decreases by a factor of about 2.5 from 21 $g.m^{-2}.s^{-1}$ to about 8 $g.m^{-2}.s^{-1}$ (see figure 2). The fuel mass loss rate decreases slightly more rapidly when CO_2 is used as diluent. In both cases, the relationship between mass loss rate and O_2 concentration in the oxidising flow is clearly linear.
This latter statement is consistent with experimental results published by **Tewarson** et **al.**[8], Santo et **al.**[9] and **Mulholland** et **al.**[10] (e.g. with **PMMA** as a fuel, and external heat flux of $15 kW.m^{-2}$). More recently, **Nikitin**[11] also deduced from theoretical considerations that the fuel mass loss rate is directly proportional to oxygen concentration. In figure 3, normalized fuel mass loss rate (which is defined here as the ratio of fuel mass loss rate to the fuel mass loss rate in normal air) is plotted as function of O_2 concentration. The correlation proposed by **Peatross** and Beyler[12] is also plotted. As can be seen, there is a good agreement between our results and the proposed correlation.

Figure 2: Pyridine mass loss rate as function of O_2 concentration

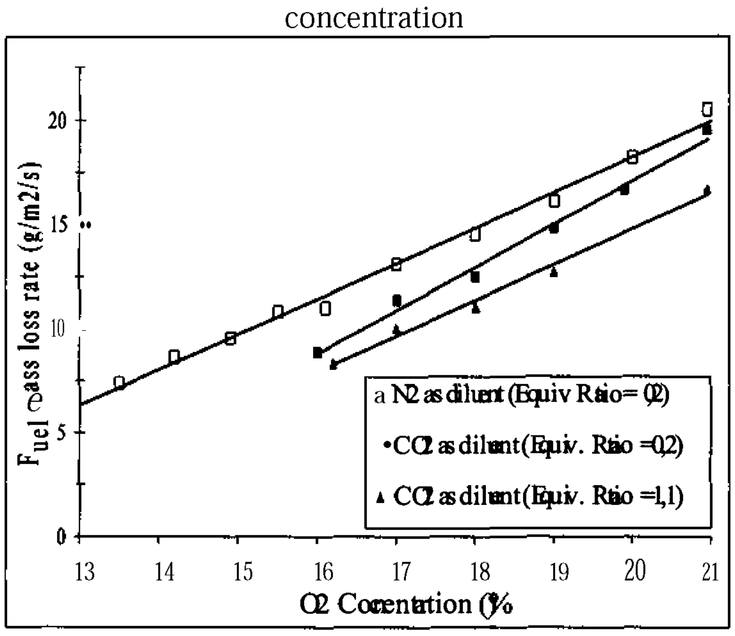
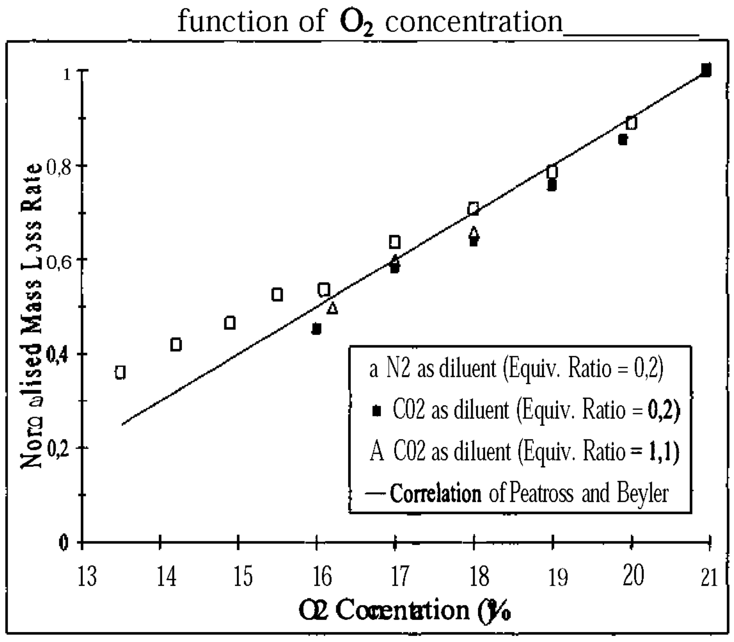


Figure 3: Normalised pyridine mass loss rate as function of O_2 concentration



It can be pointed out that the CO yields were roughly constant during the course of the combustion tests (cf. figure 4). It was observed that yield of CO is clearly dependent of oxygen molar fraction in the inlet flow stream (figure 5). As the O_2 concentration is decreased the CO yield increases by a factor of 2. When O_2 concentration is approaching the extinction limit the CO yield decreases suddenly. A shift can be observed in the curves for the CO yield as function of oxygen concentration when N_2 or CO_2 is used. This phenomenon is certainly due to the heat capacity of carbon dioxide which is larger than the one of nitrogen, leading to a flame temperature lower in the case of CO_2 used as diluent. Mulholland et al[4] conjecture that the CO yield for a given fuel is primarily determined by the flame temperature for free burn conditions (well-ventilated fire conditions). Close to the extinction limit, nearly the same flame temperature is expected for both diluents (leading to the same critical heat flux to the fuel surface); similar values are observed for the CO yields (near the extinction limit). Identical maximum values for CO yield are observed whichever diluent N_2 or CO_2 is used.

In figure 5, the correlation proposed by **Mulholland** et al is also plotted as a function of oxygen concentration. This correlation was established for solid samples with nitrogen as diluent. It can be seen that our results are consistent with the correlation of Mulholland et al except for oxygen concentrations close to the extinction limit.

Figure 4: Instantaneous CO yield as function of time for three O_2 concentrations (N_2 as diluent)

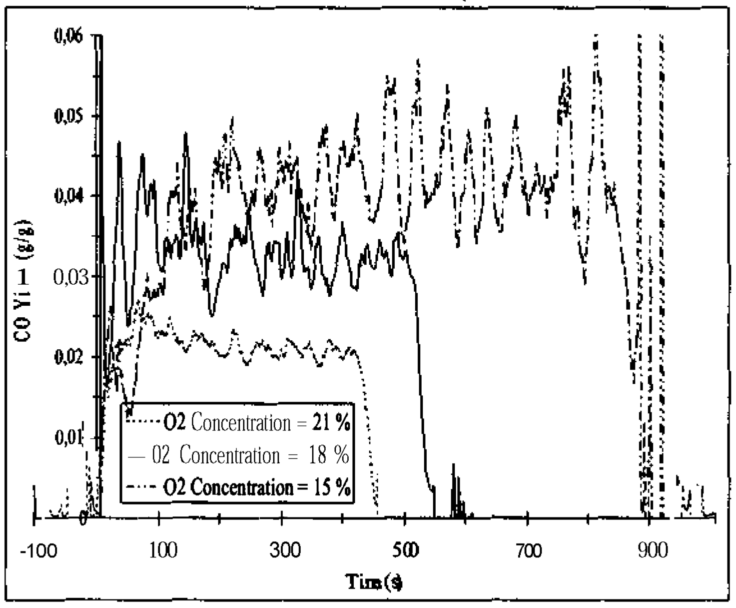
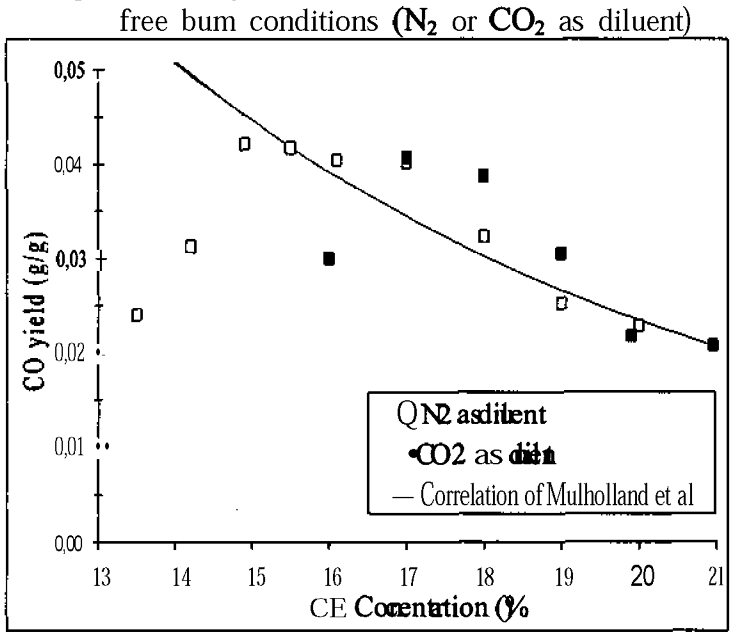


Figure 5: CO yield as function of O_2 concentration for free bum conditions (N_2 or CO_2 as diluent)



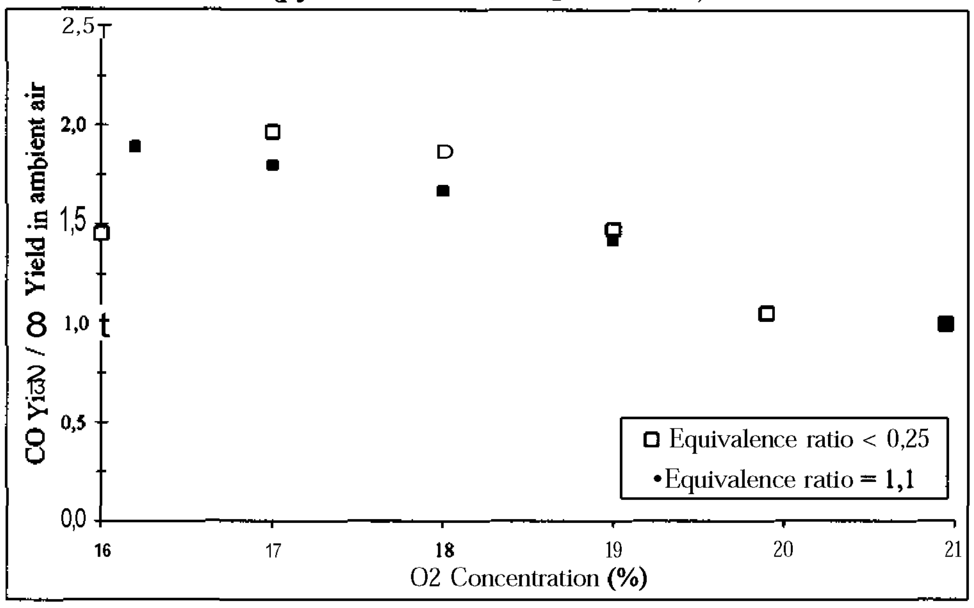
During the experiments close to the extinction limit, the flame became roughly transparent and broke up into several small flamelets moving on the pyridine surface. No soot production was observed near the extinction limit of the fire. **Zukoski**[13] previously mentioned the occurrence of this phenomenon in enclosure fire tests : he reported that when flaming combustion survives in completely vitiated air, near the extinction limit, the production of soot stops completely and the flame appears as a faint gray-blue ghost.

3.2. Under-ventilated fire conditions

A second series of experiments was performed with under-ventilated fire conditions. For these experiments, the same value of about 1.1 was targeted for the global equivalence ratio. It was not easy to obtain a set value of 1.1 for all these experiments since fuel mass loss rate decreases as the O_2 concentration is decreased. The oxidising stream consists of a mixture of air and carbon dioxide (used as the diluent). The oxygen concentration ranged from 21 % to 16 % which was the extinction limit of pyridine pool fire.

It is well known that CO yield increases with the equivalence ratio. In ambient air conditions (O_2 concentration = 21 %), CO yields of 0,02 and 0,09 were found respectively for the global equivalence ratio of 0,25 and 1,1. In figure 6, the ratio of CO yield to CO yield in ambient air is plotted as function of O_2 concentration. Results are presented for well-ventilated fire conditions ($0,1<\Phi<0,25$) as well as for the equivalence ratio value of 1,1. It can be seen that similar curves are obtained excepted near the extinction limit.
It is assumed that the oxygen depletion in the oxidising flow (vitiation) and global air inlet flow limitation (ventilation) act as independent variables on the CO yield. Both parameters should probably be taken into account in order to accurately predict the composition of fire gases in enclosures.

Figure 6: Ratio of CO yield to CO yield in ambient air as function of O_2 concentration (**pyridine** as fuel, CO_2 as diluent)



4. CONCLUSION

Experiments were performed at lab-scale making use of the Fire Propagation Apparatus at **INERIS** for studying the effect of air vitiation on the CO yield. Experiments were primarily carried out in well-ventilated fire conditions. Both nitrogen and carbon dioxide were used as diluents in order to decrease the oxygen concentration in the oxidising stream. A shift was observed in the curves plotting CO yields as functions of the oxygen concentration when nitrogen or carbon dioxide were used. However, similar values were observed for the CO yields near the extinction limit. Quite similar maximum values were also measured for the CO yields for both diluents.
Under-ventilation fire conditions were also considered with carbon dioxide used as diluent. It has been shown that the ratio of CO yield to the CO yield in ambient air plotted as function of the oxygen concentration leads to same trends as those observed in well ventilated conditions.

REFERENCES

[1] Brohez S., Delvosalle C. and Marlair G., 2000, A zone model for predicting the burning rate of liquid pool fires, gas temperature and composition in forced ventilation enclosures", 28^{th} (International) Symposium on Combustion (poster session), Edinburgh, 30 **July-4** August 2000, p.57

[2] Pitts W. M., 1995, The Global Equivalence Ratio Concept and the Formation Mechanisms of Carbon Monoxide in Enclosures Fires, **Prog.Energy** Combust. **Sci.,** , **vol.21, pp** 197-237,

[3] ASTM E 2058-00 : Standard test Method for Measurement of Synthetic Polymer Material **Flammability** Using a Fire Propagation Apparatus **(FPA),** January 2000

[4] **Mulholland G., Janssens M., Yusa S.,** Twilley W. and Babrauskas **V.,** 1991, The Effect of Oxygen Concentration on CO and Smoke Produced by Flames. Fire Safety Science, Proceedings of the Third International Symposium, pp. 585-594

[5] Marlair **G., Tewarson A.,** 2003, Effects of the Generic Nature of Polymers on their Fire Behavior, Fire Safety Science, Proceedings of the 7^{th} International Symposium, **WPI,** Ma, USA, 16-21 June 2002, D. Evans (Ed), 2003 (629-640), ISBN **0-9545348-0-8**

[6] Brohez **S.,** Delvosalle **C.,** Marlair G. and Tewarson **A.,** 1999, Soot Generation in Fires: an Important Parameter for Accurate Calculation of Heat Release, Proceedings of the 6^{th} International symposium of Fire Safety Science, Poitiers, 6/9 July 1999, France, pp. 265-276

7 Brohez **S.,** Delvosalle **C., Marlair** G. and Tewarson **A.,** 2000, The Measurement of Heat Release from Oxygen Consumption in Sooty Fires, Journal of Fire Sciences, Vol. 18, n°5, pp. 327-353

8 Tewarson **A.,** Lee J.L. and Pion R.F., 1981, The Influence of Oxygen Concentration on Fuel Parameters for Fire Modeling, Eighteenth International Symposium on Combustion, The Combustion Institute, pp. 563-570,

9 Santo G. and **Tamanini** F., **1981,** Influence of Oxygen Depletion on the Radiative Properties of PMMA Flames, Eighteenth International Symposium on Combustion, The Combustion Institute, pp. 619-631,

10 **Mulholland G., Janssens M.,** Yusa **S.,** Twilley W. and Babrauskas **V.,** 1991, The Effect of Oxygen Concentration on CO and Smoke Produced by Flames, Fire Safety Science, Proceedings of the Third International Symposium, pp. 585-594,

11 **Nikitin** Y.V., 1998, Variations of Mass Combustion Rate with Oxygen Concentration and Gas Pressure of a Milieu, Journal of Fire Sciences, 16, pp. **458-467**

12 Peatross M.J. and Beyler C.L., 1997, Ventilation Effects on Compartment Fire Characterization, Fire Safety Science, Proceedings of the Fifth International Symposium, **pp.403-414,**

13 **Zukoski** E.E., 1995, Properties of Fire Plumes, Chapter three, in Combustion Fundamentals of Fire, edited by G. Cox, Academic Press, **p.** 175