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Predicting Concentrations of Hydrogen Cyanide in Full Scale Enclosure Fires

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ABSTRACT

In this paper, a local equivalence ratio based toxicity model has been extended to include the calculation of hydrogen cyanide (HCN) by applying a generalised relationship between the normalised yields of carbon monoxide (CO) and HCN. Two full-scale nylon fires have been simulated. The concentrations of toxic gases are calculated with the extended toxicity model while the release of heat due to combustion is modelled by the eddy dissipation combustion model. The predicted concentrations of CO_2 are in good agreement with the measured data and the predicted concentrations of CO and HCN essentially follow the measured trends.

INTRODUCTION

Carbon monoxide (CO) and hydrogen cyanide (HCN) are two main toxic species leading to incapacitation and deaths in fires involving fuels containing nitrogen[1]. As a result it is desirable that toxicity models are equipped with the capability to predict the generation and transportation of both CO and HCN within fire enclosures. The flamelet-based combustion models have the capability of incorporating detailed chemistry for predicting the concentrations of CO and HCN in enclosure fires. Tuovinen et al[2] proposed a methodology for predicting toxic fire gases including HCN with solid fuels using the flamelet concept. In this methodology, the actual fuel was represented by a model fuel, a mixture of methylamine and ethylene, for which the flamelet library data are available. A key limitation of the flamelet models is their heavy reliance on data for detailed chemical kinetics, which are available for only a few gaseous or liquid fuels and notably not for common building materials at present. Therefore, a more practical approach for predicting HCN concentrations is needed in fire safety engineering applications.

In the authors' earlier studies, a toxicity model based on the concept of local equivalence ratio has been developed for the prediction of the generation and transport of CO and CO_2 within enclosure fires[3, 4]. The model incorporates correlations between the yields of species and equivalence ratio and temperature, which can be derived from small-scale experiments such as ISO TS 19700 (so-called Purser Tube Furnace) for a wide range of building materials[5]. Fire gases such as: CO, CO_2 and O_2 can be calculated with this toxicity model. In a recent study[6], a generalised relationship between the normalised yields of CO and HCN has been derived for materials containing nitrogen element. With this relationship, the toxicity model is extended including the calculation of HCN concentrations in this study.

FIRE MODELS

The basic CFD framework used in the present study is the SMARTFIRE software[3,4,6,7]. In field modelling, the fluid is governed by a set of three-dimensional partial differential equations. This set of governing equations consists of the continuity equations, the momentum equations in three space dimensions, the energy equation, the user equations for mass and mixture fraction, the equations for turbulence model, in this case the $k-\varepsilon$ model which incorporates buoyancy modification. The generalised governing equation for all variables is expressed in the form of equation [1]

$$\frac{\partial \rho \Phi}{\partial t} + div(\rho \vec{U} \Phi) = div(\Gamma_\Phi \nabla \Phi) + S_\Phi \qquad [1]$$

where Φ represents the fluid variable; ρ and $\vec{U}$ are the local density and velocity vector; Γ_Φ is the effective exchange coefficient of Φ ; S_Φ represents the source term for the corresponding variable Φ and time t is an independent variable.

Calculation of CO, CO_2 and O_2

The methodology for species calculation developed in[3, 4] is briefly described here. Denote ϕ the local equivalence ratio (LER) at a computational cell. A critical equivalence ratio, ϕ_{CR} [4], which can be derived from the combustion efficiency of the considered fire scenario, is used to partition the computational domain into two parts. A control region (CR) is defined as $\phi \geq \phi_{CR}$, in which the toxic gas levels are determined by local burning conditions

$$Y_i = \xi y_i(\phi, T) \qquad [2]$$

where ξ is the mixture fraction, $y_i(\phi,T)$ is the yield of species i and T is the temperature. The mass fraction of oxygen is calculated by the following equation

$$Y_{O2} = 0.23(1-\xi) - \xi y_{O2}(\phi, T) \qquad [3]$$

where $y_{O2}(\phi,T)$ is the consumption of oxygen per unit mass of the fuel . In the transport region (TR), where $\phi < \phi_{CR}$, the concentrations of a species are regarded as the result of transfer processes without chemical reaction and hence the mass fraction of species i (CO and CO_2) is given by a formula different from that in CR

$$Y_i = Y_i(\phi_{CR}) \cdot \xi / \xi_{CR} \qquad [4]$$

where ξ_{CR} is the mixture fraction corresponding to ϕ_{CR}. The mass fraction of oxygen in TR is given by

$$Y_{O2} = 0.23(1 - \xi / \xi_{CR}) + Y_{O2}(\phi_{CR}) \cdot \xi / \xi_{CR} \qquad [5]$$

Calculation of HCN

A generalised relationship between CO and HCN is developed in[6]. In equations [6] and [7], yields of CO and HCN are normalised with their maximum theoretical yields respectively

$$f_{CO} = y_{CO} / y_{CO}^{\max} \qquad [6]$$

$$f_{HCN} = y_{HCN} / y_{HCN}^{\max} \qquad [7]$$

Denote y_{SOFMR} the stoichiometric oxygen to fuel mass ratio (SOFMR, g/g). The normalised yields of HCN and CO can be correlated with y_{SOFMR} as

$$f_{\mathrm{HCN}} = (TANH(3.8 \times (y_{SOFMR} - 1.7) - 2.0)/1.3 + 1.2) \times f_{\mathrm{CO}} \qquad [8]$$

Correlation [8] has been validated with a wide range of nitrogen containing materials in[6]. Figure 1 shows comparison between the experimental relationships and predictions by equation [8] for six materials and it is clear that a good agreement has been achieved.

The calculation of HCN concentrations based on relationship [8] is described here. Similar to the calculation of CO and CO_2 with equation [2], the mass fraction of HCN can be calculated with its yield using equation [9]

$$Y_{HCN} = \xi \times y_{HCN}(\phi, T) \qquad [9]$$

From equation [2] for CO and equations [6-9], the mass fraction of HCN can be converted from the CO mass fraction by

$$Y_{HCN} = Y_{CO} \times y_{HCN}^{\max} \times (TANH(3.8 \times (y_{SOFMR} - 1.7) - 2.0)/1.3 + 1.2)/y_{CO}^{\max} \qquad [10]$$

The volume fractions of HCN and CO, X_{HCN} and X_{CO}, then have the following relationship

$$X_{HCN} = 1.037 \times X_{CO} \times y_{HCN}^{\max} \times (TANH(3.8 \times (y_{SOFMR} - 1.7) - 2.0)/1.3 + 1.2)/y_{CO}^{\max} \qquad [11]$$

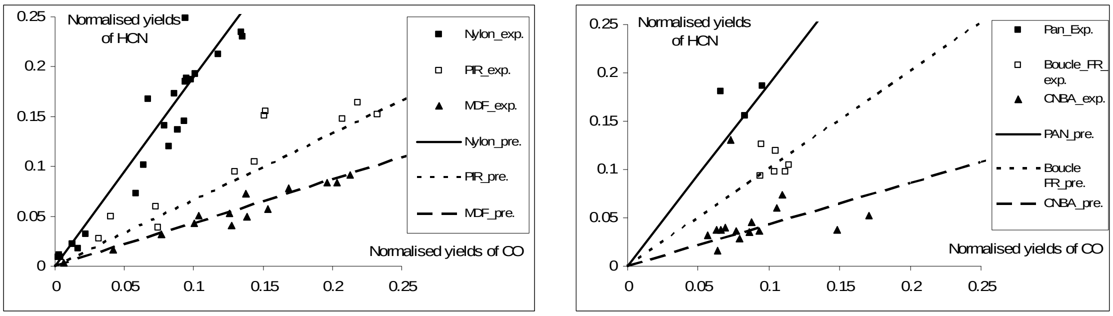


Figure 1. Measured relationship and predictions between normalised yields of CO and HCN.

SIMULATIONS AND RESULTS

Experiments and Simulations

Two fire scenarios selected from[8], the Ny4 fire and the Ny5 fire with nylon ($C_{12}H_{22}N_2O_2$) as the fuel, are simulated in this study. The schematic of the fire experiments is shown in Figure 2. The opening was 0.8 m wide with a soffit at 2.0 m. The height of the opening was 0.68 m and 0.45 m for the two scenarios respectively. A gas-sampling probe was placed diagonally from the top left corner to the middle of the other side of the opening for measuring the concentrations of species. The fire pan is 1.4 m^2. The ambient temperature was 20 ^{O}C. Figure 3 shows the fuel loss rates, which are converted from the measured HRRs with a heat of combustion of 3.0×10^7 J/kg. The simulation of the Ny5 fire excludes the complex ignition stage during the first 5 minutes.

In the simulations, the computational cells were 37,740 and 36,720 for the two fire scenarios respectively. The eddy dissipation combustion model (EDM)[9] is used for the calculation of heat release due to combustion. The extended LER toxicity model with equations [2-5] and [11] is used to calculate the concentrations of fire gases. As the inputs of the toxicity model, the yields of species are represented in the form of equation [12] and the parameters are listed in Table 1.

$$y_i(\phi) = y_{i\infty}\left[1 + \frac{\alpha}{\exp(\phi/\beta)^{-\varsigma}}\right] \qquad [12]$$

These parameters are derived from the experimental data collected from ISO TS 197000 tests from four different laboratories[5]. Figure 4 shows the derived correlation between the yields of CO and equivalence ratios and the experimental data. A default value of 1.0 for ϕ_{CR} in the toxicity model is used in this study, which means that the CR and TR are separated by the stoichiometric fuel-air interface. The averages of the predicted concentrations of fire gases at the top opening, which covers the gas probe, will be compared with the measured data.

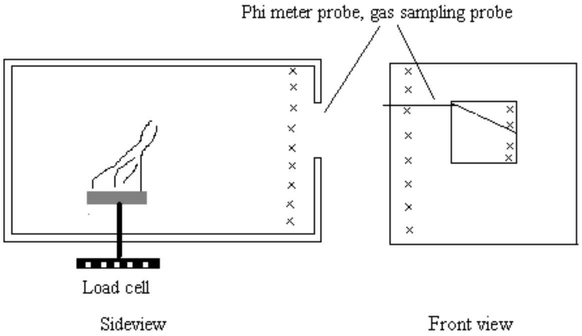


Figure 2. The test room (3.6 m × 2.4 m × 2.4 m) and the probe position in the opening

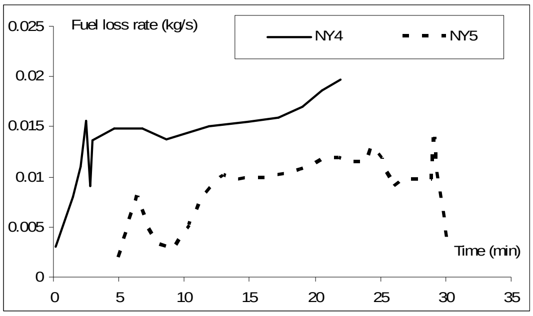


Figure 3. Fuel loss rates converted from HRRs

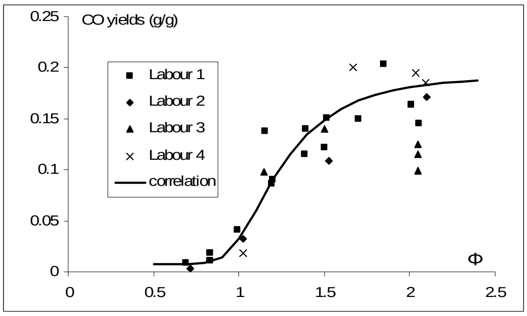


Figure 4. Yields of CO (Data from[7])

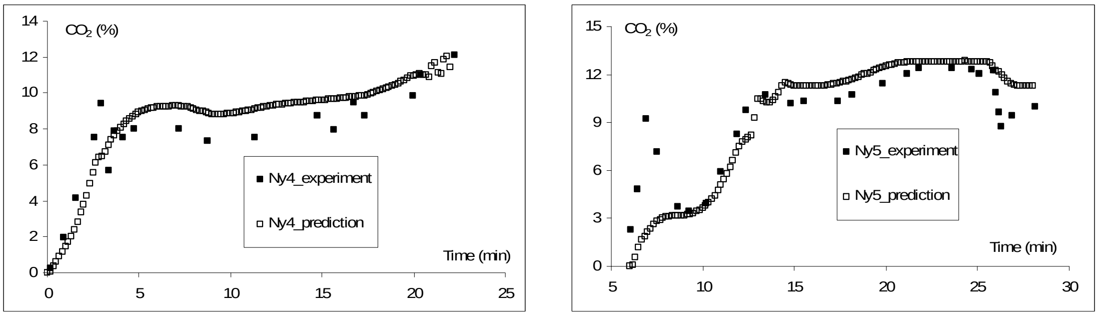
Table 1 Parameters for the yields of combustion products

	$y_{i,\infty}$ **(kg/kg)**	α	β	ς
CO	0.008	23	1.15	-5
CO_2	2.1	-1.0	1.55	-3.5
O_2	2.3	-1.0	1.55	-3.5

Results and Discussion

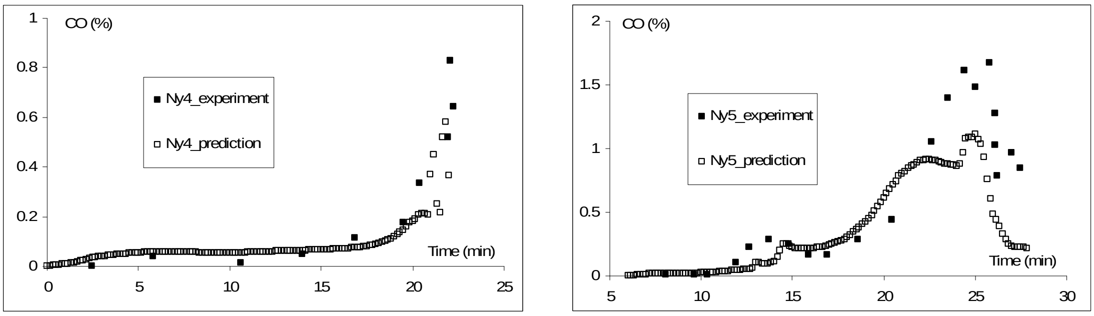
The profiles of temperatures have almost the same trends of CO_2 in the two fire scenarios and are not discussed here. The measured and predicted concentrations of CO_2, CO and HCN at the opening as functions of time are depicted in Figures 5-7. Table 2 gives the peak values of these properties. As seen in Figure 5, for the Ny4 fire, the measured CO_2 concentrations rapidly raised to 9.42% at 2.9 minutes, followed by a quasi-steady state. A maximum of 12.12% is observed just before water was added to the fire at 23 minutes. The predicted CO_2 concentrations essentially follow this trend and the peak value was under predicted by a relative error of 0.5% (Table 2). In the Ny5 fire, the measured CO_2 concentrations reaches a local maximum of 9.19% at 6.9 minutes and a local minimum of 3.43% at 9.3 minutes, and then was followed by a quasi-steady state between 14 and 25 minutes. The simulation failed to reproduce the local peak concentration of CO_2 at 6.9 minutes due to the omission of the fire during the ignition stage. However, very good agreement between the measured data and the predictions is achieved after 8 minutes. The peak concentration of 12.38% was under-predicted by a relative error of 3.6%.

As seen in Figure 6, the measured concentrations of CO in the Ny4 fire were less than 0.04% before 15 minutes and then increased to 0.83% at 22 minutes. The model predictions follow the measured trends well with a maximum of 0.64%. The measured CO concentrations in the NY5 fire were very low before 10 minutes and then increased with a local maximum of 0.28% at 13.7 minutes and a peak value of 1.67% at 25.8 minutes. The simulation has reproduced the two maximums although the peak value was under-predicted by a relative error of 33.5% (Table 2).



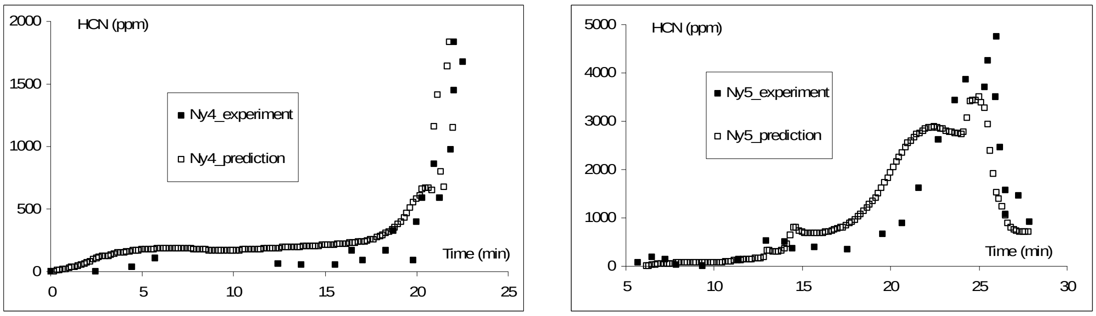
(a) (b)

Figure 5. Measured and predicted concentrations of CO_2 at opening for (a) Ny4 and (b) Ny5.



(a) (b)

Figure 6. Measured and predicted concentrations of CO at opening for (a) Ny4 and (b) Ny5.



(a) (b)

Figure 7. Measured and predicted concentrations of HCN at opening (a) Ny4 and (b) Ny5.

Table 2. Measured and predicted averages and peak temperatures and species concentrations.

	Ny4			**Ny5**		
	Experiment	**Prediction**	**Error (%)**	**Experiment**	**Prediction**	**Error (%)**
CO_2 (%)	12.12	12.06	0.5	12.38	12.83	3.6
CO (%)	0.83	0.64	22.9	1.67	1.11	33.5
HCN (ppm)	1833	1836	0.2	4746	3501	26.2

The curves of the measured HCN concentrations in the two scenarios (Figure 7) are quite similar to those observed in CO concentrations. The calculated HCN concentrations from the predicted CO concentrations using equation [11] essentially follow the measured trends in both fire scenarios. The peak HCN concentrations of 1833 ppm in the NY4 fire and 4746 ppm in the NY5 fire are over-predicted by 3 ppm and under-predicted by 1245 ppm, with relative errors of 0.2% and 26.2% respectively (Table 2). However, the measured HCN concentrations before 20 minutes in the Ny4 fire and between 15 and 22 minutes in the Ny5 fire are much over-predicted (Figure 7). As known in [8], the fires were over ventilated during these periods of time in the two fire scenarios. This further demonstrates the finding in [6] that the generalised relationship [8] produced large relative errors in strongly fuel lean fire scenarios.

CONCLUSIONS

Two fire scenarios have been simulated in this study. In the simulations, the concentrations of CO, CO_2 and O_2 are calculated with a LER based toxicity model while the concentrations of HCN are converted from the predicted CO concentrations using a simple relationship. The model predictions of all species at the opening as functions of time essentially follow the measured trends. The relative errors for peak concentrations of CO_2 are no more than 3.6% for the two fire scenarios. The predicted peak concentrations of CO and HCN are acceptable with relative errors no more than 33.5%. While the toxicity model is capable of producing reasonably accurate predictions of CO, CO2 and HCN concentrations, large errors in HCN predictions for strongly fuel lean fires may be produced.

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