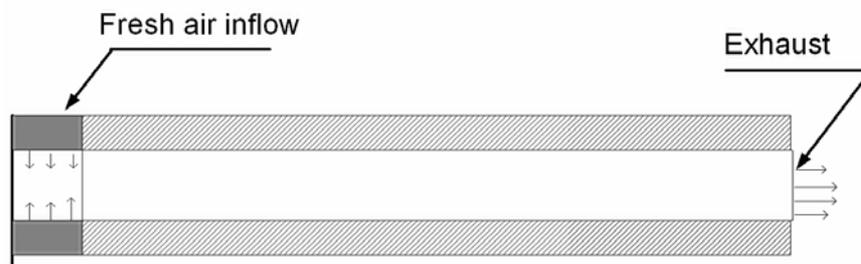
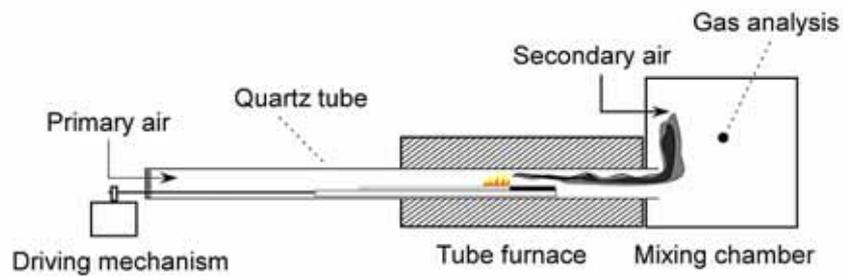


# Effect of residence time on fire gases – experiments and simulations



projekt 333-051

Heimo Tuovinen and Per Blomqvist



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## Abstract

An analysis of ageing of fire gases has been made using both laboratory tests and CFD calculations. Laboratory tests have been conducted with the so called "Purser furnace" where smoke gases were produced continuously. Residence time and temperature was varied in a mixing chamber connected to the furnace. The gases were analysed with FTIR. The fuel used was Nylon-6,6.

In the calculations the CFD code SOFIE (Simulation of Fires in Enclosures) was used. The simulations were made in a computer model of small rooms, volumes 1 and 2 m<sup>3</sup>. An exhaust pipe was connected through which the fire gases were exhausted to the open atmosphere. By varying the flow velocity in the pipe the residence time in the pipe could be varied. Fresh air inflow sources in the pipe were used to examine the effect of the air mixing to ageing of fire gases.

Lastly, a large scale simulation in the room according to ISO 9705 connected to a smoke duct was used, to reconstruct a real fire test scenario commonly used in fire laboratories.

Key words: CFD, fire products, HCN, FTIR, ageing of smoke

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## **Preface**

This project was supported by the Swedish Fire Research Board (BRANDFORSK Project 333-051) which is gratefully acknowledged. The work conducted uses a computer model that was developed in another Brandforsk project (321-011).

## Summary

Ageing of fire gases from combustion of nitrogen containing fuel is investigated. The investigation was conducted through small scale laboratory tests and CFD calculations. The test apparatus used was of "Purser furnace" type, which is capable to produce smoke continuously and vary the temperature and flow time (residence time). Gases were analysed with FTIR (Fourier Transform Infrared Spectroscopy measurement technique). The fuel used was Nylon-6,6.

CFD simulations were made using the computer code SOFIE (Simulation of Fires in Enclosures) with synthetic fuel, a mixture of methylamine and ethylene with a mixture ratio ethylene/methylamine = 3, which results in a nitrogen content comparable with Nylon-6,6. Most CFD simulations were made in a small room, volume 2 m<sup>3</sup>, except for a few initial simulations, which were made in a room with a volume of 1 m<sup>3</sup>. Two large scale simulations with a room with dimensions according to ISO 9705 were also made. A laminar flamelet model was used to calculate the chemistry.

This study focused onto investigating the production of a toxic specie, hydrogen cyanide (HCN). Also CO, CO<sub>2</sub>, and O<sub>2</sub> concentrations were calculated and results presented in the report. In the experimental part of the investigation also other pollutants such as ammonia (NH<sub>3</sub>) and NO<sub>x</sub> were measured.

Measurements show that the HCN concentration is reduced in fire gases when oxygen is present at temperatures about 600 °C, which is a representative fire gases temperature in room fires. The reduction of HCN was about a factor of 3 when the residence time was increased from 5 s to 14 s.

About the same reduction was estimated from calculations in the same temperature range also at much lower HCN concentrations. Also at 500 °C the calculated HCN concentration is reduced by a factor of 3 when the residence time is increased from 5 s to 15 s, even though the HCN concentration is very small.

Calculations show also that in rich mixtures, i.e. mixtures with low or lacking oxygen concentration, a higher temperature results in a higher HCN concentration. Thus, the HCN concentration is related to temperature and ventilation.

The large scale simulations with heat release rates of 600 kW and 900 kW showed that the gas concentration did not vary noticeably in the gas during its passage through the whole length of the exhaust gas duct.

## Sammanfattning

Åldring av brandgaser från kväveinnehållande bränslen har undersökts. Undersökningen gjordes med laborietester i liten skala samt CFD beräkningar. I experimenten användes en så kallad Purser ugn, vilken ger en kontinuerlig rökproduktion. I en kammare efter ugnen varierades temperatur och uppehållstiden. Brandgaserna analyserades med FTIR (Fourier Transform Infrared Spectroscopy). Nylon 6-6 användes som bränsle.

CFD simuleringar gjordes med datorprogrammet SOFIE (Simulation of Fires in Enclosures) med syntetiskt bränsle, en blandning av metylamin och etylen, blandningskvoten metylamin/etylen = 3, som har nära samma kväveinnehåll som Nylon 6-6. De flesta CFD simuleringarna utfördes i ett litet rum med volymen  $2\text{m}^3$ . Några inledande simuleringar gjordes i ett rum med volymen  $1\text{m}^3$ . Två simuleringar i stor skala i ett rum med dimensioner som i ISO 9705 gjordes också. Kemin beräknades med laminar flamelet modellen.

Undersökningen var koncentrerat på vätecyanid (HCN) men också koncentrationer av CO, CO<sub>2</sub> och O<sub>2</sub> beräknades och resultaten redovisas i rapporten. I den experimentella delen undersökningen omfattade också föroreningar som ammoniak (NH<sub>3</sub>) och NO<sub>x</sub> uppmättes.

Mätningar visar att HCN koncentrationen i brandgaser minskar när syre är närvarande vid temperaturer ca 600 °C, vilket är ett representativ värde i brandgaser vid rumsbränder. Reducering av HCN var ca faktor 3 när uppehållstiden ökades från 5 s till 14 s.

Ungefär samma reduktion erhöles med CFD beräkningarna vid samma temperatur även vid betydligt lägre HCN koncentrationer. Även vid 500°C minskade koncentrationer med ökning av uppehållstiden från 5 s till 15 enligt beräkningar även då HCN koncentrationen var mycket låg.

Beräkningarna visar också att vid rika blandningar, dvs. vid blandningar som innehåller lite syre eller syret saknas helt, blir HCN koncentrationen högre vid högre temperatur.. Således är HCN koncentrationen relaterad till temperaturen och ventilationen.

Simuleringar av ISO 9795 test visade att gaskoncentrationerna varierade inte märkbart under passage genom hela längden av ventilationskanalen. Således är det okönsligt var man väljer sin mätpunkt i rökkanalen.

## Introduction

There are many examples of fires in which most victims have not had any severe burns. They have been killed due to toxic gases. For example in a fire in a discotheque in Gothenburg in 1998, 63 people died mostly due to inhalation of toxic smoke [1]. In a hospital fire in Växjö in 2003 died one person in a room 40 m away from the fire, even though the fire was relatively small involving only one room [2]. The fire in the ferry Scandinavian Star in 1990 killed 159 people. Only a few had an injury due to heat from the fire.

Recently, in December 2006, a catastrophic hospital fire occurred in Moscow, which demanded 45 female person's (43 patients and two staff members) life [3]. The interior walls of this building were covered by plastic material, which generated extremely dangerous smoke. The victims lost rapidly their consciousnesses after inhaling the smoke. When the local fire brigade arrived about four minutes after the alarm were all 45 victims already dead.

Toxicity of smoke depends largely on the material that is burning, burning behaviour, fire size and ventilation conditions in the fire room. Lack of oxygen in the air is a major reason that toxic gases are formed in fires. Oxygen is always limited in rooms with small openings in relation to the fire size. Examples of locations where fires easily become under-ventilated are road tunnels, locations under ground (as under-ground stores), subway trains, buildings with long corridors, such as hospitals and passenger ships. One of the most dangerous gases is hydrogen cyanide, HCN. HCN is mainly formed from nitrogen containing fuels. Most common materials in our home and industry environment contain nitrogen [4, 5]. Many materials also emit dangerous particles as isocyanides, which in very small concentrations may cause allergies to person coming in contact with them.

The content of toxic smoke changes during the transport of the smoke-gases from the fire room. How the gas content is changed depends on several factors, such as a type of building, the length of the pathway the gases are transported, mixing of air during the transport and the temperature of the gas.

In hospitals or office buildings usually small rooms are located along a corridor. The smoke is transported more slowly in horizontal corridors and thus might aggregate and become thicker due to slower transport and slower mixing with air. The patient rooms contain mattresses (of usually polyurethane) which generate large amount of toxic products such as HCN and CO.

Fires in passenger ship cabins are also especially dangerous, because ventilation in cabins is usually low. Even a small fire in such a case would rapidly become under-ventilated, which generates gases with high content of toxic products, because the fuel in the cabin usually consists of materials such as polyurethane mattresses. Fire in a single patient room in Växjö hospital produced toxic gases much enough to be able to kill one person 40 metres from the fire [2].

Usually toxic gases are measured in one room scenarios in a duct connected to the room. One could however wonder how valid these results are since there is a possibility that the gas concentration changes during the gas transport to the measuring point.

The aim of this project is to examine how gas concentration changes as a function of transport conditions and length. In addition is the validity of the existing flamelet model for calculation of toxic species (foremost HCN and CO) in the CFD code SOFIE (Simulation of Fires in Enclosures) examined.

The investigation should clarify how the results from gas concentration measurements in large scale fire tests are interpreted best. Can the measurements in the duct be transferred to the concentrations far from a real fire?

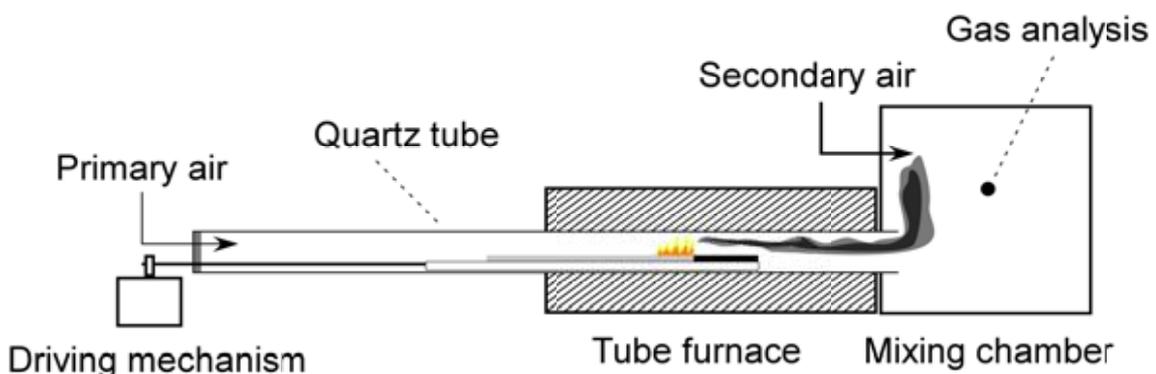
The study is conducted using small scale test together with CFD simulations. Finally a full scale test is simulated.

# 1 Experiments

The ageing of smoke gases containing HCN was studied in small scale experiments. The experimental set-up used consisted of a primary test apparatus capable of continuously producing smoke gases from constant combustion conditions. The test apparatus had a mixing/measurement chamber attached, which made it possible to make various types of experiments by changing the residence time, temperature, etc., in the chamber. In some of the tests, the smoke gases from the mixing box were led through a second tube furnace. The temperature of the second tube furnace was set to 600°C and the ageing at high temperatures could thus be studied. FTIR measurement technique was used for analysing HCN as well as other smoke gas components. All tests were made with Nylon-6,6 as fuel.

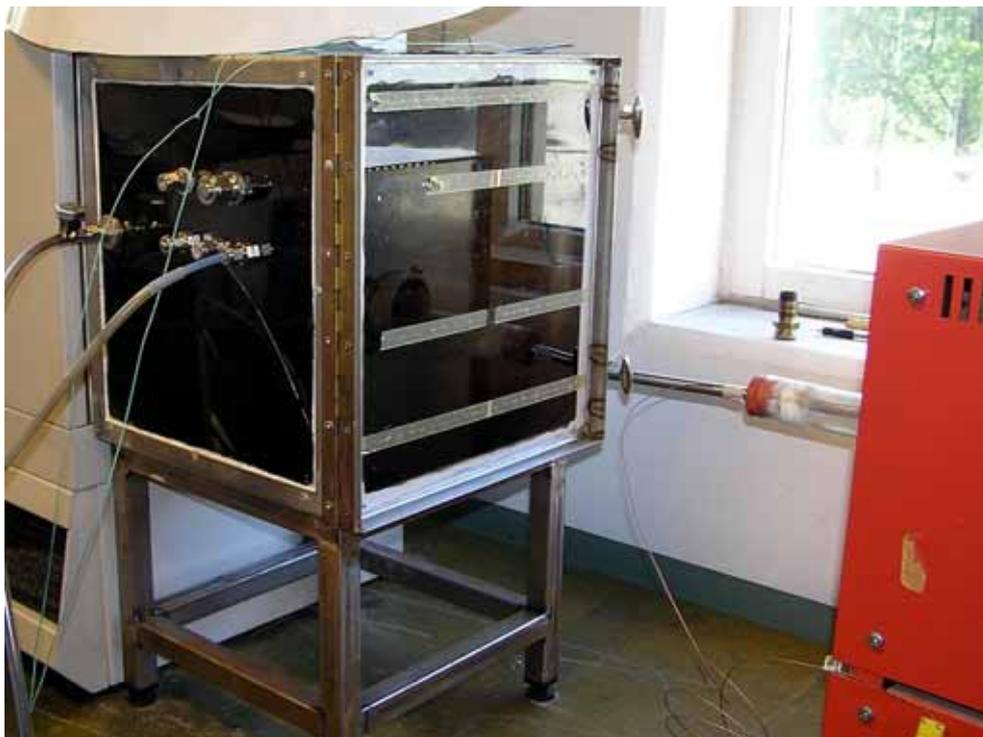
## 1.1.1 Test set-up and measurements

The primary test apparatus used was constructed in close agreement with the specifications given in BS 7990:2003 [6]. This test apparatus is commonly referred to as the “Purser furnace”. The apparatus consists of a tube furnace, a driving mechanism for continuously introducing the sample into the quartz tube of the furnace and a mixing chamber for the smoke gases from the furnace. The apparatus is schematically shown in Figure 1. The length of the tube furnace was 800 mm and the diameter was 50 mm. The quartz tube had a length of 1700 mm and an outer diameter of  $47.5 \pm 1$  mm with  $2 \pm 0.5$  mm wall thickness. A quartz sample boat with a length of 800 mm was used. The mixing chamber had part of the ceiling and the back wall in contact with the tube furnace made in stainless steel and the remaining walls and the bottom made of 4 mm thick PMMA. The dimensions of the chamber were 315 mm (depth)  $\times$  315 mm (width)  $\times$  345 mm (height), giving a volume of 34 litres. A driving mechanism with an advance rate of nominally 40 mm/min, but capable of more than 60 mm/min, was used for introducing the sample into the quartz tube. Primary air was introduced into the quartz tube with flow rates between 2 l/min and 15 l/min. Secondary air for dilution and cooling of the smoke gases was introduced in the mixing chamber.



**Figure 1** Schematic picture of the primary test apparatus.

In some of the tests the smoke gases from the mixing chamber of the primary tube furnace were led to a second tube furnace through a short length of steel pipe. The connection between the two furnaces is shown in Figure 2. The second tube furnace had a length of 900 mm and a diameter of 70 mm, a quartz tube with a diameter of 40 mm was used. The temperature of the second tube furnace was set to 600°C.



**Figure 2** The connection between the mixing chamber of the primary tube furnace (left) and the secondary tube furnace (red coloured to the right).

Measurements of the HCN concentration were normally made on the smoke gases in the mixing chamber. But in the experiments including the secondary tube furnace measurements were made on the smoke gases just before the second furnace alternatively after the second furnace. Note that the probe for gas analysis is not shown in Figure 2.

Time resolved measurements of combustion gases were made using a BOMEM MB 100 FTIR spectrometer [7]. The spectrometer was equipped with a heated gas cell (volume = 0.92 l, path-length = 4.8 m, temperature = 150°C). A spectral resolution of 4 cm<sup>-1</sup> was used, with 4 averaged spectra (based on 3 full scans) recorded per minute. Smoke gases were continuously drawn from the sampling point to the FTIR with a sampling rate of 4 l min<sup>-1</sup> using a probe with a cylindrical ceramic filter. Both the filter and the gas sampling line (4 mm i.d. PTFE, poly tetra fluoro ethylene, tubing) were heated to 180°C. The proper function of the FTIR equipment was verified by measurement on calibration gas. The FTIR data (spectra) was quantitatively evaluated for carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), hydrogen cyanide (HCN), nitrogen monoxide (NO), nitrogen dioxide (NO<sub>2</sub>) and ammonia (NH<sub>3</sub>). The oxygen concentration in the mixing chamber was continuously measured using a Servomex xentra 4100 O<sub>2</sub>-analyser.

The Purser furnace has been shown to be able to model a wide range of combustion conditions by using different combinations of temperature and ventilation [8]. The ventilation condition, *i.e.* the equivalence ratio ( $\phi$ )<sup>i</sup>, in the tube furnace is principally determined by the relation between the primary air flow rate and the fuel flow rate into the combustion zone. The fuel flow rate is dependent on the fuel loading and the feeding rate of the sample boat.

The method for managing the ventilation condition in a Purser furnace test is to determine the stoichiometric fuel-to-oxygen ratio for the test material and then selecting an actual

<sup>i</sup> The equivalence ratio ( $\phi$ ) is the quotient of the actual fuel to air ratio and the stoichiometric fuel to air ratio.

fuel-to-oxygen ratio for achieving the desired equivalence ratio [6]. The first task in the experiments was to find stable “base-line” test conditions for the primary tube furnace that would produce significant amounts of HCN.

Two series of tests were made. In the first series of tests the influence on HCN from variations of residence time of the smoke gases at rather low temperatures were investigated. In the second series of tests the influence from different residence times at 600°C was investigated. At least duplicate tests were made in all cases.

The first series of tests is described in Table 1. The concentration of HCN was measured in the mixing chamber and the temperature of the primary tube furnace was 825°C in all tests. The “base-line” test conditions selected are those of test condition 2, representing an equivalence ratio ( $\phi$ ) of 2.0, *i.e.* under ventilated conditions. The test conditions 2 produced HCN equivalent to a concentration of ~700 ppm in the mixing chamber.

The residence time in the mixing chamber for the smoke gases was 41 seconds for test condition 2. Tests conditions 3-6 do all have the same residence time as test condition 2. The influence of other parameters was investigated in these tests. For test conditions 3 the secondary air was replaced with N<sub>2</sub> as one way to investigate if any oxidation of HCN was taking place in the mixing chamber at the relatively low temperature in the chamber (< 50°C). For test conditions 4-6 the fuel flow was changed but the total flow through the box was withheld.

Test conditions 7 and 8 were attempts to regulate the concentration of HCN to keep it the same as for test condition 2, and to vary the residence time for this constant concentration. In order to do this, the measured HCN data from test condition 4 and test condition 6 was used to calculate the appropriate secondary air flows for test condition 7 and test condition 8, respectively. For test conditions 9 and 10 the settings for the tube furnace were the same as for test conditions 2, and the production of HCN from the furnace was thus theoretically the same as for test conditions 2. The secondary air flow rate was changed to half respectively double the residence time compared to test conditions 2.

For tests conditions 11 and 12 the secondary air was pre-heated by the means of heated tubing, to increase the temperature of the smoke gases in the mixing chamber to approximately 90°C. This was made in order to investigate if a moderate increase in temperature would influence HCN during ageing of the smoke gases.

**Table 1** Description of the first series of tube furnace tests.

Test condition	Test description	Fuel load (mg/mm)	Feeding rate (mm/min)	Fuel flow (mg/min)	Primary air flow (l/min)	Fuel/air ratio, tube (mg/l)	Secondary air flow (l/min)	Total flow trough box (l/min)	Fuel/air ratio, box (mg/l)	Residence time in box (s)
2	“base-line test”	25	40	1000	4.06	246	45.94	50	20	41
3	N <sub>2</sub> used for secondary flow	25	40	1000	4.06	246	45.94	50	20	41
4	Fuel flow reduced I	25	20	500	2.03	246	47.97	50	10	41
5	Fuel flow reduced II	12.5	40	500	2.03	246	47.97	50	10	41
6	Fuel flow increased	50	40	2000	8.13	246	41.87	50	40	41
7	Increased residence time, HCN <u>conc.</u> as test 2	25	20	500	2.03	246	14.87	16.9	30	121
8	Reduced residence time, HCN <u>conc.</u> as test 2	50	40	2000	8.13	246	95.56	103.7	19	20
9	Increased residence time, HCN <u>prod.</u> as test 2	25	40	1000	4.06	246	20.94	25	40	82
10	Reduced residence time, HCN <u>prod.</u> as test 2	25	40	1000	4.06	246	95.94	100	10	20
11	100°C in box, else as test 7	25	20	500	2.03	246	14.87	16.9	30	121
12	100°C in box, else as test 2	25	40	1000	4.06	246	45.94	50	20	41

The second series of tests is described in Table 2. In this series of tests the influence from different residence times at 600° was investigated by leading the smoke gases from the mixing box trough a secondary tube furnace. For test conditions 13 all settings for the primary tube furnace were the same as for test conditions 2. The gas analysis was made on the smoke gases just before the inlet to the secondary tube furnace to investigate any influence of the transport from the mixing chamber. For test conditions 14 and 15 the gas analysis was made after the secondary tube furnace to investigate the influence on HCN from different residence times at 600°.

**Table 2 Description of the second series of tube furnace tests.**

Test condition	Test description	Total flow trough box and secondary tube furnace (l/min)	Residence time in box (s)	Residence time in secondary tube furnace (s)
13	As test 2. Gas analysis <u>before</u> secondary tube furnace.	50	41	5
14	As test 2. Gas analysis <u>after</u> secondary tube furnace.	50	41	5
15	As test 7. Gas analysis <u>after</u> secondary tube furnace.	16.9	121	14

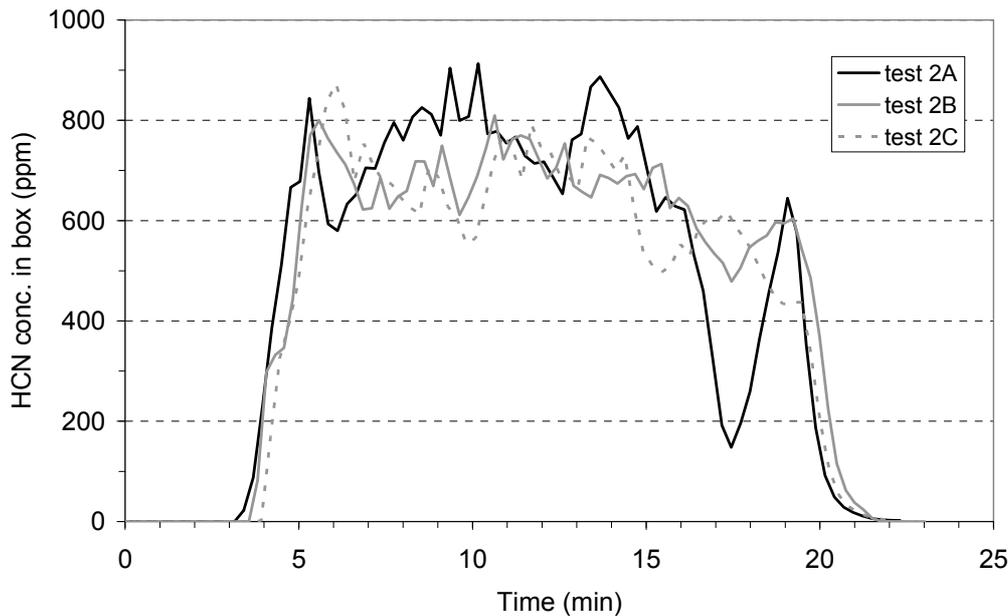
Some additional tests were made which are described in Table 3. These tests will not be specifically discussed in this report, but might be of interest for other purposes. Test conditions 1 and 1\_2 are well-ventilated tests conditions used in order to find the proper settings for the “bas-line test conditions”, test conditions 2. The conditions in 4A and 7A are strongly under-ventilated.

**Table 3 Description of supplementary tube furnace tests.**

Test condition	Test description	Fuel load (mg/mm)	Feeding rate (mm/min)	Fuel flow (mg/min)	Primary air flow (l/min)	Fuel /air ratio, tube (mg/l)	Secondary air flow (l/min)	Total flow trough box (l/min)	Fuel /air ratio, box (mg/l)	Residence time in box (s)
1	Well ventilated test I	25	40	1000	10	100	40	50	20	41
1_2	Well ventilated test II	25	40	1000	15	100	35	50	20	41
4A	Strongly under ventilated test	25	40	500	2.03	246	47.97	50	10	41
7A	Strongly under ventilated test	25	40	500	2.03	246	14.87	16.9	30	121

## 1.1.2 Results

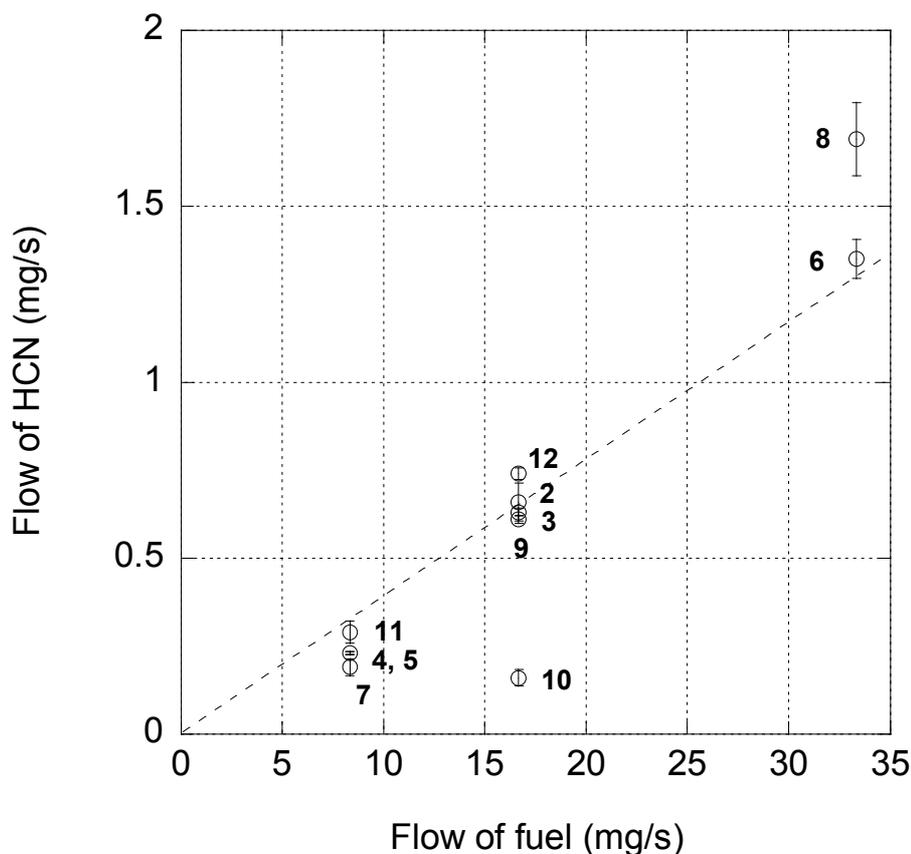
An assessment of the main results from the experiments regarding HCN will be presented here. The complete experimental data can be found in Appendix A.



**Figure 3** Concentration of HCN in the mixing chamber in the triplicate tests with “test conditions 2”.

The “base-line” test conditions (test conditions 2) produced HCN equivalent to an average concentration in the mixing chamber (from triplicate tests) of 719 ppm. The standard deviation ( $\sigma$ ) for these tests was 58 ppm which equals a relative  $\sigma$  of 8 %. The concentration data from the triplicate tests for test conditions 2 are shown in Figure 3. The average concentration was calculated from the time period 7.5 – 15 minutes where the production of HCN was the most stable. The combustion conditions were adjusted in all tests such that they would be the same as those for test conditions 2, *i.e.*, with a  $\phi$ -value of 2. If this theoretical basis was sound, any (larger) deviations in HCN would be due to reactions after the primary tube furnace.

Data on HCN from the tests in the first experimental series is presented in Figure 4. The data plotted is the fuel flow into the primary tube furnace versus the flow of HCN out from the primary tube furnace. The flow of HCN was calculated from the HCN concentration measured in the mixing chamber by considering the dilution of the primary air flow with the secondary air flow. The fuel flow was given as the feeding rate of Nylon into the tube furnace is known. The plot in Figure 4 is rather convenient as a first analysis of the data as the quotient of the flows of fuel and HCN equals the yield of HCN. Further, as combustion conditions giving a  $\phi$ -value equal of 2 were applied in all tests, the yield of HCN would be constant - that is if there are no reactions that influence HCN after the primary tube furnace. One thing to consider is, however, the different combinations of fuel load, feeding rate and primary air flow used in order to end up on a  $\phi$ -value of 2. The recommended values for these parameters [6] are those used for test conditions 2, extremes in parameter choice could influence the combustion conditions and thus the yield of HCN from the combustion.

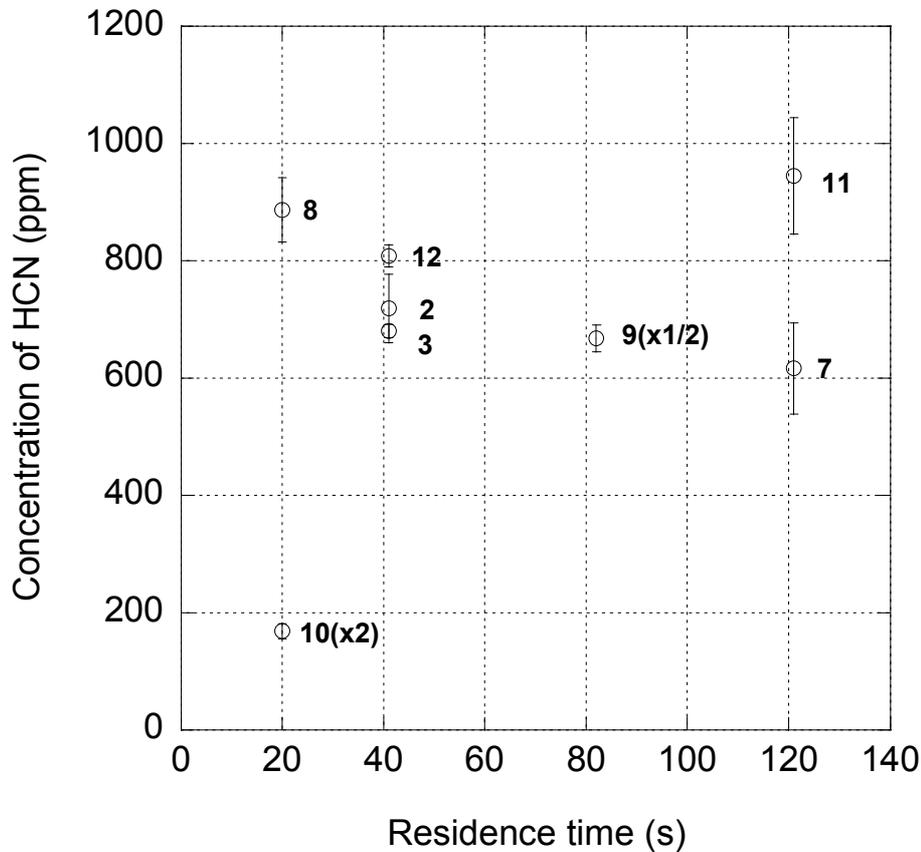


**Figure 4** Data from the first series of tests. Mean values with standard deviation are given in the plot. The flow of HCN out from the primary tube furnace as calculated from measurements of HCN in the mixing chamber is plotted vs. the flow of fuel into the primary tube furnace. The quotient of these parameters equals to the yield of HCN.

The dashed line in Figure 4 was drawn between origin and the data point for test conditions 2 and represents a constant value of the HCN-yield from different values of the fuel flow. The yield value is the slope of the line. One can see from Figure 4 that the test conditions with the data point that deviates the most from the dashed line (i.e. that have the most deviating yield value) is test conditions 10. For these conditions the settings for the primary tube furnace was identical as for test conditions 2, but the value of the secondary air flow was almost 96 l/min, the highest secondary air flow used (see Table 1). The concentration data of the tests made with these conditions was very scattered with large fluctuations. Test conditions 8 used the same settings for the tube furnace as test conditions 6, but also in this case with a secondary air flow of 96 l/min. The concentration data from these test conditions was not scattered, but the data point for test conditions 8, in Figure 4, deviates significantly from the dashed line and the data point for test conditions 6. On the basis of this information it could be reasonable to assume that the high secondary flow has influenced the combustion in the tube furnace and that the data from test conditions 10 and 8 is difficult to interpret regarding ageing effects on HCN.

Also in Figure 4, it is noteworthy that test conditions with a fuel flow of 8.3 mg/s (equally to 500 mg/min) show data points below the dashed line, *i.e.* the yields of HCN for these test conditions are lower than the yield for test condition 2. This shows that the lower fuel

flow with an accompanying lower primary air flow used for these tests actually must have influenced the combustion conditions and resulted in a lower yield of HCN.



**Figure 5** Data from the first series of tests. Mean values with standard deviation are given in the plot. The concentration of HCN in the mixing chamber is plotted vs. the residence time in the mixing chamber.

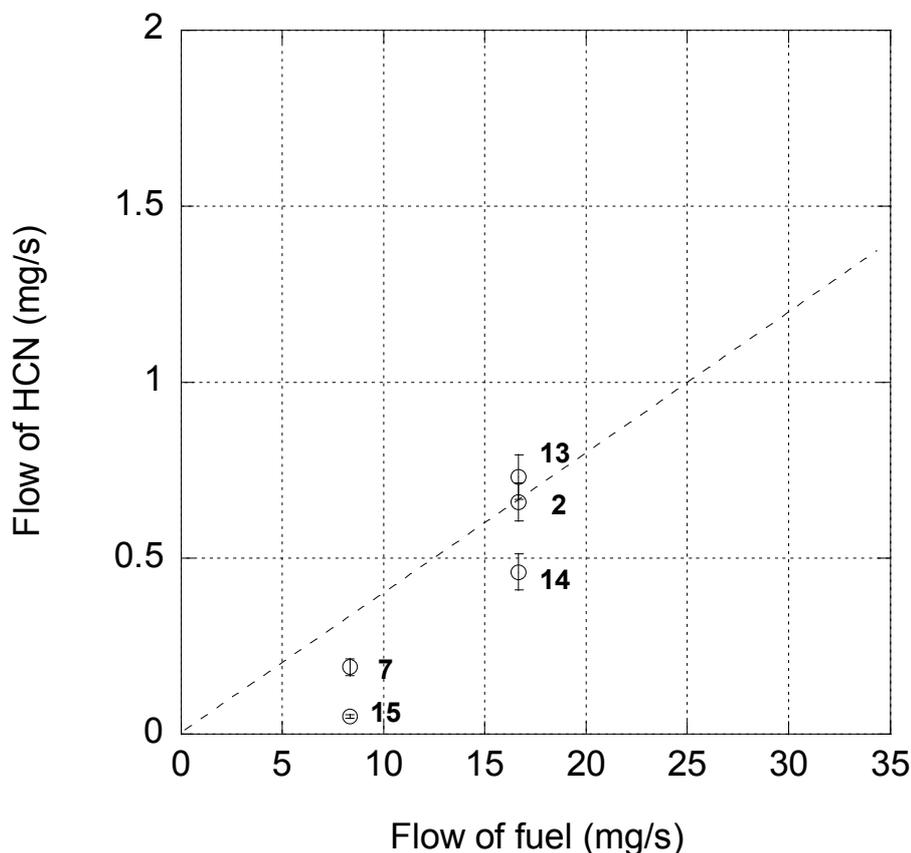
The average concentration of HCN for the resulting different residence times for the test conditions investigated are shown in Figure 5. The concentration levels shown in Figure 5 are as measured in the tests except in the cases of test conditions 10 and 9. In these cases the measured concentrations are scaled with a dilution factor compared with test conditions 2.

If disregarding the results from test conditions 10 and 8, which probably are influenced from the high secondary air flow used in these tests, it can be seen that the residence time in the mixing box with a low temperature of the diluted smoke gases does not have any traceable influence on the HCN-concentration. One can estimate that the data from both test condition 9 and test conditions 7 are on the same level as the results from test conditions 2.

For a higher temperature of the diluted smoke gases, however, the residence time seems to have an influence on the HCN-concentration. The results for test conditions 11 and 12, where the temperature in the mixing box was approximately 90°C, show an increase with increased residence time.

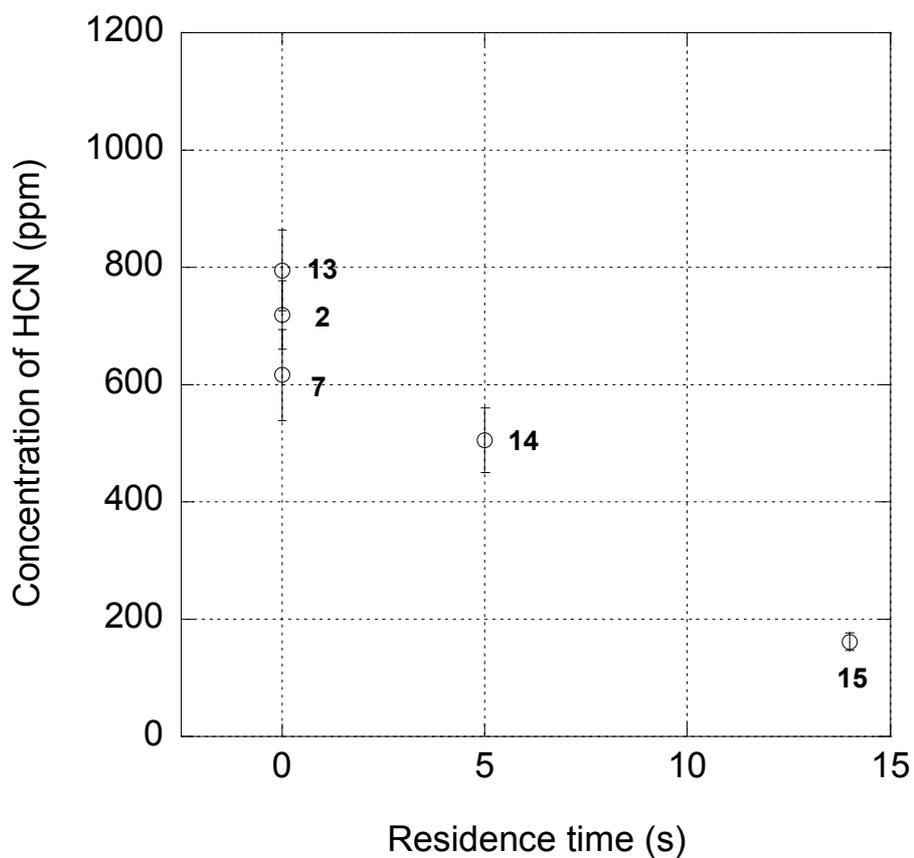
The results from test series 2 (i.e. test conditions 14 and 15) where the smoke gases from the mixing box passed a secondary tube furnace with a furnace temperature of 600°C are given in Figure 6 and Figure 7.

The flow of HCN found from measurements is plotted versus fuel flow in Figure 6. The results from test conditions 2 and 7 from measurements in the mixing box are included as reference. It can be seen from the results in Figure 6 that the amount of HCN before the secondary tube furnace (test conditions 13) are comparable with that in the mixing box (test conditions 2). It is further clear from the results for test conditions 14 and 15 that a significantly lower amount of HCN is found after the secondary tube furnace.



**Figure 6** Data from the second series of tests (test 13-15) compared to corresponding tests from the first series. Mean values with standard deviation are given in the plot. Data points 14 and 15 represent HCN data from measurement after the secondary tube furnace (furnace temperature 600°).

The concentration of HCN is plotted versus the residence time in the secondary tube furnace in Figure 7. The results from test conditions 2 and 7 from measurements in the mixing box are included as reference. The results show that the concentration of HCN clearly decreases with residence time at 600°C.



**Figure 7** Data from the second series of tests (test 13-15) compared to corresponding tests from the first series. Data points 14 and 15 represent HCN data from measurement after the secondary tube furnace (furnace temperature 600°). Mean values with standard deviation are given in the plot. The concentration of HCN is plotted vs. the residence time in the secondary tube furnace.

## 2 CFD simulations

In order to further investigate the impact transport times and transport conditions has on the gas concentrations CFD simulation both of the small scale experiments and a full-scale experiment are simulated using the CFD-code SOFIE

### 2.1 Computer code SOFIE

SOFIE has been available for fire researchers for the last decade. The code has been developed at Cranfield University in UK with contribution from several leading fire laboratories in Europe including SP Technical Research Institute of Sweden. Although it is a relatively new code, it has been successfully used to simulate fires in several types of enclosures [1, 2, 9-11].

SOFIE employs most basic features needed for computation of fluid dynamics problems and several additional sub-models specifically related to fire and combustion simulations, such as combustion, turbulence, radiation, heat transfer and soot formation. The basic code includes several optional solvers. Two widely used combustion models are: the Eddy break-up [12], modified by Magnussen [13], and the laminar flamelet model [14]. The  $k - \epsilon$  turbulence model with buoyancy production modification term is used for calculation of turbulence. For calculation of the radiation exchange between fluid and solid walls of the enclosure, a discrete transfer model (DTRM) [15] is available. Soot formation (nucleation, coagulation and surface growth) and oxidation can be modelled using Magnussen (Tesner) model or the Two-Scalar Transport model (flamelet source terms).

In a previous project [16,17] the laminar flamelet model in SOFIE was further developed to take the chemistry of nitrogen containing fuels into account. It is based on a detailed chemical kinetic of a synthetic fuel, a mixture of ethylene and methylamine [16, 17]. The chemical scheme consists of several thousands of elementary reaction steps. The flamelet model is specially made for calculation of under-ventilated fires, by taking the effect of recycling of fire gases back to fire into account. Further the radiation and the effect of turbulence are included in the calculation of chemistry.

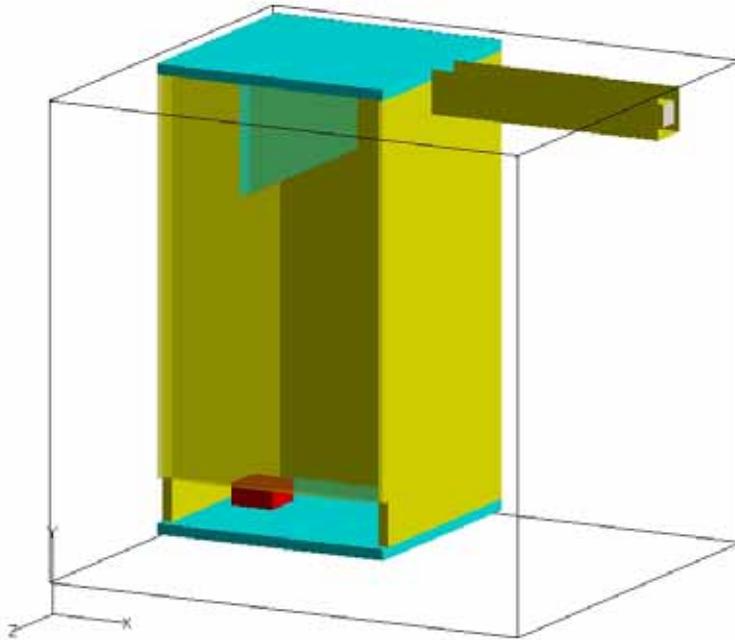
### 2.2 Simulations in a small box

The tube furnace tests used in the investigations are almost impossible to model exactly with SOFIE since the gas mixture of combustion gases estimated in the experiments cannot be used as input because the flamelet model needs a fuel exactly the same as the flamelets are calculated for. Therefore a mixture of methylamine and ethylene was used and combusted in box connected to a pipe where residence time could be varied

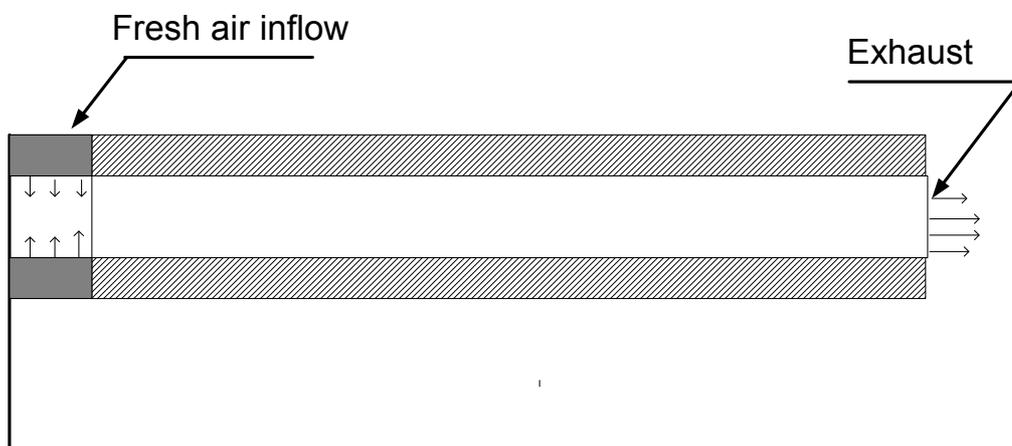
Prior to the small scale experiments a number of simulations were made in various small scale room configurations with different rate of heat releases and residence times. To simulate the ageing of fire gases a computer model of a box was needed to collect the fire gases. The box should preferably have well-stirred reactor conditions. The fire gases were then exhausted from the box through a pipe of length 1.0 or 1.5 metres. By keeping the exhaust velocity constant, a desired residence time of the gas passing the pipe was estimated. Several trial configurations were made in order to find a stable solution. These trial simulations are presented in Appendix B. Once a stable solution was found residence time and other transport properties were varied.

It was found that in most cases the gas concentration in the pipe did not change noticeably even for long residence times. The reason for this was that the fire gases, before entering into the tube, had been in the gas layer for a long time, i.e. in the same condition as in the pipe, that further residence time in the pipe was short compared to the total residence time.

Figure 8 shows the scenario with the horizontal exhaust pipe. Fresh air flows through four 10 cm x 10 cm inflow sources placed on inner boundaries of the pipe walls, just after the entrance to the pipe from the room as can be seen in Figure 9.



**Figure 8** A 2m high box used in calculations. Bottom area is 1 m<sup>2</sup> (1m x 1 m). A horizontal exhaust pipe was placed at the ceiling level. Inflow sources of fresh air was located in the pipe at the end nearest the room.



**Figure 9** A drawing showing the fresh air inflow into the exhaust pipe. Four 10 cm x 10 cm inflow sources are placed on the surfaces of the pipe interior walls.

This arrangement showed to be the best way to dilute the fire gases with air. Controlling the residence time of gases passing the whole length of the pipe is easy with this arrangement through adjusting the gas velocity at the end of the pipe. Comparison of the concentrations of the chemical species at both ends then can show whether chemical reactions occur or not in the pipe.

The temperature and species concentrations for scenario in which air of temperature 600 °C was inserted into the pipe according to Figure 9 are presented in tables 4, 5 and 6. The undiluted gas concentrations in the room before entering into pipe are shown in Table 4. Because the fire gases before entering into the pipe contained very little oxygen, the insertion of pure air caused ignition of the fire gases in the pipe. An air flow about 40 % caused ignition and a high temperature rise and expansion of the gas, so that some of the gas was pushed back to the fire room. An air inflow between 10 and 33 % of the volume flow out of the pipe gave the best dilution effect without causing a strong temperature gradient at the air inlet.

In the table 5 the gas concentrations at point 10 cm downstream from the air inlets are presented. Because the temperature at that point is higher than the temperature of air in the inflow, chemical reactions generating heat must occur. Also the concentrations of both HCN and CO are higher than a pure dilution would result in, which indicate that these gases are formed directly after the mixing of air. After mixing of 15 % air the concentrations of HCN and CO were about 200 and 8300 ppm, respectively. Corresponding values of these species after 33 % air inflow are about 21 and 750 ppm, respectively.

One metre downstream, i.e. at the end of the pipe the HCN concentrations are reduced by 34 % for residence time 5 s and 79 % for the residence time 15 s. The reduction of HCN concentrations seems to be independent of the amount of air mixed. The further reduction of CO depends in the amount of air mixed rather than the residence time. Between the two points in the pipe reduction of CO is about 32 % for the lower air mixture and about 35-40 % for the higher air mixture. However, the higher air mixing makes the CO to burn directly after the mixing, which explains the low concentrations (about 750 ppm CO) and higher temperature.

**Table 4** Temperatures and species concentrations in the room 10 cm below the ceiling

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	τ [s]
Run1	460	1035	8263	0.108	0.003	5
	460	1034	8270	0.108	0.003	15
Run 2	425	1030	8450	0.108	0.002	5
	425	1031	8435	0.108	0.002	15

**Table 5** Temperatures and species concentrations in the pipe 5 cm from the air inlet

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	τ [s]
Run 1	625	202	3527	0.103	0.028	5
	619	203	3540	0.103	0.029	15
Run 2	508	20.8	740	0.087	0.065	5
	503	20.4	732	0.088	0.065	15

**Table 6** Temperatures and species concentrations in the pipe 10 cm from the outlet

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	$\tau$ [s]
Run 1	625	133	2409	0.103	0.025	5
	620	42.6	2418	0.103	0.028	15
Run 2	495	13.7	440	0.085	0.066	5
	503	4.4	466	0.085	0.065	15

## 2.3 Large scale scenario

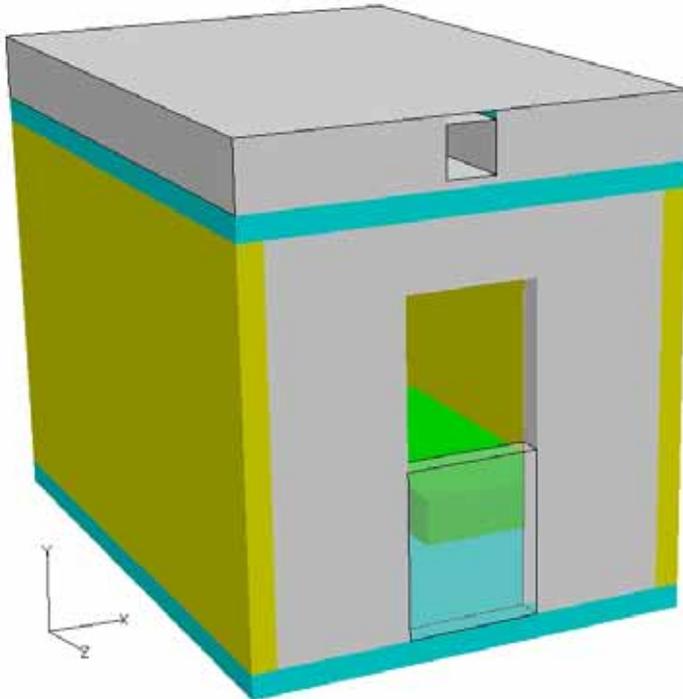
In order to study the effect of where toxic gas samples are taken in full scale experiments a fire room of size ISO 9705 (Room corner test room) was simulated including the exhaust duct where measurements of fire gases usually are made. Two simulations, one with HRR 600 kW and one with 900 kW were made. Each simulation was run for four minutes. To generate under-ventilated conditions the lower half of the door opening was blocked.

### 2.3.1 Geometry and boundary conditions

Figure 10 shows the geometry of the simulation, which includes the smoke channel. A calculation domain includes a free air region in front of the door extending to a constant pressure boundary at a distance of 1.5 m from the door wall. The lower part of the door opening, up to 1m from the floor (shown as transparent in the figure), was blocked to reach an under-ventilated situation. A ‘hole’ above the ceiling corresponds to a smoke channel leading the smoke from hood to atmosphere. Extract boundary condition was applied on the back end of the channel, which corresponds to a forced vent with desired volume flow.

The room walls including the floor and ceiling were assumed to consist of 15 cm normal density concrete. In order to save computer memory, the smoke channel was put directly above the ceiling and both sides of the smoke channel were blocked by inactive solid blockages. The material of the smoke channel walls were modified so that heat transfer through them would be about the same as the heat transfer through thin walls.

The computer model of fire source with length 180 cm, width 80 cm and height 30 cm was placed 10 cm from the right wall. Two heat release rates, one with 600 kW and the other with 900 kW were used, which are at the same level as from burning polyurethane mattress. The actual flamelet combustion model used a synthetic fuel, a mixture of methylamine and ethylene. To be able to generate HCN the fuel must contain nitrogen. Further, for the actual flamelet model the fuel must be in gas phase. The ethylene/methylamine ratio 3 contain 12.2 % (by weight) nitrogen, which is about the same as in nylon [9, 10].



**Figure 10** Geometry of a large scale scenario with a smoke channel. The room size and the door opening are equal sizes with the ISO 9705 Corner test room.

The emissivity on all solid surfaces was set to 0.9. The convective heat transfer coefficient on the inner wall surface and inner surfaces of the smoke channel were calculated automatically by SOFIE (so called conjugate heat transfer boundary conditions). On the outer wall surfaces that were bounded by the calculation domain, the convective heat transfer coefficient was set to  $5.0 \text{ W/m}^2 \text{ K}$ . Also, on the outer surfaces of the smoke channel (i.e. top surface and the surfaces faced to the solid side blockages) the heat transfer coefficient was set at that value.

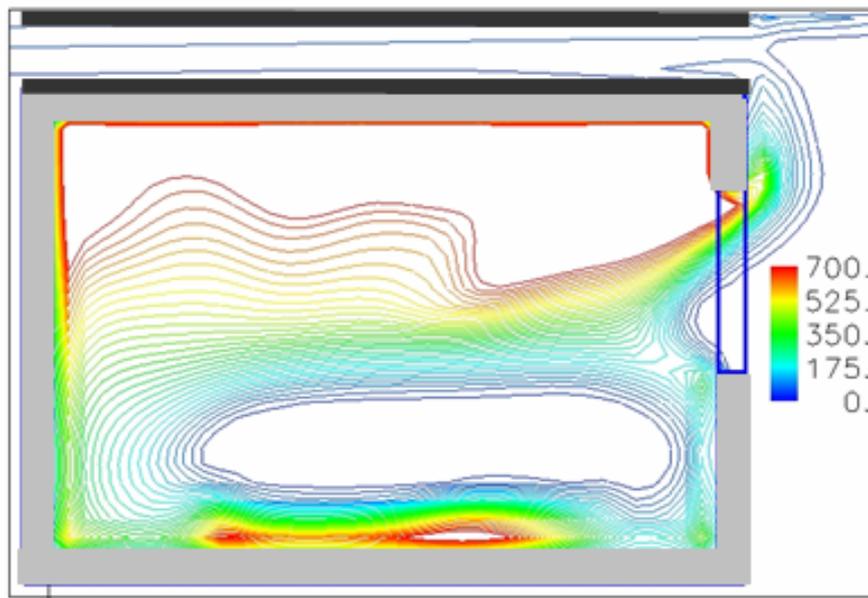
At the vertical constant pressure boundary the temperature of air was set to  $20 \text{ }^\circ\text{C}$ . The initial temperature of the whole system (i.e. all solids and air) and inflowing fuel was set to  $20 \text{ }^\circ\text{C}$ .

### 2.3.2 Simulation including the duct

The temperature and concentrations of HCN, CO, CO<sub>2</sub>, and O<sub>2</sub> was calculated for 4 minutes fire duration in each run. The results are presented in the door opening and at two different points in the smoke channel (Figures 12 through 25). The point in the door opening is 15 cm below the soffit (185 cm from the floor). NB this point represents not how much HCN the fire gases that are flowing from the room in average contain, it states only a value in one point. The points in the smoke channel are 1.2 m from the inflow to the channel and 15 cm from the exit end of the channel.

In the end of the smoke channel a forced vent with gas velocity of 23 m/s is modelled, which corresponds the volume flow of 3.0 m<sup>3</sup>/s which is the volume flow normally used in these kind of experiments.

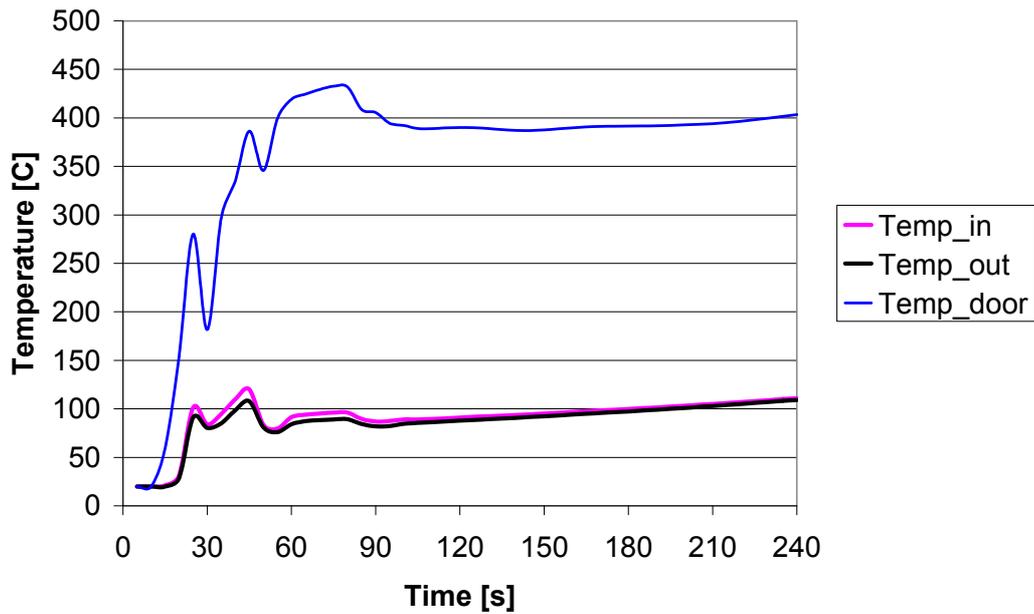
The HCN concentration is strongly reduced before the gases are sucked in to the ventilation channel. The point 15 cm below the upper edge of the opening is a location where the HCN concentration is near its maximum. The fire gases leaving the room thus have much lower average concentration of HCN. Most of the HCN is consumed when it leaves the room. Additional fresh air about a factor 5 is mixed with fire gases before the mixture is entered in the smoke channel. Figure 11 shows a contour line map och HCN concentration at the room and smoke channel centreline.



**Figure 11** HCN concentration in ppm in the room centreline including the smoke channel.

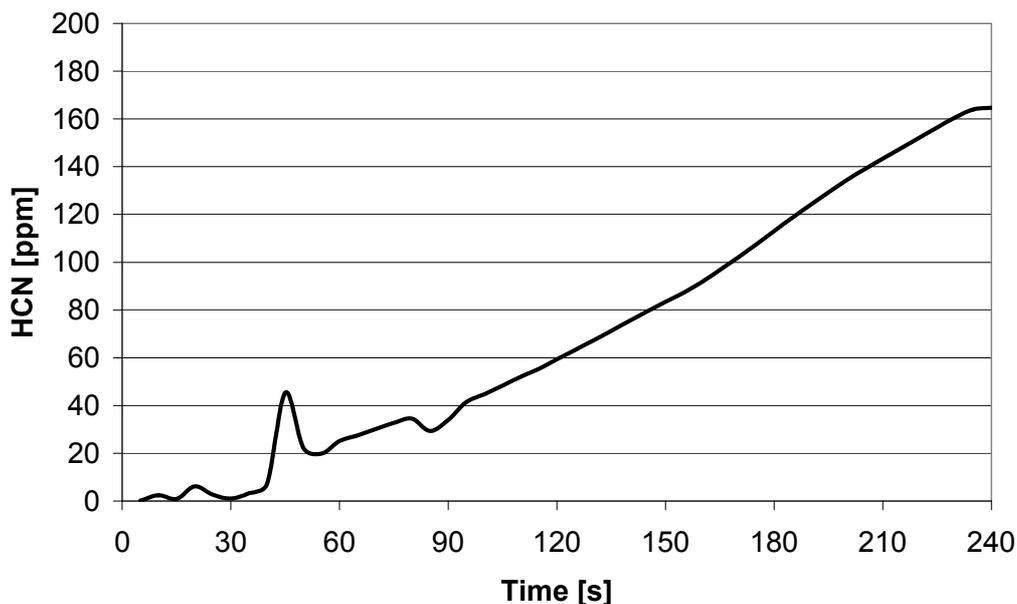
### 2.3.3 Result from 600 kW fire

In the scenario with HRR 600 kW, the temperature of the out-flowing gases from the room reaches the steady-state value about 400 °C about one minute after ignition (Figure 12). The gases are cooled considerably as they enter the smoke channel, mostly due to mixing with fresh air of ambient temperature. The temperature in the duct reaches about 90°C about one minute after ignition. The temperature in the duct is increasing nearly linearly having a value of 110°C at time 4 min (the end of the simulation). This increase can be attributed to heating up the channel walls. The temperature difference between the two points (1.2 from the smoke channel inlet and 15 cm from the outlet) is at  $t = 60$ s about 10°C. At the end of the simulation the temperature difference between the two points is negligible.

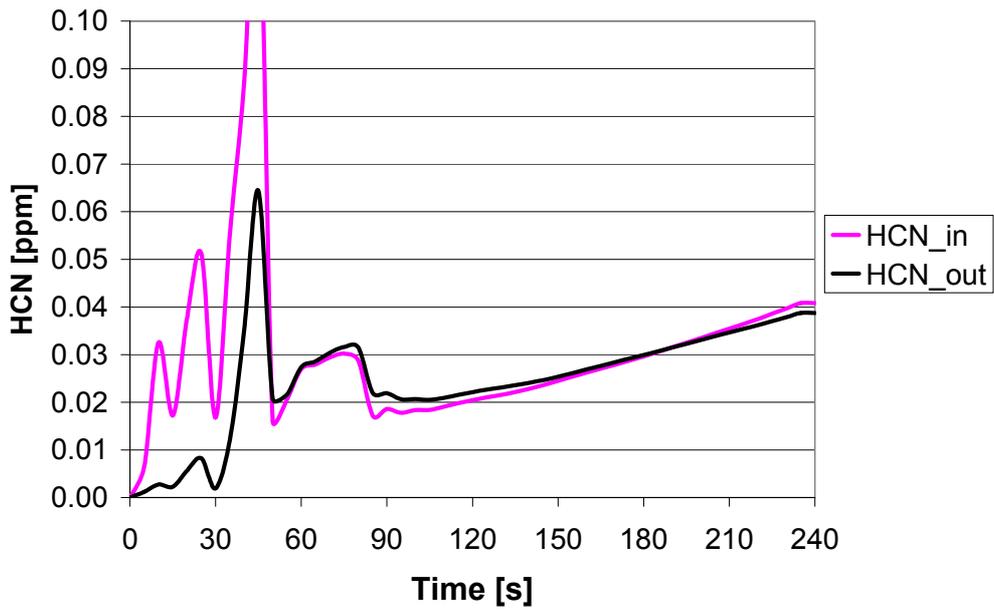


**Figure 12** Temperature of fire gases in the smoke channel 1.2 m from the inlet and 15 cm from the exit, respectively, and in fire gases flowing out from the room at 185 cm height in the door opening, HRR 600 kW.

The HCN concentration in this scenario is low, between 0.02 and 0.04 ppm in the smoke channel as can be seen in Figure 14. The concentration of the HCN does not change noticeably between points in the channel. The HCN concentration is increasing in the channel during the simulation time. In the door opening the HCN concentration is increasing strongly with time from 30 ppm at  $t = 60$  s to 160 ppm at  $t = 240$ s (Figure 13). This indicates that it takes longer time for this size of the fire to build the gas layer inside the room and extract of gas from the hood in front of the door opening is strong from the beginning,  $3.0 \text{ m}^3/\text{s}$ .

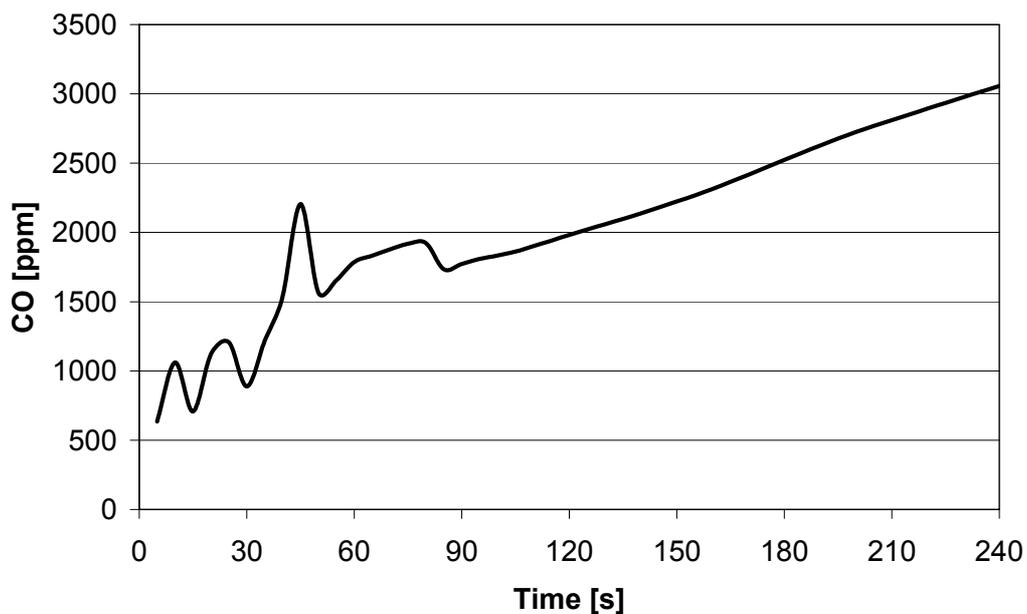


**Figure 13** HCN concentration in the fire gas outflow from the room at 185 cm height in the door opening, HRR 600 kW.

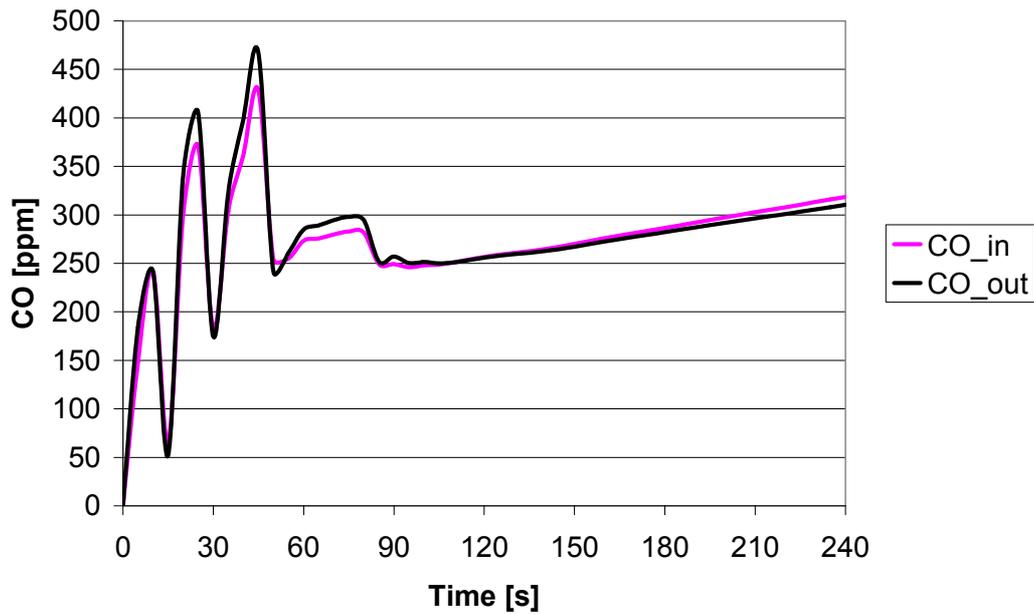


**Figure 14** HCN concentration in fire gases in the smoke channel 1.2 m from the inlet and 15 cm from the exit, respectively, HRR 600 kW.

The CO concentration follows the same pattern as HCN, i.e. it is increasing with time. At the door opening the level of CO is just below 2000 ppm at time 60 s and increases almost linearly 3000 ppm at time 240 s, see Figure 15. In the smoke channel the CO concentration is about 280 ppm one minute after the ignition. Just before 90 s the CO concentration in the smoke channel is of some reason (probably due to numerical instability in calculation) lowered to 250 ppm, after which it is increased fairly linearly to 300 ppm at time 240 s (Figure 16).

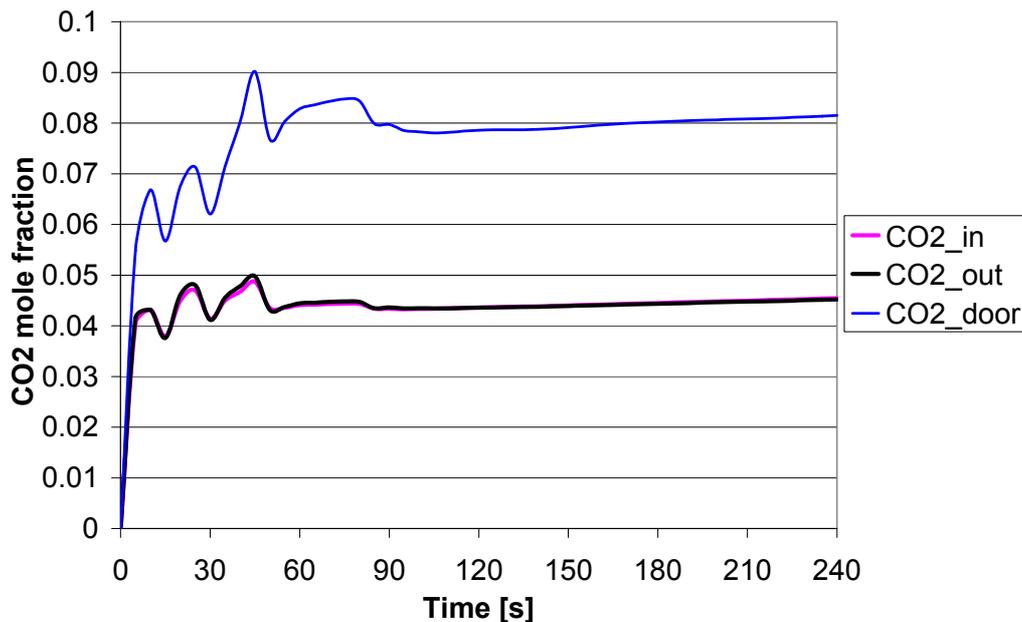


**Figure 15** CO concentration in the fire gas outflow from the room at 185 cm height in the door opening, HRR 600 kW.

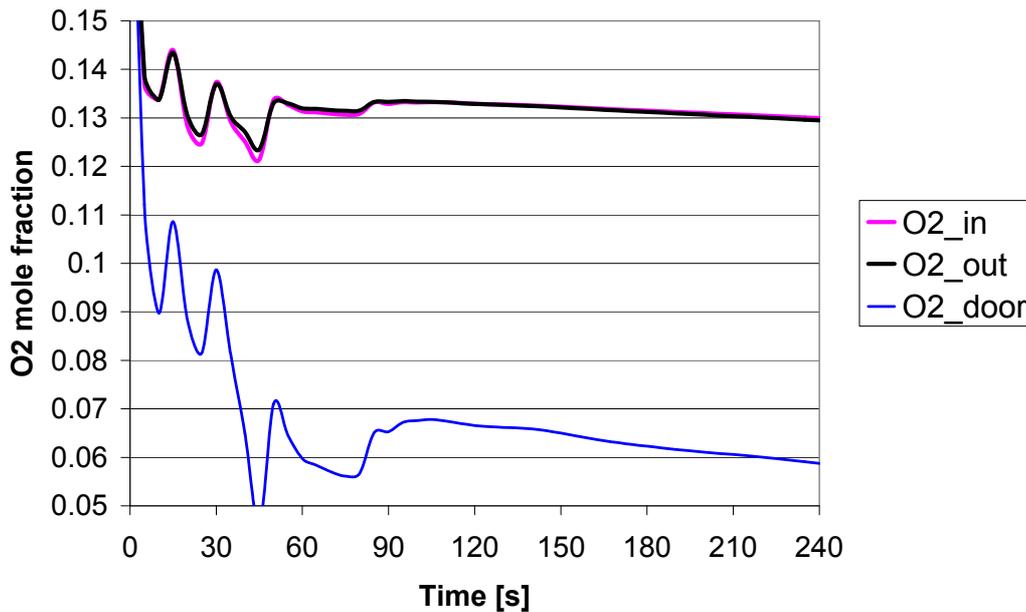


**Figure 16** CO concentration in fire gases in the smoke channel 1.2 m from the inlet and 15 cm from the exit, respectively, HRR 600 kW.

The CO<sub>2</sub> concentration is relatively constant between 60 and 240 s in the simulation. At the door opening the concentration is about 8 % by volume and in the smoke channel it is about 5 % as seen in figure 17. The oxygen concentration in the smoke channel is about 13 % as seen in figure 18. At the door opening, 15 cm below the soffit, the level of oxygen concentration is about 6 %. The concentration is slightly lowered with time. At this low temperature this cannot be due to combustion. The reason is probably that more smoke is gathered in the hood and thus more smoke is sucked in the channel later in time.



**Figure 17** CO<sub>2</sub> concentration in fire gases in the smoke channel 1.2 m from the inlet and 15 cm from the exit, respectively, and in the fire gas outflow from the room at 185 cm height in the door opening, HRR 600 kW.



**Figure 18** O<sub>2</sub> concentration in fire gases in the smoke channel 1.2 m from the inlet and 15 cm from the exit, respectively, and in the fire gas outflow from the room at 185 cm height in the door opening, HRR 600 kW.

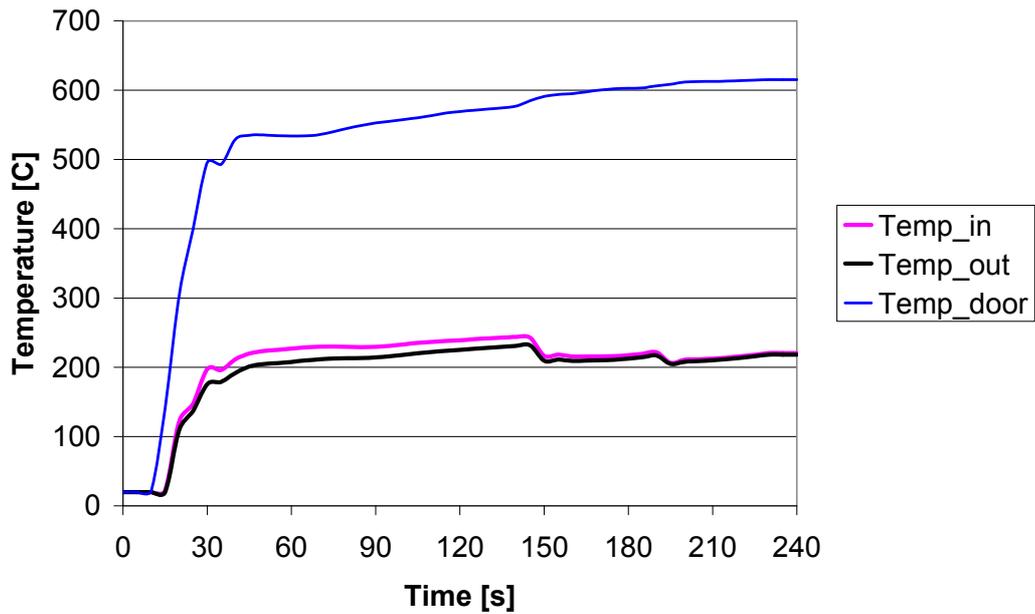
As the species concentrations and the temperature in the smoke channel have almost the same values between the two points the chemical reactions in the channel are negligible.

### 2.3.4 Result from 900 kW fire

In the scenario with HRR 900 kW the temperature of the out-flowing gas increases to about 550 °C after 60 s fire duration and at time 240 s the temperature is about 600°C, see Figure 19. In the duct the temperature reaches slightly more than 200 °C. The simulation with that higher heat release rate was more difficult to stabilize. Burning in the gas layer and in the hood in front of the room might have occurred. A much longer simulation time is required to reach a steady state.

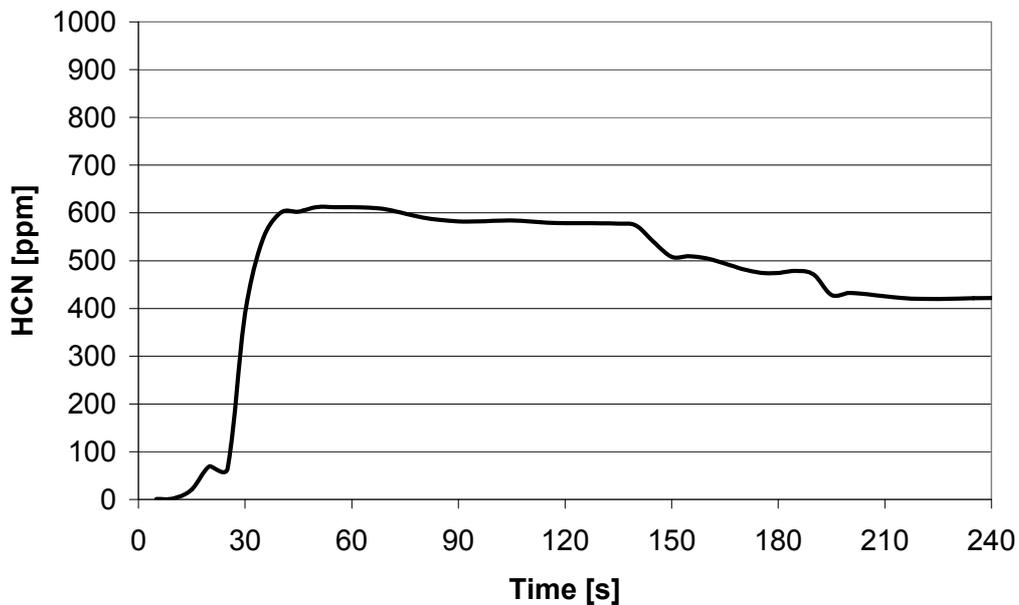
The HCN concentration in the gas flow out from the room is in the scenario considerably higher than for 600 kW fire. The concentration with time follows also a different pattern with 900 kW fire compared to 600 kW fire. At time 60 s the HCN concentration in the outflow is about 600 ppm and is reduced to about 400 ppm after four minutes, see Figure 20.

In the duct the HCN level is also considerably higher for 900 kW fire than 600 kW fire but still very low, after four minutes only between 0.1 and 0.2 ppm. From the graphs in the Figure 21 it can be seen that some consumption of HCN may occur.



**Figure 19** Temperature of fire gases in the smoke channel 1.2 m from the inlet and 15 cm from the exit, respectively, and in fire gases flowing out from the room at 185 cm height in the door opening, HRR 900 kW.

CO concentration at 900 kW-fire scenario in the gas outflow from the room is 7000 ppm at time 60 s and follows the same pattern as HCN. At time 240 s the CO in the outflow is about 5500 ppm. The higher value in the beginning is due to that the calculation of the solution has not reached a steady state.



**Figure 20** HCN concentration in the fire gas outflow from the room at 185 cm height in the door opening, HRR 900 kW.

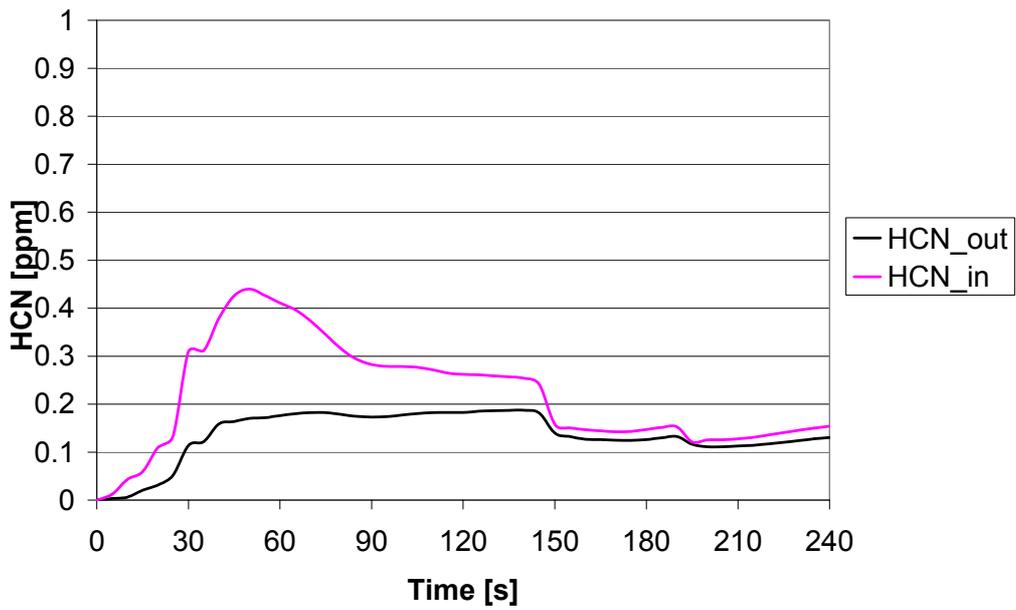


Figure 21 HCN concentration in fire gases in the smoke channel 1.2 m from the inlet and 15 cm from the exit, respectively, HRR 900 kW.

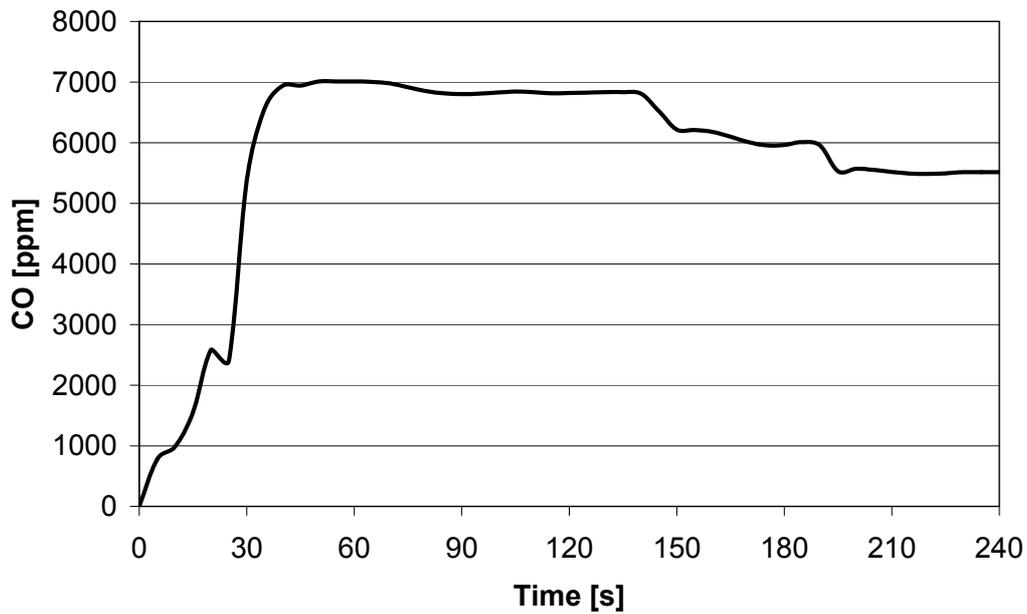


Figure 22 CO concentration in the fire gas outflow from the room at 185 cm height in the door opening, HRR 900 kW.

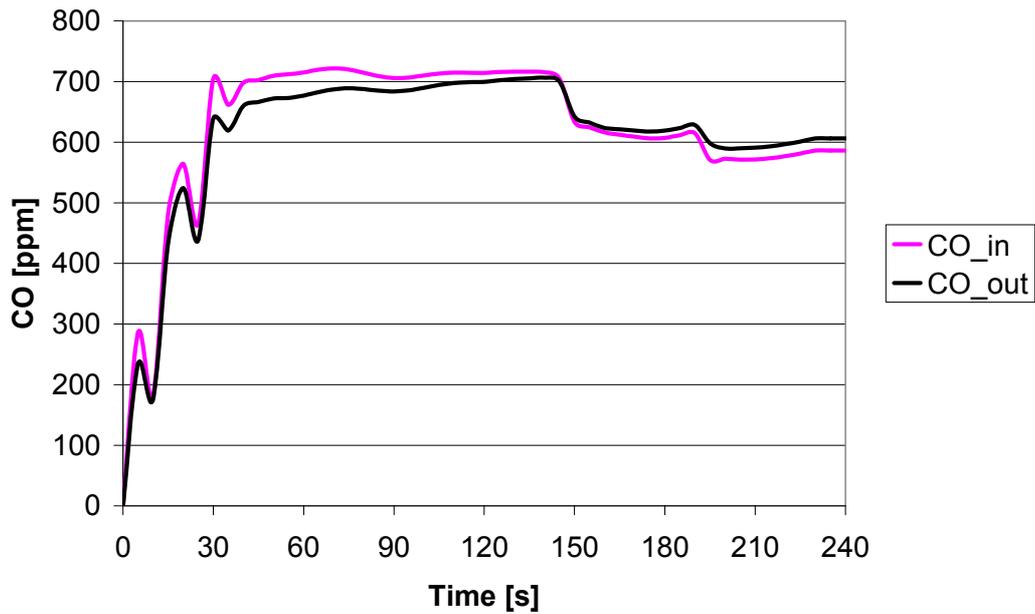


Figure 23 CO concentration in fire gases in the smoke channel 1.2 m from the inlet and 15 cm from the exit, respectively, HRR 900 kW.

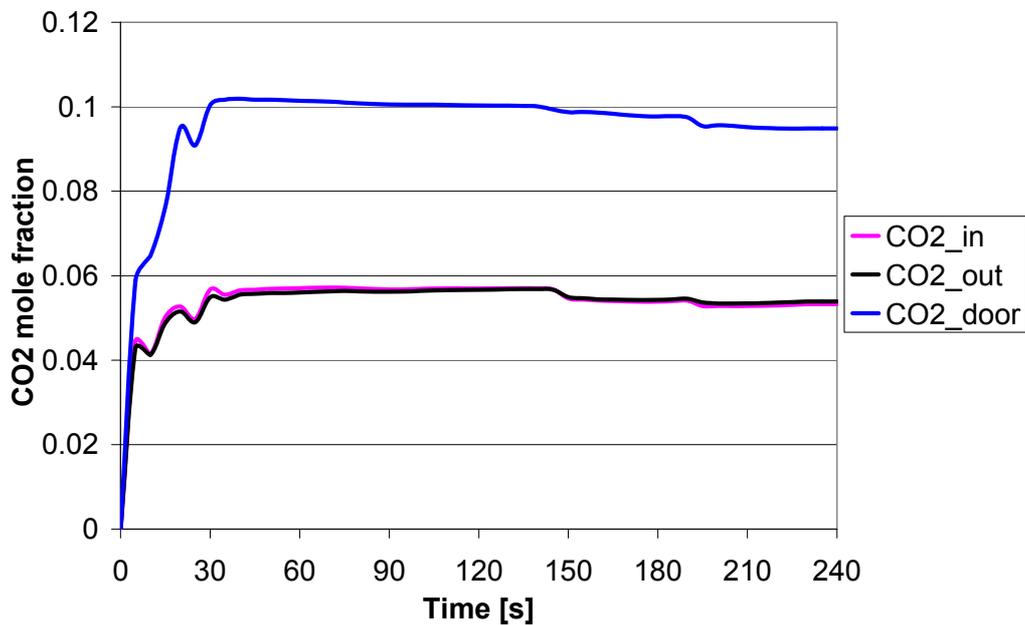
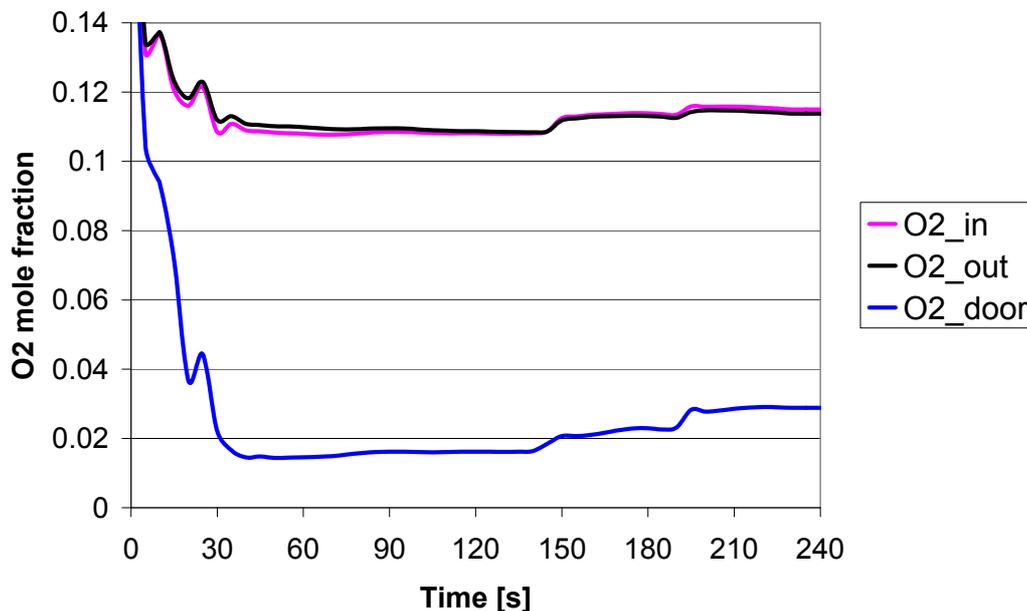


Figure 24 CO<sub>2</sub> concentration in the fire gas outflow from the room at 185 cm height in the door opening, CO<sub>2</sub> concentration in fire gases in the smoke channel 1.2 m from the inlet and 15 cm from the exit, respectively, and in the fire gas outflow from the room at 185 cm height in the door opening, HRR 900 kW.

Oxygen concentration in the outflow from the room is about 1.5 % at time 60 s after ignition and increases to about 3 % at time 240 s by volume and is relatively constant after 60 s from simulation start (Figure 25). The increase does not mean that oxygen contents in fire gases flowing out from the room increases with time. The gas flow profile

changes over time because the room is filled with gases that are increasing in temperature. In the channel the O<sub>2</sub> concentration is about 11 %.



**Figure 25** O<sub>2</sub> concentration in fire gases in the smoke channel 1.2 m from the inlet and 15 cm from the exit, respectively, and in the fire gas outflow from the room at 185 cm height in the door opening, HRR 900 kW.

### 2.3.5 Comparison between 600 and 900 kW simulations

There are quite large differences between results from simulations between 600 and 900 kW simulations (Figures 14 through 25) especially concerning HCN concentration. The larger fire (900 kW) generates HCN levels of more than 700 ppm in the gas layer. With the 600 kW fire it takes longer time to build-up the gas layer, which means that it takes longer time for the fire in the room to become under-ventilated. For example, after one minute simulation, the HCN is only 20 ppm in the outflow from the room, 15 cm below the upper edge of the opening for 600 kW fire. During the next three minutes the HCN concentration in the gas flow is increasing linearly, and after four minutes the HCN concentration is 160 ppm. This indicates that the fire is more under-ventilated at that time. The CO concentration follows the same pattern as HCN, i.e. linearly increasing from less than 2000 ppm at one minute to about 3000 ppm at four minutes.

The larger fire becomes under-ventilated quickly. The room is filled with smoke within one minute of simulation. After one minute the HCN concentration has reached a maximum value, 600 ppm 15 cm below the upper edge of the opening. After that time the HCN concentration is relatively constant up to time 2.5 min. after which it is reduced to 430 ppm at 4 minutes. The reduction does not mean that the total amount of HCN is reduced so drastically, because the thickness of the flow stream and hence the maximum point of the HCN concentration in the stream might be moved from the location.

### 3 Comparison of calculations with experiments

It was difficult to create exactly the same conditions with the CFD simulation as in the small scale laboratory tests used in this project. SOFIE needs the fuel flow as a boundary condition on the surface of the fuel source. One can define the gas composition as a net formula of simple fuel which includes the same amounts of HCN, CO, etc. at the desired temperature, but the problem is that SOFIE automatically ignites this mixture (if some amount of oxygen is present), which would generate a higher temperature than desired. Hence, such boundary conditions would be directly destroyed by the program. Therefore the comparison must be confined to analysing trends through observing scenarios with different physical conditions.

Table 1 shows the influence of residence time on HCN concentrations estimated in both experiments and calculations. According to the test at 600 °C the HCN concentration is reduced from 800 ppm to 500 ppm during the residence time 5 s, i.e. about a factor 1.6, see Table 7 and Figure 7. During the residence time of 14 s the HCN concentration is reduced by factor of 4.8.

Calculations at about the same temperature, around 620 °C (see Tables 5, 6 and 7), showed about the same relative reduction of HCN concentration for the residence time lengths of both 5 and 15 s. However, the levels of HCN were considerably lower in the calculated scenarios, 133 ppm at 5 s residence time and 42.5 ppm at 15 s, respectively.

**Table 7 Comparison of experimental and calculated values of the influence of the residence time length on HCN concentration.**

<b>Experiments</b>					
T in [°C]	T out [°C]	HCN in [ppm]	HCN out [ppm]	$\tau$ [s]	Ratio [in/out]
600	600	800	500	5	1.6
600	600	800	165	14	4.8
<b>Calculations</b>					
625	625	202	133	5	1.5
619	620	203	43	15	4.7
508	495	21	14	5	1.5
503	503	20	4	15	5.0

The residence time does not have any noticeable influence on the HCN concentration according to the experiments when the smoke gases are diluted at low temperatures. However at higher temperature the experiments show a slight increase of HCN with increased residence time, see figure 5. Simulations at low temperatures showed no noticeable influence on HCN concentration to variation of the residence time, see Appendix B.

## 4 Conclusions and discussions

Results from this investigation show that the contents of toxic gases in fire gases can change due to chemical reactions when the gases are transported away from the room of fire origin if the temperature of the gas is sufficiently high. i.e. in the order of 500-600 °C.

This survey was focused to investigate HCN and CO. It is well known that the formation of these gases is strongly dependent of the burning environment and fuel type. CO is formed in burning of practically all fuels. HCN is mainly formed if the fuel contains nitrogen. If burning occurs with lack of oxygen the formation of both gases is increased drastically. The temperature plays also an important roll. If the gas layer in the fire room has a high temperature and contains unburned fuel and uncompleted combustion products the HCN concentrations are generally high and it is also formed in the gas layer.

The residence time (that can be related to the distance the gases are transported) play an important roll in how much the concentration of HCN and CO is changed. The longer the residence time, the larger the reduction of HCN. If fire gases at about 600 °C contain low amount of oxygen the reduction of HCN due to residence time is of the same magnitude as for higher oxygen contents, according to calculations with oxygen contents of 3 and 6.5 %. Laboratory tests of much higher oxygen contents, about 18 % at 600 °C, showed that HCN concentration is reduced at the same factor due to residence time as those calculated at lower oxygen contents.

No reactions occur at gas temperatures at 200 °C and below according to this survey. Both laboratory tests and simulation showed no noticeably consumption or formation of HCN. Full scale scenario with HRR 900 kW shows, however that at the temperature slightly over 200 °C some consumption of HCN might occur, see Figure 21.

Some of the calculations showed that insertion of fresh air in hot combustion products ignited the fire gases, leading to a drastic increase of HCN and CO locally in the combustion zone. This happens certainly also when very hot fire gases containing a large amount of incomplete combustion exits from the fire room and meet fresh air outside.

The gas concentration in the pipe in the simulations is separate to that in the room, and hence the residence time for a gas in this condition is well defined and equal to the pipe length divided by gas velocity. Comparison with 5 s and 15 s residence times made in the simulated scenarios presented in section 3.2 showed a clear difference in gas concentrations, the same thing was noticed in the laboratory tests.

ISO 9705 Room corner tests results usually in gas temperatures in the duct below 100 °C which is below the temperature where reactions can take place according to this study. However, when testing a fully developed room fire and a flash over, the temperature in the smoke channel may increase above 500 °C. At so high a temperature a consumption of HCN may occur according to this study, and thus the choice of different measuring points will give different results. A possible solution to such a situation could be to increase the gas volume flow in the channel so that more fresh air (than the normal mixture ratio 5:1) is mixed in the fire gases at the entrance to the channel.

It is important to model the flame (and other regions where chemical reactions are assumed to be significant) carefully when using the flamelet model as it assumes fast chemistry. Generally the flamelet model needs a finer mesh compared to the other more

commonly used combustion models such as the eddy break-up model, in order to resolve the single chemical species distribution in space and time. Thus, especially in the fire region and in the vicinity of it, a grid cell size of a few centimetres gives different results in chemical species concentrations to that of cell sizes of a few decimetres.

In this study all small scale simulations were performed with cell sizes of a few centimetres. The large scale simulations were made using cell sizes of about 10 - 15 cm inside the fire room and less than 10 cm in the fire source. For the flamelet model a cell size of 10 cm is large. Irrespective the fire size, the cell size in the flamelet model should be small, about the size of a couple of centimetres, because chemical reactions are fast and hence not scalable like velocity and other transport properties in the fluid. On the other hand, using the same cell size in the large scale scenario as in the small scale would require several million cells, which could be impossible to calculate in a reasonable time without very large and fast computers. Therefore a question arises: was it right to simulate the large scale scenario with overall cell sizes of about a decimetre, because combustion and chemical reactions occurred also in the gas layer. The answer to this question could be given after comparing the simulation with one with smaller grid cells. The largest error introduced by using too large cells will be in calculation of the fire plume, especially the lower part of it. In the bottom cell, i.e. just above the fire source the reactants do not react correctly if the cell length is too large, especially in the flow direction. Thus, more incomplete products are transported to the next cell. If this cell is also too large the procedure continues. After a large number of cells this "error" will be reduced.

In the large scale scenario in this work we were interested in the gas contents in the duct. The possible error in calculating the flame region and part of the ceiling layer has a minor significance to what is happening in the duct. Even though the gas composition in the duct would possibly differ from that which would be calculated with smaller cells, it contained reasonable levels of HCN and CO in the temperature which was expected. So the simulations can be assumed as trustable and result useful.

This study showed that the HCN concentration is reduced at 600 °C in a magnitude which is proportional to residence time. The volume flow of 3.0 m<sup>3</sup>/s through a 3.6 m long and 40 cm diameter duct gives the residence time length of 0.16 s. If the reduction of HCN concentration is of the same magnitude as a function of residence time length as estimated for gas temperatures 600 °C in this study, it would be small, i.e. less than 5 %.

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## Appendix A - Detailed experimental results

**Table A1** Experimental results on HCN.

Test	Concentration in box (ppm)	Concentration in primary tube (ppm)	Production (mg/s)	Yield (mg/g)
1A	52.5	262	0.0483	3.00
1B	50.9	255	0.0469	2.91
<i>Mean:</i>	<i>51.7</i>	<i>258</i>	<i>0.05</i>	<i>2.95</i>
<i>Stdev:</i>	<i>1.1</i>	<i>5</i>	<i>0.001</i>	<i>0.06</i>
1A2	16.2	53.9	0.0149	0.92
1B2	14.7	49.1	0.0136	0.84
<i>Mean:</i>	<i>15.5</i>	<i>51.5</i>	<i>0.014</i>	<i>0.88</i>
<i>Stdev:</i>	<i>1.0</i>	<i>3.4</i>	<i>0.001</i>	<i>0.06</i>
2A	784	9660	0.722	44.9
2B	697	8589	0.642	39.8
2C	674	8299	0.620	38.5
<i>Mean:</i>	<i>718</i>	<i>8849</i>	<i>0.66</i>	<i>41.1</i>
<i>Stdev:</i>	<i>58.2</i>	<i>717</i>	<i>0.054</i>	<i>3.4</i>
3A	672	8276	0.619	38.4
3B	688	8475	0.634	39.4
<i>Mean:</i>	<i>680</i>	<i>8376</i>	<i>0.63</i>	<i>38.9</i>
<i>Stdev:</i>	<i>11</i>	<i>141</i>	<i>0.01</i>	<i>0.7</i>
4A	803	19780	0.739	45.9
4B	257	6342	0.237	28.9
4C	251	6189	0.231	28.2
<i>Mean:</i>	<i>254</i>	<i>6265</i>	<i>0.23</i>	<i>28.6</i>
<i>Stdev:</i>	<i>4</i>	<i>108</i>	<i>0.004</i>	<i>0.5</i>
5A	251	6184	0.231	28.7
5B	247	6074	0.227	28.2
<i>Mean:</i>	<i>248</i>	<i>6129</i>	<i>0.23</i>	<i>28.4</i>
<i>Stdev:</i>	<i>3</i>	<i>77</i>	<i>0.003</i>	<i>0.4</i>
6A	1425	8766	1.31	40.8
6B	1511	9291	1.39	43.2
<i>Mean:</i>	<i>1468</i>	<i>9029</i>	<i>1.35</i>	<i>42.0</i>
<i>Stdev:</i>	<i>60</i>	<i>371</i>	<i>0.06</i>	<i>1.7</i>
7A	1166	9708	0.363	22.5
7B	561	4673	0.175	21.6
7C	671	5584	0.209	25.9
<i>Mean:</i>	<i>616</i>	<i>5128</i>	<i>0.19</i>	<i>23.7</i>
<i>Stdev:</i>	<i>77</i>	<i>644</i>	<i>0.024</i>	<i>2.9</i>

**Table A2** Experimental results on HCN, cont.

Test	Concentration in box (ppm)	Concentration in primary tube (ppm)	Production (mg/s)	Yield (mg/g)
8A	868	11073	1.66	51.4
8B	844	10763	1.61	49.9
8C	948	12089	1.81	56.1
<i>Mean:</i>	<i>886</i>	<i>11308</i>	<i>1.69</i>	<i>52.4</i>
<i>Stdev:</i>	<i>54</i>	<i>694</i>	<i>0.10</i>	<i>3.2</i>
9A	1350	8314	0.622	38.6
9B	1318	8115	0.607	37.6
<i>Mean:</i>	<i>1334</i>	<i>8214</i>	<i>0.61</i>	<i>38.1</i>
<i>Stdev:</i>	<i>23</i>	<i>141</i>	<i>0.01</i>	<i>0.7</i>
10A	75.0	1848	0.138	8.56
10B	93.4	2302	0.172	10.67
<i>Mean:</i>	<i>84.2</i>	<i>2074</i>	<i>0.16</i>	<i>9.62</i>
<i>Stdev:</i>	<i>13</i>	<i>321</i>	<i>0.024</i>	<i>1.5</i>
11A	1015	8449	0.316	39.3
11B	875	7282	0.272	33.8
<i>Mean:</i>	<i>945</i>	<i>7865</i>	<i>0.29</i>	<i>36.5</i>
<i>Stdev:</i>	<i>99</i>	<i>825</i>	<i>0.03</i>	<i>3.8</i>
12A	821	10116	0.756	47.0
12B	795	9787	0.732	45.5
<i>Mean:</i>	<i>808</i>	<i>9951</i>	<i>0.74</i>	<i>46.2</i>
<i>Stdev:</i>	<i>19</i>	<i>232</i>	<i>0.02</i>	<i>1.1</i>
13A	776	9560	0.715	44.3
13B	738	9084	0.679	42.1
13C	871	10727	0.802	49.7
<i>Mean:</i>	<i>795</i>	<i>9790</i>	<i>0.73</i>	<i>45.4</i>
<i>Stdev:</i>	<i>69</i>	<i>845</i>	<i>0.06</i>	<i>3.9</i>
14A	544	6695	0.501	31.0
14B	466	5733	0.429	26.6
<i>Mean:</i>	<i>505</i>	<i>6214</i>	<i>0.46</i>	<i>28.8</i>
<i>Stdev:</i>	<i>55</i>	<i>680</i>	<i>0.05</i>	<i>3.2</i>
15A	149	1243	0.046	5.76
15B	183	1523	0.057	7.06
15C	155	1288	0.048	5.97
15D	160	1331	0.050	6.17
<i>Mean:</i>	<i>162</i>	<i>1346</i>	<i>0.05</i>	<i>6.24</i>
<i>Stdev:</i>	<i>15</i>	<i>123</i>	<i>0.005</i>	<i>0.57</i>

**Table A3** Experimental results on CO<sub>2</sub>.

Test	Concentration in box (ppm)	Production (mg/s)	Yield (mg/g)
1A	2.08	31.2	1934
1B	2.00	30.0	1858
<i>Mean:</i>	<i>2.04</i>	<i>30.6</i>	<i>1896</i>
<i>Stdev:</i>	<i>0.06</i>	<i>0.8</i>	<i>54</i>
1A2	2.42	36.3	2255
1B2	2.28	34.2	2125
<i>Mean:</i>	<i>2.35</i>	<i>35.2</i>	<i>2190</i>
<i>Stdev:</i>	<i>0.10</i>	<i>1.5</i>	<i>92</i>
2A	0.641	9.60	597
2B	0.626	9.38	582
2C	0.569	8.53	530
<i>Mean:</i>	<i>0.61</i>	<i>9.17</i>	<i>569</i>
<i>Stdev:</i>	<i>0.04</i>	<i>0.56</i>	<i>35</i>
3A	0.588	8.81	548
3B	0.546	8.19	509
<i>Mean:</i>	<i>0.57</i>	<i>8.50</i>	<i>528</i>
<i>Stdev:</i>	<i>0.03</i>	<i>0.44</i>	<i>27</i>
4A	0.449	6.74	419
4B	0.378	5.66	691
4C	0.429	6.43	785
<i>Mean:</i>	<i>0.40</i>	<i>6.05</i>	<i>738</i>
<i>Stdev:</i>	<i>0.04</i>	<i>0.55</i>	<i>66</i>
5A	0.425	6.36	789
5B	0.402	6.03	748
<i>Mean:</i>	<i>0.41</i>	<i>6.20</i>	<i>768</i>
<i>Stdev:</i>	<i>0.02</i>	<i>0.24</i>	<i>29</i>
6A	1.20	18.0	559
6B	1.15	17.2	536
<i>Mean:</i>	<i>1.18</i>	<i>17.6</i>	<i>548</i>
<i>Stdev:</i>	<i>0.04</i>	<i>0.54</i>	<i>17</i>
7A	2.01	10.2	633
7B	1.76	8.90	1103
7C	1.77	8.98	1112
<i>Mean:</i>	<i>1.76</i>	<i>8.94</i>	<i>1108</i>
<i>Stdev:</i>	<i>0.01</i>	<i>0.06</i>	<i>7.0</i>

**Table A4** Experimental results on CO<sub>2</sub>, cont.

Test	Concentration in box (ppm)	Production (mg/s)	Yield (mg/g)
8A	0.427	13.3	411
8B	0.410	12.7	395
8C	0.348	10.8	336
<i>Mean:</i>	<i>0.40</i>	<i>12.3</i>	<i>381</i>
<i>Stdev:</i>	<i>0.04</i>	<i>1.3</i>	<i>40</i>
9A	1.29	9.67	601
9B	1.13	8.46	525
<i>Mean:</i>	<i>1.21</i>	<i>9.07</i>	<i>562</i>
<i>Stdev:</i>	<i>0.11</i>	<i>0.85</i>	<i>54</i>
10A	0.258	7.74	480
10B	0.375	11.23	696
<i>Mean:</i>	<i>0.32</i>	<i>9.49</i>	<i>588</i>
<i>Stdev:</i>	<i>0.08</i>	<i>2.46</i>	<i>153</i>
11A	1.07	5.41	672
11B	1.15	5.85	727
<i>Mean:</i>	<i>1.11</i>	<i>5.63</i>	<i>699</i>
<i>Stdev:</i>	<i>0.06</i>	<i>0.31</i>	<i>38</i>
12A	0.553	8.29	515
12B	0.483	7.24	450
<i>Mean:</i>	<i>0.52</i>	<i>7.77</i>	<i>483</i>
<i>Stdev:</i>	<i>0.05</i>	<i>0.74</i>	<i>46</i>
13A	0.514	7.70	478
13B	0.365	5.47	339
13C	0.497	7.46	462
<i>Mean:</i>	<i>0.46</i>	<i>6.88</i>	<i>426</i>
<i>Stdev:</i>	<i>0.08</i>	<i>1.2</i>	<i>76</i>
14A	0.679	10.18	631
14B	0.581	8.71	540
<i>Mean:</i>	<i>0.63</i>	<i>9.45</i>	<i>585</i>
<i>Stdev:</i>	<i>0.07</i>	<i>1.03</i>	<i>64</i>
15A	1.63	8.24	1021
15B	1.63	8.25	1023
15C	1.34	6.78	840.7
15D	1.78	9.03	1120
<i>Mean:</i>	<i>1.59</i>	<i>8.08</i>	<i>1001</i>
<i>Stdev:</i>	<i>0.18</i>	<i>0.94</i>	<i>117</i>

**Table A5 Experimental results on CO.**

Test	Concentration in box (ppm)	Production (mg/s)	Yield (mg/g)
1A	309	0.295	18.3
1B	314	0.299	18.6
<i>Mean:</i>	<i>311</i>	<i>0.30</i>	<i>18.4</i>
<i>Stdev:</i>	<i>3.5</i>	<i>0.003</i>	<i>0.2</i>
1A2	68.5	0.0653	4.060
1B2	60.5	0.0577	3.586
<i>Mean:</i>	<i>64.4</i>	<i>0.06</i>	<i>3.82</i>
<i>Stdev:</i>	<i>5.6</i>	<i>0.005</i>	<i>0.3</i>
2A	2122	2.02	126
2B	1948	1.86	115
2C	1696	1.62	100
<i>Mean:</i>	<i>1921</i>	<i>1.83</i>	<i>114</i>
<i>Stdev:</i>	<i>214</i>	<i>0.20</i>	<i>13</i>
3A	1636	1.56	97.0
3B	1529	1.46	90.7
<i>Mean:</i>	<i>1582</i>	<i>1.51</i>	<i>93.8</i>
<i>Stdev:</i>	<i>75</i>	<i>0.07</i>	<i>4.5</i>
4A	2275	2.17	135
4B	683	0.652	79.5
4C	729	0.695	84.8
<i>Mean:</i>	<i>706</i>	<i>0.67</i>	<i>82.2</i>
<i>Stdev:</i>	<i>32</i>	<i>0.03</i>	<i>3.7</i>
5A	879	0.839	104
5B	773	0.738	91.5
<i>Mean:</i>	<i>826</i>	<i>0.79</i>	<i>97.8</i>
<i>Stdev:</i>	<i>75</i>	<i>0.07</i>	<i>8.9</i>
6A	3579	3.41	106
6B	4006	3.82	119
<i>Mean:</i>	<i>3792</i>	<i>3.62</i>	<i>112</i>
<i>Stdev:</i>	<i>302</i>	<i>0.29</i>	<i>8.9</i>
7A	5348	1.72	107
7B	2154	0.695	86.0
7C	2368	0.764	94.6
<i>Mean:</i>	<i>2261</i>	<i>0.73</i>	<i>90.3</i>
<i>Stdev:</i>	<i>151</i>	<i>0.05</i>	<i>6.0</i>

**Table A6** Experimental results on CO, cont.

Test	Concentration in box (ppm)	Production (mg/s)	Yield (mg/g)
8A	2139	4.23	131
8B	1978	3.91	121
8C	2438	4.82	150
<i>Mean:</i>	<i>2185</i>	<i>4.32</i>	<i>134</i>
<i>Stdev:</i>	<i>233</i>	<i>0.46</i>	<i>14</i>
9A	3542	1.69	105
9B	3634	1.73	107
<i>Mean:</i>	<i>3588</i>	<i>1.71</i>	<i>106</i>
<i>Stdev:</i>	<i>65</i>	<i>0.03</i>	<i>1.7</i>
10A	208	0.396	24.6
10B	285	0.545	33.8
<i>Mean:</i>	<i>246</i>	<i>0.47</i>	<i>29.1</i>
<i>Stdev:</i>	<i>55</i>	<i>0.10</i>	<i>6.5</i>
11A	3737	1.21	150
11B	3243	1.05	130
<i>Mean:</i>	<i>3490</i>	<i>1.13</i>	<i>140</i>
<i>Stdev:</i>	<i>349</i>	<i>0.11</i>	<i>14</i>
12A	2001	1.91	119
12B	1964	1.87	116
<i>Mean:</i>	<i>1983</i>	<i>1.89</i>	<i>117</i>
<i>Stdev:</i>	<i>25</i>	<i>0.02</i>	<i>1.5</i>
13A	2134	2.04	126
13B	1971	1.88	117
13C	2710	2.59	160
<i>Mean:</i>	<i>2271</i>	<i>2.17</i>	<i>134</i>
<i>Stdev:</i>	<i>388</i>	<i>0.37</i>	<i>23</i>
14A	3219	3.07	190
14B	2952	2.82	175
<i>Mean:</i>	<i>3086</i>	<i>2.94</i>	<i>182</i>
<i>Stdev:</i>	<i>189</i>	<i>0.18</i>	<i>11</i>
15A	3201	1.03	128
15B	3277	1.06	131
15C	2782	0.90	111
15D	4074	1.31	163
<i>Mean:</i>	<i>3334</i>	<i>1.08</i>	<i>133</i>
<i>Stdev:</i>	<i>539</i>	<i>0.17</i>	<i>21</i>

**Table A7** Experimental results on NH<sub>3</sub>.

Test	Concentration in box (ppm)	Production (mg/s)	Yield (mg/g)
1A	3.81	0.00221	0.137
1B	3.04	0.00177	0.109
<i>Mean:</i>	<i>3.42</i>	<i>0.0020</i>	<i>0.12</i>
<i>Stdev:</i>	<i>0.54</i>	<i>0.0003</i>	<i>0.019</i>
1A2	2.04	0.00119	0.0737
1B2	2.07	0.00120	0.0747
<i>Mean:</i>	<i>2.06</i>	<i>0.0012</i>	<i>0.074</i>
<i>Stdev:</i>	<i>0.020</i>	<i>0.00001</i>	<i>0.001</i>
2A	253	0.147	9.14
2B	213	0.123	7.66
2C	221	0.128	7.97
<i>Mean:</i>	<i>229</i>	<i>0.13</i>	<i>8.25</i>
<i>Stdev:</i>	<i>21</i>	<i>0.012</i>	<i>0.78</i>
3A	208	0.120	7.49
3B	232	0.135	8.38
<i>Mean:</i>	<i>220</i>	<i>0.13</i>	<i>7.93</i>
<i>Stdev:</i>	<i>17</i>	<i>0.010</i>	<i>0.63</i>
4A	422	0.245	15.2
4B	58.6	0.034	4.15
4C	53.8	0.031	3.81
<i>Mean:</i>	<i>56.2</i>	<i>0.03</i>	<i>3.98</i>
<i>Stdev:</i>	<i>3.4</i>	<i>0.002</i>	<i>0.24</i>
5A	66.6	0.039	4.79
5B	59.5	0.035	4.28
<i>Mean:</i>	<i>63.1</i>	<i>0.04</i>	<i>4.54</i>
<i>Stdev:</i>	<i>5.0</i>	<i>0.003</i>	<i>0.36</i>
6A	390	0.226	7.03
6B	489	0.284	8.82
<i>Mean:</i>	<i>439</i>	<i>0.25</i>	<i>7.92</i>
<i>Stdev:</i>	<i>70</i>	<i>0.04</i>	<i>1.27</i>
7A	673	0.132	8.18
7B	101	0.020	2.45
7C	139	0.027	3.39
<i>Mean:</i>	<i>120</i>	<i>0.02</i>	<i>2.92</i>
<i>Stdev:</i>	<i>27</i>	<i>0.005</i>	<i>0.66</i>

**Table A8** Experimental results on NH<sub>3</sub>, cont.

Test	Concentration in box (ppm)	Production (mg/s)	Yield (mg/g)
8A	402	0.483	15.0
8B	415	0.499	15.5
8C	623	0.750	23.2
<i>Mean:</i>	480	0.58	17.9
<i>Stdev:</i>	124	0.15	4.6
9A	443	0.129	7.99
9B	474	0.138	8.53
<i>Mean:</i>	458	0.13	8.26
<i>Stdev:</i>	22	0.006	0.38
10A	23.4	0.027	1.68
10B	30.4	0.035	2.19
<i>Mean:</i>	26.9	0.03	1.94
<i>Stdev:</i>	4.9	0.006	0.36
11A	439	0.086	10.7
11B	286	0.056	6.96
<i>Mean:</i>	362	0.07	8.84
<i>Stdev:</i>	109	0.021	2.6
12A	359	0.208	13.0
12B	381	0.221	13.7
<i>Mean:</i>	370	0.21	13.3
<i>Stdev:</i>	15	0.009	0.6
13A	364	0.211	13.1
13B	434	0.252	15.6
13C	469	0.272	16.9
<i>Mean:</i>	422	0.24	15.2
<i>Stdev:</i>	53	0.03	1.9
14A	374	0.217	13.4
14B	357	0.207	12.9
<i>Mean:</i>	365	0.21	13.1
<i>Stdev:</i>	12	0.007	0.42
15A	203	0.040	4.94
15B	220	0.043	5.35
15C	162	0.032	3.93
15D	209	0.041	5.09
<i>Mean:</i>	198	0.04	4.83
<i>Stdev:</i>	25	0.005	0.62

**Table A9** Experimental results on NO.

Test	Concentration in box (ppm)	Production (mg/s)	Yield (mg/g)
1A	59.2	0.060	3.76
1B	83.2	0.085	5.27
<i>Mean:</i>	<i>71.2</i>	<i>0.07</i>	<i>4.52</i>
<i>Stdev:</i>	<i>17</i>	<i>0.02</i>	<i>1.1</i>
1A2	183	0.19	11.6
1B2	162	0.17	10.3
<i>Mean:</i>	<i>173</i>	<i>0.18</i>	<i>10.9</i>
<i>Stdev:</i>	<i>15</i>	<i>0.02</i>	<i>0.96</i>
2A			
2B			
2C			
<i>Mean:</i>			
<i>Stdev:</i>			
3A			
3B			
<i>Mean:</i>			
<i>Stdev:</i>			
4A			
4B			
4C			
<i>Mean:</i>			
<i>Stdev:</i>			
5A			
5B			
<i>Mean:</i>			
<i>Stdev:</i>			
6A			
6B			
<i>Mean:</i>			
<i>Stdev:</i>			
7A			
7B			
7C			
<i>Mean:</i>			
<i>Stdev:</i>			

**Table A10** Experimental results on NO, cont.

Test	Concentration in box (ppm)	Production (mg/s)	Yield (mg/g)
8A			
8B			
8C			
<i>Mean:</i>			
<i>Stdev:</i>			
9A			
9B			
<i>Mean:</i>			
<i>Stdev:</i>			
10A	62.7	0.128	7.95
10B	81.8	0.167	10.4
<i>Mean:</i>	72.2	0.15	9.16
<i>Stdev:</i>	13	0.03	1.7
11A			
11B			
<i>Mean:</i>			
<i>Stdev:</i>			
12A			
12B			
<i>Mean:</i>			
<i>Stdev:</i>			
13A			
13B			
13C			
<i>Mean:</i>			
<i>Stdev:</i>			
14A	?	?	?
14B	?	?	?
<i>Mean:</i>			
<i>Stdev:</i>	<i>Interference...</i>		
15A	?	?	?
15B	?	?	?
15C	?	?	?
15D	?	?	?
<i>Mean:</i>	<i>Interference...</i>		
<i>Stdev:</i>			

**Table A11** Experimental results on NO<sub>2</sub>.

Test	Concentration in box (ppm)	Production (mg/s)	Yield (mg/g)
1A	2.50	0.00392	0.243
1B	3.03	0.00475	0.295
<i>Mean:</i>	2.77	0.00	0.27
<i>Stdev:</i>	0.375	0.001	0.036
1A2	3.55	0.00557	0.346
1B2	5.47	0.00857	0.533
<i>Mean:</i>	4.51	0.01	0.44
<i>Stdev:</i>	1.355	0.002	0.132
2A			
2B			
2C			
<i>Mean:</i>			
<i>Stdev:</i>			
3A			
3B			
<i>Mean:</i>			
<i>Stdev:</i>			
4A			
4B			
4C			
<i>Mean:</i>			
<i>Stdev:</i>			
5A			
5B			
<i>Mean:</i>			
<i>Stdev:</i>			
6A			
6B			
<i>Mean:</i>			
<i>Stdev:</i>			
7A			
7B			
7C			
<i>Mean:</i>			
<i>Stdev:</i>			

**Table A12** Experimental results on NO<sub>2</sub>, cont.

Test	Concentration in box (ppm)	Production (mg/s)	Yield (mg/g)
8A			
8B			
8C			
<i>Mean:</i>			
<i>Stdev:</i>			
9A			
9B			
<i>Mean:</i>			
<i>Stdev:</i>			
10A	2.21	0.0069	0.429
10B	3.53	0.0111	0.686
<i>Mean:</i>	2.87	0.01	0.56
<i>Stdev:</i>	0.93	0.003	0.18
11A			
11B			
<i>Mean:</i>			
<i>Stdev:</i>			
12A			
12B			
<i>Mean:</i>			
<i>Stdev:</i>			
13A			
13B			
13C			
<i>Mean:</i>			
<i>Stdev:</i>			
14A	?	?	?
14B	?	?	?
<i>Mean:</i>			
<i>Stdev:</i>			
15A	74.2	0.039	4.87
15B	40.1	0.021	2.63
15C	44.4	0.023	2.91
15D	119	0.063	7.85
<i>Mean:</i>	69	0.04	4.57
<i>Stdev:</i>	36	0.02	2.4

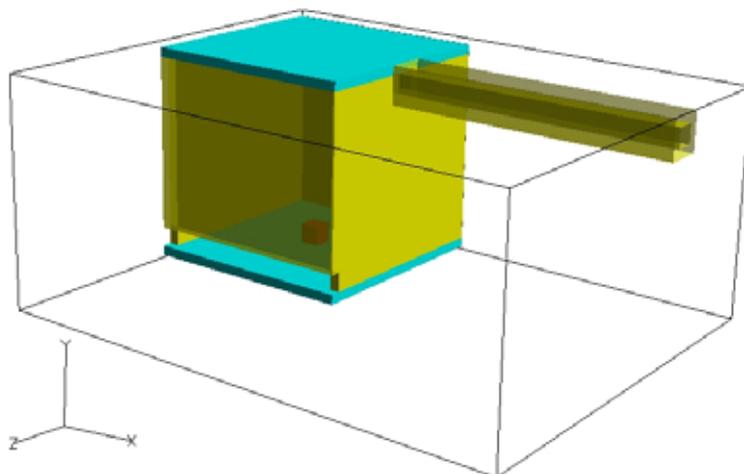
## Appendix B – Trial simulations

### B.1. Introductory simulations in 1 m high room

The first scenario was a  $1 \times 1 \times 1 \text{ m}^3$  box with 5 cm thick walls (including floor and ceiling) of thermally inactive material, i.e. the heat transfer between the wall material and gas was neglected. In the upper part of the left wall a square 10 cm (inner dimensions) exhaust pipe connected. The pipe walls were also treated as inactive solids. Lowest part of the front door was left as opening. The width of the opening was equal to the wall width to establish a smooth flow pattern of gases into and out from the room. In this first case the opening height was 10 cm, which created an under-ventilated situation, even for small fires. At a distance of one metre from the front wall a static pressure boundary was located, which provided the inflow of fresh air into and surplus gas out from the calculation domain. A square 10 cm fire source was placed in the middle of the floor. The model room is shown in Figure B1.

In this geometry most runs were made using a residence time  $\tau = 2 \text{ s}$  in the pipe. One scenario with  $\tau = 5 \text{ s}$  was made. Because in reality the combustion occurs in vitiated air in rooms with small openings, simulations with vitiation mode were also made.

This configuration showed to be unstable due to disturbance of fire plume and ceiling jet to the gas flow entering into pipe. The gas flow showed oscillating behaviour, so that it was difficult to see whether the concentration of HCN was increased or reduced during the passage of the pipe.



**Figure B1** A sketch of the first scenario. Room size  $1 \text{ m}^3$ , horizontal exhaust pipe with length 1 m and 10 cm square cross section.

It was difficult to find a simulation that generated high level of HCN at low temperature (as it was in experiments) with this small box. Low HRR generates lower temperatures, but also lowers the levels of toxic gases. Decreasing the opening size to very small would increase the toxic gases concentrations, but on the other hand, it would take longer time to get the room in steady state and small changes in flow parameters through the pipe would influence the inflow into the room too much.

Due to low the opening height the gas layer height was lowered and the fire was soon inside the smoke layer. Temperature of fire gases did not rise more than to about 180 °C since the combustion efficiency was reduced due to lack of oxygen and the HCN concentration reached to about 370 ppm and CO near 6000 ppm with the residence time  $\tau = 5$  s. For  $\tau = 2$  s the HCN concentration was reduced to 0.27 ppm. The low concentration of HCN can be explained by the increased ventilation through the pipe which raised the level of the smoke layer so that the combustion occurred in less vitiated conditions, and less HCN was formed. The concentrations of CO were also low in scenarios with  $\tau = 2$  s, about 250 ppm in non-vitiated case.

The simulations were also made using a vitiated option in SOFIE, although the gas layer did not decrease to the fire level with  $\tau = 2$  s. The vitiation simulations were made to increase the levels of HCN and CO. For  $\tau = 5$  s, however the gas layer was reduced (due to lower ventilation) so that the flame was partly in the smoke layer. This can explain that more toxic products are considerably higher. The results of simulations with the 1m high room is summarised in Tables B1 – B3.

**Table B1** Temperatures and species concentrations in the room 5 cm below the ceiling

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	$\tau$ [s]
Smoke_tau2	193	0.267	242	0.0635	0.097	2
Smoke_v05_tau2	186	0.0114	164	0.0395	0.140	2
Smoke_v10_tau2	179	0.0856	250	0.0578	0.107	2
Smoke_v15_tau2	176	0.285	481	0.0642	0.0952	2
Smoke_v20_tau2	176	7.68	1029	0.0812	0.0636	2
Smoke_tau5	209	380	5739	0.109	0.010	5

**Table B2** Temperatures and species concentrations in the pipe, 10 cm from the inlet.

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	$\tau$ [s]
Smoke_tau2	176	0.266	243	0.0635	0.097	2
Smoke_v05_tau2	181	0.0066	165	0.0395	0.140	2
Smoke_v10_tau2	175	0.0857	250	0.0581	0.107	2
Smoke_v15_tau2	173	0.284	483	0.0644	0.0950	2
Smoke_v20_tau2	176	7.72	1030	0.0813	0.0634	2
Smoke_tau5	203	373	5752	0.109	0.0099	5

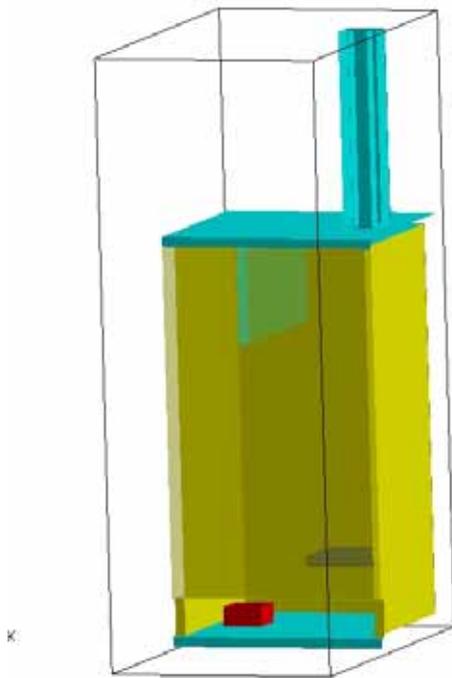
**Table B3** Temperatures and species concentrations in the pipe, 10 cm from the outlet.

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	$\tau$ [s]
Smoke_tau2	178	0.267	243	0.0635	0.097	2
Smoke_v05_tau2	183	0.0054	163	0.0393	0.140	2
Smoke_v10_tau2	177	0.0733	233	0.0579	0.107	2
Smoke_v15_tau2	176	0.280	481	0.0642	0.0954	2
Smoke_v20_tau2	176	7.72	1031	0.0813	0.0634	2
Smoke_tau5	197	368	5686	0.109	0.011	5

## B.2. Room with doubled height

To avoid instabilities due to disturbances from the plume and the ceiling jet a 0.5 m separator wall below the ceiling was inserted in this geometry. The stability was clearly better with this configuration. In the first scenarios with this configuration the opening height of 0.5 m and HRR 100 kW were used. The problem was that the generation of reasonable concentrations of HCN needed high HRR, which in turn made the temperature in the gas layer rise. An HRR of 100 kW generated not more than about 20-25 ppm HCN and a temperature of 820-950 °C.

Reducing the opening height to 0.2 m gave high levels of HCN in the gas layer. The HRR was reduced to 50 kW (100 kW was too large for this small opening). HCN levels of 1000-1400 ppm were reached in the gas layer, but the temperature was still high, i.e. about 900-950 °C. To simulate a mixture with high concentration of HCN and a low temperature is difficult. The simplest method was to cool the mixture by diluting it with air.



**Figure B2** A sketch of the two metre high room with vertical exhaust pipe. A 50 cm high separator wall is placed below the ceiling in order to stabilize the incoming flow into pipe.

One needed only to dilute the gas that was flowing into the exhaust pipe. So the best place for air inflow sources was on the inner walls at the pipe. Because the input air temperature differs to the gas temperature, the vertical pipe could not be used. Air with lower temperature would fall back into the room and could cause turbulence at the entrance and in the pipe. So the next change of the configuration was to use a horizontal pipe and otherwise keep the room geometry unchanged.

## B2.1. Horizontal pipe, opening height 0.5 m

A 20 kW fire in the two metres high box with opening height 20 cm took a long time to warm up the gases in the box. So the HRR was raised to 50 kW and the opening enlarged to 50 cm high, which generated temperatures about 300 °C in the pipe for  $\tau = 5$ . Concentrations of HCN became less than 0.1 ppm.

A doubled HRR, i.e. 100 kW, generated a smoke temperature in the pipe of about 450 °C and HCN concentrations of about 20 ppm. The slightly lower temperature at the end of the pipe as seen in tables B5 and B6 is due to radiation losses from the gas to atmosphere. At the exit, the boundary condition for emissivity,  $\varepsilon$ , was set to 0.9. In order to generate more HCN the HRR was increased to 150 kW. This gave reasonable fire gas temperatures and HCN concentrations; temperature about 600 °C and HCN concentration around 500-550 ppm. This geometry, however, was very unstable, so in the next geometry the pipe was set vertically. The results for all cases are listed in tables B4-B6.

**Table B4** Temperatures and species concentrations in the room 5 cm below the ceiling

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	$\tau$ [s]
Smoke2m tau2	200	1.29	316	0.0744	0.0779	2
Smoke50kW tau5	320	0.0825	169	0.0460	0.128	5
Smoke100kW tau5	582	21.3	877	0.0407	0.0416	5
Smoke150kW tau5	691	409	6156	0.108	0.0107	5
Smoke150kW tau2	636	455	5853	0.107	0.0101	2
Smoke150kW_tau15	565	514	6820	0.109	0.0076	15

**Table B5** Temperatures and species concentrations in the pipe 10 cm from the inlet

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	$\tau$ [s]
Smoke2m tau2	195	1.28	317	0.0744	0.0778	2
Smoke50kW tau5	297	0.024	170	0.0463	0.128	5
Smoke100kW tau5	466	23.0	930	0.0379	0.0377	5
Smoke150kW tau5	581	510	6797	0.110	0.0057	5
Smoke150kW tau2	603	480	6612	0.110	0.0063	2
Smoke150kW_tau15	565	545	7107	0.110	0.0050	15

**Table B6** Temperatures and species concentrations in the pipe 10 cm from the outlet

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	$\tau$ [s]
Smoke2m tau2	192	1.28	317	0.0744	0.0778	2
Smoke50kW tau5	289	0.024	170	0.0463	0.128	5
Smoke100kW tau5	449	23.2	935	0.0376	0.0376	5
Smoke150kW tau5	540	522	7058	0.110	0.0052	5
Smoke150kW tau2	574	507	6688	0.110	0.0060	2
Smoke150kW_tau15	517	534	6974	0.110	0.0054	15

## B2.2 Vertical pipe, opening height 0.5 m

To eliminate the disturbance from the fire plume and the ceiling jet onto gases in the pipe, the upper part of the room was sectioned by a wall according to Figure B2. The fire source was placed so that the point of impingement of the fire plume was shadowed by the wall. This arrangement stopped effectively instabilities caused by the ceiling jet. A HRR of 100 kW was used. To eliminate the temperature difference between gases at the end of the pipe and gases at pipe inlet the emissivity was set to zero at the end of the pipe.

The temperature in the pipe was considerably higher in scenarios with the vertical pipe. The omitting of the radiation from the pipe end was the main reason to this temperature rise. The other reason (probably a minor reason) was that the suction of gases into the pipe occurs through an opening in the ceiling, i.e. where the gases are hottest. Generally the gas temperature in the pipe was 950 °C. The concentrations of HCN were about 22 ppm, see Tables B8 and B9.

**Table B7** Temperatures and species concentrations in the room 5 cm below the ceiling

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	τ [s]
Smpv100kw_tauvar	952	21.00	868	0.0943	0.0425	1
	954	22.41	915	0.0955	0.0417	2
	955	23.39	937	0.0960	0.0397	5
	955	24.02	950	0.0964	0.0390	15
	955	24.18	950	0.0969	0.0399	30
	955	24.14	951	0.0965	0.0392	60

**Table B8** Temperatures and species concentrations in the pipe 10 cm from the inlet

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	τ [s]
Smpv100kw_tauvar	952	18.66	823	0.0941	0.0423	1
	953	20.59	867	0.0951	0.0404	2
	954	21.71	900	0.0959	0.0391	5
	953	22.23	912	0.0961	0.0385	15
	953	22.35	911	0.0962	0.0384	30
	952	22.39	916	0.0962	0.0384	60

**Table B9** Temperatures and species concentrations in the pipe 10 cm from the outlet

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	τ [s]
Smpv100kw_tauvar	950	18.43	813	0.0939	0.0426	1
	949	20.45	859	0.0950	0.0404	2
	944	21.66	896	0.0958	0.0394	5
	937	21.19	909	0.0961	0.0386	15
	933	22.32	913	0.0962	0.0385	30
	931	22.35	913	0.0962	0.0385	60

### B.2.3 Simulation with vitiation, horizontal pipe

A 100 kW scenario was also run with 20 % vitiation to take the effect of recycling of fire gases back to the fire into account. The effect on HCN concentrations was minimal, but CO concentration increased 60 – 70 %.

**Table B10** Temperatures and species concentrations in the room 5 cm below the ceiling, vitiation fraction 0.2.

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	τ [s]
Smpv100kw_tauvar	830	17.67	1342	0.0981	0.0361	1
	832	20.06	1430	0.0994	0.0352	2
	834	21.56	1482	0.100	0.0319	5
	834	22.28	1497	0.100	0.0315	15
	834	22.48	1510	0.100	0.0313	30
	835	22.88	1513	0.100	0.0313	60

**Table B11** Temperatures and species concentrations in the pipe, 10 cm from the inlet, vitiation fraction 0.2.

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	τ [s]
Smpv100kw_tauvar	831	16.87	1336	0.0986	0.0346	1
	833	19.27	1423	0.0995	0.0358	2
	834	20.85	1475	0.100	0.0318	5
	833	21.63	1495	0.100	0.0313	15
	833	21.88	1499	0.100	0.0312	30
	832	22.01	1500	0.100	0.0311	60

**Table B12** Temperatures and species concentrations in the pipe, 10 cm from the outlet, vitiation fraction 0.2.

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	τ [s]
Smpv100kw_tauvar	830	16.60	1428	0.0958	0.0347	1
	830	19.23	1413	0.0995	0.0329	2
	827	21.15	1456	0.100	0.0318	5
	820	22.45	1468	0.100	0.0313	15
	816	23.02	1470	0.100	0.0312	30
	813	22.33	1470	0.100	0.0312	60

### B.3. Opening height reduced to 0.2 m, horizontal pipe

#### B.3.1. Heat release rate 50 kW

In order to increase the level of HCN the size of opening was reduced to 20 cm, see Figure B2. A 100 kW fire appeared to be too large with this small opening. Therefore the HRR was reduced to 50 kW. The changes gave the desired result on HCN concentrations, which increased to about 1000-1400 ppm. The temperature was still at the same level, i.e. about 930 °C. CO concentrations up to 11 000 ppm were generated.

**Table B13** Temperatures and species concentrations in the room 5 cm below the ceiling, HRR 50 kW.

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	τ [s]
Smpv50kw_tauvar	947	1033	8566	0.107	0.00086	1
	930	989	8575	0.106	0.00041	2
	928	1240	10015	0.105	0.00012	5
	929	1360	10939	0.105	7.6x10 <sup>-5</sup>	15
	926	1378	11170	0.104	5.6x10 <sup>-5</sup>	30
	923	1361	10579	0.104	6.6x10 <sup>-5</sup>	60

**Table B14** Temperatures and species concentrations in the pipe 10 cm from the inlet, HRR 50 kW.

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	τ [s]
Smpv50kw_tauvar	949	1033	8580	0.107	0.00079	1
	931	1021	8744	0.106	0.00036	2
	929	1292	10239	0.105	6.2x10 <sup>-5</sup>	5
	929	1373	11027	0.104	2.7x10 <sup>-5</sup>	15
	925	1387	11215	0.104	1.9x10 <sup>-5</sup>	30
	920	1375	11064	0.104	2.1x10 <sup>-5</sup>	60

**Table B15** Temperatures and species concentrations in the pipe 10 cm from the outlet, HRR 50 kW.

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	τ [s]
Smpv50kw_tauvar	961	1033	8582	0.107	0.00079	1
	936	1107	9001	0.106	0.00027	2
	925	1299	10251	0.105	5.2x10 <sup>-5</sup>	5
	917	1296	10190	0.105	4.8x10 <sup>-5</sup>	15
	911	1230	9964	0.105	9.4x10 <sup>-5</sup>	30
	902	1313	10393	0.104	3.4x10 <sup>-5</sup>	60

### B.3.2 Heat release rate 20 kW

In reality the temperature of fire gases which are transported to other rooms are considerably cooler. Therefore a scenario with lower temperature and relatively high concentrations of HCN and CO is needed. An alternative scenario for this configuration was run using a HRR of 20 kW in order to get a lower temperature and keep the relatively high concentrations of toxic gases. But the formation of toxic gases seems to be very sensitive to ventilation. To reduce the temperature 200-250 °C, by reducing HRR to 20 kW, resulted in a decrease of HCN by a factor of 5000 and CO by a factor of 50. The only way to have relatively high concentrations of toxic gases at low temperatures is to cool them in some way.

**Table B16** Temperatures and species concentrations in the room 5 cm below the ceiling, HRR 20 kW.

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	τ [s]
Smpv50kw_tauvar	683	0.174	152	0.0573	0.109	1
	677	0.264	236	0.0619	0.100	2
	681	0.306	246	0.0644	0.0959	5
	683	0.321	251	0.0655	0.0941	15
	683	0.326	253	0.0659	0.0932	30
	683	0.317	253	0.0660	0.0928	60

**Table B17** Temperatures and species concentrations in the pipe 10 cm from the inlet, HRR 20 kW.

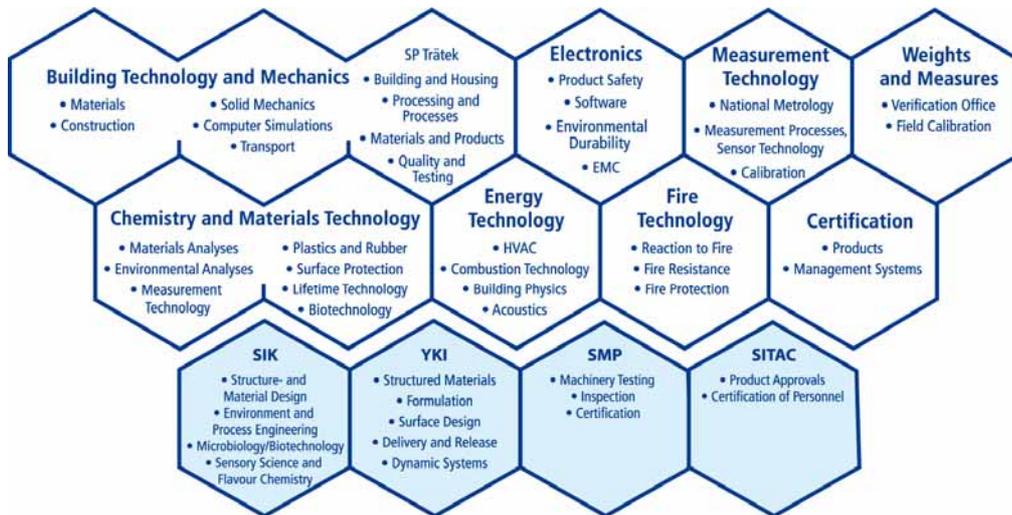
Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	τ [s]
Smpv50kw_tauvar	671	0.153	152	0.0573	0.109	1
	677	0.239	235	0.0617	0.100	2
	681	0.280	245	0.0642	0.0961	5
	683	0.300	250	0.0653	0.0941	15
	682	0.307	252	0.0657	0.0934	30
	682	0.307	252	0.0658	0.0933	60

**Table B18** Temperatures and species concentrations in the pipe 10 cm from the outlet, HRR 20 kW.

Scenario	T [°C]	HCN [ppm]	CO [ppm]	CO <sub>2</sub> [mole fraction]	O <sub>2</sub> [mole fraction]	τ [s]
Smpv50kw_tauvar	670	0.142	152	0.0572	0.109	1
	676	0.229	234	0.0616	0.101	2
	677	0.275	245	0.0640	0.0963	5
	674	0.297	250	0.0653	0.0941	15
	672	0.304	251	0.0655	0.0931	30
	668	0.307	252	0.0657	0.0933	60

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