Air Starved Wood Crib Compartment Fire Heat Release and Toxic Gas Yields

OMAR ALJUMAIAH, GORDON E. ANDREWS, HERODOTOS N. PHYLAKTOU, BINTU G. MUSTAFA, HOMHAMMEA AL-QATTAN, and VISHAL SHAH
Energy and Resources Research Institute
School of Process, Environment and Materials Engineering
University of Leeds, Leeds, LS2 9JT, UK

ABSTRACT

Pine wood crib fires (4.6 kg) were investigated in a 1.6 m^3 fire compartment with air ventilation between 3 and 40 air changes per hour (ACH). The cribs were 380 mm tall and 300 mm square. The fires rapidly self extinguished at 3ACH and struggled to continue to propagate at 5 ACH, where only 15 % of the initial crib mass was burnt. For 11, 21 and 37 ACH the cribs burned completely and the oxygen consumption HRR increased with ventilation. All three fully burned fires had rich equivalence ratios for most of the fire duration and associated high CO yields. Extremely toxic levels of CO, acrolein, formaldehyde and benzene were generated and the total toxic N on an LC_{50} basis was over 30. The combustion efficiency was very low due to the very high CO and total hydrocarbon emissions and this led to a major difference in the HRR by mass loss and that by oxygen consumption. The results demonstrate the severe toxic conditions that occur in ventilation restricted fires with wood as the main fire load.

KEYWORDS: fire chemistry, compartment fires, toxicity, heat release rate, hazard evaluation.

INTRODUCTION

Over 70 % of fire fatalities are caused by inhalation of toxic gases present in fire smoke [1–4]. Not only does smoke reduce the visibility of occupants in compartment fires, but it also is an irritant which causes respiratory problems. Purser [1] showed that in most fires the main toxic products are CO, HCN and irritant or acidic gases and the amount of each depends on the thermal decomposition of the fire load, which depends on the temperature and oxygen supply. However, HCN and HCl and HBr are normally low unless the fire load contains organic N, Cl or Br compounds [2–4], which was not the case in the present work. There are very few measurements of irritant and acidic gases in compartment wood fires and the present work uses heated Fourier transform infra-red spectroscopy (FTIR) specifically to investigate these gases.

The effect of toxic smoke can be lethal [1–4] and this is normally measured by the LC_{50} toxic limits [1–5] for 50 % deaths after 30 min exposure. However, toxic gases are often described by survivors of fires as acidic and/or irritant gases and these slow the movement of people and can lead indirectly to their death [1–4]. CO is the most common gas that kills people in fires, but this has no odour or irritant effect on people. The authors [6–8] have used COSHH 15 min exposure standards [9] as well as LC_{50} to access fire toxicity. COSHH is the European standard on occupational exposure limits, which are statutory law in Europe, and are similar to the equivalent US limits. These COSHH 15 min levels represent an impairment of the means of escape, whereas the LC_{50} limits are for 50 % people dying in a fire after 30 min exposure. The USA has introduced the Acute Exposure Guideline Levels (AEGL) with three exposure levels: 1 for non-disabling and essentially similar to the COSHH 8 h levels; 2 for disabling and impairment of escape based on 10 min exposure which is similar to the COSHH 15 min exposure limit; and 3 for life threatening health effects which are similar to LC_{50}. The $COSHH_{15min}$ [9] limits have been largely ignored in fire toxicity, apart from in the work of the authors, but are the best data set for assessing multi-component toxicity with a legally agreed methodology, which is similar to the LC_{50} N-gas method [10,11].

The toxicity assessment methods are compared in Table 1. The data for LC_{50} depends on which dataset is used and which animal exposure is used [3]. However, the data uncertainty is no more than a factor of 2 for most gases, but the ratio of the LC_{50} to impairment of escape limits are not consistent by a factor of 8. For the LC_{50} to $COSHH_{15}$ limits the ratios are again not consistent and vary by a factor close to 100. This means that the relative toxicity for LC_{50} of the different gases is completely different when impairment of means of escape limits are compared. In applying the toxic concentrations in Table 1 to the complex mixtures of toxic gases from fires the combined toxicity will be different for LC_{50} than for the three

FIRE SAFETY SCIENCE-PROCEEDINGS OF THE TENTH INTERNATIONAL SYMPOSIUM, pp. 1263-1276

Table 1. Toxicity assessment methods and their ratios (all concentrations are ppm).

Toxic gas	15 min exposure limit COSHH [9]	AEGL-2 10 min escape impairment [3]	SFPE conc. impair escape [3]	LC_{50} 30 min [1,5]	LC_{50} /Impair	LC_{50}/ AEGL-2	LC_{50}/ $COSHH_{15}$
CO	200	420		3,000		17	15
NO_2	5	20	70	350	5	17.5	70
HCN	10	17 [13]		135		8	13.5
C_6H_6	3	2000 [12]		10.000		5	3333
CH_2O	2	14	6	250	42	18	125
C_3H_5O	0.3	0.44	4	135	34	307	1000
CH_2O_2	5						
SO_2	5	0.75	24	500	20.8	667	100
HCl	5	100	200	3,700	18.5	370	740

methods of assessing the impairment of escape, because there is no consistency in the relative toxicities. LC_{50} will always place a greater relative emphasis on CO and $COSHH_{15}$ will always place a greater relative emphasis on acrolein. AEGL-2 is in agreement with this assessment of a much greater toxicity associated with acrolein than is given in LC_{50}. This means that the gas concentrations that control death are quite different from those that impair escape [5–7]. The AEGL-2 escape impairment limits in Table 1 are in most cases similar to $COSHH_{15}$, but for benzene and HCl there are large differences.

Most current information on toxic gases in fires has been obtained from well-ventilated compartment fires that simulate room fires with an open door or window or are freely-ventilated fires such as in the cone calorimeter. These essentially test the fire propagating properties of the material at conditions that represent the start of a fire, where ambient temperatures are low and the fire entrained gases are air with 21 % oxygen. These tests are suitable to rank material for fire safety purposes with tests under the same conditions [4]. However, they do not represent the behaviour of these materials in real fires, especially in the later stages of fires. Hence, toxicity measurements made in these reference tests may not be valid for use in computer modelling of fires in compartments. In a compartment fire the oxygen is depleted as the fire temperature rises and in the later stages of fires the conditions are high temperature, low oxygen and rich mixtures. This is the area of fire development that was investigated in the present work.

Information on fire toxicity has also been obtained by simulating the fire equivalence ratio in a tube furnace [14]. This has the problem that the fire temperature is separated from the fire equivalence ratio and this is not how real fires behave. In a closed room fire compartment with fire resistant walls, floor and ceiling, a closed fire door and closed double glazed windows, the air ventilation of the fire is very low and this was simulated in the present work. The present work follows the procedure in a tube furnace where the ventilation is imposed by using a forced fixed air mass flow which can be referred to in air changes per hour (ACH) ventilation terms. However, realistic fires are generated where the fire temperature and equivalence ratio are linked and not separated. The Purser furnace method [14] overcomes one disadvantage of the cone calorimeter method in that free ventilation is replaced by a controlled ventilation and controlled fire equivalence ratio.

In real compartment fires temperature, ventilation and equivalence ratio are all interdependent, which is why the present procedure was developed to give a better link between fire temperature and oxygen in studies of material behavior in fires, as well as to burn more realistic larger fire loads than in the Purser furnace method. Its principles are similar to the Purser method but on a more practical scale. It imposes the fire ventilation which is fixed, as in the Purser method, but generates a high fire temperature by heat release from the fire load and not through external heat supply.

EXPERIMENTAL EQUIPMENT

A 1.6 m^3 enclosed fire compartment [6–8] was used as shown in Fig. 1, with similar dimensions to that used by Bundy et al. [15]. The principle of air entry at floor level and fire products exiting near the ceiling level was first introduced by Gottuk et al. [16] and this has been used in this work. The principle of supplying the air ventilation at a fixed rate to the fire compartment was developed by the authors [6–8] and

has also been used in studies of pool fires by Utiskul et al. [17]. Although most compartment fires have an open door compartment [18–22] they are usually of full room height which controls the pressure difference that entrains air into the fire. In smaller compartments such as the present with a 1.5 m height natural ventilation would result in lower ventilation rates than real compartment fires and the forced ventilation technique overcomes this problem. In the fully developed fire stage of compartment fires the ventilation rate is normally relatively constant and fixed by the room height and the area of the open door [18–22] and hence the present procedures are not far away from real compartment fires.

A fixed air ventilation rate was set for each fire and 3–37 air changes per hour (ACH) were used. The bottom end of this range represents air starved fires and top end represents well ventilated fires with an open door. The air was fed into a plenum chamber under the compartment and from there into the fire compartment through four slots at the edge of the compartment. The fire gases flowed along the flat metal ceiling to exit the compartment through a small gap between the edge of the ceiling and the compartment walls. The fire products then flowed along the rear of the ceiling to exit through a 150 mm diameter short chimney discharge. Gas samples were taken from the short chimney and were the mean composition of the ceiling gases. The compartment had horizontal and vertical thermocouples arrays to determine the fire compartment mean ceiling temperature. The compartment had a high temperature glass door that was closed immediately after the methanol was ignited. The initial stages of the fire development could be photographed through the window, but this soon became covered in soot and an outer cover was closed over the window to prevent radiative heat loss.

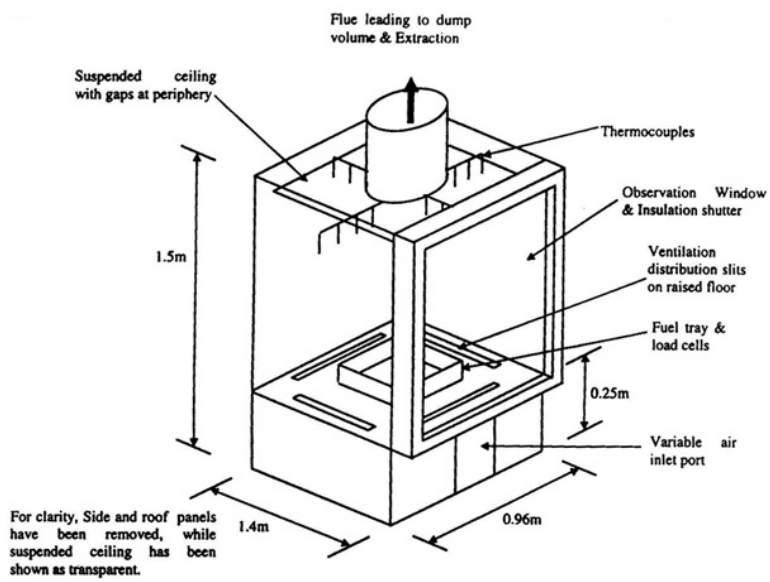


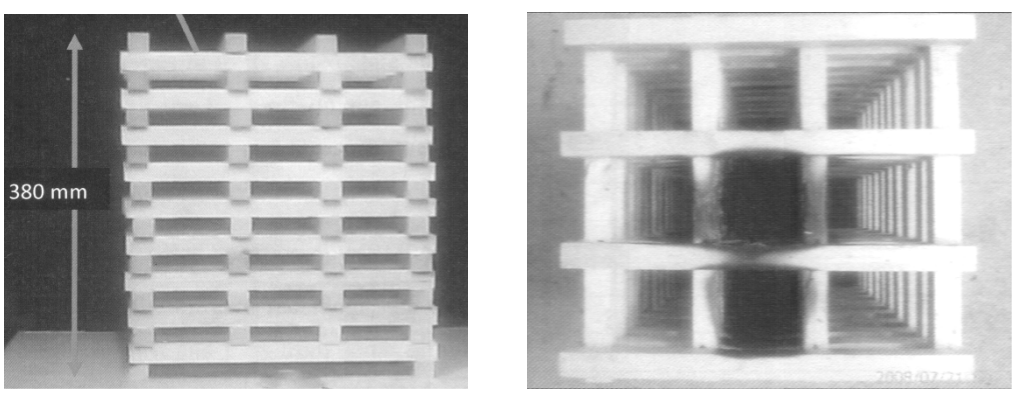
Fig. 1. Experimental 1.6 m^3 fire compartment.

Raw fire ceiling gases were sampled via 190 ºC heated sample lines and passed to a 190 ºC heated filter and pump and then to a heated FID for total hydrocarbon analysis. A heated chemiluminescence NOx analyser was used and after a 2 ºC water condenser the sample gas went to a NDIR analysers for CO and CO_2 and a paramagnetic analyser for oxygen. The oxygen analysis together with the air ventilation mass flow rate was used to determine the fire oxygen consumption and from this the HRR. The HRR was also determined by fire load mass loss measurements, as the crib was supported on a tray that rested on load cells in the air plenum chamber. The difference in the two HRR was large and this was due to the high combustion inefficiency. The gas analysis for CO_2, CO, HC and O_2 was used to determine the A/F by carbon balance, using the procedures of Chan and Zhu [23], together with the combustion inefficiency as the sum of the energy content of the CO and HC. The fire equivalence ratio was determined from the A/F by carbon balance using the stoichiometric A/F for the pine wood. The pine wood sticks were analysed for their HCO composition using an elemental analyzer, which gave the composition as 47.25 % C, 47.07 % O and 5.68 % H. This gave the chemical formula as $CH_{1.44}O_{0.75}$ where 1.44 is the H/C ratio and 0.75 is the O/C ratio. The stoichiometric A/F ratio for this composition is 5.34/1 and this was used in all the determinations of the fire equivalence ratio.

A heated TEMET GASMET CR-Series portable FTIR was used for acidic and irritant toxic gas analysis. This had a separate heated sample line, filter and pump and the FTIR sample cell was also heated at 190 ºC so that all analysis was on a hot wet basis and no acidic gases were lost by condensation. The FTIR was calibrated for over 50 species, including most of the toxic gases of interest in fire toxicity. The FTIR had a liquid nitrogen cooled detector and this gave at least 2 ppm resolution on all species. CO was calibrated to 10 % but other toxic species were calibrated to 500 ppm. The high level CO calibration was important in the present work where peak CO levels of 9 % were recorded. The parallel NDIR CO analyser was not designed to measure higher than 3 % CO and this instrument was off-scale for most of the results with ventilation levels of 11 ACH or above.

THE PINE WOOD CRIBS

The 4.6 kg pine wood cribs were identical for each fire, so that the only variable was the fire compartment ventilation rate. The cribs were three times the size of those that the authors have previously investigated [6,8] and this was to bring the fire loads closer to reality. A feature of the work with smaller cribs was that the fires had mainly lean equivalence ratios and the rich mixtures that often occur with ventilation restricted fires [18–22] were not encountered. The calorific value of pine is 17 MJ/kg and this gives 78 MJ of energy in the 4.8 kg pine cribs. The fire loading referenced to the floor area and compartment volume was 58 MJ/m^2 and 3.6 kg/m^2 or 50 MJ/m^3 and 3.1 kg/m^3 respectively. These are very light fire loads compared with the practical range for a wood processing factory of 200–800 MJ/m^2 [24], although there are some practical fire load conditions as low as 40 MJ/m^2 [24]. Other fire protection design guides quote low, medium and high fire loads [25]. Typical minimum fire loads are 230 MJ/m^2 as applied for example to a hospital [25]. The description of fire loads as a ratio to the floor area is not very realistic when the ceiling height of rooms can vary. The fire development is dependent on the air available and increases with the height of a room. However, a standard room is about 2.5m high so that fire loading in terms of floor area could simply be interpreted as a ratio to the compartment volume using this standard ceiling height. This gives 80–320 MJ/m^3 for wood processing factories [24] and 16 MJ/m^3 for the lightest fire loads [25]. It is considered that the volume based fire loading used in the present work is representative of a lightly loaded fire. The results show much higher toxic levels than in our previous work [6,8] with smaller cribs and this shows that fire loading is an important parameter in fire toxicity.



(a) (b)

Fig. 2. (a) Crib construction; (b) partially burned crib at 5 ACH.

The pine cribs were made of 74 sticks 300 mm long and 20 mm square cross section. The crib was made in layers of four sticks with the next layer at 90º to the previous one. The total height of the 19 layers was 380 mm and the gap between the sticks was 73 mm. The crib before burning is shown in Fig. 2a. The cribs were ignited by placing a small 50 mm diameter pool of 5 mm deep methanol in the centre of the crib beneath one of the pine sticks and the same position was used for each fire. The energy in the methanol was 0.4 % of the total crib heat release and hence was negligible in the fire heat release rate. Time zero in the experiments was when the compartment door was closed after placing the ignited methanol in place.

EXPERIMENTAL RESULTS

Typical 4.8 kg Pine Wood Crib Compartment Fire Results for 11 ACH

The main features of the ventilation controlled compartment fires for the 4.8 kg pine wood cribs are shown in Fig. 3 for 11 ACH. There was good agreement with the carbon balance equivalence ratio results and the metered air and fuel consumption rates. The results in Fig. 3 show a rapid fire development with the ceiling temperature increasing as the oxygen level was depleted and the CO_2 increased. There were three phases in the fire: the initial growth phase, main flaming combustion phase and finally a char burn out phase or smoldering combustion phase, which extended well beyond the time shown in Fig. 3. At 2500 s 90 % of the initial mass had been burnt, but the remaining 10 % took a further 5000s to burn out completely. This smoldering combustion phase started soon after the 1500 s time when the temperature started to fall and the oxygen to increase sharply. There was also a reduction in the toxic CO and in the total unburned hydrocarbons at this point. The mean fire equivalence ratio was different in the three phases with initially lean combustion followed by very rich conditions throughout the main flaming period of the fire and then a return to lean combustion after 1500 s when smoldering combustion was the main fire mode. It will be shown later that the toxic emissions during the first flaming fire development lean burning phase were quite different from those in the smoldering combustion lean burning phase of the fire, so that equivalence ratio is not the sole governing factor in the toxic emissions.

A key feature of Fig. 3, that was present at all the ventilations, was that the oxygen was never near 0 % even though the overall equivalence ratio was rich. The reason for this, as shown in Fig. 3, was the very high CO and total unburned hydrocarbons that occurred during the rich burning phase. The CO and HC contribute to the combustion efficiency, which is discussed later. The presence of significant oxygen during the rich high temperature fire mode leads to significant acrolein formation in this phase of the fire, as detailed later, which was unexpected as this is normally associated with lean low temperature fires.

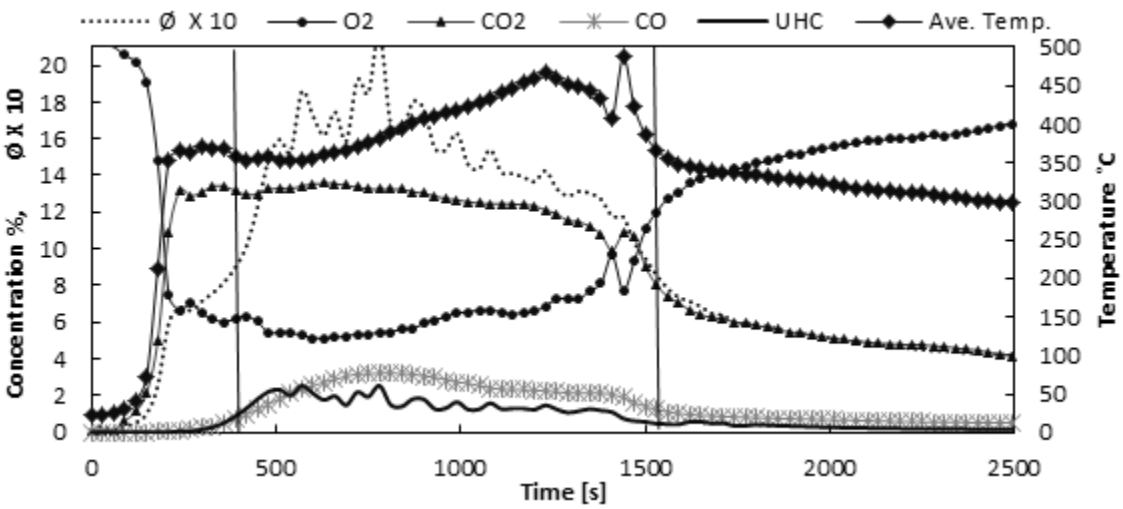
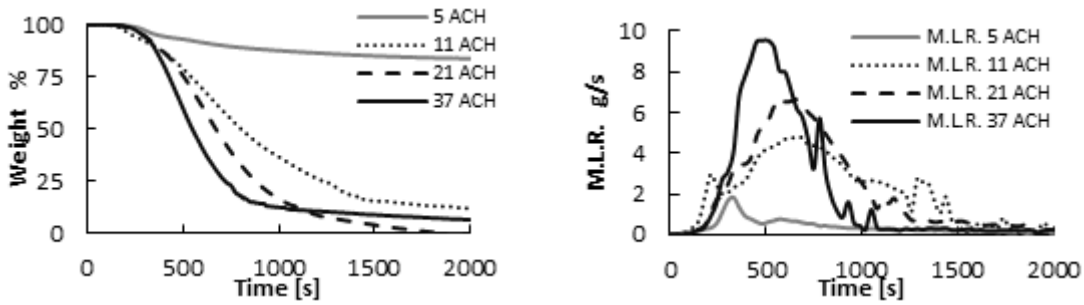


Fig. 3. Fire characteristics for 4.8 kg pine wood crib with 11ACH ventilation.

Similar results were obtained for each ventilation rate. The results show the influence of the ventilation rate on all the key fire parameters. For ventilation less than 11 ACH the crib was only partially burned, as shown in Fig. 2b for 5 ACH. The 5 ACH fire did burn sufficiently to record fire data for at least one hour, but only 17 % of the initial mass was burned and most of this in the first 20 min, as shown in Fig. 4. At 3 ACH the fire self extinguished very early in the fire. The crib did start to burn, but the lack of oxygen supply could not sustain the flame for more than 5 min. The results for this low ventilation have not been included in the graphs. In previous work [6,8] with 1.5 kg pine wood cribs, ventilation rates as low as 1 ACH could sustain a crib fire burnt lean throughout the duration. It is considered that in the present work the heat losses to the higher wood sticks resulted in cooling the post flame gases to a level that was too low to ignite the pine sticks higher up the crib. In this work there were 19 vertical layers of pine sticks compared with 10 layers, of the same stick 20 mm square cross section, in the 1.5 kg crib fires.

Compartment Weight Loss and Rate of Mass Consumption

The pine crib mass loss and rate of mass loss are shown in Fig. 4 for the four ventilation rates of 5, 11, 21 and 37 ACH. Figure 4 shows that at 5 ACH there was only a partial burn and most of this was in the Phase 3 of smoldering char combustion after about 500 s. 11 ACH was the lowest ventilation at which all the crib was burned and increasing the ventilation simply increased the rate at which the crib burned and decreased the duration of the high heat release flaming combustion phase of the fire. If combustion is complete the mass burning rate should be a linear function of the air mass flow rate as the potential heat release is ~3 MJ/kg of air irrespective of the fire load. For a given fire material, increasing the air ventilation should increase the mass burn rate linearly with the ACH. Fig. 4b shows this is not the case as increasing ACH from 11 to 21 does not double the peak mass loss rate. The reason is that all the fuel is not burned due to the presence of richer than stoichiometric mixtures, as shown in the combustion efficiency results. During most of these fires, in the Phase 2 rich burning flaming mode the pine cribs are being gasified to CO and H_2 as well as unburned volatile hydrocarbons and soot. These release heat when they encounter air outside the ceiling hot gas discharge. In a real fire this is seen as external flames from windows or roofs.

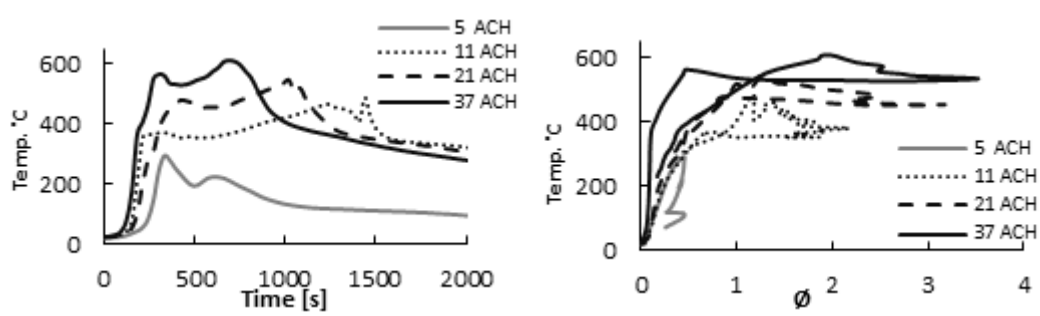


(a) (b)

Fig. 4. Pine wood crib: (a) mass loss; (b) rate of mass loss for 5, 11, 21, and 37 ACH ventilation.

Compartment Average Ceiling Temperature

The mean ceiling temperature is shown for all the air ventilations as a function of time and equivalence ratio in Fig. 5. There was a rapid temperature rise in the initial first lean burning phase and the peak temperature in this phase was limited by the air ventilation. All the fires showed a subsequent fall in temperature, which for 11–37 ACH was due to rich lower temperature combustion. This was followed by the peak temperature which occurred as the fire moved to near stoichiometric burning at lower mass burning rates in the final stages of flaming combustion before the transition to smoldering combustion. In the initial lean phase, the fire was hotter than in the final lean phase due to flaming combustion in the first lean phase and smoldering combustion in the final lean phase. Most of the 5 ACH fire occurred as smoldering combustion.

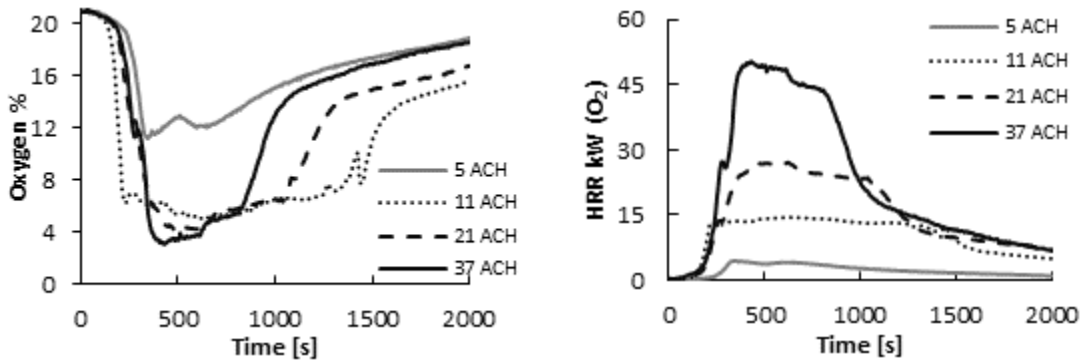


(a) (b)

Fig. 5. Compartment mean ceiling temperature as a function of: (a) time; (b) equivalence ratio.

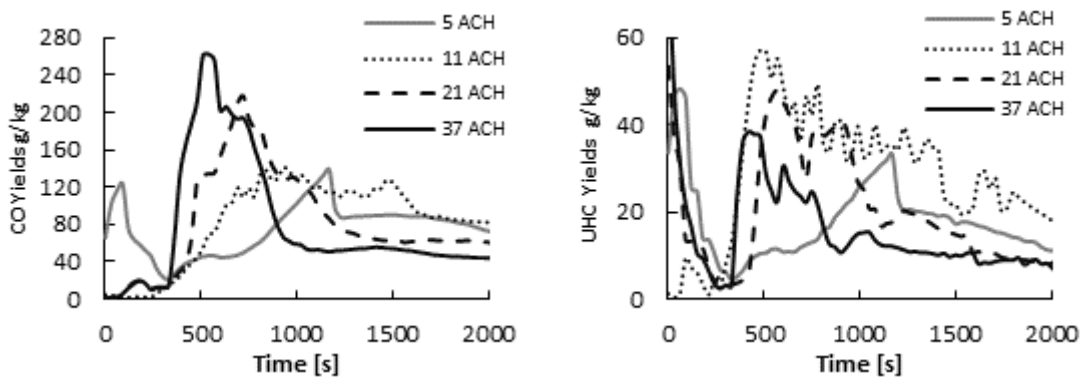
Compartment Oxygen and Oxygen Based Heat Release Rate (HRR)

The variation of oxygen with time for all the fire ventilations is shown in Fig. 6a. The HRR in Fig. 6b has been derived by oxygen mass consumption. There was very poor agreement between the HRR based on the wood mass consumption (shown later) and that based on oxygen consumption. The reason was the very poor combustion efficiency that is reflected in the high CO and HC emissions in Fig 4. When the mass loss based HRR is corrected for the poor combustion efficiency there was much better agreement with the oxygen consumption based HRR. The peak HRR by oxygen consumption for 37 ACH was 50 KW compared with 170 kW by mass consumption. The low combustion efficiency and high CO and HC that accounted for the unreleased energy are shown in Fig. 4 and for all the ventilations in Fig. 7. The high CO was due to the rich fire equivalence ratio, which was >1 for 20 min duration in Fig. 4, during which 85 % of the original mass was burned. This was the flaming combustion mode of the fire and this was where the toxic gases were at their highest, as shown later.



(a) (b)

Fig. 6. (a) Compartment oxygen (b) oxygen consumption based HRR as a function of time.



(a) (b)

Fig. 7. (a) Carbon monoxide and (b) total unburned hydrocarbons yields (kg/kg) as a function of time.

Carbon Monoxide and Total Unburned Hydrocarbon Yields

The carbon monoxide and total unburned hydrocarbon concentrations were converted to mass yields as g/kg and are shown in Fig. 7.

$$\text{Yield } C \text{ g/kg} = 1000 \text{ Cppm } MW_C/MW_{exhaust} \, [1 + A/F] \quad (1)$$

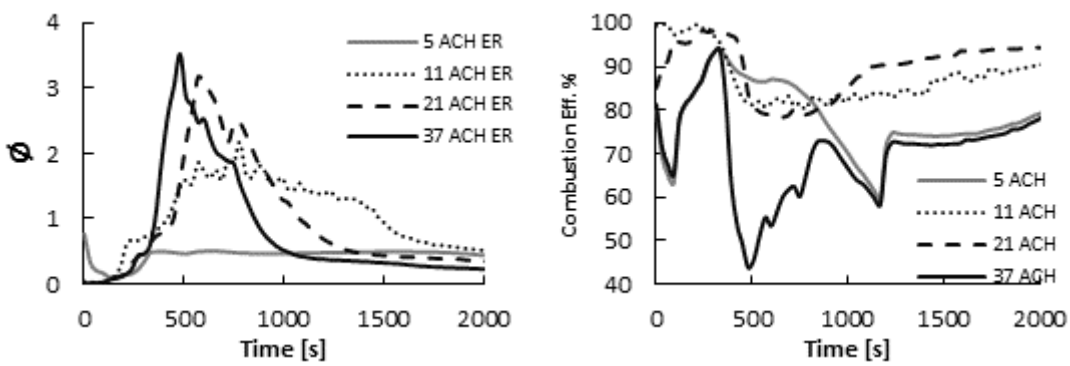
where C is the concentration of any species in ppm, MW_c is the species molecular weight and $MW_{exhaust}$ is the MW of the exhaust, which may be taken as that of air to an accuracy of better than 1 % for most fire loads. Eq. 1 has been used for all the toxic yields presented in this paper.

Figure 7 shows that CO yields are relatively low in the initial lean combustion phase, very high in the rich flaming combustion phase and relatively low in the final smoldering lean burning phase of the fires. The

peak CO yield for 37 ACH was 250 g/kg which is much greater than the 4 g/kg for freely ventilated pine wood fires [26]. Quintiere [26] quotes a value for pine wood in under-ventilated rich combustion of 138 g/kg and he also shows data for the increase in CO yield with equivalence ratio. For wood with a peak rich equivalence ratio of 4 the yield was 50 times that for a freely ventilated fire (4 g/kg) and this would give a peak yield of 200 g/kg, which is close to the present results for 21 and 37 ACH, where the peak equivalence ratio was 3–3.5, as shown in Fig. 8. Purser et al. [27] for the steady state tube furnace reported yields of 170 g/kg for pine wood rich combustion at 450 ºC, in reasonable agreement with the present results. However, these laboratory methods do not show the strong dependence of CO yield on ventilation shown in Fig. 7. Higher ventilation creates richer mixtures, as shown in Fig. 8a. Ventilation also increases the temperature, as shown in Fig. 5 and this occurs for the same rich equivalence ratio as shown in Fig. 5b. In furnace tests with wood, Purser et al. [27] showed that an increase in furnace temperature from 350 to 400 ºC increased the CO yield by a factor of 2 for the same ventilation. Fig. 5b shows for the same equivalence ratio of 2 that the temperature increased from 350 ºC to 600 ºC as the ventilation increased from 11 to 37 ACH. The peak CO yield in Fig. 7a increased from 140 to 260 g/kg over the same temperature change. This is a significant influence of temperature, but much lower than that found in the furnace work of Purser et al. [20] for a 50 ºC temperature increase. The increase in CO with temperature is a reflection of the increase in equilibrium CO with higher flame temperatures.

Combustion Efficiency, Fire Equivalence Ratio and Mass Loss Based HRR

The hydrocarbon (methane equivalent) yields in Fig. 7b are very significant and show that a substantial part of the fire load was volatilised but not burned in these fires. The HC results show a high yield during the period when the wood is being heated by the methanol accelerant, when there is little mass combustion. These volatiles suddenly ignite and burn out to zero and this gas flame is followed by heat release from the main wood flaming combustion at 200 s from the ignition of the accelerant. This occurs at the same time as this flaming combustion is driving the overall equivalence ratio rich, as shown in Fig. 8a. The subsequent high yield of HC is due to the inefficient combustion in the rich combustion.

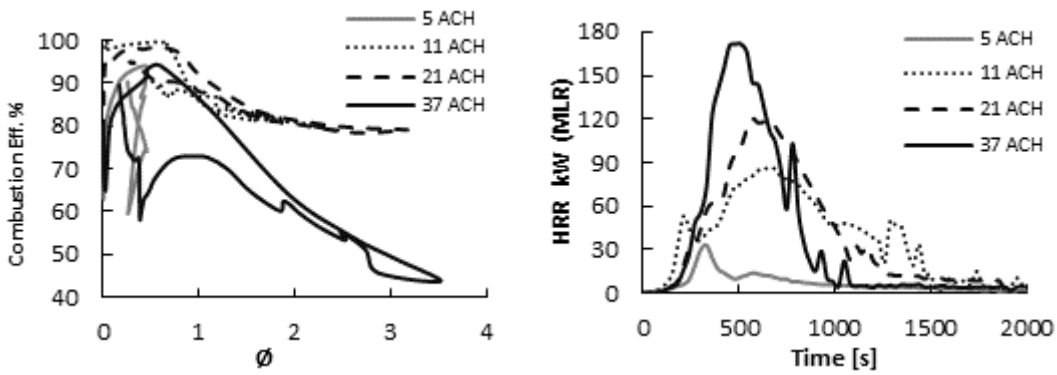


(a) (b)

Fig. 8. (a) Combustion efficiency and (b) fire equivalence ratio as a function of time.

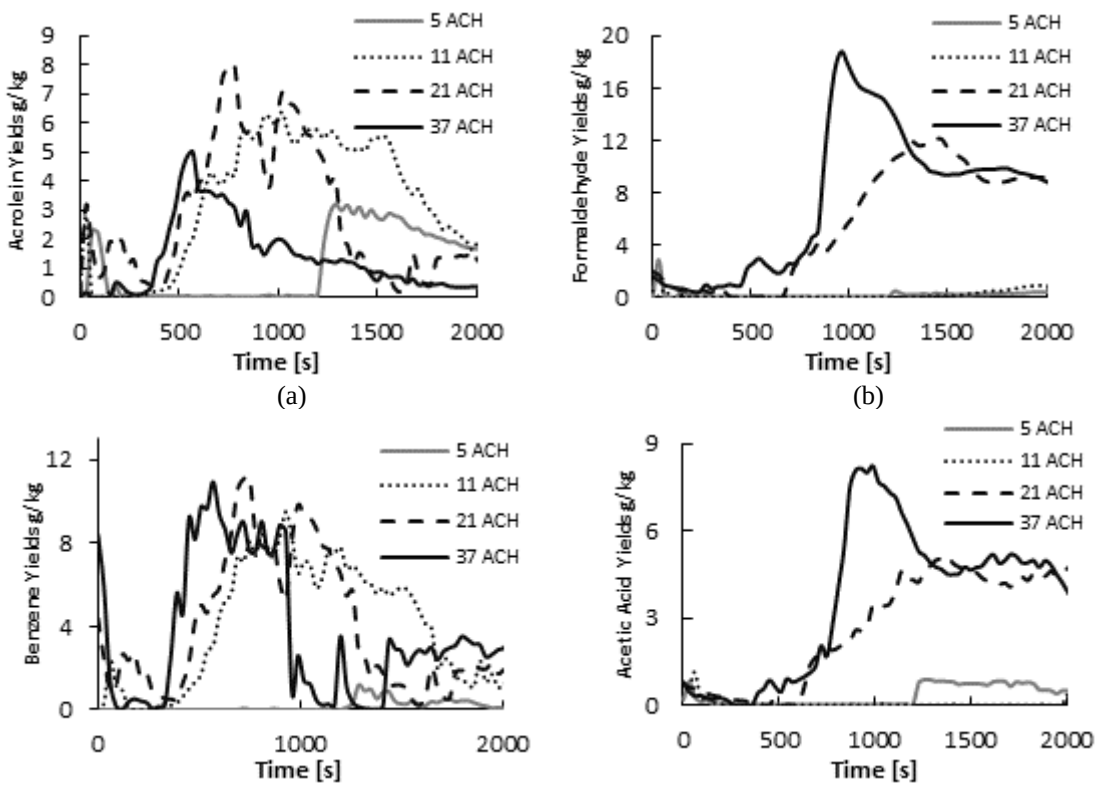
The energy content of the hydrocarbons together with the energy content of the CO represent a combustion inefficiency. The combustion efficiency variations with time are shown in Fig. 8b. These efficiencies will be high, as no account has been taken of the hydrogen or the soot energy content. However, the results show very low combustion efficiencies for all ventilation rates, but there was a decrease in the combustion efficiency as the ventilation was increased and this was related to the richer mixtures that were generated, as shown in Fig. 9a. The consequence of the very low combustion efficiencies is that not all the energy content in the fire load is released in the compartment fire, the CO, unburned hydrocarbons, hydrogen and soot energy is released outside the compartment as the discharge gases combine with external air. Consequently, there is a major difference between oxygen consumption based heat release, Fig. 6b, and that based on the fire load mass loss rate in Fig. 9b. If the peak HRR for 37 ACH of 170 kW in Fig. 9b is combined with the combustion efficiency of 45 % in Fig. 8b and 9a, the oxygen consumption HRR should be 76 kW. However, Fig. 6b shows it was 50 kW, implying that the real combustion efficiency was 29 %,

due to very high hydrogen and soot emissions. The soot emissions were measured in the experiments and were very high, but these measurements will be reported separately.



(a) (b)

Fig. 9. (a) Combustion efficiency (CO + HC energy loss) as a function of time and (b) mass loss based HRR.



(a) (b)

(c) (d)

Fig. 10. Yields of : (a) acrolein; (b) formaldehyde; (c), benzene; (d) acetic acid.

Acidic and Irritant Gas Yields

The acidic and irritant toxic gases acrolein, formaldehyde, benzene and acetic acid were all determined by the FTIR and were significant toxic gases in addition to the CO that has been discussed above. Their yields as g/kg are presented as a function of time in Fig. 10. There were other toxics generated including formic acid, toluene, methyl benzene, HCN, NO_2 and SO_2, but space does not permit this data to be included.

Acrolein, formaldehyde and acetic acid were all formed in the rich flaming combustion phase of the fire. They are products of the partial oxidation of volatiles. The oxygen present during the rich combustion was

essential for their formation. Benzene is part of the unburned hydrocarbons and its yield is about 20 % of the total hydrocarbon yield and indicates very strong production of benzene in pine wood fires.

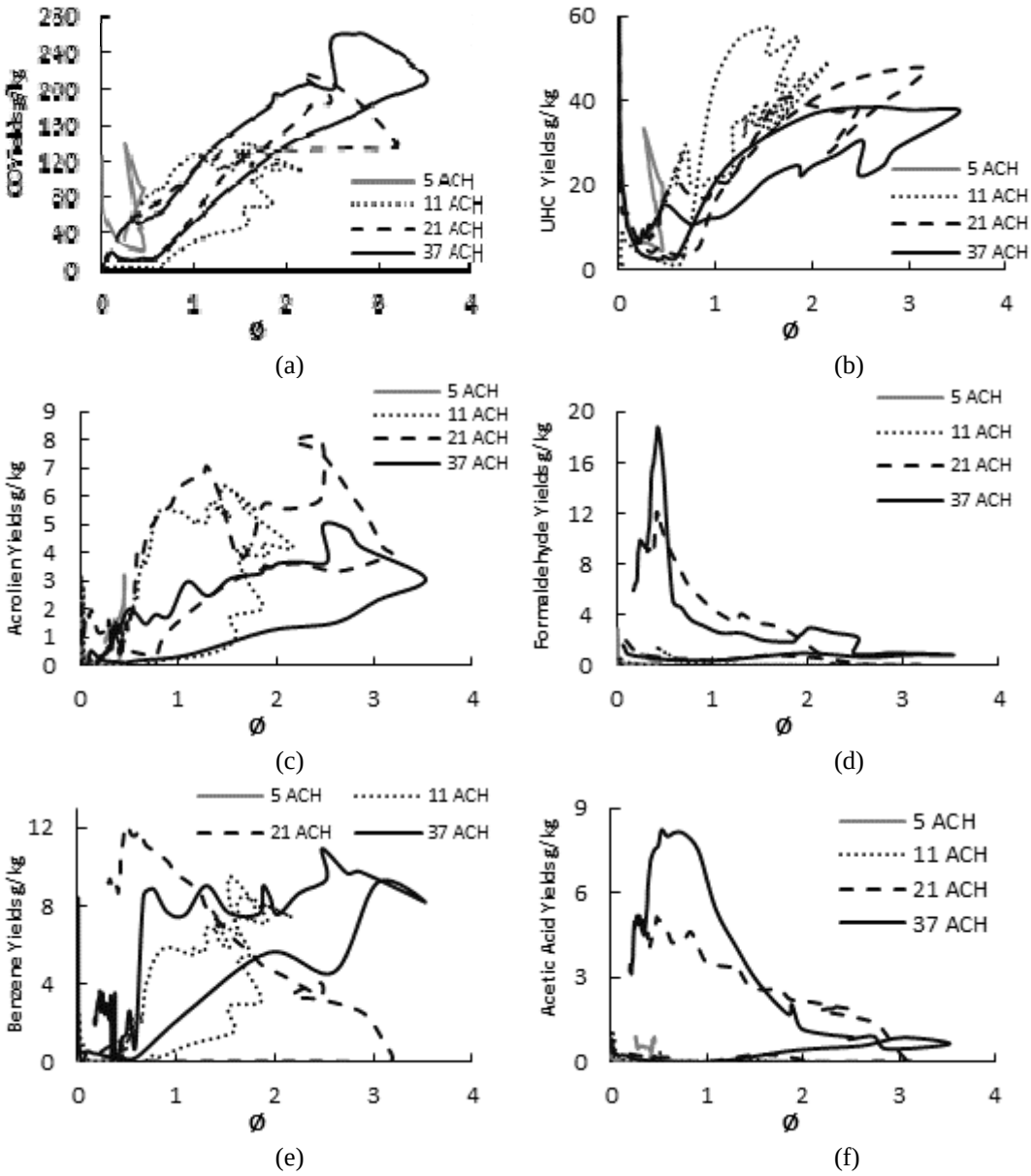


Fig. 11. Toxic yields as a fucntion of the fire equivalence ratio.

Toxic Yields as a Function of Equivalence Ratio

The yields of CO, HC, acrolein, formaldehyde, benzene and acetic acid are shown as a function of equivalence ratio in Fig. 11a–f. For CO and total hydrocarbons the high yields are for the rich flaming combustion phase. The results show two yields for the same equivalence ratio, the lower yield was for the fire growth and the higher yield was for the later stages of the fire where temperatures were higher. In the lean region the initial lean fire growth was low in CO yield but the smoldering combustion char burn out phase had much higher CO yields for the same equivalence ratio. Formaldehyde and acetic acid yields were high in the lean smoldering combustion end phase of the fire, but acrolein yield was high across the range of equivalence ratios, apart from in the initial lean flaming part of the fire. Benzene was low in the initial lean part of the fire and high in the flaming rich fire and the smoldering fire phase.

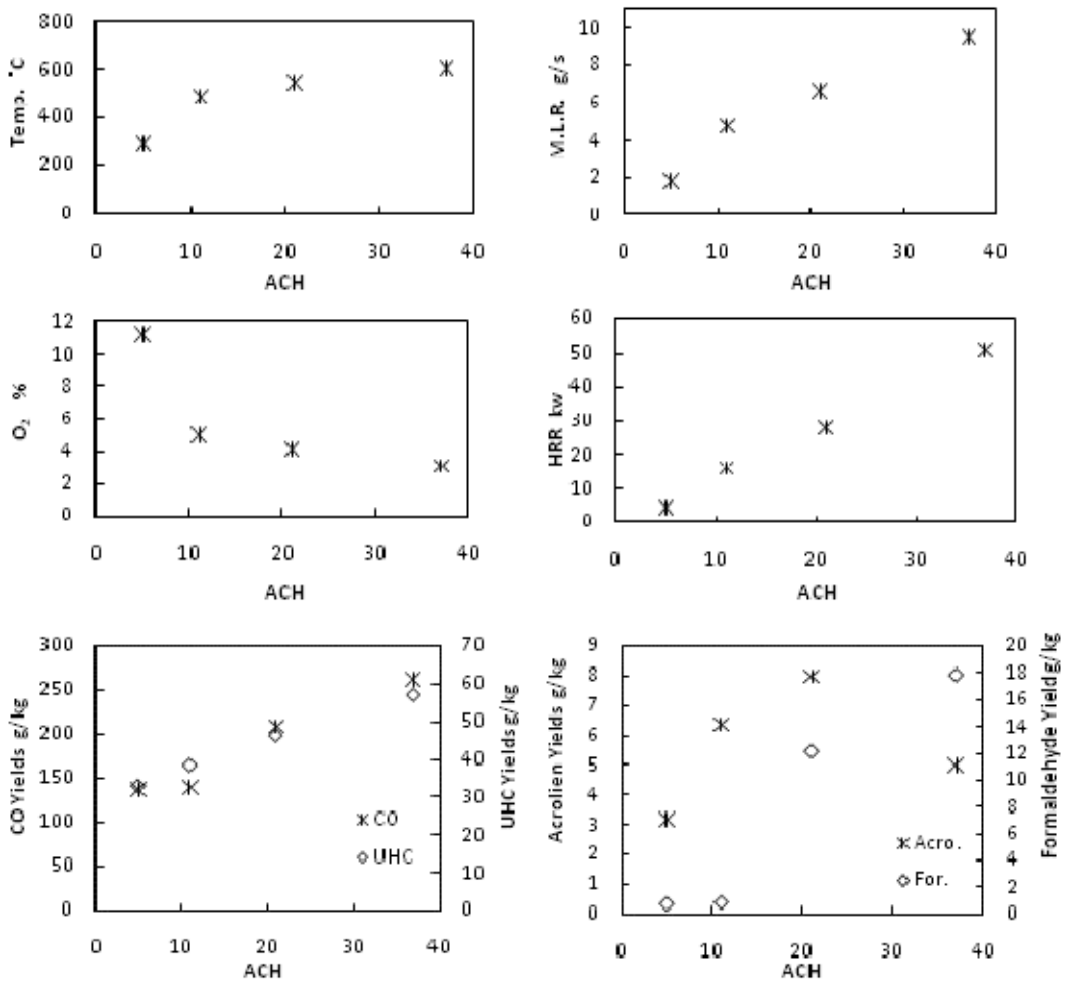


Fig. 12. Peak fire properties as a function of the air ventilation of the fire in ACH.

Peak Fire Properties as a Function of Ventilation Rate in ACH

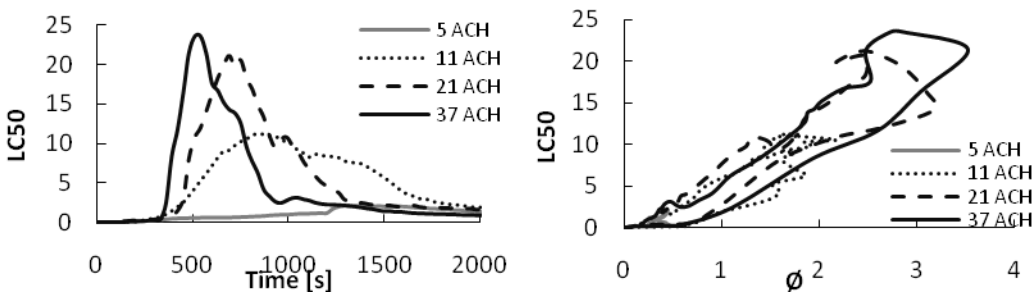
Figure 12 shows the peak value of various fire parameters as a function of the ventilation ratio in ACH. Peak fire temperature, mass loss rate and HRR all increase with increase of ACH. This is a reflection of the increased fire load combustion rate with the air mass flow increase, as a result of ~3 MJ of heat release for every kg of air supplied to a fire, provided there is sufficient oxygen to burn the fire load. This is a problem area as the minimum oxygen decreases as the ventilation increases as shown in Fig. 12. This leads to rich combustion in the fire with very poor combustion efficiency. This is shown as the peak CO and HC yields increase with ventilation in a linear relationship, as shown in Fig. 12.

Toxic yields also increase with ventilation as shown in Fig. 12 for acrolein and formaldehyde, but the trends are not linear. Acrolein has a decreased yield for the highest ventilation, as shown in Figs. 10a, 11c and 12. High temperatures and low oxygen are not conducive to acrolein formation and increasing the ventilation increases the temperature and reduces the oxygen, which results in lower acrolein formation for the 37 ACH ventilation. Formaldedyde is not generated significantly until the ventilation was above 11 ACH and then increased for 37 ACH. Formaldehyde was generated towards the end of the fires in the lean smoldering char combustion phase. This phase occurred much later in the fire and at lower temperatures.

Total Toxicity N on a LC_{50} and $COSHH_{15min}$ Basis

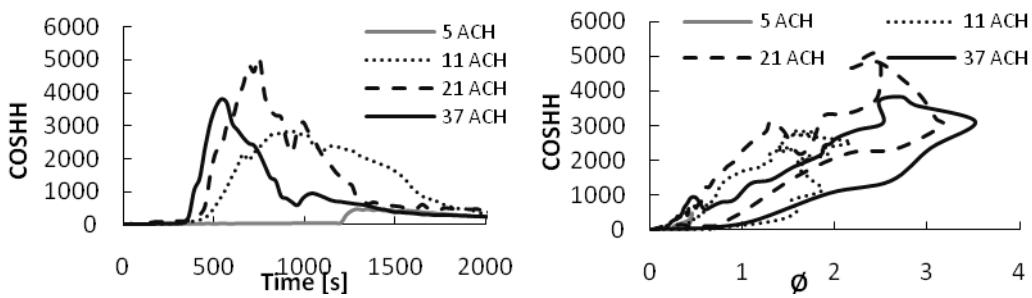
All the toxic species measured by the FTIR were normalised to their LC_{50} or $COSHH_{15min}$ toxic limits and these were summated to give the total toxicity ratio N. This is shown as a function of time and equivalence

ratio in Fig. 13 for LC_{50} toxicity and in Fig. 14 for $COSHH_{15nin}$ toxicity. The results show extremely high toxicity levels on both LC_{50} and $COSHH_{15min}$ basis, as expected from the very high yields of the toxic species. When the two toxicity assessment methods are compared they give identical shaped curves as a function of time for the same ventilation, as can be seen by comparing Figs. 13a and 14a. For the lowest ventilation the overall toxicity was low, as the fire was lean throughout and most of the time was in the smoldering char burning mode. However, for 11 ACH and higher, toxic levels increased with ventilation and all three higher ventilation fires had LC_{50} N values above 10 and $COSHH_{15\ min}$ above 2000. All the peak toxcities occurred in the flaming rich combustion phase of the fire as shown in Fig. 13b and 14b. The intial lean combustion had little toxicity, but the final smoldering lean combustion had relative high toxicity for a long period with LC_{50} values between 1 and 5 and $COSHH_{15min}$ values between 10 and 1000.



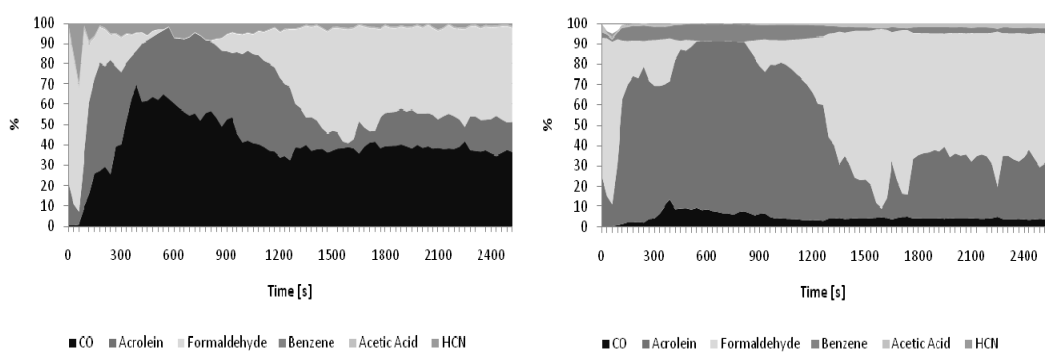
(a) (b)

Fig. 13. Normalised total toxicity N as a function of: (a) time; (b) equivalence ratio for 5–37 ACH.



(a) (b)

Fig. 14. Total normalised $COSHH_{15min}$ toxicity as a function of: (a) time; (b) equivalence ratio.



(a) (b)

Fig. 15. Contribution of the major toxic species to the overall toxicity at 21 ACH for: (a) LC_{50}; (b) $COSHH_{15min}$.

Smoke leaking from such fires (around door areas for example) would be extremely toxic and would require dilution by a factor of at least 1000 before it did not impair escape or by a factor of about 30 to make the risk of death unlikely. The species with greatest contribution to the overall toxicity are shown in Fig. 15. All fires were simlar and showed CO, acrolein, formaldehyde and benzene as the key toxic species

on both LC_{50} and $COSHH_{15min}$ basis. The main difference was that CO was more important for the LC_{50} assessment, whereas acrolein was more important on a $COSHH_{15min}$ basis. Acrolein and formaldehyde were important species for both methods of assessment. Formaldehyde was more important in the last phase of smoldering char combustion and acrolein was very important in the flaming combustion phase of the fire.

CONCLUSIONS

1. Lightly loaded wood crib fires in a ventilation controlled compartment fire did not develop at 3 ACH and only partially burned at 5 ACH. For complete combustion of load 11 ACH was required.
2. For 11–37 ACH the peak fire temperature, HRR and mass burn rate all increased linearly with ACH.
3. All the fires with 11 ACH or greater rapidly generated rich combustion with peak equivalence ratios of 3. This phase had the highest temperature, greatest toxic yields and lowest combustion efficiencies.
4. Toxic gas yields for CO were up to 250 g/kg and there were very high acrolein yields and significant yields of formaldehyde and benzene. Peak LC_{50} N values were >10 for long periods in the fires.

ACKNOWLEDGEMENTS

We thank the EPSRC for the award of the LANTERN JIF project that provided the FTIR system. The fire compartment was provided from a Leeds University development grant. Omar Aljumaiah thanks King Abdulaziz City for Science and Technology, Saudi Arabia for a research scholarship.

REFERENCES

[1] Purser, D., "Toxic assessment of combustion products," *SFPE Handbook of Fire Protection Engineering (3rd ed.)*, DiNenno P.J. (ed.), National Fire Protection Association, Bethesda, MA, 2002, p. **2**/83-**2**/171.

[2] Hartzell, G., (2001) Engineering analysis of hazards to life safety in fires: the fire effluent toxicity component, Safety Science 38(2): 147-155. http://dx.doi.org/10.1016/S0925-7535(00)00065-5

[3] Stec, A. and Hull, R., *Fire Toxicity*, Woodhead Publishing, 2010, pp. 51-117.

[4] Purser, D., (2000) Toxic product yields and hazard assessment for fully enclosed design fires, Polymer International 49(10): 1232-1255. http://dx.doi.org/10.1002/1097-0126(200010)49:10<1232::AID-PI543>3.3.CO;2-K

[5] Babrauskas, V., "Toxicity for the primary gases found in fires", 1997, Available at: http://www.doctorfire.com/toxicity.html

[6] Andrews, G.E., Daham, B., Mmolawa, M.D., Boulter, S., Mitchell, J., Burrell, G., Gunamusa, W. and Phylaktou, H.N., 2005. FTIR Investigations of Toxic Gases in Air Starved Enclosed Fires. *Fire Safety Science* 8: 1035-1046. http://dx.doi.org/10.3801/IAFSS.FSS.8-1035.

[7] Andrews, G.E., Li, H., Hunt, A., Hughes, D., Bond, S., Tucker, P., Akram, S. and Phylaktou, H.N., "Toxic Gases in Simulated Aircraft Interior Fires Using FTIR Analysis," *Fire and Explosion Hazards Seminar*, Edinburgh, 2007.

[8] Andrews, G.E., Boulter, S., Burell, G., Cox, M., Daham, B, Li, H. and Phylaktou, H.N., "Toxic Gas Measurements Using FTIR for Combustion of COH Materials in Air Starved Enclosed Fires," *Proceedings of the European Combustion Institute Meeting*, China, 2007.

[9] *Control of Substances Hazardous to Health Regulations, EH40/2005 Workplace exposure limits*, HSE Books, Health and Safety Executive, UK, 2005.

[10] Levin, B., (1996) New research avenues in toxicology: 7-gas N-gas model, toxicant suppressants, and genetic toxicology, Toxicology 115(1-3): 89-106. http://dx.doi.org/10.1016/S0300-483X(96)03497-X

[11] Babrauskas, V., (1998) A methodology for obtaining and using toxic potency data for fire hazard analysis, Fire Safety Journal 31(4): 345-358. http://dx.doi.org/10.1016/S0379-7112(98)00013-7

[12] National Advisory Committee for Acute Exposure Guideline Levels for Hazardous Substances, "Interim Acute Exposure Guideline Levels (AEGLs) for Selected Cyanide Salts," NAC/AEGL Committee, 2009, Appendix D.

[13] National Advisory Committee for Acute Exposure Guideline Levels for Hazardous Substances "Interim Acute Exposure Guideline Levels (AEGLs) for Benzene," NAC/AEGL Committee, 2009.

[14] British Standards, "Tube Furnace Method for the Determination of Toxic Product Yields in Fire Effluents," BS7990, UK, 2003.

[15] Bundy, M., Hamins, A., Johnsson, E.L., Kim, S.C., Ko, G.H. and Lenhert, D.B, "Measurement of heat and combustion products in reduced scale ventilation limited compartment fires", NIST TN 1483, Gaithersburg, MD, 2007.

[16] Gottuk, D., (1992) A study of carbon monoxide and smoke yields from compartment fires with external burning, Symposium (International) on Combustion 24(1): 1729-1735. http://dx.doi.org/10.1016/S0082-0784(06)80202-X

[17] Utiskul, Y., Quintiere, J., Rangwala, A., Ringwelski, B., Wakatsuki, K., and Naruse, T., (2005) Compartment fire phenomena under limited ventilation, Fire Safety Journal 40(4): 367-390. http://dx.doi.org/10.1016/j.firesaf.2005.02.002

[18] Tewarson, A., (1985) Fully developed enclosure fires of wood cribs, Symposium (International) on Combustion 20(1): 1555-1566. http://dx.doi.org/10.1016/S0082-0784(85)80650-0

[19] Gross, D., (1965) Experimental fires in enclosures, Symposium (International) on Combustion 10(1): 931-942. http://dx.doi.org/10.1016/S0082-0784(65)80236-3

[20] Chamberlain, G.A., (1996) The hazards posed by large-scale pool fires in offshore platforms : Major hazards onshore and offshore II, Trans IChemE 74(B): 81-87.

[21] Peatross, M.J. and Beyler, C.L., 1997. Ventilation Effects on Compartment Fire Characterization. *Fire Safety Science* 5: 403-414. http://dx.doi.org/10.3801/IAFSS.FSS.5-403.

[22] Tewarson, A., "Generation of Heat and Chemical Compounds in Fires," *SPFE Handbook of Fire Protection Engineering (2nd ed.)*, DiNenno P.J. (ed) National Fire Protection Association, Quincy, MA 02269, 1995.

[23] Chan, S., (1996) An exhaust emissions based air-fuel ratio calculation for internal combustion engines, Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering 210(34): 273-280. http://dx.doi.org/10.1243/PIME_PROC_1996_210_271_02

[24] Buchanan, A.H., *Fire Engineering Design Guide*, Centre for Advanced Engineering, University of Canterbury, Canterbury, 2001.

[25] BS7974, *Application of fire safety engineering principles to the design of buildings. Code of practice*, British Standards Institution, 2001.

[26] Quintiere, J.G., *Principles of Fire Behaviour*, Delmar Publishers, London, 1998, p. 155.

[27] Purser, D.A., Fardell, P.J., Rowley, J., Vollam, S. and Bridgeman, B., "An improved tube furnace method for the generation and measurement of toxic combustion products under a wide range of fire conditions," *Flame Retardant Conference*, Interscience Communications Ltd, 1994, pp. 263-274.