TOXICITY TOXIC PRODUCT YIELDS IN FIRE: INFLUENCE OF MATERIAL, TEMPERATURE AND VENTILATION CONDITION

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ABSTRACT

Fires can be divided into a number of stages from smouldering combustion to early well-ventilated flaming, through to fully developed under-ventilated flaming. These stages can be replicated by certain bench-scale physical fire models using different fuel-to-oxygen ratios, controlled by the primary air flow, and expressed in terms of the equivalence ratio ϕ (the actual fuel/air ratio divided by the stoichiometric fuel/air ratio).

The steady state tube furnace (BS 7990 and ISO TS 19700) is both a standard test method and a research tool that can provide building engineers and designers with valuable data related to fire hazard. The apparatus has been shown to reliably replicate different fire stages, and is capable of generating toxic product yields as a function of the equivalence ratio.

This work presents combustion product yields generated using a small-scale fire model, steady state tube furnace. The stages of fire growth, the different types of fire in terms of fire scenario and combustion conditions, and the typical toxic product yields from each stage have been calculated for a number of common polymers (LDPE, PMMA, PS, Nylon 6.6, PVC) as a function of ϕ, on which the toxicity is highly dependent.

INTRODUCTION

Despite its serious, life-threatening potential, investigating fire effluent toxicity is a fascinating multidisciplinary area where the both the fuel chemistry, and the conditions of the complex process of fire have significant influences. It requires understanding of the stages of fire growth, from ignition to ventilation controlled burning; the behaviour of fire on different scales; the product formation from flaming polymer pyrolysates; the behaviour of the aerosol particulates; the chemical quantification of those fire effluents and their relationship to the toxicity; and the application of this knowledge to fire safety [i].

Although all fires may be regarded as unique, burning behaviour and toxic product yields depends most strongly on a few of factors. Material composition, temperature and oxygen concentration are normally the most important. The generalised development of a fire has been recognised, and used to classify fire growth into a number of stages, from smouldering combustion and early well-ventilated flaming, through to fully-developed under-ventilated flaming [ii]. Although on some occasions smouldering (oxidative pyrolysis) can generate toxicologically significant quantities of effluent, the rate of reaction, and hence the amount of toxic species generated will be small, so unlikely to affect anyone outside the immediate vicinity. Similarly, well-ventilated fires are generally small, so extinguishment or escape is

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still feasible, while the fire effluent moves across the ceiling above head height. However, as they grow, fires become ventilation controlled, and fires in enclosures such as buildings rapidly change from well-ventilated to under-ventilated (or vitiated). These fires are larger, and therefore produce greater volumes of effluent, affecting occupants over a much wider part of any building. While well-ventilated fire scenarios are routinely used for assessment of flammability, because the object is to stop the fire growing to the out of control stage, where fire toxicity is concerned, the important fire stages are under-ventilated. There are two reasons for this: the volume of effluent is much greater and the yields of the major toxic products (carbon monoxide and hydrogen cyanide) will be also much greater [i].

The stages of a fire, from non-flaming to under-ventilated flaming, have been classified in terms of heat flux, temperature, oxygen concentration (to the fire, and in the fire effluent), and CO_2/CO ratio, equivalence ratio (ϕ) and combustion efficiency (the % conversion of fuel to fully oxygenated products, such as CO_2 and H_2O) and are presented in Table 1.

Table 1 ISO classification of fire stages, based on ISO 19706 [ii]

Fire Stage	**Heat /kW m^{-2}**	**Max Temp /°C**		**Oxygen %**		**Equiv-alence ratio ϕ**	**CO/ CO_2 Ratio**	**Comb-ustion Efficiency %**
		Fuel	**Smoke**	**In**	**Out**			
Non-flaming								
1a. Oxidative Pyrolysis	n.a.	450-800	25 – 85	20	0 - 20	-	0.1-1	50-90
Well ventilated flaming								
2. Well ventilated flaming	0 to 60	350-650	50 - 500	~20	0 - 20	<1	< 0.05	>95
Under ventilated Flaming								
3a. Small Under-ventilated	0 to 30	300-600	50-500	15 - 20	5 - 10	> 1	0.2-0.4	70 - 80
3b. Large Under-ventilated	50 to 150	350-650	>600	<15	<5	> 1	0.1-0.4	70 - 90

EXPERIMENTAL

Bench scale assessment and fire stages

When the formation of carbon monoxide (CO) results from combustion in oxygen depleted conditions, its concentration will also be a function of the availability of oxygen. This can be expressed in terms of the equivalence ratio, ϕ, presented below [iii,iv].

			Typical CO yield g/g
$\phi = \dfrac{actual\ \ fuel\ to\ air\ ratio}{stoichiometric\ \ \ fuel\ to\ air\ ratio}$	$\phi < 1$	fuel lean flames	0.01
	$\phi = 1$	stoichiometric flames	0.05
	$\phi > 1$	fuel rich flames	0.2

At $\phi = 0.5$ the conditions can be correlated with an early developing fire. At $\phi = 0.7$ and 1.0, the conditions correlate with those of a more developed, high ventilation fire and at $\phi > 1.5$ conditions of fully developed flaming. Whose growth rate is ventilation controlled.

Fire smoke toxicity requires suitable design generation techniques. All scale-up of fire is difficult, but particularly in combustion toxicity where product yields may differ by two orders of magnitude, depending on conditions [v,vi]. It is essential to the assessment of toxic hazard from fire that these different fire stages can be adequately replicated on the small-scale, and preferably the individual fire stages treated separately. A number of different methods exist to assess fire toxicity, but many of them fail to relate the toxicity or toxic product yields to particular fire scenarios, [vii,viii]. These different fire types have been successfully replicated using the steady state tube furnace, ISO TS 19700, the Purser furnace, [ix,x,xi], in which the air supply and rate of burning are fixed, as the sample is driven into a furnace, and subjected to an increasing applied heat flux [xii,xiii]. By varying the primary air flow rate, up to 50 litre min^{-1} with secondary air in the effluent dilution chamber, different fire conditions may be characterised as a function of equivalence ratio or ISO fire stage. Using this technique, a clear relationship has been demonstrated between the yield of toxic products and the fire condition [xiv], for a given material composition, [ix]. The apparatus has been described elsewhere [xv,xvi], and is shown in Fig.1.

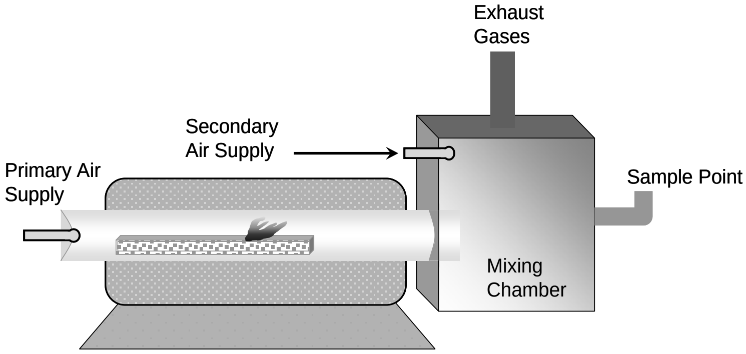

Fig. 1. The steady state tube furnace (ISO TS 19700)

Materials

All unadulterated polymers were used in the form of commercial pellets: Low Density Polyethylene (LDPE) (Cleaflex, Polimeri Europa), Polyvinyl Chloride (PVC) (Doeflex-Vitapol), Polystyrene (PS) (GPPS 1540) Atofina. Nylon 6.6 (PA 6.6) was obtained as commercial fibre extrusion grade material from Invista.

RESULTS AND DISCUSSION

The data have been normalised to an arbitrary 1 gram fuel decomposed in 50 litres of fire effluent, on a mass charge basis, based on an established standard [x,xi].

LDPE

Figure 2 presents results for LDPE. Figure 2a shows the CO_2/CO ratio plotted on a log scale expressed as a function of equivalence ratio. This shows a consistent and progressive decrease from $\phi = 0.5$ to $\phi = 1.5$, which then remains stable between $\phi = 1.5$ and $\phi = 3.0$ at CO_2/CO ratio of around 7. Figure 2b shows the CO_2 yield as a function of ϕ, showing a steady and consistent decrease in CO_2 with increase in ϕ [xiv].

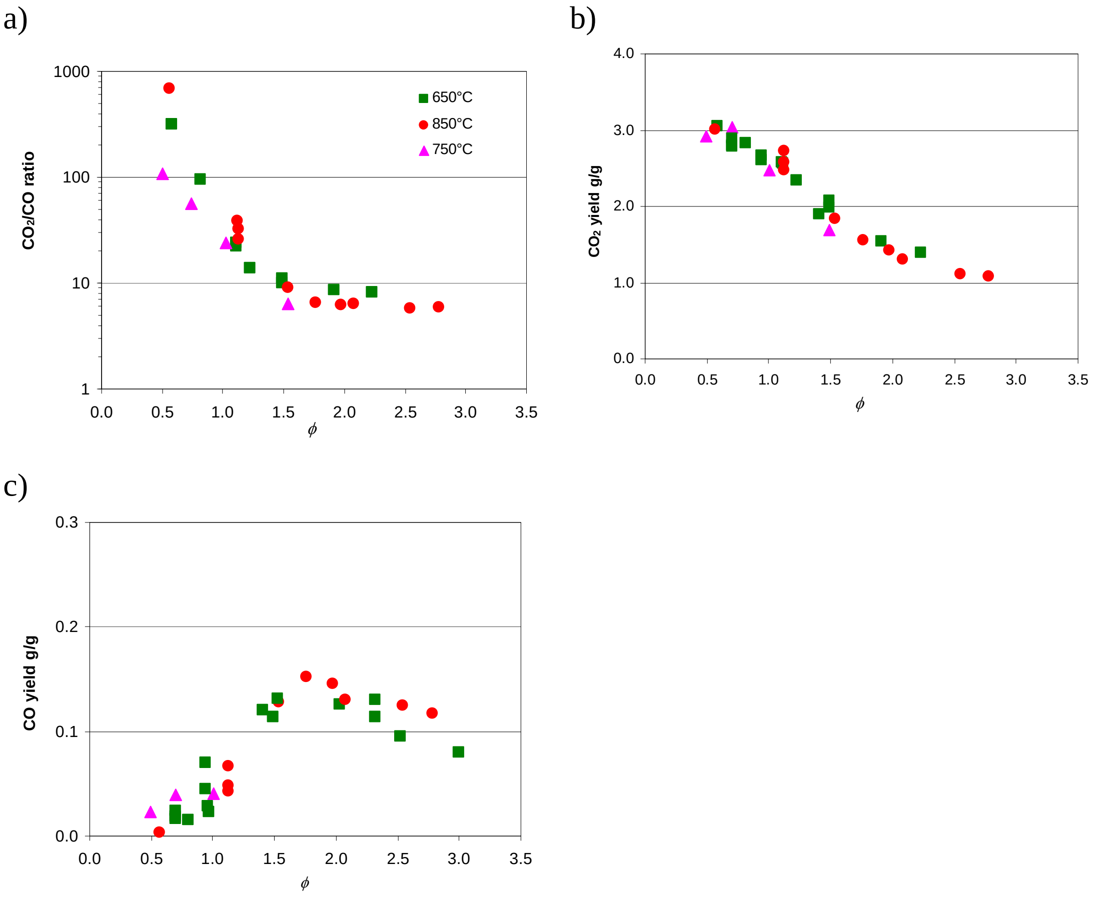

Fig. 2. CO_2/CO Ratio and Yields of b) CO_2, and CO from LDPE.

Figure 2c shows the CO yield as a function of ϕ. This shows a sharply upward trend from $\phi = 0.5$ to $\phi = 1.5$, followed by a slight downward trend from $\phi = 1.5$ to $\phi = 3.0$. It is interesting to note the consistency of the decrease of CO yield as the degree of vitiation increases.

NYLON 6.6

The results for Nylon 6.6 (PA 6.6) presented in Fig.3. Figure 3a presents the CO_2/CO ratio and CO_2 yields presented in Fig. 3b, both showing a consistent and progressive decrease from $\phi = 0.5$ to $\phi = 1.5$. The yields for CO (Fig. 3c) and HCN (Fig. 3d) yields show an increase with increase in ϕ. The NO_x yields seem to have a greater sensitivity to different fire conditions, as shown in Fig. 3e. The NO_x yields show a wide variation under conditions of low ventilation. However a downward trend from $\phi = 0.5$ to $\phi = 1.5$, and then a steady lower yields from $\phi = 1.5$ to $\phi = 3.0$ is observed. As expected, there is a higher sensitivity to furnace temperatures than for CO and HCN especially when $\phi > 1.5$ [xiv].

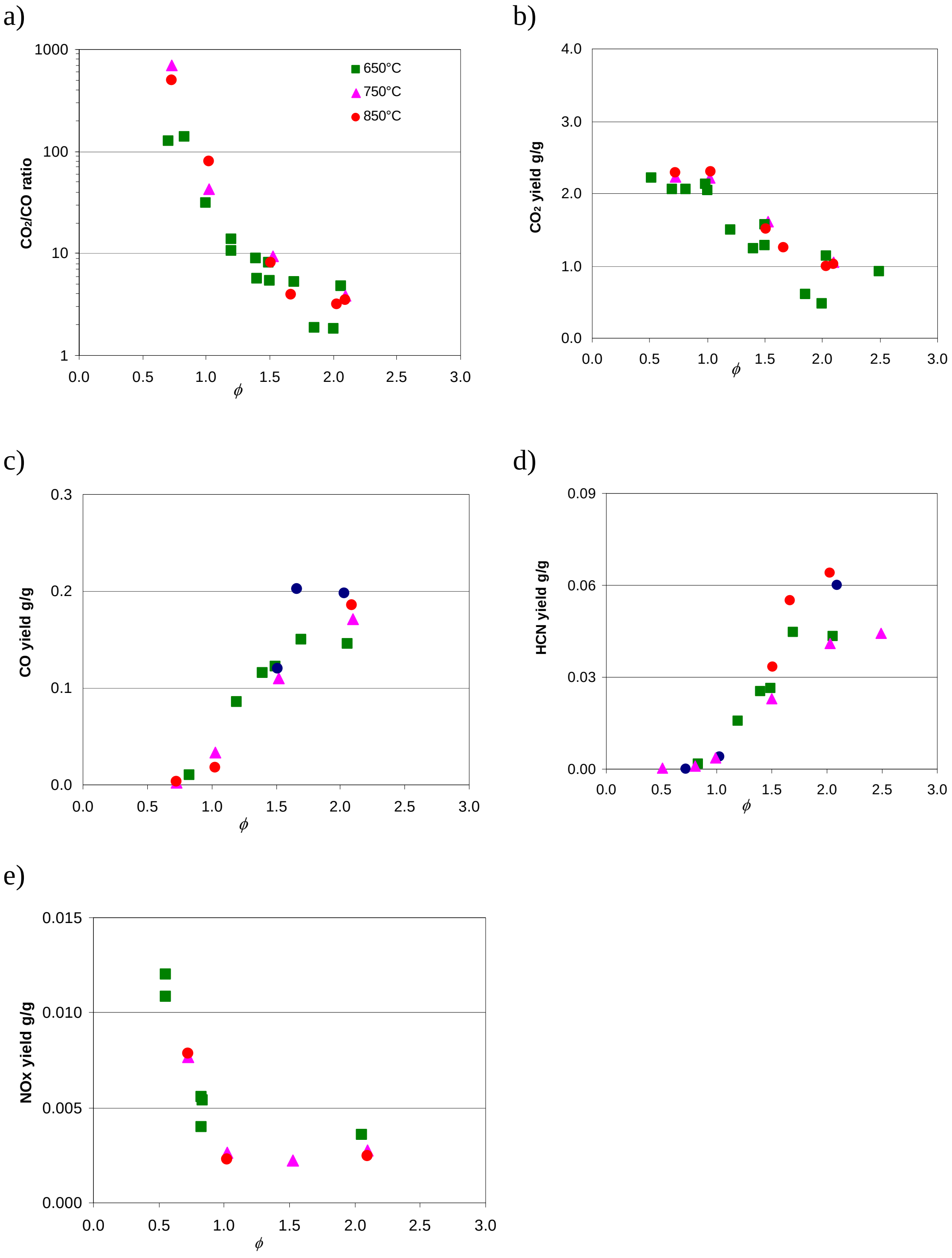

Fig. 3. CO_2/CO Ratio and Yields of b) CO_2 and c) CO d) HCN e) NO_x from Nylon 6.6.

POLYSTYRENE

PS combustion products are presented in Fig. 4. A more gradual trend for PS, presented in Fig. 4a, is observed for the CO_2/CO ratio compared to LDPE and Nylon 6.6 resulting from the greater thermal stability of the decomposition products forming more CO in well-ventilated conditions, but forming less CO in under-ventilated conditions. Figure 4b presents decreasing

CO_2 yields with the decrease of ventilation conditions. The yields for CO (Fig. 4c) show a steady increase with increase in ϕ. A sensitivity to temperature is observed for this material.

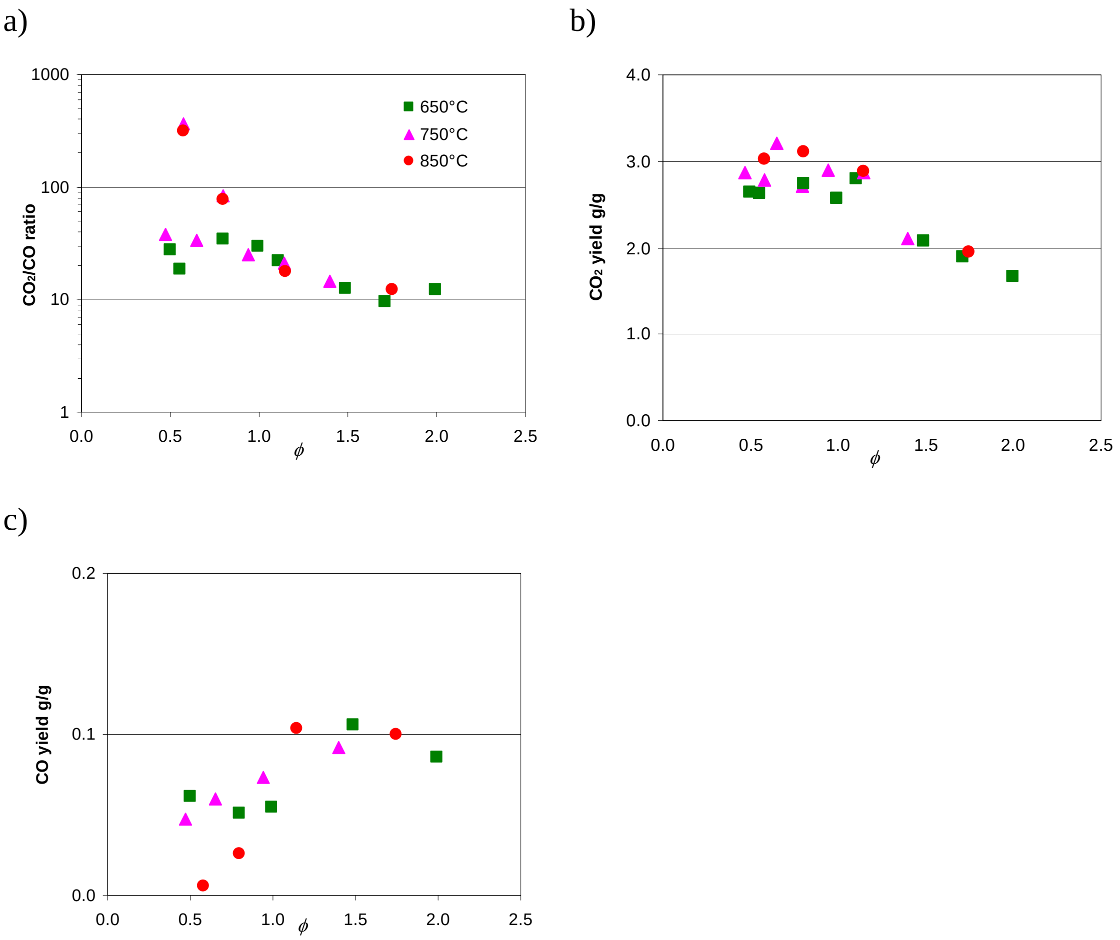

Fig. 4. CO_2/CO Ratio and Yields of b) CO_2 and c) CO from Polystyrene.

PVC

Figure 5 shows the combustion product yields for unplasticised PVC. The theoretical yield of CO_2 from unplasticised PVC is 1.4 g/g, and complete conversion of fuel carbon to CO_2 is approached at a furnace temperature of 850°C, when the CO yield also falls.

Figure 5b presents CO_2 yields as a function of equivalence ratio. Similarly to the CO_2/CO ratio, CO_2 yields decrease with increase in the ventilation conditions. The CO yields in the steady state tube furnace, presented in Fig. 5c, are almost constant with increase in ϕ, and are dependent on furnace temperature.

The most toxicologically significant species is hydrogen chloride (HCl), whose yield is almost independent of fire condition, (Fig. 5d). The theoretical yield of HCl is 0.585 g/g and it can be seen that most of the chlorine is released as HCl [xiv]. This implies that the flame quenching effect of HCl inhibits the conversion of CO to CO_2, giving much higher CO yields under well-ventilated conditions.

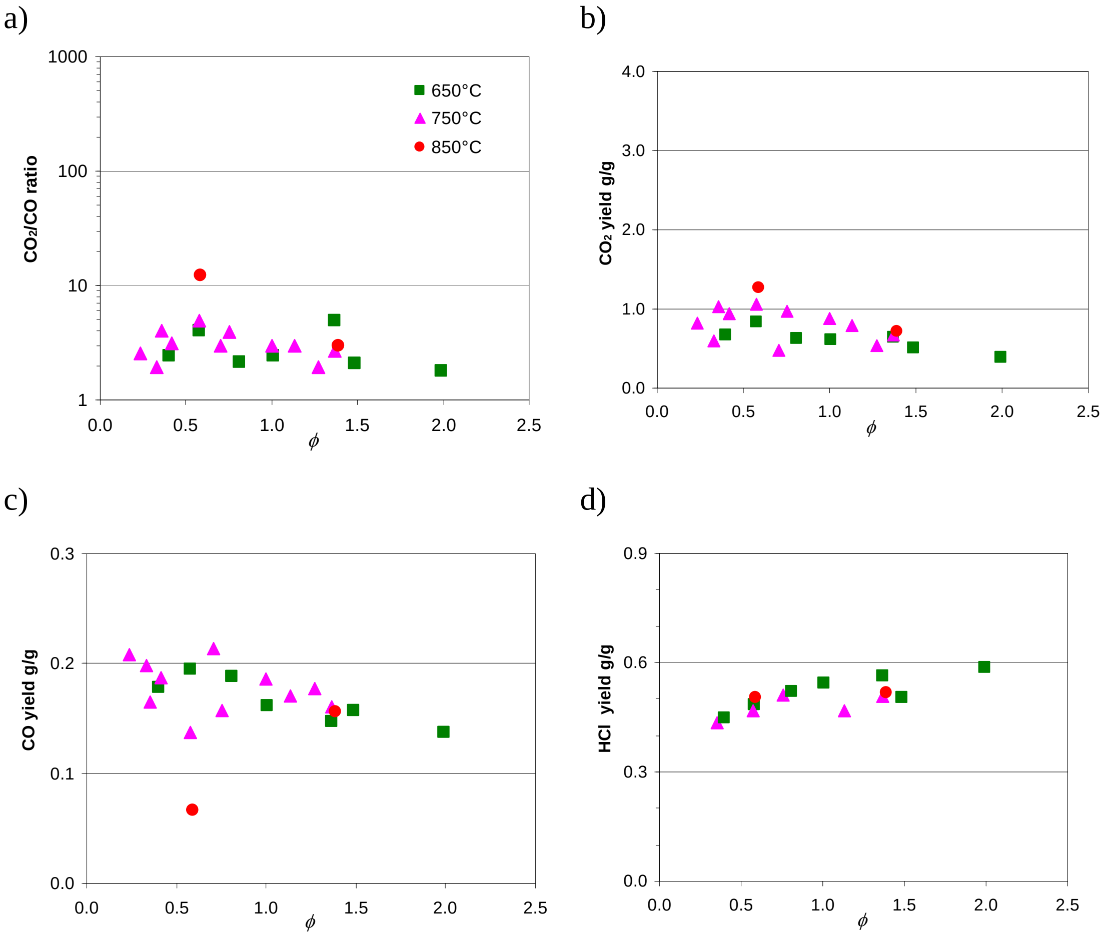

Fig. 5. CO_2/CO Ratio and Yields of b) CO_2 and c) CO d) HCl from PVC.

INFLUENCE OF TEMPERATURE

In order to investigate the influence of furnace temperature on the CO yield in well and under-ventilated conditions the data have been plotted in Fig. 6. It shows the CO for the four materials at three temperatures and at both low ϕ (0.6 to 0.8 and high ϕ (1.4 to 2.0) values.

The general picture is that for most materials the yields do not change very much as the furnace temperature is increased under either well-ventilated or under-ventilated combustion conditions. Under well-ventilated combustion conditions, where efficient combustion results in high yields of CO_2, water and heat, the effect of temperature increases are minimal on flaming decomposition of most polymers, but at ϕ values of 1 and above, there can be some changes in product yields [i].

Figure 6a clearly shows that, at low ϕ, temperature had a small influence on both LDPE and Nylon 6.6, but at high ϕ, it had a dramatic effect on PS and PVC resulting in much decreased yields at the higher temperatures. On the other hand, Fig. 6b shows an opposite trend, such that three of the materials (LDPE, Nylon 6.6 and PVC) experienced an increase in CO yield, albeit only marginal, and the fourth material (PS) had a reduced CO yield at the higher temperature [xiv].

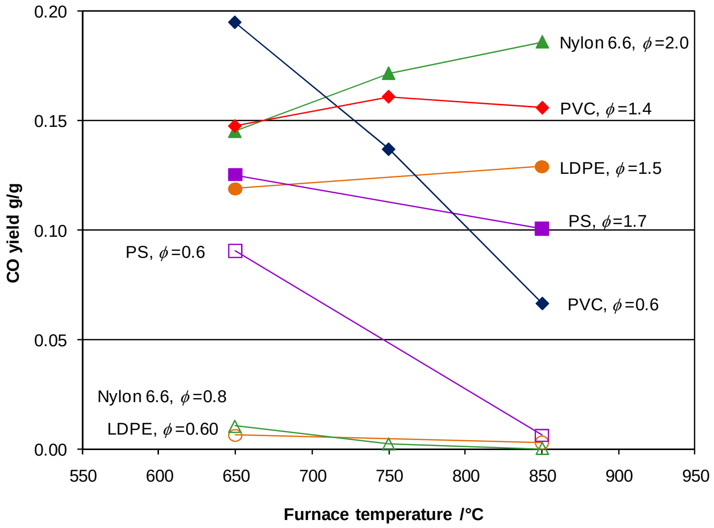

Fig. 6. Influence of Temperature on CO Yields for Different Materials.

CONCLUSIONS

Similarly to the behaviour of real fires, the yields of toxic gases in the steady state tube furnace are highly dependent on the decomposition conditions, in particular the fuel/air equivalence ratio, or the CO_2/CO ratio, which provides a measure of combustion efficiency. The exceptions are PVC and fire retarded polymers where halogens increase the CO yield under well-ventilated conditions, reducing the heat release rate. Indeed ISO 19706 notes that CO_2/CO ratio is only indicative of fire conditions for materials which do not contain halogens. This effect is clearly visible in the data from the PVC experiments.

The yields of most species for most of the polymers studied are independent of the tube furnace temperature over the range studied 650-850°C. The LDPE, PS and Nylon 6.6 results clearly show similarities in behaviour for yields of CO, HCN at the different temperatures studied. A different behaviour pattern is observed for PVC. As stated above, the toxic product yields for PVC appear to be almost independent of the fire conditions, equivalence ratio, and temperature.

The toxic product yields from different combustion scenarios, for use as a bench-scale quantification of toxic product yields, can be used to characterise the burning behaviour of materials under controlled and well-defined laboratory conditions. Since each test run represents the burning behaviour for a particular fire stage, the results are more generally applicable than those of a single large scale test, where the different fire stages can be difficult to separate in smoke gas analysis.

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