EFFECT OF TEMPERATURE AND VENTILATION CONDITION ON THE COMBUSTION EFFICIENCY OF HALOGENATED AND AROMATIC FUELS

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ABSTRACT

Carbon monoxide is an indicator of combustion efficiency. It is produced as a result of incomplete combustion, by low temperatures, flame quenching, or under-ventilation. Polymers containing halogens and aromatic rings give higher carbon monoxide yields in well-ventilated conditions, when burnt in the steady state tube furnace (ISO 19700) at a furnace temperature of 650°C. This is believed to result from flame quenching by hydrogen halides or the enhanced stability of aromatic rings in flames, respectively. This work investigates the effect of ventilation condition and furnace temperature on the yield of carbon monoxide from burning mixtures of polyvinyl chloride and polyethylene, polyamide 6 containing a brominated flame retardant and an antimony synergist, and polystyrene. In each case, the high carbon monoxide yields in well-ventilated burning reduced at higher furnace temperatures, showing a diminution of both flame retardancy and fire toxicity above 850°C.

INTRODUCTION

The various physical processes that occur during thermal decomposition depend on the nature of the material. For example, as thermosetting polymeric materials are cross-linked and therefore infusible and insoluble; simple phase changes upon heating are not possible. Thermoplastics, such as poly(vinyl chloride) (PVC), polystyrene (PS), polyamide 6 (PA6) and low density polyethylene (LDPE), can be softened by heating without irreversible changes to the material, provided heating does not exceed the minimum thermal decomposition temperature.

The pyrolysis of a polymer involves decomposition, turning chains of 10 000–100 000 carbon atoms into species small enough to be volatilised. In some cases, the chain releases groups most easily from its ends, known as end-chain scission or unzipping (e.g. PMMA). In many more cases, the chain breaks at random points along its length, known as random chain scission. A third process, where stable molecules, attached to the backbone as side chains, are lost, is known as chain stripping. The resulting chain may undergo scission to volatiles or lose further substituents forming double bonds which cross-link and undergo carbonisation, ultimately leading to char formation. Thus, the conversion of organic polymer to volatile organic molecules may follow four general mechanisms. While some polymers fall exclusively into one category, others exhibit mixed behaviour[i]. LDPE, PA6 and PS all undergo predominantly random chain scission, leading to oligomeric fragments and cylclised hydrocarbons (LDPE), a mixture of dehydrated monomers and their decomposition products (PA6) and a mixture of monomer, dimer and trimer (PS). At elevated temperatures PVC undergoes a dehydrochlorination reaction to release hydrogen chloride (HCl) and forms a

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conjugated polyene[ii] which undergoes further rearrangements and product elimination at higher temperatures to produce a complex mixture of hydrocarbons with aromatic materials predominating (Fig. 1). At temperature between 200-300°C, 80-95% of the chlorine content of rigid (or unplasticised) PVC is released as HCl, 70% within one minute at 300°C [iii]. Under combustion conditions at 650°C 75-90% of chlorine has been recovered as HCl[iv]. In some formulations, some chlorine may remain in the residue. For example calcium carbonate, a common filler in PVC, will react with HCl to produce non-volatile calcium chloride, while releasing non-fuel carbon dioxide (CO_2). In practice the chorine content of the residue has been found to depend to some extent on the decomposition conditions. When a plasticised PVC containing calcium carbonate was decomposed under non-flaming conditions 58% of chlorine was released as HCl. Under combustion at 650°C the recovery decreased to 34%, but at 1000°C calcium carbonate decomposes to calcium oxide and gas phase chloride recovery increased to 43% [v].

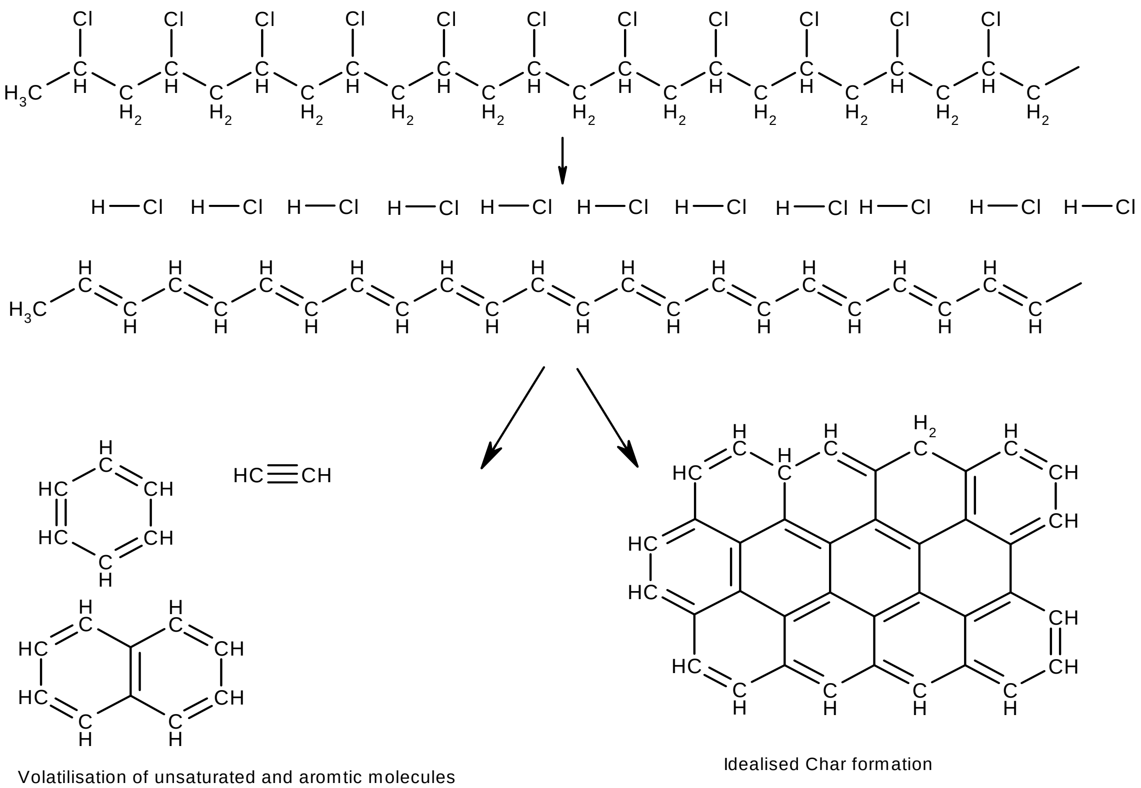

Fig. 1. PVC decomposition[i].

PVC burns with a low heat release rate, because the halogen atoms in the structure release HCl, almost 60% of its mass, which then inhibits the conversion of carbon monoxide (CO) to CO_2. This is the major heat release step in polymer combustion. When hydrogen chloride gas (HCl) comes off on heating, a double bond forms between alternate carbons, strengthening the chain in the solid residue. As this residue gets hotter, the chain either cross-links as double bonds open and attachments to neighbouring chains occur, eventually leading to char formation, or they break down and cyclise to form volatile aromatic hydrocarbons. If these only contain a few rings, they will give lots of black smoke, if they are large or cross-linked, the residue may form a stable protective char layer[vi].

A typical unwanted fire may progress through several stages which may include: non-flaming/smouldering combustion, well-ventilated flaming fires, early/ventilation-controlled (vitiated) flaming fires[vii,viii,ix]. The ventilation of flaming fires can be characterized in terms of the equivalence ratio, ϕ.

$$\phi = \frac{actual \quad fuel-to-air \quad ratio}{stoichiometric \quad fuel-to-air \quad ratio}$$

Well-ventilated flaming fires occur when there is plenty of air available so that ratio of fuel to air is low. Under these conditions, combustion is most efficient, so that for most materials, the main products are carbon dioxide, water and heat - initially the yields of smoke and toxic products tend to be low. The toxic potency and toxic hazards from simple CHO polymers are therefore also low in well ventilated flaming, but the fire is likely to grow quickly, producing considerable quantities of heat and carbon dioxide while consuming oxygen[ix]. As the fire grows, the temperature rises, the volume of effluent increases, and the oxygen becomes depleted from the surrounding atmosphere.

Ventilation-controlled flaming fires occur when the air supply is restricted compared to the fuel available for combustion. They may consist of pre-flashover fires in enclosed spaces or large post-flashover fires, where all surfaces are ignited in high temperature (often as high as 1000ºC) conflagrations in very large or ventilated spaces. Ventilation-controlled fires produce large amount of effluent, containing high yields of products of incomplete combustion (CO, HCN, organic products, and smoke)[ix].

Carbon monoxide is always present to some extent in all fires, irrespective of the materials involved or the stage (or type) of fire[x]. As an indicator of fire condition, the range of conditions favouring the formation of CO must be considered. CO results from incomplete combustion, which can arise from:

- Insufficient heat (e.g. during smouldering)[xi].
- Quenching of the flame reactions (e.g. when halogens are present in the flame, or excessive ventilation cools the flame)[xii].
- The presence of stable molecules, such as aromatics which survive longer in the flame zone, giving high CO yields in well-ventilated conditions, but lower than expected yields in under-ventilated conditions[xiii].
- Insufficient oxygen (e.g. in under-ventilated fires, large radiant heat fluxes pyrolyse the fuel even though there is not enough oxygen to complete the reaction)[vii].

The current study is focused on the transition from well-ventilated flaming (lower temperatures and adequate oxygen supplies) to fully developed flaming (higher temperatures and inadequate oxygen).

MODE OF ACTION OF HALOGENS AS FLAME RETARDANTS

Both the HCl evolved from the decomposition of PVC and the HCl or HBr evolved from the decomposition of halogenated flame retardants will interfere with the gas phase combustion process.

Flaming combustion involves a very small number of highly reactive free radicals to propagate the gas phase oxidation processes. For ignition to occur, the number of radicals must increase. This occurs in reaction 1 and 2 where each · represents an unpaired electron.

$$\mathbf{H\cdot + O_2 \rightarrow OH\cdot + O\cdot} \qquad (1)$$

$$\mathbf{\cdot O\cdot + H_2 \rightarrow OH\cdot + H\cdot} \qquad (2)$$

Halogen-containing flame retardants act by interfering with the radical chain mechanism taking place in the gas phase. The high-energy OH· and H· radicals formed by chain branching are removed by the halogen-containing flame retardant (RX). At first the flame retardant breaks down to

$$\mathbf{RX \rightarrow R\cdot + X\cdot} \qquad (3)$$

where X· is either Cl· or Br·. The halogen radical reacts to form the hydrogen halide:

$$\mathbf{X\cdot + RH \rightarrow R\cdot + HX} \qquad (4)$$

which in turn interferes with the radical chain mechanism:

$$\mathbf{HX + H\cdot \rightarrow H_2 + X\cdot} \qquad (5)$$

The removal of H· is key to elimination of the main chain branching step (when 1 unpaired electron becomes 3).

$$\mathbf{HX + OH\cdot \rightarrow H_2O + X\cdot} \qquad (6)$$

The removal of OH· blocks the main heat release step of hydrocarbon combustion, the conversion of CO to CO_2, by replacement with less reactive halogen free radicals in the gas phase[xiv]. The H· and OH· radicals are essential for many flame reactions and are involved in the main heat release in reaction 7.

$$\mathbf{CO + OH\cdot \rightarrow CO_2 + H\cdot} \qquad (7)$$

Loss of H· and OH· will reduce the CO_2/CO ratio.

The high-energy H· and OH· radicals are removed by reaction with HX and replaced with lower-energy X· radicals. The actual flame retardant effect is thus produced by HX.

The hydrogen halide consumed is regenerated by reaction with hydrocarbon:

$$\mathbf{X\cdot + RH \rightarrow R\cdot + HX} \qquad (8)$$

Thus HX could be considered to act as a catalyst.

In the condensed phase, the resulting unsaturated polyenes may act as char precursors, forming products with a tendency to cyclize and condense to yield carbonaceous products, which protect the condensed phase below the flame zone against attack by oxygen and radiant heat. In PVC, with ~60% chlorine, char formation is a significant fire retardant mechanism.

In the presence of antimony oxide, the efficiency of halogenated flame retardants is improved, although it has no flame retardant effect on its own. This is believed to result from the formation of volatile SbX_3 and other species which are more effective halogen carriers than HX.

The yield of combustion species depend on the material and on the ventilation and temperature conditions[iv]. For example for a particular material the CO yield or CO_2/CO ratio can be indicative of fire conditions.

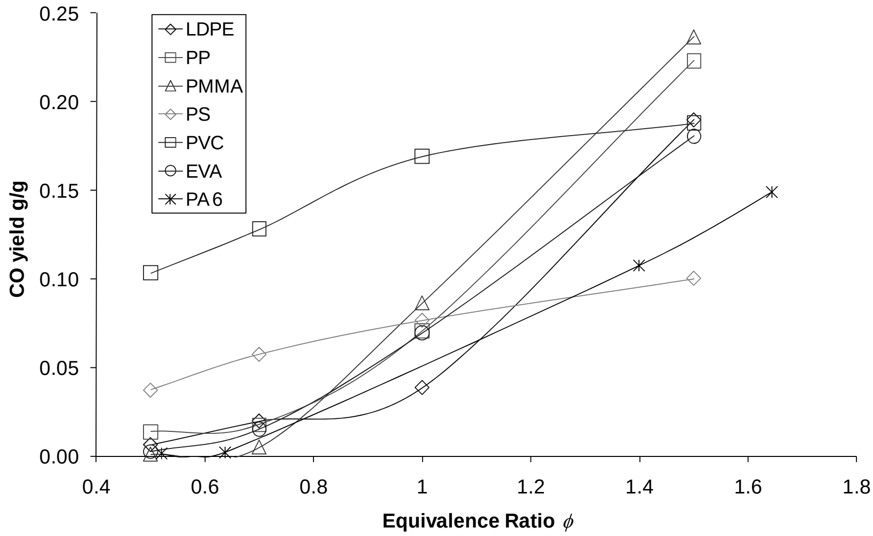

Fig. 2 CO yields from various polymers as a function of equivalence ratio at a furnace temperature of 650°C.

Figure 2 shows the carbon monoxide yield from various polymers as a function of ventilation condition, generated in the steady state tube furnace[xii, xv, xvi]. For most polymers there is a very small CO yield in well-ventilated conditions ($0.5 < \phi < 0.7$), increasing progressively with under-ventilation to give large yields when $\phi > 1.0$. There are two exceptions to this behaviour: PS, which contains a stable aromatic structure, giving incomplete combustion in well-ventilated conditions with a higher CO yield, but a lower CO yield in under-ventilated conditions, as the aromatic ring fails to decompose; PVC, which shows a consistently high CO yield, due to the trapping of H· and OH· radicals by HCl, blocking the conversion of CO to CO_2.

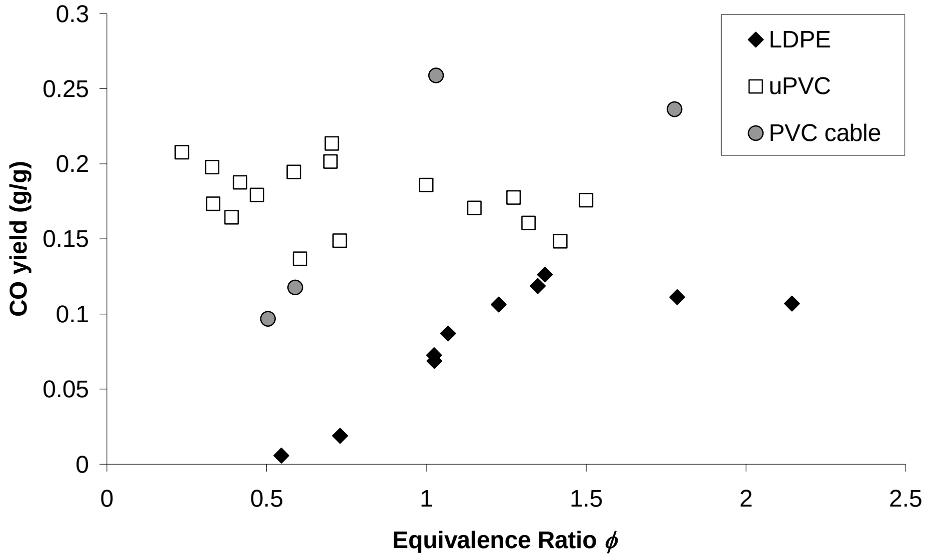

Fig. 3 Variation of CO yield for LDPE, unplasticised PVC and PVC containing plasticizer and chalk.

This effect is even more noticeable in commercial products such as plasticised PVC covered electric cable, where the PVC is compounded with an equal mass of hydrocarbon based plasticiser and chalk (Fig. 3). This shows the potency of HCl to inhibit the CO oxidation resulting in similar CO yields, when the PVC content had been reduced by a factor of 3[vi].

The Steady-State Tube Furnace (SSTF) method has been found suitable for generating fire effluents for the quantification of toxic combustion products, with particular emphasis on its use as engineering tool for quantifying the yield of toxic products under a range of fire conditions characterised by temperature and the equivalence ratio. It has been recognised as one of the only devices with such a capability by ISO, as ISO 19700[xvii].

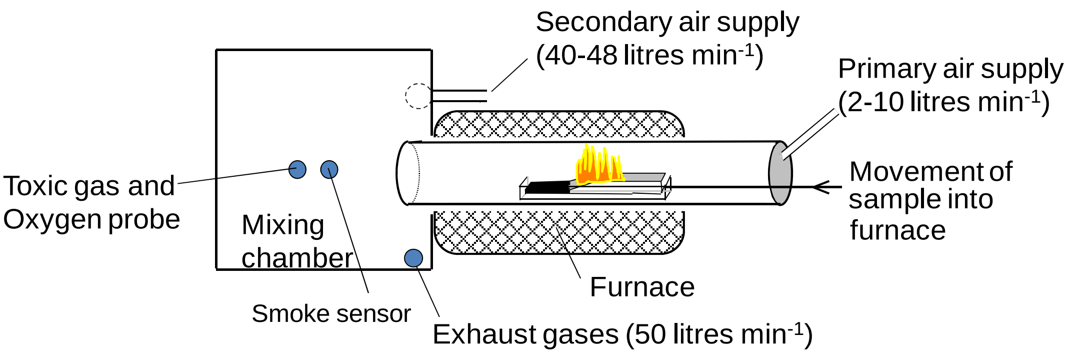

Fig. 4 – Steady State Tube Furnace apparatus ISO TS 19700 schematic.

This method was designed to replicate real fire conditions, and it is essential that proper steps are taken to ensure that those conditions are being met[xvii]. By using a range of different temperatures and airflow rates it is possible to reproduce all the different fire stages and types, including low-temperature non-flaming oxidative decomposition, well-ventilated flaming (ϕ < 0.75) and high-temperature under-ventilated (post-flashover) flaming decomposition conditions (ϕ > 2)[xvii].

Samples for the measurement of smoke and toxic gases are taken continuously from the mixing chamber and the secondary oxidiser. These gas streams are passed through a drying agent and smoke filtration system and the gas concentrations are measured using electrochemical cells, paramagnetic analysers (O_2) and non-dispersive infrared (NDIR) sensors.

The aim of the current work was to investigate the effect of temperature, and presence of halogens or aromatic species on the combustion efficiency.

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. In addition, granulated glass fibre reinforced PA6, containing brominated flame retardant and antimony oxide synergist containing 44% Polyamide 66 (Ultramid A27), 30% Glass fibres (Vetrotex EC 10 983), 20% Bromopolystyrene (Saytex HP 3010G), and 6% Antimony Trioxide (as masterbatch in PA 6 Campine 2617).

RESULTS AND DISCUSSION

In order to investigate the interaction of hydrogen chloride on the oxidation of carbon monoxide, a mixture of PVC and LDPE pellets containing equal masses of each polymer was burnt at different furnace temperatures in the steady state tube furnace. The carbon monoxide yields were determined, and are reported as a function of equivalence ratio for each temperature in Figure 5.

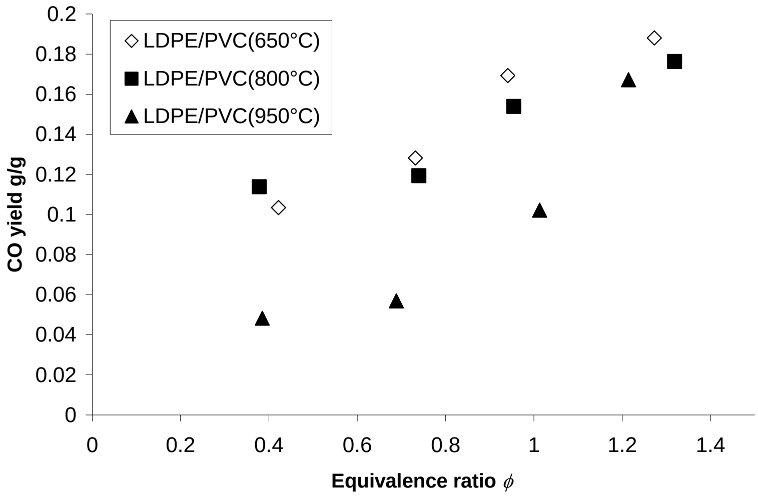

Fig. 5 CO yield of LDPE/PVC mixture at 650, 800 and 950°C.

At lower temperatures in well-ventilated conditions, conversion of CO to CO_2 is inhibited. While HCl is effective in inhibiting the conversion of CO to CO_2 from PVC/LDPE at 650 and 800°C, at 950°C the conversion of CO to CO_2 is fairly efficient. Therefore, both the fire retardant effect and the yields of products of incomplete combustion of PVC are diminishing at higher temperatures.

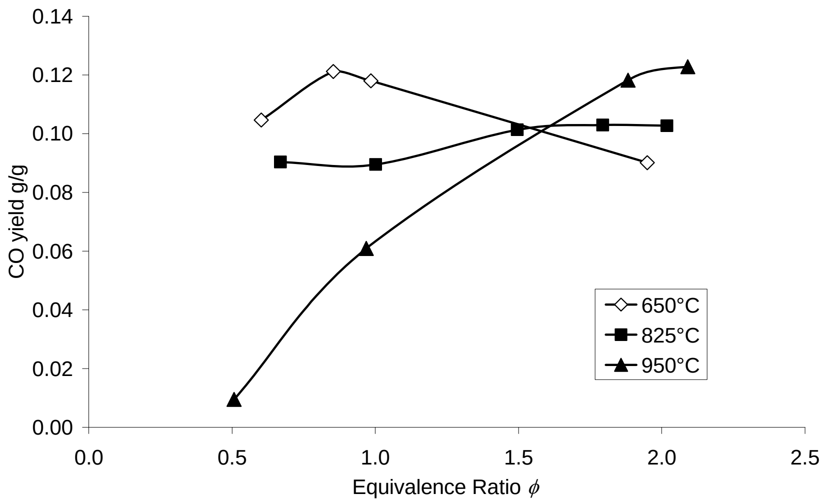

Fig. 6 Variation of CO yield with temperature and equivalence ratio for glass fibre reinforced PA6 containing brominated flame retardant.

Glass reinforced polyamide 6 containing brominated polystyrene and antimony oxide, in a typical industry formulation, was investigated to see if the same temperature dependent carbon monoxide oxidation inhibition effect was observed. The sample contained 30% glass fibre, and as the results are reported on a mass charge basis, the carbon monoxide yields would be 30% lower than they would have been if material did not contain glass fibre filler. Fig. 6 shows strong inhibition of the conversion of CO to CO_2 at 650°C and 825°C, but almost no inhibition in well-ventilated conditions at 950°C.

Finally, the enhanced stability conferred by aromatic structures (whether from polymers which already contained aromatic groups such as PS, or from polymers which decompose to form gas phase aromatic fuels, such as PVC) was investigated as a function of temperature. As shown in figure 2, polystyrene shows high CO yields in well-ventilated combustion, but lower than expected CO yields in under-ventilated combustion, at a furnace temperature of 650°C. Figure 7 shows the variation of carbon monoxide yield as a function of temperature and equivalence ratio. At 750 and 850°C the CO yield drops from the elevated level of 0.04 g/g to a very low level, around 0.005 g/g. While this increases as a function of equivalence ratio, under the conditions reported here, all the carbon monoxide yields in under-ventilated conditions are lower than those typical of other hydrocarbon polymers.

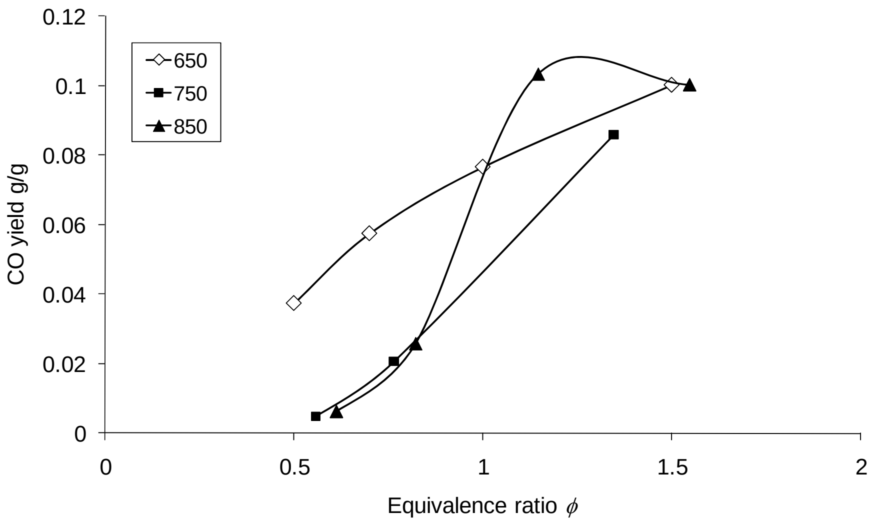

Fig. 7 Variation of CO yield with temperature and equivalence ratio for polystyrene.

CONCLUSIONS

CO and hydrocarbon yields can be used as an indicator of fire condition. Under well-ventilated conditions, combustion is most efficient, so that for most materials, the main products are carbon dioxide, water, and heat, and the CO and hydrocarbons yields tend to be low. Under-ventilated fires tend to produce large amount of effluent containing a mixture of products of incomplete combustion, such as CO and hydrocarbons. In addition, temperatures are greater, and as this work shows, this can have a dramatic effect on both the fire toxicity and the flame inhibition. Therefore, the steady state tube furnace proves to be an appropriate apparatus to reproduce the different fire types.

The equivalence ratio is a very useful factor for characterisation of fire conditions. It shows that for most materials, there is a low yield of carbon monoxide under well-ventilated ($\phi < 0.7$) conditions, and a high yield in under-ventilated conditions ($\phi > 1.5$). The anomalous flame inhibition behaviour of PVC and PS observed at 650°C becomes less apparent as the temperature increases. A comparison of carbon monoxide yields for the LDPE and PVC pellet mixture with pure LDPE and pure PVC materials as pellets as a function of equivalence ratio showed that the co-burning of the two fuels led to greater inhibition of CO oxidation per gram of HCl volatilised than for PVC alone. In well-ventilated conditions, the LDPE/PVC mixture produced greater CO yields, about 1.5 times higher than for pure LDPE, and almost in the same range as for pure PVC. This could be explained by the presence of HCl in the fire effluent which interferes with the radical chain mechanism, preventing the conversion of CO to CO_2 by the introduction of the stable chlorine radicals, which reacts with OH· or H· and results in high CO yield even for well-ventilated conditions. At very high temperatures (950ºC) the effect is reduced and both PVC and LDPE/PVC mixture show lower yields of CO.

Similar behaviour is observed for the carbon monoxide evolution from the PA6 containing 20% brominated flame retardant. At 650 and 825°C, higher yields of carbon monoxide were observed than would be expected from the pure polymer, but at 950°C the inhibition effect (and presumably the flame retardancy) disappears. This is particularly interesting because the presence of antimony is believed to produce antimony oxybromide (SbOBr) which diproportionates into various species containing progressively less oxygen, ultimately resulting in antimony tribromide ($SbBr_3$). Therefore, instead of the active agent being HBr, whose decomposition would release H· radicals which could contribute to the replenishment of ·OH radicals to oxidise CO to CO_2, the antimony-bromine species contain no hydrogen, but shows the same inhibition effect on the main heat release process of combustion The high carbon monoxide yields for PS in well-ventilated conditions and the low carbon monoxide yields for PS in under-ventilated conditions, compared to other hydrocarbon polymers has been ascribed to the stability of the aromatic ring. This enhanced stability under well-ventilated conditions, leading to only partial oxidation is also strongly temperature dependent, with a noticeable reduction at 750, and a further reduction at 850°C. The different temperature sensitivity for PS and PVC suggests that additional carbon monoxide produced in well-ventilated conditions cannot be attributed soley to the aromatic decomposition products of PVC.

Overall, the implication is that while halogens and aromatic structures may suppress ignition and reduce heat release in early stages of fires, they probably have no significant effect once the fire grows and the temperature increases.

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