Measurement of heat release in laminar diffusion flames fueled by controlled pyrolysis of milligram-sized solid samples: Impact of bromine- and phosphorus-based flame retardants

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ABSTRACT

Brominated flame retardants (BFRs) are widely used in polymers due to their high effectiveness at relatively low cost. Recent studies suggest that certain BFRs may present health and environmental hazards, yet obtaining adequate replacements is an ongoing challenge. To develop new additives, it is of paramount importance to better understand the mechanisms governing the action of flame retardants in polymers, particularly their action in the gas phase, and to develop effective screening techniques for potential candidates. To address this challenge, a novel apparatus, the Milligram-scale Flame Calorimeter (MFC), is proposed. In MFC, the pyrolysis and gas-phase combustion processes are uncoupled. Samples of 35 ± 5 mg are pyrolyzed in an anaerobic atmosphere and their pyrolysis products are burned in a laminar, near axisymmetric diffusion flame under controlled and customizable conditions in a fully enclosed system. Heat release information is obtained through the oxygen consumption calorimetry. The masses of post-combustion pyrolysis residue and solid particulate combustion products (e.g., soot) are measured. In this manuscript, a description of the design, parametric optimization of test conditions, and overall testing methodology is given. Heat release measurements are presented for polystyrene with increasing amounts of brominated polystyrene as well as poly(butylene terephthalate) with increasing concentrations of aluminum diethylphosphinate and results are compared to the Cone Calorimetry (Cone) and Microscale Combustion Calorimetry (MCC) measurements conducted on the same materials. Using combustion efficiency as a metric, the sensitivity to both bromine and phosphorus gas-phase activity is determined. The impact of these flame retardants is pronounced in the Cone experiments and largely undetected by the MCC. The MFC shows trends with respect to the flame retardant content comparable to the Cone. However, the absolute values of MFC combustion efficiencies tend to be notably higher that those observed in the Cone experiments. Overall, the MFC results demonstrate that this novel apparatus can be used to detect gas-phase activity of flame retardants using milligram-sized samples.

1. Introduction and background

While offering highly customizable mechanical properties, relatively low mass, and streamlined processing, most commercial polymers also possess inherent flammability that limits their applicability. Over the years, a variety of flame retardant additives has been introduced to address this flammability problem. These flame retardants can interfere with the pyrolysis and combustion processes through both physical and chemical mechanisms, and may act in the condensed phase, gas phase, or both. Among these additives, brominated flame retardants (BFRs) have become ubiquitous due to their high effectiveness at relatively low cost. However, as data on their

use and behavior over time have been compiled, it has been shown that some BFRs present environmental hazards due to their bioaccumulation and persistence in the environment among other reasons [1,2]. Industry is shifting towards suitable replacements [3], but the process is not trivial and testing potential replacements can be costly.

Understanding the mechanisms of action of BFRs is necessary to develop adequate replacements. Over the past five decades, a significant amount of work has been dedicated to studying the mechanisms of action of halogenated compounds as gas-phase flame inhibitors. Sheinson et al. [4] developed a methodology to quantify the modes of action of halogenated compounds and showed that brominated compounds exhibit both physical and chemical action, although the chemical action tends to outweigh the physical one. Rosser et al. [5] were the first to propose a mechanism for bromine action as a catalytic flame suppressant. Their mechanism consisted of the formation of hydrogen bromide (*HBr*) followed by two radical trapping

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reactions:

$$H + HBr \rightarrow H_2 + Br \tag{1}$$

$$OH + HBr \rightarrow H_2O + Br \tag{2}$$

The free bromine atoms are then recycled to form more HBr and the process is repeated, hence the catalytic effect.

Several researchers have built upon this proposed mechanism. Noto et al. [6] analyzed the inhibition effectiveness of various halogenated compounds using numerical modeling and suggested a procedure for differentiation between physical and chemical contributions (an alternative methodology to that proposed in [4]). These authors also showed that the ratio of physical to chemical action varies with fuel composition. Babushok and Tsang [7] used modeling to establish the dependence of burning velocity on the concentration of halogenated flame inhibitors in alkane–air mixtures and ranked the inhibitors based on their effectiveness, with brominated agents performing better than fluorinated ones for all considered fuels. A similar trend in halogenated flame inhibitor performance had been observed earlier for high temperature methane combustion [8]. Linteris et al. [9] have experimentally and numerically investigated the action of Halon 1301 (CF_3Br) and pure bromine (Br_2) in cup burner methane-air flame extinguishment experiments. Their results show that the flame is characterized by two distinct regions, a reaction kernel and a trailing diffusion flame. In the kernel, HBr formation is highly promoted; the reactions defined by Eqs. (1) and (2) dominate and are primarily responsible for radical consumption. In the trailing flame, HBr formation is hindered and the catalytic effect is reduced with respect to the kernel. More recently, Dixon-Lewis et al. [10] have improved earlier work [11] by updating the high temperature bromine chemistry and reexamining inhibition mechanisms involving HBr and Br_2. They show that hydrogen bromide and molecular bromine act differently as inhibitors in hydrogen flames. Despite these significant advances in understanding the chemistry and physics of flame inhibition by brominated compounds, extending this knowledge to polymer combustion is difficult. This is the case because neither the gaseous fuel nor brominated species formed during polymer pyrolysis are easily quantifiable and because, for many combustion scenarios, the gas-phase inhibition effects cannot be quantitatively separated from the effects of processes (initiated by the same additives) in the condensed phase.

In the search for alternative flame suppressants, researchers have identified that phosphorus-based compounds can also act as gas-phase flame inhibitors. Twarowski [12] found that phosphine (PH_3) catalyzed the recombination of H and OH radicals in hydrogen-air flames and proposed a mechanism for this process. First, PO_2 radicals are formed. Subsequently, these radicals react as follows:

$$H + PO_2 \rightarrow HOPO \tag{3}$$

$$H + HOPO \rightarrow H_2 + PO_2 \tag{4}$$

$$OH + H_2 \rightarrow H_2O + H \tag{5}$$

Further work by Korobeinichev et al. [13] expanded this mechanism to include intermediate phosphorus compounds also acting as radical scavengers. This mechanism is believed to be the main mode of action of phosphorus in the gas phase. Recently, Bouvet et al. [14] and Takahashi et al. [15] have examined the gas-phase effectiveness of dimethyl methylphosphonate (DMMP) in methane-air flames using a cup burner. Experiments and numerical simulations were carried out. Their findings show that phosphorus effectiveness is a function of concentration of DMMP (decreasing effectiveness with increasing concentration) as well as location of DMMP introduction (i.e., oxidizer versus fuel side, with fuel side introduction being ineffective). When added to polymers, phosphorus flame retardants (PFRs) have been shown to act in both the gas and condensed phases,

with relative importance of these modes of action being largely dependent on the chemical structure of the flame retardant as well as of the polymer matrix [16, 17].

To improve the understanding of the modes of action of both BFRs and PFRs in polymers, researchers have used various experimental methods, each one with its own advantages and disadvantages. Cone Calorimetry (Cone) [18] is, perhaps, the most widely used technique. This technique provides a capability to measure heat release rates (HRR), total heat release (THR) and heats of combustion (HOC) of solid materials, which gaseous decomposition products are combusted in a laminar-transitional diffusion flame. While Cone has been used to demonstrate the action of BFRs in reducing the combustion efficiency of materials [19], isolating condensed-phase and gas-phase effects is still challenging with this technique. Furthermore, test samples are quite large (on the order of 50 g) and it can become prohibitively expensive to prepare and test a variety of potential BFR replacements with such method.

A relatively new technique, the Microscale Combustion Calorimetry (MCC) [20], utilizes a heated premixed flow reactor to combust gaseous decomposition products, allowing for the measurement of HRR and HOC of 3–10 mg solid samples. The apparatus uncouples the pyrolysis process from the combustion process. However, under standard testing conditions, the gas-phase combustion reactions are essentially forced to completion [21]. As a consequence, this technique may not be sufficiently sensitive to detect the gas-phase action of flame retardants in reducing the combustion efficiency. Recently, Sonnier et al. [22] have altered the operating conditions of the MCC to investigate the effects of reactor temperature on the combustion efficiency of various polymers including those containing BFRs and PFRs. Their results show that incomplete combustion in the MCC can be achieved by decreasing the temperature, effectively creating a combustion efficiency dependence on this parameter. This development opens the door to using MCC as a tool for detecting gas-phase flame retardant activity, although modifications to operating conditions and a significant number of experiments and data analysis must be performed in order to deliver meaningful results.

Based on these observations, it is clear that there exists a need for a suitable testing technique that can provide further insight into the mechanism of action of existing additives and help identify new flame retardants. To that effect, we present the development of a novel apparatus that can measure the HRR and HOC of milligram-sized pyrolyzable solid samples, the Milligram-scale Flame Calorimeter (MFC). In this apparatus, the samples are pyrolyzed under carefully characterized heating conditions in an anaerobic environment. The gaseous pyrolysis products are subsequently combusted in a near axisymmetric laminar diffusion flame, effectively uncoupling the condensed phase from the gas phase but maintaining combustion conditions (low strain rate diffusion flames) similar to those encountered in accidental terrestrial fires. Heat release measurements of polystyrene with increasing amounts of brominated polystyrene and poly(butylene terephthalate) with increasing concentrations of aluminum diethylphosphinate are carried out in this apparatus and compared with the results of Cone and MCC measurements performed on the same materials. A definition of gas-phase combustion efficiency is introduced and employed to quantify bromine and phosphorus gas-phase activity over a wide range of scenarios realized in these tests.

2. MFC design

2.1. Description of apparatus

The MFC is a fully enclosed system composed of a control panel and four major sub-assemblies: combustor base, pyrolyzer, cylindrical combustion chamber and exhaust/gas analyzer. A schematic of the apparatus is shown in Fig. 1. From the control panel, a user-defined