



Full Length Article

A simplified model on carbon monoxide yield in burning of polymeric solids containing flame retardants

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ABSTRACT

Recent advances in Microscale Combustion Calorimetry (MCC) allow polymeric solids to be pyrolyzed and oxidized separately at the milligram scale, and the combustion gases, O₂, CO, and CO₂ to be measured using in-line gas analyzers. A simplified two-step reaction mechanism, which involves a CO generation step and a CO oxidation step, was developed to better describe the chemical reaction scheme that generates/oxidizes these products within the premixed combustor. Different incomplete combustion conditions were attained by varying the MCC combustor temperature and a numerical model of the combustor was developed to simulate the species evolution. Kinetics parameters were found by minimizing the errors in fitting the simulated results with the experiments. The two-step method was employed to examine halogen- and phosphorous-containing polymers of known compositions. The halogen additives were found to decrease gas phase reaction rate, whereas the phosphorous additives do not show significant effect. In cone calorimeter fire tests, both additives inhibit combustion efficiency by promoting soot formation.

1. Introduction

Halogen-containing, especially bromine-containing, flame retardants (FR) have played an important role in the polymer industry. Recently, environmental concern about bromine's persistence, bioaccumulation, and toxicity has emerged [1]. Particularly in the aircraft industry, a highly effective flame-inhibiting compound, decabromodiphenyl oxide (DBDPO) was banned [2]. There is an increased interest in halogen-free products. Phosphorus-containing compounds are promising because of their association with gas phase reaction as well as condensed phase char promoting reactions.

Unlike halogen-containing FRs which are relatively insensitive to fuel type and combustion environment, phosphorus-containing FRs are sensitive to both. For example, Bouvet et al. [3] found that effectiveness of dimethyl methyl phosphonate (DMMP) as an inhibitor decreased in going from a premixed flame to a diffusion flame, and finally a cup-burner flame. In contrast, Korobeinichev et al. [4,5] found that DMMP, trimethyl phosphate (TMP), and diisopropyl methylphosphonate (DIMP) promoted combustion in a premixed H₂/O₂/Ar flame. Similar behavior was also observed in the work of Glaude et al. [6] with a H₂/O₂ flame. Later on, TMP and Triphenylphosphate (TPP) were found to inhibit combustion in hydrocarbon flames in the work of Korobeinichev

et al. [7,8] and other researchers [3,9,10].

These studies of gaseous fire suppressing agents are narrowly focused on well-characterized liquid or gaseous fuels but a steady fuel supply cannot be easily extended to solid polymeric fuels. Stolarov et al. [11] used Microscale Combustion Calorimetry (MCC) to isolate gas-phase activity of FR from its condensed-phase activity. Incomplete combustion was achieved by reducing the combustor temperature [2,11,12]. A one-step global gas-phase mechanism was proposed [11]. Halogen was found to inhibit reaction, while phosphorous was found to inhibit reaction only at low FR loading. Further increasing the phosphorous FR loading reduced the inhibition effect. Recently, Walters et al. [2] have equipped the MCC with in-line CO and CO₂ analyzers in addition to the standard O₂ analyzer, due to their interest in toxic products especially CO from burning polymeric solids in the aircraft industry. A broader combustor temperature range (550–1000 °C) was explored. It was obvious from these MCC studies that there were competing mechanisms involving CO formation and oxidation for polymers in pre-mixed combustion.

In this study our objective is to incorporate a more detailed gas-phase reaction mechanism than the one-step global mechanism using the MCC and correlating these results with fire calorimeter tests.

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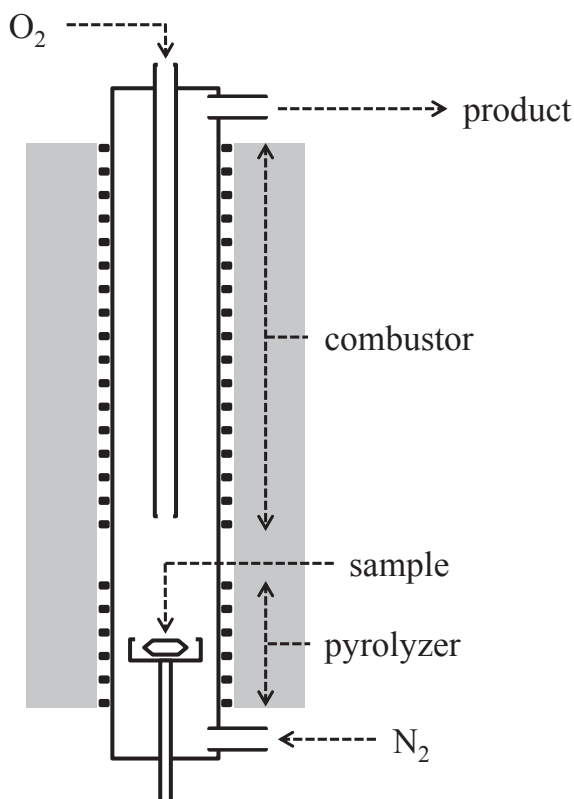


Fig. 1. Schematic of the MCC.

2. Approach

Polystyrene (PS) and three blends of PS with DBDPO were examined in this study. The mass fraction of DBDPO in the blends was 10, 15, and 20%. In addition, a diglycidyl ether of bisphenol-A epoxy (DER-322) and triethylenetetramine (TETA) hardener in 1:1 stoichiometric ratio was mixed with triphenylphosphine oxide (TPPO) at 0, 9 and 18% weight percent and cured at 200 °C.

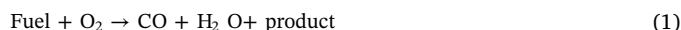
The MCC apparatus following the ASTM D7309 [13] standard was used. A schematic of the MCC is shown in Fig. 1. Details of the MCC setup can be found in Refs. [2,11,14]. Sample (about 3 mg weight) was heated at a constant heating rate of 1 °C/s from 100 to 800 °C. The specimen chamber was continuously purged with 80 cm³/min (20 °C, 1 bar) N₂. The purge gas carrying gaseous pyrolyzates was mixed with O₂ and burned either completely or incompletely by varying the temperature of the combustor. The oxygen flow rate was maintained at 20 cm³/min (20 °C, 1 bar). The MCC was modified to allow extra in-line measurements of CO and CO₂ concentrations besides O₂ concentration in the original design.

The temperature profile along the 21 cm long combustor tube was measured by replacing the oxygen inlet tube with an identical tube equipped with a 0.5 mm diameter bead Type-K thermocouple. The thermocouple was positioned along the axial direction in the combustor at 1 cm intervals at each combustor set point temperature. The combustor temperature was set between 550 and 900 °C in 50 °C increments. The measured temperature profiles were fit with respect to combustor set point temperature and combustor position. The uncertainties in the temperature data were about ± 5 °C. Complete combustion tests were performed for each material to determine the stoichiometric yield of CO₂ and O₂ consumed. Materials achieved complete combustion at temperatures between 900 °C and 1000 °C. Incomplete combustion tests were then performed by reducing the combustor temperature to as low as 550 °C. Each test was repeated three times. And the yields/consumptions of CO, CO₂ and O₂ were averaged

respectively.

Pyrolyzed gaseous fuels were assumed to have the form of the monomer that comprises the polymeric solid. Initial fuel concentration was estimated from the measured CO₂ yield in the complete combustion test based on material stoichiometry. Species concentrations were measured on a dry-basis and corrected for any condensed phase product removed in the cold trap. The flow becomes fully developed before entering the combustor [11], and the reacting species diffuse sufficiently fast radially in the combustor. A pre-mixed plug flow is assumed. Heat release from the combustion process was found to be negligible compared to the total heat delivered by the heating coil of the combustor.

A two-step reaction mechanism, involving CO generation and CO oxidation, was proposed to represent the chemical reaction between gaseous pyrolyzates (fuel) and oxygen.



Both reactions were assumed to be first-order dependent on both fuel and oxygen. The first-order dependence of the sequential fuel oxidation reactions in our paper on fuel and oxygen was derived from the work of Stolarov et al. [11]. Further reaction order optimization was not implemented because some preliminary simulations show that the current optimization is less sensitive to the reaction order. The rate constants, k , were assumed to follow an Arrhenius form $k = A \exp(-E/RT)$, where A is pre-exponential factor, E is activation energy, R is ideal gas constant, and T is temperature. Local residence time was estimated with the bulk flow velocity at ambient temperature and corrected for the local combustor temperature. The combustor model uses a constant grid size of 0.1 mm. Evolution of the species along the combustor was simulated following the proposed 2-step reaction mechanism using MatLab. The appropriate value for A and E was found by minimizing the error in fitting the measured and simulated species concentrations (i.e. CO, CO₂ and O₂).

In addition, a fire calorimeter (Fire Testing Technology), operating on the oxygen consumption principle, was used for bench scale testing of the samples following the standard of ASTM E1354 [15]. The samples were cut to 10 cm square and 0.3 cm in thickness, and were subject to 50 kW/m² of radiant heat flux. Similar to the MCC tests, species concentrations of O₂, CO, and CO₂, were measured. Soot mass was determined from laser extinction with a soot refractive index of $m = 1.57 - 0.56i$ [16,17]. It is assumed the flow in the duct is fully developed and the soot concentration is uniform radially. Soot volume fraction, f_v , is then expressed with:

$$f_v = \frac{\ln(I_0/I)\lambda}{6\pi E(m)L}, \quad (3)$$

where $E(m)$ is the refractive index absorption function, I and I_0 are the laser intensity with/without extinction respectively, L is the optical path length, and λ is laser wavelength. Soot mass is then calculated by integrating the soot volume fraction over the cross-sectional area, assuming a soot density of 1850 kg/m³ [18].

3. Results and discussion

Total yields of CO, CO₂, and O₂ in MCC tests were calculated by integrating the measured species concentration and the flow rate. The total yields were normalized by the mass of pyrolyzed sample. Char yields in all tests of PS and brominated PS are negligible. The measured yields of CO, CO₂, and O₂ in MCC tests of PS and brominated PS are shown in Fig. 2. The O₂ yields are negative as they correspond to consumption.

Also shown in Fig. 2 as lines are the simulated results using the optimized kinetics parameters. It is seen that as bromine loading increases, the minimum combustor temperature required for complete

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