

TIME RESOLVED MEASUREMENTS OF PYROLYSIS PRODUCTS FROM THERMOPLASTIC POLY-METHYL-METHACRYLATE (PMMA)

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ABSTRACT

The goal of this research is to obtain quantitative information on chemical speciation over time during high temperature material thermal decomposition. The long term goal of the research will be to impact structural fire safety by developing a data base of characteristic “burn signatures” for combustible structural materials. In order to establish procedure and to generate data for benchmark materials, the first material tested in these preliminary tests is poly-methyl-methacrylate (PMMA). Material samples are heated in an infrared (IR) heating chamber until they undergo pyrolysis. Time resolved quantitative measurements of the exhaust species CO₂, O₂, HC, and CO were obtained. During heating the PMMA sample undergoes two distinct processes. First, pre-combustion pyrolysis is characterized by the appearance a peak in the THC signal between 600-650 °C. Secondly, at about 900 °C flaming combustion occurs as evidenced by an exothermic reaction reported by the thermocouples. The time sequence of the production of HC, O₂ depletion and CO₂ production are consistent with combustion in an excess-oxidizer environment.

NOMENCLATURE

PMMA	Poly-methyl-methacrylate
HC	Hydrocarbons
THC	Total HC's (same as HC)
O ₂	Oxygen
CO ₂	Carbon dioxide
CO	Carbon monoxide
IR	Infra Red
BeO	Beryllium Oxide
OD	Outer diameter
T1, T2, T3, T4	Thermocouples in furnace

INTRODUCTION

Unwanted fire poses a serious threat to structures, property, and human life. The general goal of this research is to develop a technique for creating a library of burn signatures for various materials. Though research has been done in examining which gases are produced during combustion, there has been little work quantifying these combustion products in the form of a “signature” of that material. This goal is complicated by the fact that the same material may produce different signatures under different test conditions. Nevertheless, our intent is at least partly to determine whether or not certain chemical features remain intact across a variety of heating conditions. If that is the case, a “signature” can be said to exist for that material and not simply the particular test.

Although there have been many efforts at quantifying the products of combustion and pyrolysis, these efforts have been primarily directed firstly at determining the products themselves and secondly at determining whether or not their concentrations, over the course of an experiment, exceed a threshold value. An extensive review of the pyrolysis and combustion of materials is provided in Wichman (2003)^[1]. The emphasis is chiefly on materials used in transportation applications, but the principles for structural materials are essentially the same. Additional emphases in Wichman (2003) were ignitability, smoke generation, retardants and, of course, the complicated issue of toxicity. Toxicity is generally quantified by estimating expressions such as LD₅₀, which is the time required to generate a lethal dose of the toxicant under question at the measurement site. Numerous ASTM and ISO tests have been developed to achieve this goal. Some of the benefits and many of the drawbacks of such an approach are discussed in Wichman (2003).

The material examined here, PMMA, has been referred to for many reasons as an “ideal gasifying solid,”

among them the “unzipping” of the polymer, the comparative absence of melting, dripping and running during heating, the lack of formation of char layers, and the general cleanliness of the pyrolysis and combustion of this material. Details are provided in Wichman (1992) [2].

Since PMMA behaves “ideally” in the thermal modeling sense, many if not most of the modeling efforts in the theory of flame spread use PMMA as the representative material. In addition, many scientific experiments on material ignition and combustion and flame spread employ PMMA as the first test case during initial apparatus evaluations [Cordova, et al., 1997] [3]. This will be the intent of this research.

In this article the emphasis is on the development of a transient, temporally evolving real-time metric for the pyrolysis and thermal decomposition of PMMA in what amounts to the *pre-combustion* or *pre-ignition* decomposition stage. The goal is to obtain a complete transient description (as opposed to a static definition) of material combustibility including specifically a quantitative characterization of the chemical “burn signatures” of this particular material. Additional materials other than PMMA will be examined in our future research.

EXPERIMENT

A. Materials

For the first phase of the research, the material chosen for testing was poly-methyl-methacrylate (PMMA). PMMA is a thermoplastic with chemical formula of $(C_5O_2H_8)_n$ [Polymers, 2008] [4]. PMMA is more commonly referred to as ‘acrylic glass’ or ‘Plexiglas’, and can be found in shatter-proof windows as well as in hard plastic for furniture.

These products can be commonly found in many buildings and homes. Due to its regular and predictable burning properties, PMMA has been called an “ideal gasifying solid” of the kind that can be characterized in the simplest and most elegant theoretical models [de Ris, 1969, Wichman and Williams, 1983] [5][6]. An extensive discussion of the “ideal gasifying solid” is provided in the review article by Wichman, 1992.

B. Heating System

The samples are examined in an IR radiant heating chamber. The equipment chosen for this function was the ChambIR Model E4 Infrared Heating System. The Model E4 focuses high-density IR energy, generated by ‘T3-style’ halogen lamps, onto a cylindrically shaped target area. The ‘T3-style’ lamp configuration is displayed in Figure 1. The target area has a length of 63.5 mm, with a diameter of 6 mm. The geometry of the chamber means that the sample is heated with radial symmetry. Within this target area, transient product temperatures of 1100°C and continuous product temperatures of 815°C can be achieved [ChambIR, 2001] [7].

The system can heat to 90 percent of full operating temperature within 3 seconds, and cool down to 10 percent of operating temperature within 5 seconds with the assistance of an

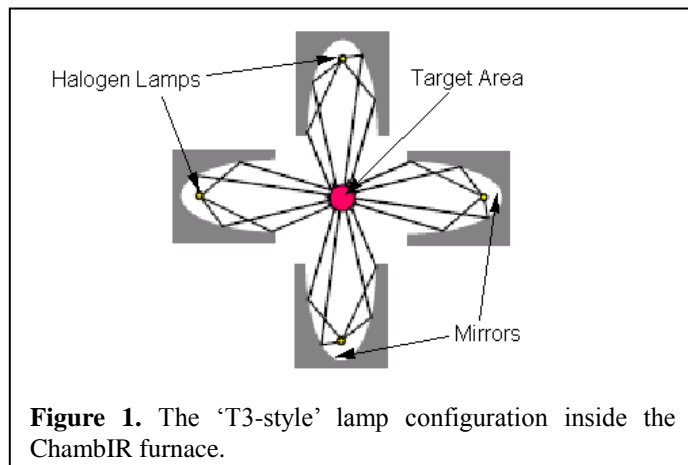


Figure 1. The ‘T3-style’ lamp configuration inside the ChambIR furnace.

external water-cooling device. The sample is skewered on a rod made of beryllium oxide (BeO), which, as it is heated by the IR lamps also provides an internal direct-contact or conductive heat supply to the PMMA sample.

C. Temperature Monitoring

While the materials are heated, both their temperature and exhaust gases are monitored in real time. The temperature of various positions within and surrounding the chamber are measured by type-K thermocouples (TC’s). Type-K TC’s measure temperatures up to 1350°C, 250°C higher than the maximum value attainable by the furnace. One TC is placed directly in the middle of the heated area, another measures the expelled (i.e., exhaust) gas temperature and a third TC measures the quartz rod temperature. The fourth TC is located within the tip of the gas analyzer’s probe, which monitors the sample gas temperature. The quartz and BeO apparatus holds the sample in place. The measurement rate is 2 samples/second.

D. Exhaust Gas Analysis

The exhaust gases are monitored by a model IMR 1400-IR combustion gas analyzer with measurement rate 1 sample/second. The data is then displayed in real-time and logged. The analyzer measures the concentration of O₂, CO₂, CO, and total hydrocarbons (HC’s or THC’s) through the use of sensors displayed in Table 1 [8].

Gas	Sensor Type	Relative Accuracy	Absolute Accuracy	Range
O ₂	Electrochemical	0.1%	+/-0.2%	0-20.9%
CO ₂	NDIR	0.01%	5%	0-30.00%
CO	Electrochemical	1ppm	Z	0-2000ppm
HC	Solid State	0.1%	5%	0-100%LEL

Z: 0-6% Volume: 0.3% absolute accuracy
6-30% Volume: 1.5% absolute accuracy

Table 1. IMR 1400-IR gas analyzer’s respective gas sensing mechanism, resolution, accuracy, and range.

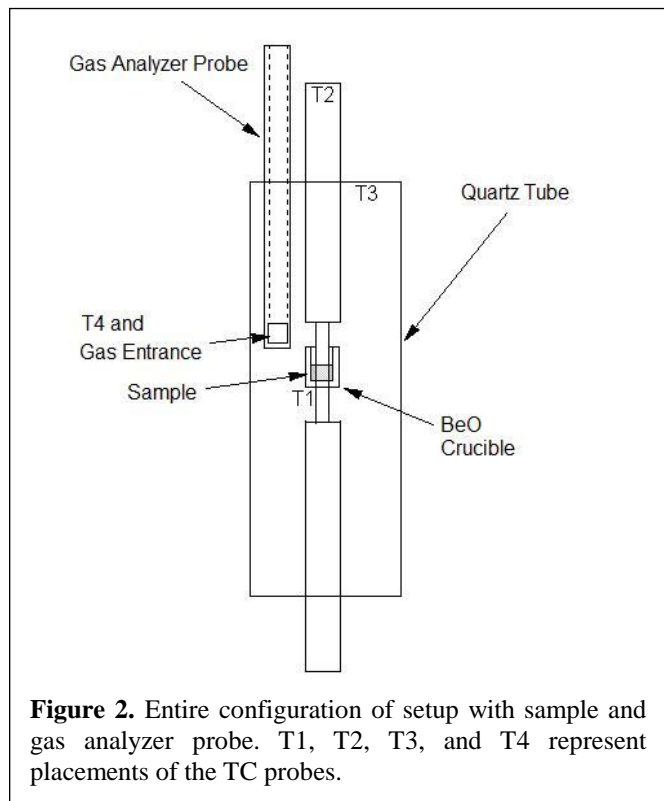


Figure 2. Entire configuration of setup with sample and gas analyzer probe. T1, T2, T3, and T4 represent placements of the TC probes.

The exhaust gas is drawn into the analyzer through a sampling probe placed 1 cm downstream from the sample. The gas flows through a filter which removes moisture [IMR, 2004]^[8]. This analyzer directly measures CO₂ concentration.

Both O₂ and CO are measured with an electrochemical cell. The sample gas is absorbed into two electrodes which produces a potential difference between the electrodes, and then a current is produced which can be directly correlated to gas concentration [Anderson, 1999]^[9].

HC's are measured by a solid-state cell which consists of one or more transition metal oxides. In the presence of HC's, the oxide causes the gas to dissociate into charged ions, which results in the transfer of electrons [Lowe, 2008]^[10], which produces a change in its conductivity, measured as a signal. This signal is correlated to the HC concentration.

Carbon dioxide is measured using a nondispersive infrared (NDIR) sensor consisting of an IR lamp, a sample chamber or light tube, a wavelength filter, and the IR detector.

CO₂ diffuses into the sample chamber, and its concentration is measured electro-optically by its absorption of a specific wavelength in the IR range [Gilway, 2002]^[11].

The setup of the experiment is in a vertical configuration. A quartz tube with a 1" OD is suspended directly in the center of the heating chamber. Quartz was used instead of regular glass. Since quartz has fewer impurities than glass at high temperatures, there are insufficient defects and potential reaction sites to cause unwanted chemical reactions. Quartz also has a low optical absorption, thus much more of the IR

radiation passes through the tube. Finally, quartz can withstand temperatures up to 1200°C, almost four times higher than glass.

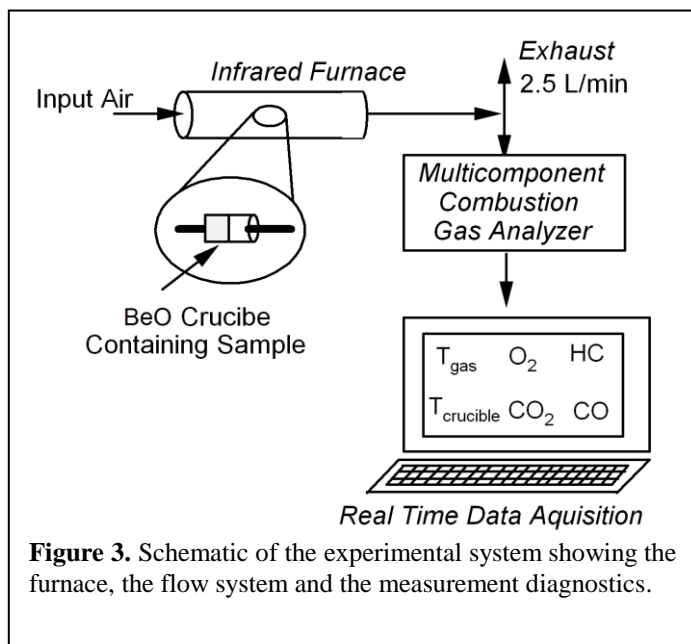
At both ends of the 1" quartz tubes are stainless steel plenum chambers. These chambers allow for gases and measurement devices to be inserted and removed while still maintaining a closed system. On the bottom plenum chamber are designated areas for TC's and input gases. Initially, the input gases will be either ambient air or synthetic air. In future work, other inlet gases will be introduced such as O₂ enriched environments or O₂ depleted (extinction) environments. A centered hole with a ¼" diameter is present in both the input and output plenum chambers. This holds a quartz rod in the center of the heated chamber so the sample may be properly heated (see Figure 1). In the center-end of the quartz rod, a ½" groove is carved to hold a beryllium oxide (BeO) rod with a 1/8 in diameter. This BeO rod passes through both the sample and a BeO crucible with a ¼" OD and a 1" length. The BeO crucible ensures that the sample stays in the center of the heated chamber, even while pyrolysis, decomposition and possibly combustion occur. The configuration of all the pieces is displayed in Figure 2. The TC labeled 'T1' is located in the center of the target area, wrapped around the crucible. 'T2' is located at the end of the quartz rod, which is exposed to ambient air outside the furnace. 'T3' is located in a small gas exhaust hole towards the end of the furnace. 'T4' is a thermocouple located at the tip of the gas probe, and it measures the gas temperature that is given in Figures 4-6.

BeO was specifically chosen because it is a machinable ceramic with high mechanical strength. BeO has a thermal conductivity of 265 W/m·°K, thus it is an excellent conductor of heat. This ensures the heat radiated by the lamps is efficiently absorbed and transferred to the pyrolysis sample. In addition, BeO is chemically non-reactive even at very high temperatures.

Ambient air is drawn into the furnace from the bottom, please refer to the lower section of Figure 2. In the current experiments the moisture in the input air was not controlled; the sample uses the O₂ in the air for combustion. The combustion gases, as well as the remaining ambient gases, flow up the quartz tube. These gases pass into the output plenum chamber. In this chamber, there is a TC which measures the exhaust gas temperature. A hole allows the gas analyzer probe to pass near the test crucible. The probe enters through a 1/8" OD hole, see Figure 2. The probe runs parallel to the quartz rod, which is centered in the heated chamber. The product gases flow directly into the gas analyzer and no undesired chemical reactions can occur before they reach the sensors

A schematic of our time-resolved materials characterization furnace system is shown in Figure 3. A real-time LabVIEW based data acquisition system (1s updates) monitors the crucible and gas temperatures, as well as directly measures O₂, CO₂, CO and HC's with resolutions 0.1 % Vol, 0.01 % Vol, 1 ppm, and 0.1 % Vol, respectively.

Prior to each set of measurements, solid residues from previous tests were burned off using a propane torch, followed



by ultrasonic baths in acetone and methanol. The empty crucible was then heated to operational temperature. The output for all four test gases was found to yield readings at the resolution/noise limit of the analyzer, thus verifying the cleanliness of the crucible.

RESULTS

Measurements were made on four "identical" PMMA samples of mass 0.25 ± 0.05 g (Figure 4). The heating sequence was as follows. Test A: rapid heating to 650 °C and hold until all four gas levels have fallen to approximately 10% of their peak values. Test B: rapid heating to 730 °C and hold (same criteria as Test A). Test C: slow heat to 800 °C without any hold. Test D: rapid heat to 900 °C and hold (same criteria as Tests A & B). The rationale for designing these tests in this manner was to determine whether different heating rates and heating profiles served to alter various "signature" metrics. If the "signature" characteristics remained intact, it was inferred that they were robust and thus meaningful and largely independent of the details of the heating protocol. For this reason, none of the tests follow an established ASTM or ISO heating protocol.

Figure 4 shows the HC signal (mole fraction or equivalently, volume fraction) as a function of time. During the first three lower temperature tests A, B and C the PMMA specimen underwent pre-combustion pyrolysis. In test D the sample self ignited at the temperature spike resulting in flaming combustion. The rise in gas temperature between 220 and 270

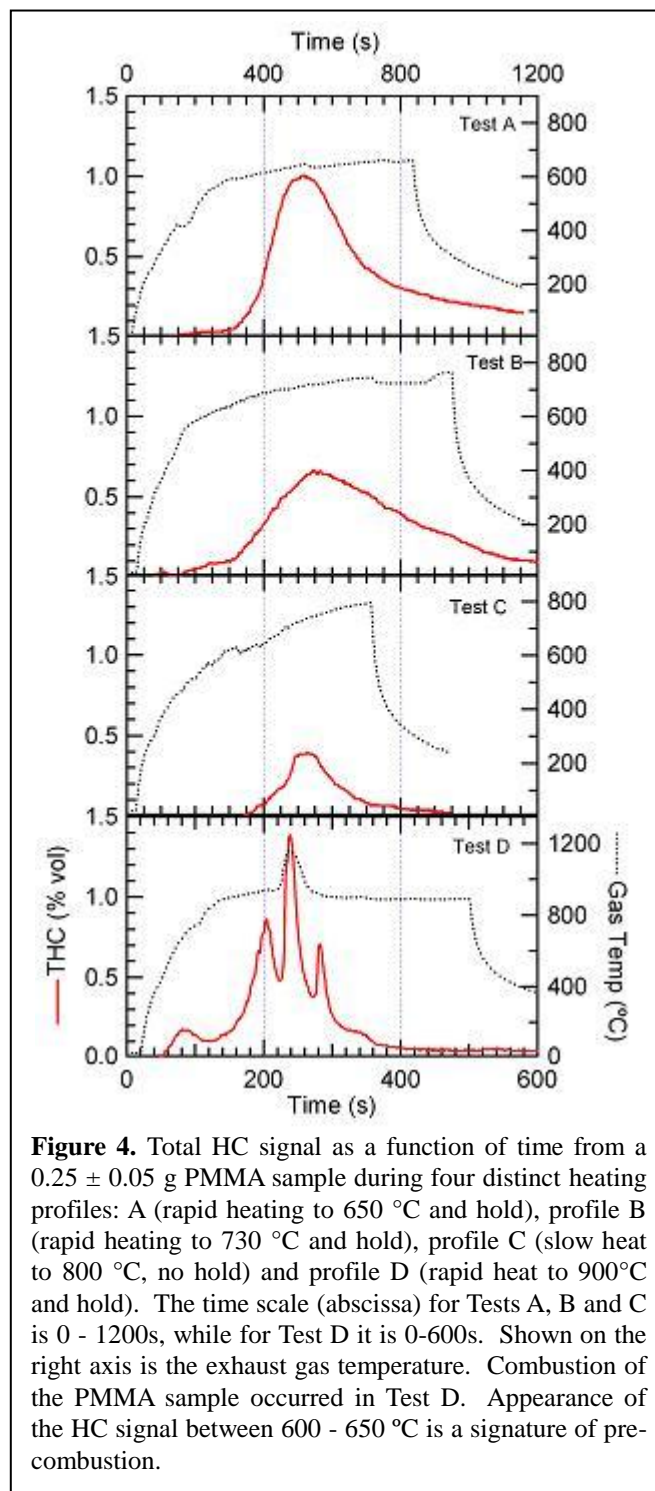


Figure 4. Total HC signal as a function of time from a 0.25 ± 0.05 g PMMA sample during four distinct heating profiles: A (rapid heating to 650 °C and hold), profile B (rapid heating to 730 °C and hold), profile C (slow heat to 800 °C, no hold) and profile D (rapid heat to 900 °C and hold). The time scale (abscissa) for Tests A, B and C is 0 - 1200s, while for Test D it is 0-600s. Shown on the right axis is the exhaust gas temperature. Combustion of the PMMA sample occurred in Test D. Appearance of the HC signal between $600 - 650$ °C is a signature of pre-combustion.

seconds is due to self ignition since the heater power was kept constant from 150 seconds onwards.

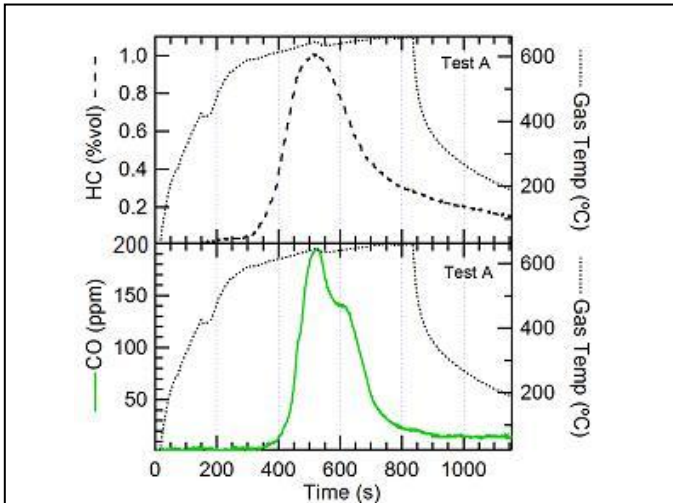


Figure 5. HC and CO signals as a function of time during Test A. The peaks are separated by 8 s and occur at a temperature of 645 °C and 647 °C for HC and CO, respectively. The appearance of the CO signal at 600 °C is a potential signature of pre-combustion.

The peak values of HC decrease with increase of the temperature from Tests A-C. In Test A HC acquires a maximum of approximately 1% Vol whereas in Tests B and C it is approximately 0.67 % Vol and 0.4 % Vol, respectively. A complete explanation cannot yet be provided, but it is reasonable to speculate that for these pyrolysis experiments (in which there was no flaming combustion), as the ambient temperature of the oxidizing gases is increased the consumption of the HC pyrolysis gases correspondingly increases, resulting in a diminished product gas mole fraction (or % Vol). The important factor for Tests A-C thus appears not to be the magnitude of the HC peak, or the total area under the HC versus time curve, but instead the temperature at first appearance of the HC's. In all of Tests A-C shown in Figure 4, the first appearance of HC's occurs in the same approximate range, namely 600-650 °C. Consider now Test A in more detail. Shown in Figure 5 is a plot identical to the first panel of Figure 4, with the addition of the CO signal. The peaks of the HC and CO signals are essentially coincident, being separated by less than 10 seconds. Within the instrumental resolution of the gas analyzer and the scale of the heating process (of order 1,000 seconds) the time difference is negligible. The appearance of CO in the 600 - 650 °C temperature range can be interpreted, in this preliminary study, as a characteristic *signature* of pre-combustion.

CO is in general the most potent (deadly) toxicant released by the pyrolysis and eventual combustion of hydrocarbon materials [Wichman, 2003]^[1]. The results of Tests A-D show in addition (Figure 5) that CO acts as a marker or indicator of potentially impending combustion or ignition of the released THC gases from the pyrolyzing sample. For both of these reasons (toxicity and impending potential ignition) CO detection is crucial. This fact has been known for a very long

time. Nevertheless, the dynamic relationship is only now being quantified.

Figure 6 shows almost all of the exhaust gas profiles for the case of complete combustion (Test D of Figure 4) of the PMMA sample. These results were verified by repeating test D (not shown). The HC signal is multiplied by a factor of 10 and for oxygen the magnitude of *depletion* is shown. The major HC (or THC) coincides with the location of the combustion event which takes place between 220-270 seconds. Note the appearance of the temperature spike and the maximum value of the temperature at 1160 °C ~ 1430 °K. This was a self ignition event, brought on without a “pilot” flame but likely caused by ignition originating from the hot surface temperature of the crucible and other surfaces (Figures 2, 3). Note also that only the Oxygen depletion is shown. For this reason the zero value is unimportant. Depletion is measured relative to that initial standard.

The time evolution of the HC signal indicates several distinct events are occurring. The initial HC rise between 65 - 80 seconds occurs when the gas temperature measured by T4 (Figure 2) is between approximately 600 – 650 °C as already mentioned in our discussions of Figure 4 Tests A-C. As the temperature of the surrounding gases increases the measured HC's decrease (consistent with the trend for Tests A, B, C in Figure 4) but eventually, at a sufficiently high furnace temperature in the vicinity of 900 °C (between approximately 150 and 170 seconds) the HC's once again begin to rise. The rise is interrupted by gas phase ignition, which occurs at approximately 200 seconds at a temperature of approximately 940 °C. The combined influences of the furnace and flame heating serve to increase HC production, producing the peak seen at approximately 240 seconds with T4 gas temperature 1160 °C = 1430 °K. The flame consumes the HC's, producing the sharp decline between 240 – 270 seconds, after which the flame presumably extinguishes. The pyrolyzing sample in the 900 °C furnace continues to produce HC gases which, however, are not consumed by any flame. After approximately 280 seconds the HC's decline steeply and eventually by about 400 seconds essentially disappear.

O₂ depletion and CO₂ production are of nearly the same magnitude on a % Vol basis (i.e., a mole fraction basis) but are separated by an approximately 50 second time interval. Slightly after the appearance of the HC's and the CO, the oxidation of these substances takes place, depleting the O₂. Approximately 1 minute thereafter, at 260 seconds, CO₂ production reaches its peak value and then drops rapidly to zero. At approximately 300 seconds the conversion of additional HC's to CO₂ has ceased.

Not shown in Figure 6 is the CO signal which has a first peak at 210 s followed by a rapid rise in signal level at about 230 seconds to well above 0.2 % vol. At this point the CO detector saturated and shut down. From this partial data set, it is observed that the first CO peak is coincident with the first THC peak, and the inference of a second CO peak that may

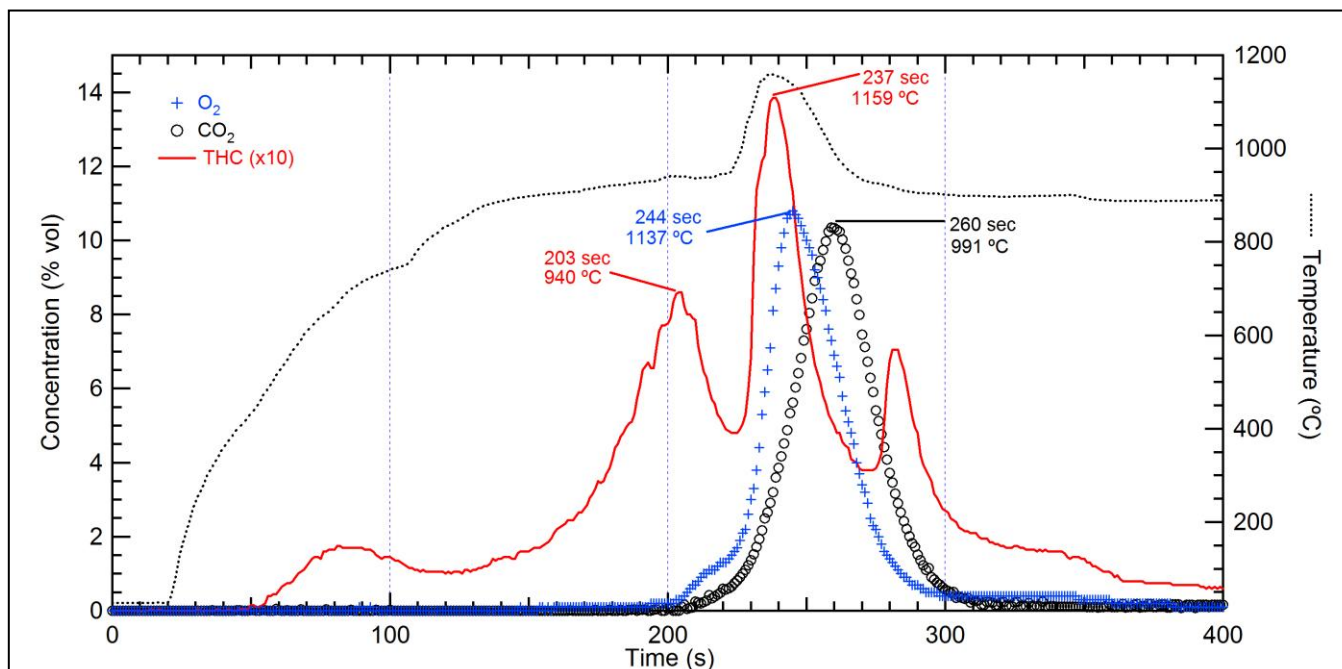


Figure 6. O₂, CO₂, HC and gas temperature profiles during rapid heating and hold of a PMMA sample to 900 °C. This sample first undergoes pre-combustion pyrolysis followed by flaming combustion as evidenced by the exothermic event between 220-270 seconds, which is coincident with the HC peak. As expected for combustion the HC peak is followed by O₂ depletion and then by CO₂ production. Note that (i) the HC signal was multiplied by a factor of 10 and (ii) the magnitude of the O₂ depletion is shown.

be coincident with the second THC, which occurs during the combustion event between 220-270 seconds.

DISCUSSION

Although it is possible to explain the time-sequence of various events (see discussion of Figure 6), it is more difficult to explain and to interpret the magnitudes of the effects and the relationship of the integral quantities to one another. In what follows the relative magnitudes will be examined for the O₂ depletion and CO₂ production curves in Figure 6. According to the chemical formula for the PMMA monomer, C₅H₂O₈ stoichiometric combustion in air would require (3/2) O₂ in order to produce 5 CO₂ on the product side¹. Pyrolysis and combustion in the IR radiant furnace occurs with a great excess of oxidizer. An equal Vol % reduction in O₂ and increase in CO₂ suggests that each carbon lost from the PMMA monomer is combined with the O₂ in such a proportion as to form an equal number of moles of CO₂. Thus, with respect to the surrounding gas the loss of the moles of O₂ is compensated by the gain of the moles of CO₂. This suggests that the oxygen that is bound in the PMMA monomer does not participate in the oxidation process, and that these O atoms appear, ultimately, in the compounds designated as HC (or THC). A more careful and

detailed assessment of these observations and measurements is necessary in future work, along with examination of the literature of PMMA degradation and oxidation kinetics to be certain that our furnace is reproducing the correct trends.

With respect to the main features concerning which the experiments are unambiguous, namely the temporal appearance of species peaks in a fixed, definite sequence (see Figure 6), the IR furnace produces satisfactory results that are compatible with a limited and recent body of work in the fire literature on this subject. Chemical “signature” development is a comparatively new topic. The authors are familiar with only one such work in the literature (Note that this is unpublished work that cannot presently be referenced), which produces results quite similar to the present work. The previous work, however, uses the open Cone Calorimeter (CC) whose control and specificity of heating rate is not as accurate as our small-scale furnace. The agreement between the data is encouraging and bodes well for future research.

CONCLUSION

Future work will utilize control of moisture in the samples and in the gas. The gas moisture can very easily be controlled by using laboratory air in gas cylinders. The samples, if they absorb moisture, will need to be placed in a humidity

¹ The stoichiometric reaction would be C₅H₂O₈ + (3/2)(O₂ + 3.76 N₂) → 5CO₂ + H₂O + (3/2)3.76 N₂.

controlled chamber for a specified length of time to control for their moisture content.

An important quantity that was not discussed in the present research is the HRR or Heat Release Rate. HRR is a calculated quantity that utilizes some of the quantities that are measured here to determine its magnitude. The basic idea is one of oxygen consumption, with a multiplication factor that depends upon the CO₂ and O₂ mole fractions (which were measured in Figure 6). It is anticipated that the HRR will correlate approximately with the CO₂ curve of Figure 6. In other words, the HRR peak will lag the CO, HC and O₂ peaks.

Through the data collected by this research, a library of burn signatures will be created. Each material will have a burn signature, which consists of an auto-ignition temperature and the expected concentration of each of the combustion gases based on the current temperature.

Future work will address materials other than the “test” material PMMA. One such material is cellulose, for which some measurements have already been made. The difficulty with cellulose, however, is that under slow heating it produces large quantities of tars which foul air filters. Under rapid heating (e.g., as in Tests A and D) these problems will likely be diminished. Future work will also address nontraditional materials and new materials. Among these materials are composites such as thermoplastic/wood fiber blends (which have many applications in structures and buildings) and new composite materials. Composites often have excellent strength properties, but their thermal properties, including resistance to ignition and fire, can negate the gains made in the area of strength. Some of these materials will be examined very carefully in future research.

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