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Reproducing the Products of Flaming Combustion in the Microscale Combustion Calorimeter

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16. Abstract

The FAA microscale combustion calorimeter (MCC) operates by burning the evolved gases from a thermally degrading sample and measuring the oxygen consumption to calculate a heat release rate. Recent method developments using hyphenated MCC techniques enables measurements of the effect of vitiation on toxic combustion gas yields. Stoichiometric fuel to oxygen ratio tests were performed where a constant fuel to oxygen ratio relative to the stoichiometric ratio, Φ, in the combustor is controlled throughout the sample decomposition. When $\Phi < 1$, combustion is fuel lean (over ventilated). When $\Phi > 1$, combustion is fuel rich (vitiated).

The MCC was coupled with an infrared spectrometer (MCC-IR) and a multigas analyzer (MCC-Testo), which were used to monitor gases and evaluate combustion toxicity at different Φ and combustion temperature set points. These hyphenated techniques demonstrate a unique capability to elucidate the effect of constant fuel to oxygen ratios on combustion product yields. Measurements made at different Φ's will help to better understand the flame chemistry and the mix of complete/incomplete combustion products for various aircraft materials throughout the different stages of a full-scale fire. Combustion equivalence ratios of 0.5, 1.0 and 1.5 were evaluated in this study. A set of hydrocarbon materials with elemental compositions, including C, H, N, O, and S, were examined to provide a spectrum of gaseous combustion products where a small set of potential toxic combustion products could be evaluated. Yields of the gaseous decomposition/combustion products were compared as a function of equivalence ratio for the set of materials. Trends in combustion products produced at different oxygen ratios correlate with large-scale fire test data from the literature and showed an increase in toxic product yields with increasing Φ.

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Acronyms

Acronym	**Definition**
ABS	Acrylonitrilebutadienestyrene
ASTM	American Society for the Testing of Materials
FAA	Federal Aviation Administration
FEP	Fluorinatedethylenepropylene copolymer
FR	Flame retardant
FTIR	Fourier-transform infrared spectroscopy
HDPE	High-density polyethylene
HIPS	High-impact polystyrene
HRR	Heat release rate
MCC	Microscale combustion calorimeter
MCT	Mercury cadmium telluride
MCC-IR	Microscale combustion calorimeter with infrared spectrometer
MCC-Testo	Microscale combustion calorimeter with multiple gas analyzer
NDIR	Nondispersive infrared sensor
PA66	Polyhexamethyleneadipamide
PC	Polycarbonate
PEI	Polyetherimide
PET	Polyethyleneterphthalate
PMMA	Polymethylmethacrylate
POM	Polyoxymethylene
PP	Polypropylene
PPS	Polyphenylenesulfide
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PVC	Polyvinylchloride
PVDF	Polyvinylidenefluoride
PVF	Polyvinylfluoride
TEM	Tunneling electron microscopy
UHP	Ultra-high purity
ZnSe	Zinc selenide

Executive summary

The FAA microscale combustion calorimeter (MCC) operates by burning the evolved gases from a thermally decomposing sample and measuring the oxygen consumed by the evolved gases in oxygen at high temperature to calculate a heat release rate in Watts per gram of sample. Recent method developments using hyphenated MCC techniques enables measurements of the effect of vitiation on toxic combustion gas yields. Stoichiometric fuel-to-oxygen ratio tests were performed, where a constant fuel-to-oxygen ratio relative to the stoichiometric ratio, Φ, in the combustor was controlled throughout the sample decomposition. When $\Phi < 1$, combustion was fuel lean (overventilated). When $\Phi > 1$, combustion was fuel rich (vitiated).

The MCC was coupled with an infrared spectrometer (MCC-IR) and a multiple gas (multigas) analyzer (MCC-Testo), which were used to monitor gases and evaluate combustion toxicity at different Φ values and combustion temperatures. These hyphenated techniques demonstrate a unique capability to elucidate the effect of constant fuel-to-oxygen ratios on combustion product yields. Measurements made at different Φ values will help to better understand the flame chemistry and the mix of complete/incomplete combustion products for various aircraft materials throughout the different stages of a full-scale fire. Combustion equivalence ratios of 0.5, 1.0, and 1.5 were evaluated in this study. A set of hydrocarbon materials with elemental composition C, H, N, O, and S, were examined to provide a spectrum of gaseous combustion products where a small set of potential toxic combustion products could be evaluated. Yields of the gaseous complete and incomplete combustion products were compared as a function of equivalence ratio for the set of materials. Trends in combustion products produced at different fuel/oxygen ratios correlate with large-scale fire test data from the literature that show an increase in toxic product yields with increasing Φ.

1 Introduction

The microscale combustion calorimeter (MCC) was developed by FAA researchers to evaluate materials for flammability on a milligram scale and was standardized by ASTM in 2007 and revised several times, most recently as D7309-21 in 2021 (ASTM International, 2021). The MCC operates by separating sample pyrolysis from combustion of the evolved gases. A ceramic tube with a small wound heater (pyrolyzer) is used to thermally decompose a solid sample under nitrogen. Oxygen is then added in a second, larger wound heater (combustor), held at a constant high temperature, to thermally oxidize the volatile decomposition products. The pyrolyzer is programmed to heat the sample at a constant rate of temperature rise, usually 1°C/s, from 70 °C to 1200 °C. In the newly modified device, a commercial molybdenum disilicide furnace replaces the standard wound combustor for premixed oxidation of pyrolysis products at flame temperatures of up to 1600 °C.

Recent method developments using hyphenated MCC techniques enables measurements of the effect of vitiation on combustion gas yields (Patent No. US11579103B2, 2023). In practice, a preliminary test is conducted using the MCC standard test method, ASTM D7309 (2021), where the oxygen depletion as a function of sample temperature is recorded. Data produced from the MCC has proven to be repeatable for many materials, providing an accurate oxygen consumption history in the combustor over the entire temperature range of the pyrolysis. This history then serves as the control file for the subsequent stoichiometric fuel/oxygen ratio tests. The control file, with the use of mass flow controllers, generates a constant fuel/oxygen ratio relative to the stoichiometric ratio, Φ, in the combustor throughout the sample decomposition. When $\Phi < 1$, combustion is fuel lean (over ventilated). When $\Phi > 1$, combustion is fuel rich (vitiated).

Continuing efforts focus on recreating combustion chemistry from a burning material in a non-flaming milligram-scale test. Earlier work (Walters, Safronava, & Lyon, 2015) focused on the analysis of the combustion gases using infrared analyzers and varying the combustor temperature to generate incomplete combustion products and combustion efficiencies similar to those generated during flaming in a cone calorimeter. Similar studies were performed by Sonnier, Dorez, Vahabi, Longuet, and Ferry (2014). Even though the combustor temperature settings used to obtain identical combustion efficiencies in the MCC were found, the chemistry involved did not produce the mix of combustion products found in a diffusion flame, as evidenced by the high CO/CO_2 ratios and lack of soot generated in the MCC. Carbon monoxide levels generated in these studies were several orders of magnitude greater than that which occurs in flaming combustion tests using a cone calorimeter (ASTM International, 2023).

Two hyphenated techniques, MCC with infrared spectral analysis of combustion gases (MCC-IR) and MCC with multiple chemical gas sensors (MCC-Testo), were used to monitor gases and evaluate combustion toxicity at different fuel/oxygen equivalence ratios and different combustion temperatures. Changes in MCC flow control eliminated some of the alignment problems described previously (Speitel, Walters, & Lyon, 2016). These hyphenated techniques demonstrate the unique capability to elucidate the effect of constant fuel/oxygen ratios on combustion product yields for materials. Measurements made at different Φ will help to better understand the flame chemistry and the mix of complete/incomplete combustion products for various polymers throughout the different stages of a full-scale fire. In addition to the equivalence ratio, the temperature of the standard MCC combustor was varied to examine the composition of the products in an attempt to correlate with bench scale flaming combustion tests. Even with varying the equivalence ratio and combustor temperature up to 1000°C, the chemistry of premixed MCC combustion did not correspond to the combustion chemistry of a diffusion flame, as evidenced by the lack of soot formation for materials known to produce a lot.

Discussions with colleagues and other experts in the flame retardant (FR) industry led to the topic of temperature (Schartel, 2019). Previous experiments performed at the FAA showed that changes in the oxidation rate of pyrolysis gases were easily observed for halogen FRs and quantitative results obtained, but not for other non-halogenated additives that contained phosphorous. This was due to the temperature in the MCC combustor not reaching the elevated temperatures that occur in a diffusion flame. These temperatures, above 1200 °C, could not be obtained in a standard MCC. Commercial thermal analysis equipment, capable of reaching temperatures of over 1600 °C, was required. Further investigation found that, even though these heaters could reach diffusion flame temperatures, they could not maintain them for long periods without degradation of the heating elements.

A commercial heater was found that was applicable to the scale and dimensions of the MCC and that could maintain temperatures of 1600-1700 °C for long periods without degradation of the element. Preliminary tests at elevated temperatures were performed and the CO/CO_2 ratios measured. Data was obtained for several different polymer types that contained carbon and hydrogen, as well as other polymers that contained nitrogen and sulfur, respectively. It was found that the CO/CO_2 ratio did not change systematically above 1000 °C to 1500 °C and stayed about the same for unmodified hydrocarbon polymers. However, soot formation as occurs in diffusion flames occurred only at the higher temperatures, as evidenced by its accumulation on the in-line filters.

2 Materials and equipment

All ultra-high purity (UHP)-grade supply gases, certified calibration gases, and liquid nitrogen were obtained from local suppliers. Polymeric test samples were additive-free solid polymers obtained from commercial sources. The FAA MCC was constructed in house using off-the-shelf components and custom parts that were fabricated on-site and contracted out. A high-temperature MHI Robust Radiator, model RHUL-MP1125-4, was used as the combustor for all ultra-high temperature experiments, and a smaller, custom-wound Kanthal heater was used for the high-temperature experiments. The heaters were made as small as possible to provide a very high temperature for a very short duration. All software for control, acquisition and analysis was written in house using LabVIEW.

Two Edinburgh Sensors Gascard NGs were used for measuring the CO and CO_2. Both sensors were configured with a 0-10% range with an accuracy of 0.2%.

A Midac Model I1813 Fourier-transform infrared spectrometer (FTIR) with a 2-m cell was used for all tests. The optical path of this cell is about 1000 times longer than the 3-mm CO and CO_2 nondispersive infrared sensor (NDIR) analyzer cells, contributing to a much greater sensitivity and lower limit of detection. The sample cell is nickel, the mirrors are coated with gold, and the windows are zinc selenide (ZnSe). The cell volume is approximately 90 ml. The interferometer, beam splitter, and windows are constructed of ZnSe with a germanium coating for moisture protection. The detector is a sterling engine-cooled mercury cadmium telluride (MCT) detector, providing more than an order of magnitude additional sensitivity. All interface optics are gold-coated for high light throughput and corrosion resistance. The sample cell has a horizontal orientation to minimize buildup of soot on the cell mirrors.

A Testo model 350 was used for additional gas analysis. The Testo 350 measures six gases simultaneously. Oxygen and CO_2 are permanently defined analyzers, but there are four other slots that can be used for a number of gases. For this study, CO, NO, NO_2, and SO_2 chemical sensors were used. Specifications for the various analyzers used for this study are listed below.

- CO_2 (NDIR) sensor, 0 to 50 Vol %, resolution 0.01 Vol %,
- O_2 measurement 0 to +25 Vol. % O_2 ±0.2 Vol. % 0.01 Vol. % O2
- CO sensor, 0 to 10,000 ppm, resolution 1 ppm
- SO_2 and NO sensor, 0 to 5,000 ppm, resolution 1 ppm
- NO_2 sensor, 0 to 1000 ppm, resolution 0.1 ppm

A Mettler Toledo XPR2 microbalance, with a capacity of 2.1 g and readability of 1 µg, was used to weigh the polymer samples and for the gravimetric soot analysis.

3 Methods

3.1.1 Microscale combustion calorimetry

3.1.1.1 Controlling the equivalence ratio

The FAA microscale combustion calorimeter was constructed in house according to ASTM D7309 (2021) specifications, and tests were conducted according to the standard method, with the exception that the concentration of oxygen during the test was set by the equivalence ratios. In the standard MCC method (ASTM International, 2021), the sample temperature increases linearly from about 80 °C to 1000 °C at a constant rate of 1 K/s, and the pyrolysis/fuel gases are mixed with excess oxygen and combusted for a few seconds at 1000 °C. In the standard test, the equivalence ratio is $\Phi = 0$ at the beginning and end of the test (fuel pulse) and about $\Phi = 0.5$ at the peak rate of heat release (oxygen consumption), so there is typically at least twice as much oxygen available at any time in the combustor than is required to completely convert the fuel gases to carbon dioxide, water, and acid gases. Figure 1 shows the Φ history during a standard test of polystyrene (PS). For the rest of this study, the equivalence ratio Φ was held constant by varying the oxygen and nitrogen flow rates to obtain $\Phi = 0.5$, 1.0, 1.5 and 2.0 for the gas analysis, with additional values of 0.75 and 1.25 added for the gravimetric soot analysis. The Initial experiment for each polymer was performed using method A of the ASTM standard to generate the oxygen consumption versus sample temperature history that was needed to control the oxygen fraction in the constant 100 cm^3/min flow rate of O_2 and N_2 combustion stream for subsequent controlled fuel/oxygen tests.

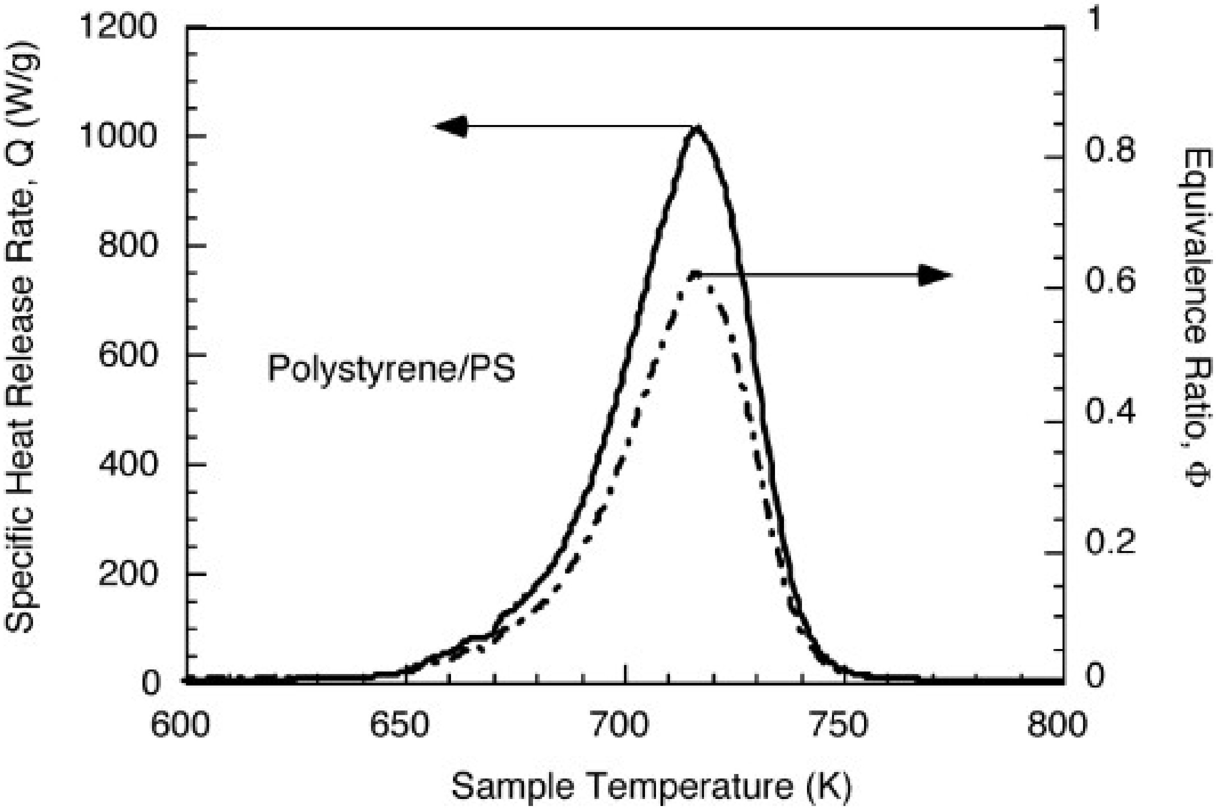


Figure 1. Specific heat release rate Q and equivalence ratio Φ for PS in the standard test

Triplicate analyses were performed for each material using the standard method, and the data was either averaged or the most representative test was used for the control file. From this file, the stoichiometric oxygen consumption per unit mass (specific oxygen demand) of sample at each temperature throughout the sample decomposition range can be generated. The control file was stored as a look-up table and used to control the flow rate of oxygen that would result in the desired Φ. For the tests using the FTIR, the oxygen consumption module of the MCC (cold trap to remove volatiles and water , flow meter and oxygen sensor) was connected to the outflow of the FTIR to check for leaks, but only the total heat could be obtained from the oxygen consumption data due to distortion of the transient signal in the relatively large-volume FTIR gas cell.

The control file, with the use of mass flow controllers, generates a constant fuel/oxygen ratio in the combustor throughout the sample decomposition. Φ is the fuel/oxygen mass ratio relative to the stoichiometric mass ratio. When $\Phi < 1$, combustion is fuel lean (over ventilated). When $\Phi > 1$, combustion is fuel rich (vitiated). Equation 1 shows how the equivalence ratio is calculated, where m has units of moles.

$$\Phi = \frac{m_{fuel}/m_{O_2}}{(m_{fuel}/m_{O_2})_{stoichiomtric}} \qquad 1$$

The MCC was coupled separately with a FTIR multigas analyzer as well as CO and CO_2 analyzers. A picture of the experimental configuration with the FTIR is shown in Figure 2. The CO and CO_2 analyzers can be used as a simple, low-budget tool for assessing the combustion toxicity by looking at the CO/CO_2 ratio for comparison to values obtained in bench scale flaming combustion (fire) tests. However, in this study, it was also used to calibrate the more expensive FTIR results obtained. The FTIR also provided data for additional gases programmed in the method discussed below. Additionally, a new high-temperature combustor, shown in Figure 3, was installed to increase the maximum MCC combustion temperature to 1600 °C, which is well within the range of flame temperatures of 1300 °C-1800 °C so that soot (an important component of incomplete combustion) could be produced.

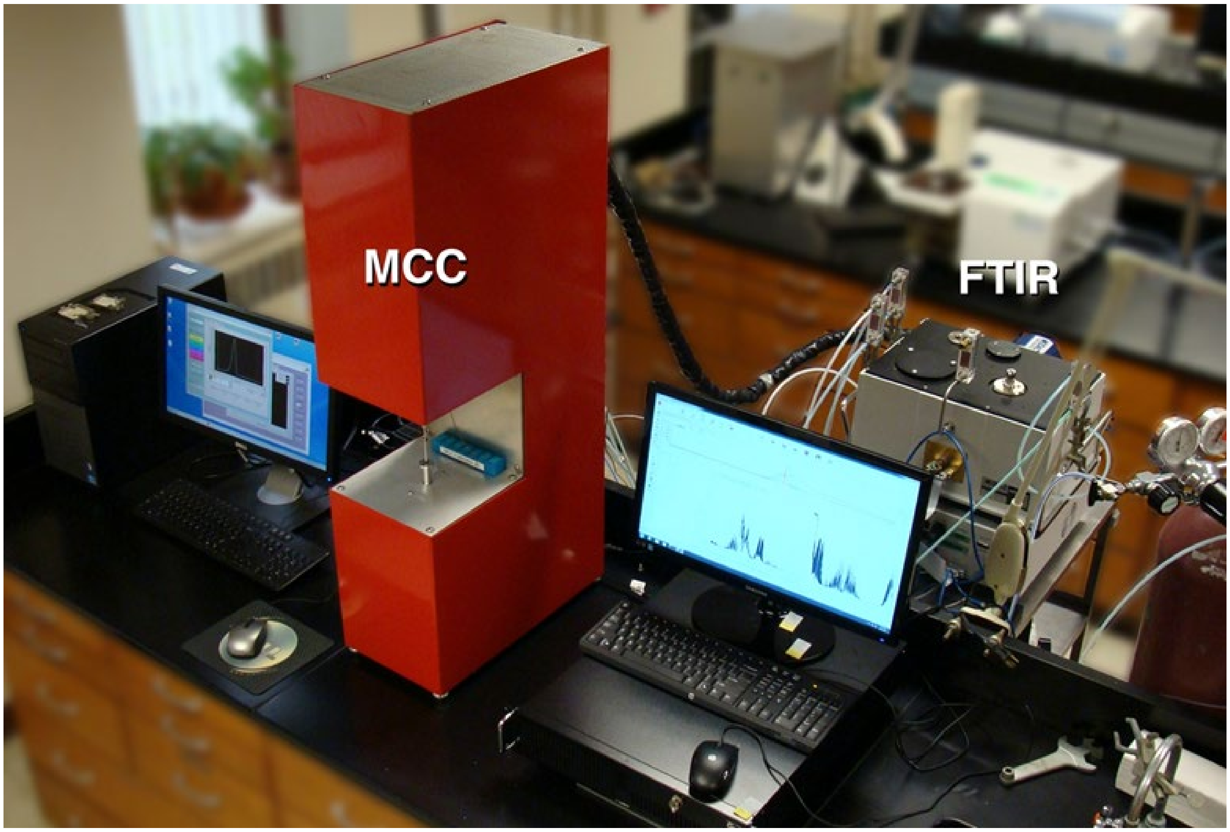


Figure 2. The coupled MCC-IR used for generating and measuring combustion products of polymers at different fuel/oxygen (equivalence) ratios

Figure 3. High-temperature MCC combustor

3.1.2 Infrared spectroscopy and gas analysis

3.1.2.1 Measuring the combustion products using FTIR

The MCC was coupled to an FTIR for gas analysis by a 6 ft (1.83 m)-long heated transfer line maintained at a temperature of 165 °C. An in-line, heated, stainless-steel filter housing was inserted at the end of the heated line prior to the inlet port of the FTIR gas cell. The stainless steel housing contained a 0.2-µm Teflon filter to remove particulates and any possible condensates from the gas stream and was maintained at a temperature slightly below 165 °C to trap organics. A plastic tube filled with desiccant was attached to the outlet of the gas cell to remove water from the combustion stream prior to it entering the flow meter and oxygen sensor of the MCC for oxygen consumption measurements. Basically, the FTIR was inserted between the combustor and the oxygen consumption module of the MCC.

All calibration spectra and test spectra were obtained at unit gain. A triangular apodization, a Mertz phase correction, and a resolution of 0.5 cm^{-1} were used for all calibration and test spectra, with the exception of CS_2. The method creates a spreadsheet with the time profiles of the concentration and error (residuals) data for the analyte gases. Gas concentrations are reported as zero for each gas and spectra if the residuals for the spectral region are 50% or greater than the calculated concentration. Cell pressure and temperature are monitored and recorded with each spectrum. The Autoquant Pro software performs piecewise-linear Beer's Law calculations for each analyte in each test spectra to correct the analyte concentration for any pressure and temperature variations from the calibration spectra.

All tests were conducted in an extractive mode at 170 °C and 0.5 cm^{-1} resolution with 8 bidirectional scans every 6 seconds, on average. Calibration spectra for most gases were obtained under these conditions, except that 256 scans were run. Most calibration spectra were obtained at 170 °C using a Midac FTIR. H_2O and CO_2 spectra were prepared in house using the same FTIR as was used for the MCC tests. CO, HF, HCl, HBr, SO_2, NO, NO_2, $COCl_2$, COF_2 were prepared by Midac Corporation at 170 °C using a 10-m path cell. COS and C_3H_8 calibration spectra were prepared by Midac at 121 °C. NH_3 and N_2O calibration spectra were prepared by Midac at 25 °C. CS_2 was prepared by the United States Environmental Protection Agency at 25 °C.

A quantitative analysis method containing 24 gases, including CO, CO_2, HF, HCl, HBr, SO_2, COS, NO, NO_2, $COCl_2$, COF_2, NH_3, and N_2O was developed by FAA researchers to support full-scale fire tests. A gas of concern that is considered nonquantitative but is in the method is CS_2. The carbon disulfide spectrum was from an EPA spectral library taken at a different temperature and was only used to correct for the gases with absorbances in the same spectral region. A subset of these gases is reported because pure materials of known composition were tested and did not contain the elements to produce some of the gases in the method. Other gases that are in the method but not reported are H_2O, C_2H_2, CH_4, C_2H_4, C_2H_6, and C_3H_8. Yields of combustion products are in units of g/kg. These yields can be used to calculate the concentration of a toxic gas evolved in a volume for a unit mass of a sample. Data were collected, analyzed, and plotted using the following commercial software: Midac Autoquant Pro™ software, Operant LLC: Essential FTIR®, and Microsoft® Excel®. Spectral bands for all quantified gases were selected to have minimal common absorbance. Another requirement for spectral band selection is low absorbance so that the calibration is linear over a wide concentration range. Broad nonoverlapping bands were selected when possible.

Yields of the gaseous complete/incomplete combustion products were compared as a function of Φ for a selection of materials. It is hoped that this technique, combined with an appropriate toxicity model, can be used as a part of a toxicity assessment for polymers.

A set of hydrocarbon materials with elemental compositions including C, H, O, N, and S were evaluated to provide a spectrum of gaseous combustion products where a small set of potential combustion products could be evaluated. Spectra were acquired continuously during each test at 8 scans every 12 seconds. The following gases were measured: CO, CO_2, NO_2, NO, N_2O, HCN, NH_4, SO_2, COS, CS_2 and C_6H_5OH. A piecewise linear, classical least-squares analysis was performed by the FTIR software for obtaining quantitative yields. FTIR interferences including H_2O, CH_4, C_2H_6, C_2H_4 and C_2H_2 were subtracted out in the piecewise classical least-squares method of analysis. Figure 4 shows a portion of the method with the regions used to quantify each component in the gas mixture. The method also utilized different regions for different concentrations, determined by signal intensity and potential interferences as shown for CO in Figure 5. Yields of the gaseous decomposition/combustion products were compared as a function of Φ for a selection of materials. The yields of the combustion products at different combustion temperatures but the same Φ were also compared using this method.

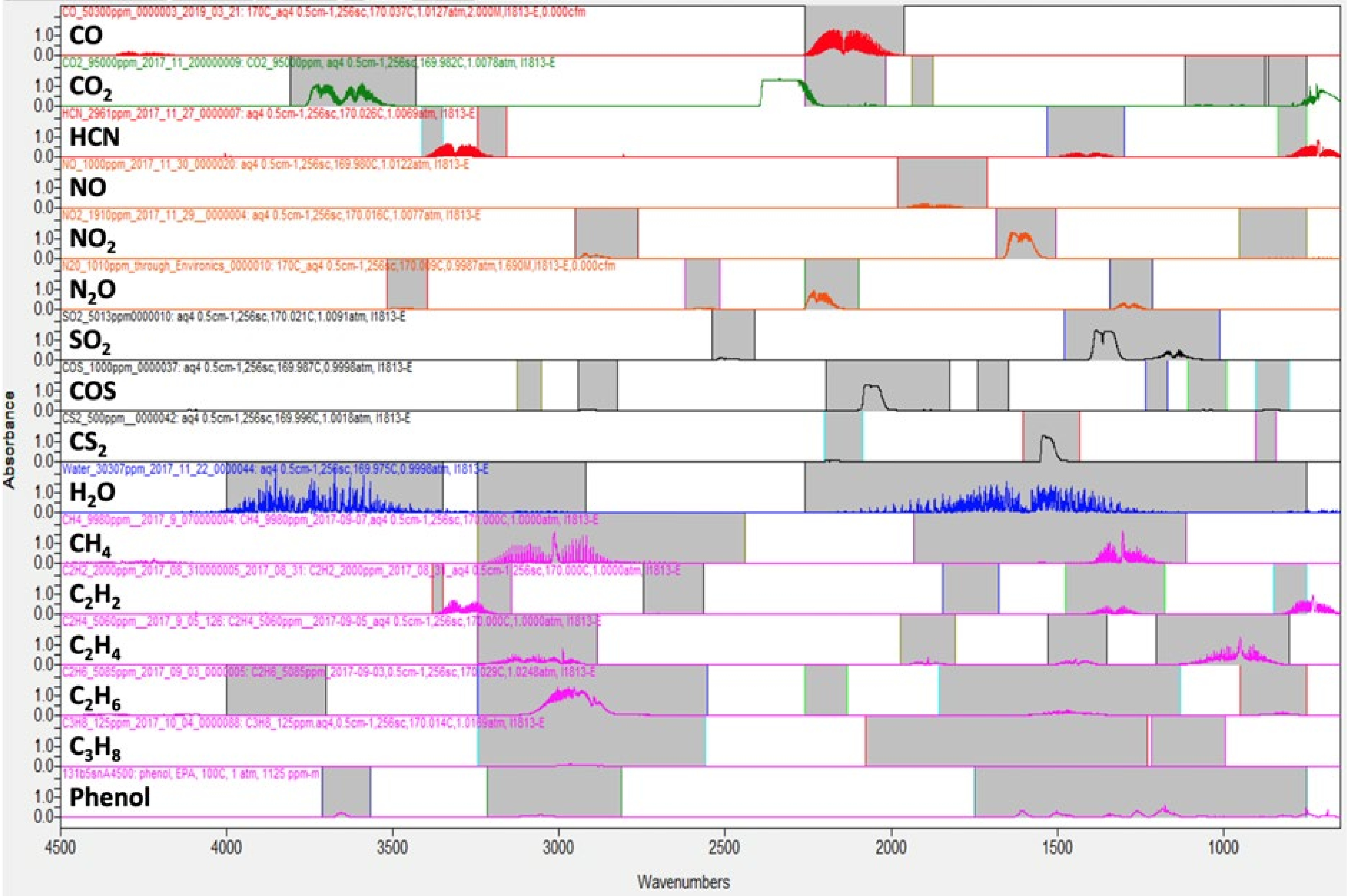


Figure 4. Regions used in the infrared for quantification of 16 gases of interest

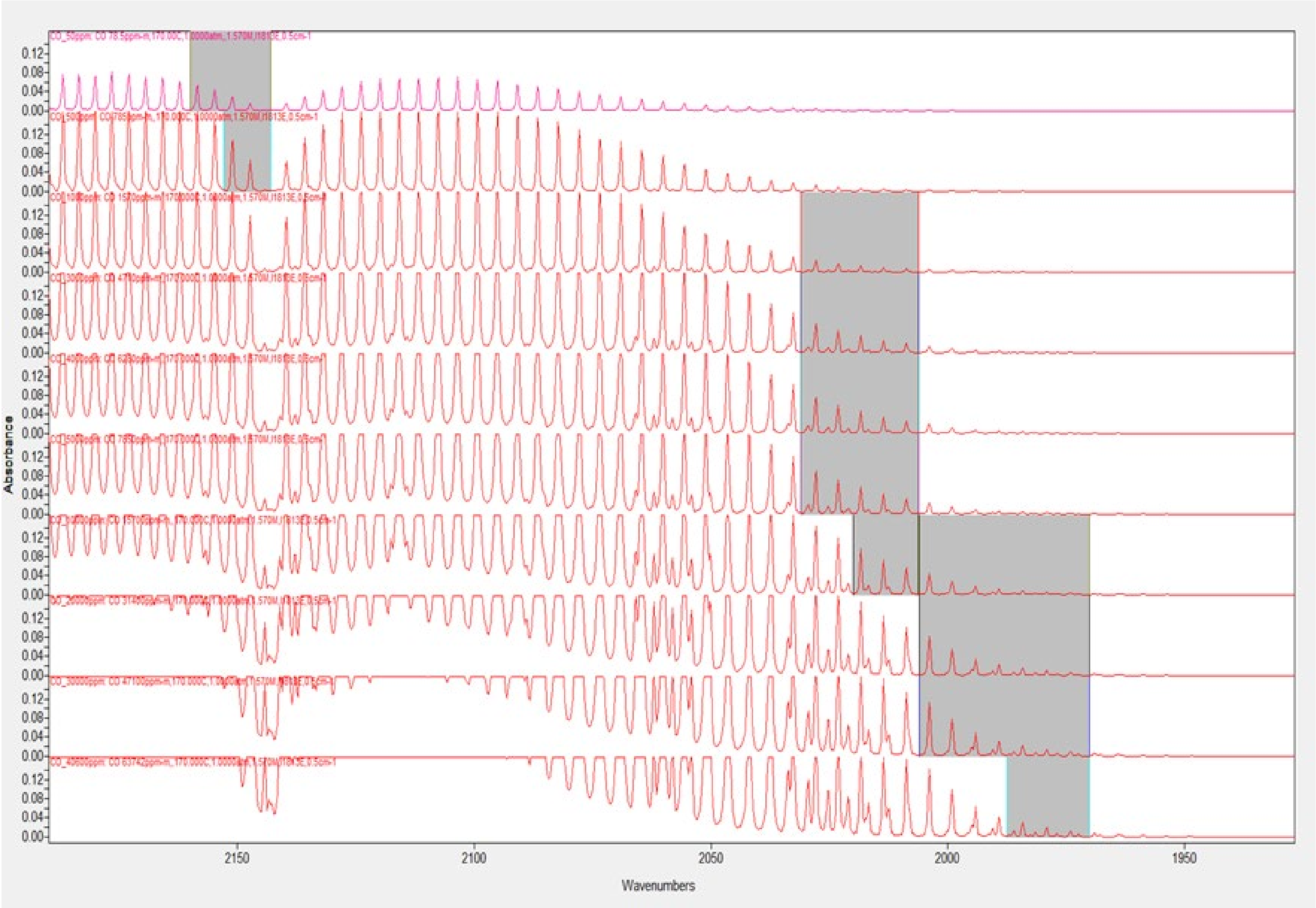


Figure 5. Spectral regions used at different gas concentrations based on signal intensity and potential interferences for CO

3.1.2.2 Measuring the combustion products using a multigas analyzer

Additional gas analysis tests were performed with a Testo 350 multi-gas analyzer, shown in Figure 6. The in-line placement of the analyzer was similar to the FTIR layout, except for the gas flow rates sent to the analyzers. The FTIR was able to utilize the 100-mL/min flow that is supplied by the MCC. However, the Testo requires around a 1-L/min flow rate that is drawn by an internal pump that is integral to the unit. A tee was installed so the analyzer could draw the flow it needed by making up the difference with room air. Data was logged on the Testo unit interfaced with a computer that utilized the Testo easyEmission software. Carbon mass balance calculations were used to validate the gas collection efficiency using samples of known composition, combusted in excess oxygen.

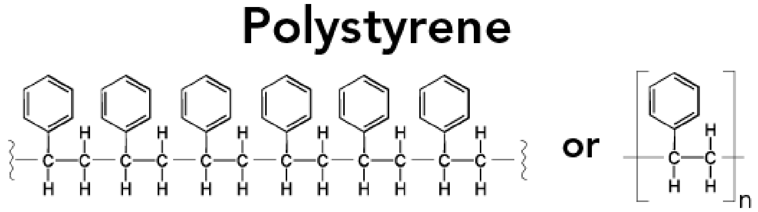
Figure 6. Testo multigas analyzer connected to MCC exhaust

3.1.3 Gravimetric soot analysis

A separate series of tests was performed to measure the mass of soot generated at different temperatures and stoichiometric fuel-to-oxygen ratios. Single-ply polytetrafluoroethylene (PTFE) membrane filters having 0.2 micron pore size and 25-mm diameter were vacuum dried and weighed prior to inserting into an in-line stainless-steel filter holder for testing. The entire filter assembly was encased in an oven to prevent condensation of any volatiles on the filter or walls of the filter housing prior to reaching the analyzer. Ten replicate tests were performed at each specified temperature and reaction stoichiometry in order to accumulate enough soot mass for an accurate gravimetric analysis of the PTFE filters. Then the filters were vacuum dried and weighed again after each set of ten tests was performed. The weight difference was used to determine a quantitative average soot yield at each stoichiometric ratio.

4 Results and discussion

Preliminary tests were run during the development of the controlled fuel/oxygen ratios with the MCC configured with the additional CO and CO_2 analyzers only. These analyzers (Edinburgh Instruments) were placed after the flow meter and oxygen sensor so the MCC oxygen consumption history was well resolved. A series of FAA database thermoplastics were tested to evaluate the algorithm for well-characterized samples in the MCC. In order to expand the parameter space for the study of the effect of material composition (including FRs) on incomplete combustion, tests were conducted at different fuel/air (Φ) ratios and combustion temperatures (T_c). Measured flow rates and concentrations were used to calculate the yields of CO and CO_2 by integrating the signal and normalizing for initial sample mass. The accuracy of the yields from the CO and CO_2 analyzers were checked using a carbon mass balance for samples of known composition that were completely combusted at $T_c \geq 900$ °C, shown in Table 1. A char composition of C_5H_2 was found to best correlate to the CO_2 yield of the volatile component of charring polymers. An example of the mass balance calculation for polystyrene is shown below. The atomic composition of a polymer repeat unit is used in a stoichiometric reaction with oxygen to determine the mole ratios of reactant to products. The moles and the molecular weights are used to calculate the mass of carbon dioxide that should be produced from a known mass of a sample. The same theory applies for CO.



$$1C_8H_8 + 10O_2 \rightarrow 8CO_2 + 4H_2O$$

$$Y_{CO_2} = \frac{(8\ mol\ CO_2)(\frac{44\ g}{mol\ CO_2})}{(1\ mol\ PS)(\frac{104\ g}{mol\ PS})} = 3.38\,\frac{g\ CO_2}{g\ PS}$$

Table 1. Experimental values measured in the MCC and theoretical values calculated from the chemical composition and sample weight

				O_2 Demand (g/g)		CO_2 Yield (g/g)		Char Yield (%, w/w)	
Polymer	**Formula**	**MW (g/mol)**	**HR (kJ/g)**	**Theory (no char)**	**Experiment (char)**	**Theory**	**Experiment**	**Theory**	**Experiment**
POM	CH_2O	30.03	14.5	1.07	1.11	1.47	1.59	0.00	0.02
PMMA	$C_5H_8O_2$	100.12	24.7	1.92	1.89	2.20	2.40	0.00	0.03
PP	C_3H_6	42.08	42.9	3.42	3.27	3.14	3.29	0.00	0.13
HDPE	C_2H_4	28.06	43.2	3.42	3.30	3.14	3.25	0.00	0.23
ABS	$C_{15}H_{17}N$	211.31	36.9	2.92	2.82	3.12	3.44	0.00	0.75
PVDF	$C_2H_2F_2$	64.02	28.5	1.25	2.18	1.37	2.86	0.00	1.10
PA66	$C_{12}H_{22}O_2N_2$	226.32	28.9	2.33	2.21	2.33	2.89	1.68	1.16
HIPS	$C_{12}H_{14}$	158.24	38.3	3.13	2.92	3.34	3.50	2.34	2.52
PET	$C_{10}H_8O_4$	192.17	16.8	1.67	1.28	2.29	1.97	13.55	13.02
PVC	C_2H_3Cl	62.48	10.7	1.41	0.82	1.41	1.00	20.84	19.71
PC	$C_{16}H_{14}O_3$	254.28	21.1	2.27	1.61	2.77	2.03	24.41	23.94
PPS	C_6H_4S	108.15	15.5	2.07	1.18	2.44	1.24	46.28	41.97
PEI	$C_{37}H_{24}O_6N_2$	592.61	10.5	2.16	0.80	2.75	1.16	53.71	56.80

The Φ control algorithm for the oxygen and nitrogen flow meters was checked for accuracy by running a test without a sample and comparing the program response to the measured response for a fictitious sample of identical weight. A composite material was selected for this check because it had a complex heat release rate (HRR) history. The composite sample exhibited three peaks, with two of them overlapping. The stoichiometric amount of oxygen was calculated from the measured HRR curve. A blank was then run for the composite using the Φ-control file, and the output for the mass flow controller along with the measured oxygen concentration were recorded. Figure 7 shows that there is excellent agreement between the experimental and programmed oxygen profiles for this complicated oxygen consumption history.

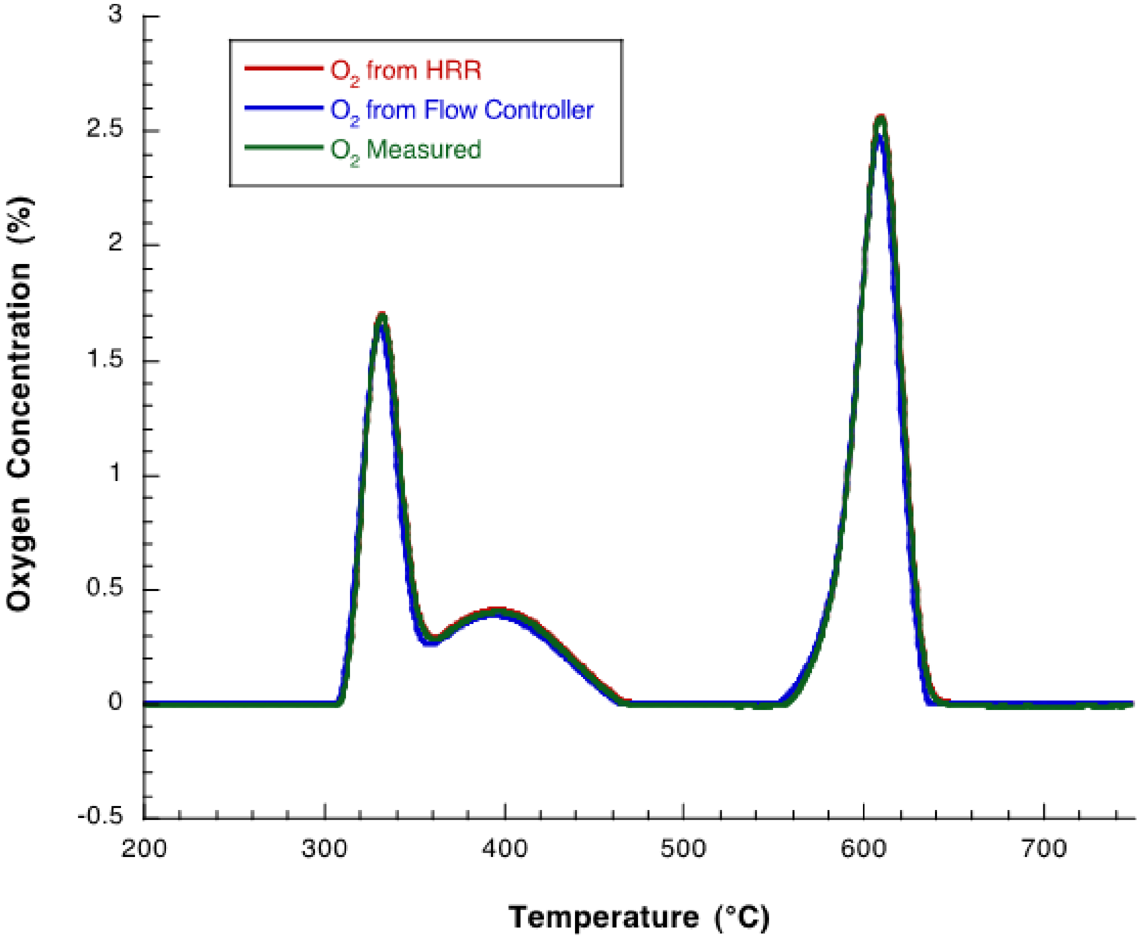


Figure 7. Programmed and measured oxygen concentration for complete combustion of a composite sample for Φ = 1

Samples of FAA database plastics and aircraft materials were selected for chemical composition and tested at several different Φ values. Initially only O_2, CO, and CO_2 were measured using the in-line analyzers and validated with a CO_2 mass balance as described earlier. Figure 8 shows a plot of the CO/CO_2 ratio over a rage of Φ values for these materials. As expected, the CO levels increased drastically with increasing fuel/O_2 ratios.

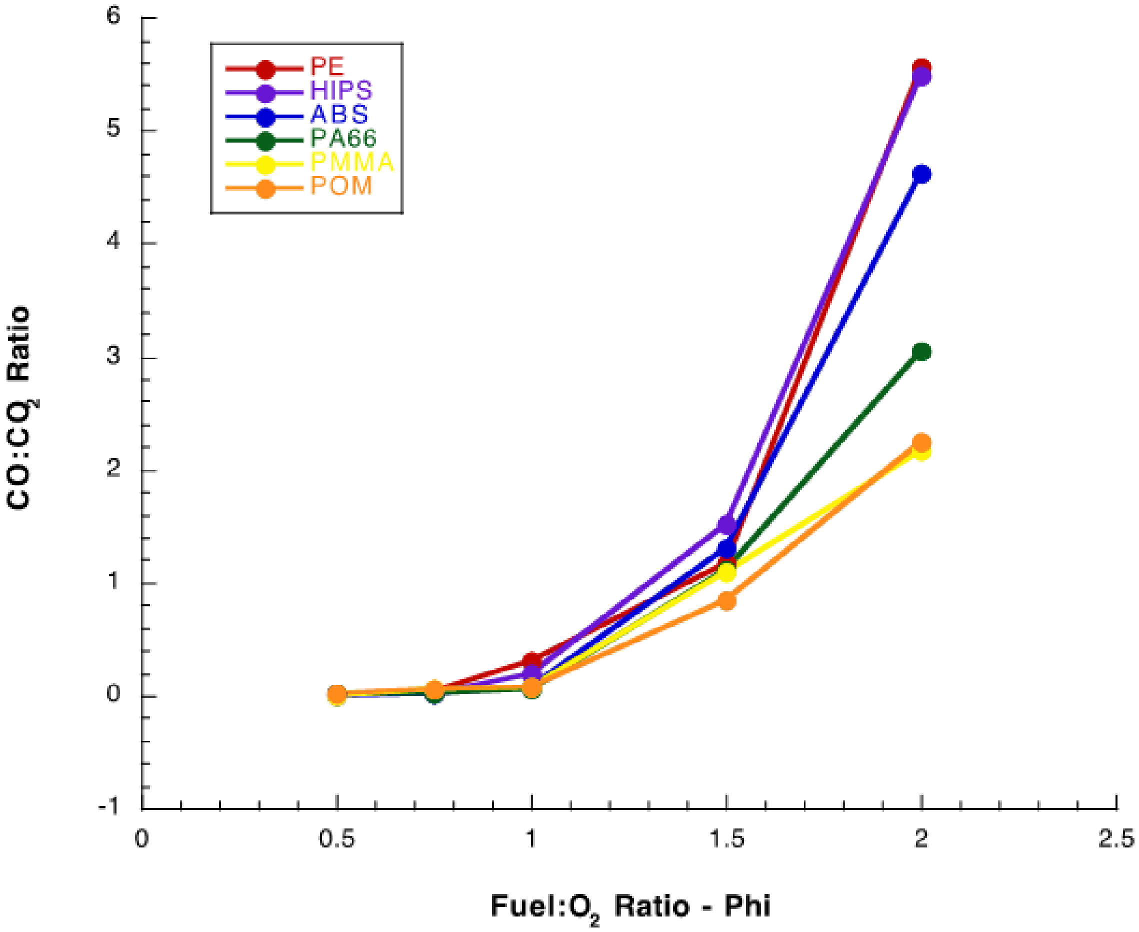


Figure 8. CO/CO_2 ratio changes over the fuel/O_2 (Φ) range

These data were used to benchmark the CO and CO_2 yields obtained for the same materials in the FTIR and Testo methods as follows. The CO and CO_2 analyzers were removed, and either the FTIR or Testo was connected to the outlet of the combustor, as described previously. Initial results from the comparison of the CO and CO_2 yields (grams of gas species per gram of sample) from the MCC with dedicated gas analyzers indicated the FTIR and Testo yields of CO and CO_2 were comparable. Several nitrogen-containing samples were tested at multiple Φ, and the yield results for NO and NO_2 from FTIR and Testo for polyhexamethyleneadipamide (PA66) are shown in Figure 9. There was good agreement between the analyzers for the NO, but not for NO_2. This could be due to the Testo giving artificially high readings, the FTIR method not detecting the signal due to poor region selection, or other interferences.

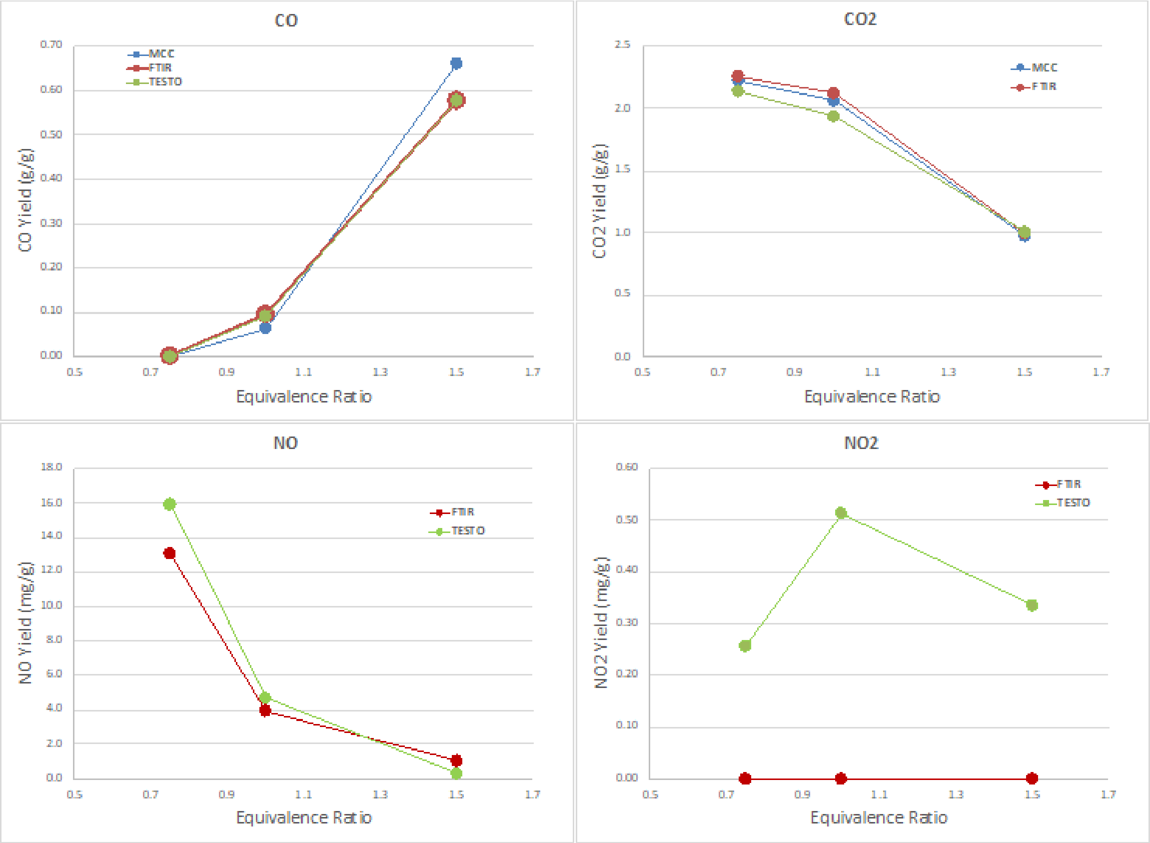


Figure 9. Combustion gas yields for PA66 from Testo and FTIR

Yields of HCN are shown in Figure 10. Most of the samples produced little or none of the asphyxiant gas HCN in well-ventilated conditions ($\Phi < 1$), with the exception of a flame-retarded polyphthalamide. In contrast, polyurethane and the non-FR polyphthalamide produced HCN at a stoichiometric fuel/oxygen ratio ($\Phi = 1$), while all nitrogen-containing polymers produced HCN under oxygen-starved/vitiated ($\Phi > 1$) conditions.

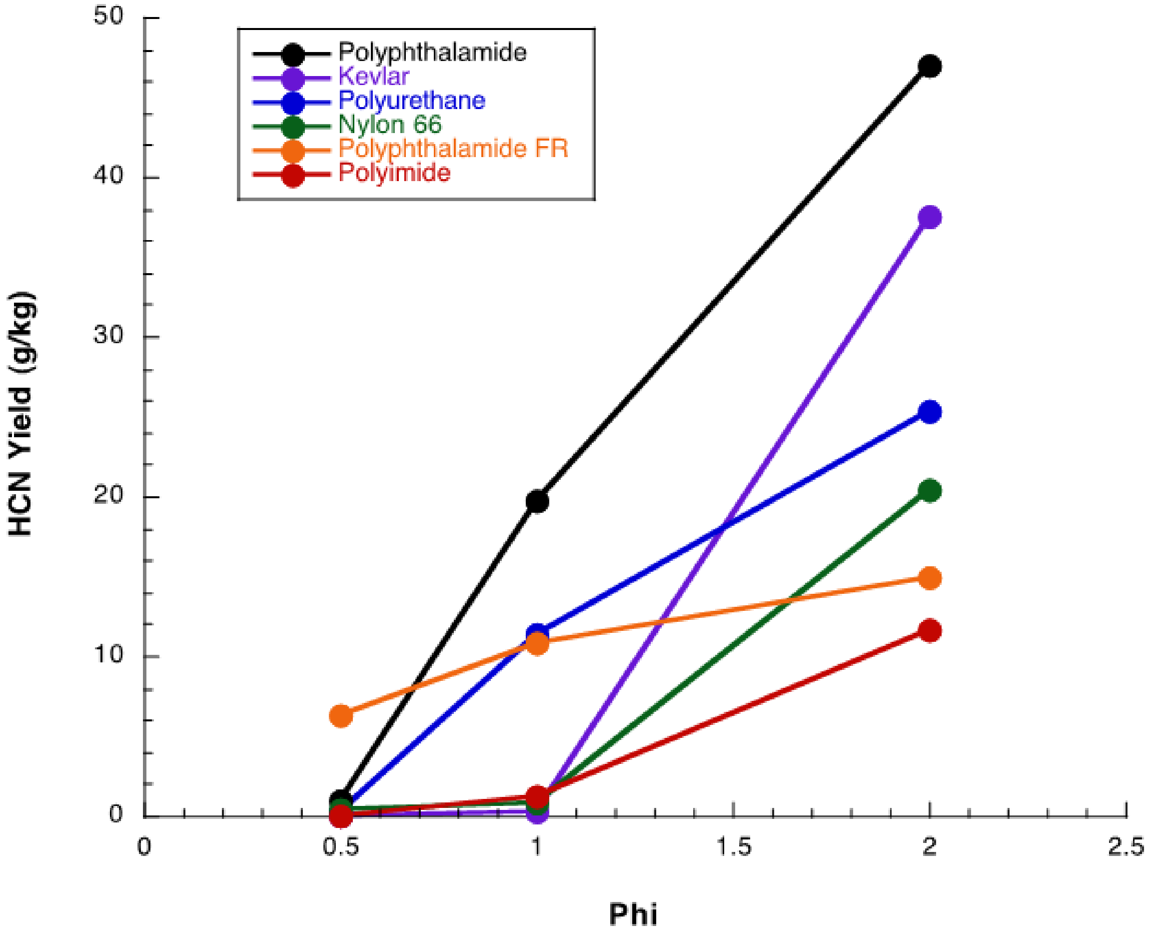


Figure 10. Yields of HCN for several nitrogen-containing polymers

Yields of hydrogen fluoride (HF) and hydrogen bromide (HBr) acid gases remained fairly constant throughout the different Φ as expected, since oxygen plays no role in their formation. For example, brominated polystyrene yielded an average of 41.3 g-HBr/kg-sample over the range $\Phi = 0.5\text{-}2$. Several fluorinated polymers had similar Φ-independent yields. For example, fluorinated ethylenepropylene copolymer (FEP) had a yield of 24.9 g-HF/kg-sample, and polyvinylfluoride (PVF) yielded 57.3 g-HF/kg-sample. Three different grades of proprietary PVF films currently used in aircraft had HF yields of 19.9 g/kg, 49.6 g/kg and 79.1 g/kg at $\Phi = 0.5\text{-}2$.

Figure 11 shows the yields of toxic combustion products SO_2 and COS for some sulfur-containing polymers as measured by FTIR. Yields of CS_2 were high, but there is not enough confidence in the CS_2 values to report them here. Most of 24 gases analyzed in the FTIR method are not reported here, because they were not present in the spectra or there was not enough confidence in the results.

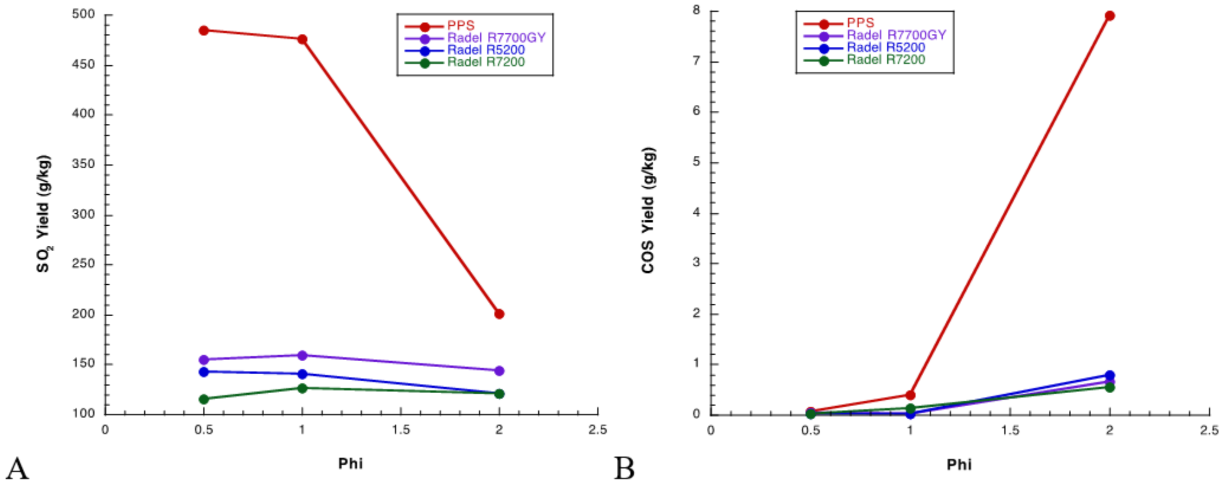


Figure 11. FTIR yields of SO_2 and COS for sulfur-containing polymers at different equivalence ratios

Tests were conducted at equivalence ratios of 0.5, 1, and 1.5 for all samples. Additional ratios of 0.75, 1.25, and 1.75 were conducted for the nitrogen- and sulfur-containing samples. Combustor temperatures of 750 °C, 1000 °C, 1250 °C, and 1500 °C were used to react the polymer pyrolysis products at the different fuel to oxygen ratios. Unlike the previous study (Speitel, Walters, & Lyon, 2016), where only single test values were reported, this study had multiple tests at each setting. Several replicate tests were performed to get an idea of the sample homogeneity and repeatability of the results.

The tests run at 750 °C provided no useful results other than showing that tests should not be run at that low a temperature due to the inefficiency of combustion. The other tests, however, showed more promising results that provided more insight into the combustion chemistry. CO and CO_2 values were found to be consistent at the different equivalence settings above 1000 °C for most samples, as shown in Figure 12. The different temperatures at a particular Φ are illustrated by the different dashed lines. Values in Figure 12 are the yields in grams measured by the independent analyzers normalized by the theoretical grams of CO_X possible if all carbon was converted to CO or CO_2, respectively. At low Φ, where there is excess oxygen, almost all carbon is converted to CO_2. At $\Phi \geq 1$, CO starts to appear and increases as the CO_2 decreases. The sum remains fairly constant, indicating all the gaseous carbon is accounted for. CO and CO_2 numbers in Table 2 are reported as CO_2/CO, so values could be expressed on the order of integers as opposed to small fractions. Table 2 shows these ratios were fairly constant as well for all materials, with the exception of PPS. While CO remained fairly consistent across the increasing temperatures, CO_2 increased. Values for the CO_2/CO ratios of $\Phi < 1$ showed inconsistencies due to the fact that little to no CO was produced/measured in those tests. Similar values were obtained using the FTIR, but the trends were not as well resolved as the independent analyzers.

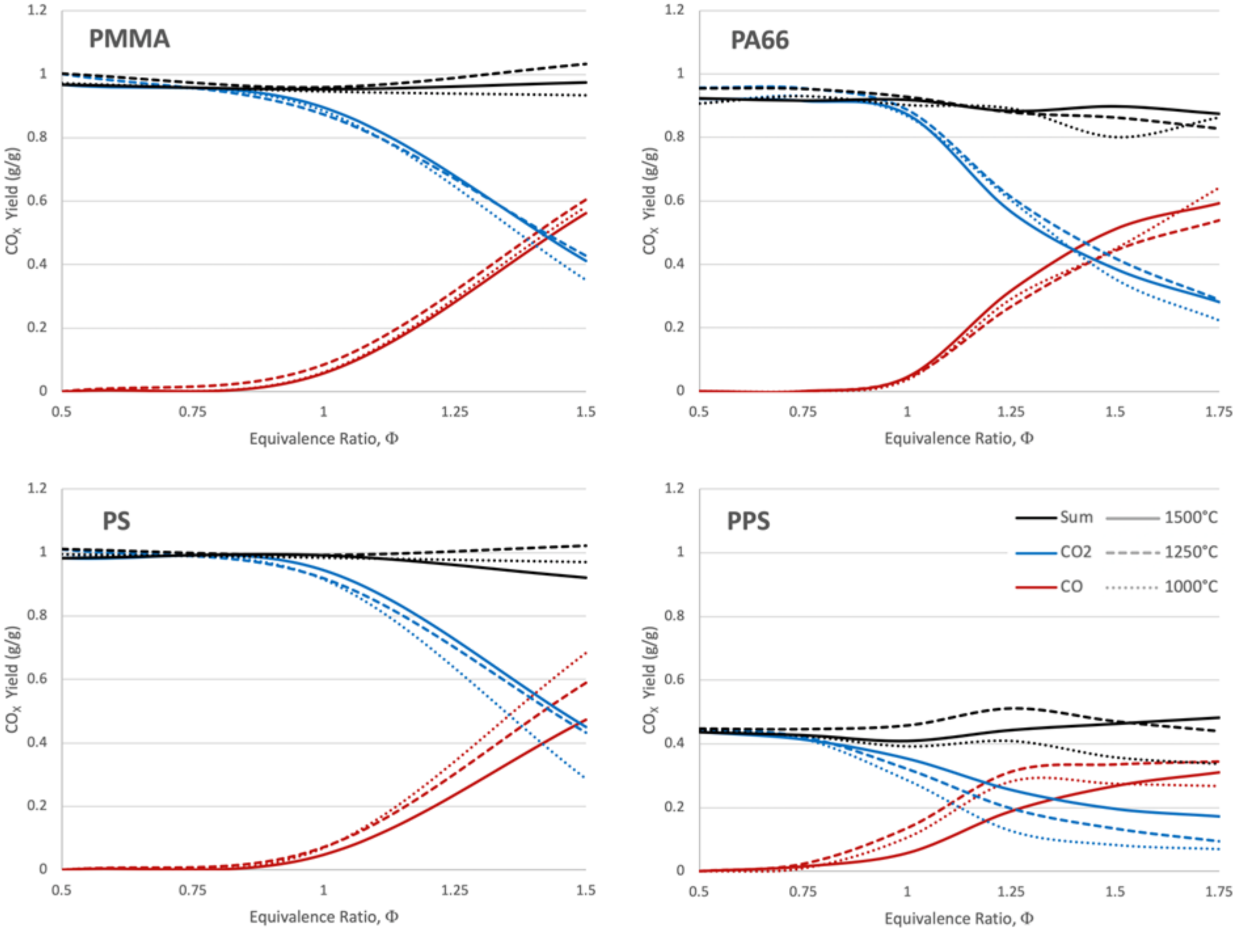


Figure 12. Yield of gaseous carbon, normalized for the theoretical maximums at combustor temperatures of 1000 °C, 1250 °C, and1500 °C, measured with CO and CO_2 analyzers

Table 2. CO_2/CO ratio for polymers at different equivalence ratios and combustor temperatures

	Φ	**750 °C**	**1000 °C**	**1250 °C**	**1500 °C**
PMMA	**0.50**	1.2	713	2203	2128
	1.0	0.33	22	16	24
	1.50	0.34	0.95	1.1	1.2
PS	**0.50**	1.1	841	3416	3321
	1.0	0.13	21	20	32
	1.50	0.11	0.67	1.2	1.5
PA66	**0.50**	3.5	353	1114	2150
	0.75	0.76	217	1112	2134
	1.00	0.45	38	33	30
	1.25	0.30	3.2	3.6	2.8
	1.50	0.27	1.2	1.5	1.2
	1.75	0.30	0.54	0.83	0.74
PPS	**0.50**	0.38	120	1090	1066
	0.75	0.32	67	29	44
	1.00	0.34	4.2	3.7	9.7
	1.25	0.29	0.71	0.99	2.1
	1.50	0.45	0.48	0.63	1.1
	1.75	0.42	0.41	0.43	0.87

It was anticipated that more samples would be tested for the report. Complications with the FTIR optical bench prevented a more thorough analysis of samples with more variety in the composition. Upon recalibration of several gases and optimization of the method, excellent agreement was obtained between the FTIR and the independent CO_X analyzers. Some of the toxic gases quantified using the FTIR method are shown in Figure 13. PA66 shows a steady increase in CO and HCN above Φ = 1 for 1000 °C and 1250 °C and not until Φ > 1.25 for 1500 °C. At 750 °C, where the combustion efficiency is extremely low, the HCN measured is fairly consistent across the equivalence ratios examined. PPS showed fairly consistent values of SO_2, CS_2, and SO_2 across the equivalence ratios and temperatures measured, with a slight increase in COS with increasing Φ and CS_2 at a combustor temperature of 1250 °C. The products of complete combustion were measured to check the IR method against theoretical yields. Table 3 shows the measured yields of CO_2 and water measured divided by the maximum possible based upon the polymer repeat unit structure. The independent analyzer is in good agreement with the

FTIR values for CO_2. The yields of the gaseous combustion products for the charring materials are lower, as expected, due to some carbon and hydrogen remaining in the char.

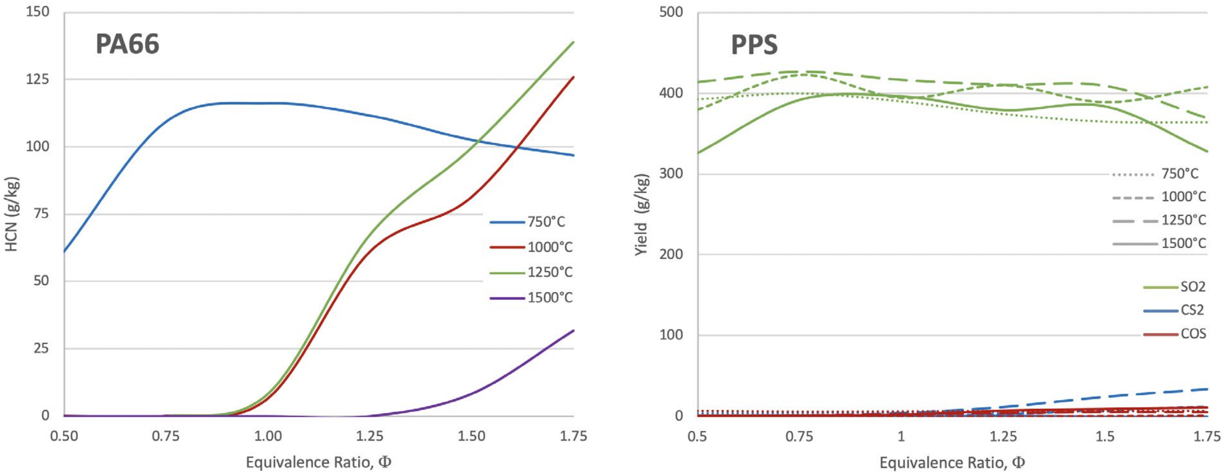


Figure 13. FTIR combustion gas yields of HCN for PA66 and SO_2, CS_2, and COS for PPS at four different temperatures

Table 3. Theoretical yields per gram of sample and fractional yields of CO2 and water, measured using an independent analyzer and FTIR at 1500 °C and Φ = 0.5

Sample	Theoretical CO_2 (g)	Theoretical Water (g)	CO_2 MCC Meas/Calc (g/g)	CO_2 FTIR Meas/Calc (g/g)	Water FTIR Meas/Calc (g/g)
PMMA	2.20	0.72	0.97	0.97	1.02
PS	3.38	0.69	0.98	0.89	0.81
PA66	2.33	0.87	0.92	0.97	0.86
PPS	2.44	0.33	0.44	0.42	0.90

Values from the hyphenated MCC techniques were found to agree reasonably well with literature data (Stec & Hull, 2010) for the main toxicants of interest, CO and HCN, over a range of equivalence ratios, as shown in Figure 14. Although yields of CO and HCN measured in the MCC are local equivalence ratios for premixed combustion, the MCC-IR results fell within the range of reported values from bench- and large-scale tests where equivalence ratios are global values for diffusion limited combustion.

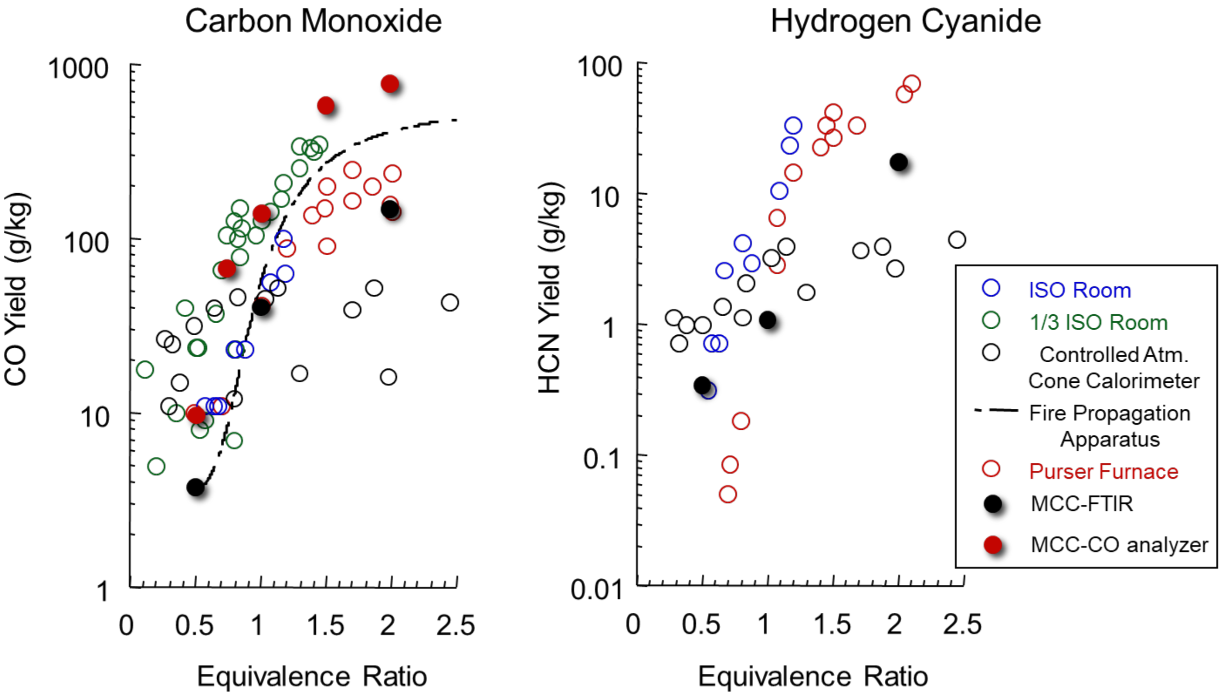


Figure 14. Comparison of FAA results compared to range of literature values reported

Gravimetric soot analysis showed promising results that the combustion products are similar to those generated in a real fire. The difference is that combustion in a flame (fire) is a diffusion-controlled process, whereas combustion in the MCC is premixed. Initially borosilicate fiberglass filters were used for the soot collection. Although soot was deposited quantitatively on the fiberglass filters, the filters were friable, and too much filter material was lost during handling. The PTFE filters described in the method did not have this problem. Although the edge of the filter was crushed in the stainless-steel housing shown in Figure 15, none was lost during handling. Once this filter was found to be suitable, quantitative measurements could be made. Since polystyrene is a good soot former, it seemed like a good material to start with. Figure 15 also shows cross-sections of soot deposition across 1375 °C at different equivalence ratios and at an equivalence ratio of 1.25 at temperatures ranging from 1000 °C to 1500 °C.

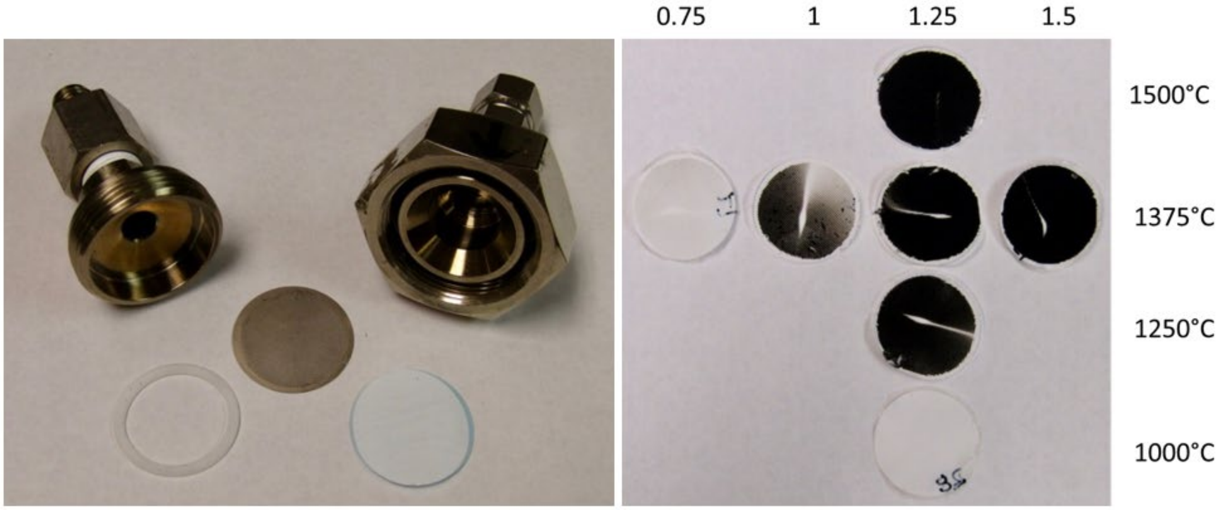


Figure 15. In-line filter assembly and cross-sections of soot collected under different conditions

Soot samples collected in the MCC were analyzed by the Department of Polymer Science & Engineering at the University of Massachusetts using tunneling electron microscopy (TEM) to see if the oily black residue collected on the filters was, in fact, soot. Images displayed in Figure 16 show the correct morphology for soot, validating the assumption.

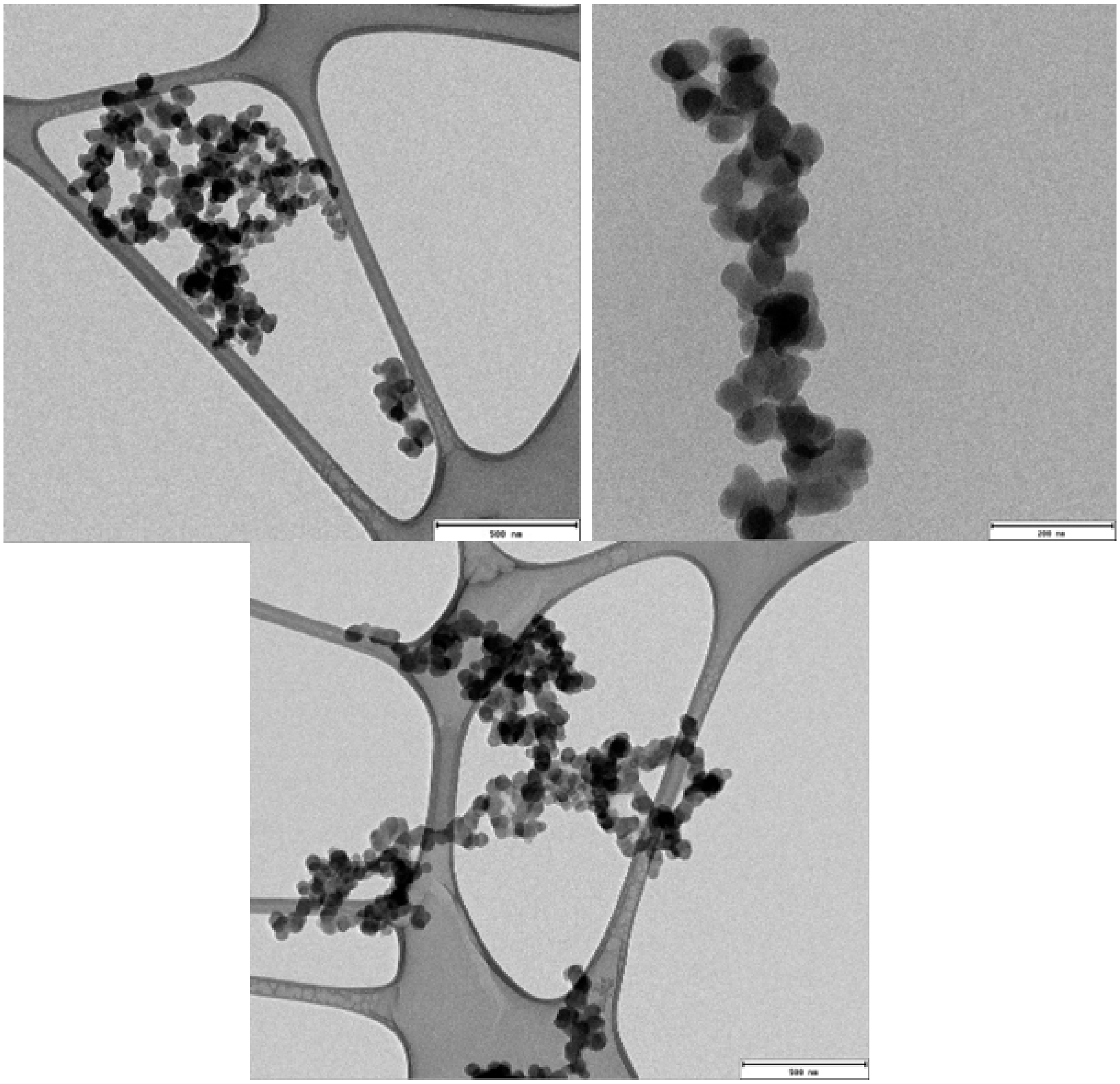


Figure 16. TEM of soot particles collected using the high-temperature, vitiated conditions in the MCC

Table 4 presents the carbon mass balance for polystyrene from measuring the soot, CO, and CO_2 yields. The soot was assumed to have the atomic composition of char C_5H_2, which was used to calculate the moles of carbon from the masses collected for each configuration. The theoretical moles of CO and CO_2 were calculated using the method described earlier. It was found that all the carbon was accounted for in the measurements and was within the specified accuracies of the components with an average measured/theoretical yield of 1.01g/g over all conditions evaluated.

Table 4. Normalized carbon yields from soot formation and CO and CO_2 generation and at different temperatures and stoichiometric fuel/oxygen ratios

	Phi			
Temperature	**0.75**	**1**	**1.25**	**1.5**
	Soot Yield (g/g)			
1000	-	0.00	0.00	0.00
1250	-	0.00	0.01	0.02
1375	0.00	0.00	0.03	0.04
1500	0.00	0.01	0.05	0.07
	Measured/Theoretical CO+CO_2 Yields (g/g)			
1000	-	1.03	1.04	1.06
1250	-	1.02	0.99	0.97
1375	1	1.01	0.98	0.97
1500	1.03	1.01	0.96	0.91
	Measured/Theoretical Total Carbon Yield (g/g)			
1000	-	1.03	1.04	1.06
1250	-	1.02	1.00	0.99
1375	1.00	1.01	1.01	1.01
1500	1.03	1.01	1.01	0.98

Figure 17 shows a 3-axis plot of equivalence ratio, temperature, and soot yield. The soot yield is represented as a percentage of the total amount of vacuum dried, desiccated soot divided by the sum of the 10 initial sample weights. As Figure 17 shows, soot is not generated in any appreciable amount until temperatures above 1250 °C and $\Phi \geq 1$ are achieved, and it increases with temperature and Φ.

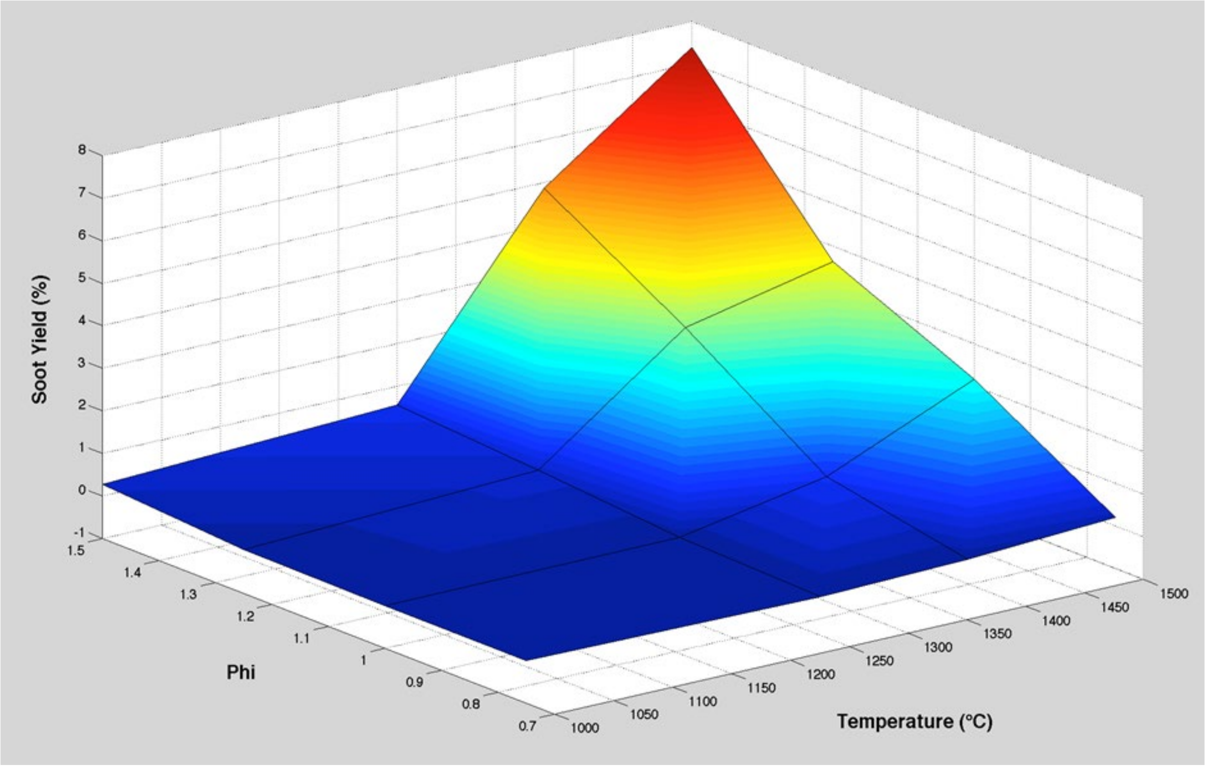


Figure 17. Soot yields from polystyrene in the MCC

Preliminary results show an equivalence ratio in the range of 1.05 to 1.20 in the MCC seems to give the right combustion efficiency and CO/CO_2 ratio that correlates well with bench-scale fire calorimetry. CO and CO_2 ratios did not change much with temperatures above 1000 °C. The gravimetric soot values should identify the correct combustor temperature needed to obtain the same yields as measured in bench-scale fire calorimetry tests. More tests are needed to acquire more data points for the three-axis plot to better illustrate the trends. Once the trends are established, a set of conditions can be determined to produce the identical combustion efficiencies, soot formation, CO/CO_2 ratios, and hopefully the rest of the chemistries that occur in a diffusion flame. Once those parameters are identified, infrared spectroscopy can be done on both the MCC and bench-scale fire calorimeters for the definitive answer to whether this methodology works to accurately recreate the chemistry of combustion.

5 Conclusions

Work continues on the development of the FTIR method to have a robust method for toxic gas quantification. Work also continues on the MCC with the additional CO_X analyzers to provide a simple method for evaluating the toxicity of materials under different ventilation conditions. The CO/CO_2 ratio, along with the gravimetric soot analysis, will help to refine the temperature and fuel-to-oxygen ratio that correlates with the results from flaming combustion tests. This work will be extended to high-performance and flame-retarded materials to quantify the effectiveness, efficiency, and relative toxicity. This information will be used to better understand how to make materials better and safer for aircraft, other modes of public transportation, and any other applications where there is a need for improved fire safety.

Future work will include testing materials possessing other elements for the generation of different combustion gases not examined in this study. Other materials will include halogenated and non-halogenated flame-retarded samples. It is planned that this technique, combined with an appropriate toxicity model, can be used as a part of a toxicity assessment for polymers.

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