

# Accuracy of the Heat Release Rate Measured in Microscale Combustion Calorimetry

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16. Abstract  The ASTM standard method for measuring heats of combustion of plastics in microscale combustion calorimetry by the oxygen consumption principle uses only the volumetric flow rate and O <sub>2</sub> volume fraction exiting a premixed combustor in the calculation. The carbon dioxide (CO <sub>2</sub> ) generated by complete combustion replaces some or all of the O <sub>2</sub> consumed from the dry gas stream, depending on the atomic composition of the fuel, so it can change the volumetric flow rate and affect the flow meter response, which is typically calibrated for pure nitrogen. Consequently, the presence of CO <sub>2</sub> in the combustion stream causes a systematic error (bias) in the heat of combustion measurement that increases monotonically with the initial O <sub>2</sub> concentration. Accounting for volume changes using the combustion stoichiometry is sensitive to the atomic composition of the fuel and is still subject to the CO <sub>2</sub> bias in flow meter response, which can be up to 3%. Accounting for volume changes using both the initial and instantaneous flow rates measured at the terminal flow meter in the calculation and correcting the flow meter response for CO <sub>2</sub> using an average combustion stoichiometry is more accurate and less sensitive to material composition. Heats of combustion computed by the new method are in quantitative agreement with theoretical values.					
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## LIST OF SYMBOLS AND ACRONYMS

$\Delta O_2$	Oxygen consumed by combustion
$Q'_c$	Specific heat release rate
$X_{CO_2}$	Mole fraction of carbon dioxide
MCC	Microscale combustion calorimetry
CO	Carbon monoxide
CO <sub>2</sub>	Carbon dioxide
N <sub>2</sub>	Nitrogen
O <sub>2</sub>	Oxygen
O <sub>2</sub> C	Oxygen consumption calorimetry
PE	Polyethylene
PMMA	Poly(methylmethacrylate)
POM	Polyoxymethylene
PP	Polypropylene
PS	Polystyrene

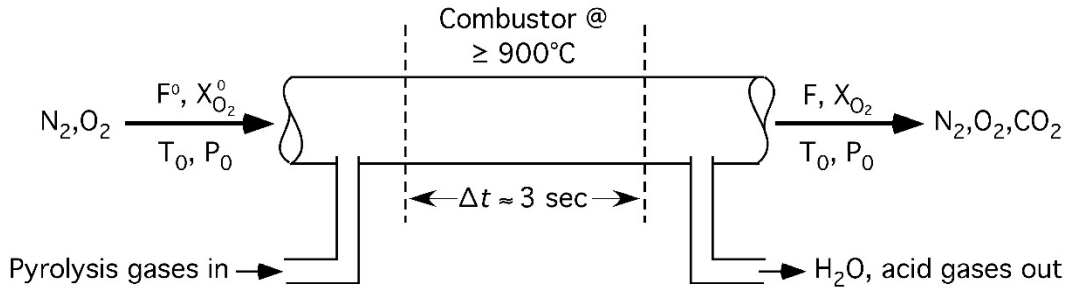
## EXECUTIVE SUMMARY

This report analyzes the accuracy of heat release rate measured in microscale combustion calorimeter (MCC), and proposes an optimum approach for determining heat release rate. MCC was developed by the FAA in the 1990s, licensed to two manufacturers in 2005, and has been sold worldwide by them since that time. As opposed to standard fire tests that use kilogram-size samples and provide qualitative results, the MCC is a quantitative, milligram scale test used by industrial laboratories, national research institutions, and universities to determine flammability characteristics of plastics and other solid materials. The MCC became an ASTM Standard Test Method (D7309) in 2007 and has been used mainly as a research tool since then. Recently, Underwriters Laboratories adopted the MCC for product surveillance, The Boeing Company began using the MCC for quality control of incoming materials and production articles, and the FAA is considering MCC as a means of demonstrating compliance of material substitutions with flammability requirements for large passenger aircraft. A high degree of accuracy is needed for the MCC to satisfy these voluntary standards, quality control programs, and regulatory requirements, and to support the development of fire-safe polymers and non-hazardous flame retardants by industry. The research in this report focuses on the accuracy of MCC as currently practiced in ASTM D7309. Two sources of systematic error (bias) were discovered that bias the specific heat release rate measured in the test, and computational strategies to correct for these errors are proposed. The recommended approach increases the relative accuracy of MCC by as much as 6%, as demonstrated by newly computed heats of combustion that are in quantitative agreement with theoretical values.



## INTRODUCTION

In oxygen consumption calorimetry (O2C), the heat released by combustion is computed from the difference in the mass flow rate of oxygen (O<sub>2</sub>) entering and exiting the process zone [1]. In microscale combustion calorimetry (MCC), the process zone is a premixed combustor at  $\geq 900^\circ\text{C}$ , in which pyrolysis gases are thermally oxidized to completion in a nitrogen (N<sub>2</sub>)/O<sub>2</sub> mixture and O2C is implemented by measuring the volumetric flow rate and O<sub>2</sub> concentration of the gas stream exiting the combustor after water is removed [2]. Figure 1 is a schematic drawing of the MCC process zone. The dry gases exiting the combustor contain carbon dioxide (CO<sub>2</sub>) that replaces some or all of the O<sub>2</sub> consumed by combustion ( $\Delta\text{O}_2$ ) on a molar/volume basis, depending on the atomic composition of the fuel. CO<sub>2</sub> in the gas mixture can also change the thermal and transport properties of the gas stream and affect output of the flow meter, which is typically calibrated for pure N<sub>2</sub> or air. The stoichiometric ratio of CO<sub>2</sub> to  $\Delta\text{O}_2$  for complete combustion is determined by the atomic composition of the fuel, but it affects the actual and apparent flow rates used to calculate the specific heat release rate ( $Q'_c$ ) in the test. This systematic error (bias) in  $Q'_c$  results from changes in the volume of the gas stream and changes in the flow meter response when CO<sub>2</sub> is present in the dry combustion gases.



**Figure 1. The MCC process zone**

The rate at which heat is released by combustion in O2C is computed from the difference between the mass flow rate of O<sub>2</sub> into and out of the combustion zone ( $\dot{m}_{\text{O}_2}$ , kg/s) multiplied by the average net heat of complete combustion of O<sub>2</sub> with hydrocarbon fuels,  $E = 13.1 \pm 0.6$  kJ/g-O<sub>2</sub> [1]:

$$q'_c = E(\dot{m}_{\text{O}_2, \text{in}} - \dot{m}_{\text{O}_2, \text{out}}) = E(\rho_{\text{O}_2, \text{in}} F_{\text{in}} X_{\text{O}_2, \text{in}} - \rho_{\text{O}_2, \text{out}} F_{\text{out}} X_{\text{O}_2, \text{out}}) \quad (1)$$

The last term on the right side of equation 1, which has units of Watts (W), expresses the difference in the mass flow rates as the difference between the product of the volumetric flow rate of the combustion stream  $F$  and the O<sub>2</sub> mole (volume) fraction,  $X_{\text{O}_2}$ , entering (in) and exiting (out) the combustion zone. The volumetric flow rate and the O<sub>2</sub> volume fraction of the gases entering the combustor prior to any chemical reaction with fuel will be denoted,  $F_{\text{in}} = F^0$  and  $X_{\text{O}_2, \text{in}} = X_{\text{O}_2}^0$ , respectively, and the corresponding values exiting the combustor as,  $F_{\text{out}} = F$  and  $X_{\text{O}_2, \text{out}} = X_{\text{O}_2}$ . If,  $F^0$  and  $F$  are measured at standard temperature (298 K) and pressure (1 bar), and  $\rho_{\text{O}_2, \text{in}} = \rho_{\text{O}_2, \text{out}} = \rho_{\text{O}_2}$  is the density of O<sub>2</sub> at the standard temperature and pressure where  $X_{\text{O}_2}$  is

also measured, the heat release rate normalized for the initial mass of the sample,  $m^0$ , is the specific heat release rate:

$$Q'_c = \frac{E\rho_{O_2}}{m^0} (F^0 X_{O_2}^0 - F X_{O_2}) \quad (2)$$

In the standard procedure [3], it is assumed that  $F = F^0$ , so the heat release rate is computed from the instantaneous exit flow  $F$  and the change in the oxygen volume fraction  $\Delta X_{O_2}$  only:

$$Q'_{c,ASTM} = \frac{E\rho_{O_2}}{m^0} F (X_{O_2}^0 - X_{O_2}) = \frac{E\rho_{O_2}}{m^0} F \Delta X_{O_2} \quad (3)$$

Recently, it was shown that  $Q'_{c,ASTM}$  was sensitive to  $X_{O_2}^0$  because, in general,  $F^0 \neq F$ , and that the difference in flow rates is related to the atomic composition of the fuel [4]:

$$\frac{F^0 - F}{F} \approx \Delta X_{O_2} - X_{CO_2} = (1 - \frac{X_{CO_2}}{\Delta X_{O_2}}) \Delta X_{O_2} = (1 - \alpha) \Delta X_{O_2} \quad (4)$$

Substituting equation 4 into an expansion of equation 2 shows that the volume-corrected specific heat release rate in the MCC using only the final flow rate  $F$  in the calculation is [4]:

$$Q'_c = \frac{E\rho_{O_2}}{m^0} F \Delta X_{O_2} \left\{ 1 + \frac{(F^0 - F)}{F} \frac{X_{O_2}^0}{\Delta X_{O_2}} \right\} = \frac{E\rho_{O_2}}{m^0} F \Delta X_{O_2} \left\{ 1 + (1 - \alpha) X_{O_2}^0 \right\} \quad (5)$$

Equation 5 uses a stoichiometric correction term,  $\alpha = X_{CO_2}/\Delta X_{O_2}$ , to account for the difference between  $F^0$  and  $F$  when only the latter is used in the calculation of  $Q'_c$  as per ASTM [3]. Unfortunately, the ratio of the moles of  $CO_2$  produced to the moles of  $O_2$  consumed by complete combustion,  $\alpha$ , is sensitive to the atomic composition of the fuel through the combustion stoichiometry, and it is not clear if equation 5 will eliminate the systematic error (bias) in  $Q'_c$  due to volume changes when an average  $\alpha$  is used for general purpose testing. Moreover, it was recently discovered that the output of the flow meters used to measure  $F$  in the MCC is also subject to a small, systematic error due to the presence of  $CO_2$  in the gas stream when it is calibrated for  $N_2$  or air. This paper explores computational strategies to eliminate the systematic errors in  $Q'_c$  caused by volume changes and flow meter error when  $CO_2$  is present in the dry combustion gases of ASTM D 7309 [3].

## APPROACH

To obtain accurate flow rates, most gas flow meters—regardless of operating principle—require a correction factor if the composition of the dry combustion gases is different from the reference gases used for calibration. The MCC used in this study was made by the FAA. The instrument has a thermal type flow meter (MKS Instruments: 179A) and an electrochemical oxygen sensor (Teledyne Analytical Instrument: R-17A), with N<sub>2</sub> or air as a reference gas. Mixing the N<sub>2</sub> with residual O<sub>2</sub> and added CO<sub>2</sub> in the combustion gases affects the calibration constant of the flow meter and, therefore, the accuracy of the flow rate measurement, which is calibrated for N<sub>2</sub>. For the thermal type mass flow meter most commonly used in MCC construction, the flow correction factor,  $k_i$ , for any species,  $i$ , is [5]:

$$k_i = \frac{\rho_{ref} c_{p,ref} s_i}{\rho_i c_{p,i} s_{ref}} \quad (6)$$

In equation 6,  $c_{p,i}$  and  $\rho_i$  are the specific heat and density of gas  $i$  at 20°C and 1 bar, respectively;  $s$  is a molecular structure correction factor equal to 1.030 for monatomic gases, 1.000 for diatomic gases, 0.941 for triatomic gases, and 0.880 for polyatomic gases; and subscript  $ref$  denotes the reference gas. Table 1 shows the gas properties [5, 6] and the correction factors calculated using equation 6. Carbon monoxide (CO) is negligible when combustion is complete in the standard MCC method, but CO<sub>2</sub> in the combustion gases is appreciable and has a significant impact on the change in the volumetric flow rate as per equation 5. In test conditions in which incomplete combustion is a concern, CO concentration increases. The gas properties and thermal correction factor for CO shown in table 1 are almost identical to those of pure nitrogen, and the flow rate reading is not affected by CO.

**Table 1. Property and thermal correction factor for selected gases at 1 bar and 20°C [5, 6]**

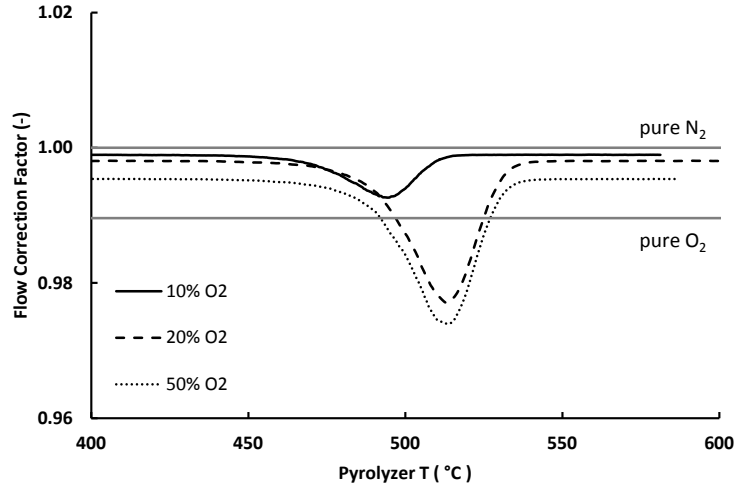
		N <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	CO
Molecular Structure Factor	$s$	1.000	1.000	0.941	1.000
Density	$\rho$ (g/L)	1.150	1.314	1.816	1.150
Specific Heat	$c_p$ (cal/g °C)	0.249	0.220	0.202	0.249
Correction Factor (N <sub>2</sub> ref.)	$k_i$	1.00	0.99	0.73	1.00

For the mixture of gases in the combustion stream after water is removed, the correction factor,  $k_m$ , is calculated using the following equation [5]:

$$k_m = \frac{0.286 \sum X_i s_i}{\sum X_i \rho_i c_{p,i}} \quad (7)$$

In equation 7,  $X_i$  is the volume fraction of species  $i = \text{N}_2, \text{O}_2$  and  $\text{CO}_2$ , and the coefficient  $0.286 = \rho_{ref} c_{p,ref} / s_{ref}$ , is the value for pure N<sub>2</sub> using the properties in table 1. The correction factors calculated from the measured O<sub>2</sub> and CO<sub>2</sub> concentrations for polyethylene (PE) combusted in MCC are shown in figure 2. Tests were performed at various initial O<sub>2</sub> volume

fractions  $X_{O_2}^0 = 0.1, 0.2,$  and  $0.5$  with a combustor temperature of  $900^\circ\text{C}$ , a pyrolyzer heating rate of  $1^\circ\text{C/s}$ , and an initial sample mass of approximately 2 mg. Heating rate and initial sample mass are reduced to  $0.5^\circ\text{C/s}$  and 1 mg respectively for the  $X_{O_2}^0 = 0.1$  to ensure excess  $O_2$  for complete combustion. Figure 2 shows that the measured flow is as much as 3% too low at the highest  $O_2$  fraction,  $X_{O_2}^0 = 0.5$ , when testing high-density PE.



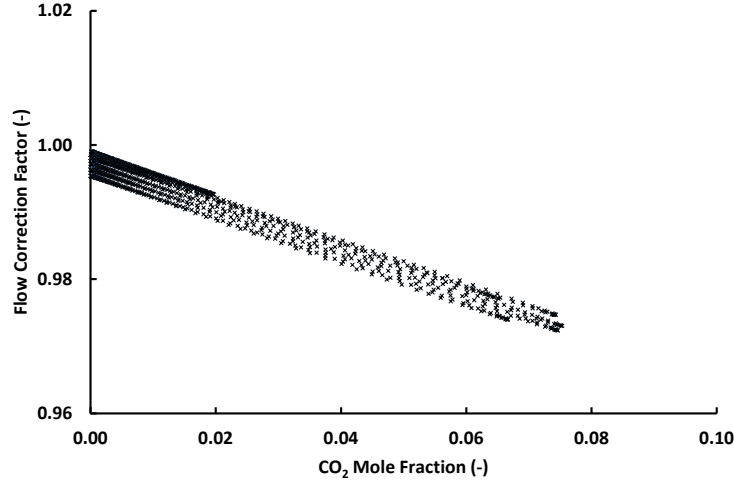
**Figure 2. Calculated correction factors for complete combustion of PE in MCC at  $X_{O_2}^0 = 0.1, 0.2,$  and  $0.5$**

The flow correction factors for  $O_2$  mole (volume) fractions,  $X_{O_2}^0 = 10\%, 15\%, 20\%, 30\%, 40\%$ , and  $50\%$ , in a mixture with  $N_2$  and  $CO_2$  are plotted against the  $CO_2$  volume fraction in figure 3. The deviation of the correction factor from unity increases as the  $CO_2$  volume fraction increases in the combustion gases. By comparison, substituting  $O_2$  for  $N_2$  in the reference and combustion gas streams results in a relatively small decrease in  $k_m$ , as illustrated by the band of  $O_2$  contours projected on the ordinate at a particular  $X_{CO_2}$ . Neglecting the small effect of  $O_2$  on the correction factor, a fit of the data in figure 3 forced through an ordinate value of unity yields:

$$k_m = 1 - 0.38X_{CO_2} \quad (8)$$

To express this result in terms of the  $O_2$  volume fraction,  $X_{O_2}$ , measured in ASTM D 7309, recall that the moles of  $CO_2$  produced ( $X_{CO_2}$ ) per mole of  $O_2$  consumed by complete combustion ( $\Delta X_{O_2}$ ) is a characteristic of the fuel, as is the ratio  $X_{CO_2}/\Delta X_{O_2} = \alpha$ . In this case, equation 8 becomes:

$$k_m = 1 - 0.38\alpha\Delta X_{O_2} \quad (9)$$



**Figure 3. Calculated flow correction factors for PE combustion in MCC vs. CO<sub>2</sub> volume fraction**

Both  $X_{CO_2}$  and  $\Delta X_{O_2}$  depend on the atomic composition of the fuel and the combustion stoichiometry; in general,  $\alpha \equiv X_{CO_2}/\Delta X_{O_2} \neq 1$ . As an example,  $\alpha = 0.67$  for PE,  $\alpha = 0.8$  for polystyrene (PS),  $\alpha = 0.83$  for poly(methylmethacrylate) (PMMA), and  $\alpha = 1$  for polyoxymethylene (POM) [4, 7]. Defining a volumetric correction factor that is the bracketed term on the right side of equation 5:

$$k_s = 1 + (1 - \alpha)X_{O_2}^0 \quad (10)$$

Substituting equations 9 and 10 into equation 5 gives the true specific heat release rate in terms of the ASTM D 7309 value:

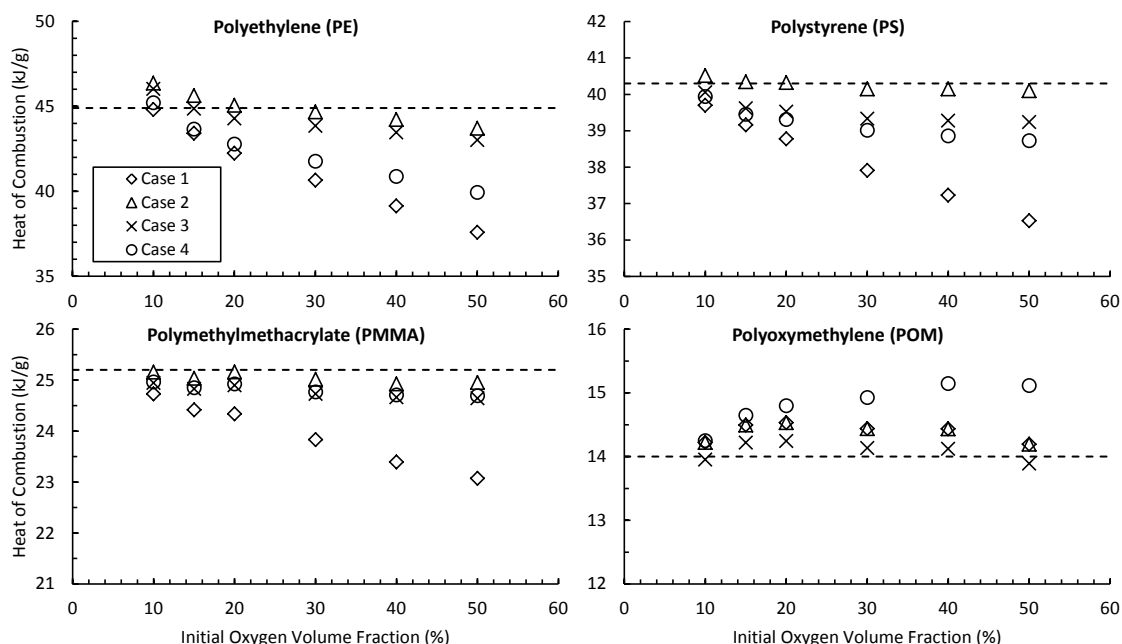
$$Q_c = k_s k_m Q'_{c,ASTM} = \frac{k_s k_m E \rho_{O_2}}{m^0} F \Delta X_{O_2} \quad (11)$$

Equation 11 includes the CO<sub>2</sub> stoichiometric coefficient,  $\alpha$ , in both the volumetric correction factor,  $k_s$ , and the calibration correction factor,  $k_m$ , when only  $F$  and  $\Delta X_{O_2}$  are used to calculate  $Q'_c$ . The average value of  $\alpha$  for PE, PS, PMMA, and POM is  $\alpha = 0.83$ , which is the same value obtained for a larger population that includes most of the common polymers,  $\langle \alpha \rangle = 0.83 \pm 0.12$  ( $n = 120$ ). The net heat of complete combustion,  $\Delta h_c$  is obtained by time integration of equation 11.

## RESULTS AND DISCUSSION

Figure 4 contains experimental results for the specific heat release rate  $\Delta h_c$  for PE, PS, PMMA, and POM as per equation 11, at different initial  $O_2$  volume fractions. The dashed lines in figure 4 are the theoretical values of the net heat of complete (stoichiometric) combustion,  $\Delta h_c$ , of each of these non-charring, hydrocarbon polymers producing only  $CO_2$  and water. Each symbol represents the average of three replicates with a coefficient of variation (COV) of less than 1%. The following cases were studied:

- Case 1: Only  $F$  used in calculation with  $k_m = 1$  and  $k_s = 1$  (current ASTM D 7309 algorithm).
- Case 2: Only  $F$  used in calculation with  $k_m = 1$  and  $k_s$  evaluated using  $\alpha$  (no flow correction for  $CO_2$  effect).
- Case 3: Only  $F$  used in calculation with  $k_m$  and  $k_s$  both evaluated using  $\alpha$ .
- Case 4: Only  $F$  used in calculation with  $k_m$  and  $k_s$  both evaluated using  $\alpha = \langle \alpha \rangle = 0.83$ .



**Figure 4. Heats of combustion  $\Delta h_c$  by equation 11 vs. incoming  $O_2$  volume fraction  $X_{O_2}^0$  for PE, PS, PMMA, and POM, calculated without incoming flow measurement  $F^0$ ; theoretical  $\Delta h_c$  is indicated by the dashed line**

In the ASTM D 7309 method [3],  $F^0$  is not used in the calculation and the effect of  $CO_2$  on the flow meter calibration (and, therefore,  $F$ ) is neglected, resulting in a large and systematic decrease in  $\Delta h_c$  with increasing  $X_{O_2}^0$  (Case 1). Case 2 shows the effect of using the polymer-specific stoichiometric factor  $\alpha$  in table 2 to correct the flow volume when  $CO_2$  replaces  $O_2$  without accounting for the effect of  $CO_2$  on the flow meter calibration. Case 3 shows the effect of using  $\alpha$  to account for the flow volume and the effect of the flow meter calibration on  $F$ . It is seen that when the polymer-specific  $\alpha$  is used to account for the volume change when  $CO_2$  replaces  $O_2$ , the computed  $\Delta h_c$  approximates the theoretical value with (Case 3) or without

(Case 2) accounting for the effect of CO<sub>2</sub> on the flow meter calibration,  $F$ . However, when the atomic composition of the sample is unknown, the average stoichiometric coefficient  $\langle\alpha\rangle$  must be used to correct the flow volume and the flow meter calibration (Case 4). Using  $\langle\alpha\rangle$  results in a relatively large error, even with CO<sub>2</sub>-corrected  $F$ , and this error is greatest for PE and POM, which have the largest difference between  $\alpha$  and  $\langle\alpha\rangle$ . Because of the uncertainty in  $\langle\alpha\rangle$ , the accuracy of  $\Delta h_c$  increases as the O<sub>2</sub> fraction entering the combustor decreases [4, 7], primarily because of its effect on  $k_s$ . Following the engineering uncertainty propagation approach [8], using average  $\langle\alpha\rangle$  instead of the stoichiometric  $\alpha$  results in a bias on  $k_s$  of approximately 7%, at 50% incoming O<sub>2</sub> volume fraction for the worst case in PE. If high accuracy is desired, a fuel-specific  $\alpha$  and  $\Delta h_c$  can be obtained from the slope and intercept, respectively of equation 3 plotted as  $Q'_{c,ASTM}$  versus  $X_{O_2}^0$  [4, 7].

In general, the exact composition of the fuel is unknown and the O<sub>2</sub> fraction is  $X_{O_2}^0 = 0.2$  [3], in which case the bias in  $\Delta h_c$  and  $Q'_{c,max}$ , obtained by the ASTM D 7309 procedure, will be approximately -5% when the mean stoichiometric correction factor,  $\langle\alpha\rangle = 0.83$ , is used. The experimental data at different initial O<sub>2</sub> concentrations in figure 4 are averaged in table 2 ( $\pm 1$  standard deviation) for comparison.

**Table 2. Stoichiometric coefficients and heats of combustion of PE, PS, PMMA, and POM calculated without measuring incoming flow rate**

Polymer	$\alpha$	Heats of Combustion, $\Delta h_c$ in Figure 4				
		Case 1	Case 2	Case 3	Case 4	Theory
PE	2/3	41.3 $\pm$ 2.7	44.9 $\pm$ 1.0	44.2 $\pm$ 1.1	42.4 $\pm$ 1.9	44.9
PS	4/5	38.2 $\pm$ 1.2	40.3 $\pm$ 0.2	39.5 $\pm$ 0.3	39.2 $\pm$ 0.4	40.3
PMMA	5/6	24.0 $\pm$ 0.6	25.0 $\pm$ 0.1	24.8 $\pm$ 0.1	24.8 $\pm$ 0.1	25.2
POM	1	14.4 $\pm$ 0.1	14.4 $\pm$ 0.1	14.1 $\pm$ 0.1	14.8 $\pm$ 0.3	14.0

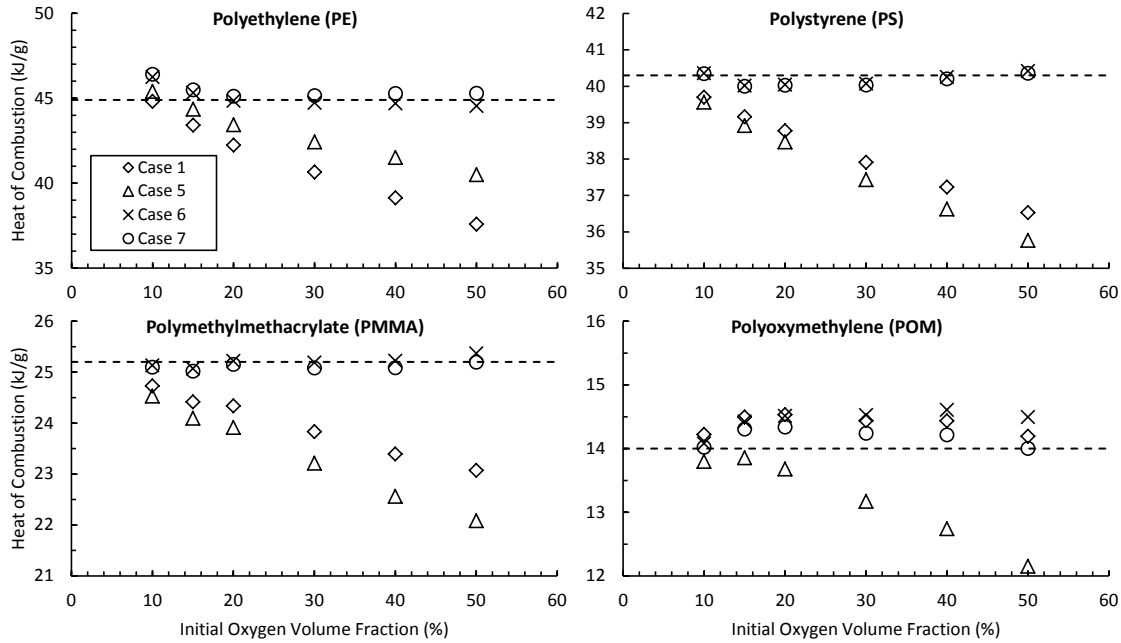
When both  $F^0$  and  $F$  are measured and used to calculate  $Q'_c$  instead of using  $k_s$  to account for the difference, the specific heat release rate  $Q'_c$  is calculated from equations 2 and 9, using an average value,  $\alpha = \langle\alpha\rangle = 0.83$  in equation 9 to correct for CO<sub>2</sub> in the outflow  $F$ :

$$Q'_c = \frac{E\rho_{O_2}}{m^0} (F^0 X_{O_2}^0 - k_m F X_{O_2}) \quad (12)$$

The effect of CO<sub>2</sub> bias on  $F$  was evaluated using the net heat of combustion,  $\Delta h_c$ , obtained by time integration of equation 12. The following cases were studied using equation 12 as the basis:

- Case 5:  $F^0$  and  $F$  used in calculation with  $k_m = 1$  (no correction for CO<sub>2</sub> bias on  $F$ ).
- Case 6:  $F^0$  and  $F$  used in calculation with  $k_m$  evaluated using  $\alpha$ .
- Case 7:  $F^0$  and  $F$  used in calculation with  $k_m$  evaluated using  $\alpha = \langle\alpha\rangle = 0.83$ .

The results for Cases 5–7 are shown graphically as  $\Delta h_c$  versus  $X_{O_2}^0$  for PE, PS, PMMA, and POM in figure 5. Standard ASTM D7309 method (Case 1) is also included for comparison. Using both flow measurements in the calculation without correcting for CO<sub>2</sub> bias in flow meter reading (Case 5) reduces the bias in PE heats of combustion with  $X_{O_2}^0$ , but increases the bias for PS, PMMA, and POM. Using both flow measurements and correcting  $F$  for CO<sub>2</sub> bias in the flow meter reading essentially removes the dependence of  $\Delta h_c$  on  $X_{O_2}^0$ , using either the exact stoichiometric coefficient,  $\alpha$  (Case 6), or the average stoichiometric coefficient,  $\langle\alpha\rangle$  (Case 7), and an accurate value of  $\Delta h_c$  is obtained at all  $X_{O_2}^0$ .



**Figure 5. Heats of combustion  $\Delta h_c$  by equation 12 vs. incoming O<sub>2</sub> volume fraction  $X_{O_2}^0$  for PE, PS, PMMA, and POM calculated with incoming flow measurement  $F^0$ ; the theoretical  $\Delta h_c$  is indicated by a dashed line**

The experimental data at each initial O<sub>2</sub> concentration in figure 5 is averaged in table 3 ( $\pm 1$  standard deviation). The net heat of complete combustion computed from the combustion stoichiometry,  $\Delta h_c$  (theory), is also listed in table 3. The results with flow meter correction (Cases 6 and 7) show less variation than those without the flow meter bias correction (Cases 1 and 5), and the mean values of  $\Delta h_c$  are equal to the theoretical values. Therefore, when equation 12 (Case 7) is used to calculate  $Q_c$  using the O<sub>2</sub>-consumption method with the measured flow rate prior to combustion,  $F^0$ , the instantaneous flow rate exiting the combustor,  $F$ , and an average material stoichiometric coefficient,  $\langle\alpha\rangle = 0.83$ , the recommended equation for calculating the specific heat release rate in oxygen consumption flow calorimetry is,

$$Q_c = \frac{E\rho_{O_2}}{m^0} \left\{ F^0 X_{O_2}^0 - F X_{O_2} \left( 1 - 0.32(X_{O_2}^0 - X_{O_2}) \right) \right\} \quad (13)$$



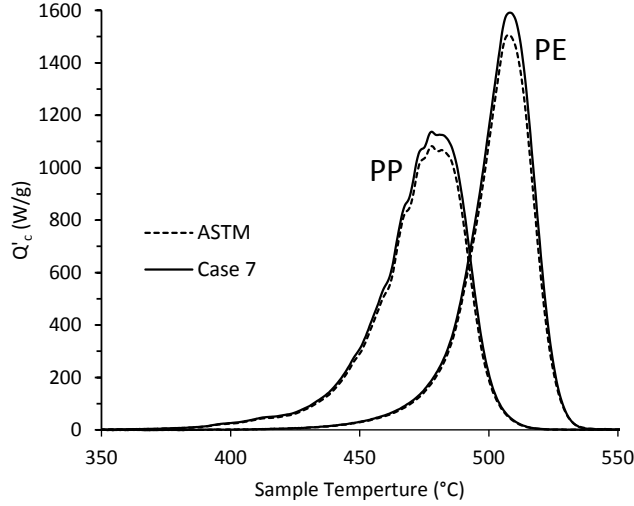
**Table 3. Stoichiometric factors and heats of combustion of PE, PS, PMMA, and POM calculated measuring incoming flow rate**

Polymer	$\alpha$	Heats of Combustion, $\Delta h_c$ in Figure 5				
		Case 1	Case 5	Case 6	Case 7	Theory
PE	2/3	41.3 $\pm$ 2.7	42.9 $\pm$ 1.8	45.1 $\pm$ 0.6	45.5 $\pm$ 0.5	44.9
PS	4/5	38.2 $\pm$ 1.2	37.8 $\pm$ 1.4	40.2 $\pm$ 0.2	40.2 $\pm$ 0.2	40.3
PMMA	5/6	24.0 $\pm$ 0.6	23.4 $\pm$ 0.9	25.2 $\pm$ 0.1	25.1 $\pm$ 0.1	25.2
POM	1	14.4 $\pm$ 0.1	13.2 $\pm$ 0.7	14.4 $\pm$ 0.2	14.2 $\pm$ 0.1	14.0

Equation 13 is implemented in the method by recording and averaging  $F$  and  $X_{O_2}$  for several seconds prior to the start of sample heating to obtain  $F^0$  and  $X_{O_2}^0$ . Table 4 lists  $\Delta h_c$  for the 15 common polymers in the FAA database [7], using the standard ASTM D7309 method (Case 1) at an initial  $O_2$  volume fraction  $X_{O_2}^0 = 0.2$  (20% v/v  $O_2$  in  $N_2$ ) and using the recommended method (Case 7) with constants evaluated (Equation 13). The specific heat release rate history  $Q_c'$  of two selected polymers, PE and polypropylene (PP), using the standard ASTM method [3] and the optimum method (Case 7/Equation 13) are shown in figure 6, which shows that the revised calculation (Equation 13) has a similar impact on the peak heat release rate and  $\Delta h_c$ .

**Table 4. Specific heat of combustion of 15 common polymers using the ASTM method [3] and the optimum method (Case 7)**

FAA Database Polymer		$\Delta h_c$ (ASTM) [7] (kJ/g)	$\Delta h_c$ (Case 7) (kJ/g)
High-Density Polyethylene	PE	42.2	45.5
Polypropylene	PP	41.0	45.4
Polystyrene	PS	40.1	40.2
High-Impact Polystyrene	HIPS	38.4	39.8
Acrylonitrile-Buatdiene-Styrene Terpolymer	ABS	36.1	37.9
Polyhexamethylenedipamide	PA66	28.4	29.9
Polymethylmethacrylate	PMMA	24.5	25.1
Polycarbonate of Bisphenol-A	PC	20.5	20.7
Polyethyleneterephthalate	PET	16.6	15.9
Polyphenylenesulfide	PPS	14.7	15.5
Polyoxymethylene	POM	14.0	14.2
Polyphenylsulfone	PPSU	12.8	13.4
Polyvinylchloride (rigid)	PVC	11.1	11.3
Polyetherimide	PEI	9.6	10.2
Fluorinated Ethylene-Propylene	FEP	4.5	3.2



**Figure 6. Specific heat release rate,  $Q'_c$  of PE and PP using ASTM method [3] and revised calculation (case 7/Equation 13)**

It has been shown that the flow meter has a bias of up to 3% because of the presence of  $\text{CO}_2$  in the gas mixture and that the bias propagates and affects the determination of heat of combustion in Case 5 without flow correction. It should be noted that the approach in Case 5 is theoretically identical to the stoichiometric  $\alpha$  method (Case 2) in the previous section. Neither approach corrects for the  $\text{CO}_2$  effect on the flow meter reading. The following analysis shows how a bias of up to 3% in flow meter reading propagates through the method and results in a total bias of approximately 14% in  $\Delta h_c$  at an initial  $\text{O}_2$  volume fraction,  $X_{\text{O}_2}^0 = 0.5$ , and the bias in heat of combustion increases with the increase of  $X_{\text{O}_2}^0$ .

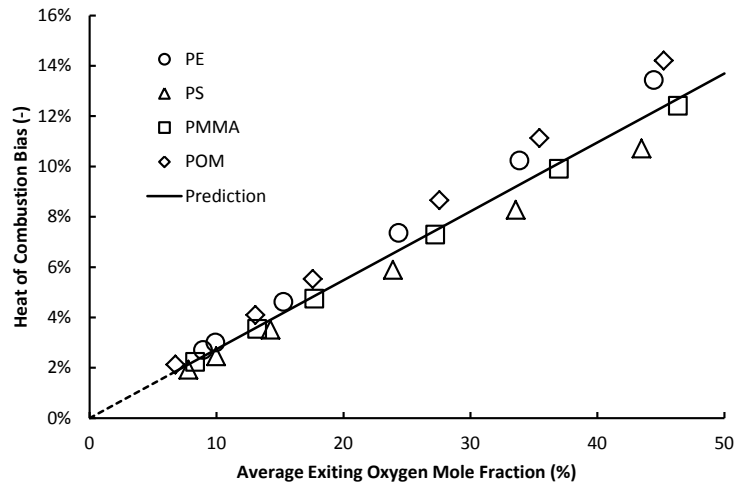
Following the experimental error propagation approach [8], and neglecting the error from the  $\text{O}_2$  measurement and initial flow measurement (no  $\text{CO}_2$ ), the relative total bias,  $\varepsilon_h$ , in heat of combustion (equation 2) is:

$$\varepsilon_h = \frac{X_{\text{O}_2} \sigma_F}{F^0 X_{\text{O}_2}^0 - F X_{\text{O}_2}} = \frac{\sigma_F / F}{F^0 X_{\text{O}_2}^0 / F X_{\text{O}_2} - 1} \quad (14)$$

In equation 14,  $\sigma_F$  is the absolute bias of flow meter, and  $\varepsilon_F = \sigma_F / F \approx 0.38 X_{\text{CO}_2}$  is the relative bias of the flow meter estimated from the fitting correlation. When the relative change in flow rate is small compared to the relative change in  $\text{O}_2$  volume fraction,  $F^0 X_{\text{O}_2}^0 / F X_{\text{O}_2} \approx X_{\text{O}_2}^0 / X_{\text{O}_2}$ . Replacing  $X_{\text{CO}_2}$  with  $\alpha \Delta X_{\text{O}_2}$ , the negative bias in  $\Delta h_c$  for PE, PS, PMMA, and POM is:

$$\varepsilon_h = \frac{0.38 \alpha \Delta X_{\text{O}_2}}{(X_{\text{O}_2}^0 - X_{\text{O}_2}) / X_{\text{O}_2}} = 0.38 \alpha X_{\text{O}_2} \approx 0.38 \alpha X_{\text{O}_2}^0 \quad (15)$$

Equation 15 indicates that the bias in  $\Delta h_c$ , without correcting  $F$  for  $\text{CO}_2$ , is proportional to the  $\text{O}_2$  volume fraction. The computed negative bias for an average  $\alpha = \langle \alpha \rangle = 0.83$  are compared to the experimental bias (open symbols) in figure 7, which shows that  $\Delta h_c$  will be under-predicted by as much as 14% at high  $\text{O}_2$  volume fractions if the effect of  $\text{CO}_2$  on thermal flow meter response is not taken into account. Reducing the heating rate in the pyrolyzer to reduce the rate of  $\text{CO}_2$  production will have little effect on bias because  $\alpha$  is a stoichiometric coefficient, so  $\Delta X_{\text{O}_2}$  is correspondingly reduced. This behavior is described by equation 15, and was validated by conducting tests at different heating rates and at different  $X_{\text{O}_2}^0$ . In addition, the signal-to-noise ratio for  $F$  and  $X_{\text{O}_2}$  increases at a lower heating rate, so the method is less sensitive.



**Figure 7 Predicted and experimental determined heat of combustion bias in MCC**

The analysis in the previous section has shown that in a typical MCC  $\text{O}_2$  consumption calorimeter using a thermal type flow meter, the negative flow rate bias from  $\text{CO}_2$  in the combustion gases when both  $F$  and  $F_0$  are measured is as high as 3% and increases with  $X_{\text{O}_2}^0$ , such that  $\Delta h_c$  can be under-predicted by as much as 14% at  $X_{\text{O}_2}^0 = 0.5$ .

Another type of flow meter suitable for low flow rates uses a differential-pressure operating principle in which the flow is calculated from the pressure drop across a tube. The correction factor for the differential pressure flow meter is calculated [9]:

$$k_i = \frac{\mu_{ref} \beta_i}{\mu_i \beta_{ref}} \quad (16)$$

In equation 16,  $\beta$  is the compressibility of the gas, and  $\mu$  is its dynamic viscosity. These properties for selected gases at  $20^\circ\text{C}$  and 1 bar are listed in table 5 [6]. Using  $\text{N}_2$  as the reference gas, the correction factor is  $k_i = 1.757 \beta_i / \mu_i$ . Unlike the thermal flow meter, the difference between  $\text{O}_2$  and  $\text{N}_2$  cannot be neglected with the differential pressure type of flow meter because of the difference in viscosity. Consequently, use of a differential pressure flow meter in the MCC

that is calibrated for N<sub>2</sub> will result in significant bias in  $\Delta h_c$  from both O<sub>2</sub> and CO<sub>2</sub>. The CO effect on flow rate in the incomplete combustion condition is small because of the similar viscosity of N<sub>2</sub> and CO.

**Table 5 Property and pressure correction factor for selected gases at 1 bar and 20°C [6]**

		N <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	CO
Dynamic Viscosity	$\mu$ (10 <sup>-5</sup> Pa s)	1.757	2.017	1.468	1.743
Compressibility	$\beta$	1.000	0.999	0.995	1.000
Correction Factor (N <sub>2</sub> ref.)	$k_i$	1.00	0.87	1.19	1.01

If the flow meter is empirically calibrated for a particular  $X_{O_2}^0$  (e.g., 20% O<sub>2</sub>/80% N<sub>2</sub> as per ASTM D 7309), and the viscosity of the gas mixture is calculated using Wilke's expression [10], the flow correction coefficient for CO<sub>2</sub> is  $k_m = 1 - 0.42 X_{CO_2}$ , which is identical in form and similar in magnitude to equation 8. Therefore, the negative bias in  $\Delta h_c$  for the differential pressure flow meter is approximately 17% at  $X_{O_2}^0 = 0.50$ , following the previously used procedure.

## CONCLUSIONS

The current ASTM D 7309 test standard for the microscale combustion calorimetry was found to have two sources of systematic error (bias) when calculating the specific heat release rate  $Q_c'$  from the final flow rate,  $F$ , and the change in the oxygen (O<sub>2</sub>) volume fraction of the dried combustion gases  $\Delta X_{O_2}$ . These sources of error are the effect of carbon dioxide (CO<sub>2</sub>) generated by combustion of the fuel on the volume change of the flow stream and the effect of CO<sub>2</sub> on the flow meter output during the test. Several computational approaches were examined to eliminate the systematic errors due to volume changes and flow calibration when CO<sub>2</sub> is present in the combustion gases, of which two were selected as viable strategies.

Volume Changes: Measuring only the final flow rate of the dry combustion gases  $F$  precludes a determination of the change in volume when the mole fraction of carbon dioxide ( $X_{CO_2}$ ) generated by combustion of the fuel is different from the mole fraction of O<sub>2</sub> consumed ( $\Delta X_{O_2}$ ). A material-specific stoichiometric coefficient,  $\alpha = X_{CO_2}/\Delta X_{O_2}$ , can largely account for the difference,  $F^0 - F$ , using the measured  $\Delta X_{O_2}$  as long as the atomic composition of the fuel is known. However, for general-purpose testing, for charring materials, or where the composition of the fuel gases is unknown, an average value,  $\langle \alpha \rangle = 0.83 \pm 0.12$  for 120 polymers must be used, which has an uncertainty of 14% that propagates to the specific heat release rate,  $Q_c'$ , and heat of combustion,  $\Delta h_c$ , regardless of whether the initial flow rate  $F^0$  is used in the calculation of  $Q_c'$  and the final flow rate  $F$  is corrected for the effect of CO<sub>2</sub> on the flow meter calibration. This approach is therefore unacceptable for general testing.

Flow Meter Signal: The terminal flow meter signal during the test  $F$ , is affected by CO<sub>2</sub> in the combustion gases when  $F^0$  is calibrated for N<sub>2</sub> or air. This bias in  $F$  increases monotonically with increasing initial O<sub>2</sub> concentration as demonstrated by  $\Delta h_c$  for the non-charring polymers

(polyethylene [PE], polystyrene [PS], poly(methylmethacrylate) [PMMA], and polyoxymethylene [POM]) at initial O<sub>2</sub> concentrations ranging from  $X_{O_2}^0 = 0.10$  to 0.50. An average stoichiometric coefficient,  $\langle\alpha\rangle = 0.83 \pm 0.12$ , was sufficient to adjust the flow meter calibration factor for  $X_{CO_2}$  using the measured  $\Delta X_{O_2}$  during the test. The combination of this  $F$  correction and the incorporation of  $F^0$  in the calculation of  $Q_c'$  as per Equation 13, resulted in  $\Delta h_c$  that were in quantitative agreement with theoretical values for the net heat of complete combustion of the non-charring polymers PE, PS, PMMA, and POM.

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