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An Exploratory Study on a High-Energy  
Flux (HEF) Calorimeter  
to Characterize Flammability  
of Advanced Engineered Polymers:  
Phase 1 - Ignition and Mass Loss Rate

by Archibald Tewarson, Wai Chin,  
and Richard Shuford

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# **Army Research Laboratory**

Aberdeen Proving Ground, MD 21005-5066

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## **An Exploratory Study on a High-Energy Flux (HEF) Calorimeter to Characterize Flammability of Advanced Engineered Polymers: Phase 1 - Ignition and Mass Loss Rate**

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## Abstract

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This report describes a newly designed *high-energy flux (HEF) calorimeter* for the flammability evaluation of high fire resistant plastics exposed to high heat flux typical of combat field scenarios and large-scale fires. Small samples are exposed to heat fluxes as high as  $150 \text{ kW/m}^2$  in co-flowing air with oxygen concentration in the range of 0–100%. A pilot flame ignites the vapors, a load cell measures mass loss, and an FTIR spectrometer identifies and quantifies the concentration of products generated in the tests. Standard relationships routinely used in the FMRC flammability apparatus are used to obtain the release rates of heat and products and fire parameters associated with ignition, combustion, and fire propagation.

Polymers with high fire resistance (two halogenated and four high-temperature polymers) and low fire resistance (six ordinary polymers) have been tested at 50, 100, and  $150 \text{ kW/m}^2$  in normal co-flowing air. The HEF calorimeter data at  $150 \text{ kW/m}^2$  was found useful in comparing the differences between the high fire-resistant halogenated and high-temperature polymers.

Literature data for the combustion of polymers with and without fire retardants and inorganic materials as fillers and nanocomposites have been analyzed. The analysis indicates that for the realistic evaluation of the effectiveness of fire retardants and nanocomposites, it is necessary to expose the polymers to high heat flux values typical of large-scale fires ( $120\text{--}150 \text{ kW/m}^2$ ).

## Acknowledgments

The authors gratefully acknowledge Mr. James R. Markham, Chief Executive Officer and Manager, New Technology, Advanced Fuel Research, East Hartford, CT, for the active participation and supervision in the assembly of the *high-energy flux (HEF) calorimeter* and in the performance of all the tests in the HEF calorimeter at the Advanced Fuel Research Laboratories in East Hartford, CT.

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# 1. Introduction

In fires, hazards to life and property are due to release of heat and products. For example, a fire started by a direct hit to stored munitions by firebrands can lead to catastrophic results with extensive thermal damage. Fire involvement of a composite structure of a combat vehicle can have severe consequences to personnel safety due to release of heat, smoke, and toxic and corrosive products. A fire can disrupt signals from delicate electronic components of guidance and control systems of vehicles and control rooms due to nonthermal damage by smoke and corrosive products released in the fire.

For lowering or eliminating hazards due to fires, the U.S. Army has been pursuing two complementary technologies: (1) material modifications, and (2) flame extinction [1]. Several experimental techniques, apparatuses, products, and hardware have been developed. Fundamental understanding of ignition, combustion, fire propagation, flame extinction processes, and thermal and nonthermal contamination are being pursued by the U.S. Army [1].

Utilization of highly fire- and chemical-resistant<sup>1</sup> polymers provides one of the several avenues to reduce or eliminate thermal and nonthermal damage [1]. Along with the U.S. Army [1], several other agencies [2-4] are developing and exploring the use of highly fire-resistant polymers with or without fixed fire protection. The Federal Aviation Administration (FAA) is investigating highly fire-resistant cabin materials for commercial aircraft) [2]. The Factory Mutual Research Corporation (FMRC) [3] and the semiconductor industry [4] are investigating highly fire- and chemical-resistant polymers for wafer processing equipment in clean rooms.

Polymers with high fire resistance increasingly require high heat flux exposure to initiate a fire (ignition). The heat flux requirements for ignition and fire propagation for the highly fire-resistant polymers in many cases are beyond the heat flux exposure limits of the conventional flammability

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<sup>1</sup>In this report, high fire resistance is defined as high combined resistance to ignition, combustion, fire propagation, and release of smoke, toxic, and corrosive products. High chemical resistance is defined as high resistance to leaching and extraction of ions, elements, and total oxidizable carbon from the polymers by process chemicals.

apparatuses. As a result, FMRC has developed techniques to simulate large-scale fire conditions in the FMRC flammability apparatus for flame radiation, external heat flux, and ventilation [5, 6]. In the current study, these techniques have been utilized by the U.S. Army and FMRC to develop a *high-energy flux (HEF) calorimeter*, where external heat flux range has been extended to 150 kW/m<sup>2</sup>. Note that in large-scale fires, the heat flux could be as high as 120–150 kW/m<sup>2</sup> [6]. This report presents details of the HEF calorimeter and limited data obtained from the tests in the calorimeter for highly fire-resistant advanced engineered polymers (halogenated and high-temperature polymers) and low fire-resistant ordinary polymers (thermoplastics). Fire resistance of polymers and fire parameters of polymers are discussed in Appendices A and B, respectively.

Results from the HEF calorimeter have been compared with the results obtained from the tests in the FMRC flammability apparatus<sup>2</sup> and in the cone calorimeter. This report explores the use of the HEF calorimeter as a tool to quantify properties associated with ignition, combustion, fire propagation, and release of heat and products from low to highly fire-resistant polymers of interest to the U.S. Army.

## 2. The HEF Calorimeter

Figure 1 shows a schematic, and Figure 2 shows a photograph of the HEF calorimeter. The calorimeter consists of a lower section where a sample is exposed to heat flux and an upper section where fire products are captured, analyzed, and exhausted. In this preliminary exploratory study, quantitative measurements were made for only time to ignition and mass loss rate in the lower section of the calorimeter. In the upper section of the calorimeter, products were analyzed qualitatively by a Fourier transform infrared (FTIR) spectrometer.<sup>3</sup>

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<sup>2</sup> A draft standard of the Fire Propagation Apparatus has been submitted to the National Fire Protection Association (NFPA) Fire Test Committee (1999) and the American Society for Testing and Materials (ASTM) Fire Standard Committee (1999).

<sup>3</sup> The design of the exhaust duct for the HEF calorimeter has not been finalized.

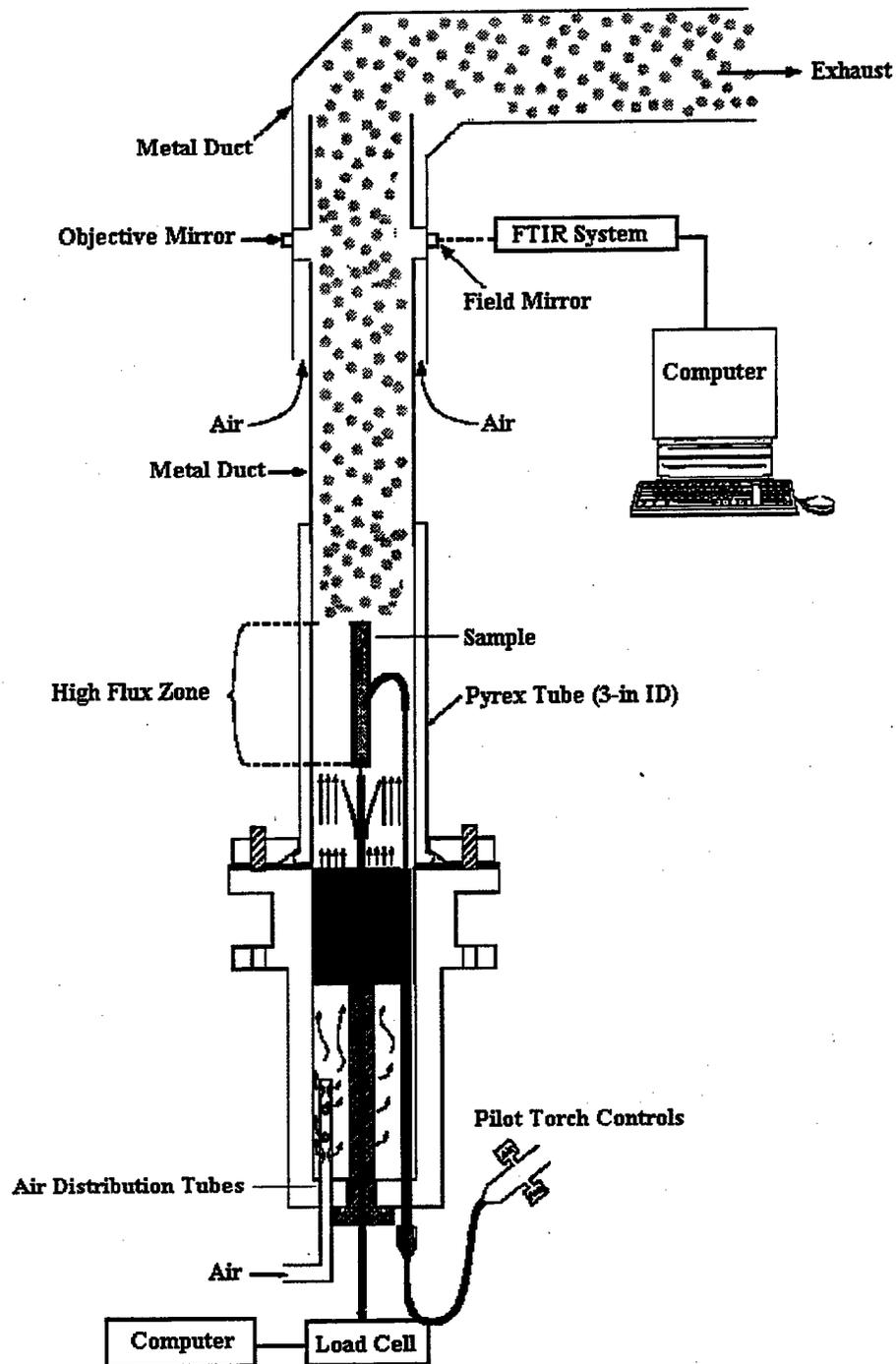
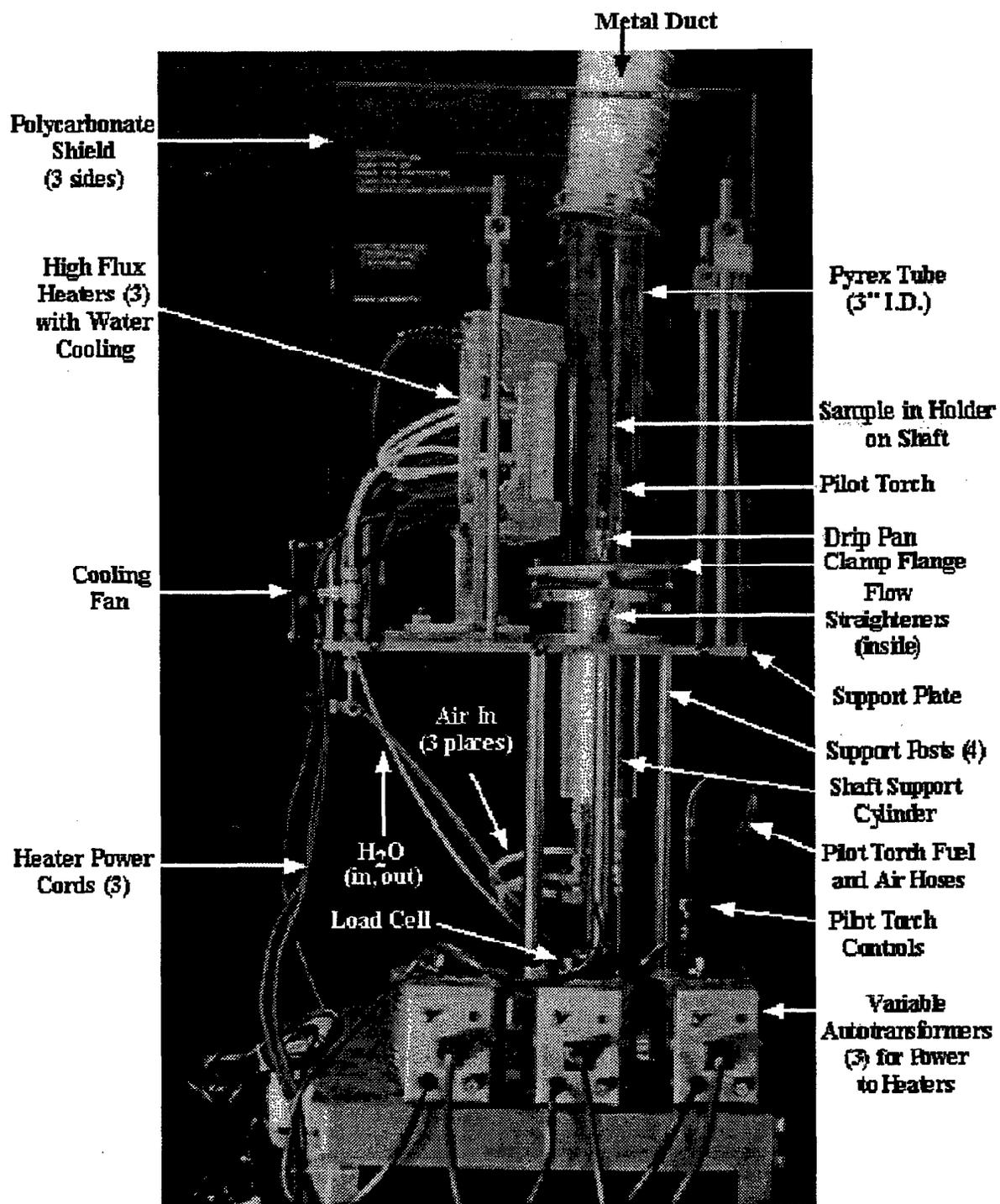


Figure 1. The HEF Calorimeter. The FTIR System Is Located About 3 ft (0.9 m) Away From the Top of the Pyrex Tube.



**Figure 2. Photograph of the HEF Calorimeter.**

**2.1 The Lower Section of the HEF Calorimeter.** Figure 3 shows the lower section of the HEF calorimeter. The sample used in the tests was 5 in (130 mm) long, 0.5–1.5 in (13–38 mm) wide, and 0.12–0.5 in (3–13 mm) thick and was placed on a stainless steel holder in a vertical configuration. A 1.4-in (35 mm)-diameter and 1.75-in (44 mm)-tall drip pan was provided to collect the molten mass of thermoplastics.

The sample was placed inside an 18-in (457 mm)-long, 3-in (76 mm)-id Pyrex glass tube. Details of the components associated with the Pyrex tube are listed in Table 1. The bottom of the tube had a metal flange and a gasket, which was attached to the metal base by two bolts to reduce the air leaks. The glass tube was surrounded on three sides by three 50-in (1.3 m)-square polycarbonate shields bolted to the base support table of the calorimeter. The sample surface was exposed to external heat flux by three vertical tungsten-quartz radiant heaters, in the range of 0–150 kW/m<sup>2</sup> (high-flux zone). The top view of the arrangement of the heaters is shown in Figure 4, and details of the components associated with the heaters are listed in Table 1. All the other sides of the sample protected by the ceramic paper insulated walls of the sample holder were not exposed to heat flux.

The stainless steel sample holder was attached to a load cell via a 20-in (508 mm)-tall and 1/4-in (6 mm)-diameter stainless steel shaft and a ceramic sphere. The shaft was supported by metal bearings, contained within a shaft support cylinder (10 in [254 mm] tall with a 4 in [102 mm] diameter at the bottom and a 7 in [178 mm] diameter at the top).

Air was introduced into a 10-in (254 mm)-long, 3-in (76 mm)-diameter tube inside the shaft support cylinder by three air-distribution tubes made of 1/4-in (6 mm)-diameter copper tubes with multiple outlets. Air in the tube flowed vertically upward toward the sample via a 3-in (76 mm)-wide and 2.5-in (64 mm)-long metal honeycomb flow straightener. A maximum inlet airflow of 200 liters/min ( $3.3 \times 10^{-3} \text{ m}^3/\text{s}$ ) with an oxygen concentration of 0–100% (operation limited to 60%) can be used in the HEF calorimeter. In this study, normal air at 200 liter/min ( $3.3 \times 10^{-3} \text{ m}^3/\text{s}$ ) was used.

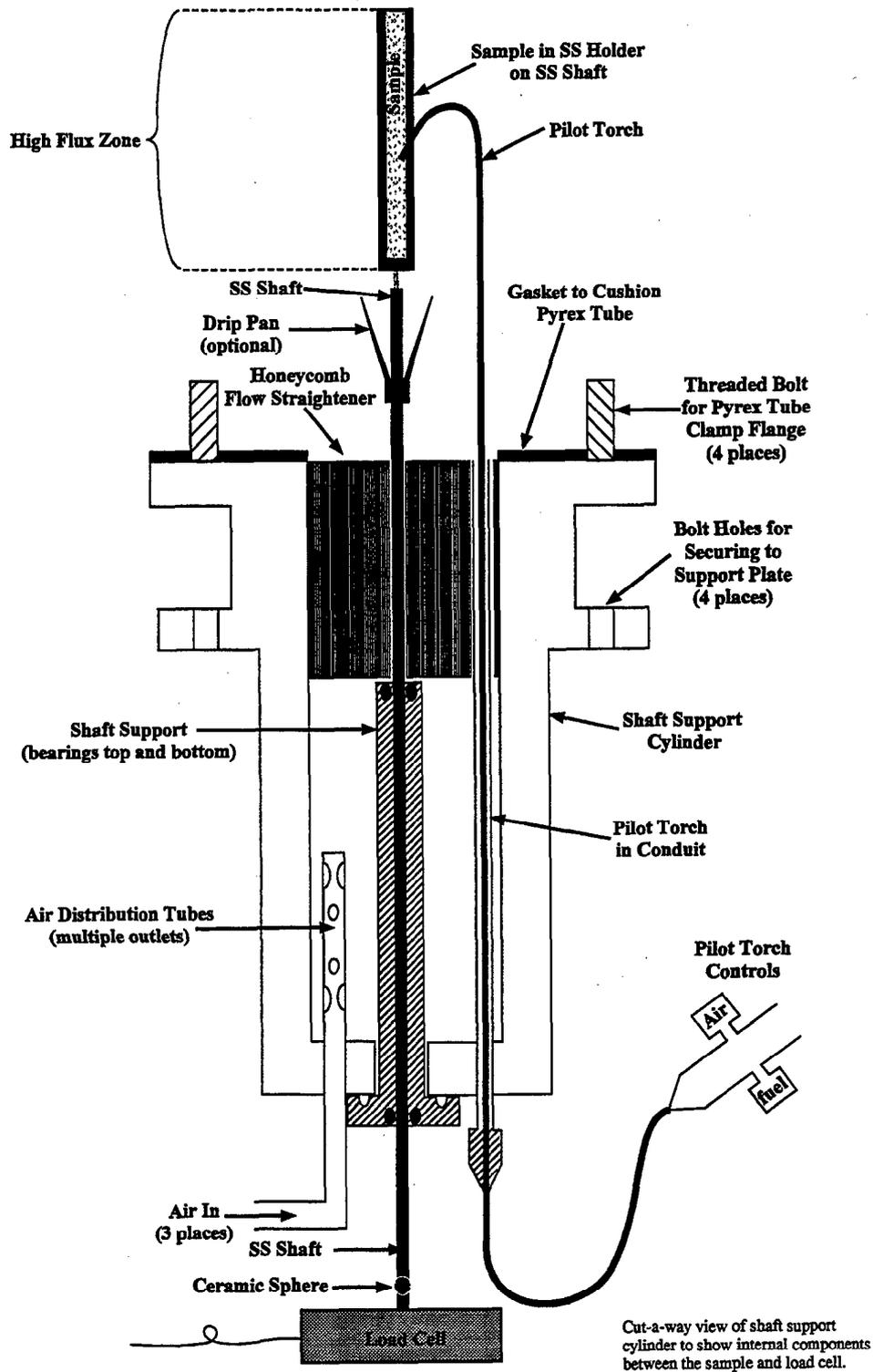
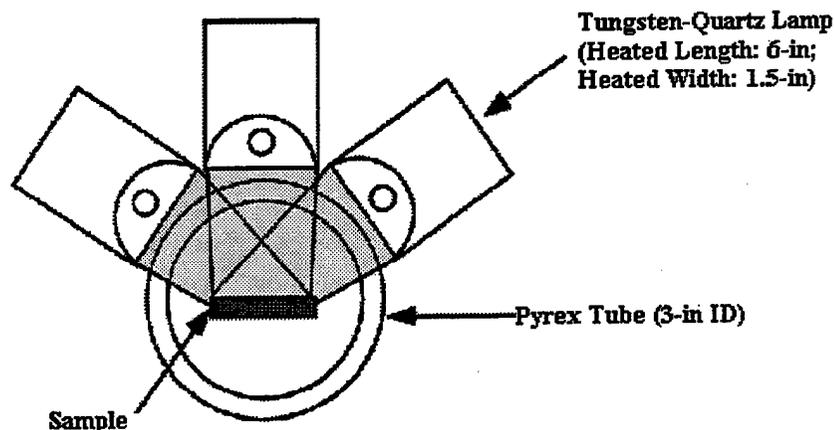


Figure 3. Lower Section of the HEF Calorimeter. The Pyrex Tube Is Not Shown.



**Figure 4. Top View of High Flux Zone and the Pyrex Tube. All Three Lamps Are Focused Onto the Sample Surface to Produce High-Energy Flux.**

A pilot torch (1/8-in [3 mm] stainless steel tube) within 0.4 in (10 mm) from the surface of the sample was used to ignite the vapors generated from the sample as it was exposed to external heat flux. Details of the components associated with load cell and sample support, support body, and pilot torch are listed in Table 1.

**2.2 The Upper Section of the HEF Calorimeter.** The products generated in the combustion of the sample were exhausted from the top of the Pyrex glass tube through the upper section of the calorimeter, where an FTIR spectrometer was located 12 tube diameters downstream of the Pyrex tube. In this study, the FTIR spectrometer was used only for qualitative analysis.

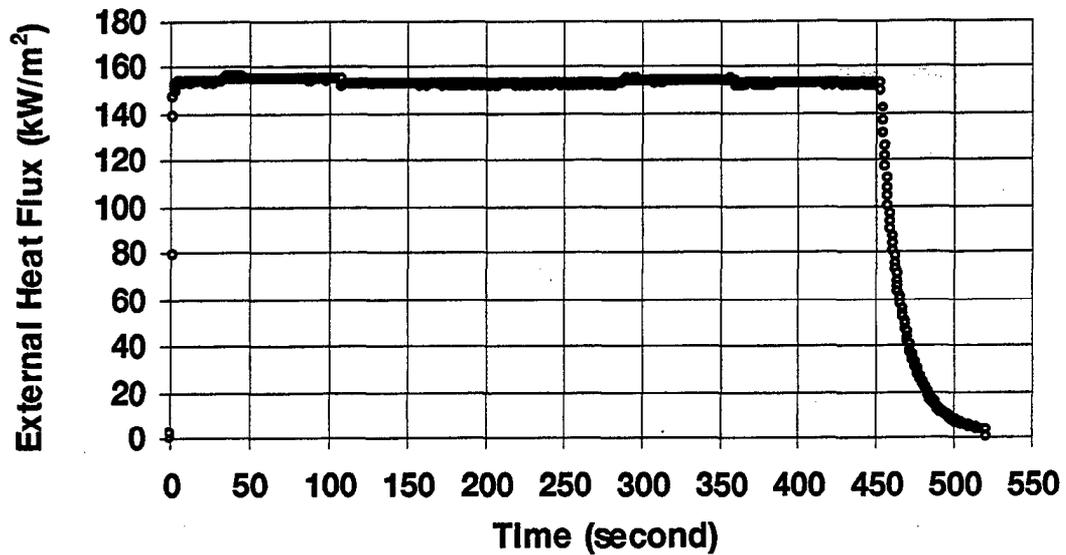
**2.3 Heat Flux.** The maximum heat flux at the center of the exposure zone vs. time in the HEF calorimeter is shown in Figure 5. Figure 6 shows the heat flux, also at the center of the exposure zone, at the maximum voltage (140 V) vs. the controller setting. The external heat flux in Figure 5 remains fairly constant for the exposure duration in the HEF calorimeter with an average value of  $153 \text{ kW/m}^2 \pm 1\%$ . The external heat flux increases rapidly as the power is turned on (time - 0 s in the figure) and decreases as the power is turned off (450 s). The maximum heat flux that can be achieved in the HEF calorimeter is close to  $158 \text{ kW/m}^2$  (Figure 6).

**Table 1. Component Details of the HEF Calorimeter**

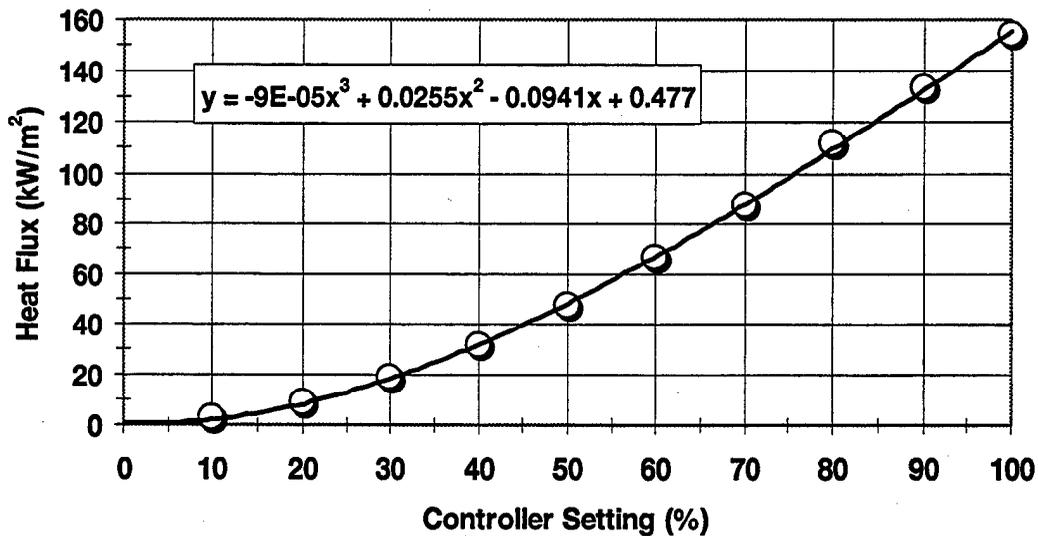
Components	Details	Manufacturer
Heaters	<ol style="list-style-type: none"> <li>1. 5305-05 heaters with tungsten-quartz lamps with 1.15-<math>\mu</math> spectral energy peak at rated voltage (2200° C) Overall length: 9.80 in. Heated length: 6 in. Heated Width: 1.5 in. Uniform heating area: 5 in long <math>\times</math> 1 in wide</li> <li>2. Lamp plate</li> <li>3. Lamp clamps - two</li> <li>4. Lamp supports - three</li> <li>5. Replacement lamps</li> <li>6. Variable output transformers - three</li> <li>7. Power cords, skirts, fittings - three</li> <li>8. Safety shield no. 1 - two</li> <li>9. Safety shield no. 2 - two</li> <li>10. Thumbscrews and shield material</li> <li>11. Shield connectors</li> <li>12. Shield support rods - four</li> <li>13. Fitting and lines for water cooling</li> <li>14. Full lamp support plate</li> <li>15. Cooling fan</li> </ol>	<p>Parabolic Strip Research Inc.</p> <p>Elks Manufacturing Elks Manufacturing Elks Manufacturing Research Inc. McMaster-Carr McMaster-Carr Elks Manufacturing Elks Manufacturing McMaster-Carr Elks Manufacturing Deadal Hartford Valve &amp; Fitting Elks Manufacturing McMaster-Carr</p>
Load Cell and Sample Support	<ol style="list-style-type: none"> <li>1. 200-g load cell (4850-154850-000-20)</li> <li>2. Signal conditioning package</li> <li>3. Load cell top bar</li> <li>4. Load cell bottom bar</li> <li>5. Bearing support</li> <li>6. Linear bearings - two</li> <li>7. Shaft - 20 in tall, 0.25 in diameter</li> <li>8. Melt catch no. 1</li> <li>9. Melt catch no. 2</li> <li>10. Sample holders</li> <li>11. Shaft machining</li> <li>12. Misc. electronic components</li> <li>13. Ceramic sphere</li> </ol>	<p>GSE</p> <p>—</p> <p>Elks Manufacturing Elks Manufacturing Elks Manufacturing McMaster-Carr McMaster-Carr Elks Manufacturing Elks Manufacturing Elks Manufacturing Elks Manufacturing Newark Electronics McMaster-Carr</p>
Support Body (10 in tall; bottom diameter: 4 in; top diameter: 7 in)	<ol style="list-style-type: none"> <li>1. Baseplate material</li> <li>2. Baseplate machining</li> <li>3. Drilled fittings</li> <li>4. Aluminum fixture</li> <li>5. Support rods - four</li> <li>6. Misc. fittings, fasteners, nuts, bolts</li> <li>7. Shaft support cylinder</li> <li>8. Air distribution tubes (3/8-in copper tubing with drilled holes)</li> </ol>	<p>McMaster-Carr Elks Manufacturing Elks Manufacturing Elks Manufacturing Oriol McMaster-Carr Elks Manufacturing —</p>

**Table 1. Component Details of the HEF Calorimeter (Continued)**

Components	Details	Manufacturer
Pyrex Glass Tube	1. Kimax process pipe - 8 in id × 18 in long	Ace Glass
	2. Process pipe coupler	Ace Glass
	3. RTV rubber gasket	McMaster-Carr
	4. Exhaust duct	—
Pilot Torch (3-mm Stainless Steel Tube)	1. Mini torch and tip extensions	Smith Equipment
	2. Flash arrestors	Local welding supply
	3. Fuel/air support hose	Local welding supply
	4. Fittings	Hartford Valve & Fitting



**Figure 5. Maximum External Heat Flux at the Sample Surface in the HEF Calorimeter. The Heat Flux Was Turned on at Time Zero and Was Turned Off at 450 s.**



**Figure 6. Heat Flux From the Radiant Heaters at the Center of the Exposure Zone at the Maximum Voltage (140 V) as a Function of the Controller Setting in the HEF Calorimeter.**

The variations of the maximum heat flux along the length and width of the exposure zone are shown in Figures 7 and 8, respectively. The average maximum heat flux for the exposure zone lengths of 2.5 in (60 mm), 3.2 in (80-mm), and 5 in (120 mm) are  $148 \pm 3\%$ ,  $145 \pm 5\%$ ,  $135 \pm 13\%$  kW/m<sup>2</sup>, respectively (Figure 7). The average maximum heat flux for an exposure zone width of 0.8 in (20 mm) is  $148 \pm 4\%$  (Figure 8).

**2.4 Operation of the HEF Calorimeter.** Diagrams, photographs, operating steps, and a list of components associated with the HEF calorimeter were submitted for the FMRC's HAZOP (Hazard and Operability) study by Advanced Fuel Research [7]. Based on the review of the documents, FMRC performed the HAZOP study of the HEF calorimeter [8, 9]. This safety review information is presented in Appendix C.

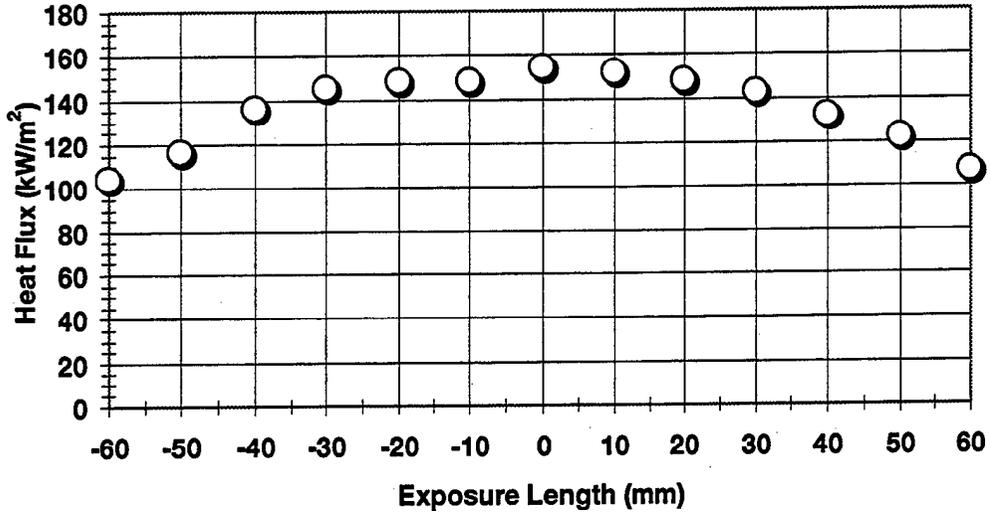


Figure 7. Heat Flux at the Maximum Power at the Center of the Exposure Zone vs. the Length of the Exposure Zone in the HEF Calorimeter.

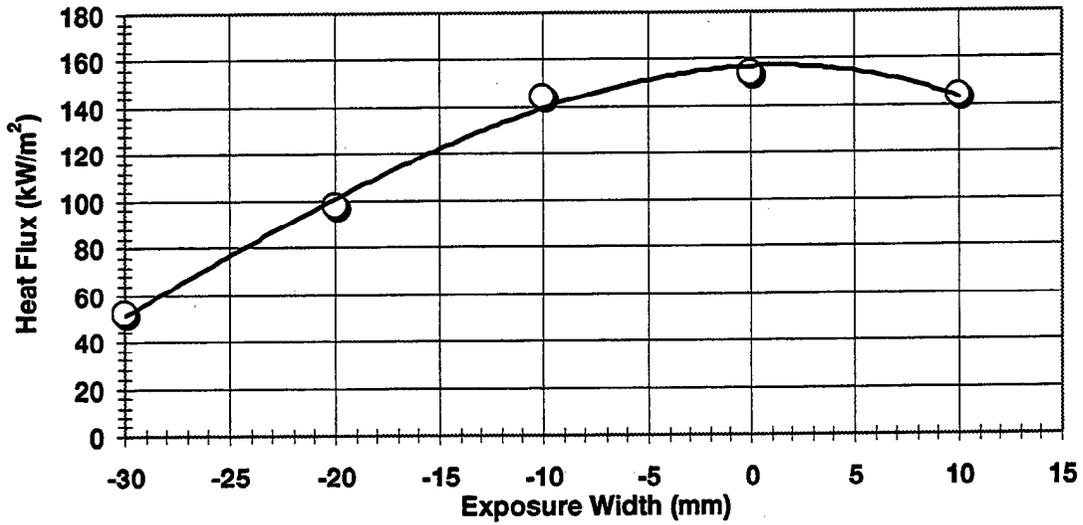


Figure 8. Heat Flux at the Maximum Power at the Center of the Exposure Zone vs. the Width of the Exposure Zone in the HEF Calorimeter.

### 3. Test Polymers and Experimental Data

**3.1 Polymer Samples Used in the Study.** In this study, two halogenated polymers, four high-temperature polymers, and six thermoplastics (ordinary polymers) were examined to test the operation of the HEF calorimeter.<sup>4</sup> The polymers are listed in Table 2.

**Table 2. Commercial Polymers Used in the Study**

Sample	Polymer	Symbol	Dimensions (mm)			Weight (g)
			Length	Width	Thickness	
Halogenated Polymers						
1	Poly (vinylchloride) (rigid)	PVC	127	16	9	25.15
2	Poly (vinylidene fluoride)	PVDF	126	17	6	16.48
High-Temperature Polymers						
3	Phenolic	Phenolic	128	15	4	11.49
4	Polyetherimide	PEI	127	16	3	7.98
5	Polypropylene (modified)	PP	126	16	6	12.38
6	S2 glass-epoxy composite <sup>a</sup>	None	128	17	6	23.04
Thermoplastics (Ordinary Polymers)						
7	Polyethylene	PE	127	15	6	10.98
8	Polypropylene-1	PP	133	17	3	5.57
9	Polypropylene-2	PP	128	17	3	4.59
10	Fire-retarded polypropylene-3	FRPP	132	17	5	10.29
11	Polycarbonate	PC	126	17	4	7.80
12	Filled polyester <sup>b</sup>	FPST	125	17	4	9.68

<sup>a</sup>Sample was used for ignition tests only. Mass loss was not measured.

<sup>b</sup>64% (CaCO<sub>3</sub>).

<sup>4</sup>In the study, measurements were made for only time to ignition and mass loss rate in pyrolysis and combustion. Products were analyzed qualitatively by the FTIR spectrometer.

The fire parameters of the polymers, measured in the FMRC flammability apparatus, are listed in Table 3. The halogenated and high-temperature polymers are inherently fire resistant, whereas the thermoplastics (ordinary polymers) are weakly fire resistant.

The polymers selected for the study are expected to burn with different efficiencies (Tables 3, A-1, and A-2), which are listed in Table 4. The combustion efficiency is the ratio of the chemical heat of combustion (measured) to the net heat of complete combustion (theoretical), and the release efficiency of a product is the ratio of the yield of the product to its theoretical yield.

The halogenated polymers have lower combustion efficiency, lower CO<sub>2</sub> release efficiency, and higher CO and smoke release efficiencies compared to the high-temperature and ordinary thermoplastics. Combustion efficiency of halogenated polymers is close to 0.30, indicating predominance of nonflaming combustion (mostly white/gray vapors with intermittent flames) [5, 6]. High combustion and CO<sub>2</sub> release efficiencies and low CO and smoke release efficiencies, such as for high-temperature polymers and ordinary thermoplastics, are indicators of predominance of flaming combustion.

**3.2 Time-to-Ignition and Mass Loss Measured in the HEF Calorimeter.**<sup>5</sup> The mass loss vs. time measured by a load in the HEF-calorimeter is shown in Figures 9–19 for the polymers selected for the study. Initial weight and mass loss reported in the figure captions were determined by a laboratory balance. Time to ignition for each polymer corresponds closely to the time for the initiation of mass loss in the figure for the polymer.

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<sup>5</sup>Data were not measured for sample no. 6.

**Table 3. Fire Parameters of Polymers Selected for Testing in the HEF Calorimeter<sup>a</sup>**

Polymer Type	Highly Halogenated		High Temperature				Ordinary Thermoplastics					
Sample No.	1	2	3	4	5	6	7	8	9	10	11	12
Polymer/ Property	PVC	PVDF	Phenolic	PEI	Mod-PP	Epoxy	PE	PP	PP	FR-PP	PC	FPST
CHF	20	30	15	25	25	20	15	15	15	10	20	20
TRP	603	465	635	435	1029	1000	454	333	415	310	357	483
$\Delta H_g$	2.5 <sup>b</sup>	2.5 <sup>b</sup>	5.4 <sup>b</sup>	3.4 <sup>b</sup>	6.9 <sup>b</sup>	—	0.93 <sup>b</sup>	1.1 <sup>b</sup>	0.90 <sup>b</sup>	2.0 <sup>b</sup>	1.1 <sup>b</sup>	2.1 <sup>b</sup>
$\Delta H_{ch}$	4.9	4.0	16.3	27.1	29.3	—	32.7	35.5	33.3	25.8	20.2	25.5
$y_{CO}$	0.055	0.054	0.032	0.026	0.011	—	0.032	0.056	0.080	0.040	0.051	0.061
$y_{CO_2}$	0.580	0.504	1.37	2.03	2.46	—	2.33	2.52	2.51	2.01	1.86	1.86
$y_{Smoke}$	0.070	0.060	0.012	0.019	0.063	—	0.042	0.080	0.108	0.091	0.105	0.100
HRP	2	2	3	8	13	—	35	32	37	13	8	12
PRP <sub>CO</sub>	0.022	0.027	0.006	0.008	0.005	—	0.036	0.051	0.084	0.024	0.065	0.029
PRP <sub>CO<sub>2</sub></sub>	0.232	0.252	0.254	0.597	1.07	—	2.65	2.29	2.64	1.18	2.35	0.886
PRP <sub>Smoke</sub>	0.028	0.030	0.002	0.006	0.027	—	0.048	0.073	0.114	0.054	0.133	0.048
FPI	4	6	5	8	5	—	16 <sup>b</sup>	21 <sup>b</sup>	18 <sup>b</sup>	17 <sup>b</sup>	16 <sup>b</sup>	10 <sup>b</sup>

<sup>a</sup>Part of the data taken from Tewarson et al. [3–6].

<sup>b</sup>From Tewarson [5].

- Notes: CHF: Critical heat flux (kW/m<sup>2</sup>).  
 TRP: Thermal response parameter (kW-s<sup>1/2</sup>/m<sup>2</sup>).  
 $\Delta H_g$ : Heat of gasification (kJ/g).  
 $\Delta H_{ch}$ : Heat of combustion (kJ/g).  
 $y_j$ : Yield of product j (g/g).  
 CI: Corrosion index (A/min)/(g/m<sup>3</sup>).  
 HRP: Heat release parameter (kJ/kJ).  
 PRP: Product release parameter (g/kJ).  
 FPI: Fire propagation index (m/s<sup>1/2</sup>)/(kW/m)<sup>2/3</sup>.  
 nm: Not measured.

**Table 4. Combustion Efficiency and Release Efficiencies of Products for Polymers Selected for Testing in the HEF Calorimeter**

Polymer Type	Highly Halogenated		High Temperature			Ordinary Thermoplastics					
Sample No.	1	2	3	4	5	7	8	9	10	11	12
Polymers	PVC	PVDF	Phenolic	PEI	Mod-PP	PE	PP	PP	PP	PC	PST
Combustion Efficiency	0.30	0.30	0.42	0.90	0.68	0.75	0.82	0.77	0.59	0.64	0.78
CO Release Efficiency	0.061	0.061	0.017	0.014	0.0055	0.016	0.028	0.040	0.020	0.027	0.064
CO <sub>2</sub> Release Efficiency	0.41	0.37	0.47	0.72	0.78	0.74	0.80	0.80	0.64	0.63	0.78
Smoke Release Efficiency	0.18	0.16	0.024	0.025	0.073	0.049	0.093	0.13	0.11	0.13	0.25

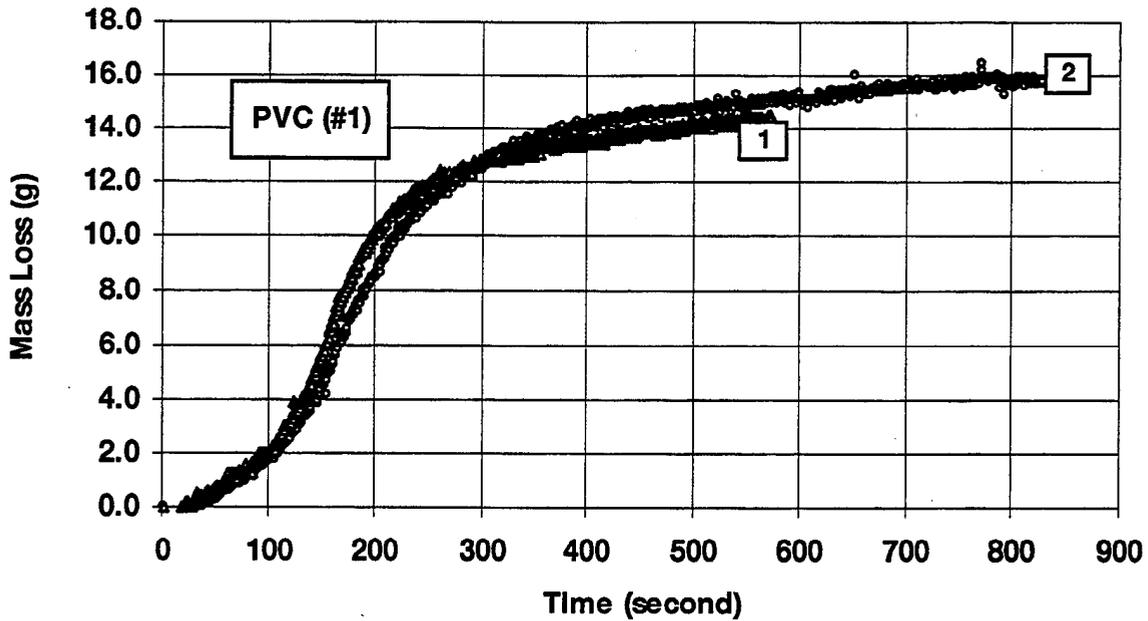


Figure 9. Mass Loss in the Combustion of Halogenated Polymer: Rigid Poly (Vinylchloride) (Sample No. 1) in the HEF Calorimeter in Normal Air at  $150 \text{ kW/m}^2$ . 1 and 2 Represent Repeat Tests. Average Initial Weight: 24.5 gm; Mass Loss: (1) 14.9 gm and (2) 16.2 gm.

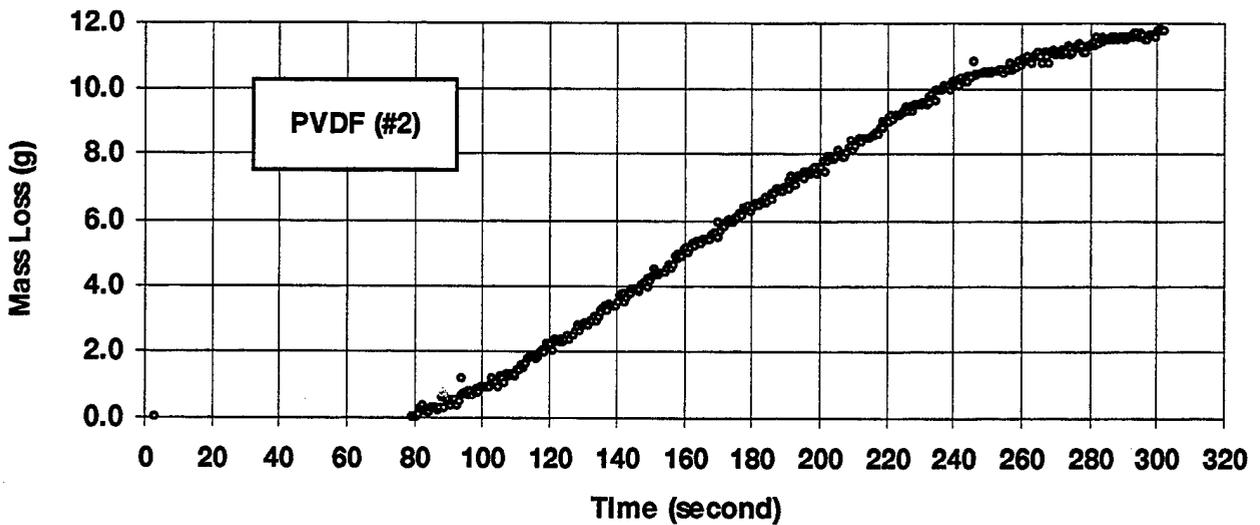


Figure 10. Mass Loss in the Combustion of Highly Halogenated Polymer Poly (Vinylidene fluoride) (Sample No. 2) in the HEF Calorimeter in Normal Air at  $150 \text{ kW/m}^2$ . Initial Weight: 16.5 gm; Mass Loss: 11.7 gm.

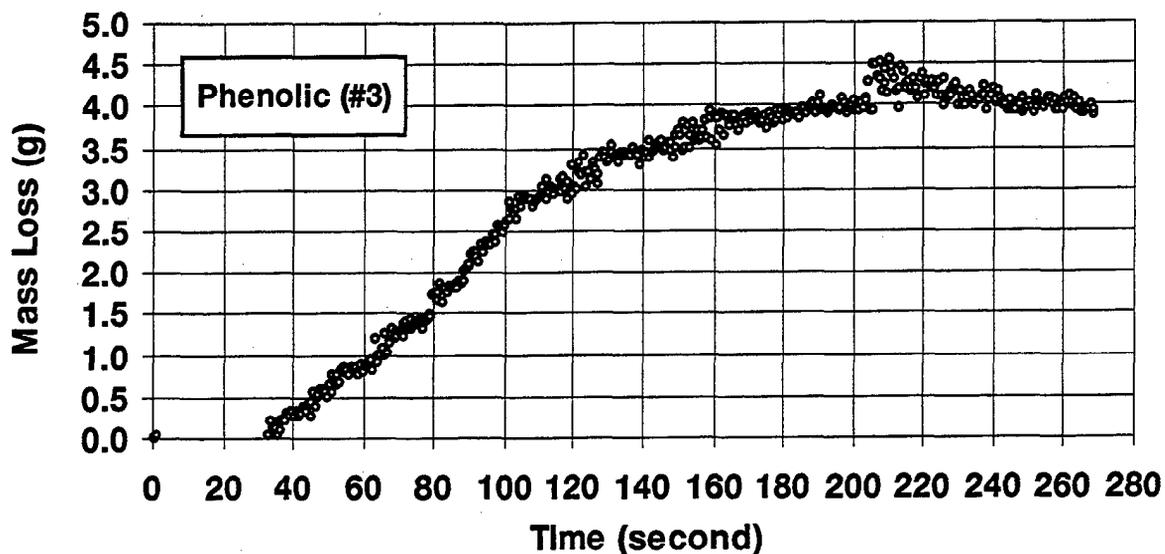


Figure 11. Mass Loss in the Combustion of High-Temperature Polymer Phenolic (Sample No. 3) in the HEF Calorimeter in Normal Air at  $150 \text{ kW/m}^2$ . Initial Weight: 11.5 g; Mass Loss: 4.3 gm.

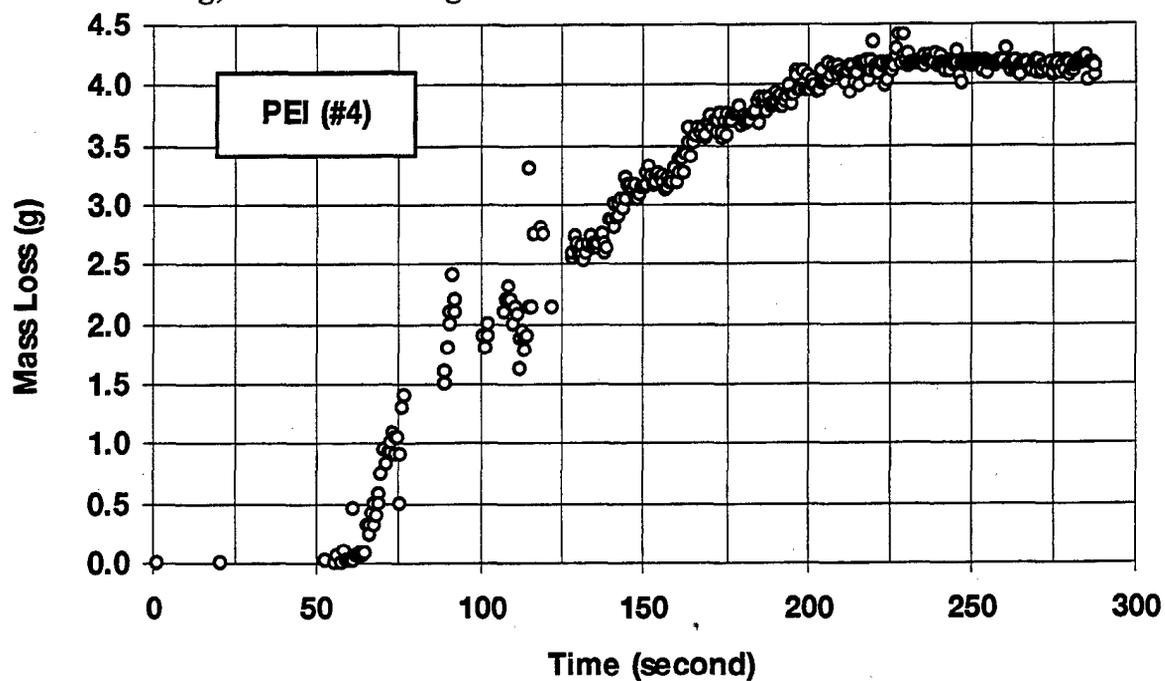


Figure 12. Mass Loss in the Combustion of High-Temperature Polymer Polyetherimide (Sample No. 4) in the HEF Calorimeter in Normal Air at  $150 \text{ kW/m}^2$ . Initial Weight: 8.0 gm; Mass Loss: 4.2 gm. The Scattering of the Data Between About 75 and 125 s Is Due to the Sample Touching the Pyrex Glass Tube as It Was Softening.

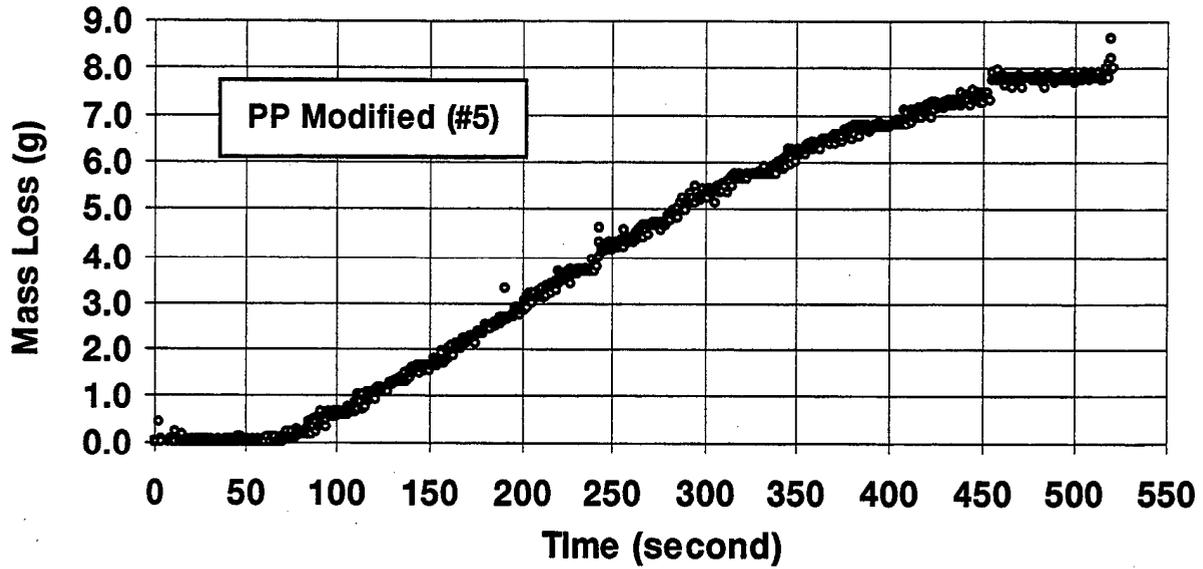


Figure 13. Mass Loss in the Combustion of High-Temperature Polymer Modified PP (Sample No. 5) in the HEF Calorimeter in Normal Air at  $150 \text{ kW/m}^2$ . Initial Weight: 12.4 g; Mass Loss: 8.4 gm.

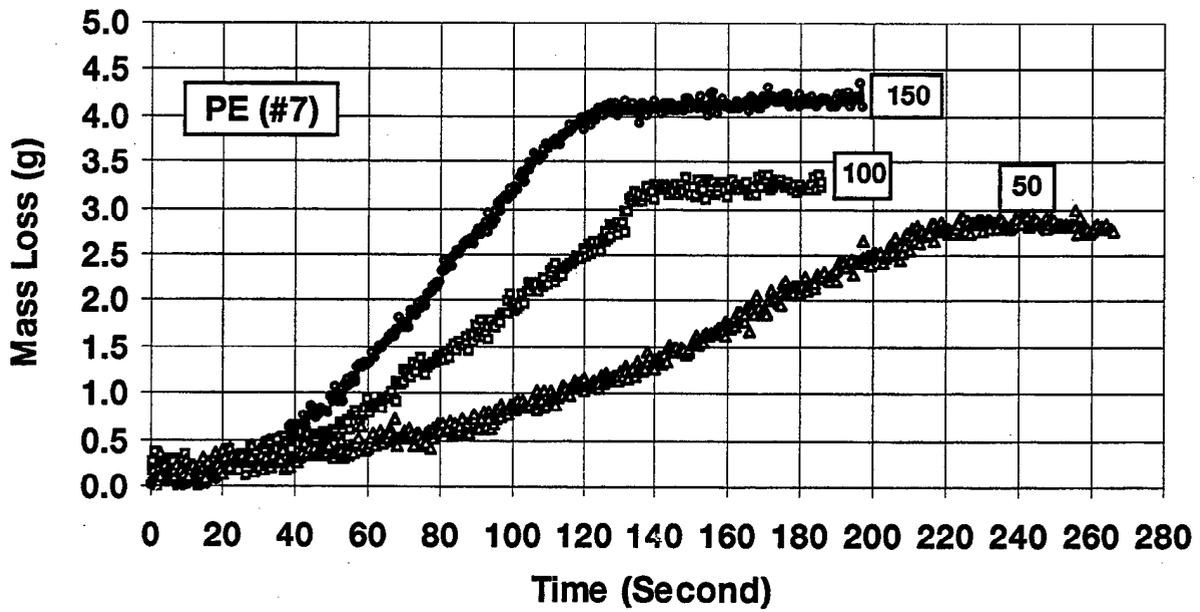


Figure 14. Mass Loss in the Combustion of Ordinary Polymer PE (Sample No. 7) in the HEF Calorimeter in Normal Air at 50, 100, and  $150 \text{ kW/m}^2$ . Initial Weight:  $50 \text{ kW/m}^2$ : 10.6 gm;  $100 \text{ kW/m}^2$ : 11.1 gm;  $150 \text{ kW/m}^2$ : 11.2 gm.

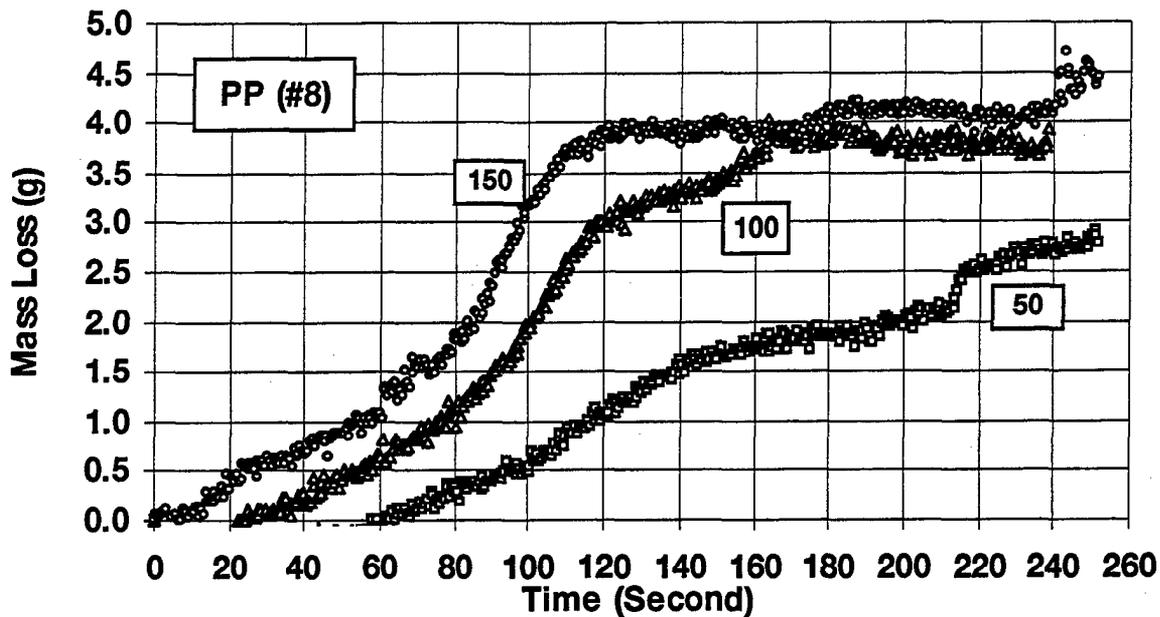


Figure 15. Mass Loss in the Combustion of Ordinary Polymer Polypropylene-1 (Sample No. 8) in the HEF Calorimeter in Normal Air at 50, 100, and 150 kW/m<sup>2</sup>. Initial Weight: 50 kW/m<sup>2</sup>: 5.3 gm; 100 kW/m<sup>2</sup>: 5.8 gm; 150 kW/m<sup>2</sup>: 5.6 gm. The Anomaly in the Data at 150 kW/m<sup>2</sup> Is Due to Loss of Sample From the Holder.

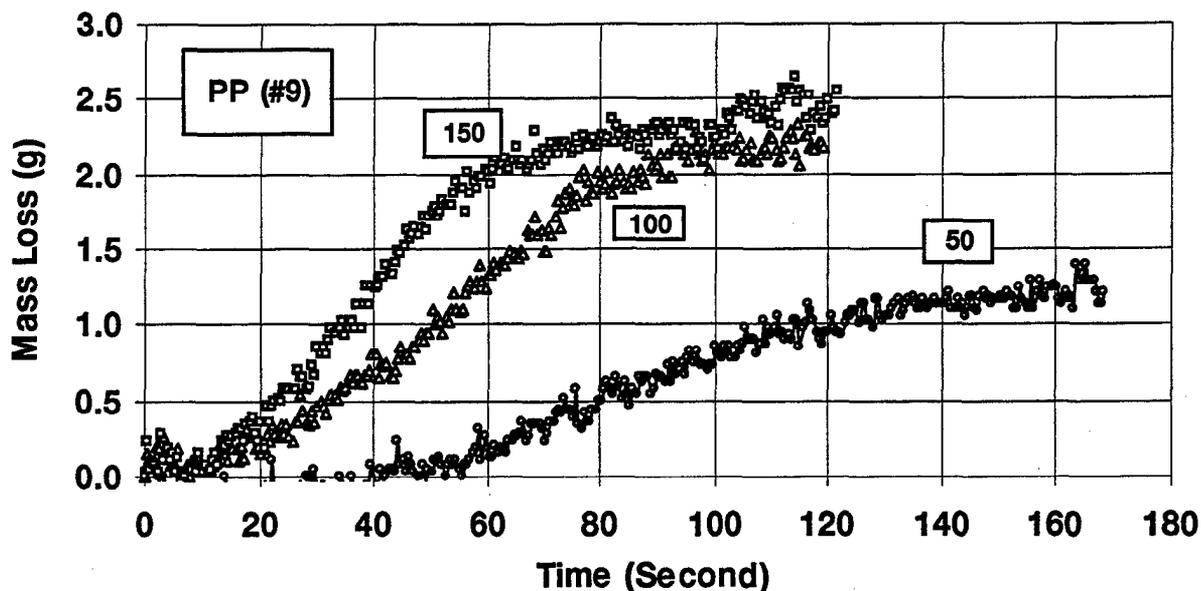


Figure 16. Mass Loss in the Combustion of Ordinary Polymer Polypropylene-2 (Sample No. 9) in the HEF Calorimeter in Normal Air at 50, 100, and 150 kW/m<sup>2</sup>. Initial Weight: 50 kW/m<sup>2</sup>: 4.4 gm; 100 kW/m<sup>2</sup>: 4.9 gm; 150 kW/m<sup>2</sup>: 4.5 gm.

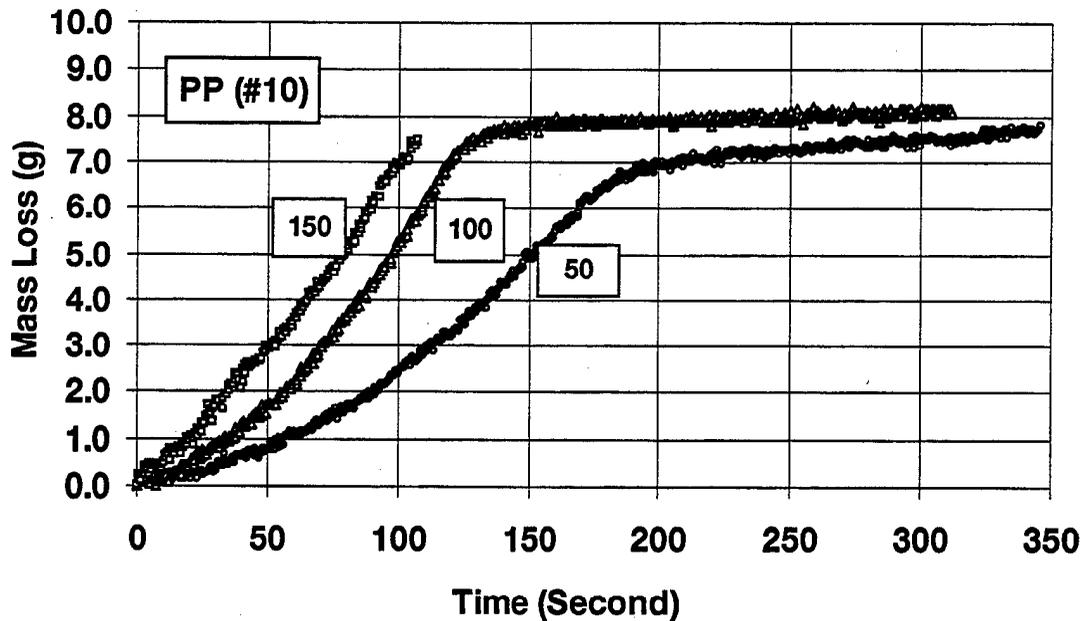


Figure 17. Mass Loss in the Combustion of Ordinary Fire-Retarded Polymer Polypropylene-3 (Sample No. 10) in the HEF Calorimeter in Normal Air at 50, 100, and 150 kW/m<sup>2</sup>. Initial Weight: 50 kW/m<sup>2</sup>: 10.3 gm; 100 kW/m<sup>2</sup>: 10.7 gm; 150 kW/m<sup>2</sup>: 9.9 gm.

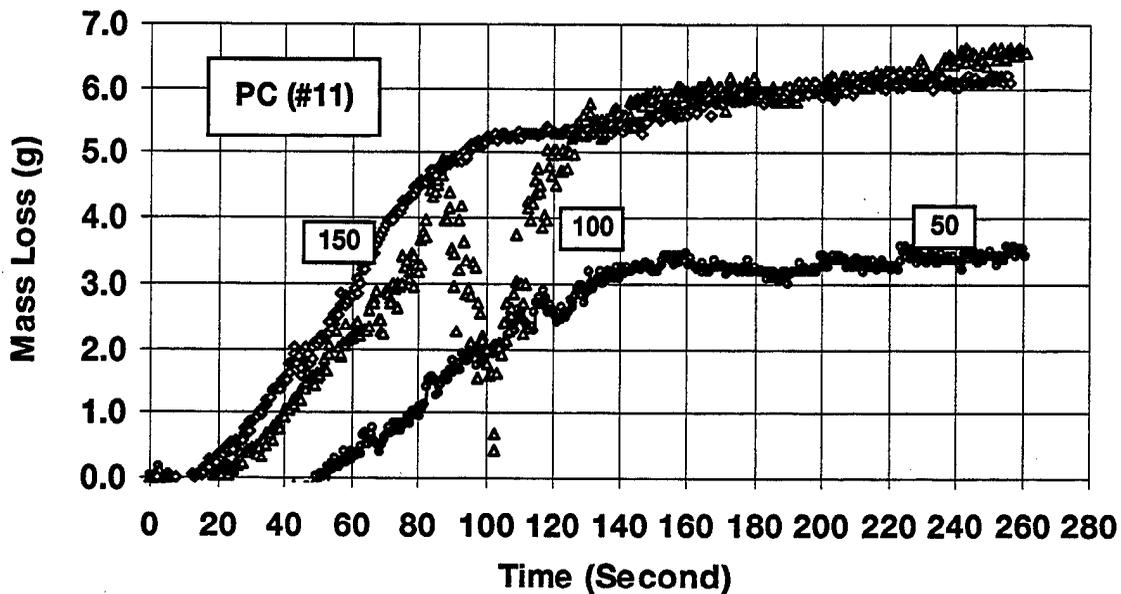
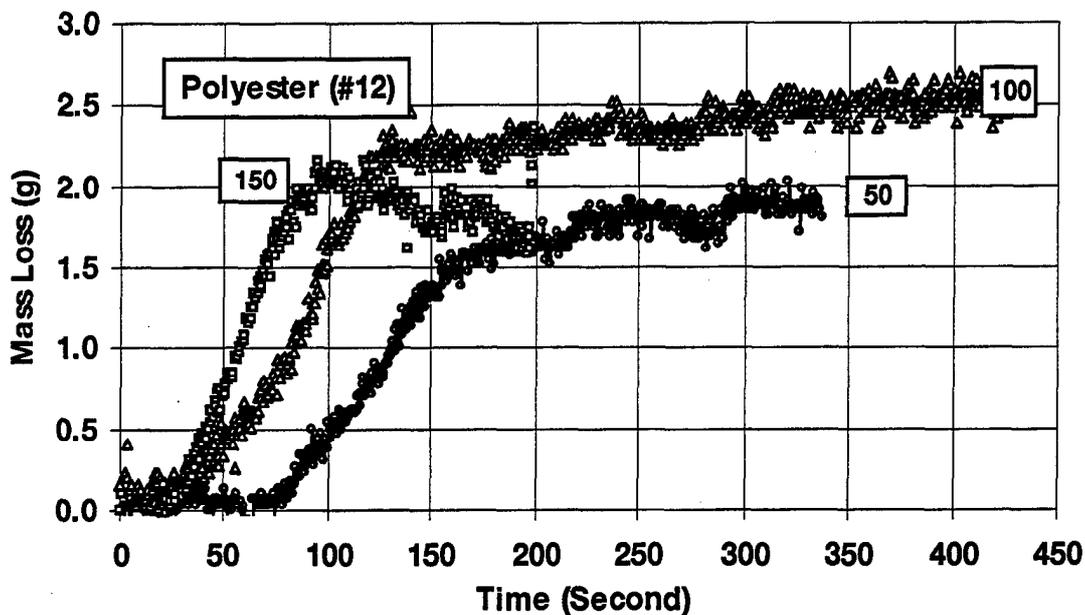


Figure 18. Mass Loss in the Combustion of Ordinary Polymer Polycarbonate (Sample No. 11) in the HEF Calorimeter in Normal Air at 50, 100, and 150 kW/m<sup>2</sup>. At 100 kW/m<sup>2</sup> Between 90 and 110 s, the Fire Had Almost Gone Out, but There Was Auto-Ignition and Combustion for a Short Time. Initial Weight: 50 kW/m<sup>2</sup>: 7.9 gm; 100 kW/m<sup>2</sup>: 8.2 gm; 150 kW/m<sup>2</sup>: 7.3 gm. The Scatter of 100 kW/m<sup>2</sup> Data Between About 80 and 120 s Is Due to the Sample Touching the Pyrex Glass Tube.



**Figure 19. Mass Loss in the Combustion of Ordinary Polymer Polyester (Sample No. 12) in the HEF Calorimeter in Normal Air at 50, 100, and 150 kW/m<sup>2</sup>. Initial Weight: 50 kW/m<sup>2</sup>: 9.8 gm; 100 kW/m<sup>2</sup>: 9.6 gm; 150 kW/m<sup>2</sup>: 9.6 gm. The Anomaly for the 150 kW/m<sup>2</sup> Data Is Due to Loss of Sample From the Holder.**

A comparison of the data for total mass loss and residue in the combustion of the polymers from the HEF calorimeter, measured by the load cell and by the laboratory balance, is reported in Table 5 (also in Figures 9–19). The load cell and the laboratory balance provide very similar data.

Data in Table 5 show that a significant amount of residue is formed even at 150 kW/m<sup>2</sup> by the halogenated and high-temperature polymers, an inherent property of these types of polymers. The thermoplastics either melt or soften, except sample 12, which is a nonmelting type polymer due to the presence of large amounts of CaCO<sub>3</sub>. Thus, during combustion, most of the mass of the melting polymers dripped away or was collected in the drip pan in the HEF calorimeter, which could not be distinguished as a loss by the load cell. For the softening polymers, part of the polymer mass was collected in the drip pan. Sample no. 12 with 64% CaCO<sub>3</sub> was found to char with the amount of residue higher than the mass of CaO (decomposition product of CaCO<sub>3</sub>).

**Table 5. Total Mass Loss and Total Residue in the Combustion of Polymers in the HEF Calorimeter**

Sample	Heat Flux (kW/m <sup>2</sup> )	Initial Weight (gm)	Mass Loss (gm)		Residue (%)	
			Load Cell	Balance	Load Cell	Balance
<b>Halogenated Polymers</b>						
1 (PVC)	150	24.5	14.5; 16.0	14.9; 16.2	41; 36	39; 34
2 (PVDF)	150	16.5	11.8	11.7	29	29
<b>High-Temperature Polymers</b>						
3 (Phenolic)	150	11.5	4.3	4.3	63	63
4 (PEI)	150	8.0	4.3	4.2	46	48
5 (PP)	150	12.4	8.2	8.4	36	32
<b>Ordinary Polymers (Thermoplastics)</b>						
7 (PE) - melting type	50	10.6	2.9	Most of the polymer melted rapidly and dripped away or collected in the drip pan.		
	100	11.1	3.3			
	150	11.2	4.3			
8 (PP) - melting type	50	5.3	4.0	Most of the polymer melted rapidly and dripped away or collected in the drip pan.		
	100	5.8	4.5			
	150	5.6	2.9			
9 (PP) - melting type	50	4.4	2.5	Most of the polymer melted rapidly and dripped away or collected in the drip pan.		
	100	4.9	2.5			
	150	4.5	1.3			
10 (PP) - softening type	50	10.3	NM	Rapid softening. Part of the polymer collected in the drip pan.		
	100	10.7	8.0			
	150	9.9	7.9			
11 (PC) - softening type	50	7.9	6.5	Rapid softening. Part of the polymer collected in the drip pan.		
	100	8.2	6.2			
	150	7.3	3.4			
12 (polyester) - 64% CaCO <sub>3</sub> - nonmelting	50	9.8	2.5	NM	75	NM
	100	9.6	2.5	NM	74	NM
	150	9.6	2.0	NM	79	NM

Note: NM - not measured.

**3.3 Qualitative Analysis of Combustion Products in the HEF Calorimeter by the FTIR Spectrometer.** The location of the FTIR spectrometer used in the study is shown in Figure 1. The mixture of combustion products and air was extracted from the sampling duct and directed into the cell of the FTIR spectrometer. The cell had mirrors on the opposite sides of the sampling duct. A clean gas flow was maintained over the mirrors for optical integrity. The mirrors on the opposite

sides of the sampling duct provided a long effective path length for good sensitivity for the measurements of trace compounds.

The analysis of combustion products by the FTIR spectrometer is based on the fact that every molecule, except homonuclear diatomics, has a unique set of rotational and vibrational frequencies that absorb and emit infrared energy in a characteristic manner. The absorbed infrared energy can be recorded as infrared absorption bands from the range of about  $500\text{ cm}^{-1}$  ( $20\text{ }\mu\text{m}$ )– $5000\text{ cm}^{-1}$  ( $2\text{ }\mu\text{m}$ ). The location and magnitude of the infrared absorption bands can be used to identify a variety of compounds and quantify their concentrations over a very wide range, from sub-ppm to percent.

The FTIR spectrometer calibration requires the generation of a spectral library containing all the compounds of interest over a range of concentrations. This library is usually generated only once and can be used over the life of the instrument. When analysis for a new compound is desired, it is a simple matter of measuring a new set of references for that compound. In order to verify the calibration on a day-to-day basis, only one or two calibration compounds need to be analyzed to verify proper operation of the spectrometer.

Figure 20 shows an example of typical FTIR spectrometer data obtained from the combustion of PVC in the HEF calorimeter.

## 4. Analysis

**4.1 Ignition.** For each polymer, there is a characteristic relationship between the time to ignition and external heat flux. When the surface of a polymer is exposed to heat flux, a thermal wave penetrates the interior of the polymer to different depths, depending on the thermally thick or thermally thin behavior.

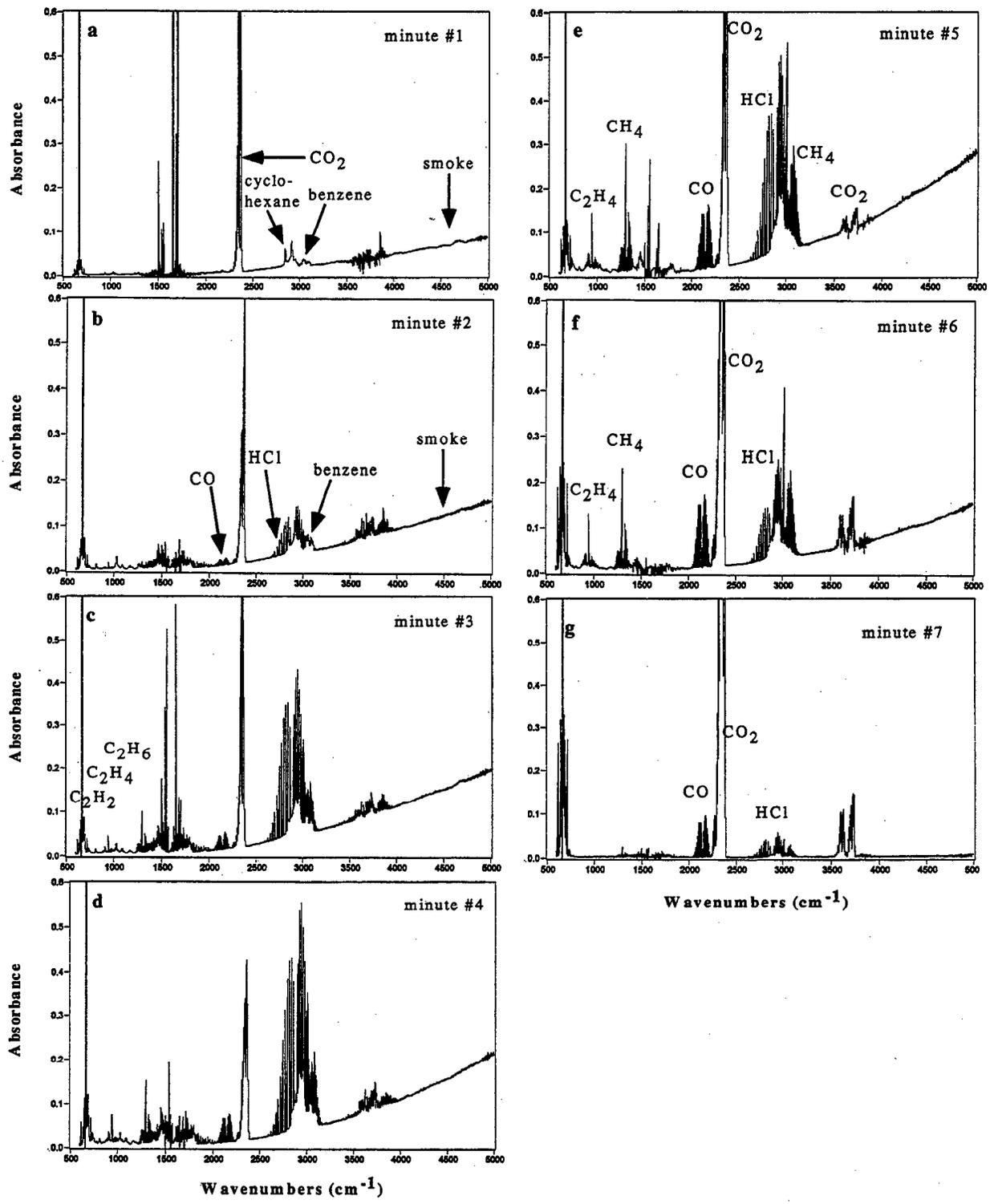


Figure 20. FTIR Spectrometer Data for the Combustion Products of PVC Burning in the HEF Calorimeter.

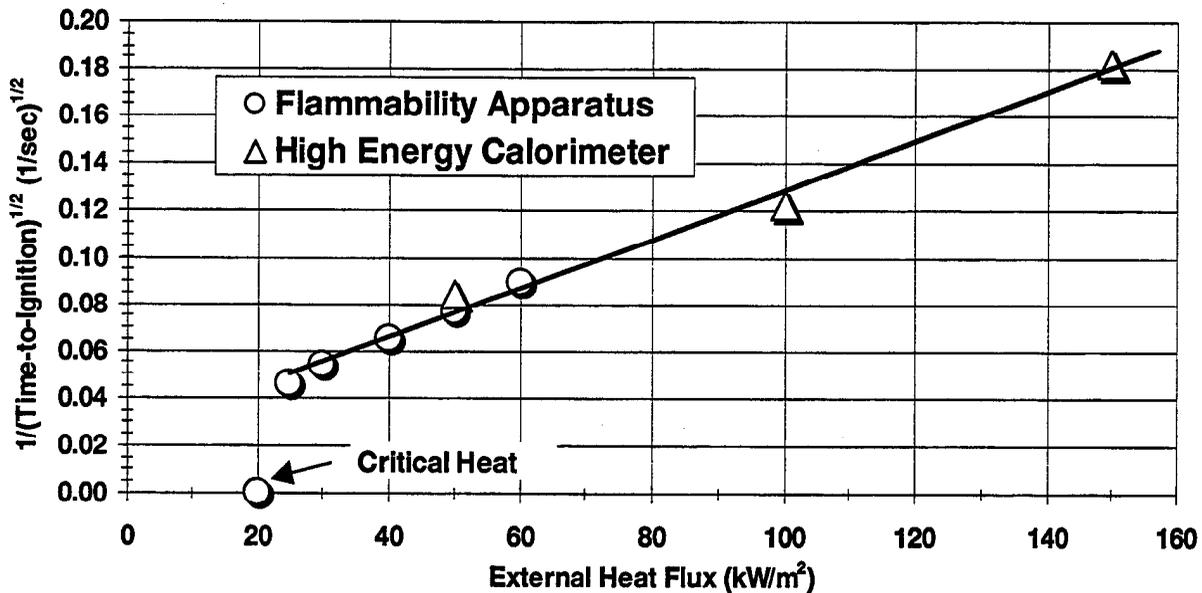
A polymer sample is *thermally thick* if the thermal penetration depth ( $\delta$ ) is less than the actual thickness of the sample. The thermal penetration depth is expressed as the square root of the product of thermal diffusivity ( $\alpha$  in  $\text{m}^2/\text{s}$ ) and exposure time ( $t$  in sec), i.e.,  $\delta \approx \sqrt{\alpha t}$  [10]. The thermal diffusivity,  $\alpha$ , is  $k/\rho c_p$ , where  $k$  is the thermal conductivity of the material ( $\text{kW}/\text{m}\cdot\text{K}$ ),  $\rho$  is the density of the material ( $\text{g}/\text{m}^3$ ), and  $c_p$  is the heat capacity of the material ( $\text{kJ}/\text{g}\cdot\text{K}$ ). When the thermal penetration depth is much greater than the actual thickness of the polymer sample, it behaves as *thermally thin* material. The actual thickness of each test sample used in the study (see Table 2) was expected to satisfy the thermally thick condition for the range of heat fluxes used in the study.

For a thermally thick polymer, inverse of the square root of time to ignition is a linear function of the applied heat flux and the inverse of the slope is defined as the TRP for the thermally thick polymer sample ( $\text{TRP}_{\text{thick}}$ ), which is modeled as  $\Delta T_{\text{ig}} (\pi k \rho c_p / 4)^{1/2}$  [5, 6]. This relationship holds for applied heat flux values away from the CHF value, defined as a flux at or below which there is no ignition.

For a thermally thin polymer, inverse of the time to ignition is a linear function of the applied heat flux and the inverse of the slope is defined as the TRP for the thermally thin polymer ( $\text{TRP}_{\text{thin}}$ ).  $\text{TRP}_{\text{thin}}$  is modeled as  $\rho c_p d \Delta T_{\text{ig}}$ , where  $d$  is the sample thickness (m) and  $\Delta T_{\text{ig}}$  is the ignition temperature above ambient (K).

Ignition data for the glass-epoxy composite sample no. 6, measured in the HEF calorimeter, are plotted in Figure 21 along with the ignition data measured in the FMRC flammability apparatus. The ignition data from the HEF Calorimeter correlate with the ignition data from the FMRC flammability apparatus, as expected.

From the inverse of the slope in Figure 21, the TRP value for the glass-epoxy composite sample no. 6 is  $1000 \text{ kW}\cdot\text{s}^{1/2}/\text{m}^2$  and  $\text{CHF} = 20 \text{ kW}/\text{m}^2$  (these values agree with the values from the FMRC flammability listed in Table 3).



**Figure 21.** Ignition Data Measured in the HEF Calorimeter and the FMRC Flammability Apparatus for the Glass-Epoxy Composite (Sample No. 6). TRP = 1000 kW-s<sup>1/2</sup>/m<sup>2</sup> and CHF = 20 kW/m<sup>2</sup>.

The ignition data presented here indicate that the HEF calorimeter provides ignition data consistent with the ignition data from the FMRC flammability apparatus and extends the measurement range to heat fluxes as high as 150 kW/m<sup>2</sup>, a range needed for halogenated and high-temperature polymers with high fire resistance.

**4.2 Mass Loss Rate.** Mass loss rate for each polymer was obtained from the mass loss measured as a function of time in the HEF calorimeter. Figure 22 shows the data for PVC from the HEF calorimeter at 150 kW/m<sup>2</sup> and from the FMRC flammability apparatus at 50 kW/m<sup>2</sup>. Figure 23 shows the data for the halogenated and high-temperature polymers, and Figure 24 shows the data for an ordinary thermoplastic.

**4.2.1 Mass Loss Rate for Halogenated and High-Temperature Polymers.** The peak mass loss rates at 150 kW/m<sup>2</sup> from the HEF calorimeter are listed in Table 6, under the experimental mass loss rate column. The peak mass loss rates for the halogenated polymers are higher than they are for the

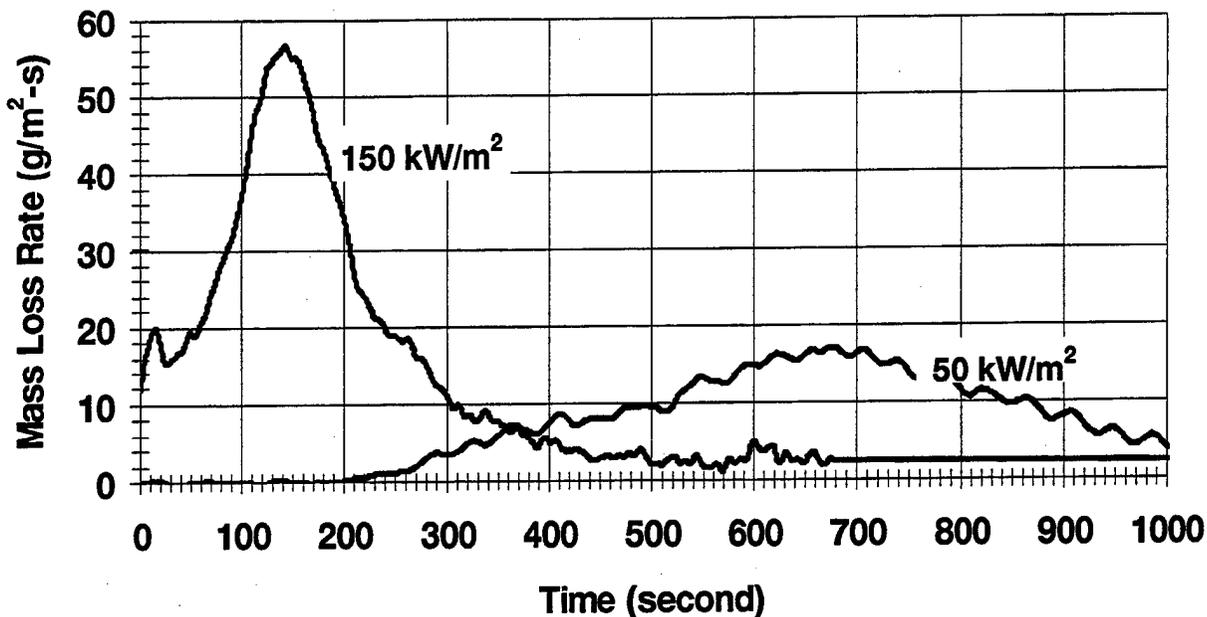


Figure 22. Mass Loss Rate Profile for the Combustion of Poly (Vinylchloride) in Normal Air at  $150 \text{ kW/m}^2$  in the HEF Calorimeter and at  $50 \text{ kW/m}^2$  in the FMRC Flammability Apparatus. Data in This Figure Are 15-s Running Averages.

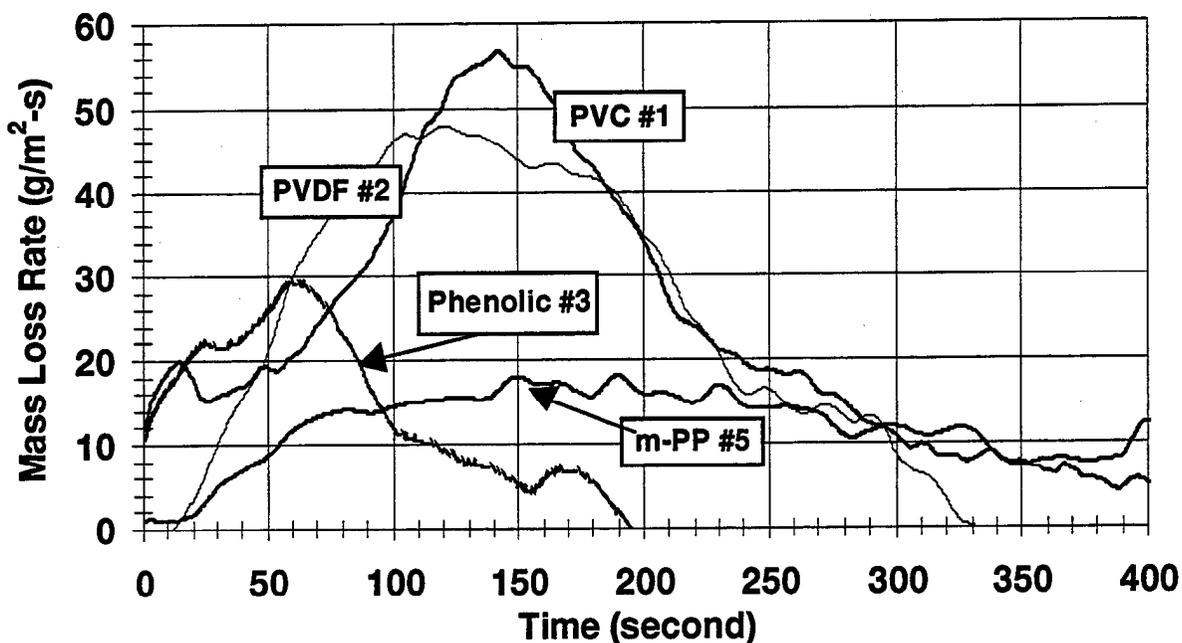


Figure 23. Mass Loss Rate Profiles for the Combustion of Halogenated and High-Temperature Polymers at  $150 \text{ kW/m}^2$  in the HEF Calorimeter. Data Reported in This Figure Are 15-s Running Averages.

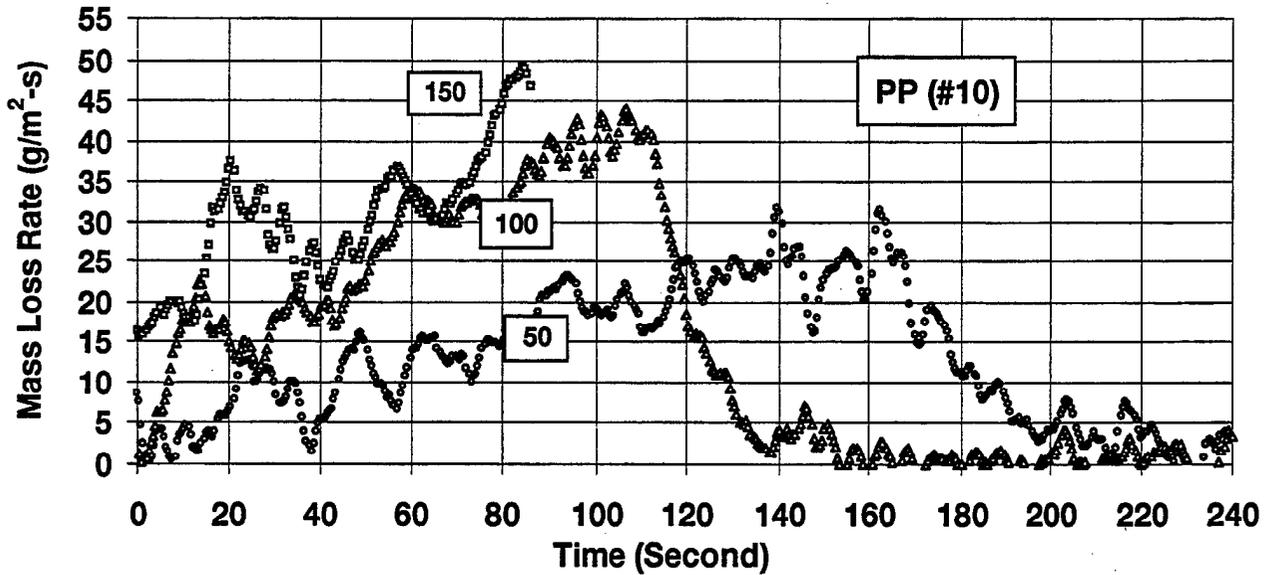


Figure 24. Mass Loss Rate in Normal Air Combustion of Fire-Retarded Polypropylene Sample No. 10 at 50, 100, and 150 kW/m<sup>2</sup> of External Heat Flux in the HEF Calorimeter. Data Reported in the Figure Are 15-s Running Averages.

Table 6. Peak Mass Loss Rates at 150 kW/m<sup>2</sup> for Halogenated and High-Temperature Polymers

Sample	Polymer	Symbol	Peak Mass Loss Rate (g/m <sup>2</sup> -s)	
			Experimental <sup>a</sup>	Calculated <sup>b</sup>
Halogenated				
1	Poly (vinylchloride), rigid	PVC	58	52
2	Poly (vinylidene fluoride)	PVDF	48	48
High Temperature				
3	Phenolic	Phenolic	29	25
5	Polypropylene (modified)	m-PP	18	18

<sup>a</sup>From the HEF calorimeter.

<sup>b</sup>From Equation 1 and data from Table 3 with an assumption that flame heat flux is negligibly small and that surface re-radiation loss is equal to the critical heat flux.

high-temperature polymers. For PVC, the peak mass loss rate at 150 kW/m<sup>2</sup> is about three times the peak mass loss rate at 50 kW/m<sup>2</sup>.

The relationship between the steady-state mass loss rate and external heat flux, flame heat flux, and surface re-radiation loss is expressed as [5, 6]:

$$\dot{m}'' = \frac{\dot{q}_e'' + \dot{q}_f'' - \dot{q}_r''}{\Delta H_g} \quad (1)$$

where  $\dot{m}''$  is the mass loss rate ( $\text{g}/\text{m}^2\text{-s}$ ),  $\dot{q}_e''$  is the external heat flux ( $\text{kW}/\text{m}^2$ ),  $\dot{q}_f''$  is the flame heat flux transferred to the surface from the burning polymer ( $\text{kW}/\text{m}^2$ ),  $\dot{q}_r''$  is the surface re-radiation loss ( $\text{kW}/\text{m}^2$ ), and  $\Delta H_g$  is the heat of gasification ( $\text{kJ}/\text{g}$ ).

Mass loss rates calculated for an external heat flux of  $150 \text{ kW}/\text{m}^2$  from Equation 1, using heat of gasification and critical heat flux values for the polymers from Tewarson [5] (Table 3), are included in Table 6 under the calculated mass loss rate column. In these calculations, it is assumed that flame heat flux is negligibly small and that surface re-radiation loss is equal to the critical heat flux.

The experimental and calculated mass loss rates at  $150 \text{ kW}/\text{m}^2$  in Table 6 for the halogenated and high-temperature polymers are in excellent agreement. These data (in Figures 22 and 23 and Table 6) indicate that the HEF calorimeter is capable of providing data consistent with the data from the FMRC flammability apparatus, but over a wider range of external heat flux values up to a maximum value of  $150 \text{ kW}/\text{m}^2$ .

**4.2.2 Mass Loss Rate for Thermoplastics.** The ordinary thermoplastics examined in the study were mostly softening- and melting-type polymers, except the polymer sample no. 12, which was a nonmelting type as it contained large amounts of  $\text{CaCO}_3$  (see Table 5). Samples no. 7 (polyethylene) and no. 8 and no. 9 (polypropylene) were melting types, and samples no. 10 (fire-retarded polypropylene) and no. 11 (polycarbonate) were softening-type polymers.

The melting-type polymers burned with melting, dripping, and pooling, whereas the softening-type polymers burned as vertical sheets maintaining their shapes, although part of the polymer mass

did collect in the drip pan. It was thus possible to define the burning area for the softening/nonmelting-type polymers and to determine the peak mass loss rates per unit surface area, which are listed in Table 7 in the rows identified "experimental." For 150 kW/m<sup>2</sup>, data are reported up to about 90 s, as beyond that time there was too much scatter in the data, possibly due to sample breaking and falling from the sample holder. Under the rows identified as calculated in Table 7, mass loss rates calculated from Equation 1 and data from Table 3 are listed. In the calculations, it was assumed that flame heat flux is negligibly small and that surface re-radiation loss is equal to the critical heat flux.

**Table 7. Peak Mass Loss Rates for Softening/Nonmelting Ordinary Thermoplastics**

Sample	Polymer	Type	Peak Mass Loss Rate (g/m <sup>2</sup> -s)		
			50 kW/m <sup>2</sup>	100 kW/m <sup>2</sup>	150 kW/m <sup>2</sup>
10	Fire-retarded polypropylene, PP-3	Experimental <sup>a</sup>	22.0	44.1	nm
		Calculated <sup>b</sup>	20.0	45.0	70.0
11	Polycarbonate, PC	Experimental	26.2	70.6	119.8
		Calculated	27.3	72.8	118.0
12	Filled polyester (commercial), PST	Experimental	14.2	40.9	65.0
		Calculated	14.3	38.1	61.9

<sup>a</sup>Experimental from the HEF calorimeter.

<sup>b</sup>Calculated from Equation 1 and data from Table 3 with an assumption that flame heat flux is negligibly small and that surface re-radiation loss is equal to the critical heat flux.

Note: nm - not measured.

The experimental and calculated mass loss rates in Table 7 for softening/nonmelting-type thermoplastics are in excellent agreement. The mass loss rate data suggest that the HEF calorimeter is capable of providing data consistent with those from the FMRC flammability apparatus for a wider range of external heat values up to a maximum of 150 kW/m<sup>2</sup>.

**4.3 Implications of Heat and Product Release From Mass Loss Measurements.** The release rates of heat and products are expressed as [5, 6]:

$$\dot{Q}_{ch}'' = \Delta H_{ch} \dot{m}'' \quad (2)$$

$$\dot{G}_j'' = y_j \dot{m}'' \quad (3)$$

where  $\dot{Q}_{ch}$  is the chemical heat release rate (kW/m<sup>2</sup>),  $\dot{G}_j$  is the release rate of product j (g/m<sup>2</sup>-s),  $\dot{m}$  is the mass loss rate (g/m<sup>2</sup>-s),  $\Delta H_{ch}$  is the chemical heat of combustion (kJ/g), and  $y_j$  is the yield of product j (g/g). Literature data listed in Table 8 indicate that the values of  $\Delta H_{ch}$  and  $y_j$  from the FMRC flammability apparatus for well-ventilated fires appear to be independent of the fire size. Thus, the values of  $\Delta H_{ch}$  and  $y_j$  from the FMRC flammability apparatus can be used along with the mass loss rates measured in the HEF calorimeter in Equations 2 and 3 to estimate release rates of heat and products under well-ventilated conditions.

The combustion tests in the HEF calorimeter were performed under well-ventilated conditions, as indicated by the equivalence ratios listed in Table 9. The values of  $\Delta H_{ch}$  and  $y_j$  for the polymers examined in the study were determined in the FMRC flammability apparatus under well-ventilated conditions (Table 3). We have thus used the mass loss rate values from the HEF calorimeter and  $\Delta H_{ch}$  and  $y_j$  for the polymers from the FMRC flammability apparatus (Table 3) in Equations 2 and 3 to estimate the release rates of heat and products up to a maximum of 150 kW/m<sup>2</sup>.

**Table 8. Literature Data for the Average Heats of Combustion and Yields of Products for Well-Ventilated Fires<sup>a</sup>**

Material	Surface Area (m <sup>2</sup> )	$\Delta H_{ch}$ (kJ/g)	$y_i$ (g/g)	
			CO <sub>2</sub>	CO
Methanol	4.68 <sup>b</sup>	18.7	1.29	<0.001
	2.32 <sup>b</sup>	18.8	1.30	<0.001
	0.008 <sup>c</sup>	19.4	1.32	<0.001
Rigid Polyurethane Foam	7 <sup>b</sup>	16.4	1.50	0.027
	0.008 <sup>c</sup>	15.8	1.51	0.036
Polymethylmethacrylate	2.37 <sup>b</sup>	24.2	2.11	0.008
	0.073 <sup>b</sup>	23.8	2.10	0.010
	0.008 <sup>c</sup>	24.4	2.15	0.011
Heptane	0.920 <sup>b</sup>	26.8	2.83	0.015
	0.059 <sup>b</sup>	26.2	2.92	0.009
	0.041 <sup>b</sup>	26.9	2.82	0.008
	0.008 <sup>c</sup>	24.8	2.84	0.009

<sup>a</sup>Data taken from the Handbook of Plastic and Elastomers [11].

<sup>b</sup>Large-scale data.

<sup>c</sup>FMRC flammability apparatus data.

**Table 9. Equivalence Ratios in the HEF Calorimeter Tests at 150 kW/m<sup>2</sup>**

Sample	Polymer	Symbol	$\dot{m}_f$ (g/s)	s	$\Phi^a$
1	Poly (vinylchloride)	PVC	0.103	5.5	0.14
2	Poly (vinylidene fluoride)	PVDF	0.085	4.3	0.09
3	Phenolic	Phenolic	0.052	12.9	0.17
5	Polypropylene (modified)	m-PP	0.032	14.6	0.12
7	Polyethylene	PE	0.042	14.6	0.16
8	Polypropylene-1	PP	0.061	14.6	0.23
9	Polypropylene-2	PP	0.042	14.6	0.16
10	FR polypropylene-3	FRPP	0.159	14.6	0.60
11	Polycarbonate	PC	0.249	10.6	0.68
12	Filled polyester	FPST	0.134	10.0	0.34

<sup>a</sup> $\Phi = \dot{m}_f s / \dot{m}_{air}$ ,  $\dot{m}_f$  is the mass loss rate for the polymer (g/s), s is the stoichiometric mass air-to-fuel ratio (g/g), and  $\dot{m}_{air}$  is the mass air flow rate (3.9 g/s). For well-ventilated fires,  $\Phi \ll 1.0$ , and for ventilation controlled fires,  $\Phi > 1.0$ .

**4.3.1 Heat Release Rate.** The estimated heat release rate profiles for the halogenated and high-temperature polymers are shown in Figure 25, whereas for thermoplastics, the peak values for the estimated heat release rates are listed in Table 10.

The peak estimated heat release rates at 150 kW/m<sup>2</sup> for thermoplastics are in the range of 1700–2400 kW/m<sup>2</sup>, whereas for the halogenated and high-temperature polymers, they are less than 500 kW/m<sup>2</sup>. Amongst the halogenated and high-temperature polymers, the estimated heat release rate is highest for the high-temperature polymer (phenolic, sample no. 3) and lowest for one of the halogenated polymers (PVDF, sample no. 2). Heat release rates for the PVC (sample no. 1) and high-temperature m-PP (sample no. 5) are comparable.

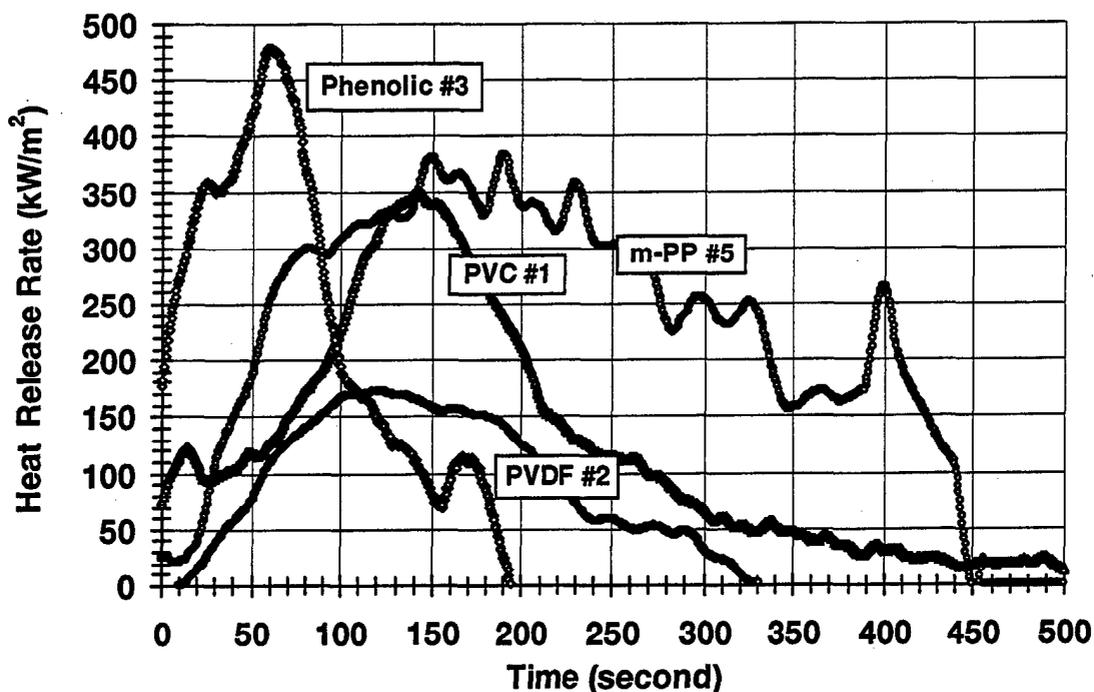


Figure 25. Heat Release Rate Profiles at 150 kW/m<sup>2</sup> for the Halogenated and High-Temperature Polymers Estimated From the Mass Loss Rate From the HEF Calorimeter and the Heat of Combustion From the FMRC Flammability Apparatus.

Table 10. Estimated Peak Release Rates of Heat, CO, and Smoke From the Combustion of Thermoplastics at 150 kW/m<sup>2</sup> in the HEF Calorimeter

Sample	Polymer	Peak Release Rates		
		Heat (kW/m <sup>2</sup> )	CO (g/m <sup>2</sup> -s)	Smoke (g/m <sup>2</sup> -s)
10	FR polypropylene <sup>a</sup>	1800	2.8	6.4
11	Polycarbonate <sup>b</sup>	2400	6.1	12.6
12	Filled polyester <sup>c</sup>	1700	4.0	6.5

<sup>a</sup>Mass loss rate = 70.0 g/m<sup>2</sup>-s (calculated).

<sup>b</sup>Mass loss rate = 119.8 g/m<sup>2</sup>-s (experimental).

<sup>c</sup>Mass loss rate = 65.0 g/m<sup>2</sup>-s (experimental).

Comparisons of the peak estimated heat release rates indicate that the differences between the halogenated, high-temperature polymers and thermoplastics are magnified and that they provide insights into the fire behavior of polymers at  $150 \text{ kW/m}^2$  of heat exposure in the HEF calorimeter.

**4.3.2 CO and Smoke Release Rates.** The estimated CO and smoke release rate profiles for the halogenated and high-temperature polymers are shown in Figures 26 and 27, whereas for thermoplastics, the peak estimated values for the CO and smoke release rates are listed in Table 10.

Release rates of CO for thermoplastics are in the range of  $2.8\text{--}6.1 \text{ g/m}^2\text{-s}$ , whereas for the halogenated and high-temperature polymers, they are less than  $3.2 \text{ g/m}^2\text{-s}$ . The smoke release rates for thermoplastics are in the range of  $6.4\text{--}12.5 \text{ g/m}^2\text{-s}$ , whereas for halogenated and high-temperature polymers, they are less than  $5 \text{ g/m}^2\text{-s}$ . Amongst the halogenated and high-temperature polymers, CO and smoke release rates are highest for the halogenated polymers (PVC sample no. 1 and PVDF sample no. 2) and lowest for m-PP (sample no. 5).

Comparisons of the estimated CO and smoke release rates indicate that the differences between the halogenated, high-temperature polymers and thermoplastics are magnified and that they provide insights into the fire behavior of polymers at  $150 \text{ kW/m}^2$  of heat exposure in the HEF calorimeter.

The significance of the fire parameters for the assessment of fire resistance of polymers over a wide range of external heat flux values is enumerated in Appendix D.

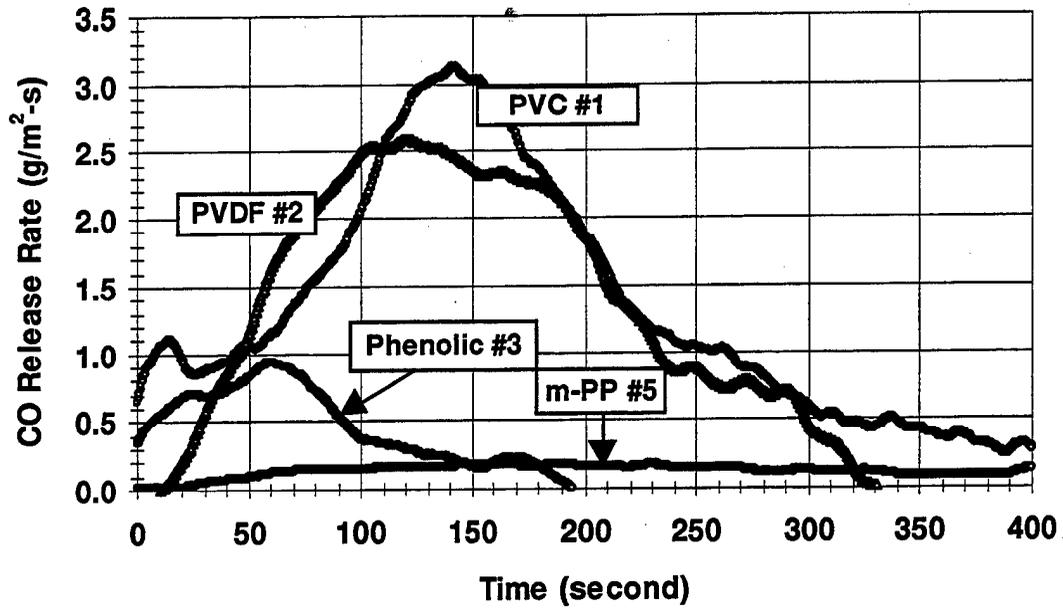


Figure 26. CO Release Rate Profiles at 150 kW/m<sup>2</sup> for the Halogenated and High-Temperature Polymers From the Mass Loss Rate From the HEF Calorimeter and the Yield of CO From the FMRC Flammability Apparatus.

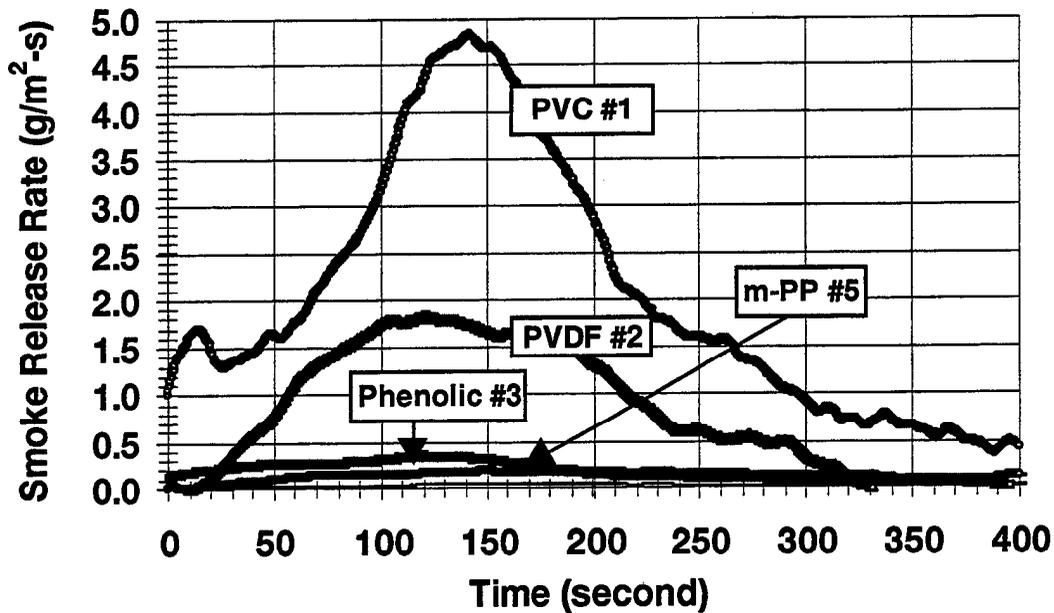


Figure 27. Smoke Release Rate Profiles at 150 kW/m<sup>2</sup> for the Halogenated and High-Temperature Polymers From the Mass Loss Rate From the HEF Calorimeter and the Smoke Yield From the FMRC Flammability Apparatus.

## 5. Summary

1. An HEF calorimeter has been designed to examine the fire resistance of potential plastics for use by the U.S. Army under high heat flux exposure typical of combat field scenarios and large-scale fires.

2. The fire resistance of plastics can be examined in the HEF calorimeter under: (1) external heat flux values from 0–150 kW/m<sup>2</sup>; (2) co-airflow rate from 0–200 liter/min (0.0033 m<sup>3</sup>/s); and (3) oxygen concentration in the co-flowing air around the sample from 0–60%.

3. The sample mass loss is measured by a load cell, and the products flowing out of the Pyrex glass tube are analyzed by a FTIR spectrometer.

4. The time to ignition vs. external heat flux relationship established in the FMRC flammability apparatus has been found on a limited testing to be applicable for the ignition data from the HEF calorimeter up to 150 kW/m<sup>2</sup>.

5. The steady-state relationship between the mass loss rate and external heat flux established in the FMRC flammability apparatus has been found to be applicable for the data from the HEF calorimeter up to 150 kW/m<sup>2</sup>.

6. It is possible to examine minor differences between the high fire-resistant halogenated and high-temperature polymers due to enhanced effects at 150 kW/m<sup>2</sup> in the HEF calorimeter. This, however, needs to be investigated further.

7. There is a need to design a sampling duct to use the FTIR spectrometer quantitatively for the tests in the HEF calorimeter.

## 6. References

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**Appendix A:**

**Fire Resistance of Polymers**

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The fire resistance of polymers is governed by:

- Inherent Chemical Factors. Strength of chemical bonds, ratios of halogen, and other atoms, to carbon atoms, and ratio of hydrogen-to-carbon atom in the products released in the gas phase or the flammability of the products.
- Additives. Presence of inorganic materials as fillers and nanocomposites, fire retardants, and other materials interacting with the polymer in the solid phase or with the products in the gas phase.

Based on the thermal behavior, polymers are categorized into two classes: thermosets and thermoplastics.<sup>1</sup> Thermosets are cured, set, or hardened into a permanent shape. The curing is an irreversible chemical reaction known as cross-linking. Thermoplastics differ from thermosets in that they do not cure or set under heat. Thermoplastics soften when heated to a flowable state take the shape of the surrounding as they cool, and can be remelted and remolded many times.

In general, thermoplastics have low fire resistance due to weaker chemical bonds, whereas the thermosets have higher fire resistance due to stronger chemical bonds. The fire resistance of thermoplastics, however, increases with an increase in the ratio of halogen-to-carbon atoms and decrease in the ratio of hydrogen-to-carbon atoms.<sup>2</sup> Inorganic materials as fillers and nanocomposites and fire retardants are used primarily in thermoplastics to increase their fire resistance.

Tables A-1 and A-2 list examples of advanced-engineered polymers (halogenated thermoplastics and high-temperature thermosets). Chemical formulae, values of the net heat of complete combustion ( $\Delta H_T$ ), stoichiometric mass air-to-fuel ratio (s), and maximum theoretical yields are included in the tables. Stoichiometric mass air-to-fuel ratio is defined as the mass of

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<sup>1</sup>Harper, C. A. (editor-in-chief). Handbook of Plastic and Elastomers. New York, NY: McGraw-Hill Book Company, 1975

<sup>2</sup>Tewarson, A. "Generation of Heat and Chemical Compounds in Fires." *The SFPE Handbook of Fire Protection Engineering*, Section 3, Chapter 4, pp. 3-53 to 3-124. The National Fire Protection Association Press, Quincy, MA, 1995.

air required for the complete combustion of a unit mass of a polymer. Maximum theoretical yield of a product is defined as the maximum possible conversion of an atom in the polymer to that product. For halogenated polymers in Table A-1, the ratio of halogen-to-carbon atoms is high and the ratio of hydrogen-to-carbon atoms is low. For high-temperature polymers in Table A-2, oxygen, sulfur, or nitrogen atoms are present in the structures, along with carbon and hydrogen atoms. The  $\Delta H_T$  values are estimated from the  $\Delta H_T/s$  value, which is approximately constant for all the nonhalogenated polymers ( $2.98 \text{ kJ/g} \pm 7\%$ ).<sup>2, 3</sup> Hydrofluoric (HF) and hydrochloric (HCl) acids from halogenated polymers and nitric (HNO<sub>3</sub>) and sulfuric (H<sub>2</sub>SO<sub>4</sub>) acids and gases such as HCN, SO<sub>2</sub>, and NO<sub>x</sub> from the high-temperature thermosets are expected to be released.

The properties listed in Tables A-1 and A-2 are interrelated: the theoretical yields of CO, hydrocarbons, and soot are respectively equal to 0.64, 0.30, and 0.27 times the theoretical yield of CO<sub>2</sub>. The ratio of the net heat of complete combustion to the theoretical yield of CO<sub>2</sub> is approximately constant, agreeing with an average ratio of  $13.3 \text{ kJ/g} \pm 11\%$  reported in the literature.<sup>2, 3</sup> An example of the interrelationship between the properties (stoichiometric mass air-to-fuel ratio and theoretical yield of CO<sub>2</sub>) is shown in Figure A-1. Similar interrelationships have been developed between the stoichiometric mass air-to-fuel ratio and theoretical yields of CO, hydrocarbons, and soot and net heat of complete combustion.

The interrelationships between the properties in Tables A-1 and A-2 and in Figure A-1 provide insights into the fire resistance of polymers. For example, polymers with high halogen or nitrogen or sulfur-to-carbon atoms ratios and low hydrogen-to-carbon atoms ratios have low theoretical yields and net heat of complete combustion. These polymers, all else being equal, are expected to have lower release rates of heat and products and higher fire resistance and would require higher intensity environments for testing than the ordinary polymers. The HEF calorimeter has been designed to satisfy this need of high-intensity environment testing not possible in other apparatuses.

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<sup>2</sup>Tewarson, A. "Generation of Heat and Chemical Compounds in Fires." *The SFPE Handbook of Fire Protection Engineering*, Section 3, Chapter 4, pp. 3-53 to 3-124. The National Fire Protection Association Press, Quincy, MA, 1995.

<sup>3</sup>Tewarson, A. "Flammability." Chapter 42 in *Physical Properties of Polymers Handbook*, pp. 577-604, edited by J. E. Mark, The American Institute of Physics, Woodbury, NY, 1996.

**Table A-1. Net Heat of Complete Combustion and Maximum Theoretical Yields of Products for Halogenated Polymers<sup>a</sup>**

Polymer	Formula	$\Delta H_T$ (kJ/g)	s (g/g)	Maximum Theoretical Yield (g/g)					
Name (Trade Name)				CO	CO <sub>2</sub>	THC	Soot	HF	HCl
<b>Fluoropolymers</b>									
Poly (vinylfluoride) (Tedlar, PVF)	CH <sub>1.5</sub> F <sub>0.50</sub>	13.5	7.5	1.22	1.91	0.59	0.52	0.44	0
Poly (vinylidene fluoride) (Kynar, PVDF)	CHF	13.3	4.3	0.88	1.38	0.41	0.38	0.63	0
Poly (ethylenetrifluoroethylene) (Tefzel, ETFE)	CHF	12.6	4.3	0.88	1.38	0.41	0.38	0.63	0
Poly (ethylenechlorotrifluoroethylene) (Halar, ECTFE)	CHF <sub>0.75</sub> Cl <sub>0.25</sub>	12.0	3.8	0.78	1.22	0.36	0.33	0.42	0.25
Poly (tetrafluoroethylene) (Teflon TFE)	CF <sub>2</sub>	6.2	2.7	0.56	0.88	0	0.26	0	0
Poly (chlorotrifluoroethylene) (Kel-F, CTFE)	CF <sub>1.5</sub> Cl <sub>0.50</sub>	5.0	2.4	0.48	0.76	0	0.21	0	0
Poly (perfluoroalkoxy) (Teflon PFA)	CF <sub>1.6</sub> O <sub>0.01</sub>	5.0	3.2	0.66	1.0	0	0.28	0	0
Poly (fluorinated ethylene propylene) (Teflon FEP)	CF <sub>1.8</sub>	4.8	3.0	0.61	0.95	0	0.26	0	0
<b>Chloropolymers</b>									
Poly (vinylchloride) PVC	CH <sub>1.5</sub> Cl <sub>0.50</sub>	16.4	5.5	0.90	1.42	0.44	0.39	0	0.58
Chlorinated poly (vinylchloride) (Corzan, CPVC)	CH <sub>1.3</sub> Cl <sub>0.70</sub>	12.8	4.2	0.74	1.16	0.34	0.32	0	0.67 <sup>b</sup>
Poly (vinylidenechloride) (Saran, PVDCI)	CHCl	9.0	2.9	0.58	0.92	0.27	0.25	0	0.75

<sup>a</sup>  $\Delta H_T$ : Net heat of complete combustion from Handbooks of Chemistry, Physics, and Polymers.

<sup>b</sup> Typical.

Notes: s: Stoichiometric mass air-to-fuel ratio.

THC: Total hydrocarbons.

**Table A-2. Net Heat of Complete Combustion and Theoretical Yields of Products for High-Temperature Polymers**

Polymer	Formula	$\Delta H_T^a$ (kJ/g)	$s^b$ (g/g)	Maximum Theoretical Yield (g/g)					
				CO	CO <sub>2</sub>	THC <sup>c</sup>	Soot	HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>
Phenol-formaldehyde, Bakelite	CHO <sub>0.14</sub>	38.4	12.9	1.84	2.89	0.85	0.79	0	0
Polycarbonate, PC	CH <sub>0.88</sub> O <sub>0.13</sub>	31.6	10.6	1.88	2.94	0.86	0.80	0	0
Polyetheretherketone, PEEK	CH <sub>0.63</sub> O <sub>0.16</sub>	31.3	10.5	1.84	2.90	0.54	0.79	0	0
Polyphenylenesulfide, PPS	CH <sub>0.67</sub> S <sub>0.17</sub>	30.3	10.2	1.55	2.43	0.75	0.66	0	0.92
Polysulfone, PSO	CH <sub>0.81</sub> O <sub>0.15</sub> S <sub>0.04</sub>	29.0	9.7	1.70	2.67	0.78	0.73	0	0.24
Polyethersulfone, PES, Radel	CH <sub>0.67</sub> O <sub>0.21</sub> S <sub>0.08</sub>	25.2	8.5	1.51	2.37	0.68	0.65	0	0.42
Polybenzimidazole, PBI	CH <sub>0.67</sub> N <sub>0.33</sub>	35.4	11.9	1.62	2.54	0.73	0.69	1.20	0
Polyarylamide, PA MXD 6	CH <sub>1.29</sub> O <sub>0.14</sub> N <sub>0.14</sub>	32.6	11.0	1.60	2.52	0.76	0.69	0.50	0
Polyetherimide, PEI	CH <sub>0.68</sub> N <sub>0.05</sub> O <sub>0.14</sub>	30.1	10.1	1.79	2.82	0.81	0.77	0.20	0

<sup>a</sup>  $\Delta H_T$ : Net heat of complete combustion estimated using an average value of net heat of complete combustion per unit mass of air.

<sup>b</sup> Stoichiometric mass air-to-fuel ratio.

<sup>c</sup> Total hydrocarbons.

Note:  $\Delta H_T/s = 2.98$  kJ/g.<sup>2,3</sup>

<sup>2</sup>Tewarson, A. "Generation of Heat and Chemical Compounds in Fires." *The SFPE Handbook of Fire Protection Engineering*, Section 3, Chapter 4, pp. 3-53 to 3-124. The National Fire Protection Association Press, Quincy, MA, 1995.

<sup>3</sup>Tewarson, A. "Flammability." Chapter 42 in *Physical Properties of Polymers Handbook*, pp. 577-604, edited by J. E. Mark, The American Institute of Physics, Woodbury, NY, 1996.

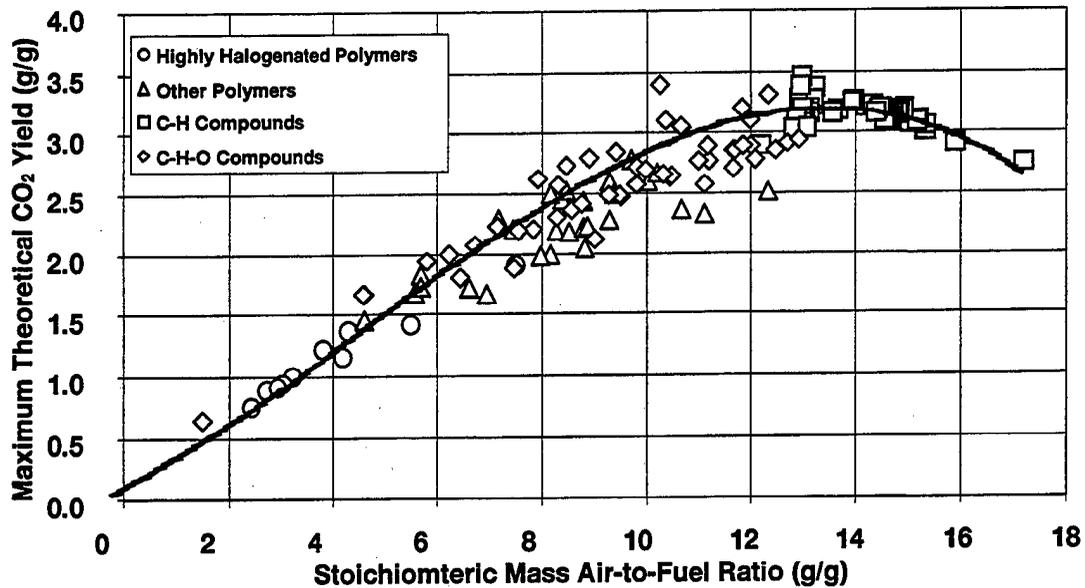


Figure A-1. Correlation Between the Stoichiometric Mass Air-to-Fuel Ratio and Maximum Theoretical Yield of CO<sub>2</sub>. Data Are Taken From Tewarson.<sup>2,3</sup>

<sup>2</sup>Tewarson, A. "Generation of Heat and Chemical Compounds in Fires." *The SFPE Handbook of Fire Protection Engineering*, Section 3, Chapter 4, pp. 3-53 to 3-124. The National Fire Protection Association Press, Quincy, MA, 1995.

<sup>3</sup>Tewarson, A. "Flammability." Chapter 42 in *Physical Properties of Polymers Handbook*, pp. 577-604, edited by J. E. Mark, The American Institute of Physics, Woodbury, NY, 1996.

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## **Appendix B:**

### **Fire Parameters of Polymers**

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Fire parameters are defined in this report as the principal characteristics of polymers associated with ignition, combustion, fire propagation, and release of heat and products.<sup>1,2</sup>

**B.1 Ignition.** The ignition characteristic of a polymer is expressed by:

- **Critical Heat Flux (CHF)** - The maximum flux at or below which there is no sustained ignition and is related to the ignition and decomposition temperatures of the polymer ( $\text{kW}/\text{m}^2$ ).
- **Thermal Response Parameter (TRP)** - The ignition propensity of a polymer, related to the physico-chemical properties of the polymers (thickness, ignition temperature, thermal conductivity, density, and heat capacity) ( $\text{kW}\cdot\text{s}/\text{m}^2$  or  $\text{kW}\cdot\text{s}^{1/2}/\text{m}^2$ ).

CHF and TRP values are obtained from the measurements for time to ignition at various external heat flux values. Standard procedure is to use maximum heat flux at which there is no ignition for 15 min as the CHF value of the polymer.

**B.2 Combustion and Release of Heat and Products.** The combustion characteristic of a polymer, which includes release of heat and products, is expressed by:

- **Heat of Gasification ( $\Delta H_g$ )** - The energy required to gasify a unit mass of a polymer from ambient temperature ( $\text{kJ}/\text{g}$ ). It is obtained from the measurement for the steady-state mass loss rate in  $\text{g}/\text{m}^2\cdot\text{s}$  at several external heat flux values in  $\text{kW}/\text{m}^2$  in an inert environment.
- **Chemical Heat of Combustion ( $\Delta H_{ch}$ )** - The energy released in the combustion of a unit mass of a polymer originally at ambient temperature ( $\text{kJ}/\text{g}$ ). It is obtained from the ratio of

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<sup>1</sup>Tewarson, A. "Generation of Heat and Chemical Compounds in Fires." *The SFPE Handbook of Fire Protection Engineering*, Section 3, Chapter 4, pp. 3-53 to 3-124. The National Fire Protection Association Press, Quincy, MA, 1995.

<sup>2</sup>Tewarson, A. "Flammability." Chapter 42 in *Physical Properties of Polymers Handbook*, pp. 577-604, edited by J. E. Mark, The American Institute of Physics, Woodbury, NY, 1996.

the cumulative energy released in kJ and the total mass loss in grams in the combustion of the polymer determined in the tests.

- **Yield of a Product ( $y_j$ )** - The mass of a product released in the combustion of a unit mass of a polymer originally at ambient temperature (g/g). It is obtained from the ratio of the measured total mass of the product released in gram and total mass loss in gram in the combustion of the polymer.
- **Heat Release Parameter (HRP)** - The ratio of the heat of combustion to the heat of gasification or the energy released per unit amount of energy required to gasify a unit mass of the polymer (kJ/kJ). It is obtained from the ratio of the measured heat of combustion to the heat of gasification or from the measurements for the heat release rates at several external heat flux values.
- **Product Release Parameter (PRP)** - The ratio of the yield of the product to the heat of gasification of the polymer or the mass of a product released per unit amount of energy required to gasify a unit mass of the polymer (g/kJ). It is obtained from the ratio of the measured yield of the product to the heat of gasification or from the measurements for the release rate of the product at several external heat flux values.

**B.3 Fire propagation.** The fire propagation characteristic of a polymer is expressed by:

- **Fire Propagation Index (FPI)** - The fire propagation propensity of a polymer, related to the heat release rate and the TRP value. It is obtained from the ratio of the measured heat release rate during upward fire propagation on a vertical surface of a polymer sheet in 40% oxygen concentration and the TRP value measured in the ignition test.

The HEF calorimeter has been designed to operate in the external heat flux range of 0 to 150 kW/m<sup>2</sup>, oxygen concentration in the range of 0 to 60% in the air co-flowing around the sample, and airflow rate in the range of 0 to 200 l/min (0 to  $3.3 \times 10^{-3}$  m<sup>3</sup>/s) (velocity in the range of 0 to 2.4 ft/s [0–0.73 m/s]).

**Appendix C:**  
**Operation of the HEF Calorimeter**

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The hazard and operability (HAZOP) study on the HEF calorimeter, performed by FMRC,<sup>1, 2</sup> is summarized in the following sections. The analysis of failure modes and their effect [9] are listed in Table C-1.<sup>2</sup>

### C.1 Safety

1. During the operation of the HEF calorimeter, high radiant energy is imposed on the sample. Components heat up during the operation. The operator of the HEF calorimeter thus must allow components to cool down before handling to avoid skin burn hazard.
2. Necessary water and airflow must be provided during the operation of the HEF calorimeter, otherwise it will be damaged.
3. Safety glasses for eye protection from high radiation must be worn during the operation of the HEF calorimeter.
4. Exhaust ventilation above the top of the Pyrex glass tube of the HEF calorimeter must be on to remove heat and products generated in the test.
5. A pilot torch is used to ignite the sample vapors. Torch gases (fuel and air) must not be allowed to concentrate in the glass tube, otherwise an explosion hazard can occur. An open system with flowing air around the sample and exhaust ventilation eliminates this risk. When not lit, the torch gas supply valves must be in the closed position (oxygen should never be used in the pilot torch). At the end of test, the pilot gas systems should be isolated properly at the regulators.
6. Operators must read the following publications: (1) *Operation of the Radiant Heaters*: publication provided by Research, Inc: "Parabolic Strip Heater Model 5305," publication

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<sup>1</sup> Alpert, R. "Safety Review Meeting for the High Energy Calorimeter." Notes, 22 May 1998.

<sup>2</sup> Kumar, B. "The Failure Modes and Effects for High Energy Calorimeter - Updated Version." Memorandums to A. Tewarson, 2 and 6 June 1998.

KA063274-001 C, Research, Inc., Minneapolis, MN, April 1987 (phone: 1-800-328-6184) and (2) *Operation of the Pilot Torch*: publication provided by Smith Equipment "Instructions and Operation Manual for Soldering, Welding, and Heating," Watertown, SD.

7. Operator should follow the checklist items in the sequence provided in the operation procedure.

## **C.2 Flow Specifications**

1. Cooling water for the parabolic strip heaters: 2 liter/min through the three heaters connected in series for water flow.
2. Inlet airflow to the Pyrex tube: up to a maximum of 200 liter/min. The airflow out of the top of the glass tube must not be restricted.
3. Airflow to cool the space between the glass tube and the exterior polycarbonate panels: as supplied by the fan (standard 120 VAC, 60 Hz).

## **C.3 Operation Procedure**

1. Turn on the exhaust flow (do not start the test if there is a problem with the exhaust flow system).
2. Turn on the cooling water to the parabolic strip heaters (2-liter/min minimum). Lamps will burn out without the cooling water.
3. Remove the polycarbonate side panel (allows access to the tube/heater).
4. Slide assembly of the parabolic strip heaters back from the glass tube by removing one hold-down bolt at the rear of the base, and then grasp the support base and slide to the end of the slots (do not hold the lamp itself, as it will damage the lamps).

5. Remove glass tube by removing wing nuts and lift glass tube straight up over the sample holder (jarring the sample holder could damage the load cell or crack the glass tube).
6. Carefully lift the sample holder and the shaft straight up until they clear the internal bearing assembly and flow straightener (to avoid damage to the load cell).
- 6a. Optional: Unscrew the sample holder from the shaft, insert the preweighed sample into the holder, and record the weight of the sample and the holder. Replace onto the shaft.
7. Insert the preweighed sample into the sample holder.
8. Carefully insert the shaft through the flow straightener and through the bearing assembly. Gently make contact with the load cell (hard impact can damage the load cell).
9. Turn on the fuel, ignite using a match, and slowly turn on air until a small 5-mm blue flame is present at the tip of the pilot tube. If there is no ignition with the fuel alone, stop the fuel flow and check the problem (keep the torch directed away from the sample).
10. Turn on the specified inlet airflow at the bottom of the Pyrex tube. Turn on the inlet flow of oxygen if required to obtain the desired concentration of oxygen as indicated by the analyzer and flow rates.
11. Replace the glass tube and snug wing nuts (be careful to avoid hitting the glass tube or exhaust funnel, otherwise the glass tube may break). Avoid close contact between the torch flame and the glass tube, and maintain inlet airflow through the glass tube and around the sample.
12. Slide the parabolic strip heaters into position and lock them in place using the hold-down bolt.
13. Turn on the cooling fan for the heaters.
14. Replace the polycarbonate side panel. (Note: The polycarbonate side panels expand when heaters are on; do not tighten or snug thumbscrews, leave loose for expansion.)

15. Adjust the load cell tare and initiate the data acquisition procedure.
16. Rotate the pilot torch such that the flame is within 100 mm from the surface.
17. Put on the dark glasses for eye protection (exposure to infrared radiation may cause eye damage).
18. Turn on the radiant heaters using the settings on the controller for the desired heat flux.
19. When vapors are observed, rotate the pilot torch to ignite the vapors, rotate the pilot torch back, and turn off the pilot flame after the sample starts burning.
20. At end of the test, stop data acquisition, turn off the power to the heaters, and allow the HEF calorimeter to cool (the Pyrex glass tube and the sample holder can get very hot). Cooling time can be 15 min or longer.
21. Turn off the inlet airflow through the glass tube and around the sample and the exhaust blower.
22. Disassemble and remove the shaft, the sample holder, and the burned sample.
23. Record the final weight of the sample holder and the burned sample.

Clean and prepare for the next test.

**Table C-1. Failure Modes and Effects Analysis<sup>a, b</sup>**

<i>S.no</i>	Component	Failure Modes - Effects	Safety Systems Available and Comments	Actions
1.	Pilot torch system	Absence/failure of ignition - accumulation of the gases - may lead to explosion.	Pilot is ignited only in open atmosphere without the Pyrex tube. The flammability zone will not be more than 5-mm from the tip. (For gas jets, including laminar jets, in open atmosphere, it is presumed that flammable zone length will be approximately equal to the length of the flame.) The airflow is established before the Pyrex tube is placed. Hence no accumulation of fuel expected. For any possible accumulation, two failures, i.e., failure of the airflow and failure of the flame, have to occur simultaneously. Further, in view of the open system, no explosion expected even in case of failure of procedures.	<ol style="list-style-type: none"> <li>1. Obtain correct and complete information about pilot system.</li> <li>2. Ensure that flame will not be more than 5 mm away from the tip at the maximum flow. If the pilot system turns out to be different from that reviewed by the team, further review may be necessary.</li> <li>3. Ensure that the stepwise procedures finalized will be followed.</li> </ol>
2.		Low fuel gas pressure - backfire.	Flash arrestors available.	<ol style="list-style-type: none"> <li>4. Provide metallic (preferably SS) hoses for fuel lines instead of rubber/plastic make.</li> </ol>
3.		Flow through the valve - entry of fuel when not intended - may lead to explosion.	Closing the valves will turn off the pilot. Any flow (valve does not stop the flow even when closed) through the valve will be known. At the end of the day, the main valves on the cylinder regulator will be closed.	<ol style="list-style-type: none"> <li>5. Document the procedure to properly isolate the pilot gas system at the end of the test.</li> <li>6. Ensure to follow the procedures provided by the pilot torch manufacturer.</li> </ol>

<sup>a</sup> Taken from Kumar, B. "The Failure Modes and Effects for High Energy Calorimeter - Updated Version." Memorandums to A.Tewarson, 2 and 6 June 1998.

<sup>b</sup> The user manual of the previous version of the equipment may be reviewed (referred to in the accident investigation report) for any additional inputs.

**Table C-1. Failure Modes and Effects Analysis (continued)**

S.no	Component	Failure Modes - Effects	Safety Systems Available and Comments	Actions
4.	Air /oxygen mixture control	Accumulation of contaminants in the flow straightener - may result in higher pressure drop, higher back pressure, and lower flow rates.	The container is made of steel - hence, no safety concern from higher pressure. Lower flows rates - may lead to explosion in combination with other failures, i.e., pilot and exhaust failures.	
5.		Error in the oxygen analyzer - high oxygen concentration in air flow.	Flow meter and analyzer help to countercheck the oxygen flows and the compositions. With higher concentrations, burning rate of the material will be higher - no safety concern.	
6.	Heater, including water and airflow systems	Failure of cooling water - results in lamp burning out - results in equipment shutdown.	Emergency procedure to shut down the apparatus safely.	Document the emergency procedure to shutdown the equipment. Include details of N2 system in the documentation.
7.		Improper handling of the heater - may result in bulb damage.	Not a safety concern..	
8.	Cooling fan	Failure of the fan - reduction in the external cooling of the heaters.		
9.	Pyrex tube	Improper handling - may result in breakage - may cause injury to the operator.		At appropriate location, include safety precaution in the procedures.
10.	Load cell and sample support	Impingement - results in load cell damage.	No safety concern.	

**Table C-1. Failure Modes and Effects Analysis (continued)**

<i>S.no</i>	Component	Failure Modes - Effects	Safety Systems Available and Comments	Actions
11.	Exhaust duct and associated systems	Failure of blower - results in the release of products - operator may be exposed to the products.	Blower failure is noticeable by the operator. Emergency procedures to handle the situation.	Establish emergency procedures to shut down the heater and introduce N2 in case of failure of blower. Document the emergency procedures.
12.		Blockage of flow through any other failure mode, e.g., failure of main exhaust system or openings on exhaust duct - may contribute to the accumulation of gases in case of pilot failure.		Ensure that the test will not be started or conducted if there is any problem with the exhaust system.
13.	Exhaust duct instrumentation	Failure of instrumentation such as smoke meter, thermocouples, corrosion probe, flow measuring device, FTIR - no measurement of the parameters.	No safety concern.	
14.	Variable transformers and heater power cords	Exposed electrical wiring and connections - electric shock to the operator.	Checks by the operator about the integrity of the electrical wiring and equipment.	Include periodical checking of electrical equipment in the procedures.
15.	Specimen	Unknown properties of specimen - possible release of smoke and toxic gases.	Experimentation will be done only for specific type of polymers for which the general properties are known.	Ensure, through procedures and training, that only specified materials will be tested.

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**Appendix D:**  
**Significance of Fire Parameters**

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## D.1 Introduction

Thermally stable polymers have high decomposition temperatures and high bond dissociation energies [1–5]. Cyclic structures, cross-linking, ratio of branched to linear structures, and copolymerizations are other factors affecting thermal stability of the polymer. Differences in the thermal stability, retention of carbon at the surface (surface charring), and release of products with reduced flammability are reflected in the degree of fire resistance of the polymers.

In general, halogenated and high-temperature polymers have high fire resistance, whereas ordinary polymers (thermoplastics) have lower fire resistance. Fire retardants, inorganic materials as fillers and nanocomposites, and others [6, 7–9], however, can enhance the fire resistance of thermoplastics. Recently, inorganic materials as nanocomposites, especially polymer-layered silicate nanocomposites, have been proposed as alternatives to conventionally filled polymers [6, 8, 9]. Because of their nanometer-size dispersion, the nanocomposites exhibit markedly improved properties when compared to their pure polymer constituents or their macrocomposite counterpart [8].

Due to high thermal stability, surface charring, and reduced release of heat and products, highly fire resistant polymers may burn when exposed to higher heat flux values (120–150 kW/m<sup>2</sup>) typical of large-scale fires. It is thus necessary to simulate the large-scale fire conditions of high-heat fluxes in small-scale test apparatuses. *The HEF calorimeter allows simulation of large-scale fire conditions:*

- External Heat Flux: With an upper limit of 150 kW/m<sup>2</sup>.
- Flame Heat Flux: Air with oxygen concentration up to 100% (operation limit - 60%).
- Ventilation: Airflow with an upper limit of 200 liter/min (0.0033 m<sup>3</sup>/s).

## D.2 Ignition (Critical Heat Flux and Thermal Response Parameter)

The ignition resistance of a polymer depends on the critical heat flux (CHF) and thermal response parameter (TRP) values. CHF value is indicative of the magnitude of the heat flux required to initiate the fire. TRP value is indicative of the delay in fire initiation as the polymer is heated beyond the CHF value. The CHF and TRP values of the polymers examined in the study are shown in Figures D-1 and D-2, respectively. Table D-1 lists the CHF and TRP values for halogenated polymers from Tewarson [10, 11].

The CHF and TRP values indicate that halogenated and high-temperature polymers are expected to resist ignition (as well as fire propagation) to a greater extent than ordinary polymers (thermoplastics) when exposed to heat flux in real fires.

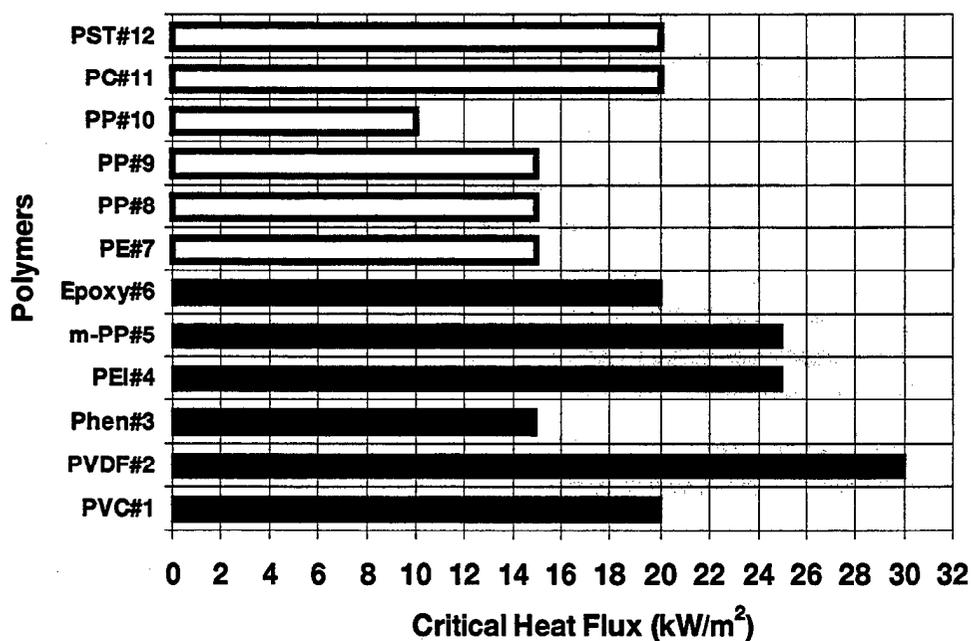


Figure D-1. Critical Heat Flux Values for Halogenated and High-Temperature Polymers (Black Bars) and Ordinary Polymers (Open Bars).

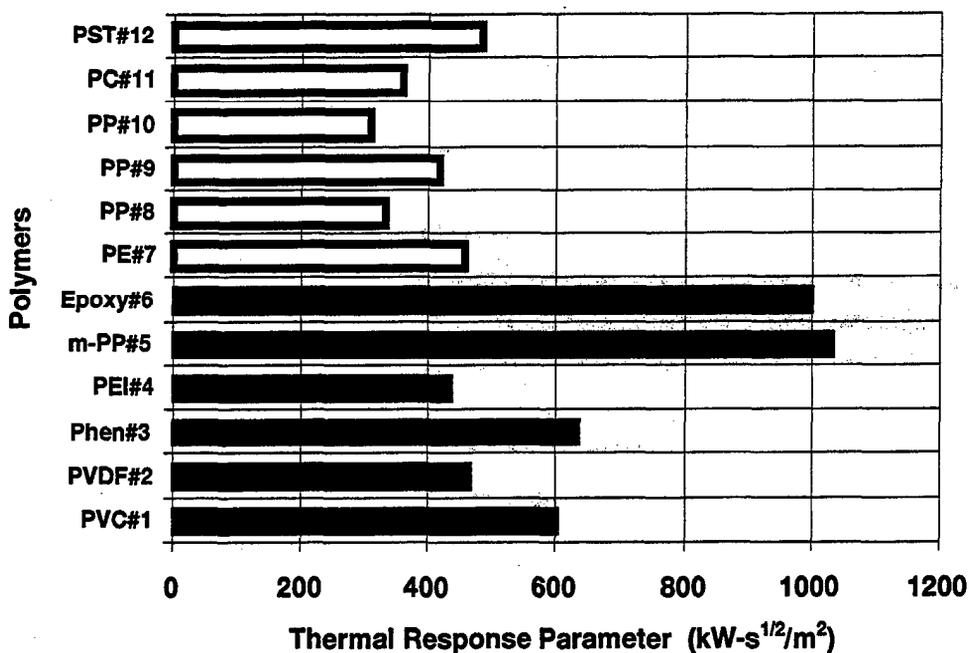


Figure D-2. Thermal Response Parameter Values for Halogenated and High-Temperature Polymers (Black Bars) and Ordinary Polymers (Open Bars).

Table D-1. Thermal and Ignition Properties of Fluorinated and Chlorinated Polymers<sup>a</sup>

Properties	Teflon TFE	Teflon FEP	Tefzel ETFE	Kel-F CTFE	Halar ECTFE
Ignition temperature (°C)	699	700	540	580	613
CHF (kW/m <sup>2</sup> )	50	50	25	30	38
Density (g/cm <sup>3</sup> )	2.18	2.15	1.7	2.11	1.69
Thermal conductivity (W/m-K)	0.25	0.25	0.23	0.22	0.15
Heat capacity (kJ/kg-K)	1.0	1.2	0.9	0.9	1.0
$\Delta T_{ig}$ (°C)	679	680	520	560	593
$(\pi k \rho c_p / 4)^{1/2}$ (kW-s <sup>1/2</sup> /m <sup>2</sup> -K)	0.654	0.712	0.526	0.573	0.446
TRP (Theoretical) <sup>b</sup> (kW-s <sup>1/2</sup> /m <sup>2</sup> -K)	444	484	273	321	265
TRP (Experimental) (kW-s <sup>1/2</sup> /m <sup>2</sup> -K)	654	680	481	460	450

<sup>a</sup> Data taken from Tewarson et al. [12].

<sup>b</sup> Calculated from the density, thermal conductivity, heat capacity, and the ignition temperature and  $\pi/4$ .

Additives such as fire retardants, inorganic materials as fillers and nanocomposites, and others are used to enhance the ignition resistance of ordinary polymers (thermoplastics). These additives have minor effects on the CHF values but do increase the TRP values [10–12]. Large amounts of inorganic fillers (> 40%) with higher thermal conductivity values are effective in increasing the TRP values, such as shown in Figure D-3 [12]. For similar amounts of inorganic fillers, the TRP value of epoxy increases with the thermal conductivity values, which are 0.20 for Kevlar, 1.05 for glass, and  $5.02 \text{ kW/m-K} \times 10^{-3}$  for graphite [12].

Smaller amounts of inert fillers in the form of nanocomposites, however, are not effective in enhancing ignition resistance. Examples of some of the literature data on nanocomposites, taken from Gilman, Kashiwagi, and Lichtenhan [9], Pape and Romenesko [13], and Buch, Page, and Romenesko [14], are listed in Table D-2. There is a significant decrease in the heat release rate by  $\leq 5\%$  of clay and silicone nanocomposites in the thermoplastics. The ignition behavior of the thermoplastics, as indicated by the time-to-ignition, however, is not affected by the nanocomposites because of small amounts.

The effect of inert fillers can also be noted in the ignition data for the polymers examined in this study. For example, in Table 3, the TRP value of polyester sample no. 12 is  $483 \text{ kW-s}^{1/2}/\text{m}^2$ . This sample contains 64% of  $\text{CaCO}_3$ , and its TRP value is between the TRP values of polyester with glass fibers and graphite fibers as fillers (Figure D-3).

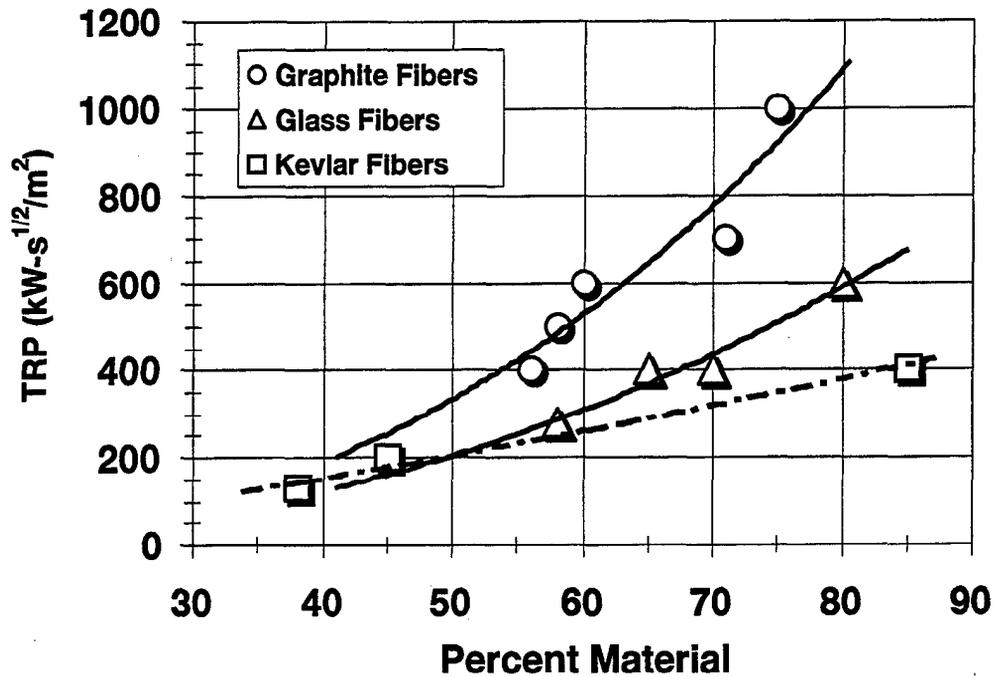


Figure D-3. Thermal Response Parameter vs. Percent Fillers in Polyester Composites. Data are taken from Tewarson et al. [12].

### D.3 Combustion (Release Rates of Heat and Products)

The expressions for the release rates of heat and products from Equations 1, 2, and 3 in the main body of this report are:

$$\dot{Q}_{ch}'' = (\Delta H_{ch} / \Delta H_g)(\dot{q}_e'' + \dot{q}_f'' - \dot{q}_r'') , \quad (D-1)$$

and

$$\dot{G}_j'' = (y_j / \Delta H_g)(\dot{q}_e'' + \dot{q}_f'' - \dot{q}_r'') , \quad (D-2)$$

where  $\dot{Q}_{ch}''$  is the heat release rate per unit polymer surface area (kW/m<sup>2</sup>);  $\dot{q}_e''$  is the external heat flux (kW/m<sup>2</sup>);  $\dot{q}_f''$  is the flame heat flux (kW/m<sup>2</sup>);  $\dot{q}_r''$  is the surface re-radiation loss (kW/m<sup>2</sup>) that is close to the CHF value [10, 11],  $\Delta H_{ch}/\Delta H_g$  is the *heat release parameter* (HRP) (kJ/kJ),  $\dot{G}_j''$  is the release rate of product *j* (g/m<sup>2</sup>-s); and  $y_j / \Delta H_g$  is the *product release parameter* (PRP) (g/kJ).

**Table D-2. Time to Ignition, Heat Release Rate, and Its Reduction by Fillers and Nanocomposites in Thermoplastics<sup>a</sup>**

Heat Flux (kW/m <sup>2</sup> )	Ref.	Polymer	Filler	Nanocomp (%)	Time to Ignition <sup>a</sup> (s)	HRR (kW/m <sup>2</sup> )	HRR Reduction (%)
35	18	Nylon6	None	0	368	1011)	0
				2 <sup>b</sup>	198	686	32
				5 <sup>b</sup>	330	378	63
40	20, 21	Nylon66	None	0	270	1190	0
				3 <sup>c</sup>	255	440	63
				5 <sup>c</sup>	255	476	60
				8 <sup>c</sup>	255	369	69
40	20, 21	Polyethylene terephthalate (PET)	None	0	130	1600	0
				3	94	400	75
				5	109	352	78
				8	105	352	78
30	20, 21	Polypropylene	None	0	30	1400	0
			30% APP	0	60	952	32
			15% APP	5 <sup>c</sup>	53	532	62
			25% MHO	0	80	462	67
			20% MHO	5 <sup>c</sup>	106	378	73
			35% MHO	0	80	266	81
			30% MHO	5 <sup>c</sup>	80	266	81
			50% MHO	0	80	266	81
			45% MHO	5 <sup>c</sup>	80	210	85
		Polystyrene (PS)	None	0	70	780	0
				1 <sup>c</sup>	80	499	36
				3 <sup>c</sup>	60	296	62
				3 <sup>c</sup>	94	nr	nr
				5 <sup>c</sup>	109	nr	nr
8 <sup>c</sup>	105	nr	nr				

<sup>a</sup> Data measured in the cone calorimeter. Time to ignition derived from the heat release rate profiles.

<sup>b</sup> Clay nanocomposite.

<sup>c</sup> Silicone nanocomposite.

Notes: APP - Ammonium pyrophosphate.

MHO - Magnesium hydroxide.

nr - Not reported.

The relative importance of flame and external heat flux depends on the combustion within and beyond the ignition zone.

Figures D-4, D-5, and D-6 show calculated release rates of heat, CO, and smoke at 150 kW/m<sup>2</sup>, respectively. The rates are calculated from Equations D-1 and D-2 and HRP, PRP, and CHF values listed in Table 3 for the polymers examined in the study. The release rates of heat, CO, and smoke for halogenated and high-temperature polymers are significantly lower than the rates for the ordinary thermoplastics. This condition is expected within the ignition zone where  $\dot{q}_e'' \gg \dot{q}_f''$ .

Beyond the ignition zone,  $\dot{q}_f'' \gg \dot{q}_e''$  and thus flame heat flux from the burning polymer has to satisfy the CHF and TRP values for the combustion and fire propagation to continue. Flame heat flux is strongly dependent on the generic nature of the polymer, surface area of the burning polymer, its orientation, and airflow conditions. For large pool fires of ordinary polymers (thermoplastics), flame heat flux is in the range of about 50–75 kW/m<sup>2</sup> [10, 11]. Thus, for combustion beyond the ignition zone, the release rates of heat, CO, and smoke would be about one half to one third times the rates in the ignition zone (shown in Figures D-4, D-5, and D-6).

#### D.4 Low Fire-Resistant Polymers

Ordinary polymers (thermoplastics) soften, melt, and burn as pool fires. Figure D-7 shows a typical heat release profile for the combustion of thermoplastic (product release rate profiles are similar). In the figure, three burning zones are identified, based on the observations during the combustion process for a 1-in (25-mm)-thick, 4-in (100-mm)-diameter solid slab of polypropylene in the FMRC flammability apparatus:

- **Solid Zone:** A thin molten polymer layer is present at the surface during combustion. The thermoplastic burns at a steady state with the experimental heat release close to the theoretical rate shown by the dashed line. The theoretical rate is calculated from the HRP value of 19 kJ/kJ and CHF value of 15 kW/m<sup>2</sup> for polypropylene given in Drysdale [10] and equation 6, assuming flame heat flux to be negligibly small and using CHF value for surface re-radiation loss.

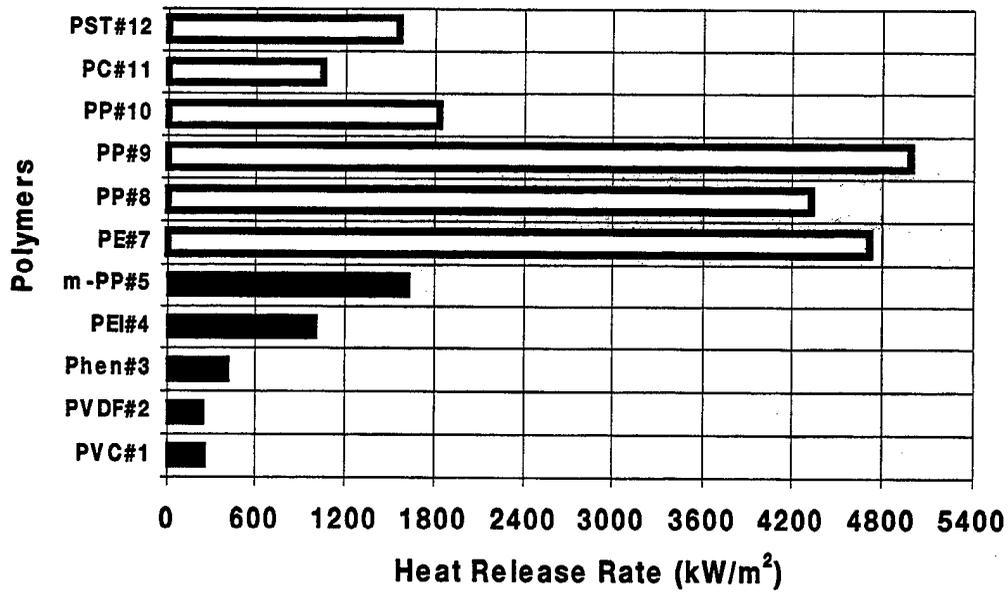


Figure D-4. Heat Release Rate at 150 kW/m<sup>2</sup> for the Halogenated and High-Temperature Polymers (Dark Bars) and Ordinary Polymers (Open Bars).

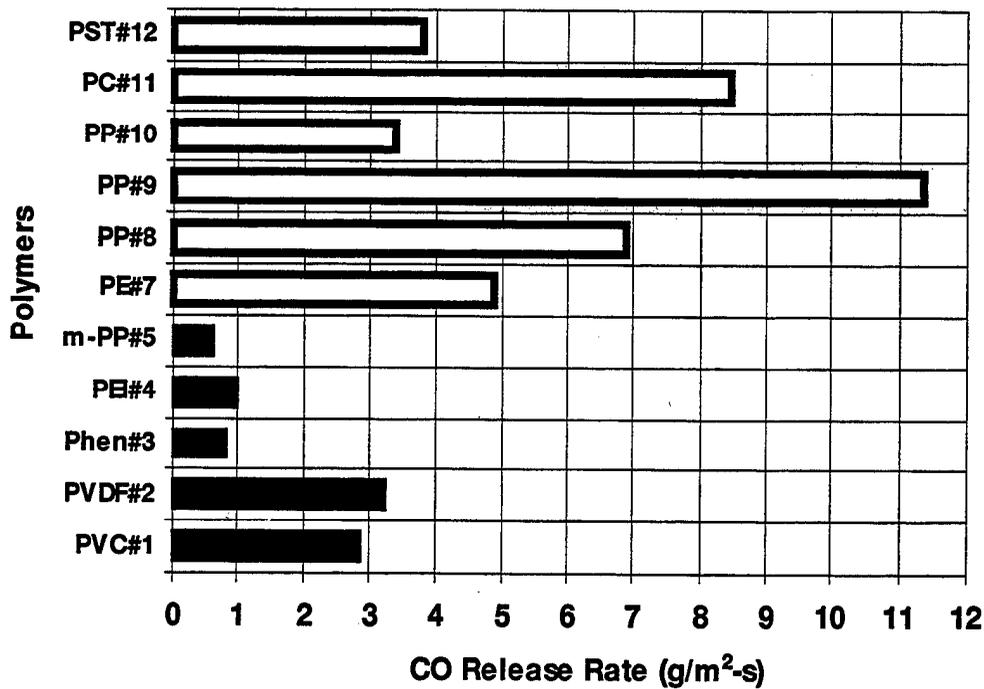


Figure D-5. CO Release Rate at 150 kW/m<sup>2</sup> for the Halogenated and High-Temperature Polymers (Dark Bars) and Ordinary Polymers (Open Bars).

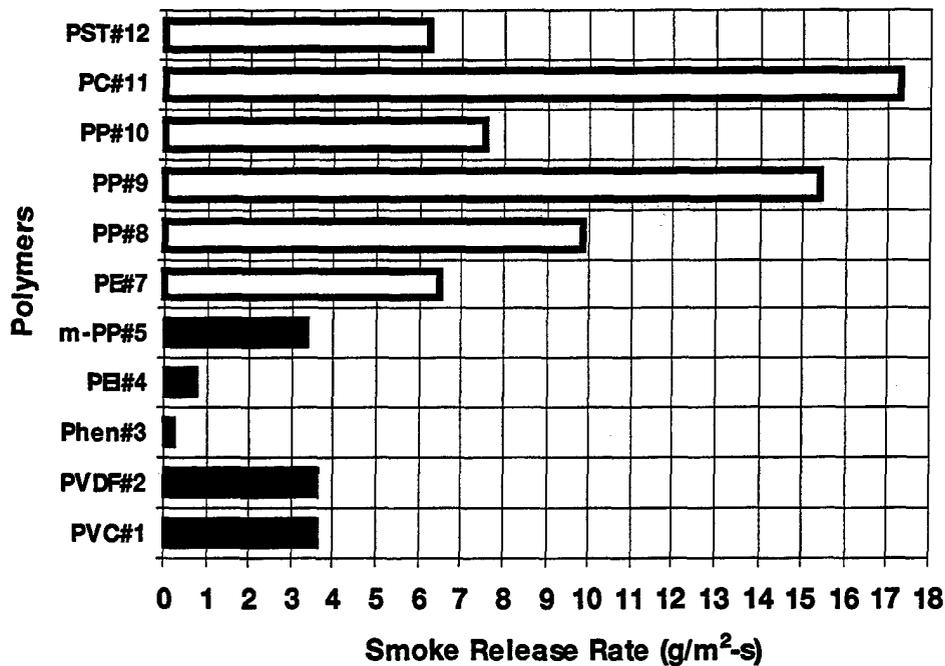


Figure D-6. Smoke Release Rate at 150 kW/m<sup>2</sup> for Halogenated and High-Temperature Polymers (Dark Bars) and Ordinary Polymers (Open Bars).

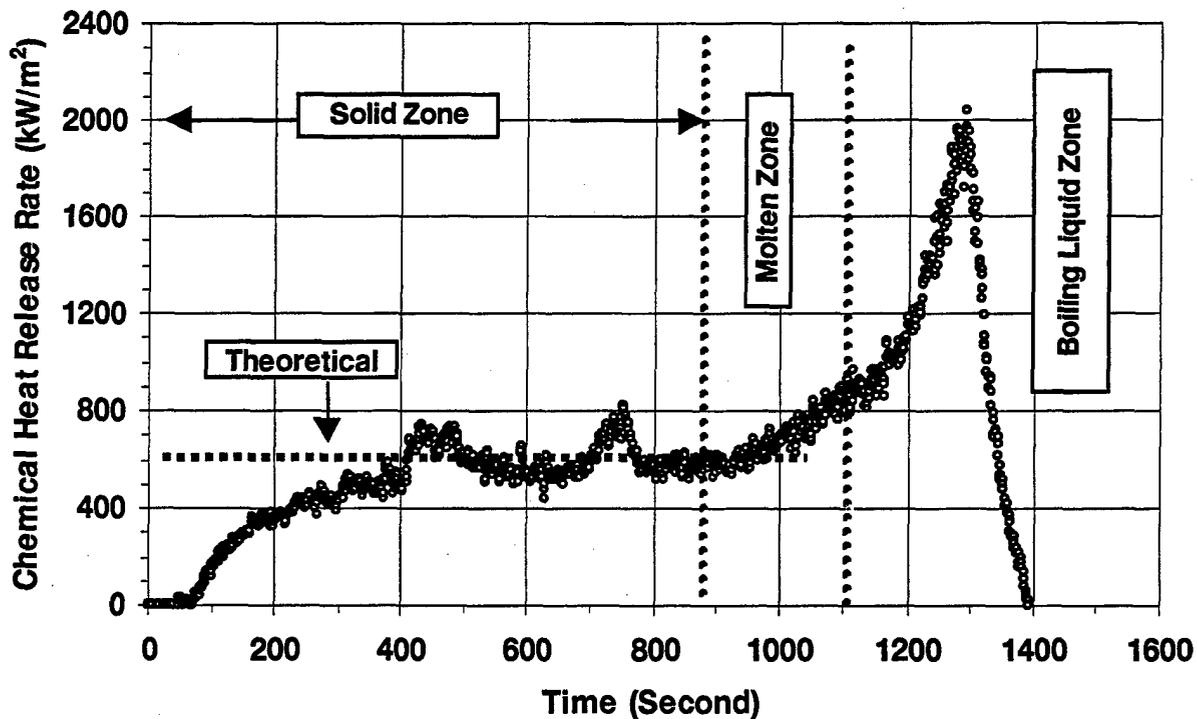


Figure D-7. Chemical Heat Release Rate in the Normal Air Combustion of a 100-mm-Diameter and 25-mm-Thick Slab of Polypropylene Exposed to 50 kW/m<sup>2</sup> in the FMRC Flammability Apparatus.

- **Molten Zone:** Thickness of the molten polymer layer increases during combustion. Heat release rate starts to increase.
- **Boiling Liquid Zone:** All the solid polymer changes into a liquid pool and burns as a boiling liquid pool fire with very high heat release rate (three times the theoretical value). The depth of the liquid pool decreases rapidly changing to a thin liquid film just before the polymer is consumed. At this stage, heat release reaches a peak momentarily and then decreases rapidly.

With a decrease in the thickness of the polymer, the duration of each zone decreases, and for about 2- to 3-mm-thick polymer, the solid and molten zones almost disappear and the boiling liquid zone is observed for a short time after ignition. Incorporation of fire retardants, inorganic materials as fillers and nanocomposites, into the thermoplastics eliminates the molten and boiling liquid zones and, in some cases, reduces the steady-state release rates of heat and products in the solid zone. In this respect, the fire behavior change of thermoplastics with fire retardants and fillers is similar to the fire behavior of thermosets.

#### **D.5 Use of Fire Retardants to Reduce Heat Release Rates**

Fire retardants generally interact chemically with the polymers during combustion and reduce heat release rate and heat of combustion by shifting chemical reactions toward incomplete combustion. Thus, the fire-retarded thermoplastics have higher yields and release rates of products of incomplete combustion. Extensive data on the affects of fire retardants on the combustion of polymers exist in the literature [7, 15, 16, 17]. Table D-3 lists data from a recent study [18] on the effectiveness of fire retardants<sup>1</sup> on the combustion of thermoplastics.

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<sup>1</sup>Fire retardants incorporated in the polymers were organic bromine and chlorine compounds, phosphorous alone, or as a part of an organic molecule, sometimes in combination with bromine, antimony as an oxide in combination with bromine, and metal hydrates (aluminum trihydrate or other metal hydrates) [17].

**Table D-3. Heat Release Rates for Thermoplastics With and Without the Fire Retardants<sup>a</sup>**

Polymer	Heat Flux (kW/m <sup>2</sup> )	HRR (kW/m <sup>2</sup> ) (% Reduction)		$\Delta H_{ch}$ (kJ/g)		TRP (kW-s <sup>1/2</sup> /m <sup>2</sup> )	
		NFR <sup>b</sup>	FR <sup>c</sup>	NFR <sup>b</sup>	FR <sup>c</sup>	NFR <sup>b</sup>	FR <sup>c</sup>
Acrylonitrile-Butadiene-Styrene (ABS)	25	671	439 (35)	29.0	10.3	339	330
	50	1005	414 (59)	28.3	10.0		
	75	1215	494 (59)	29.4	10.0		
High-Impact Polystyrene (HIPS)	25	834	304 (64)	29.8	11.0	372	351
	50	1039	252 (76)	28.2	10.2		
	75	1218	301 (75)	26.4	9.8		
Polycarbonate (PC) - ABS Copolymer	25	436	351 (20)	22.4	17.8	344	391
	50	469	321 (32)	22.4	18.4		
	75	590	453 (23)	22.2	17.0		
Cross-Linked Polyethylene (XPE)	25	931	227 (76)	36.1	20.0	442	581
	50	1517	293 (81)	39.9	22.0		
	75	-	494	-	20.7		

<sup>a</sup>Data taken from Priest [18]. Data were measured in the cone calorimeter for 100-mm × 100-mm × up to 50-mm thick samples.

<sup>b</sup>NFR: No fire retardant.

<sup>c</sup>FR: With the fire retardant.

The heat release rates for the thermoplastics without the fire retardants are about 2–4 times the theoretical rates (calculated from the HRP and CHF values of the polymers from Tewarson [10]). The fire retardants reduce the heat release rates significantly with rates close to theoretical rates, indicative of the elimination of the molten and boiling liquid zones (Figure D-7). The HEF calorimeter data show similar results. For example, for FRPP (sample no. 10), the fire retardant modifies polypropylene from an ordinary melting thermoplastic to a softening polymer with higher fire resistance.

#### D.6 Use of Inorganic Materials as Fillers to Reduce Release Rates of Heat and Products

Inorganic materials as fillers are used in large amounts to reduce release rates of heat and products. For example, in Table D-2, 30% of ammonium pyrophosphate in polypropylene reduces the heat release rate by 32% and 25–50% of magnesium hydroxide reduces the heat release rate by 67–81%. Similar results are found from the HEF calorimeter. For example,

about 40% of an inorganic material as a filler modifies polypropylene (sample no. 5) from an ordinary thermoplastic to a high-temperature polymer with high fire resistance.

#### **D.7 Use of Inorganic Materials as Nanocomposites to Reduce Release Rates of Heat and Products**

Nanocomposites are inorganic materials dispersed in thermoplastics in nanometer-size and are effective in small amounts compared to fillers that require large amounts to be effective. The effectiveness and mode of operation of the nanocomposites have been examined by the literature data listed in Table D-4 for the combustion of nylon, with and without clay nanocomposites [9].

Nylon is thermoplastic. Thus, with zero-percent clay nanocomposite, the heat release rate is 4.2 times the theoretical heat release rate ( $240 \text{ kW/m}^2$  at  $35 \text{ kW/m}^2$  [10]), indicative of the boiling liquid zone. The heat release rate is reduced by 2.9 times the theoretical heat release rate by 2% clay nanocomposite and by 1.6 times the theoretical heat release rate by 5% clay nanocomposite, indicative of elimination of the molten and boiling liquid zones in the combustion of nylon.

The literature data on the combustion of thermoplastics with and without nanocomposites, listed in Table D-2, also indicate that nanocomposites eliminate molten and the boiling liquid zone. For example, for nylon, polypropylene, and polystyrene, the heat release rates without the nanocomposites are 4.2, 4.9, and 2.9 times their respective theoretical heat rates ( $240$ ,  $285$ , and  $272 \text{ kW/m}^2$ , respectively). The rates decrease with an increase in the amount of nanocomposite, as can be noted in Table D-2 and Figure D-8.

For nylon6 and nylon66, about 5%, and for polystyrene, about 3% silicone nanocomposite appears to be effective.

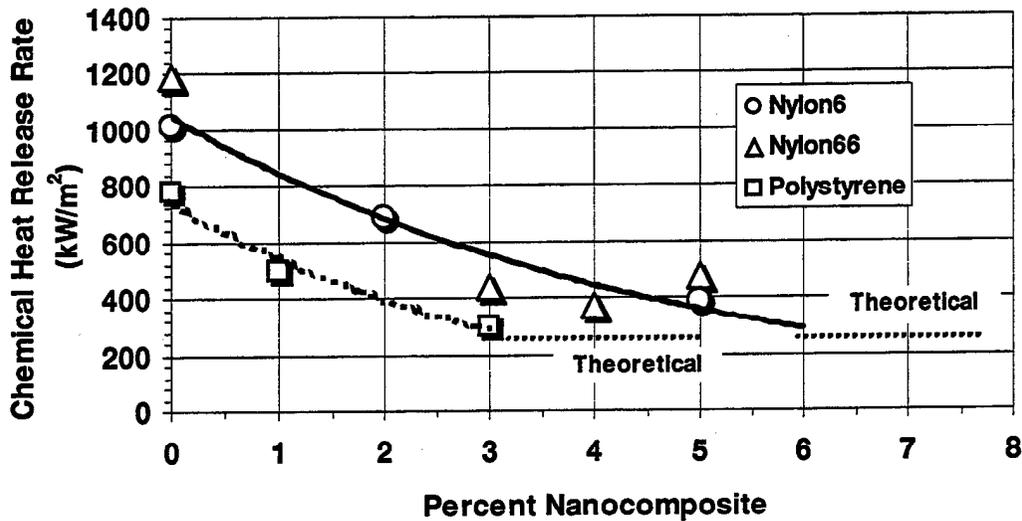
Data for char, heat of combustion, smoke, and CO in Table D-4 indicate that the clay nanocomposite does not affect the combustion chemistry in the gas phase, but does affect the chemistry in the solid phase as char formation is increased.

**Table D-4. Nylon Combustion Data With and Without the Clay-Nanocomposite<sup>a</sup>**

% Clay Nanocomposite	Residue (%)	Heat Release Rate (kW/m <sup>2</sup> )	$\Delta H_{ch}$ (kJ/g)	$\sigma^b$ (m <sup>2</sup> /g)	$y_{co}$ (g/g)
0	0.3	1011	27	0.197	0.01
2	3.4	686	27	0.271	0.01
5	5.5	378	27	0.296	0.02

<sup>a</sup>Data are taken from Gilman, Kashiwagi, and Lichtenhan [9]. Data measured in the cone calorimeter at 35 kW/m<sup>2</sup> for 75 × 50-mm × 15-mm-thick samples.

<sup>b</sup> $\sigma$  - Specific extinction area for smoke.



**Figure D-8. Chemical Heat Release Rate in the Combustion of Thermoplastics Measured in the Cone Calorimeter vs. Percent Nanocomposite. Data Are Taken From Gilman, Kashiwagi, and Lichtenhan [9], Pape and Romenesko [13], and Buch, Pate, and Romenesko [14]. Theoretical Heat Release Rate Is Calculated From the HRP and CHF Values From Tewarson [10].**

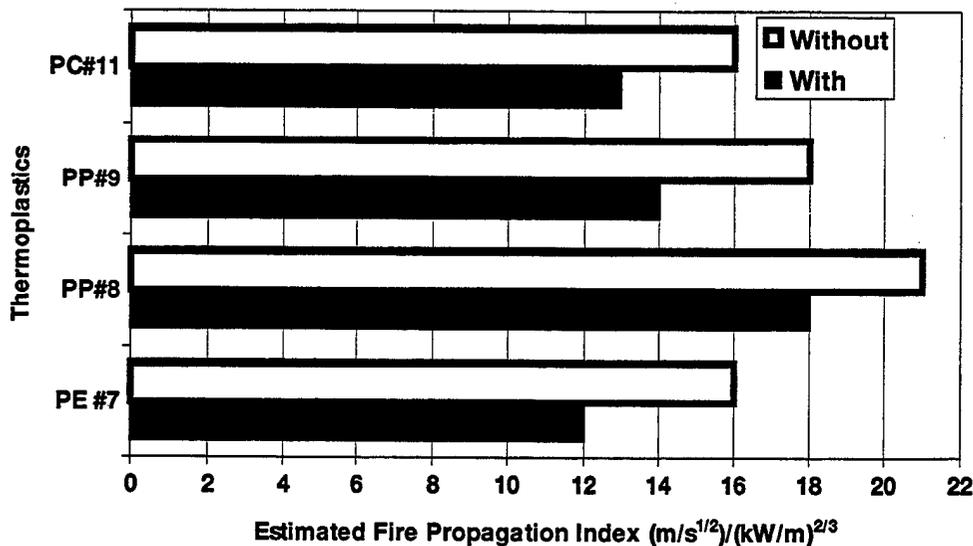
### D-8 Resistance to Fire Propagation

The Fire Propagation Index (FPI) expresses the fire propagation propensity of a polymer. FPI is a function of the heat release rate and the TRP value of the polymer (10, 11). Polymers

with FPI values less than or equal to  $6 \text{ (m/s}^{1/2})/(\text{kW/m})^{2/3}$  have no fire propagation beyond the ignition zone. The extent and rate of fire propagation beyond the ignition increases with increase in the FPI values.

The estimated FPI values listed in Table 3 in the main body of this report indicate that fire is not expected to propagate beyond the ignition zone for halogenated and high-temperature polymers with the exception of PEI (sample no. 4), whereas, it is expected to propagate beyond the ignition zone for all thermoplastics examined in the study (sample nos. 7–12).

Figure D-9 is constructed with estimated FPI values for thermoplastics, where it is assumed that incorporation of 3–6% of nanocomposites would decrease the heat release rate to the theoretical rate for the thermoplastics and that the TRP values would not be affected. FPI values from Table 3 in the main body of this report are also shown in Figure D-9. The data in the figure indicate that there is some decrease in the FPI values by incorporating the nanocomposites, but the decrease is not sufficient to change the fire propagation behavior of the polymers from propagating to nonpropagating.



**Figure D-9. Estimated FPI Values for Thermoplastics With and Without the Nanocomposite.**

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## List of Abbreviations

<b>APP</b>	ammonium pyrophosphate
<b>ASTM</b>	American Society for Testing and Materials
<b>CHF</b>	critical heat flux ( $\text{kW/m}^2$ )
<b>CI</b>	corrosion index
$c_p$	heat capacity of the polymer ( $\text{kJ/g-K}$ )
<b>CPVC</b>	chlorinated poly (vinylchloride) (Corzan)
<b>CTFE</b>	chlorotrifluoroethylene (Kel-F)
<b>d</b>	polymer thickness (m)
<b>ECTFE</b>	ethylenechlorotrifluoroethylene (Halar)
<b>ETFE</b>	ethylenetrifluoroethylene (Tefzel)
<b>FAA</b>	Federal Aviation Administration
<b>FEP</b>	fluorinated ethylene propylene (Teflon)
<b>FMRC</b>	Factory Mutual Research Corporation
<b>FPI</b>	Fire Propagation Index ( $\text{m/s}^{1/2}/(\text{kW/m})^{2/3}$ )
<b>FPST</b>	filled polyester
<b>FR</b>	fire retarded
<b>FRPP</b>	fire-retarded polypropylene
<b>FTIR</b>	Fourier transform infrared
$\dot{G}_j$	release rate of product j per unit surface area of the polymer ( $\text{g/m}^2\text{-s}$ )
<b>HAZOP</b>	hazard and operability
<b>HCl</b>	hydrochloric
<b>HEF</b>	high-energy flux
<b>HF</b>	hydrofluoric
<b>HRP</b>	heat release parameter, $\Delta H_{\text{ch}}/\Delta H_g$ ( $\text{kJ/kJ}$ )
$\Delta H_{\text{ch}}$	chemical heat of combustion of the polymer ( $\text{kJ/g}$ )
$\Delta H_g$	heat of gasification of the polymer ( $\text{kJ/g}$ )
$\Delta H_T$	net heat of complete combustion of the polymer ( $\text{kJ/g}$ )

<b>id</b>	inside diameter
<b>k</b>	thermal conductivity of the polymer (kW/m-K)
<b><math>\dot{m}''</math></b>	mass loss rate per unit surface area of the polymer (g/m <sup>2</sup> -s)
<b><math>\dot{m}_{air}</math></b>	mass airflow rate (g/s)
<b><math>\dot{m}_f</math></b>	mass loss rate in the combustion of the polymer (g/s)
<b>MHO</b>	magnesium hydroxide
<b>NFPA</b>	National Fire Protection Association
<b>PBI</b>	polybenzimidazole
<b>PC</b>	polycarbonate
<b>PE</b>	polyethylene
<b>PEEK</b>	polyetheretherketone
<b>PEI</b>	polyetherimide
<b>PES</b>	poly (ethersulfone) (Radel)
<b>PET</b>	polyethylene terephthalate
<b>PFA</b>	perfluoroalkoxy (Teflon)
<b>PP</b>	polypropylene
<b>PPS</b>	polyphenylenesulfide
<b>PRP</b>	Product Release Parameter, $y_f/\Delta H_g$ (g/kJ)
<b>PS</b>	polystyrene
<b>PSO</b>	poly (sulfone)
<b>PST</b>	polyester
<b>PVF</b>	poly (vinylfluoride) (Tedlar)
<b>PVC</b>	poly (vinylchloride)
<b>PVDCI</b>	poly (vinylidenechloride) (Saran)
<b>PVDF</b>	poly (vinylidene fluoride) (Kynar)
<b><math>\dot{Q}_{ch}''</math></b>	chemical heat release rate (kW/m <sup>2</sup> )
<b><math>\dot{q}_e''</math></b>	external heat flux (kW/m <sup>2</sup> )
<b><math>\dot{q}_f''</math></b>	flame heat flux per unit surface area of the polymer (kW/m <sup>2</sup> )
<b><math>\dot{Q}_i''</math></b>	heat release per unit surface area of the polymer (kW/m <sup>2</sup> )

$\dot{q}_{rr}$	surface re-radiation loss (kW/m <sup>2</sup> )
s	stoichiometric mass air-to-fuel ratio (g/g)
SS	stainless steel
TFE	tetrafluoroethylene (Teflon)
TRP <sub>thin</sub>	thermal response parameter for thermally thin polymers (kW-s/m <sup>2</sup> )
TRP <sub>thick</sub>	thermal response parameter for thermally thick polymers (kW-s <sup>1/2</sup> /m <sup>2</sup> )
$\Delta T_{ig}$	ignition temperature above ambient (°C)
y <sub>j</sub>	yield of product j (g/g)

**Greek**

$\alpha$	thermal diffusivity, $k/\rho c_p$ , (m <sup>2</sup> /s)
$\delta$	thermal penetration depth (m)
$\rho$	density of the polymer (g/cm <sup>3</sup> )
$\Phi$	equivalence ratio

**Super and Subscripts**

'	per unit time (s <sup>-1</sup> )
"	per unit area (m <sup>-2</sup> )

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