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SCREENING FLAME RETARDANT ADDITIVES FOR PLASTICS USING MICROSCALE COMBUSTION CALORIMETRY

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SCREENING PLASTICS FOR FLAMMABILITY

PROBLEM

Need Small Scale (milligram) Screening Test for FR Additives to *Reduce Development Costs* and *Accelerate Discovery*.

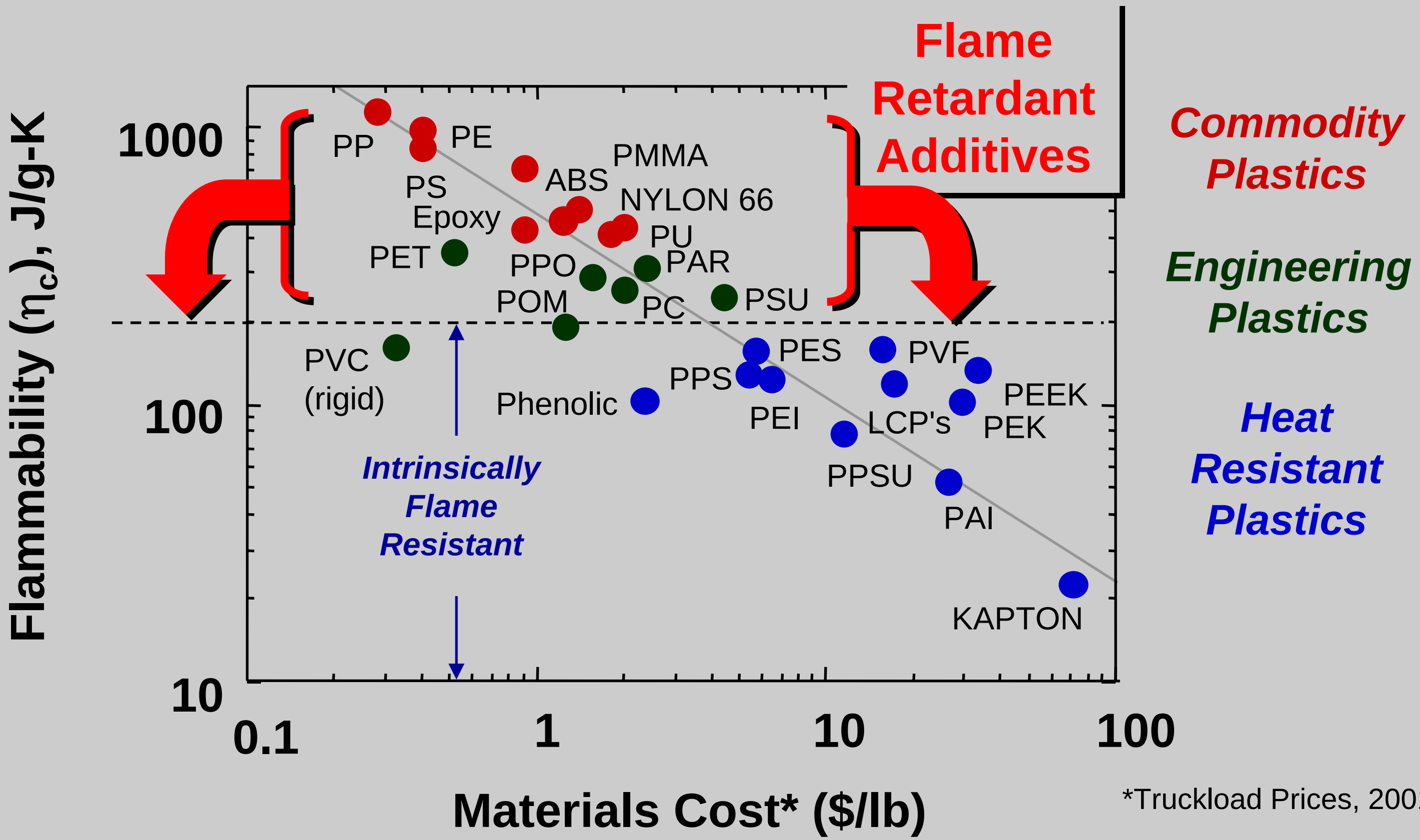
APPROACH

- Measure Properties of Complete Combustion using Microscale Combustion Calorimetry.
- Use a “Burning Efficiency” to Account for Incompleteness of Flaming Combustion.
- Account for Uncertainty Using Probability.

RESULTS

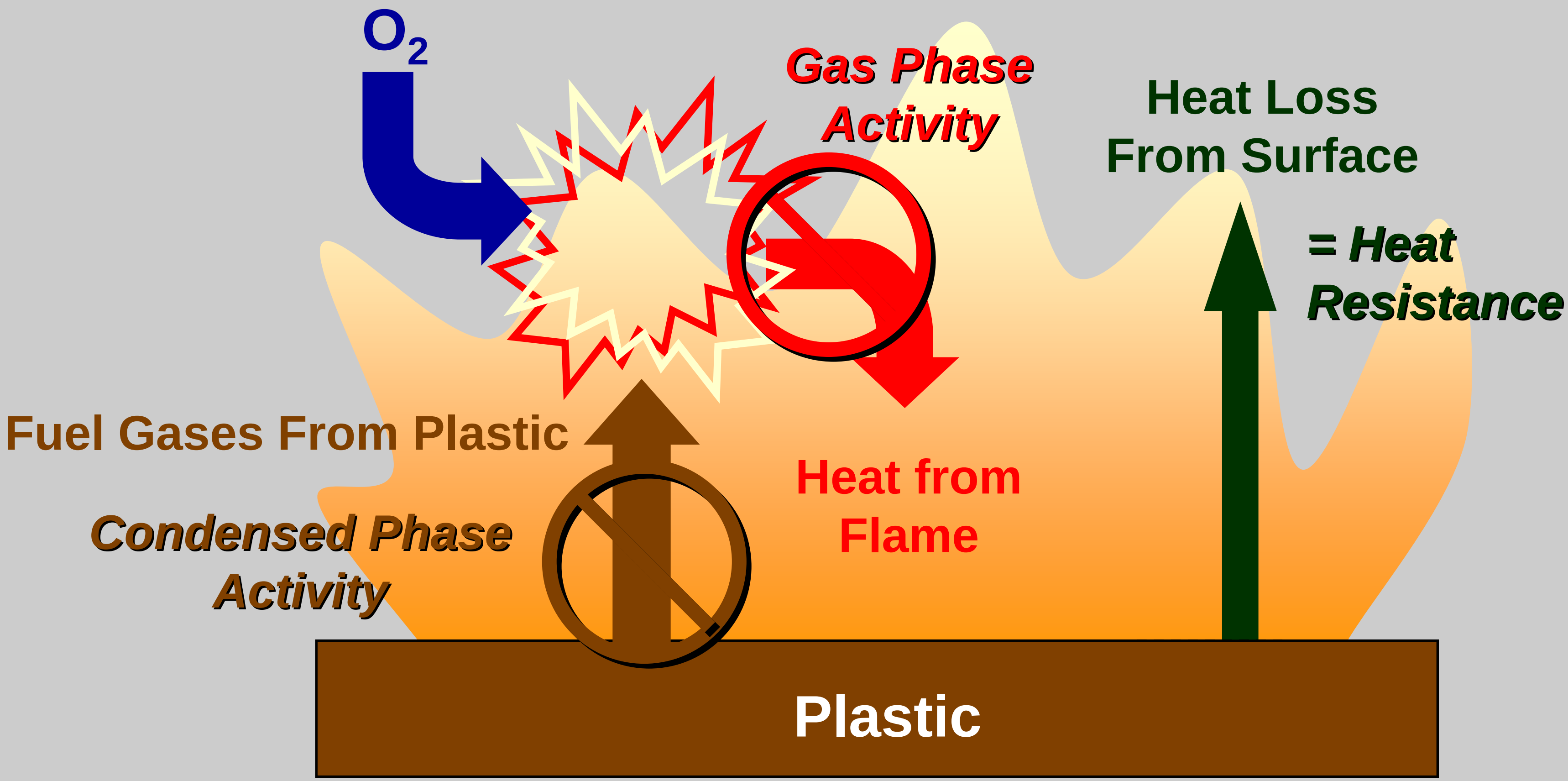
CONCLUSIONS

THE GOAL OF THE FR ADDITIVE APPROACH



*Truckload Prices, 2001

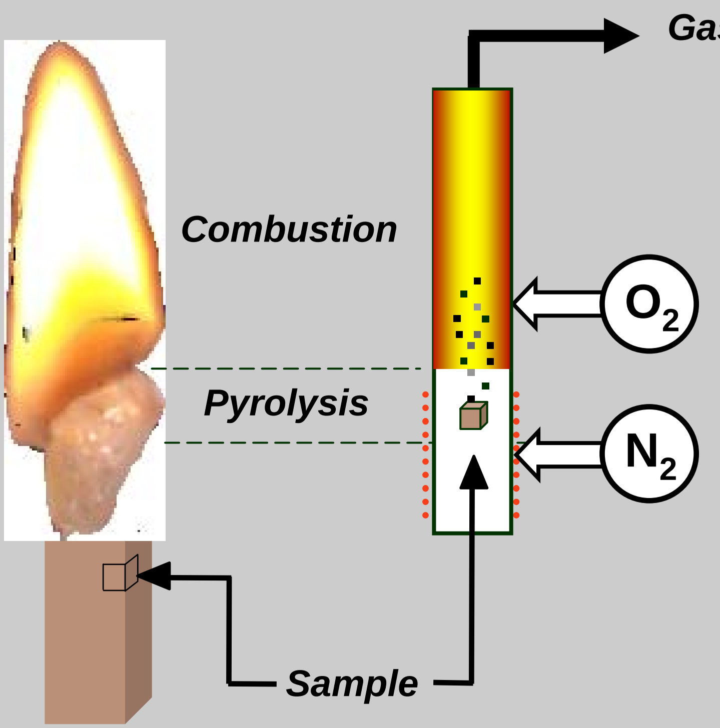
FLAME RETARDANTS WORK IN TWO WAYS



Need to quantify the efficiency of these modes of action

APPROACH

1) **Reproduce elements of flaming combustion in non-flaming test**



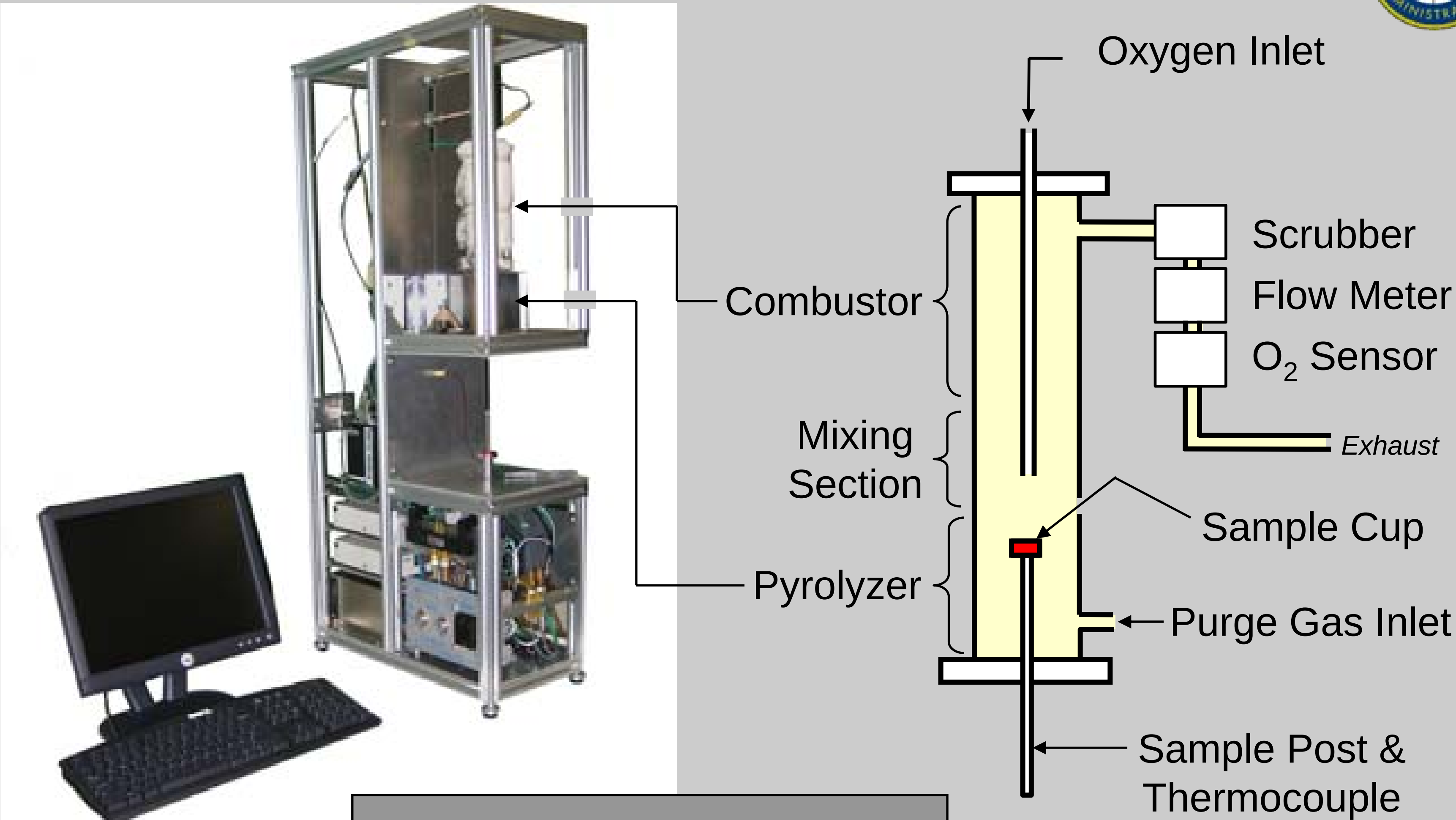
Flaming Combustion

Microscale Combustion Calorimeter

2) **Measure thermal combustion properties of materials**

3) **Relate thermal combustion properties to fire and flame tests using deterministic and probabilistic models**

MICROSCALE COMBUSTION CALORIMETER (MCC)

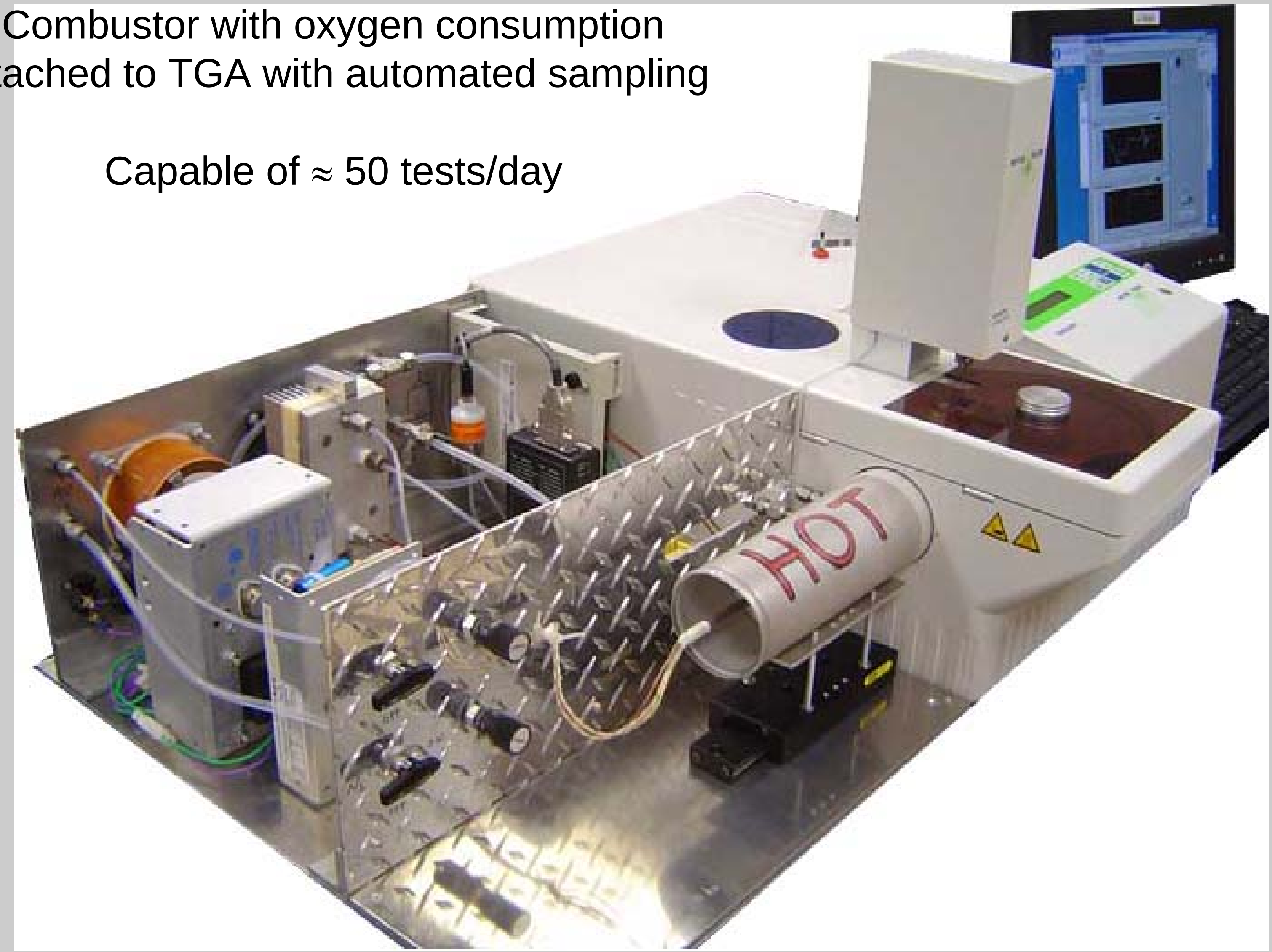


Heat release rate by oxygen consumption

AUTOMATED / HIGH THROUGHPUT MCC

Combustor with oxygen consumption attached to TGA with automated sampling

Capable of ≈ 50 tests/day



Designation: D 7309 – 07

Standard Test Method for Determining Flammability Characteristics of Plastics and Other Solid Materials Using Microscale Combustion Calorimetry[1]

This standard is issued under the fixed designation D 7309; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method, which is similar to thermal analysis techniques, establishes a procedure for determining flammability characteristics of combustible materials such as plastics.

1.2 The test is conducted in a laboratory environment using controlled heating of milligram specimens and complete thermal oxidation of the specimen gases.

1.3 Specimens of known mass are thermally decomposed in an oxygen-free (anaerobic) or oxidizing (aerobic) environment at a constant heating rate between 0.2 and 2 K/s.

1.4 The heat released by the specimen is determined from the mass of oxygen consumed to completely oxidize (combust) the specimen gases.

1.5 The rate of heat released by combustion of the specimen gases produced during controlled thermal or thermoxidative decomposition of the specimen is computed from the rate of oxygen consumption.

1.6 The specimen temperatures over which combustion heat is released are measured.

1.7 The mass of specimen remaining after the test is measured and used to compute the residual mass fraction.

1.8 The specimen shall be a material or composite material in any form (fiber, film, powder, pellet, droplet). This test method has been developed to facilitate material development and research.

1.9 *This standard is used to measure and describe the response of materials, products, or assemblies to heat and flame under controlled conditions, but does not by itself incorporate all factors required for fire hazard or fire risk assessment of the materials, products, or assemblies under actual fire conditions.*

1.10 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

NOTE 1—There is no ISO equivalent to this test method.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D 883 Terminology Relating to Plastics

D 5865 Test Method for Gross Calorific Value of Coal and Coke

E 176 Terminology of Fire Standards

E 1591 Guide for Obtaining Data for Deterministic Fire Models

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms relating to plastics, refer to Terminology D 883.

3.1.2 For definitions of terms relating to fire, refer to Terminology E 176.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *combustion res*… cies remaining after co… tion of a specimen.

3.2.2 *combustion te*… ture at which the specifi… controlled thermal oxid…

3.2.3 *controlled hea*… gram used to effect therr… decomposition in whic… uniform throughout and…

3.2.4 *controlled ther… tion, n*—thermal (oxid… heating.

MCC became ASTM Standard April 1, 2007

3.2.5 *heat release capacity, n*—the maximum specific heat release rate during a controlled thermal decomposition divided by the heating rate in the test.

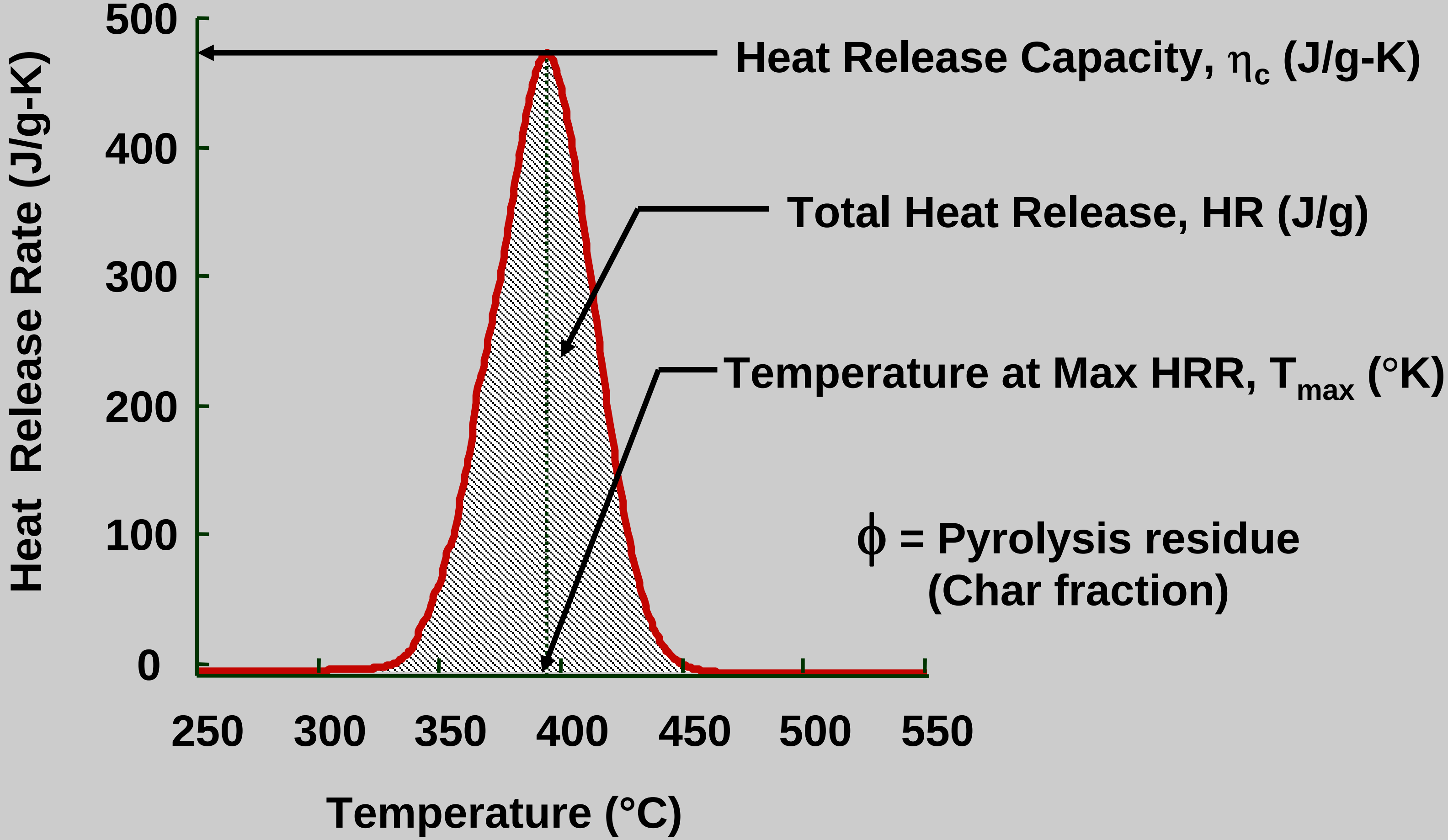
3.2.6 *heating rate, n*—the constant rate of temperature rise of the specimen during the controlled temperature program.

3.2.7 *heat release temperature, n*—the specimen temperature at which the specific heat release rate is a maximum during controlled thermal decomposition.

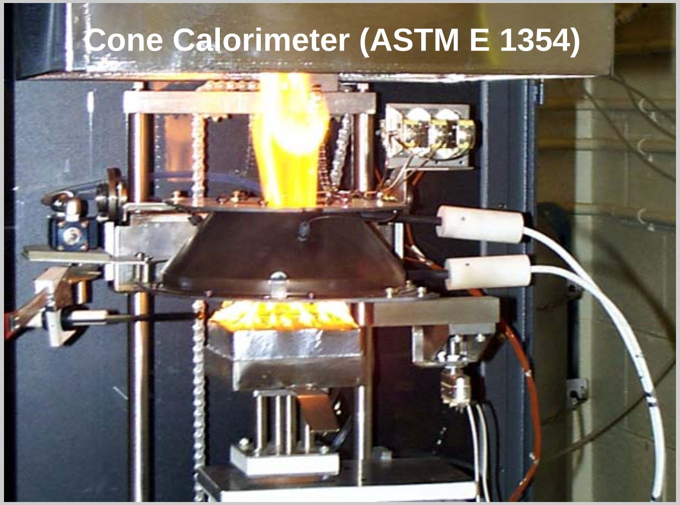
[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.30 on Thermal Properties.
Current edition approved April 1, 2007. Published April 2007.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

THERMAL COMBUSTION PROPERTIES (MCC)



FORCED AND UNFORCED COMBUSTION


Cone Calorimeter (ASTM E 1354)


Vertical Flame Test
(ASTM D 3801)

Unforced Combustion


OSU Calorimeter
(14 CFR Part 25)

Forced Combustion


Oxygen Index (ASTM D 2863)

FLAMING COMBUSTION: Gas Phase Chemistry

Complete Combustion (Oxidation) of Fuel Gases

$$C_cH_hO_mN_nX_x + m\,O_2 \xrightarrow[10\ sec]{900\ ^\circ C} CO_2 + H_2O + N_2 + HX$$

Fuel Gases

} Microscale Combustion Calorimetry

Incomplete Combustion of Fuel Gases in Diffusion Flame

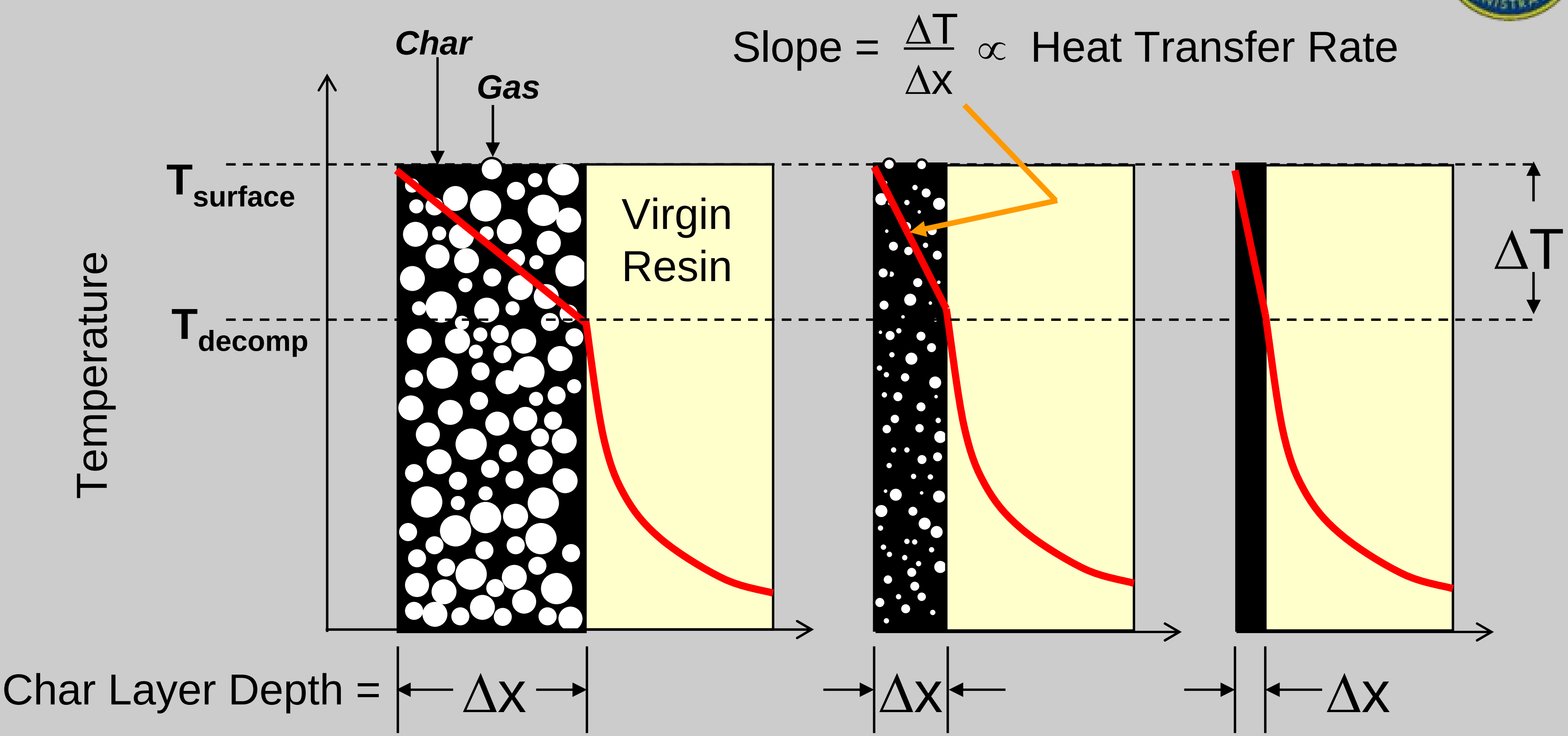
$$C_cH_hO_mN_nX_x + n\,O_2 \xrightarrow{Flame} CO_2 + H_2O + N_2 + HX + CO + C_xH_y + soot$$

Fuel Gases

} Fires and Flames

Flaming Combustion Efficiency, $\chi = \dfrac{n\,O_2}{m\,O_2} < 1$

FLAMING COMBUSTION: Condensed Phase Physics



Heat Transfer Efficiency, θ **=** $\dfrac{\{-\kappa(\Delta T/\Delta x)\}_{\text{char layer}}}{\{-\kappa(\Delta T/\Delta x)\}_{\text{resin}}} = \dfrac{q''_{net}}{q''^{0}_{net}}$

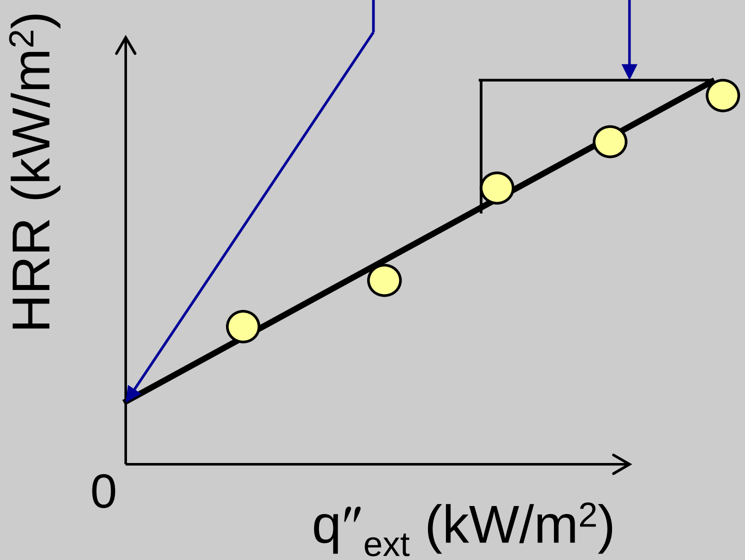
STEADY BURNING MODEL: Macro

Heat Release Rate (HRR) for Steady Burning:

$$HRR = \chi \frac{H_c^0}{L_g} \theta \left(q''_{flame} - q''_{rerad} \right) + \chi \frac{H_c^0}{L_g} \theta \, q''_{ext}$$

Cone Calorimeter Data

HRR_0 ***HRP***



H_c^0 = Heat of Combustion Of Fuel Gases

χ = Combustion Efficiency in Flame

θ = Heat Transfer Efficiency at Surface

HRR AND THERMAL COMBUSTION PROPERTIES

Heat Release Capacity

$$HRP = \chi\theta \frac{H_c^0}{L_g} = \chi\theta \frac{\eta_c}{\eta_g}$$

Flaming Combustion Efficiency

$$\frac{h_g}{\Delta T_p}$$

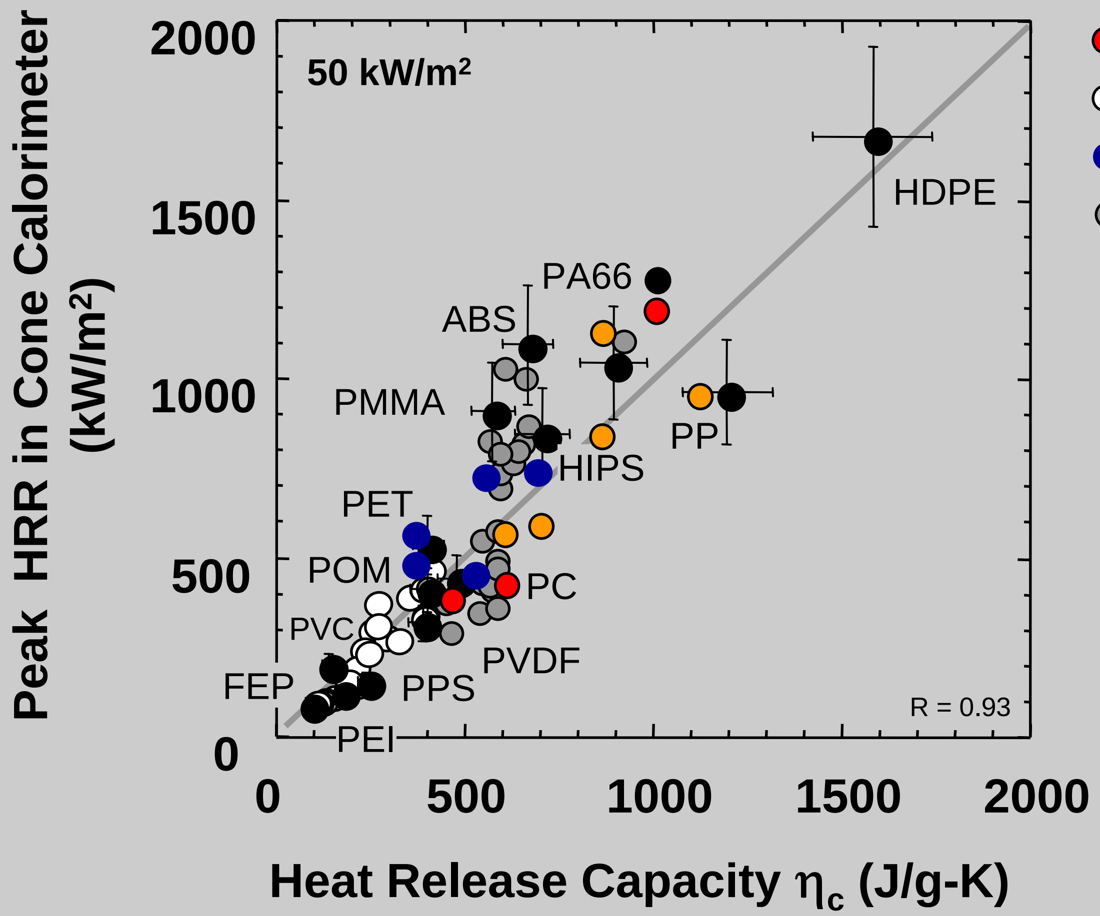
Heat Release Rate:

$$\mathbf{HRR} = \frac{\eta_c}{\eta_g}\left(q''_{flame} - q''_{rerad}\right) + \frac{\eta_c}{\eta_g} q''_{ext}$$

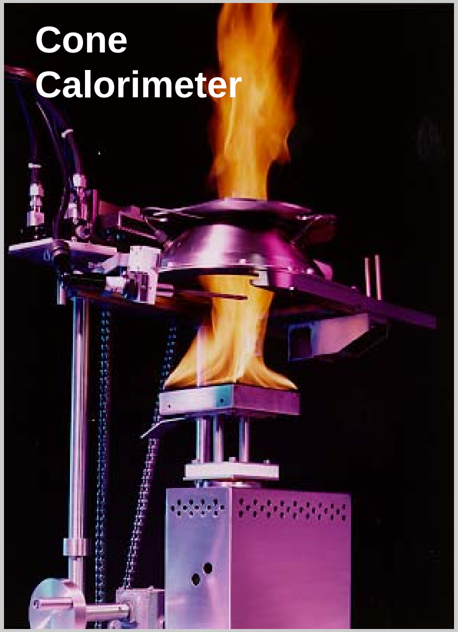
Fire Response

HEAT RELEASE RATE: Macro Vs. Micro

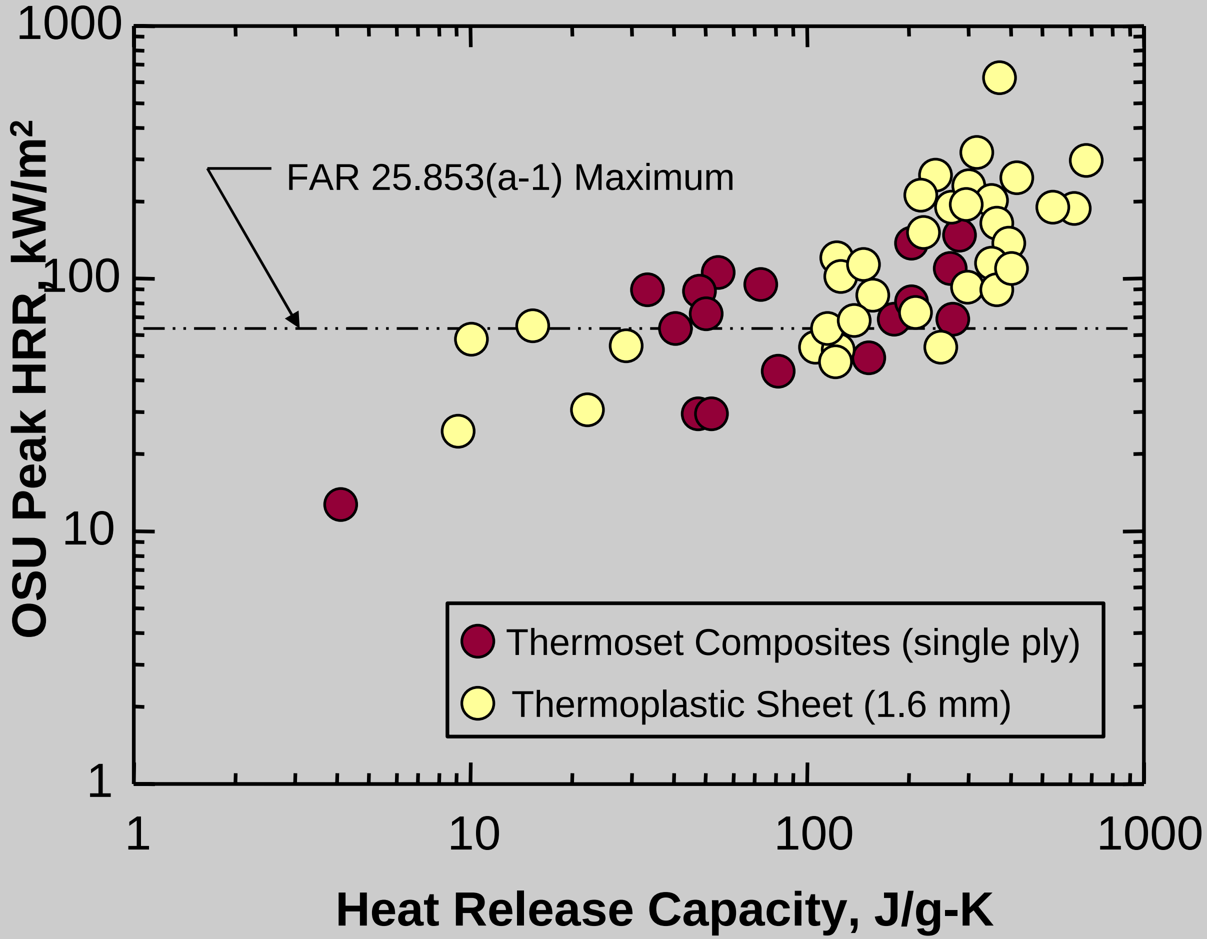
At large external heat flux, HRR $\propto \eta_c$



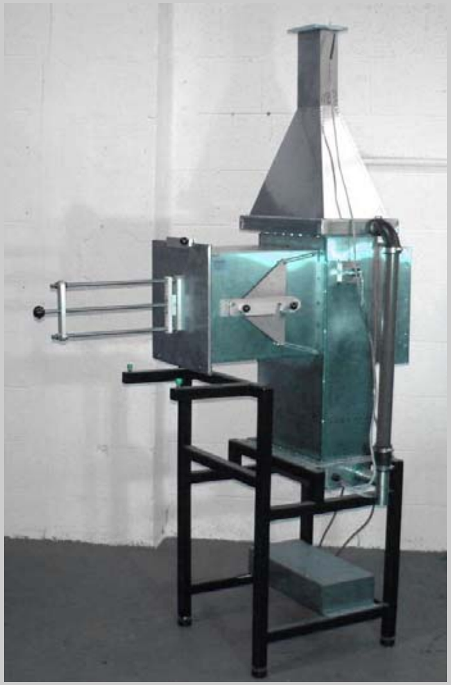
- Natural Plastics
- Micro-composites
- Nano-composites
- GFRP (PA6, PBT, PC, PPS)
- PC/ABS Blends
- FR Compounds



OSU HEAT RELEASE RATE: Macro Vs. Micro



ASTM E 906/OSU Rate of Heat Release Apparatus



Flame Resistance

FLAME EXTINCTION CRITERIA

Flame Extinction Occurs at Critical HRR:

$$HRR^* \approx \begin{cases} 100\ kW/m^2 \ \ \text{(Downward Burning)} \\ 60\ kW/m^2 \ \ \text{(Upward Burning)} \end{cases}$$

- **MACRO Extinction Criterion for Flame Tests**

$$HRP \leq \frac{HRR^*}{(q''_{flame} - q''_{loss})}$$

- **MICRO Extinction Criterion for Flame Tests**

$$\eta_c \leq \frac{\eta_g\ HRR^*}{(q''_{flame} - q''_{rerad})} = \eta_c^*$$

FLAME RESISTANCE TEST (ASTM D2863)

Limiting Oxygen Index (LOI) = $[O_2^*]$

HRR = 100 kW/m² (downward burning)*

$q''_{flame} \propto [O_2] = a\,[O_2]$ $\qquad q''_{rerad} = \sigma T^4_{max} \approx 17 kW/m^2$

$a = 1.4\ kW/m^2\text{-}\%O_2$

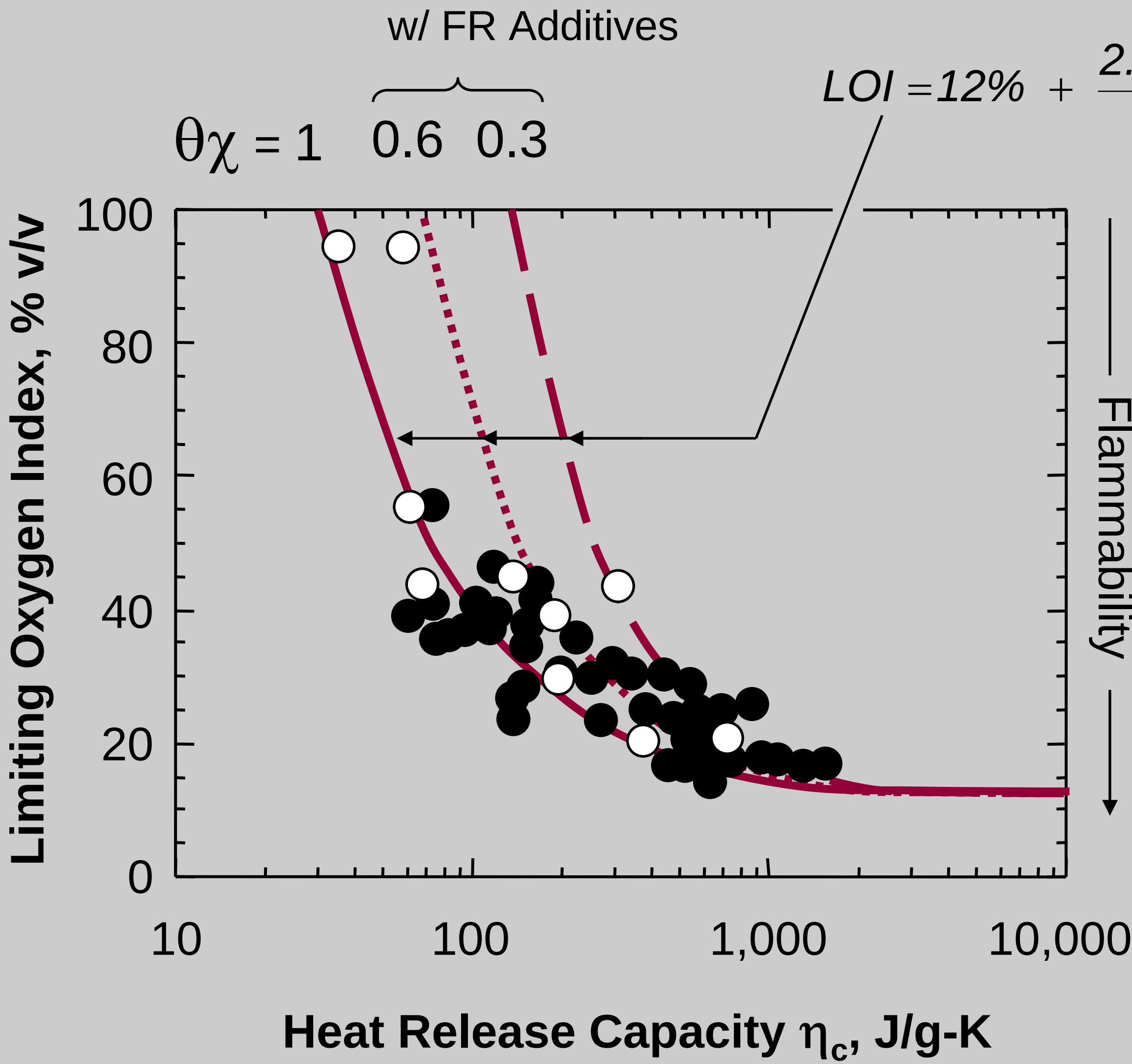
$$\eta_g = \frac{h_g / \Delta T_p}{\chi\theta} = \frac{(2\,kJ/g)/(50K)}{\chi\theta} = \frac{40\,J/g-K}{\chi\theta}$$

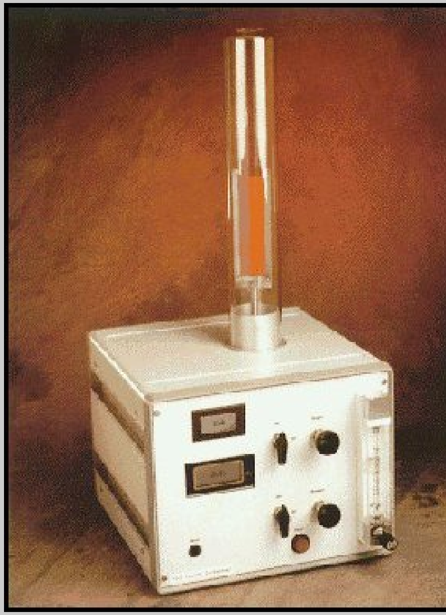
LOI EXTINCTION CONDITION:

$$[O_2^*] = \frac{q''_{rerad}}{a} + \frac{HRR^*\,\eta_g / a}{\eta_c} \approx 12\% + \frac{2.8\,kJ/g-K}{\theta\,\chi\,\eta_c}(\%)$$

EFFECT OF BURNING EFFICIENCY ON L.O.I.

$$LOI = 12\% + \frac{2.8\,kJ/g-K}{\theta\chi\eta_c}(\%)$$





FLAME RESISTANCE: UPWARD BURNING

Comparative Burning Characteristics of Plastics in Vertical Position (UL 94 V or ASTM D 3801):

$$HRR^* = 60\ kW/m^2$$

$$q''_{rerad} = CHF \approx \varepsilon\sigma T_{max}^4$$

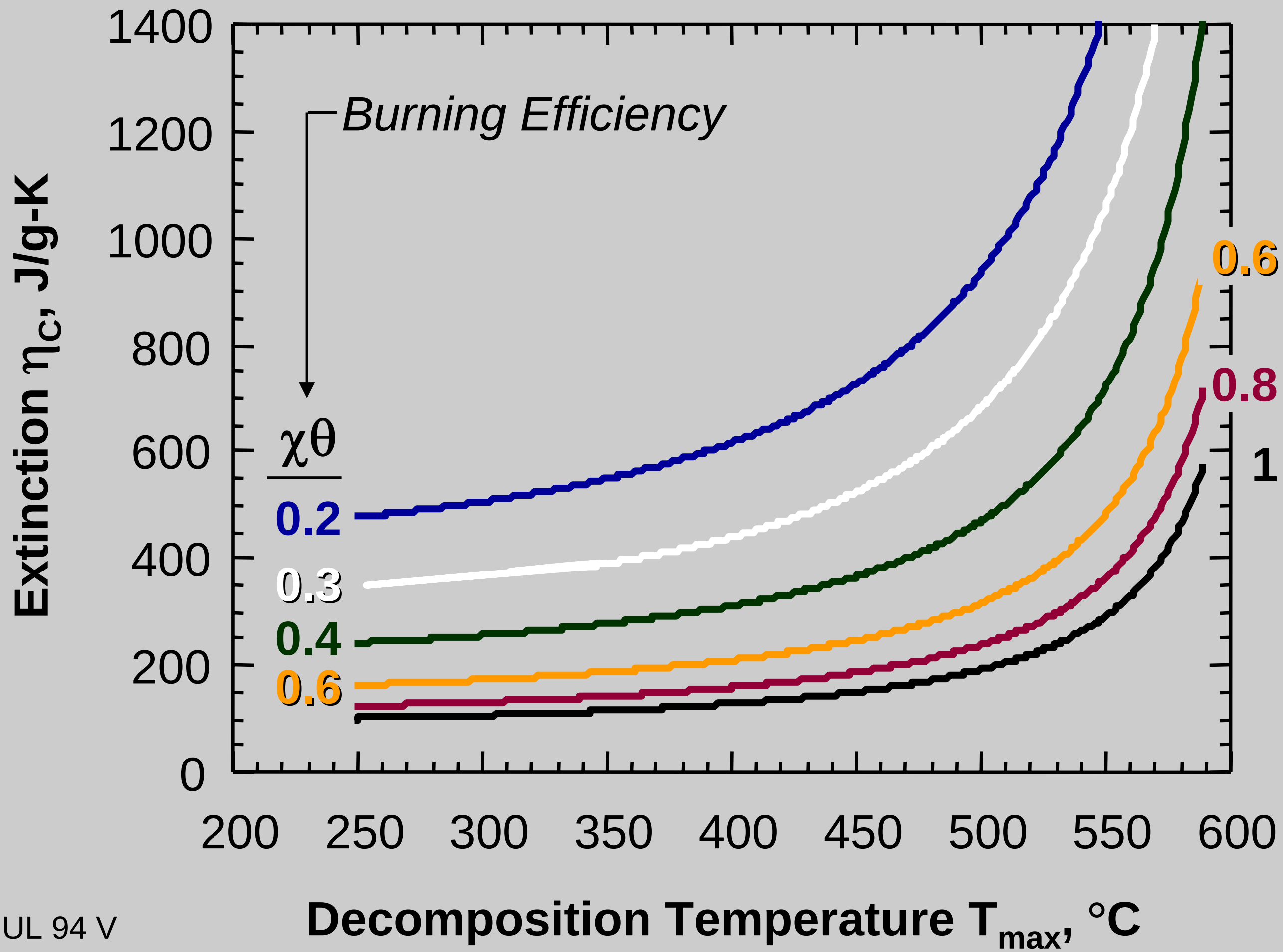
$$q''_{flame} \approx 30\ kW/m^2$$

$$\eta_g = \frac{h_g / \Delta T_p}{\chi\theta} = \frac{(2\,kJ/g)/(50K)}{\chi\theta} = \frac{40\,J/g-K}{\chi\theta}$$

UL 94 V EXTINCTION CONDITION:

$$\eta_c \quad \leq \quad \frac{HRR^*\ \eta_g}{\chi\theta(q''_{flame} - \varepsilon\sigma T_{max}^4)} \approx \frac{2.4\ MW\,J\,m^{-2}\,g^{-1}K^{-1}}{\chi\theta(q''_{flame} - \varepsilon\sigma T_{max}^4)}$$

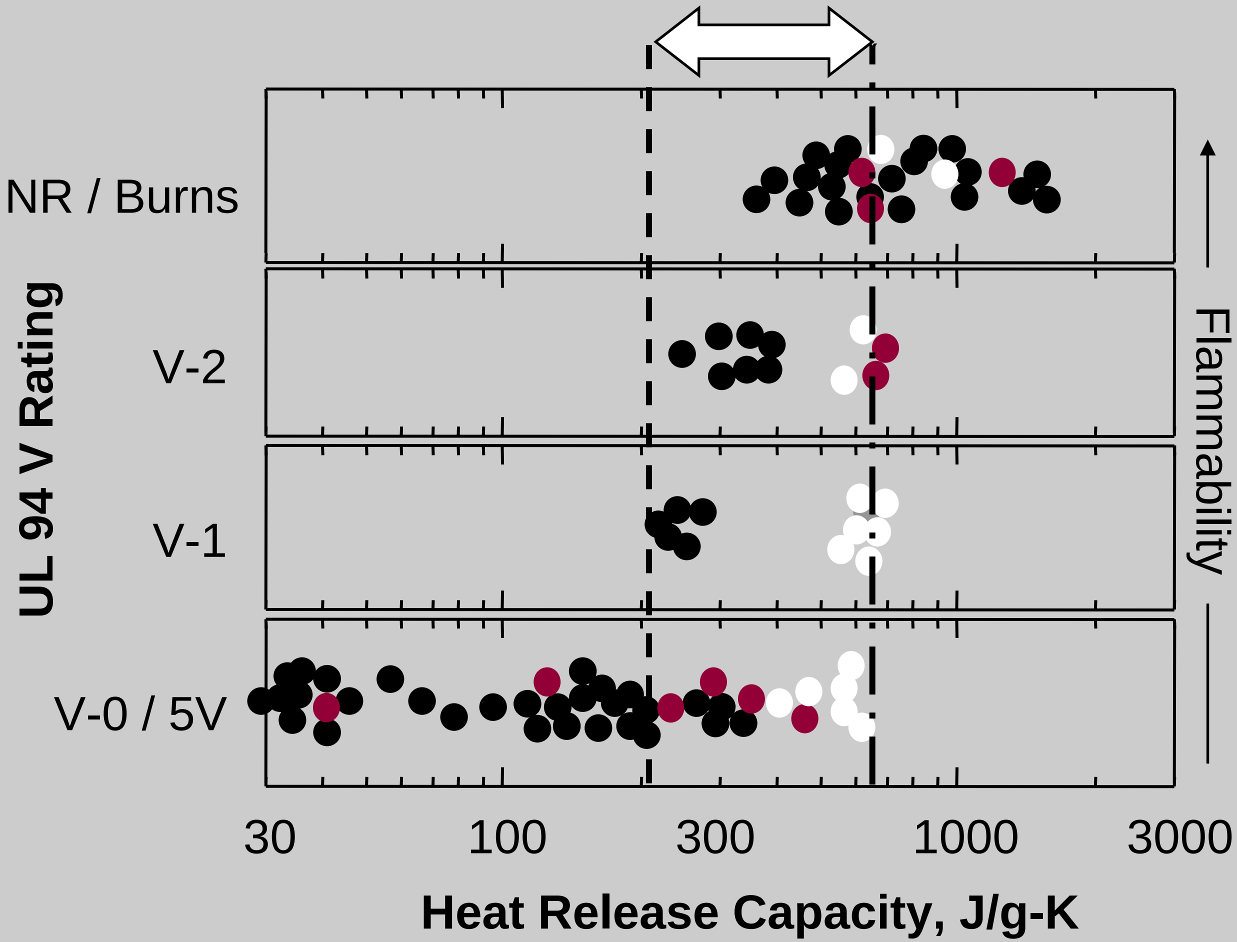
EFFECT OF $\chi\theta$ AND T_{max} ON EXTINCTION η_c



UL 94 V
Flame Test

EFFECT OF BURNING EFFICIENCY ON UL 94

UNCERTAINTY DUE TO BURNING EFFICIENCY



ODDS OF BURNING AND HRR

Assume that *Odds of Burning* is related to HRR and **probability of burning, p_B**

$$\textbf{Odds of Burning} = \frac{p_B}{1 - p_B} = \left(\frac{HRR}{HRR^*}\right)^3$$

Then,

$$p_B = \frac{(HRR/HRR^*)^3}{1 + (HRR/HRR^*)^3}$$

$\frac{HRR}{HRR^*}$	p_B
10	0.999
5	0.99
2	0.89
1	0.5
1/2	0.11
1/5	0.008
1/10	0.001

$$\textbf{HRR} = \chi\theta \frac{\eta_c}{\eta_g} q''_{net} \quad ; \qquad \textbf{HRR*} = \frac{\eta_c^*}{\eta_g} q''_{critical} \approx 60 \text{ kW/m}^2$$

Then,

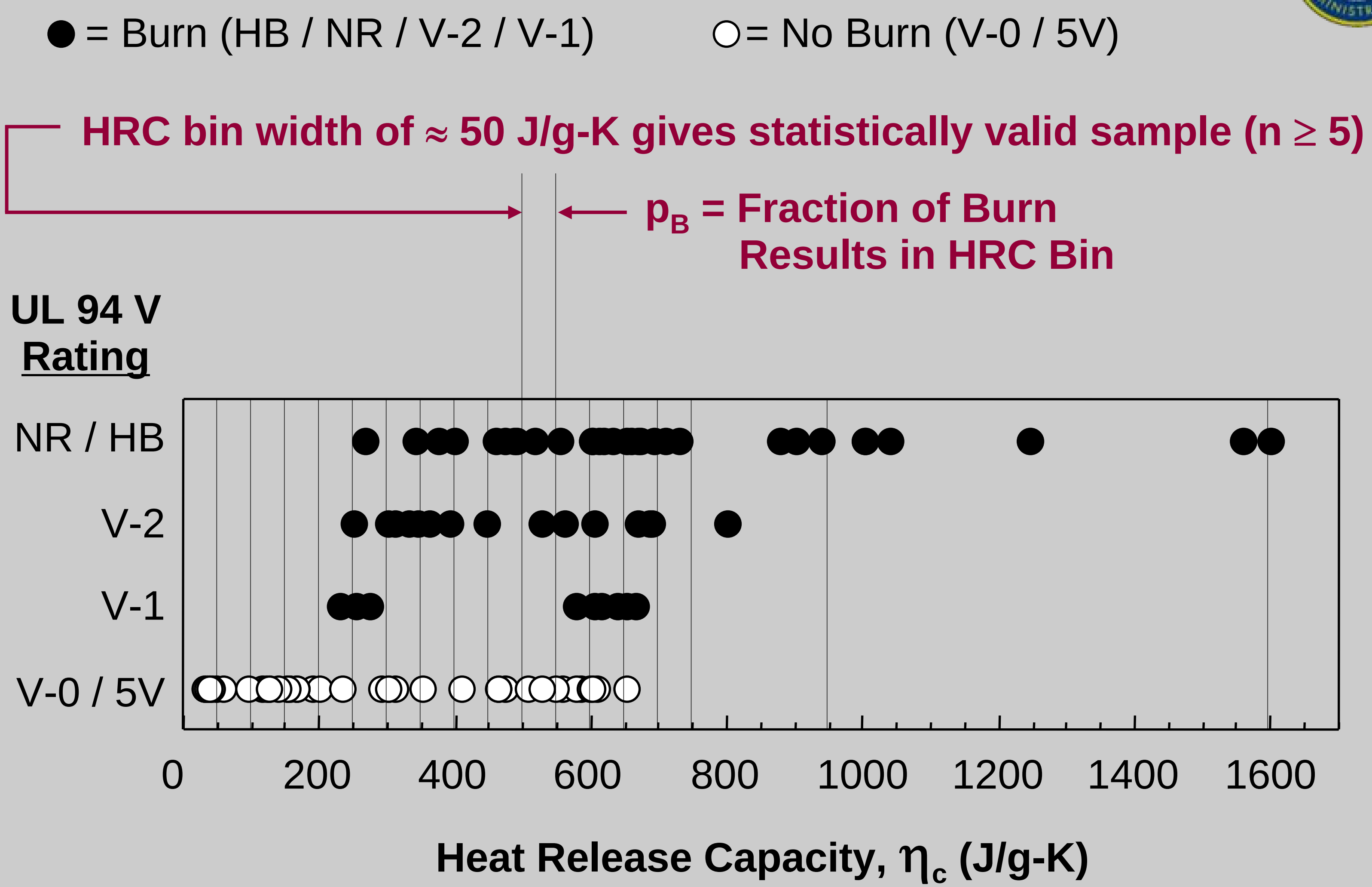
$$\frac{p_B}{1-p_B} = \left(\frac{HRR}{HRR^*}\right)^3 = \left(\chi\theta \frac{\eta_c}{\eta_c^*}\right)^3 \left(\frac{q''_{net}}{q''_{critical}}\right)^3 \approx \left(\chi\theta \frac{\eta_c}{\eta_c^*}\right)^{3/\chi\theta}$$

And:

$$p_B = \frac{(\chi\theta\,\eta_c / \eta_c^*)^{3/\chi\theta}}{1+(\chi\theta\,\eta_c / \eta_c^*)^{3/\chi\theta}}$$

Depends only on burning efficiency ($\chi\theta$)
and heat release capacity (η_c)

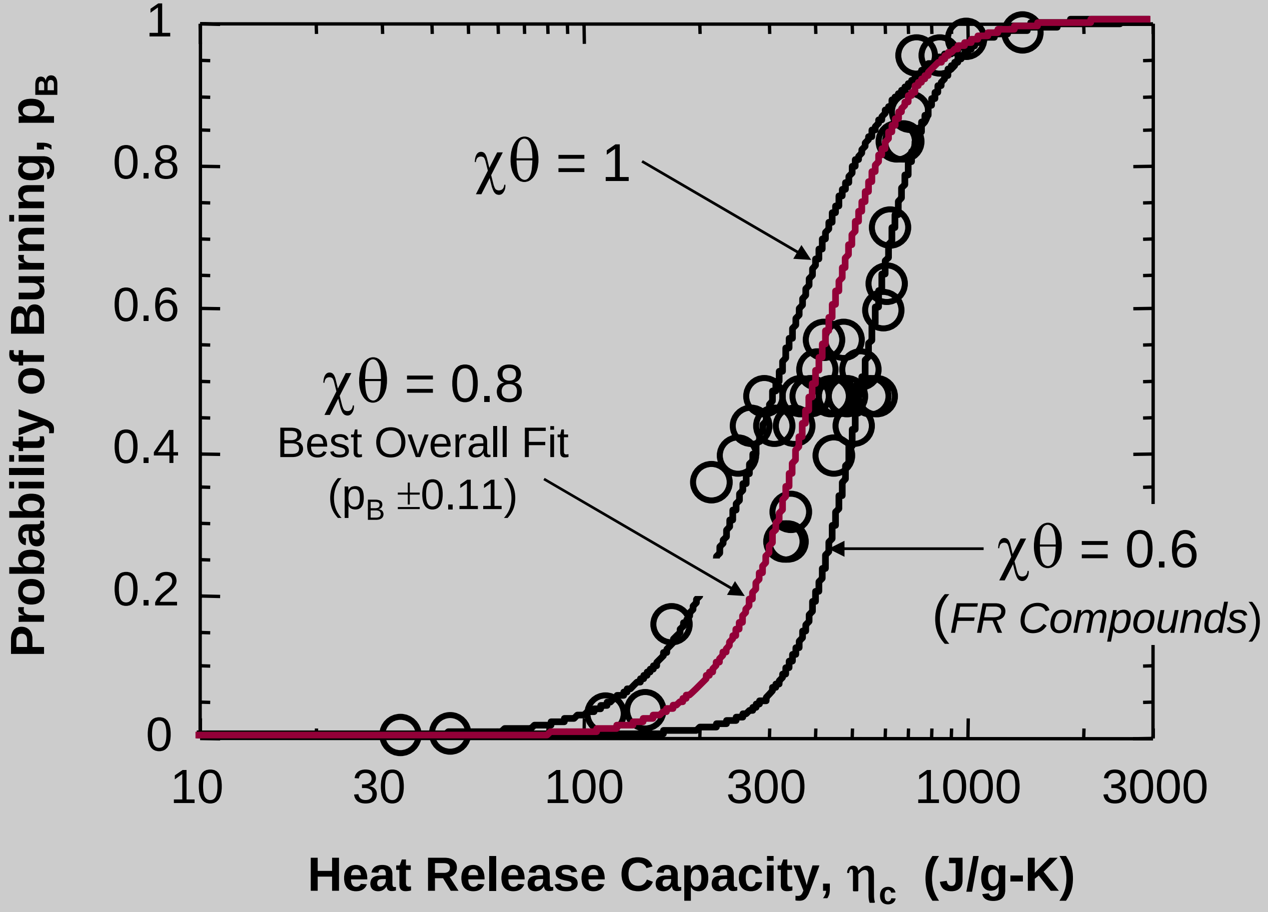
MEASURE PROBABILITY OF BURNING, p_B



184 test results

EFFECT OF BURNING EFFICIENCY ON PROBABILITY OF BURNING

$$p_B = \frac{(\chi\theta\,\eta_c / 325)^{3/\chi\theta}}{1 + (\chi\theta\,\eta_c / 325)^{3/\chi\theta}}$$



CONCLUSIONS

- **Deterministic Models** using thermal combustion properties appear adequate for *forced flaming combustion*.

- **Probabilistic Models** are required to reconcile MCC data with *flame resistance* tests because

  - Intumescence, charring (θ)
  - Gas phase inhibition (χ)
  - and Dripping

  } *Incomplete combustion in flame*

  are comparable in magnitude and effect to thermal combustion properties at extinction.