Heat Release Capacity

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Outline

- Background
  - Flammability Testing & Fire Processes
  - PCFC Instrument Description

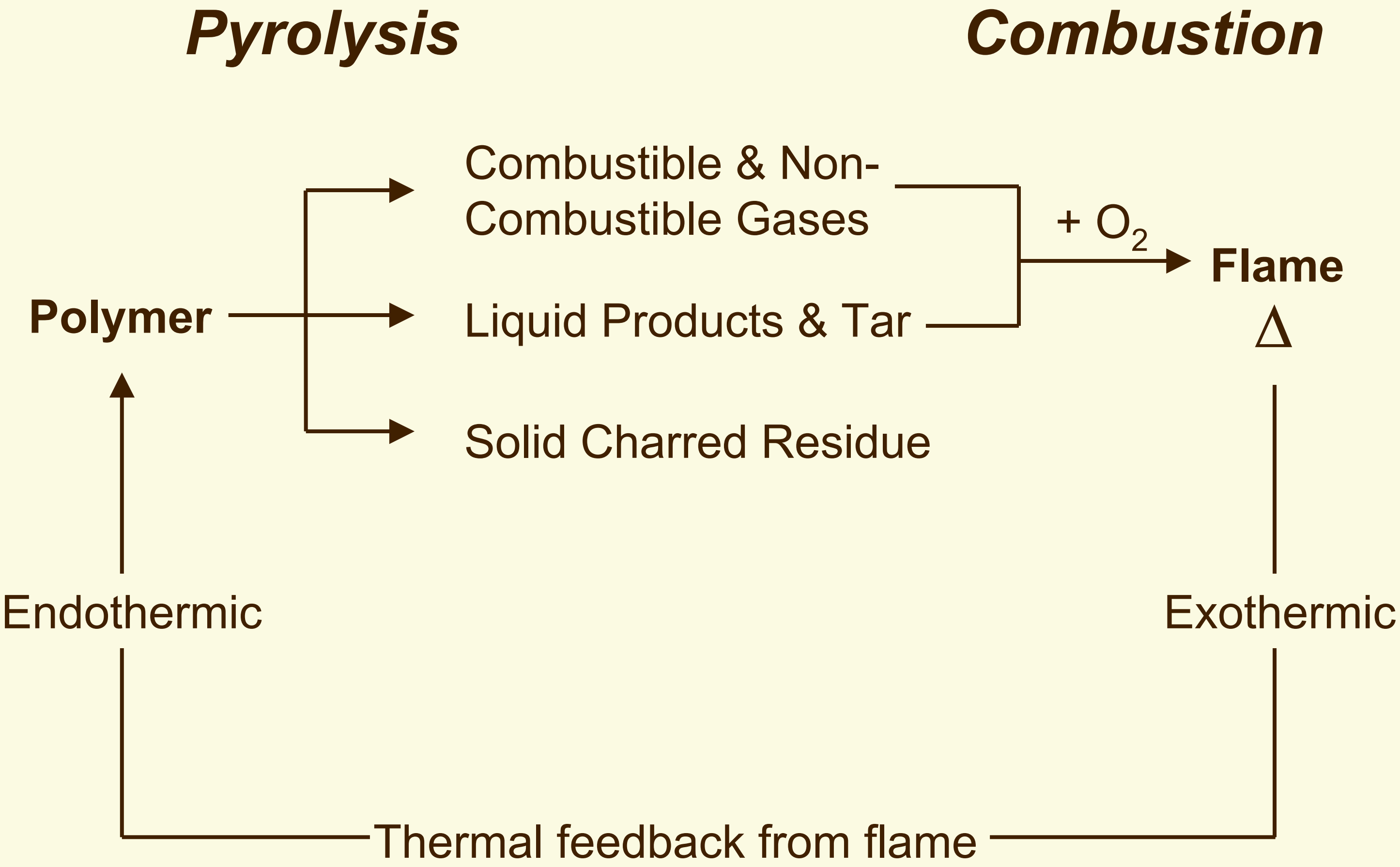
- Theory
  - PCFC
  - Heat Release Capacity
  - Fire Test Theory & Correlations
  - Molar Group Contributions

- Conclusions

Flammability Testing

- Extrinsic quantities resulting from the reaction of a macroscopic polymer sample to a severe thermal exposure
  - Burning Rate
  - Flammability
  - Ignitability
  - Fire Performance
- Fire test results are dependent on
  - Orientation
  - Color
  - Geometry
  - Ambient Conditions
  - Sample Size
  - Operator
- Thermal and mass diffusion effects dominate the fire behavior in large sample tests
- An intrinsic material property is needed to correlate fire performance

Fuel Generation Process



Pyrolysis

Combustion

Combustible & Non-Combustible Gases

Polymer

Liquid Products & Tar

Solid Charred Residue

+ O_2

Flame

Δ

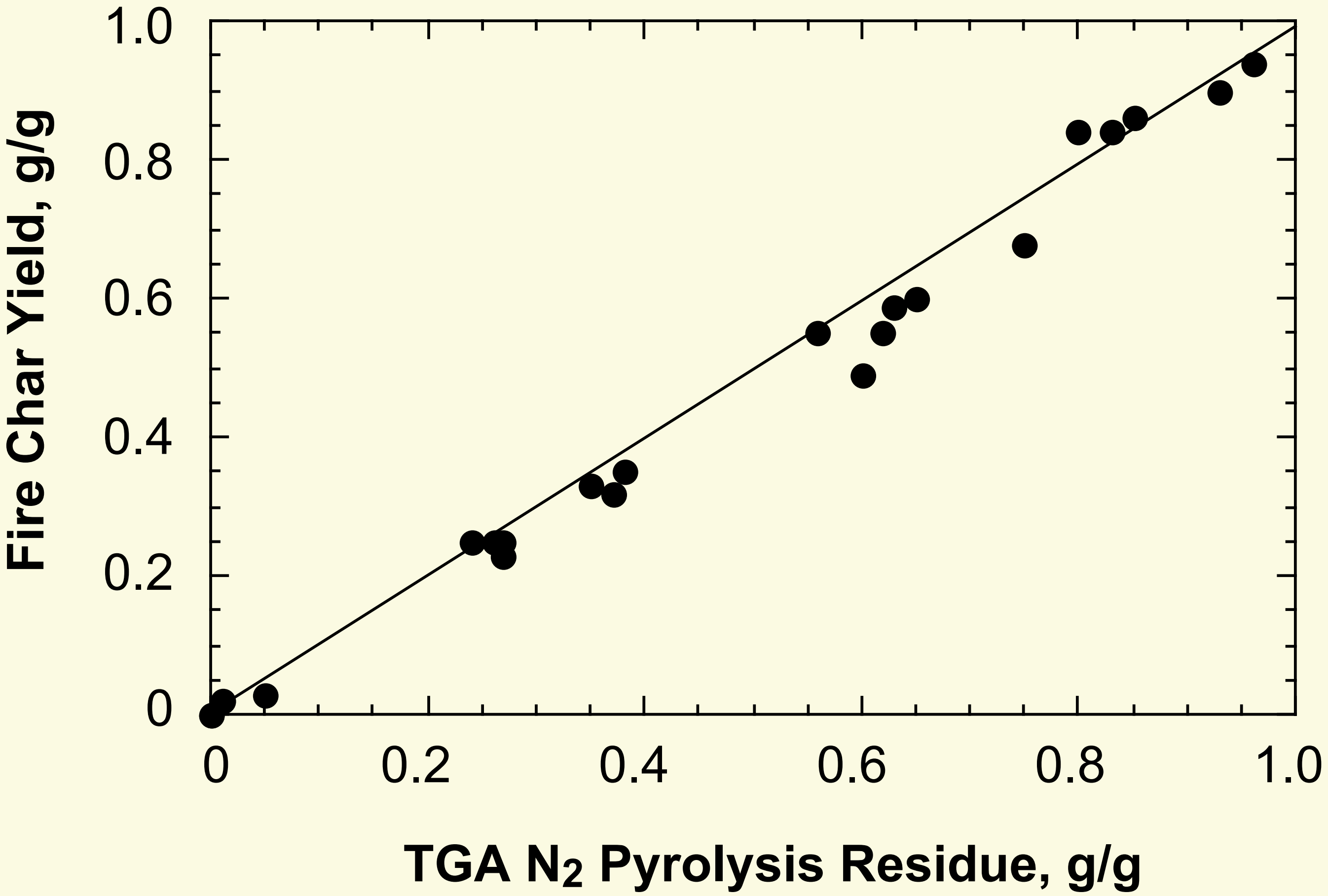
Endothermic

Exothermic

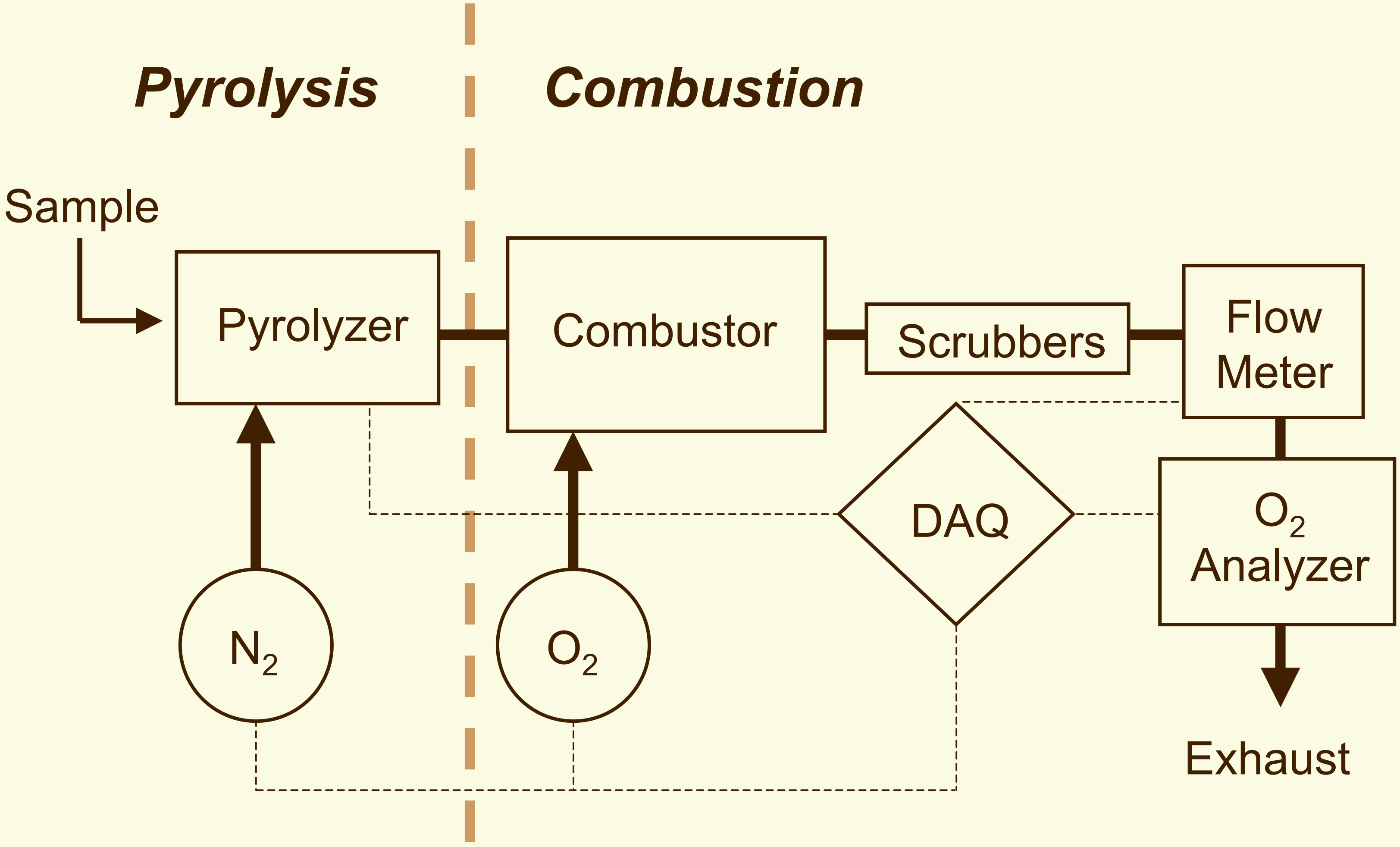
Thermal feedback from flame

Char Formation

Charring in fires is an **anaerobic** process



Microcalorimeter Schematic



Pyrolysis-Combustion Flow Calorimeter

Forced Non-Flaming Combustion Test

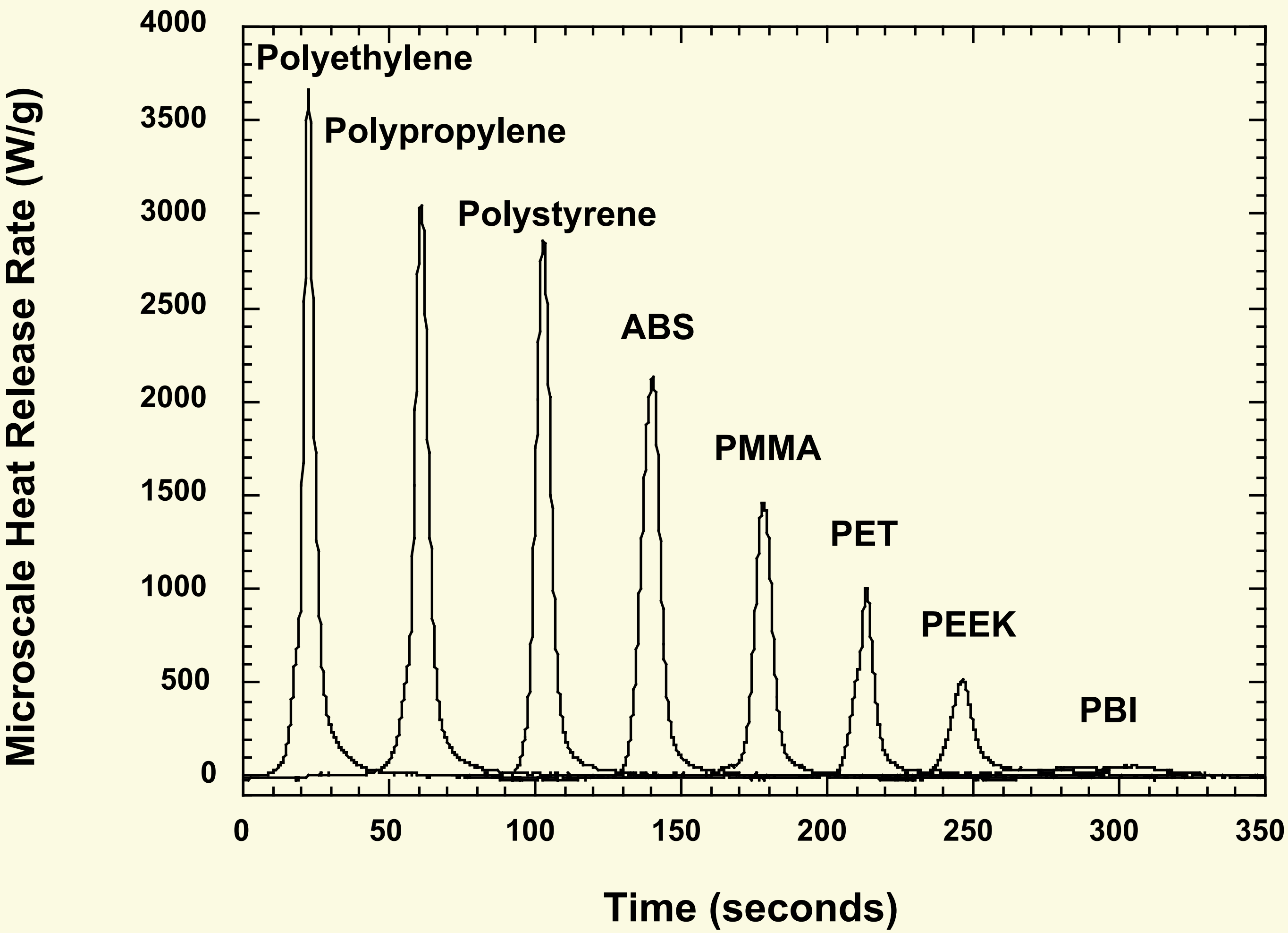
Small Sample Size: ~1mg

Rapid Screening of Materials

Measured Values:
- Heat Release Rate
- Total Heat Release
- Char Yield

Calculated Values:
- Heat Release Capacity
- Global E_a

Measured Heat Release Rates



Microcalorimeter Theory

Heat release rate by oxygen consumption normalized to initial sample mass

$$\dot{Q}_c(t) = \frac{E\Delta O_2}{m_o} = h^o_{c,v}(t)\left[\frac{-1}{m_o}\frac{dm(t)}{dt}\right]$$

Peak rate of heat release

$$\dot{Q}_c^{\max} = \left[\frac{E\Delta O_2}{m_o}\right]_{\max} = h^o_{c,v}\left[\frac{-1}{m_o}\frac{dm}{dt}\right]_{\max} = h^o_{c,v}\frac{\beta\left(1-\mu\right)E_a}{eR\,T_p^2}$$

Heat Release Capacity

$$\eta_c = \frac{\dot{Q}_c^{\max}(\beta)}{\beta} = \frac{h^o_c\left(1-\mu\right)E_a}{eR\,T_p^2}$$

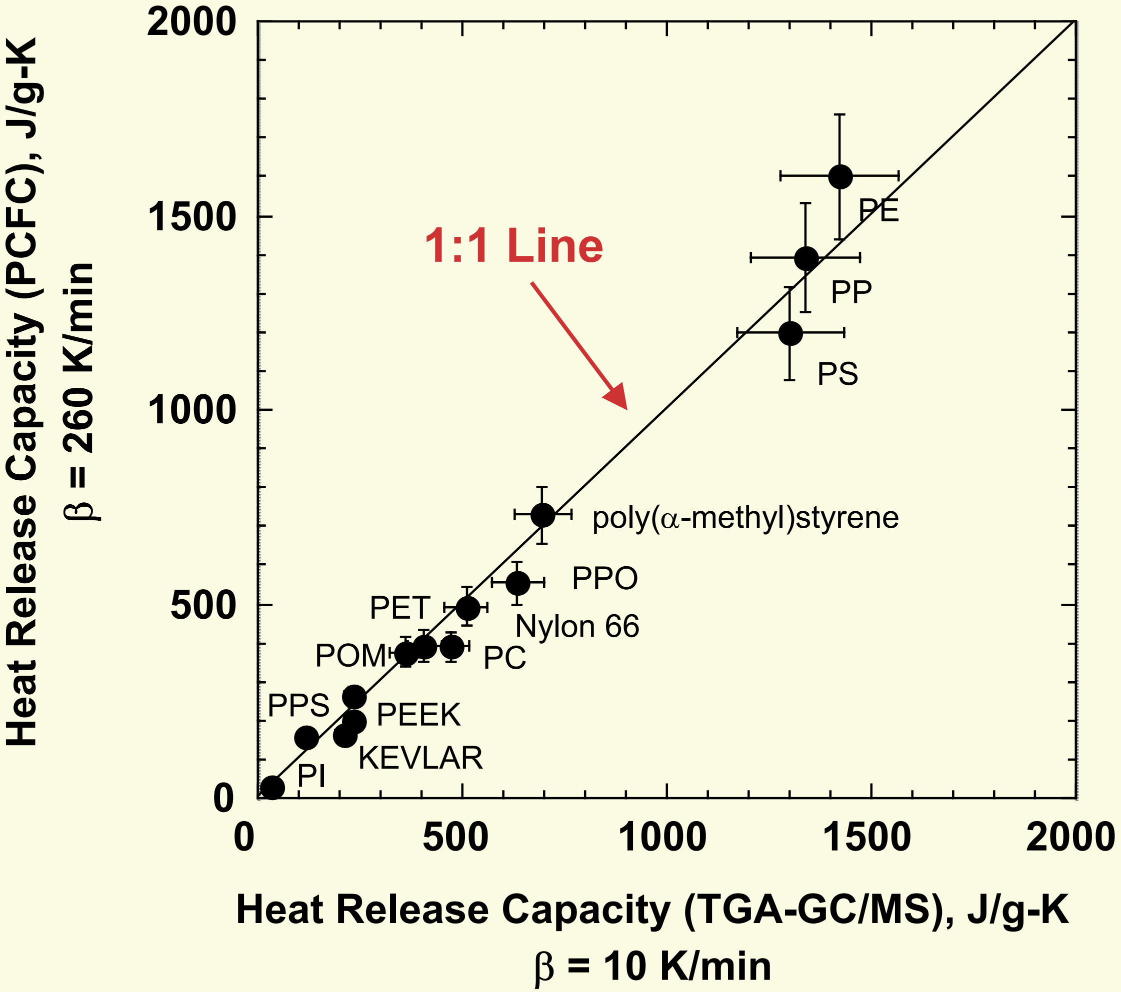
… dependent only on material properties

Material Property

Must satisfy the following conditions:

1. Independent of sample mass
2. Independent of heating rate
3. Measurable by different methods

Heat Release Capacity by TGA-GC/MS

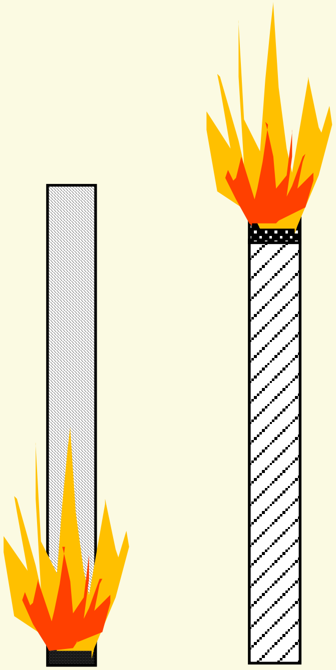


***T.V. Inguizilian**, Correlating Polymer Flammability Using Measured Pyrolysis Kinetics, MS Thesis, University of Massachusetts, Amherst, January 1999.*

Flammability Character - UL-94V vs. LOI

UL-94 - Vertical Bunsen Burner test based on operator observation where materials are classified by their burning behavior

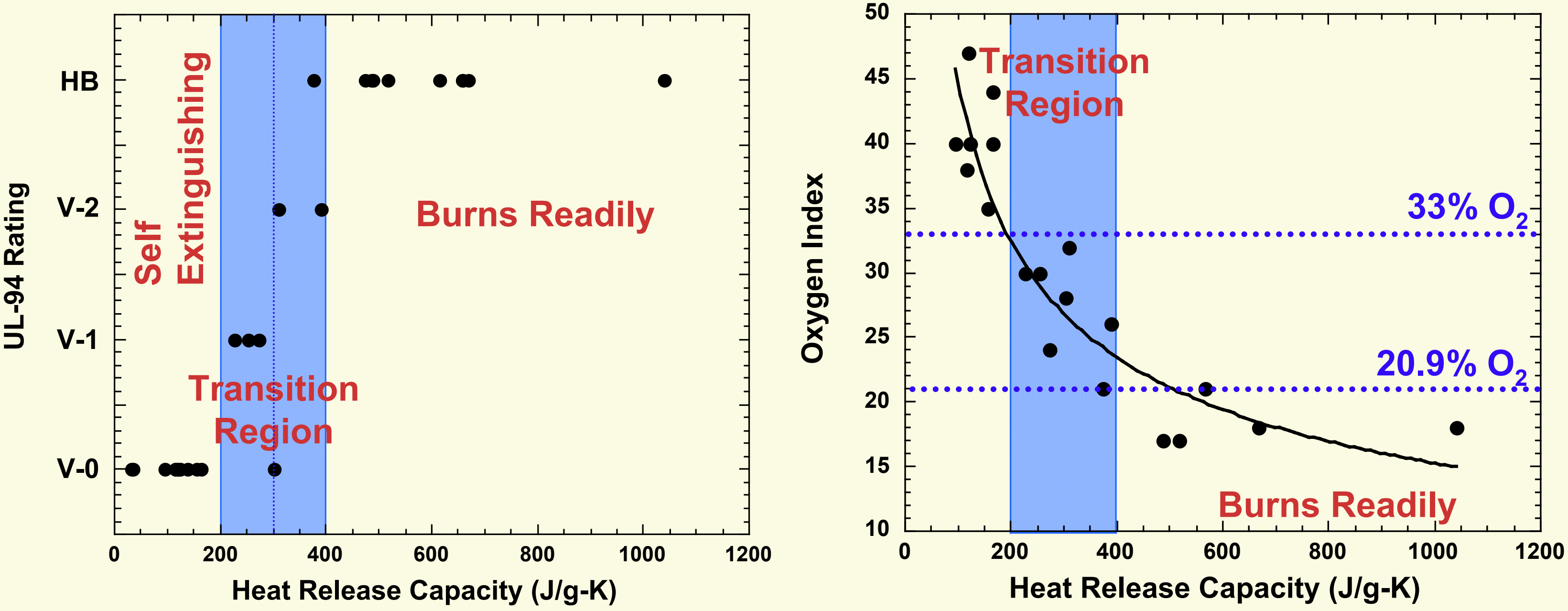
Oxygen Index - Minimum amount of oxygen needed to sustain a candle-like flame for 3 minutes based on operator observation



	UL-94	LOI
Vertical Test	X	X
Preheating of sample	X	
Radiant component	X	
Convective component	X	
Conductive component	X	X

***Upward** versus **Downward** flame spread*

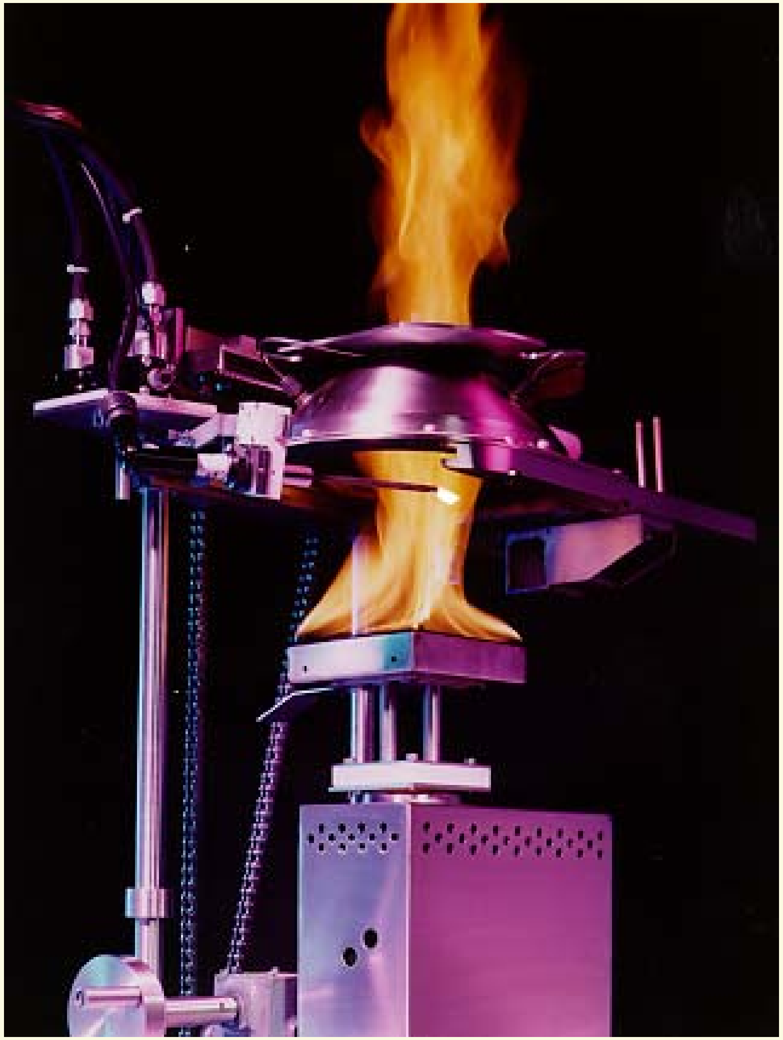
Fire Test Correlations - UL-94 & LOI



Transition Region from self-extinguishing to readily burning: 200-400 J/g-K

Transition Region corresponds to 21-33 $\%O_2$ in LOI

Cone Calorimeter



Bench Scale Flaming Combustion Test

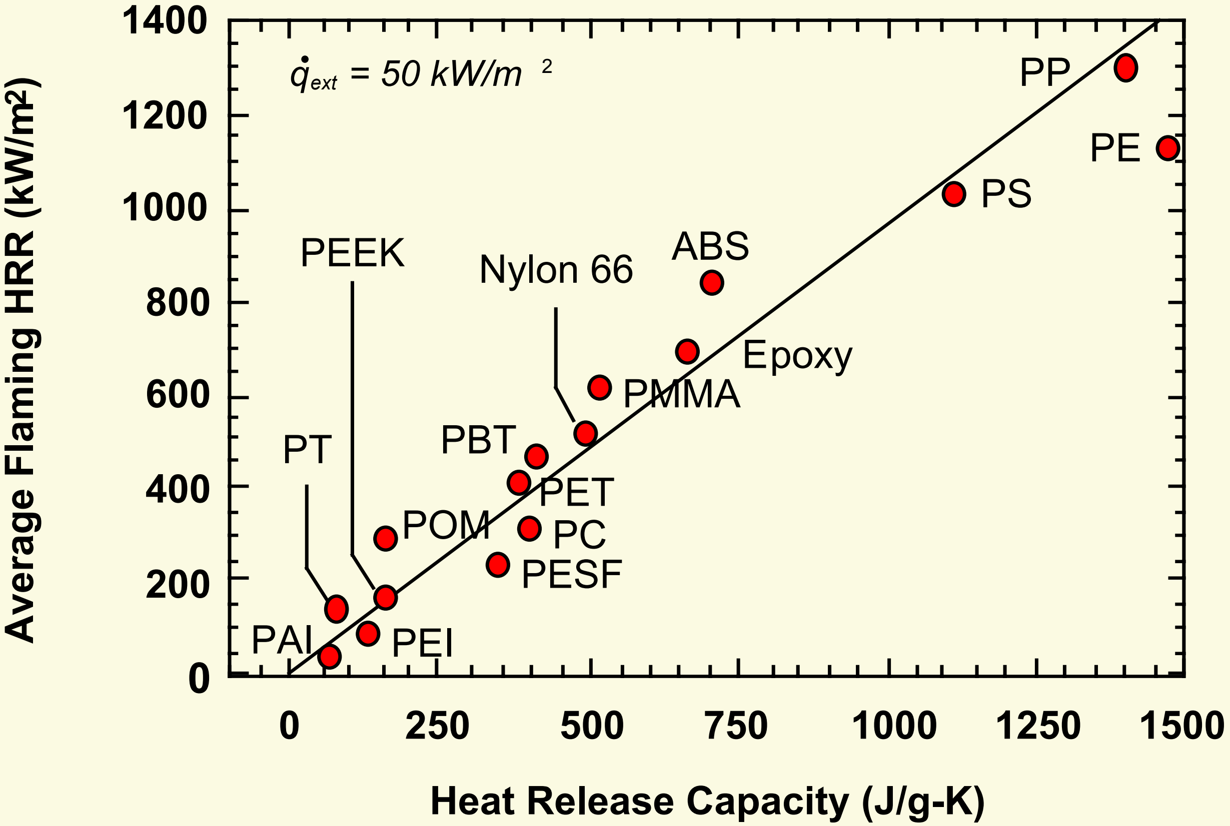
Sample Dimensions:
- 10cm x 10 cm x 0.3cm

0-100 kW/m^2 incident heat flux

Measured Values:
- heat release rate - O_2 consumption
- mass loss rate
- time to ignition
- CO & CO_2
- smoke generation

Calculated Values:
- critical heat flux
- heat of gasification
- ignition temperature
- thermal inertia ($\kappa\rho c$)

Fire Test Correlations - Cone Calorimeter



Cone Calorimetry - Bench scale flaming combustion test measuring heat release by oxygen consumption

Fire Test Summary

- ✓ Fire Tests
  - Flaming combustion tests where physical attributes influence the flammability
  - Samples can be designed to give false passes in the tests
  - Tests are hard to run and do not give quantitative results
  - Multiple tests and rigorous calculations needed to obtain material properties

- ✓ PCFC
  - Provides a material property directly
  - Quantitative results that represent the total fuel value of a sample
  - Quick & easy to run

Group Contribution Background

- ✓ Methods for predicting thermochemical data from molecular structure (Bensen 1968)
- ✓ Interactions of several atoms summed and approximated by structural groups (VanKrevelen 1972)
- ✓ Atomic-level bond topology used to predict molecular properties using connectivity indices (Bicerano, 1996)
- ✓ Structural group contribution method for flammability (Walters 2000)
- ✓ Group Contribution calculations can predict thermodynamic quantities such as:
  - Heat of Combustion
  - Char Yield
  - Heat Capacity
  - Thermal Decomposition Temperature
  - Glass Transition Temperature
- ✓ Theories of group contributions based on empirical correlations

Molar Group Contributions to η_c

Heat Release Capacity

$$\eta_c = \frac{\dot{Q}_c}{\beta} = \frac{h_c^o(1-\mu)E_a}{eR\,T_p^2}$$

Approach: Write the heat release capacity terms as additive molar quantities

$$\Psi = \frac{\boldsymbol{H}\,\boldsymbol{V}\,\boldsymbol{E}}{eR\,\boldsymbol{T}^2} = \frac{\left(\sum_i n_i H_i\right)\left(\sum_i n_i V_i\right)\left(\sum_i n_i E_i\right)}{eR\left(\sum_i n_i T_i\right)^2}$$

Expand summations over chemical groups, i, j, k… and neglect terms with mixed indices

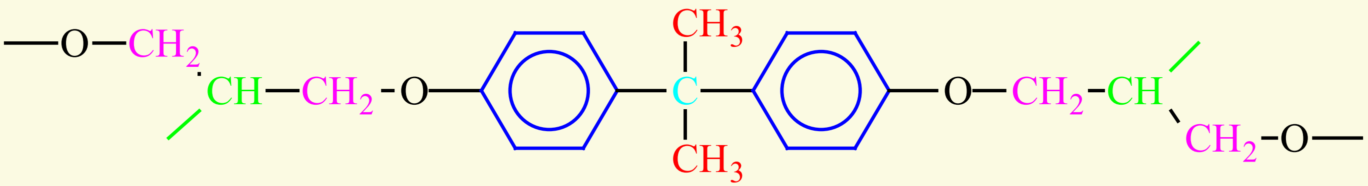
$$\Psi = \sum_i n_i \frac{H_i\,V_i\,E_i}{eR\,T_i^2} = \sum_i n_i \Psi_i$$

Obtain η_c in correct units from molar mass of component groups

$$\eta_c = \frac{\Psi}{M_o} = \frac{\sum_i n_i \Psi_i}{\sum_i n_i M_i} = \frac{\sum_i N_i \Psi_i}{\sum_i N_i M_i}$$

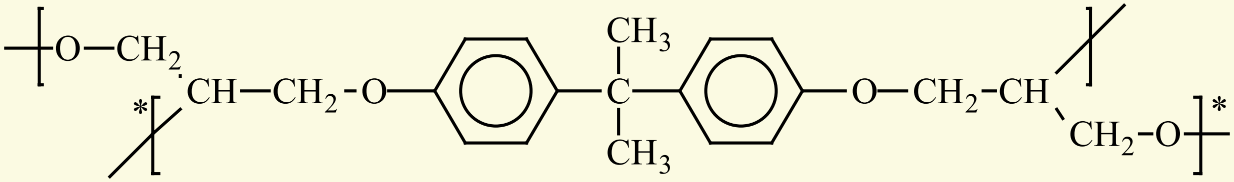
Calculating Heat Release Capacity

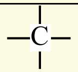
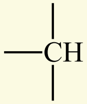
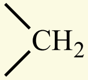
If η_c is a material property it should be calculable from additive molar group contributions like other polymer properties (e.g., heat capacity, refractive index, solubility parameter, etc.)



Example: Bisphenol A Epoxy has 6 distinct chemical groups comprising the polymer repeat unit.

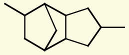
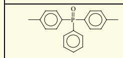
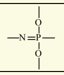
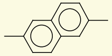
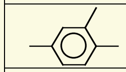
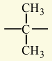
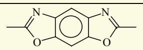
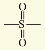
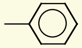
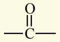
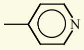
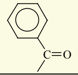
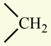
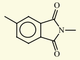
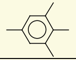
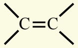
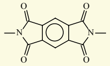
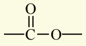
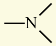
Calculating Heat Release Capacity



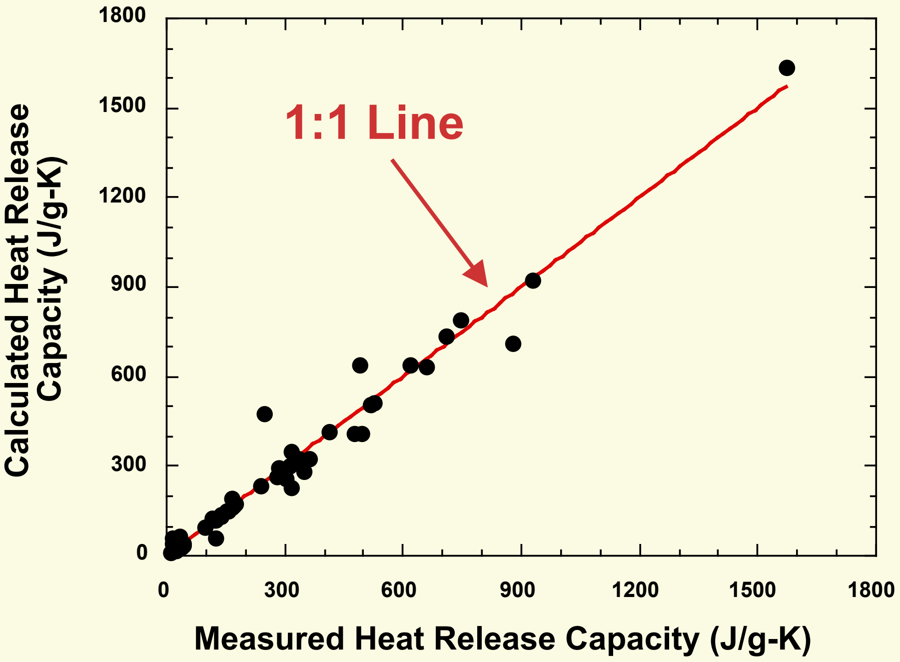
Chemical Group *i*	***N***	**M_i (g/mole)**	**Ψ (kJ/mole-K)**	**$N_i M_i$ (g/mole)**	**$N_i \Psi$ (kJ/mole-K)**
 $-\overset{\mid}{\underset{\mid}{C}}-$		**12**	**28.3**	**12**	**28.3**
 $-\overset{\mid}{\underset{\mid}{C}}H$	**2**	**13**	**26.6**	**26**	**53.2**
	**4**	**14**	**16.7**	**56**	**66.8**
$-CH_3$	**2**	**15**	**22.5**	**30**	**45.0**
	**2**	**76**	**28.8**	**152**	**57.6**
$-O-$	**4**	**16**	**–11.6**	**64**	**–46.4**
		Total:		**340**	**204.5**

$$\eta_c = \frac{\Psi}{M} = \frac{\sum_i n_i \Psi_i}{\sum_i n_i M_i} = \frac{\sum_i N_i \Psi_i}{\sum_i N_i M_i} = \frac{204.5\ kJ/mole\text{–}K}{340\ g/mole} = 601\ J/_{g\text{–}K}$$

Molar Group Contributions to η_c

Group	Contribution (kJ/mol-K)	Group	Contribution (kJ/mol-K)
	118*	$-\mathrm{O}-$	-11.6
	77.0	 $-\mathrm{N}=\mathrm{P}(\mathrm{O}-)_2-$	-13.8
	69.5	$-\mathrm{NH_2}$	-13.9*
	30.6	$-\mathrm{CF_3}$	-14.8
 $-\mathrm{C}(\mathrm{CH_3})_2-$	29.5	$-\mathrm{C{\equiv}N}$	-17.6
	28.8		-18.9*
 $>\mathrm{C}<$	28.3	 $-\mathrm{SO_2}-$	-19.2
 $>\mathrm{CH}-$	26.6	$-\mathrm{OH}$	-19.8
$-\mathrm{CH_3}$	22.5	$-\mathrm{Br}$	-22.0
	19.0	 $-\mathrm{C}(=\mathrm{O})-$	-22.0
	18.7		-23.2*
 $>\mathrm{CH_2}$	16.7		-25.5
	15.1	$-\mathrm{Cl}$	-34.7
 $>\mathrm{C}=\mathrm{C}<$	9.7		-36.4*
$-\mathrm{H}$	8.1	 $-\mathrm{C}(=\mathrm{O})-\mathrm{O}-$	Pendant -39.5 Backbone: -13.7
 $>\mathrm{NH}$	7.6	 $-\mathrm{N}<$	-43.0*

$$\eta_c = \frac{\Psi}{M_o} = \frac{\sum_i n_i\Psi_i}{\sum_i n_iM_i} = \frac{\sum_i N_i\Psi_i}{\sum_i N_iM_i}$$



Conclusions

- ✓ **Heat Release Capacity is:**
  - A **rate independent** flammability parameter
  - An **intensive quantity** (independent of sample mass)
  - **Measurable** by different laboratory techniques
  - A good **predictor of fire and flammability** behavior
  - **Calculable** from chemical structure
  - A **material property**: dynamic combustion potential

Acknowledgements

- **FAA**
- **Dr. Stanislav Stoliarov**