Solid State Thermochemistry of Flaming Combustion

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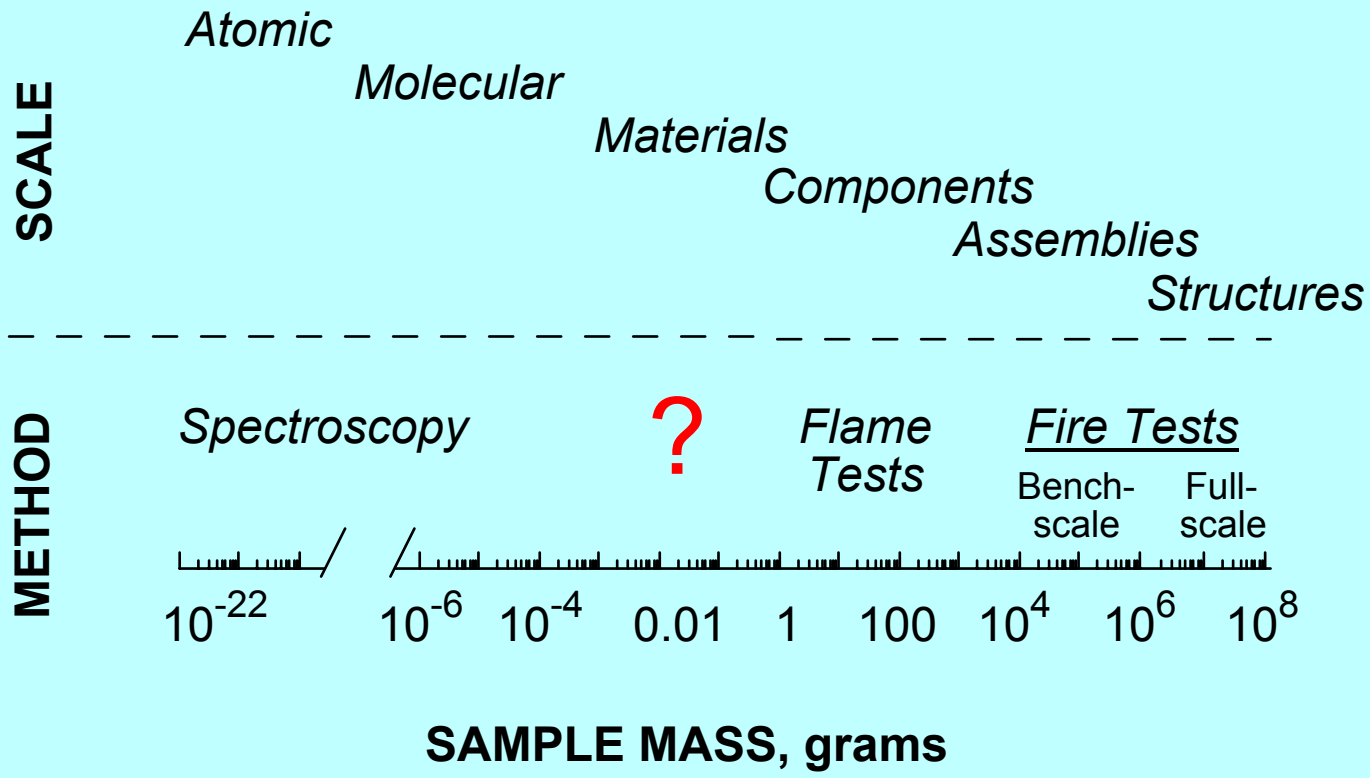
OUTLINE OF TALK

Solid State Thermochemistry of Flaming Combustion

- Scaling: Molecules to Motor Vehicles
- Fire Behavior of Combustible Solids
- Solid State Thermochemistry
  - Thermodynamics
    - -Char Yield
    - -Heat of Combustion
    - -Heat of Gasification
    - -Thermal Decomposition Temperature
  - Kinetics
    - -Mass loss rate
    - -Pyrolysis zone depth
- Heat Release Capacity

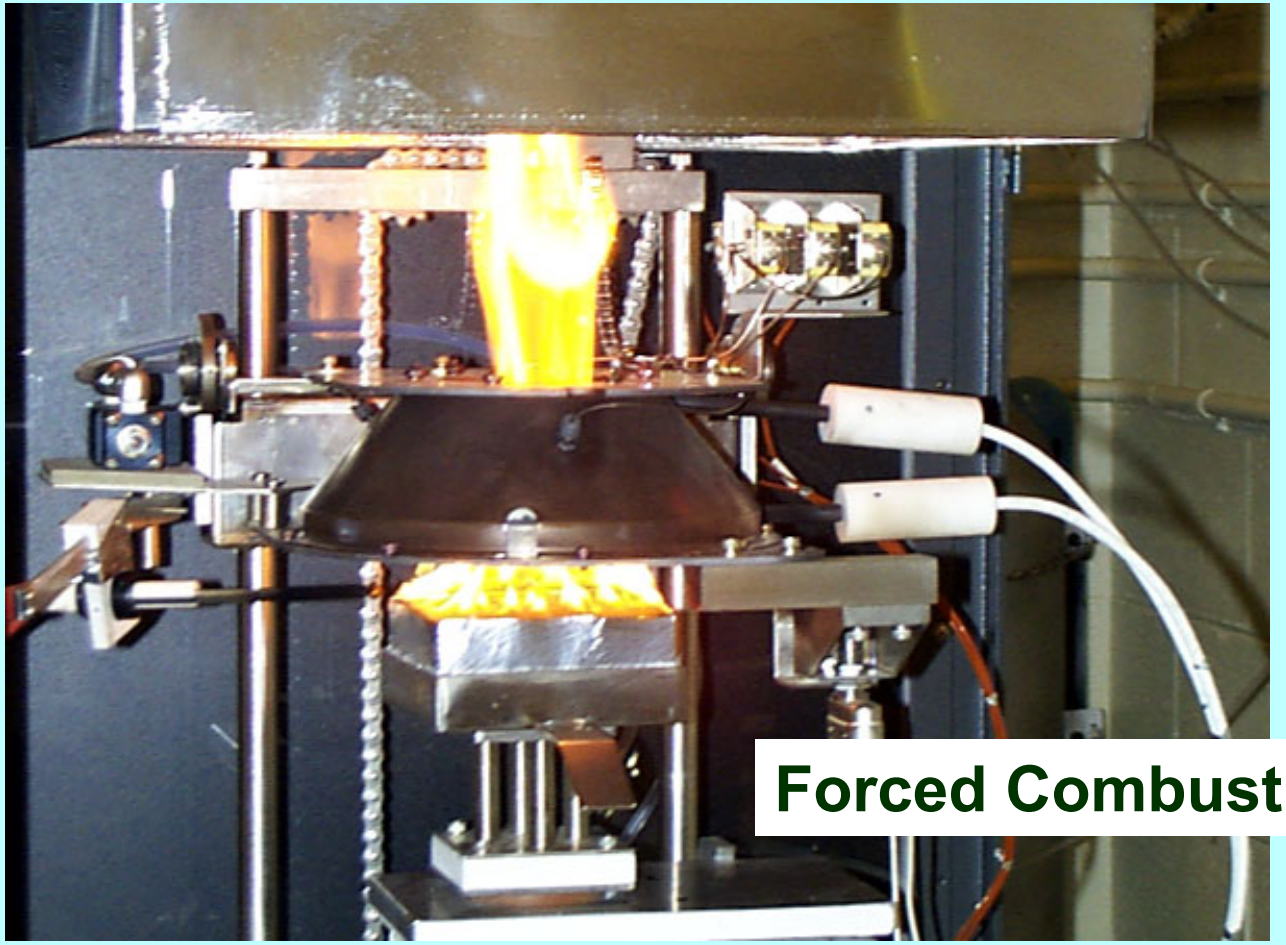
SCALES OF THE FIRE PROBLEM



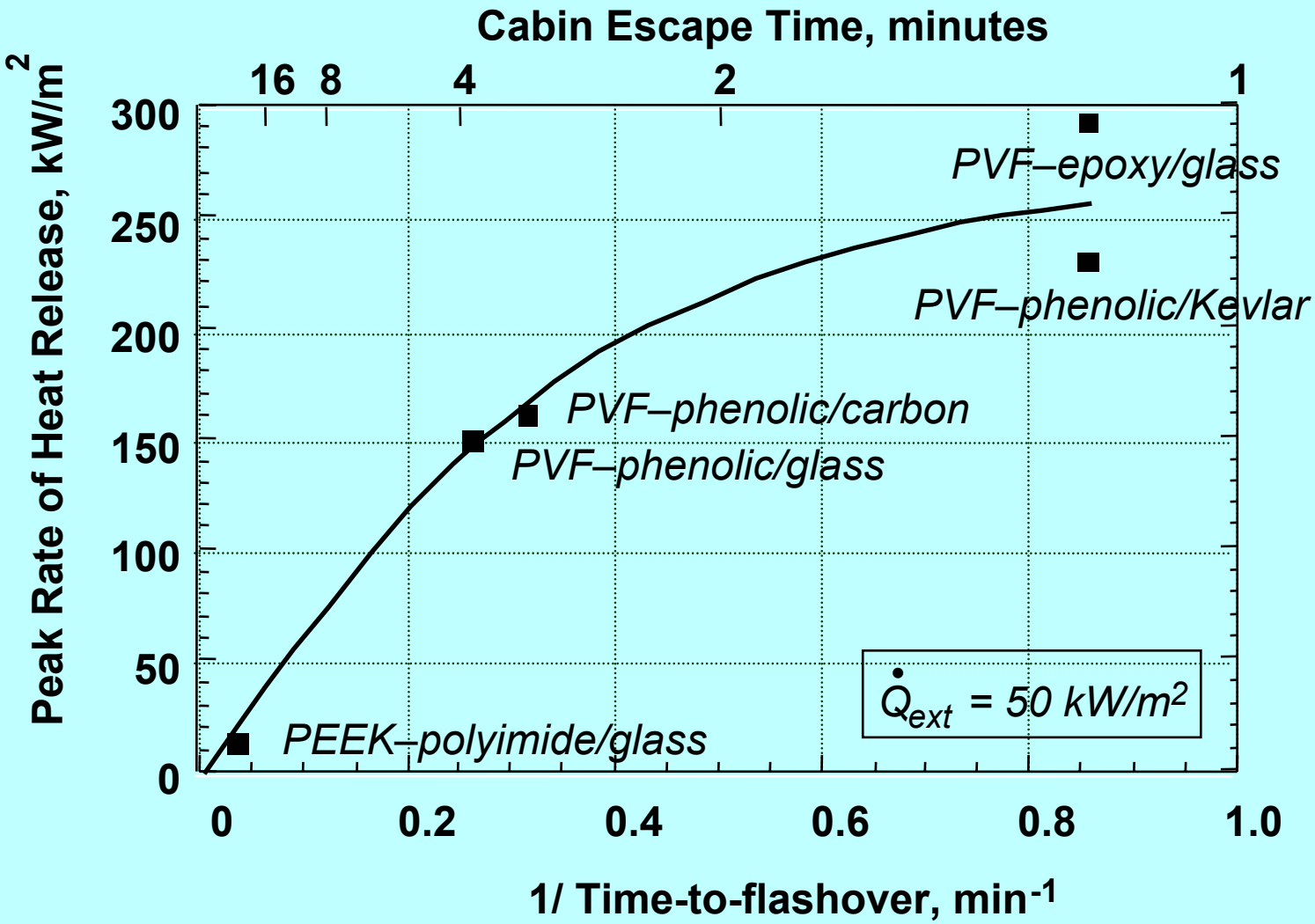
POST-CRASH FUEL FIRE: Structures

FULL-SCALE FIRE TEST: Assemblies

FIRE (CONE) CALORIMETER: Components



SCALING: Components vs. Structures

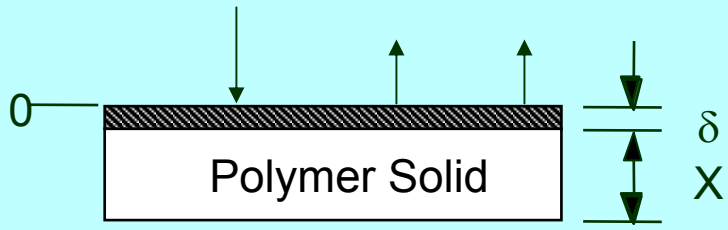


FLAME TEST: Materials

Unforced (self-propagating) Combustion

FIRE BEHAVIOR: Ignition

$$\dot{q}_{net} = \dot{q}_{ext} - \dot{q}_{rerad} - \dot{q}_{conv}$$



Unsteady Heat Conduction

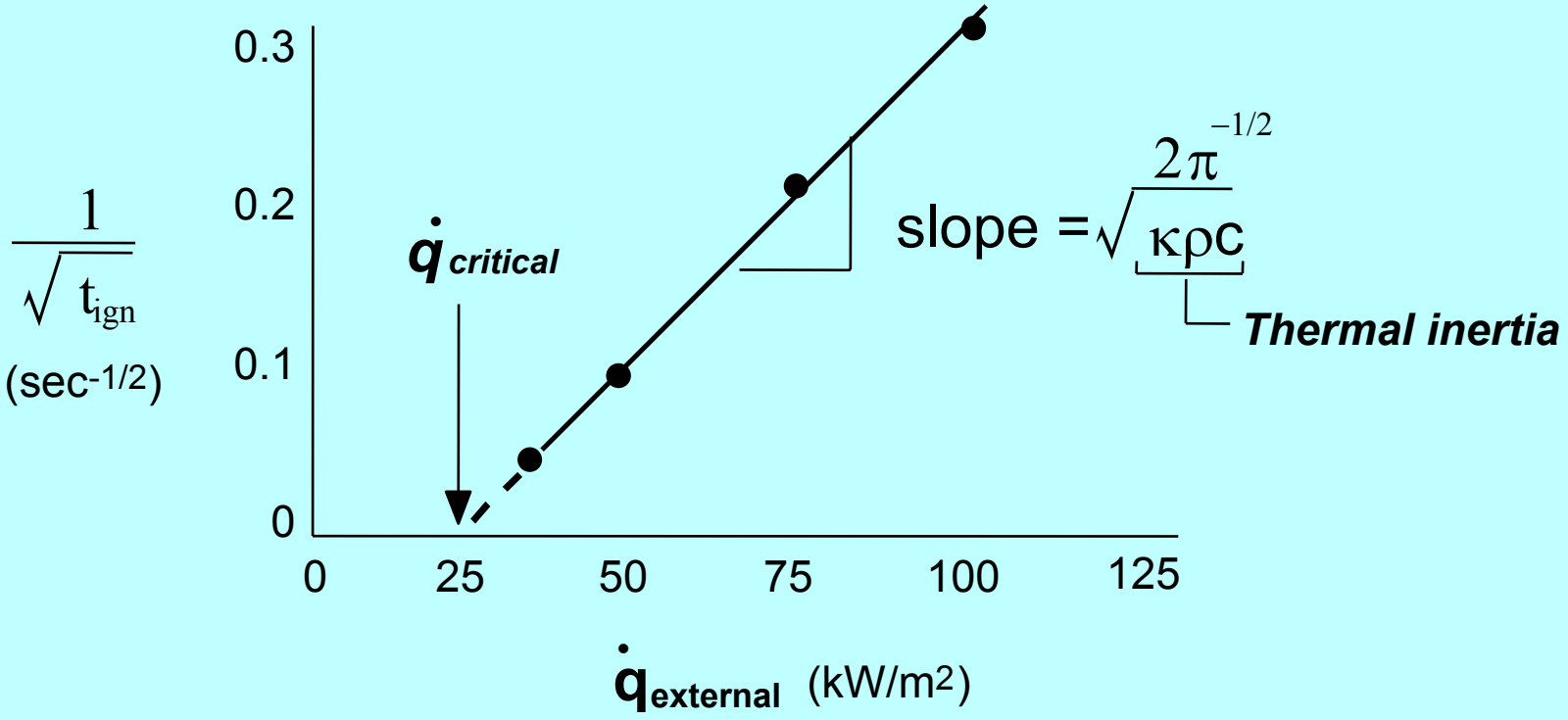
$$\frac{\partial^2 T}{\partial x^2} - \frac{1}{\alpha}\frac{\partial T}{\partial t} = 0$$

Time-to-Ignition: $$t_{ign} = \frac{\pi}{4}\kappa\rho c\left[\frac{T_{ign} - T_o}{\dot{q}_{net}}\right]^2$$

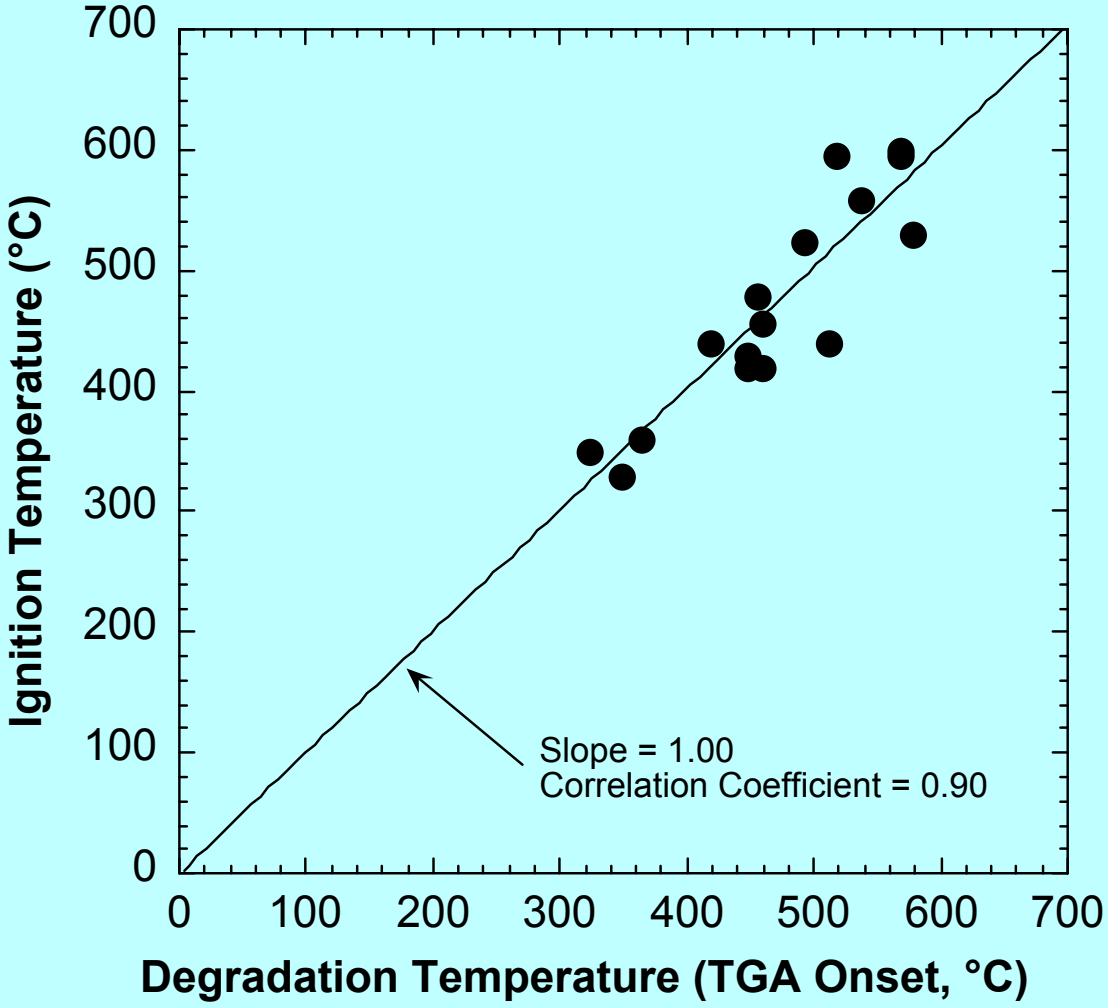
Critical Heat Flux: $$\dot{q}_{critical} = \dot{q}_{external} - \dot{q}_{net}$$

or… $$\frac{1}{\sqrt{t_{ign}}} = \frac{\dot{q}_{external}}{\sqrt{\pi\kappa\rho c/4\,(T_{ign} - T_o)}} - \frac{\dot{q}_{critical}}{\sqrt{\pi\kappa\rho c/4\,(T_{ign} - T_o)}}$$

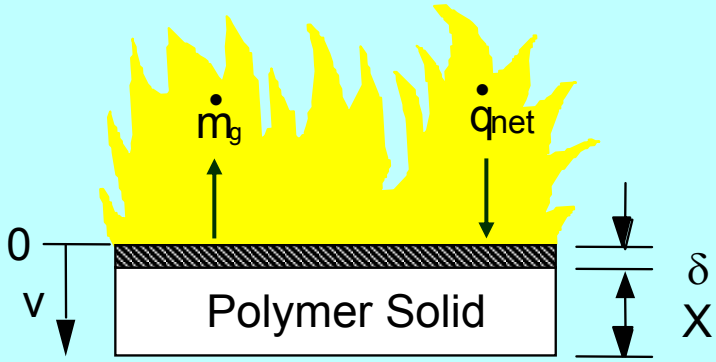
FIRE BEHAVIOR: Ignition Delay



FIRE BEHAVIOR: Ignition Temperature



FIRE BEHAVIOR: Steady-Burning



Moving Boundary @ v

Steady-State Heat Conduction

$$\frac{\partial^2 T}{\partial x^2} + \frac{v}{\alpha}\frac{\partial T}{\partial x} = 0$$

Conservation of Mass

$$(1-\mu)\rho v = \dot{m}_{gas}$$

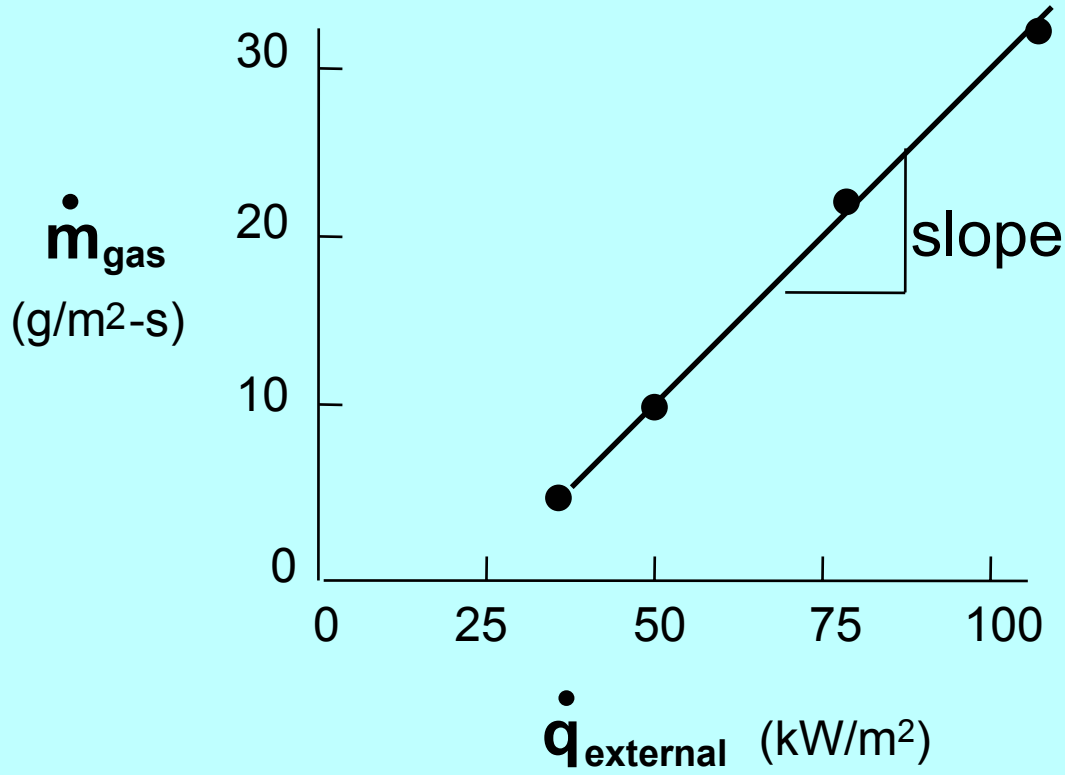
Conservation of Energy

$$\dot{q}_{net} = \dot{m}_{gas}\frac{h_g}{(1-\mu)} = \dot{m}_{gas} L_g$$

Heat Release Rate for Steady Burning:

$$\boxed{\dot{q}_c = \chi\, \overset{\circ}{h}_c\, \dot{m}_{gas} = \chi(1-\mu)\frac{\overset{\circ}{h}_c}{h_g}\dot{q}_{net} = \chi\frac{\overset{\circ}{h}_c}{L_g}\dot{q}_{net}}$$

FIRE BEHAVIOR: Steady-Burning

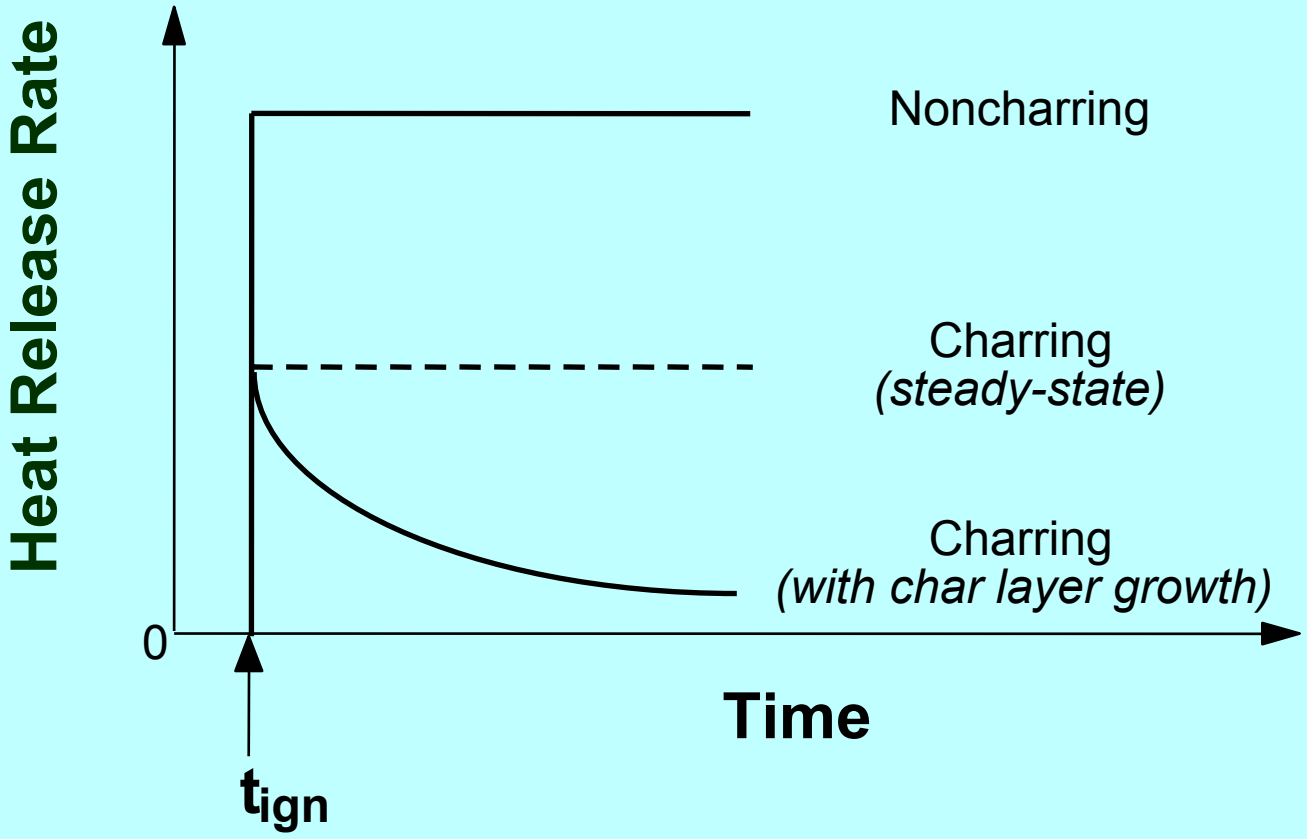


$$\text{slope} = \frac{1}{L_g} = \frac{(1-\mu)}{h_g}$$

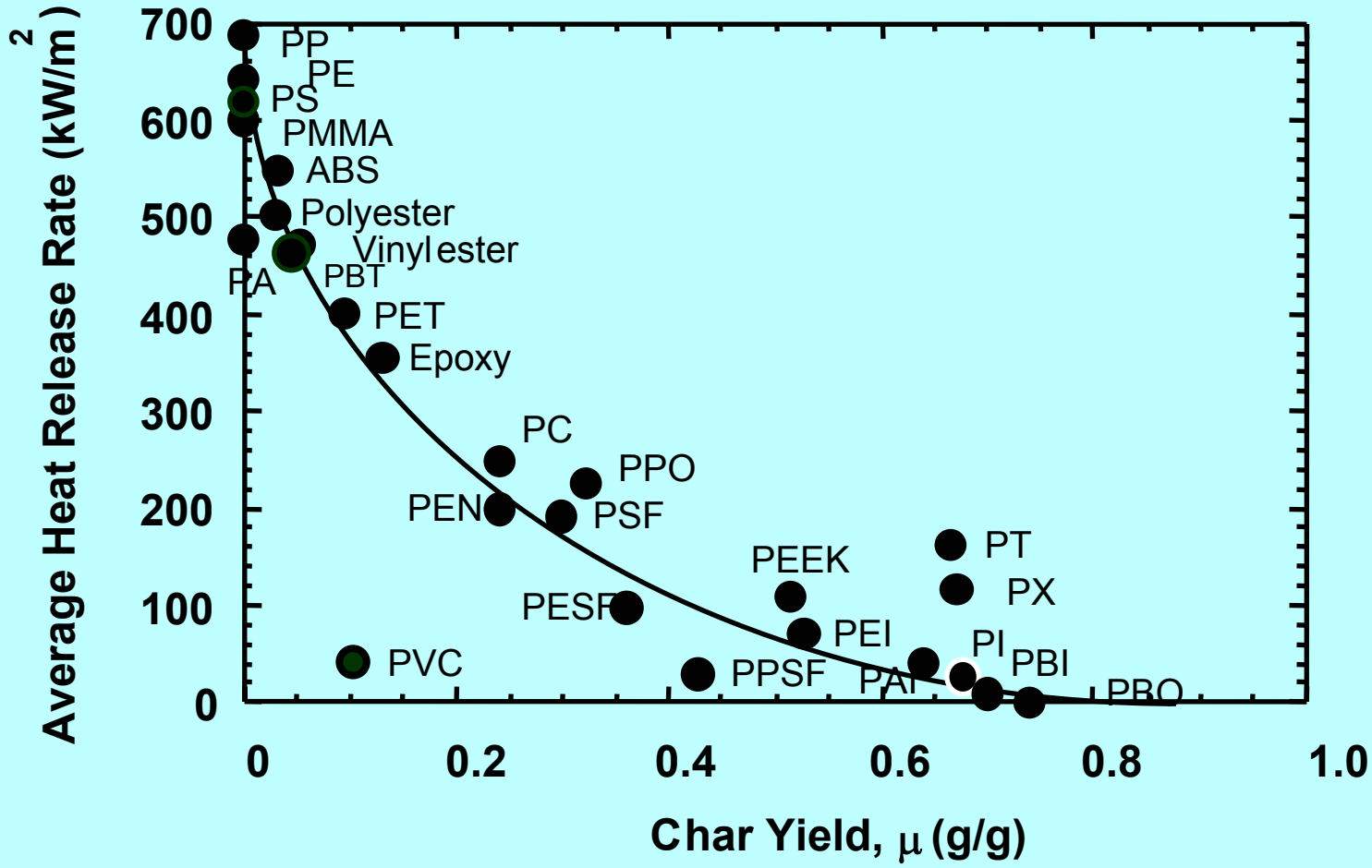
μ = Char Yield

h_g = Enthalpy of Gasification

FIRE BEHAVIOR: Steady-Burning



FIRE BEHAVIOR: HRR *versus* Char Yield



FIRE BEHAVIOR: Temperature Profile

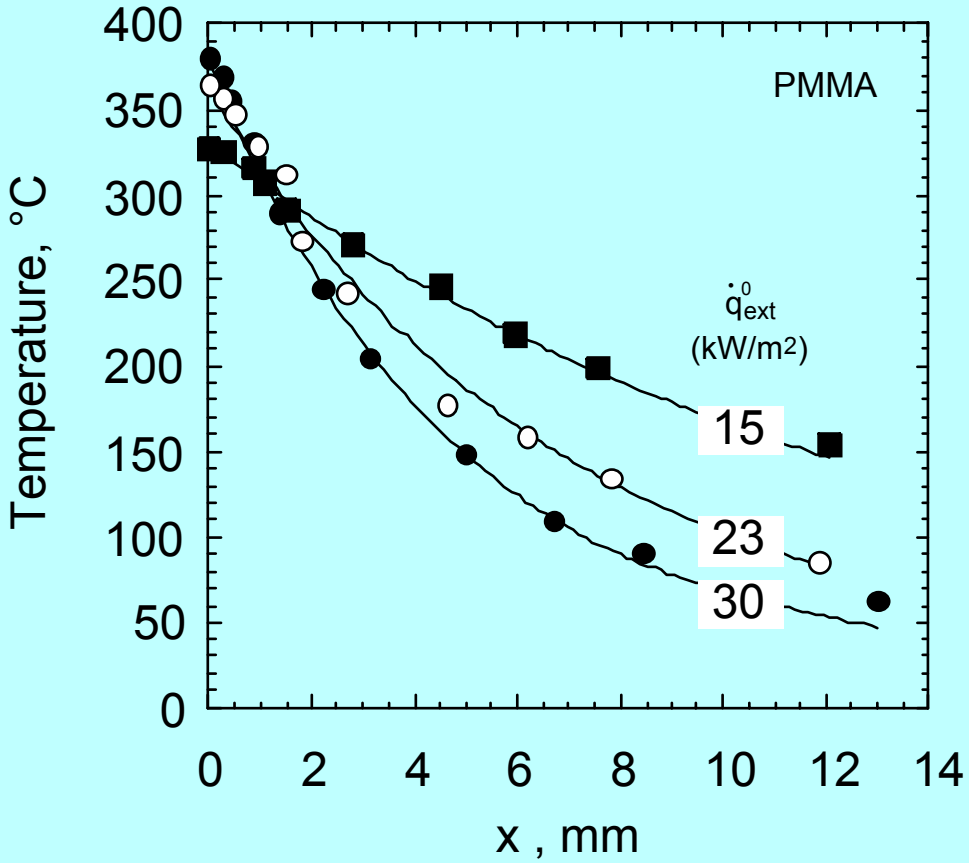
Temperature profile (steady burning):

$$\frac{T(x) - T_o}{T_s - T_o} = \exp\left[-\frac{c\dot{q}_{net}}{\kappa h_g} x\right]$$

Calculated (——)
and measured temperature*
profiles for steady burning
*of **non-charring***
poly(methylmethacrylate)
(PMMA)

κ = *0.185 W/m-K*
c = 2.5 kJ/kg
h_g = *1.7 MJ/kg*

*Data of Vovelle, et. al. Comb. Sci. Tech., 53, 187-201 (1987)



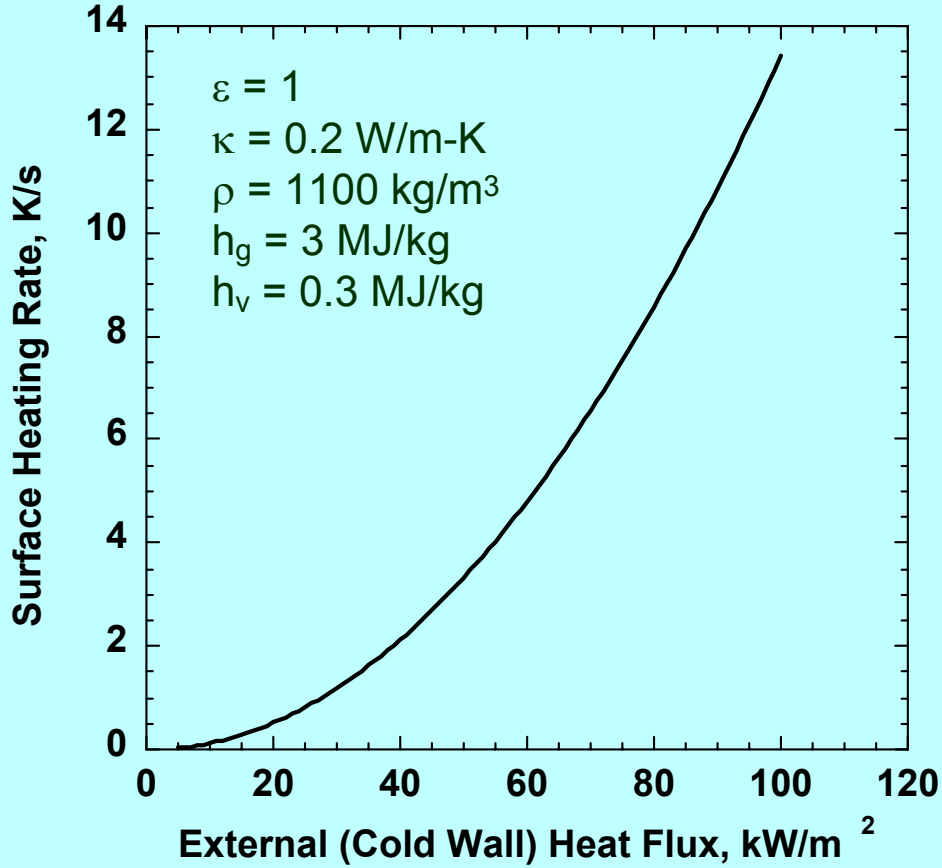
FIRE BEHAVIOR: Surface Heating Rate

Surface heating rate, β:

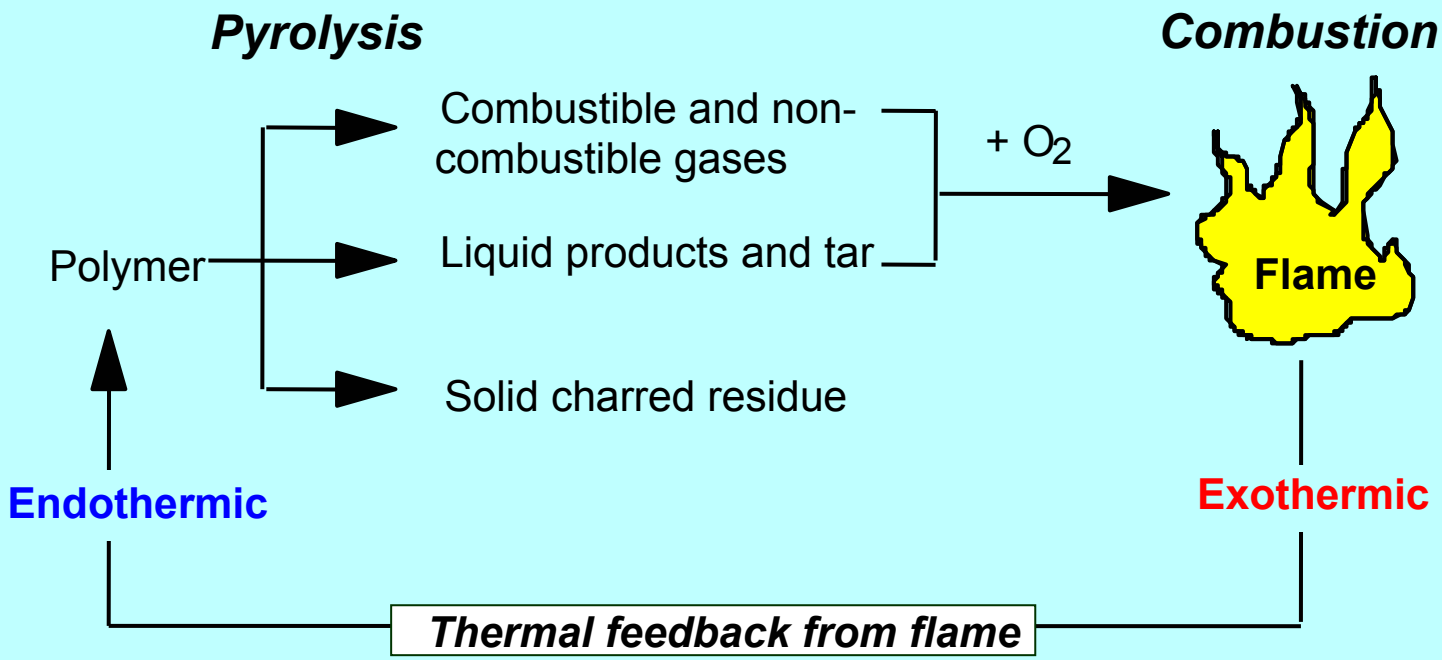
$$\beta = \left.\frac{dT(x)}{dt}\right|_{x=0} = v \left.\frac{dT(x)}{dx}\right|_{x=0}$$

$$\approx \frac{\dot{q}^2_{net}}{\kappa \rho h_g}\left(1 - \frac{\Delta h_v}{h_g}\right)$$

$$\approx \frac{\dot{q}^2_{net}}{\kappa \rho h_g}$$

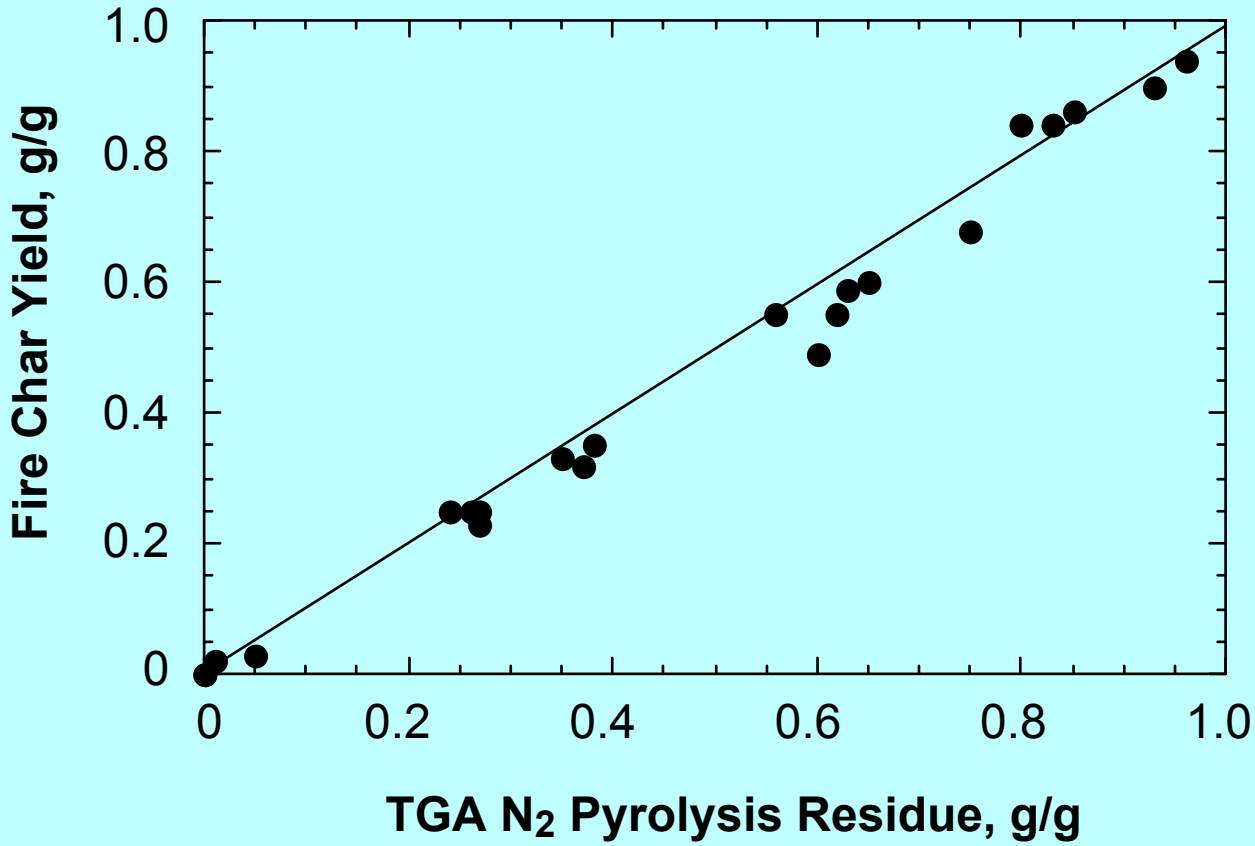


FUEL GENERATION PROCESS



FUEL GENERATION THERMODYNAMICS

<u>CHARRING</u>: in fires is anaerobic, rapid (equilibrium) process.

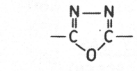
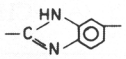
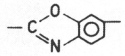
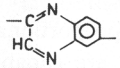
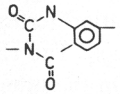
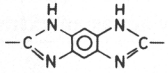
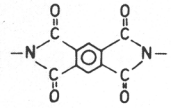
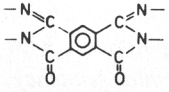
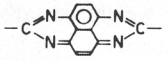


THERMODYNAMICS: Char Yield

<u>CHAR YIELD</u> is and equilibrium property which is calculable from molar group contributions.

c.f., Van Krevelen

TABLE 21.4
Group contribution to char formation

Group	Contribution to residue per structural unit (FC)	Do. in C-equiv.
"All" aliphatic groups*)	0	0
–CHOH–(exception)	4	1/3
	12	1
	24	2
	36	3
	48	4
	60	5
	72	6
	96	8
	60	5
	72	6
	120	10
	168	14
Corrections due to disproportioning (H-shift):		
Next to aromatic nucleus		
>CH_2 and >CH–CH_2–	–12	–1
–CH_3	–18	–1½
>$C(CH_3)_2$	–36	–3
–$CH(CH_3)_2$	–48	–4
	12	1
	36	3.5
	42	3.5
	42	3.5
	84	7
	84	7
	108	9
	132	11
	120	10
	144	12
	120	10
	180	15

*) No halogen groups included

Table | GROUP CONTRIBUTIONS TO PYROLYSIS | 14

THERMODYNAMICS: Heats of Combustion

$h^0_{c,\,s}$ **= Heat of Complete Combustion of Solid**

$h^0_{c,\,\mu}$ **= Heat of Complete Combustion of Char**

Calculable from:

1) Molar Group Contributions
2) Free energies of formation of products and reactants
3) Oxygen Consumption (± 5%)

Heat of Complete Combustion of Fuel Gases

$$h^0_{c,\,g} = \frac{h^0_{c,\,s} - \mu h^0_{c,\,\mu}}{(1-\mu)}$$

THERMODYNAMICS: Heat of Gasification

Molar Heat of Gasification

Heat Melt to Decomposition Temperature

$$h_g = \frac{\Delta H_g}{M} = \int_{T_0}^{T_m} c_p^{xl}\,dT + h_m + \int_{T_m}^{T_d} c_p^{melt}\,dT + h_d + h_v \overset{?}{=} \frac{E_a}{M}$$

Heat to Melting Temp — **Heat of Crystal Melting**

Latent heat

Heat of Vaporization

Break Secondary Bonds

Heat of Dissociation

Break Primary Chemical Bonds

Avg. Molar Mass Of Fuel Gases

THERMODYNAMICS: Heat of Gasification

$$\frac{E_a / h_g}{M_o} = \frac{M}{M_o}$$

> 1: Random scission / chain breaking

- 1: Depolymerization / unzipping

< 1: Small molecule cleavage

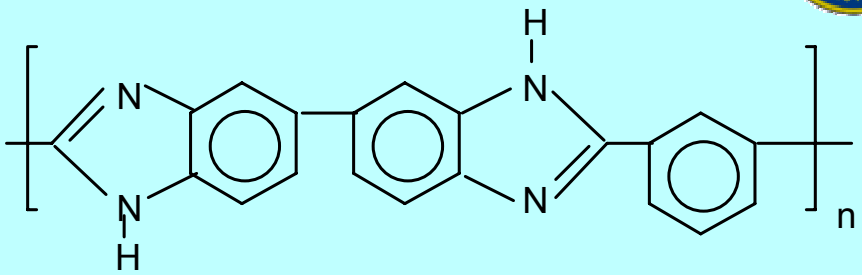
POLYMER	M_o (g/mol)	h_g (kJ/g)	E_a (kJ/mol)	$\frac{M}{M_o}$	PYROLYSIS PRODUCTS
polypropylene	42	2.5	243	**2.3**	C_2 – C_{90}
polyethylene	28	2.4	264	**3.9**	hydrocarbon fragments
polystyrene	104	2.2	230	**1.0**	>60% monomer
PMMA	100	1.6	160	**1.0**	100% monomer
polyoxymethylene	30	2.7	84	**1.0**	100% monomer
nylon 6,6	226	2.6	160	**0.3**	H_2O , CO_2 , C_5 HC's
cellulose	162	3.2	200	**0.4**	H_2O , CO_2 , CO
polyvinylchloride	62	2.5	110	**0.7**	HCl, benzene, toluene

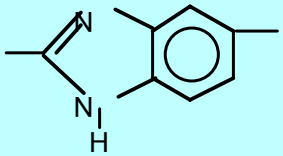
THERMODYNAMICS: Heat of Gasification

Polymer	PMMA	PS	PE	
M (g/mol)	100	104	28	
M_g (g/mol)	100	104	112	
J/g				
$^2 h_s$	740	813	803	
$^2 h_f$	amorphous	amorphous	243	
$^2 h_d$	550	644	910	
$^2 h_v$	375	387	345	
$h_g = \Sigma\, ^2 h_i$	1665	1850	2301	***Calculated***
$h_g = E_a/M_g$	1550 ± 300	1930	2230 ± 630	***From TGA MLR***
h_g (measured)	1600	1800	2300	***From Fire MLR***

THERMODYNAMICS: Decomposition Temperature

Polybenzimidazole (PBI):
T_d = 900 K (measured)

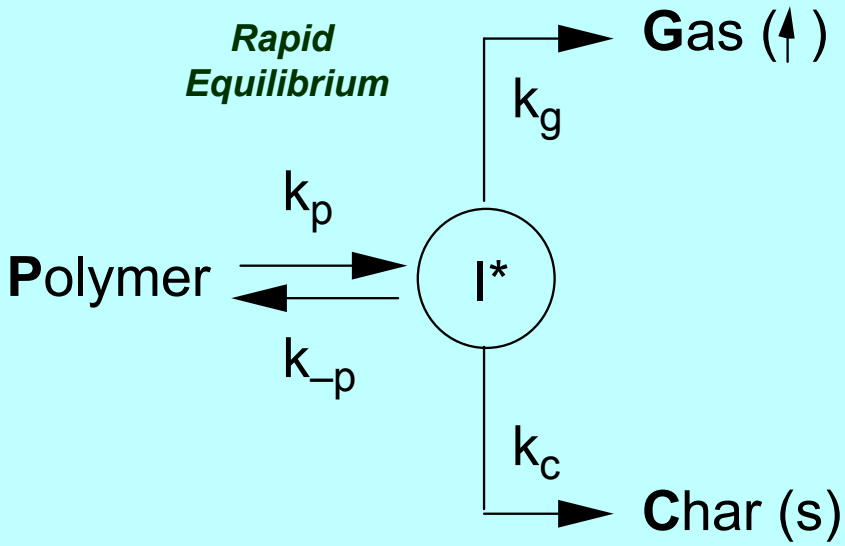


Group	Quantity	M_i (g/mol)	$Y^i_{d,\,1/2}$ (K-kg/mol)
	2	116.12	105
	1	76.09	65

$$T_d = \frac{Y_d}{M_0} = \frac{\sum_1^n n_i Y_d^i}{\sum_1^n n_i M^i} = \frac{275\ \text{K–kg/mol}}{308\ \text{g/mole}} \times 1000 = 892\ \text{K}\ \ \text{(calculated)}$$

FUEL GENERATION KINETICS

Mass Loss Model



Total mass

$$m_o = P + G + C + I^*$$
$$\approx P + G + C$$

Sensible mass,

$$m = P + C + I^*$$
$$\approx P + C$$

FUEL GENERATION KINETICS

Isothermal Mass Fraction

$$\frac{m(t)}{m_o} = Y_c(T) + \left(1 - Y_c(T)\right) \exp\left[-k_p\, t\right]$$

Non-Isothermal Mass Fraction @ $\beta = \frac{dT}{dt}$ = constant

$$\frac{m(T)}{m_o} = Y_c + (1 - Y_c)\exp\left[-\frac{ART^2 e^{-E_a/RT}}{\beta\,(E_a + 2RT)}\right]$$

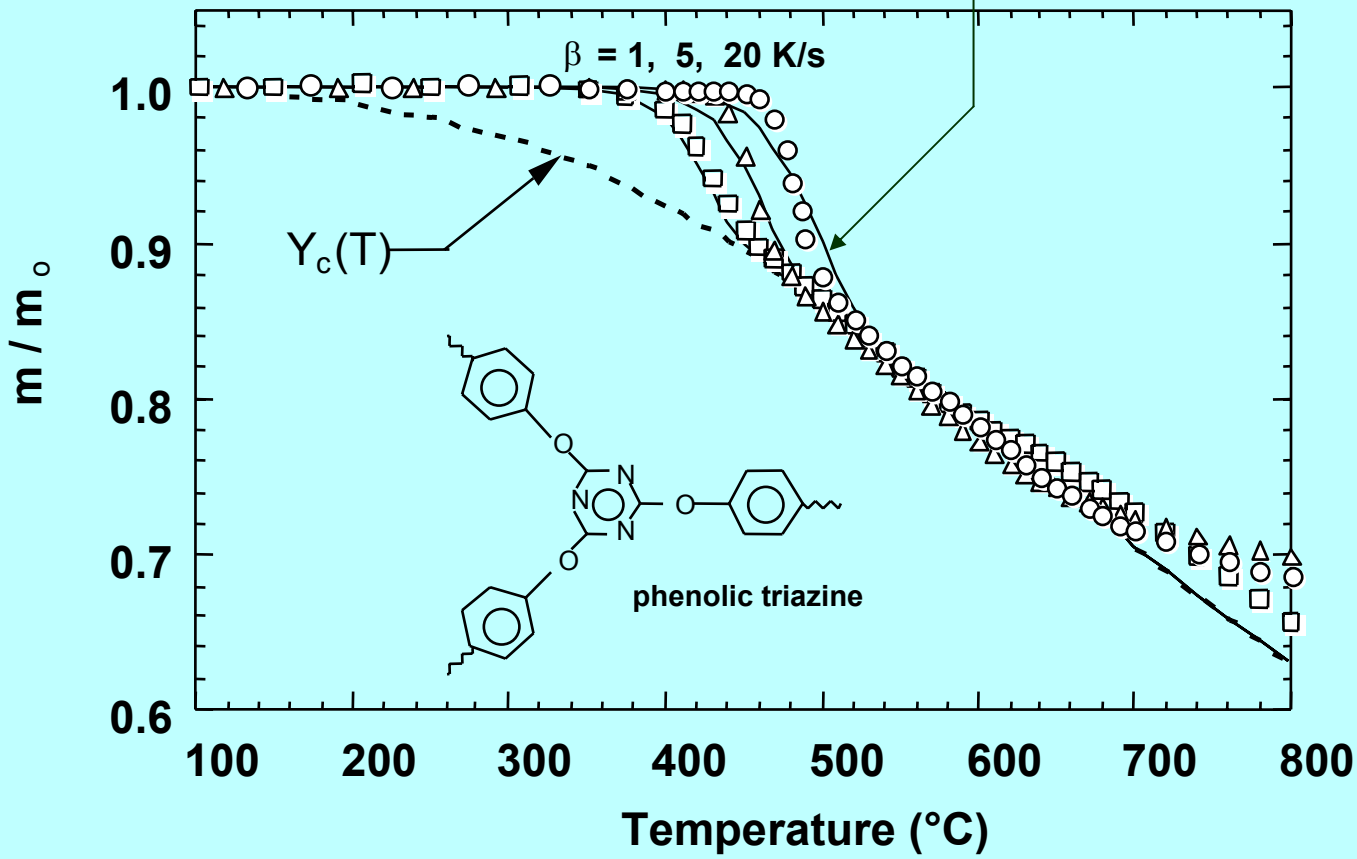
Equilibrium Char Yield

$$Y_c(T,t) = Y_c(T,\infty) = \frac{k_c}{k_c + k_g}$$

KINETICS: Mass Fraction

Comparison to Experiment:

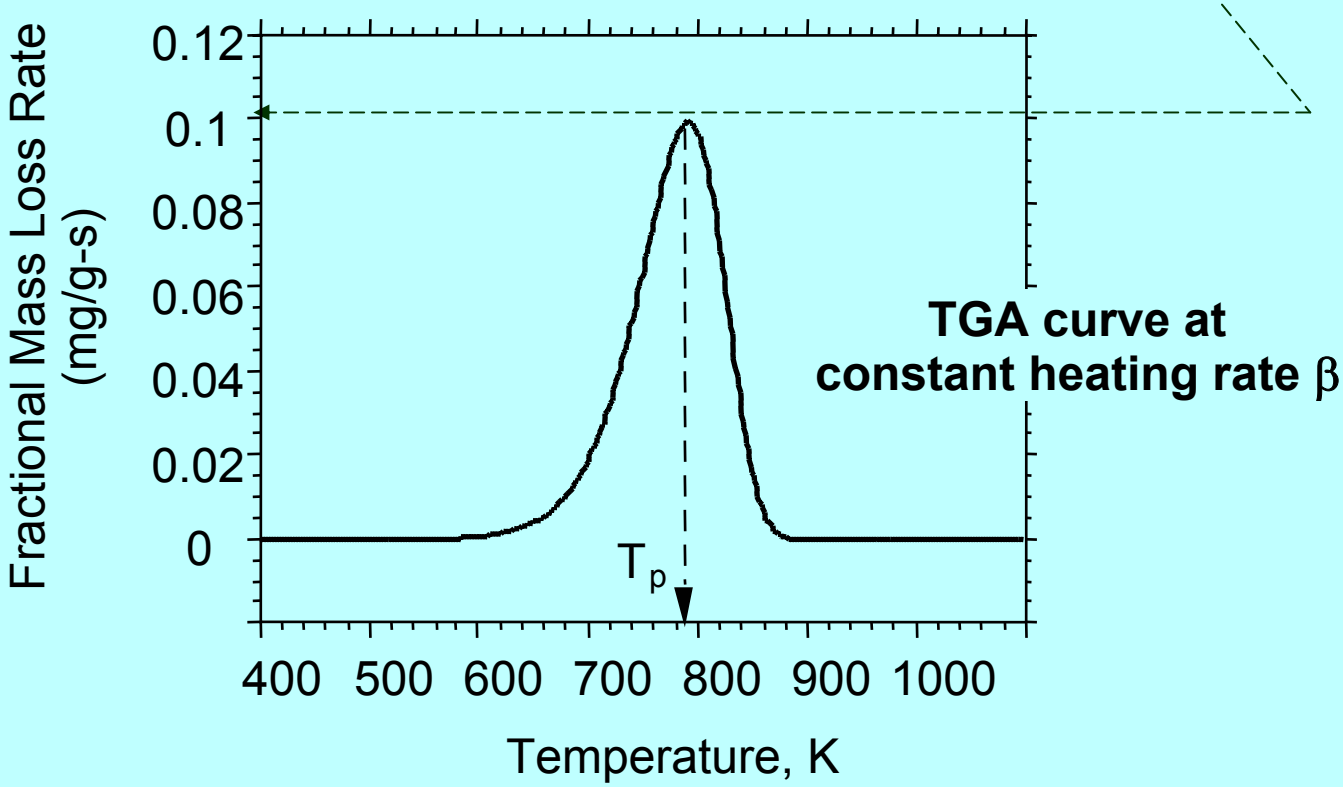
$$\frac{m(T)}{m_o} = Y_c + (1 - Y_c)\exp\left[-\frac{ART^2 e^{-E_a/RT}}{\beta\,(E_a + 2RT)}\right]$$



FUEL GENERATION KINETICS

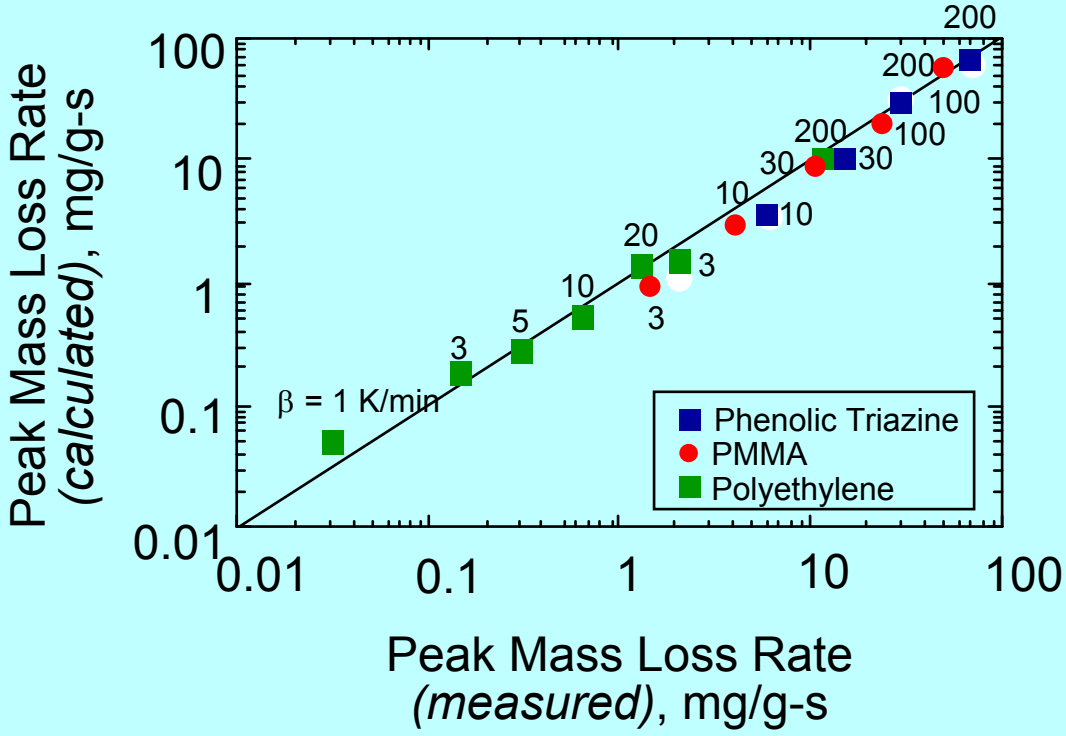
Peak Mass Loss Rate:

$$\left[-\frac{1}{m_o}\frac{dm}{dt}\right]_{max} = (1-\mu)\frac{\beta E_a}{eRT_p^2}$$



FUEL GENERATION KINETICS

Peak Mass Loss Rate: *Calculated vs. TGA Experiments*



THERMAL-CHEMICAL COUPLING: Pyrolysis Zone

Assume:

1) **Mass loss rate falls to 1/e of surface (max) value at 1/e of pyrolysis zone thickness**

2) **Mass loss rate has Arrhenius form**

$$\frac{\dot{m}(\delta/e)}{\dot{m}(0)} = \frac{1}{e} = \exp\left[-\frac{E_a}{R}\left(\frac{1}{T(\delta/e)} - \frac{1}{T_{max}}\right)\right]$$

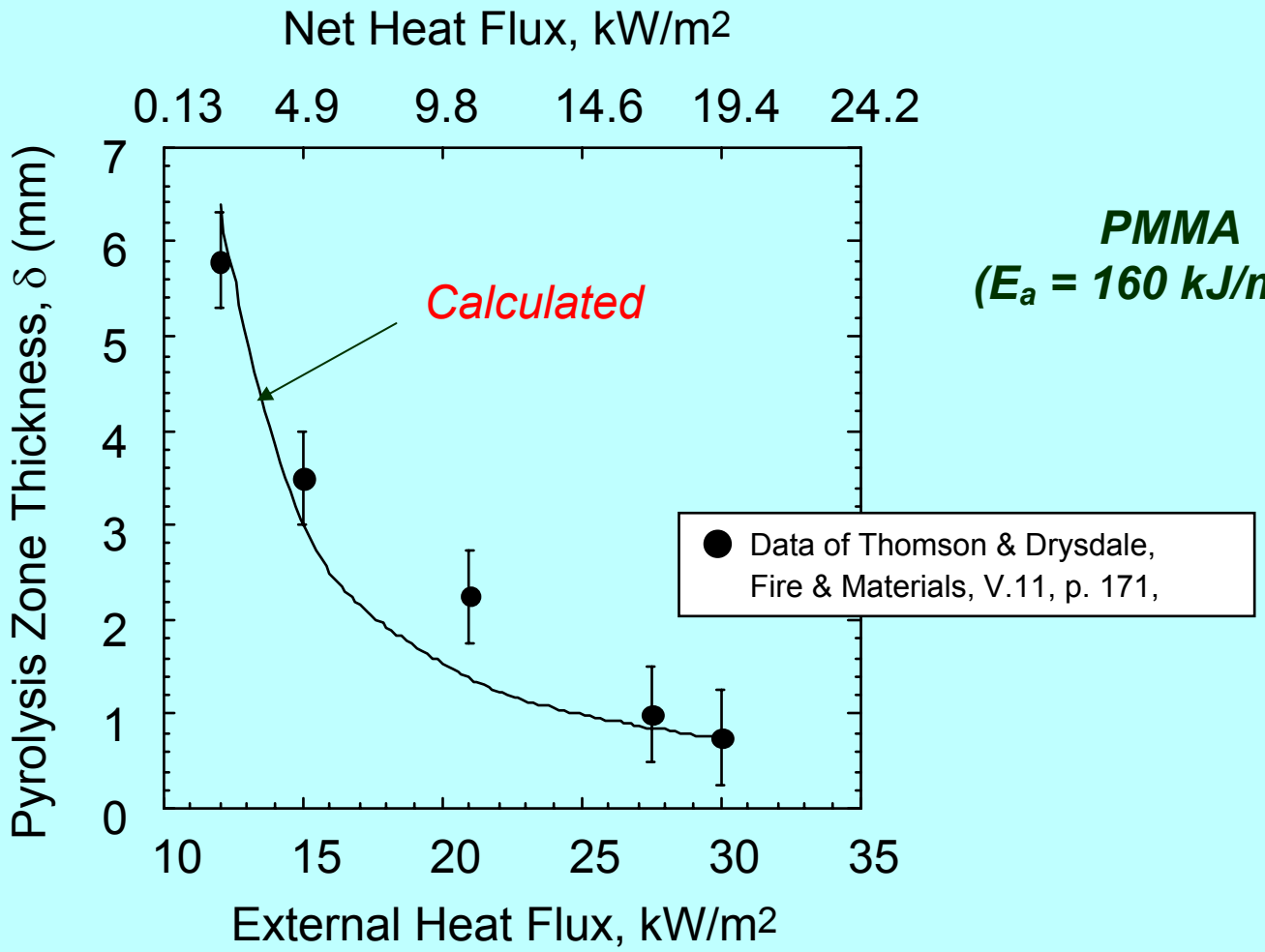
From temperature distribution at, x = δ/e, during steady mass loss rate

$$T_{max} - T(\delta/e) \approx (T_{max} - T_o)\left(1 - \exp\left[-\frac{v}{\alpha}\frac{\delta}{e}\right]\right)$$

Eliminating, $T_{max} - T(\delta/e)$, between the above equations

$$\delta = \frac{\kappa}{\dot{q}_{net}}\frac{eRT_p^2}{E_a}\left(1 + \frac{\Delta h_v}{c(T_p - T_0)}\right) \approx \frac{\kappa}{\dot{q}_{net}}\frac{eRT_p^2}{E_a}$$

PYROLYSIS ZONE DEPTH



PMMA
(E_a = 160 kJ/mole)

FUEL GENERATION KINETICS

- Multiplying the mass loss rate by the heat of combustion of the fuel gases gives the <u>kinetic heat release rate</u>.

- For a constant heating rate, the <u>peak kinetic heat release rate</u> contains only β and material properties.

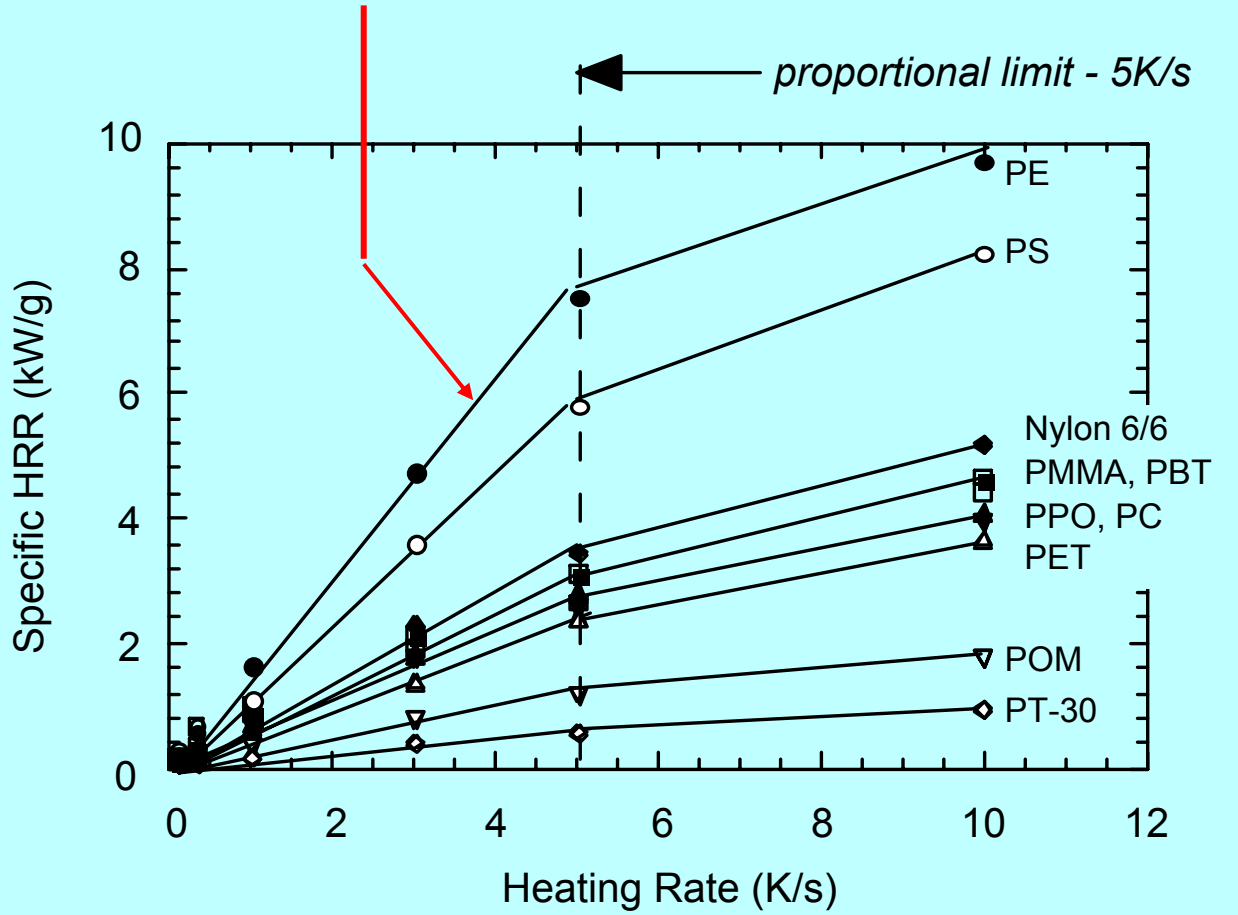
$$\dot{Q}_c^{max} = h_c^o \frac{\dot{m}_{max}}{m_0} = \beta \left[\frac{h_c^o (1 - \mu) E_a}{eRT_p^2} \right]$$

Heat of Combustion of fuel gases from
– GC-MS & thermochemical calcs.
– Oxygen consumption calorimetry

Peak fractional mass loss rate from TGA

FUEL GENERATION KINETICS

Kinetic HRR proportional to β as predicted



1 mg sample

HEAT RELEASE CAPACITY

Dividing the peak kinetic heat release rate by β gives a material property, the <u>Heat Release Capacity</u>

$$\eta_c \equiv \frac{\dot{Q}_C^{max}}{\beta} = h_c^0 \frac{(1-\mu)E_a}{eRT_p^2}$$

(J/g-K)

h_c^0 = Heat of Combustion of Fuel Gases

E_a = Global Activation Energy for Pyrolysis

μ = Char Fraction

T_p = Temperature at Peak Mass Loss Rate

e = The natural number 2.7183…

R = Gas Constant

HEAT RELEASE CAPACITY (continued)

Derived Relationships:

- $T_p \propto \dfrac{E_a}{R}$ — Peak mass loss rate temperature at constant heating rate

- $E_a = M_g h_g$ — M_g = Molecular weight of gases; h_g = Heat of gasification per unit mass of solid

- $L_g \equiv \dfrac{h_g}{(1-\mu)}$ — Latent heat of gasification per unit mass of fuel

$$\eta_c = h_c^0 \frac{(1-\mu)E_a}{eRT_p^2} \propto \frac{h_c^0}{E_a/(1-\mu)} \propto \frac{h_c^0}{L_g}$$

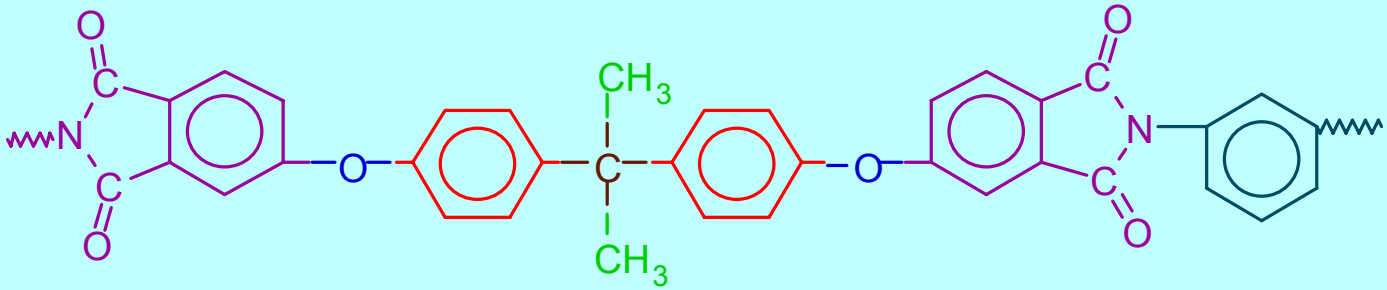
"Combustibility Ratio" from fire science

CALCULATING HEAT RELEASE CAPACITY

Hypothesis:

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.)

c.f., S.W. Benson, D.W. Van Krevelen, J. Bicerano, etc.



Example: ULTEM™ has six (6) distinct chemical groups comprising the polymer repeat unit.

MOLAR GROUP CONTRIBUTIONS TO η_c

<u>Approach</u>: Write the heat release capacity terms as additive molar quantities

$$\Psi = \frac{\mathbf{HVE}}{eR(\mathbf{Y/M})^2} = \frac{\left(\sum_i n_i H_i\right)\left(\sum_i n_i V_i\right)\left(\sum_i n_i E_i\right)}{eR\left(\sum_i n_i Y_i/M_i\right)^2}$$

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

$$\Psi = \sum_i n_i \frac{H_i V_i E_i}{eR(Y_i/M_i)^2} = \sum_i n_i \Psi_i$$

Obtain η_c in correct units from molar mass of component groups

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

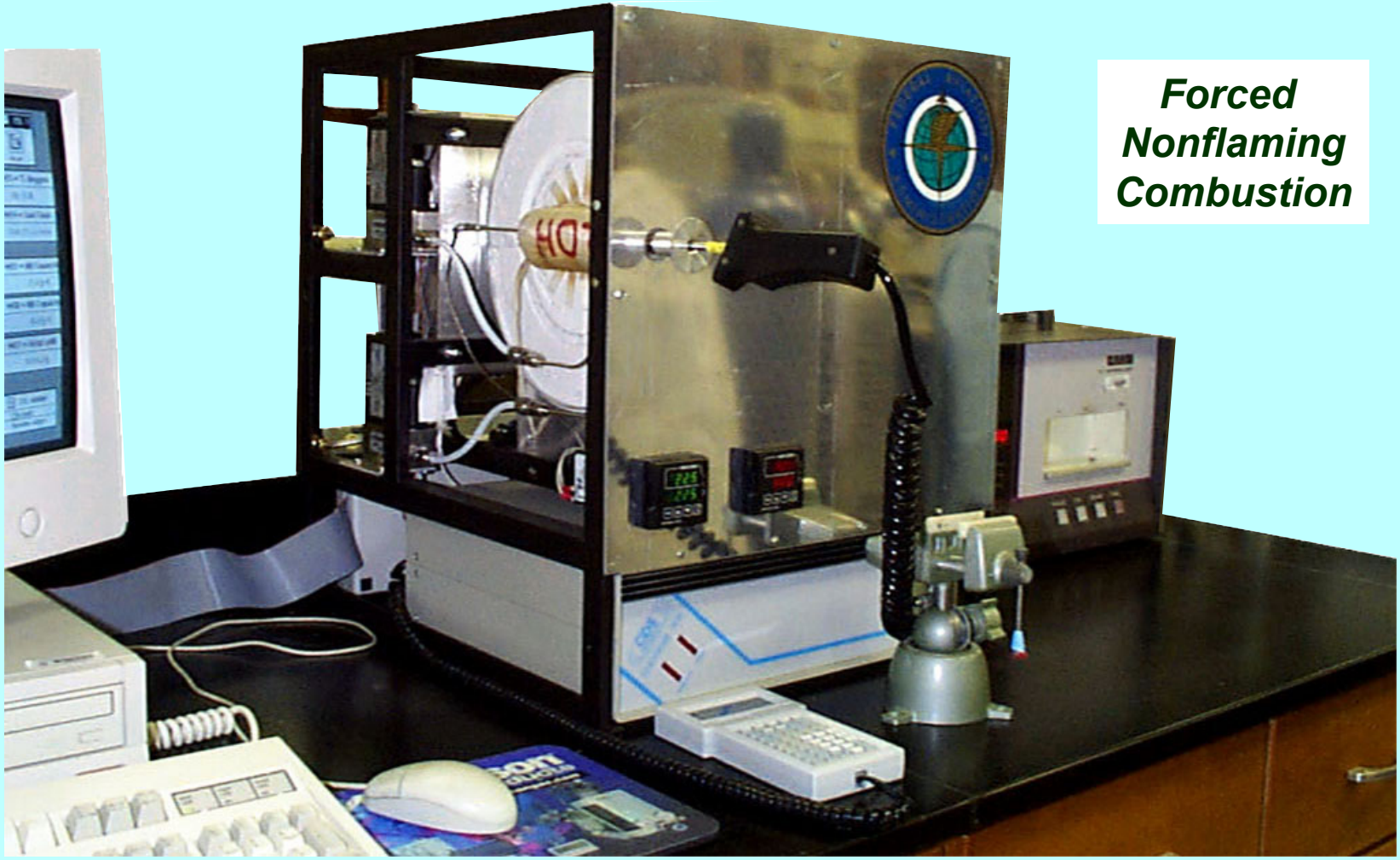
DETERMINING GROUP CONTRIBUTIONS TO η_c

Empirical Method:

- Measure η_c for polymers with known chemical structure, $C_pH_qO_rX_s$.
- Calculate Ψ_i which give best-fit to η_c, $C_pH_qO_rX_s$

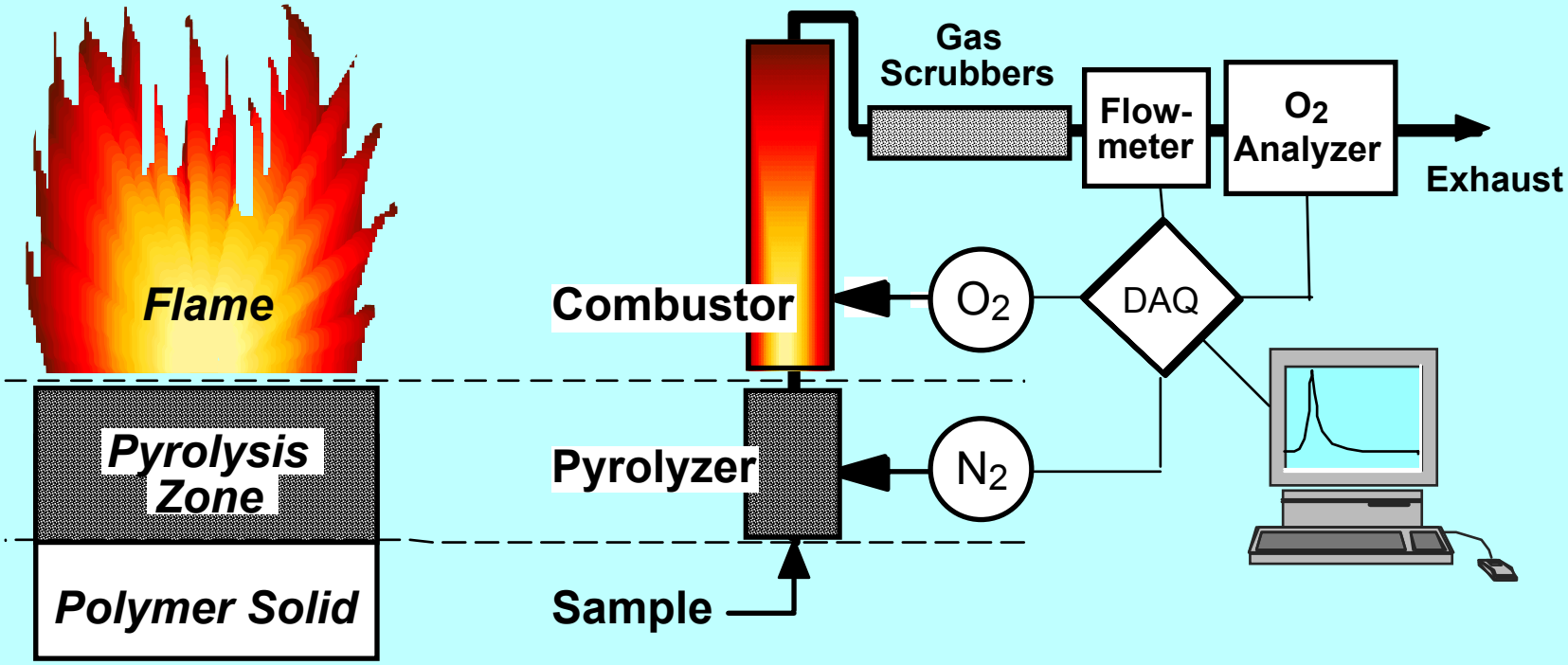
How to Measure (Molecular) Heat Release Capacity?

MEASUREMENT OF HEAT RELEASE CAPACITY



Forced Nonflaming Combustion

MICROSCALE HEAT RELEASE RATE TEST

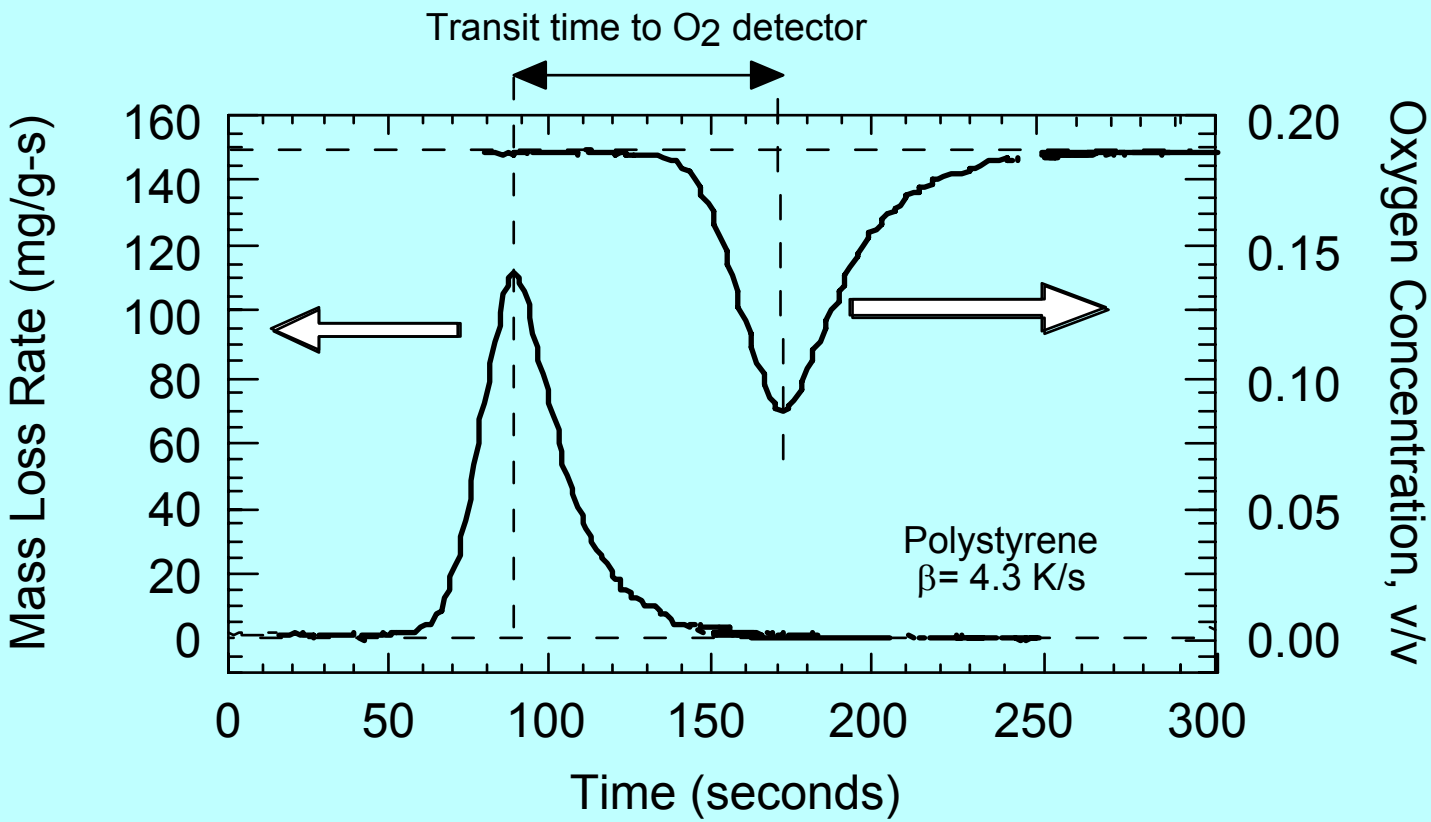


Flaming Combustion

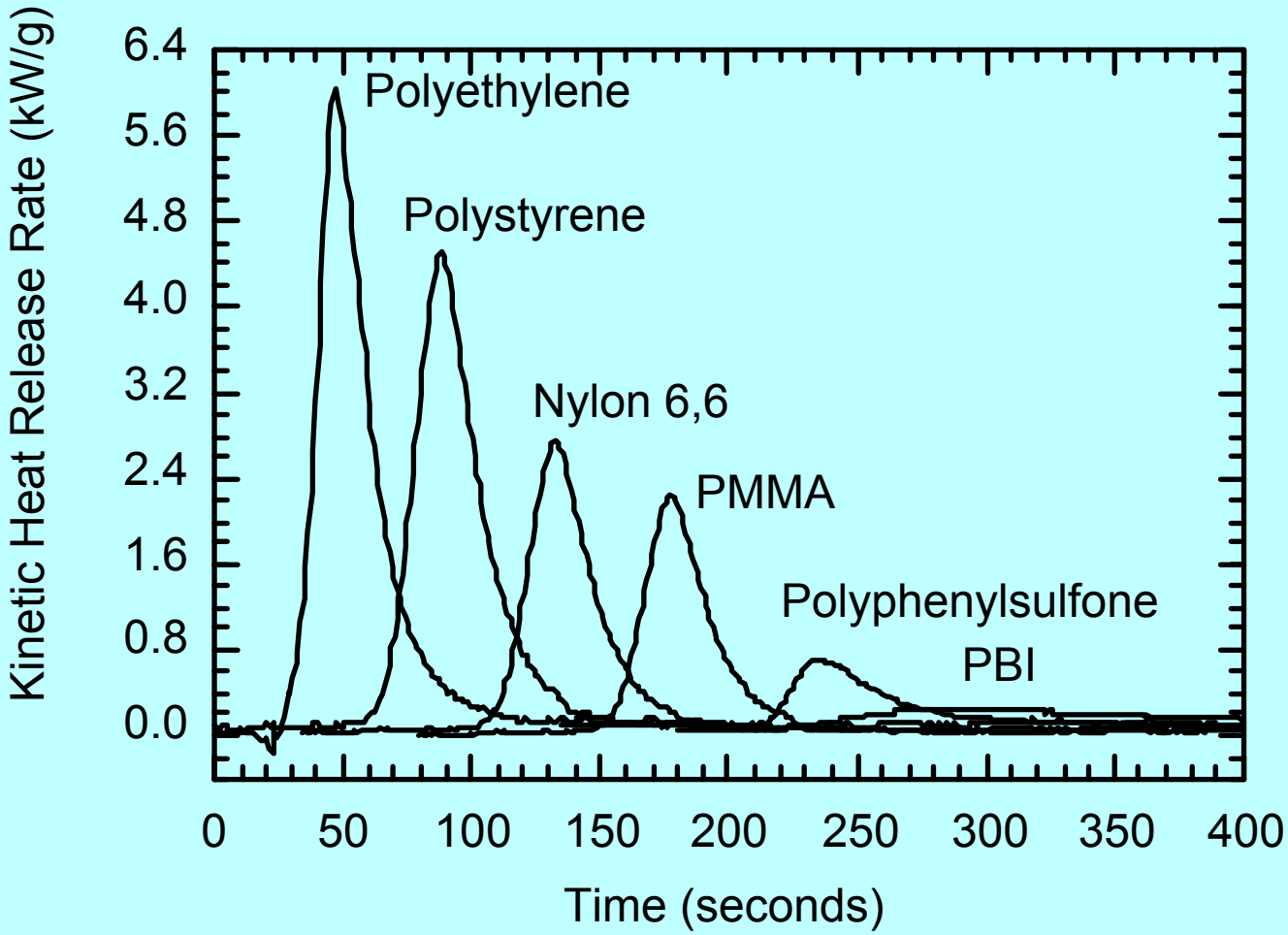
Pyrolysis-Combustion Flow Calorimetry

KINETIC HEAT RELEASE RATE BY O_2 CONSUMPTION

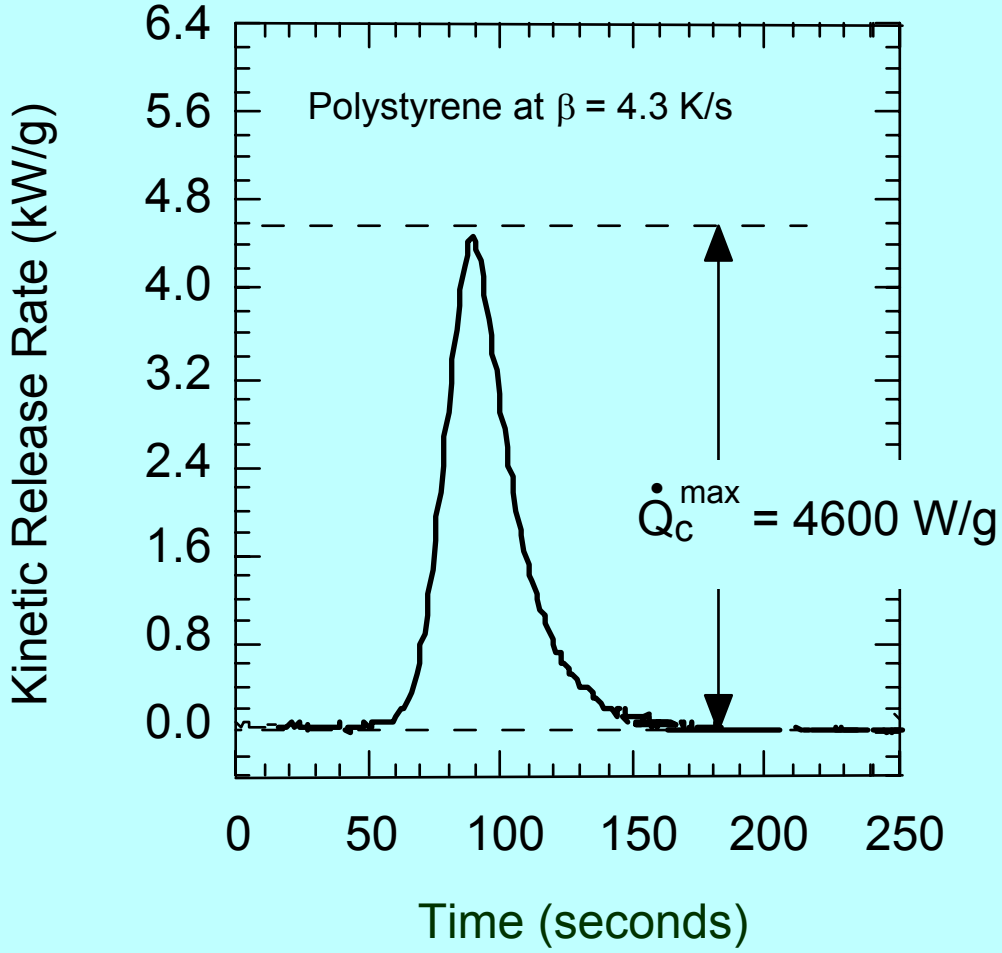
$$\dot{Q}_c^{max} = h_c^o \frac{\dot{m}_{max}}{m_0} = \beta \left[\frac{h_c^o (1-\mu) E_a}{eRT_p^2} \right] = \frac{E}{m_0} \Delta \dot{m}_{O_2}^{max}$$



KINETIC HEAT RELEASE RATE BY PCFC



HEAT RELEASE CAPACITY FROM KINETIC HRR



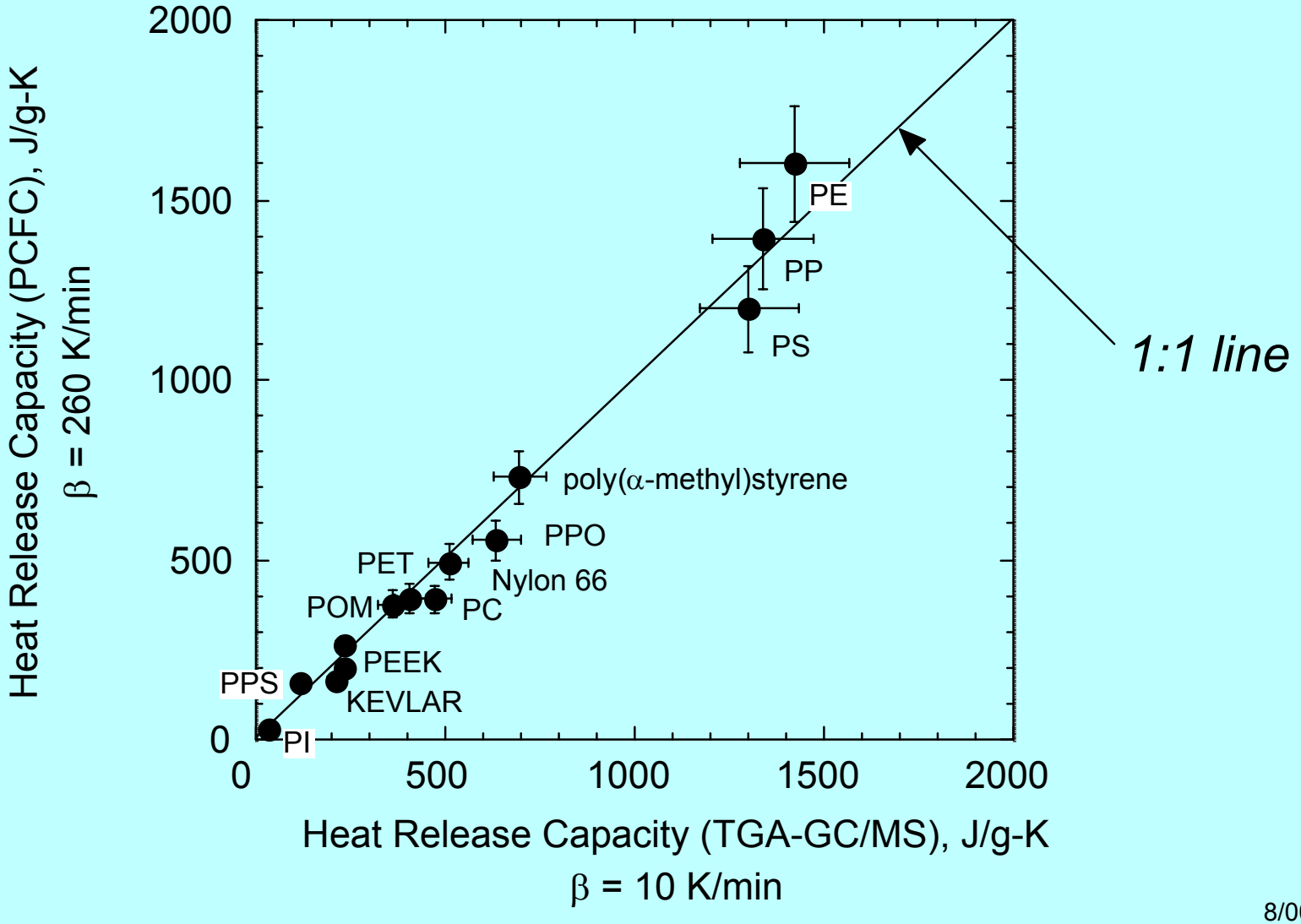
Heat Release Capacity, η_c

$$\eta_c \equiv \frac{\dot{Q}_c^{max}}{\beta} = \frac{4600\ \text{W/g}}{4.3\ \text{K/s}}$$

$$= 1100\ \text{J/g-K}$$

(Polystyrene)

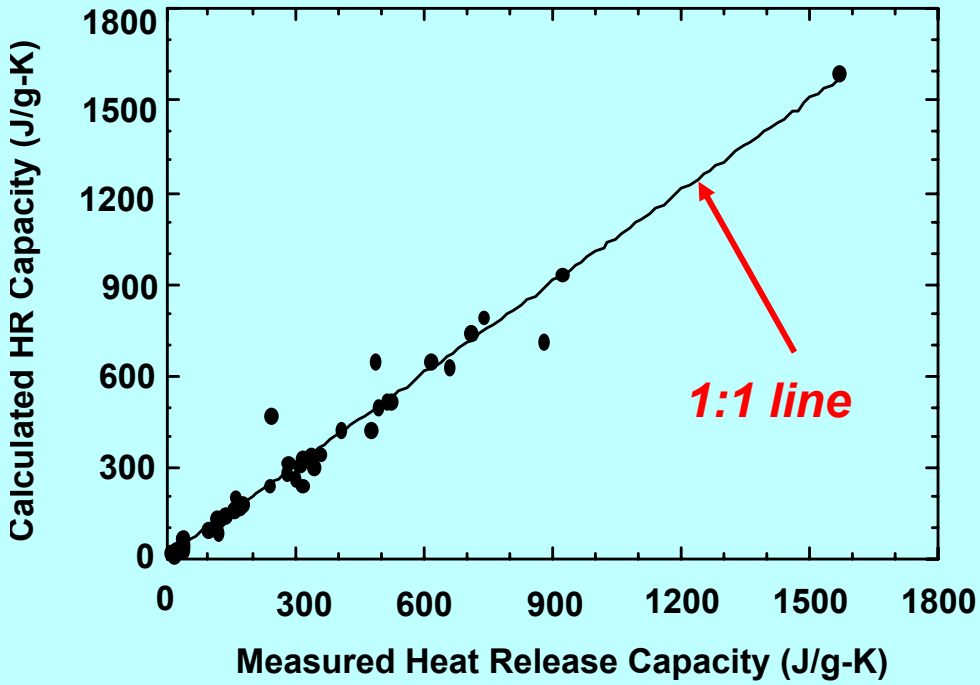
HEAT RELEASE CAPACITY: PCFC vs. TGA-GC/MS

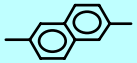
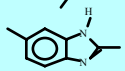
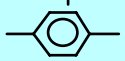
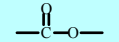
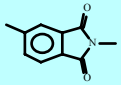
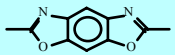
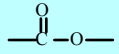
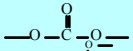
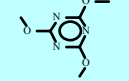


MOLAR GROUP CONTRIBUTIONS TO η_c

Results:

- Good correlation (r = 0.98) between calculated and experimental values.
- Unique Ψ_i (stable solutions to linear system of equations).
- Over 30 Ψ_i determined to date from > 100 polymers.



Group	Ψ_i (kJ/mol-K)	Group	Ψ_i (kJ/mol-K)
	67		–8
	52		–9
	31	—O—	–9
	30	—S—	–10
	28		–11
	28		–14
	26		–18
—CH_3	23		–24
	15	—OH	–36
	14		–39
	13		–43
—CH_2-O—	4		–49
CF_2	2		–71
	1		–121

HRR AND HEAT RELEASE CAPACITY

Average Flaming Heat Release Rate

$$\dot{q}_c = \chi h_c^0 \dot{m}_g = \chi h_c^0 \left[\rho_g \int_0^\infty k(x)\, dx \right] = \chi \rho \delta \dot{Q}_c^{max} = \chi \rho \delta \beta \eta_c$$

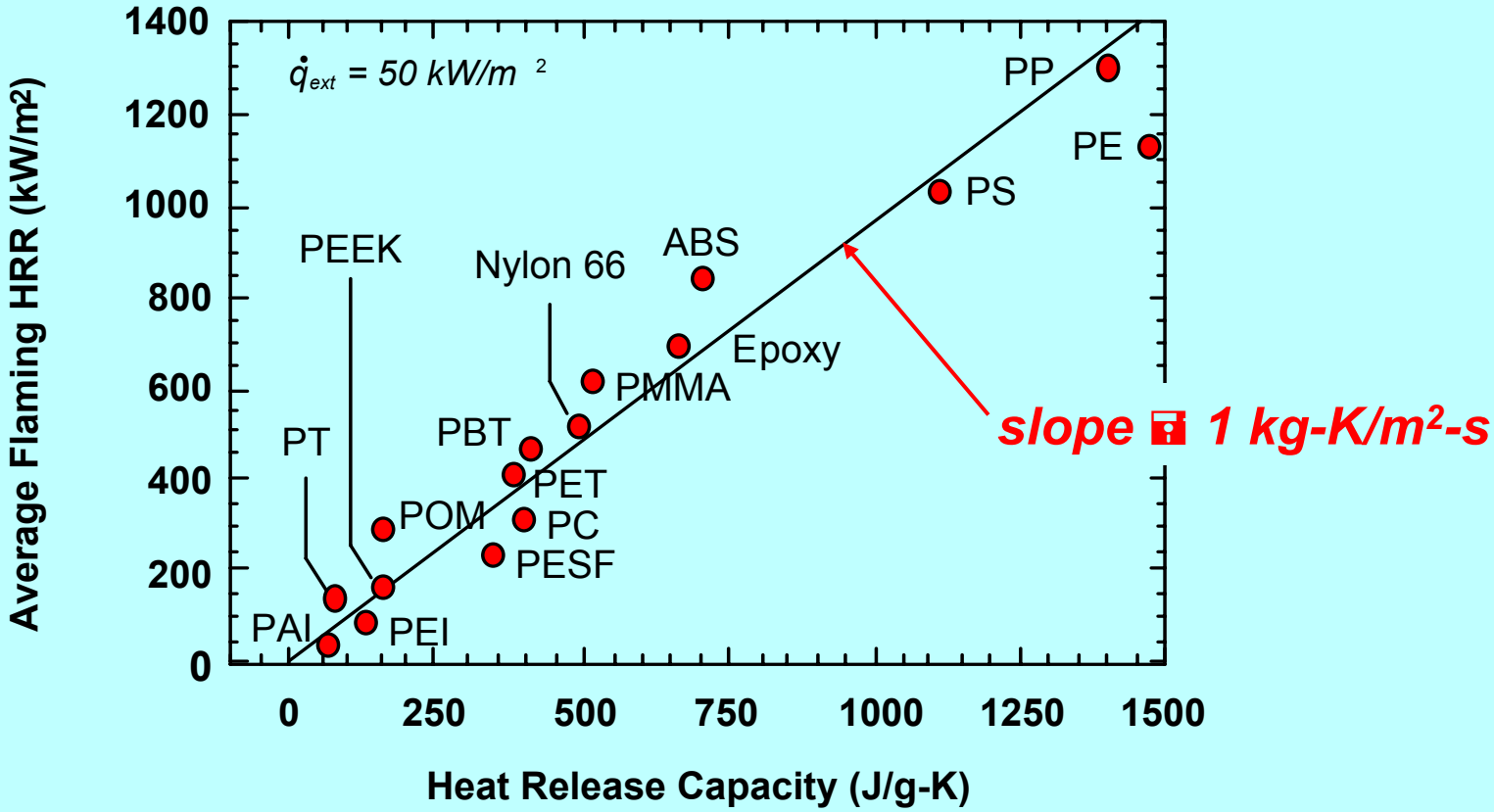
(χ = flaming combustion efficiency)

Flaming HRR / Heat Release Capacity Ratio

$$\frac{\dot{q}_c}{\eta_c} = \chi \rho \delta \beta \approx (0.75)(1100\ \text{kg/m}^3)(400\ \mu\text{m})(3\ \text{K/s})$$

$$= 1\ \text{kg-K/m}^2\text{-s}$$

HEAT RELEASE- *RATE versus -CAPACITY*



HEAT RELEASE PARAMETER

Steady Heat Release Rate

From Thermochemistry

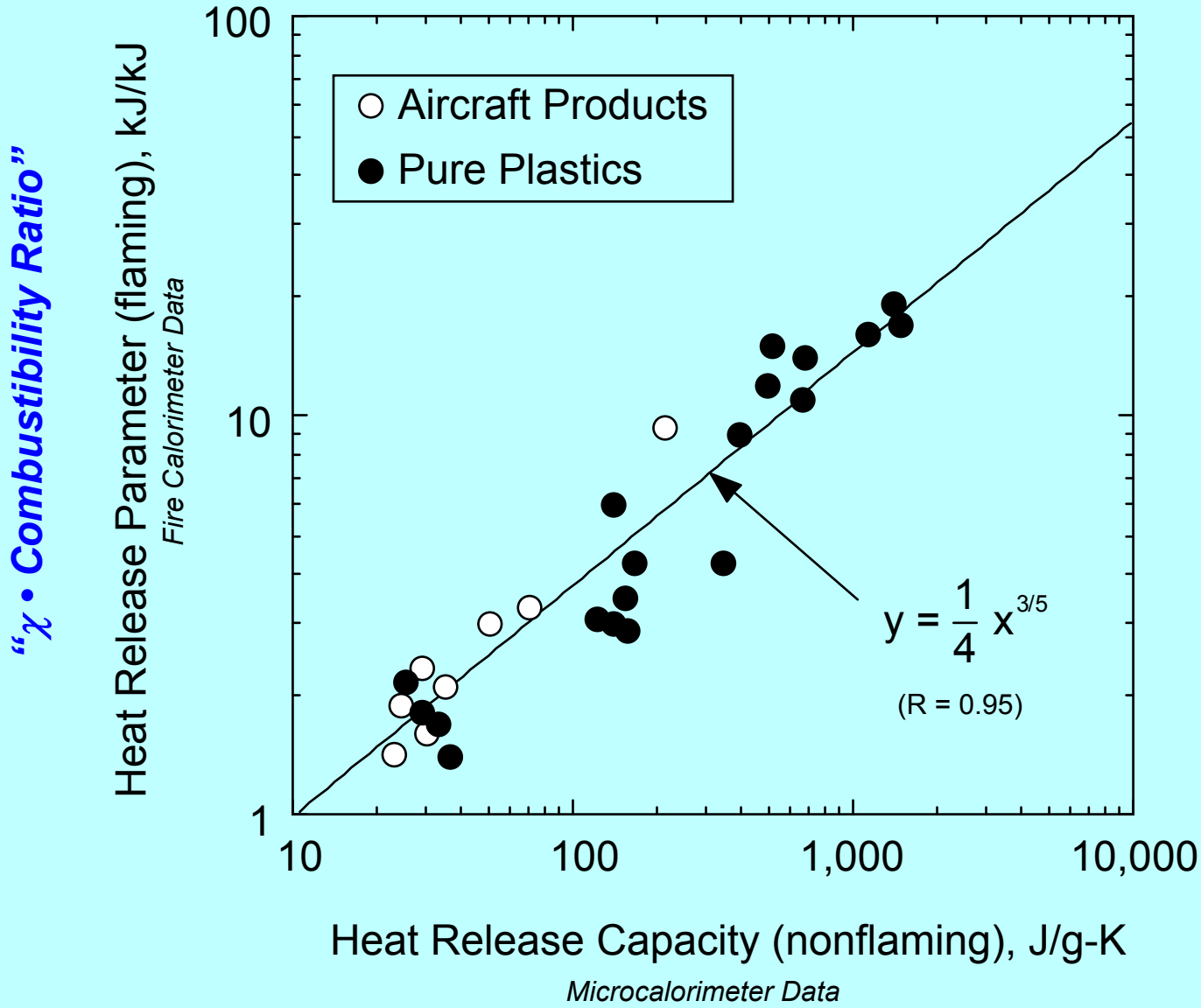
$$\dot{q}_c = \chi(1-\mu)\frac{h_c^0}{h_g}\dot{q}_{net} = (\chi\rho\delta\beta)\,\eta_c$$

Heat Release Parameter (HRP)

$$\mathbf{HRP} = \left(\frac{\chi\rho\delta\beta}{\dot{q}_{net}}\right)\eta_c = \left(a\eta_c^{-b}\right)\eta_c$$

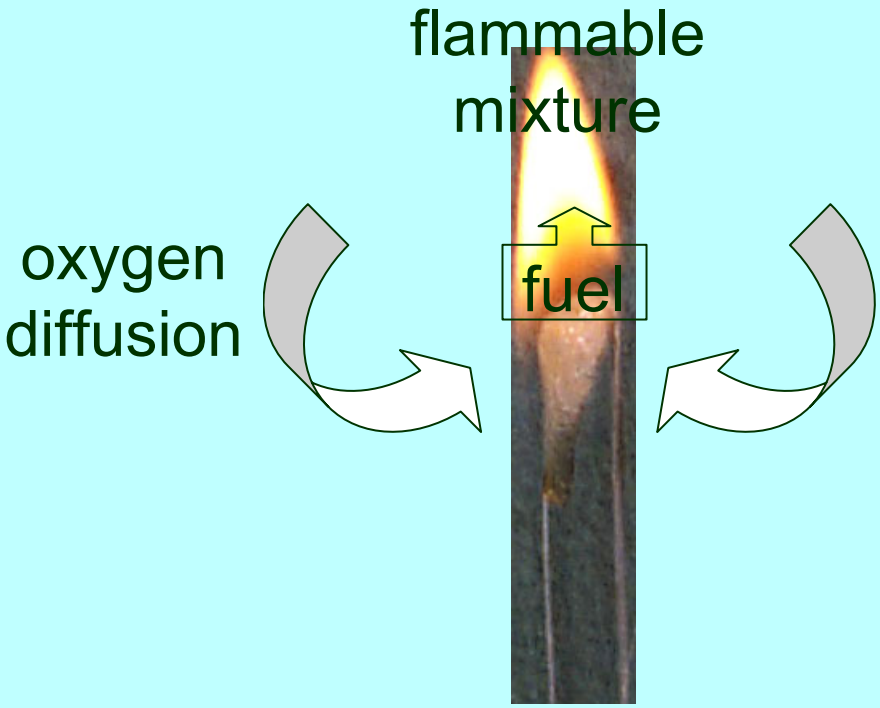
$$\mathbf{HRP} = a\,\eta_c^{1-b}$$

FLAMING *versus* NONFLAMING HEAT RELEASE



FLAMMABILITY

Flame tests measure extinguishment condition (flammability limit) for self-propagating diffusion flame.



FLAMMABILITY

Assume critical heat release rate criterion and express in terms of η_c

$$\dot{q}_c^* = 100\ \mathrm{kW/m^2} = \chi \frac{h_c^0}{L_g} \dot{q}_{net} = \chi \rho \delta \beta \eta_c$$

OR:

$$\frac{\dot{q}_c^*}{\chi \rho \delta \beta} \leq \eta_c$$

Must calculate δ and β in <u>flame test</u> to evaluate criterion.

FLAMMABILITY

FOR UPWARD FLAME TEST UL-94 V, q_{net} ≈ *15 kW/m²*

Pyrolysis zone depth:

$$\delta = \frac{\kappa}{\dot{q}_{flame}} \frac{eRT_p^2}{E_a} \approx \frac{0.2\ \text{W/m-K}}{15\ \text{kW/m}^2} \frac{eR(750\ \text{K})^2}{200\ \text{kJ/mole}} \approx 1\ \text{mm}$$

Effective heating rate of material particle at surface:

$$\beta = \frac{\dot{q}_{net}^2}{\kappa \rho h_g} \approx \frac{(15\ \text{kW/m}^2)^2}{(0.2\ \text{W/m-K})(1000\ \text{kg/m}^3)(3\ \text{MJ/kg})} = 0.4\ \text{K/s}$$

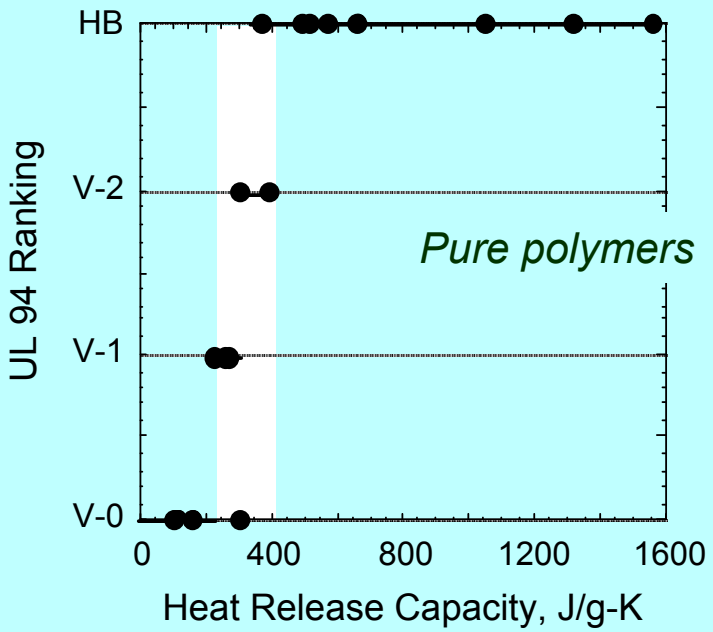
FLAMMABILITY CRITERION: UL- 94

The criterion for incipient burning in an upward flame test:

$$\frac{\dot{q}_c^*}{\chi\rho\delta\beta} = \eta_c^* = \frac{100\ \mathrm{kW/m^2}}{(0.75)(1000\ \mathrm{kg/m^3})(10^{-3}\mathrm{m})(0.4\ \mathrm{K/s})}$$

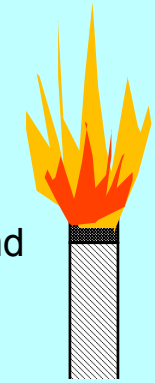
Flame extinguishment (ignition resistance) when:

η_c ≈ **300-400 J/g-K**



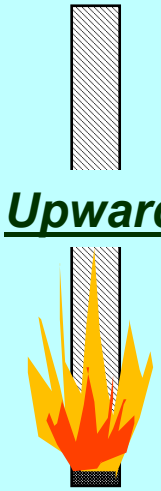
FLAMMABILITY CRITERION: L.O.I. vs UL 94V

$$\dot{q}_{ext} = \dot{q}_{cond}$$



$$\eta_c^* = \frac{\dot{q}_c^*}{\chi \rho \delta \beta} \propto \frac{1}{\dot{q}_{ext}}$$

Downward *versus* ***<u>Upward</u>*** *flame spread…*



$$\dot{q}_{ext} = \dot{q}_{cond} + \dot{q}_{conv} + \dot{q}_{rad}$$

LOI **UL 94 V**

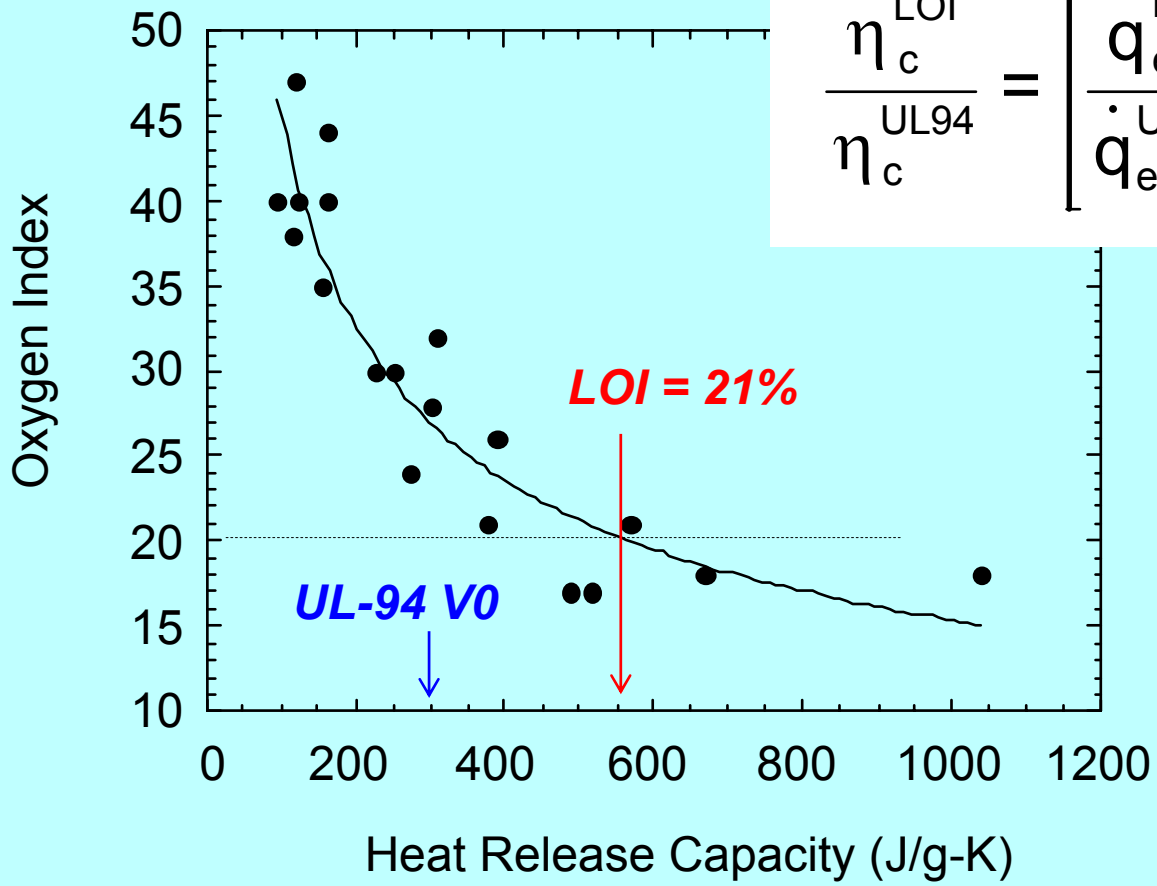
…should have different η^*_c because:

1. ***External heat flux is different.***
2. ***Time to extinguish is different***

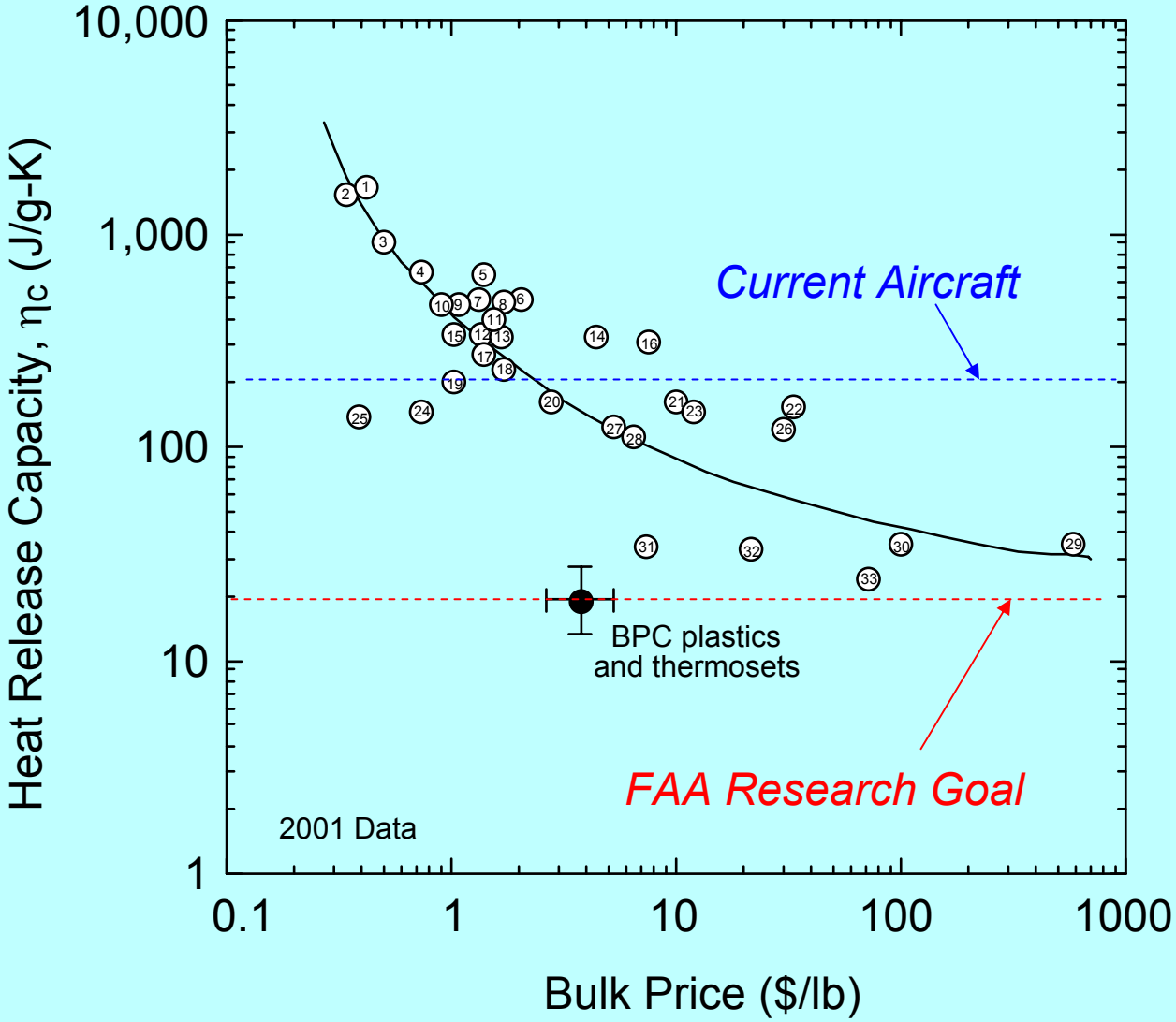
RELATIVE FLAMMABILITY CRITERION

η_c^* for L.O.I. vs UL 94-V0

$$\frac{\eta_c^{LOI}}{\eta_c^{UL94}} = \left[\frac{\dot{q}_{ext}^{LOI}}{\dot{q}_{ext}^{UL94}}\right]^{-1} > 1$$



THE PRICE OF FIRE RESISTANCE



POLYMER
(ranked by η_c)

1. PE
2. PP
3. PS
4. ABS
5. BPA Epoxy
6. PU
7. Nylon 6
8. Polyarylate
9. PBT
10. PMMA
11. PPO
12. Polycarbonate
13. Nylon 66
14. Polysulfone
15. PET
16. PVDF
17. SMA
18. PC/ABS
19. POM
20. PPS
21. LCP
22. PEEK
23. Polyphenylsulfone
24. Phenolic
25. PVC (rigid)
26. PEK
27. PEI
28. PES
29. PBI
30. PBO
32. PTFE
33. PAI
34. Polyimide

CONCLUSIONS

Solid state thermochemistry provides a measurable, calculable, rate-independent material flammability parameter

$$\eta_c = \frac{\dot{Q}_c}{\beta} = \left[\frac{h_c^o (1-\mu) E_a}{eRT_p^2}\right]$$

For simple materials (pure polymers) η_c correlates fire and flammability data reasonably well using a critical heat release rate criterion for burning.