

Fire & Materials 2017  
San Francisco, CA, February 6-8, 2017

# Ignition Temperature by Dynamic Thermal Analysis



Richard E. Lyon, Natallia Safronava\* and Sean Crowley

Aviation Research Division  
Federal Aviation Administration  
William J. Hughes Technical Center  
Atlantic City International Airport, NJ 08405

\*Technology & Management International, LLC  
Toms River, NJ

# **Specific Issues**

What is “Ignition Temperature?”

How is ignition temperature ( $T_{\text{ign}}$ ) measured?

How does  $T_{\text{ign}}$  relate to flammability?

Is  $T_{\text{ign}}$  a material property?

# Definitions of Ignition Temperature, $T_{ign}$

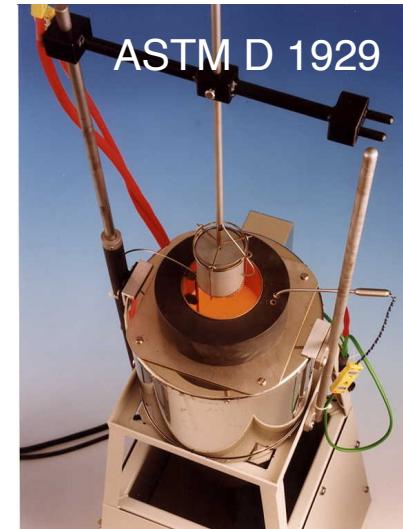
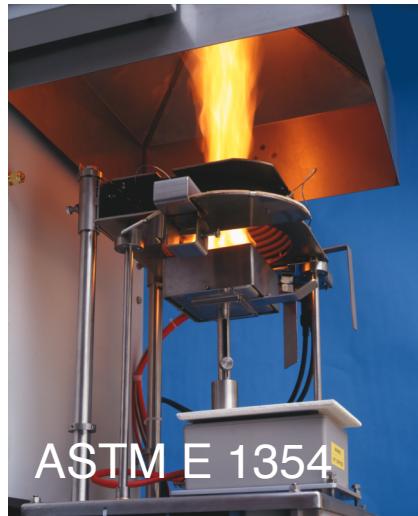
Minimum temperature at which combustion can be initiated under specified test conditions (ISO 13943)

The lowest temperature at which sustained combustion of a material can be initiated under specified test conditions (ASTM E 176)

Minimum temperature a substance must attain in order to ignite under specific test conditions (NFPA 921)

*“Minimum temperature for [sustained] combustion under specific test conditions”*

# Ignition Temperatures in Fire Tests



*Surface  
Temperature  
Measurements*

*Furnace  
Temperature  
Measurements*

# Ignition Temperature and Fire Behavior

## Ignitability

*Ignition delay at external heat flux,  $\dot{q}''_{ext}$*

$$t_{ign} = \frac{\pi}{4} \kappa \rho c \left[ \frac{T_{ign} - T_0}{\dot{q}''_{ext} - CHF} \right]^2$$

*$b > 2 \text{ mm thick}$   
 $\text{or } \dot{q}''_{ext} \gg CHF$*

$$= \rho c b \frac{T_{ign} - T_0}{\dot{q}''_{ext} - CHF}$$

*$b \leq 2 \text{ mm thick}$   
 $\text{or } \dot{q}''_{ext} \approx CHF$*

*Critical heat flux for ignition,  
CHF ( $\text{W/m}^2$ )*

$$CHF = \varepsilon \sigma (T_{ign}^4 - T_0^4) + h (T_{ign} - T_0)$$

## Heat Release Rate, $HRR = (H_c/L_g)\dot{q}''_{net}$

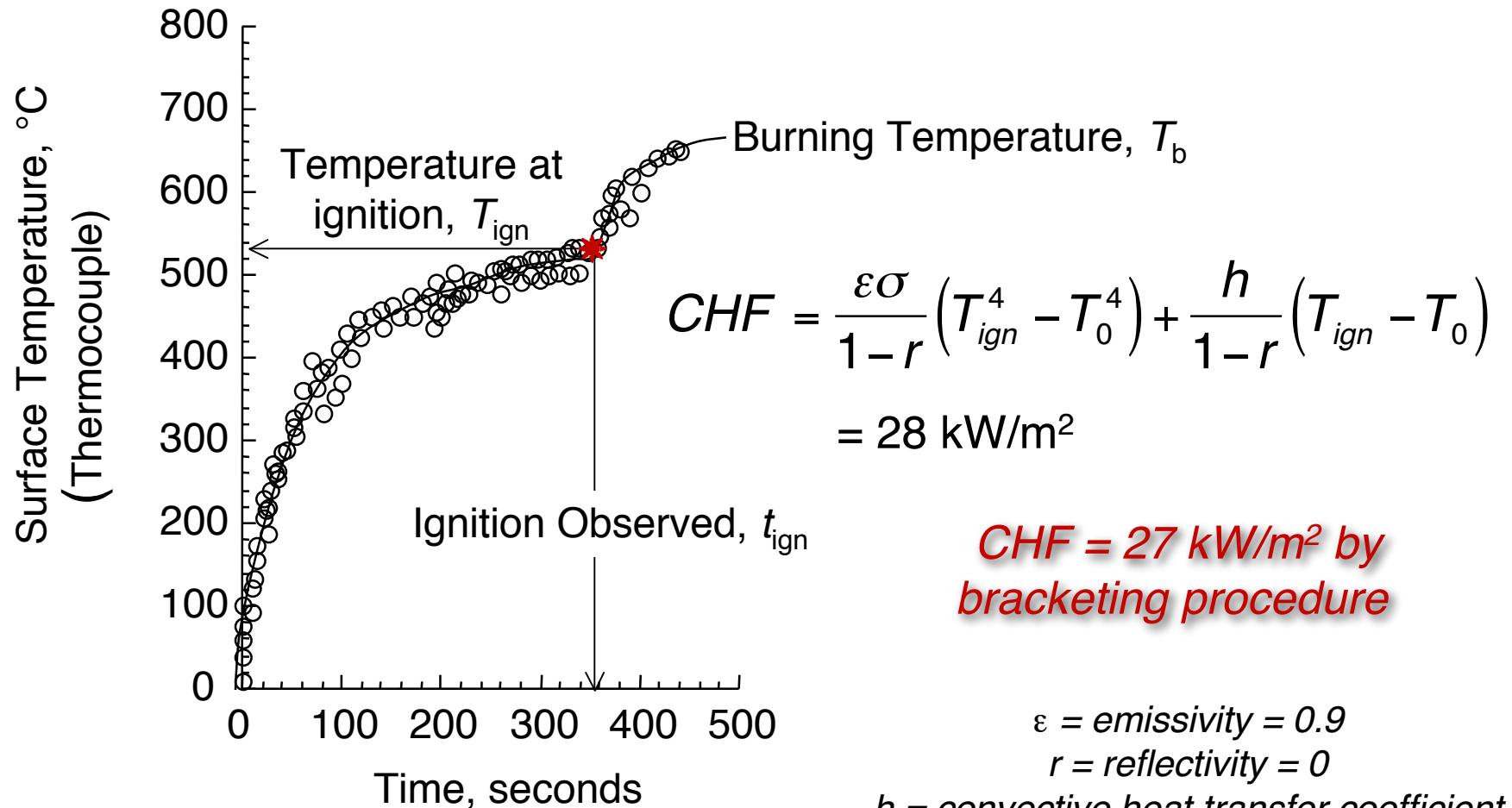
*Energy required to generate gaseous fuel,  $L_g$  ( $\text{J/kg}$ )*

$$L_g = \int_{T_0}^{T_{ign}} c(T) dT + \Delta h_v$$

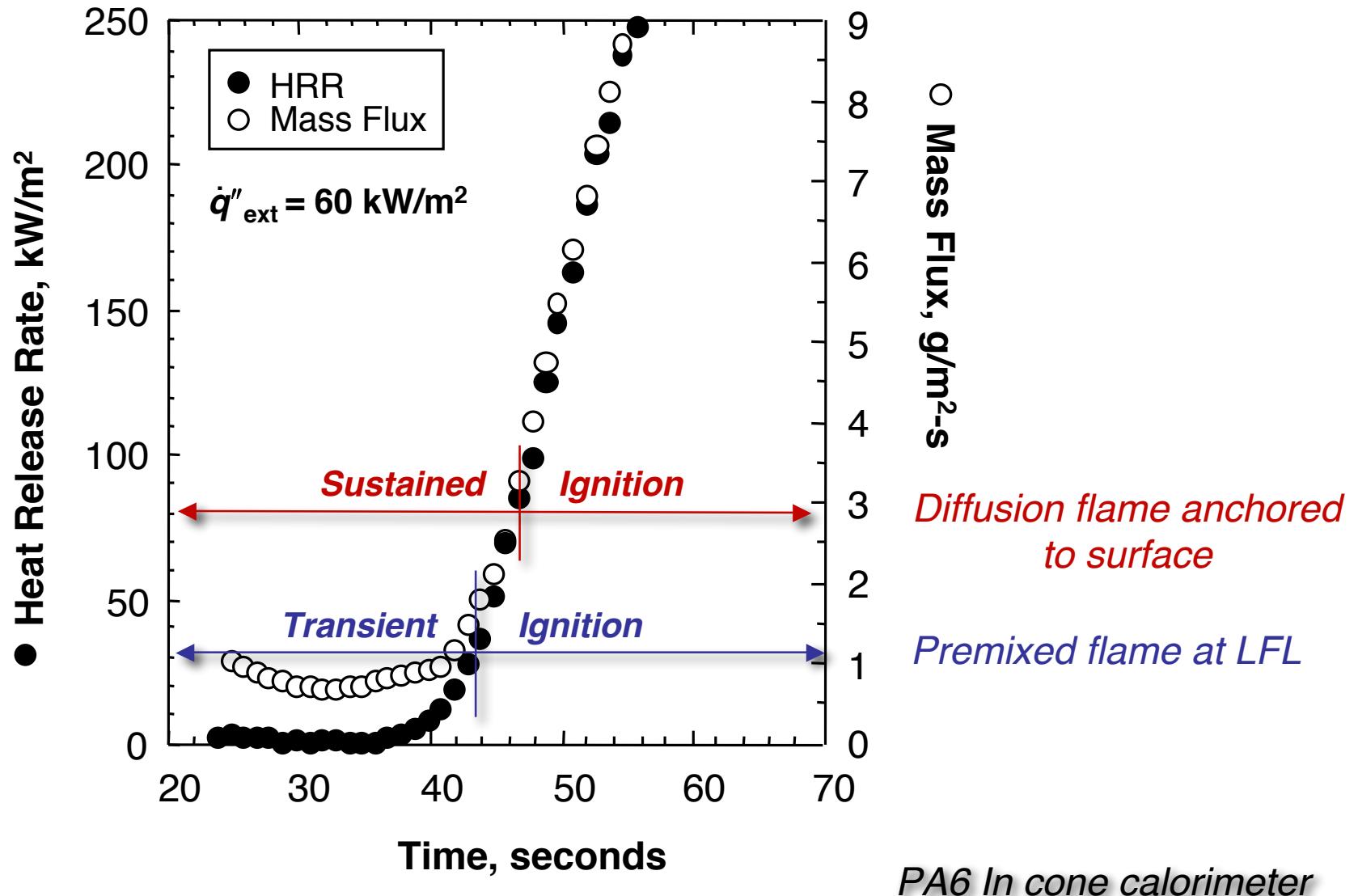
*Upper bound on short term thermal stability*

# Measuring Ignition Temperature in Fire Test

ASTM E 1354, Triplicate measurements of PEEK at  $q''_{ext} = 50 \text{ kW/m}^2$ , 10 mm samples



# Experimental Determination of Gas Phase Ignition Criteria



# Gas Phase Criteria for Ignition of Solids\*

*Typical polymers in cone calorimeter with  $\bar{h} = 10 \text{ W/m}^2\text{-K}$*

## **Critical Energy Flux ( $\text{W/m}^2$ )**

$$HRR^* = \frac{\bar{h}Q''_{cr}}{(\rho c_p)_{air}} \left( 1 - \frac{T_{ign} - T_0}{T_{flame} - T_0} \right) = \begin{cases} 21 \pm 6 \text{ kW/m}^2 & \text{Transient Ignition} \\ 66 \pm 17 \text{ kW/m}^2 & \text{Sustained Ignition} \end{cases}$$

*Theory* *Experiment*

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## **Critical Mass Flux ( $\text{W/m}^2$ )**

$$MLR^* = \frac{hQ''_{cr}}{H_{c,fuel}(\rho c_p)_{air}} \left( 1 - \frac{T_{ign} - T_0}{T_{flame} - T_0} \right) = \begin{cases} 1.0 \pm 0.4 \text{ g/m}^2\text{-s} & \text{Transient Ignition} \\ 3.2 \pm 1.2 \text{ g/m}^2\text{-s} & \text{Sustained Ignition} \end{cases}$$

*Theory* *Experiment*

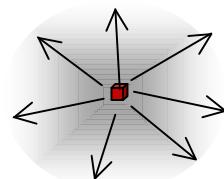
\*R.E. Lyon and J.G. Quintiere, "Criteria for Piloted Ignition of Combustible Solids," *Combustion & Flame*, 151, 551-559 (2007)

# Thermal Analysis Vs. Cone Calorimeter

## Thermal analysis

3-D fuel generation

$$h = 4\epsilon\sigma T_s^3 \approx 100 \text{ W/m}^2\text{-K}$$



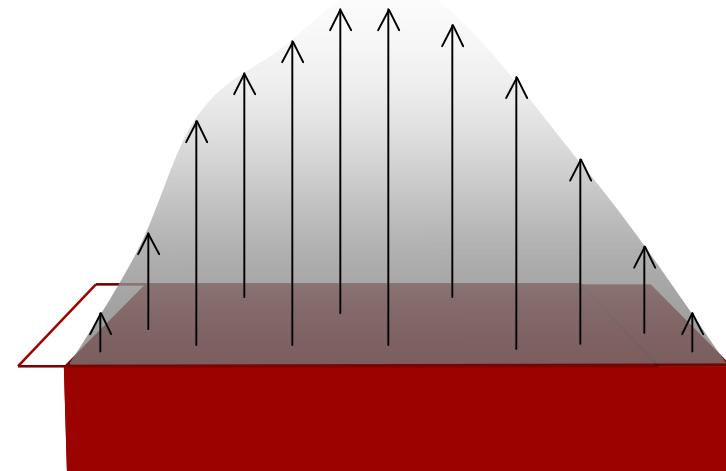
**Specific (scalar)  
Mass Loss Rate (s<sup>-1</sup>)**

$$\frac{\dot{m}}{m_0} = \frac{\text{Mass Loss Rate (g/s)}}{\text{Initial Mass (g)}}$$

## Fire (calorimeter)

1-D fuel generation

$$h \approx 10 \text{ W/m}^2\text{-K}$$



**Mass Flux (g/m<sup>2</sup>-s)**

$$\dot{m}'' = \frac{\text{Mass Loss Rate (g/s)}}{\text{Initial Area (m}^2)}$$

# Mass and Energy Fluxes in Thermal Analysis

*Uniform TA sample temperature requirement :*

$$\frac{hV}{\kappa S} \leq 1$$

V = sample volume ( $\text{m}^3$ ) =  $m/\rho$

m = sample mass (kg)

$\rho$  = sample density ( $\text{kg}/\text{m}^3$ )

S = sample surface area ( $\text{m}^2$ )

$\kappa$  = thermal conductivity ( $\text{W}/\text{m}\cdot\text{K}$ )

h = heat transfer coefficient in TA

$$\approx 4\sigma T^3 = 100 \text{ W}/\text{m}^2\cdot\text{K}$$

## DTG Criterion

$$\frac{\dot{m}}{m_0} (\text{s}^{-1}) \geq \frac{\dot{m}_{ign}''}{\rho\kappa/h} = \frac{\text{MLR}^*}{3 \text{ kg}/\text{m}^2}$$

## MCC Criterion

$$\dot{Q} (\text{W}/\text{kg}) \geq \frac{\dot{q}_{ign}''}{\rho\kappa/h} = \frac{\text{HRR}^*}{3 \text{ kg}/\text{m}^2}$$

# Specific Rates in TA Corresponding to MLR\* and HRR\* in Cone Calorimeter

## DTG

*Specific Mass Loss Rates*

## MCC

*Specific Heat Release Rates*

*Transient  
Ignition*

$$M'_{\text{flash}} = \frac{\text{MLR}^*_{\text{flash}}}{\rho\kappa/h} = 0.3 \frac{mg}{g-s}$$

$$Q'_{\text{flash}} = \frac{\text{HRR}^*_{\text{flash}}}{\rho\kappa/h} = 7 \frac{W}{g}$$

*Sustained  
Ignition*

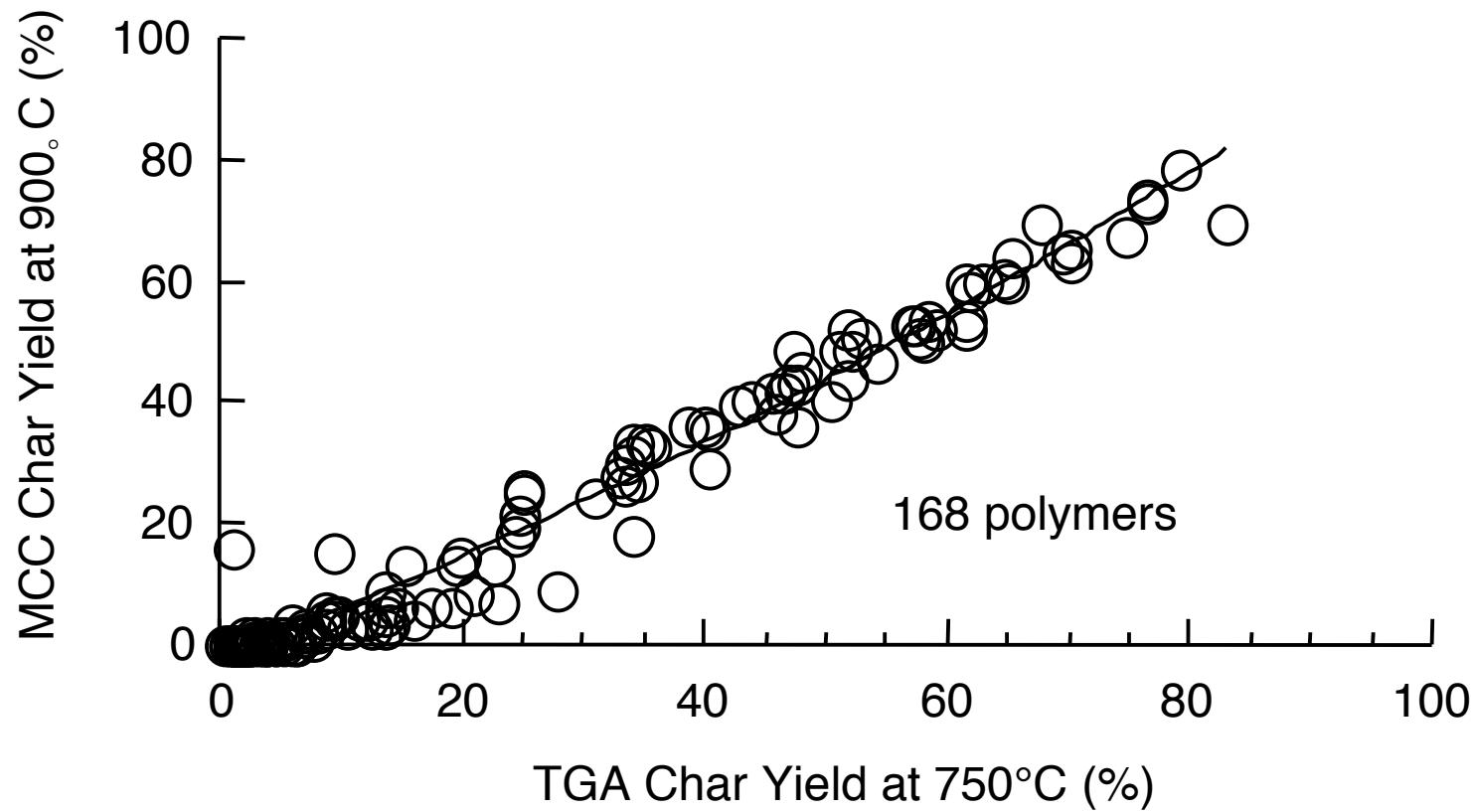
$$M'_{\text{fire}} = \frac{\text{MLR}^*_{\text{fire}}}{\rho\kappa/h} = 1 \frac{mg}{g-s}$$

$$Q'_{\text{fire}} = \frac{\text{HRR}^*_{\text{fire}}}{\rho\kappa/h} = 20 \frac{W}{g}$$

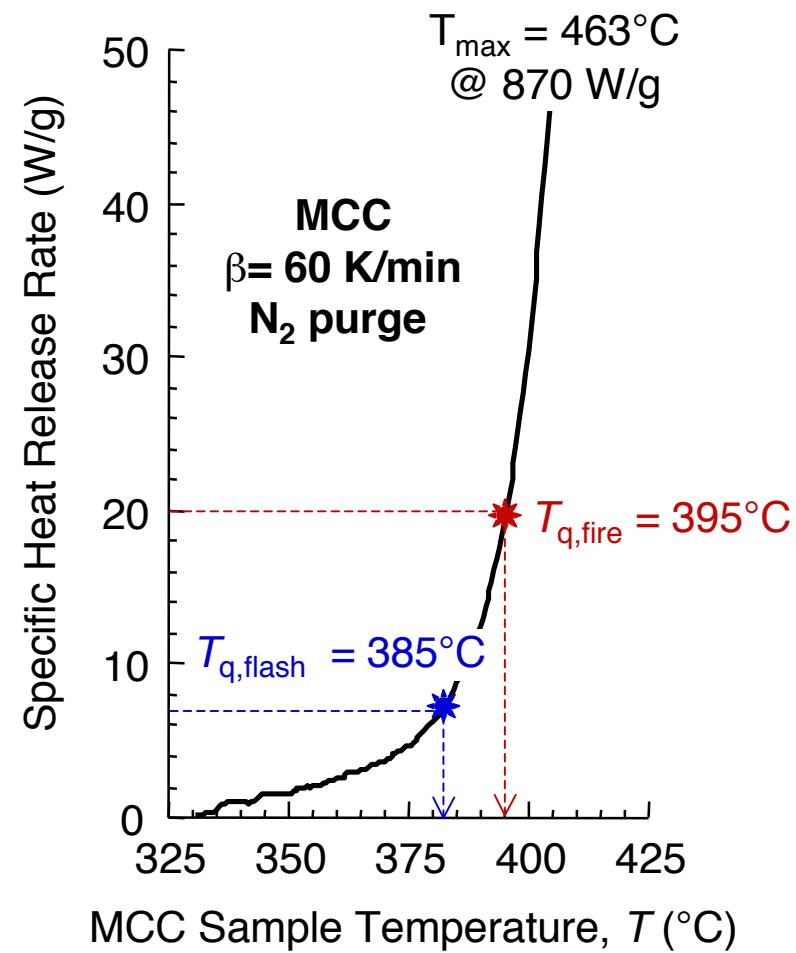
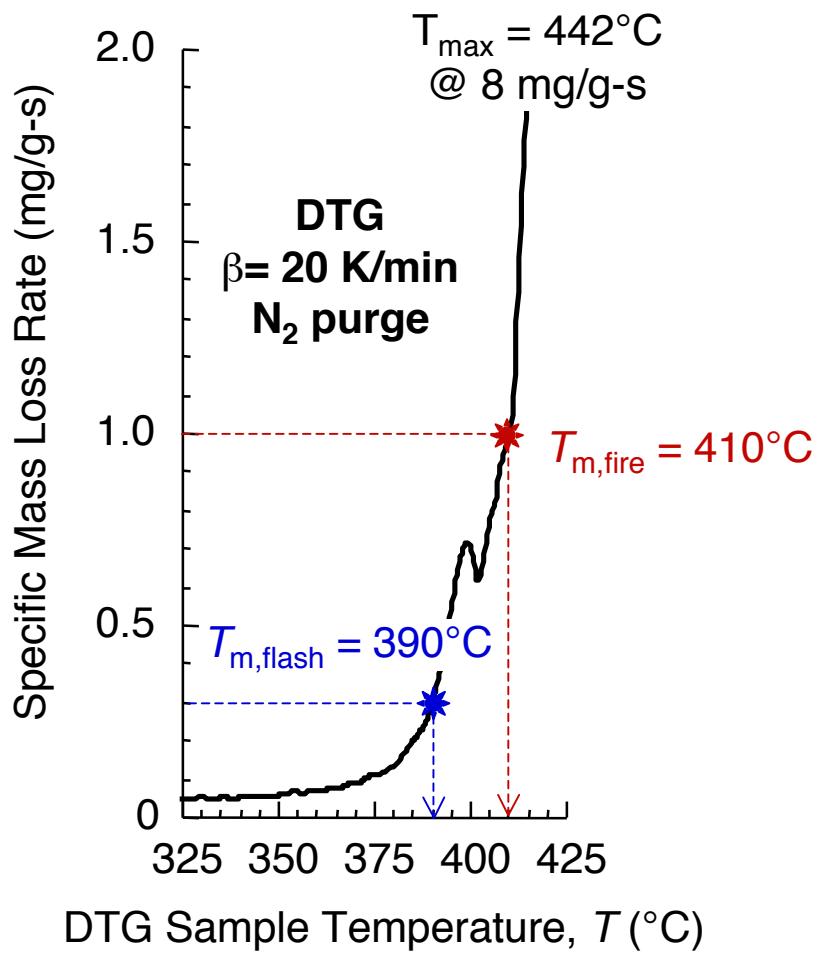
$$\rho = 1300 \text{ kg/m}^3; \kappa = 0.24 \text{ W/m-K}; h = 100 \text{ W/m}^2\text{-K}$$

# Pyrolysis Environment is Same for MCC and TGA

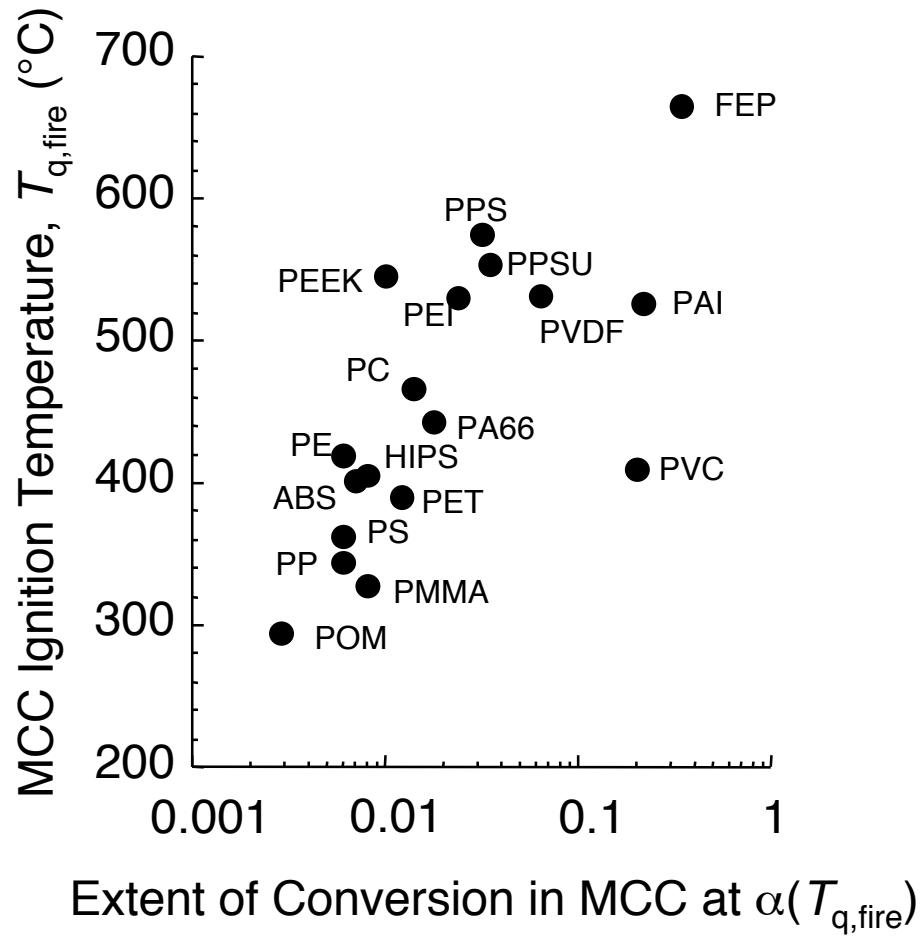
*Char Yield in MCC = TGA*



# TA Temperatures for Gas Phase Ignition of HIPS in Fire Test



# Extent of Conversion at $T_{q,\text{fire}}$ and Single-Point Kinetic Parameters

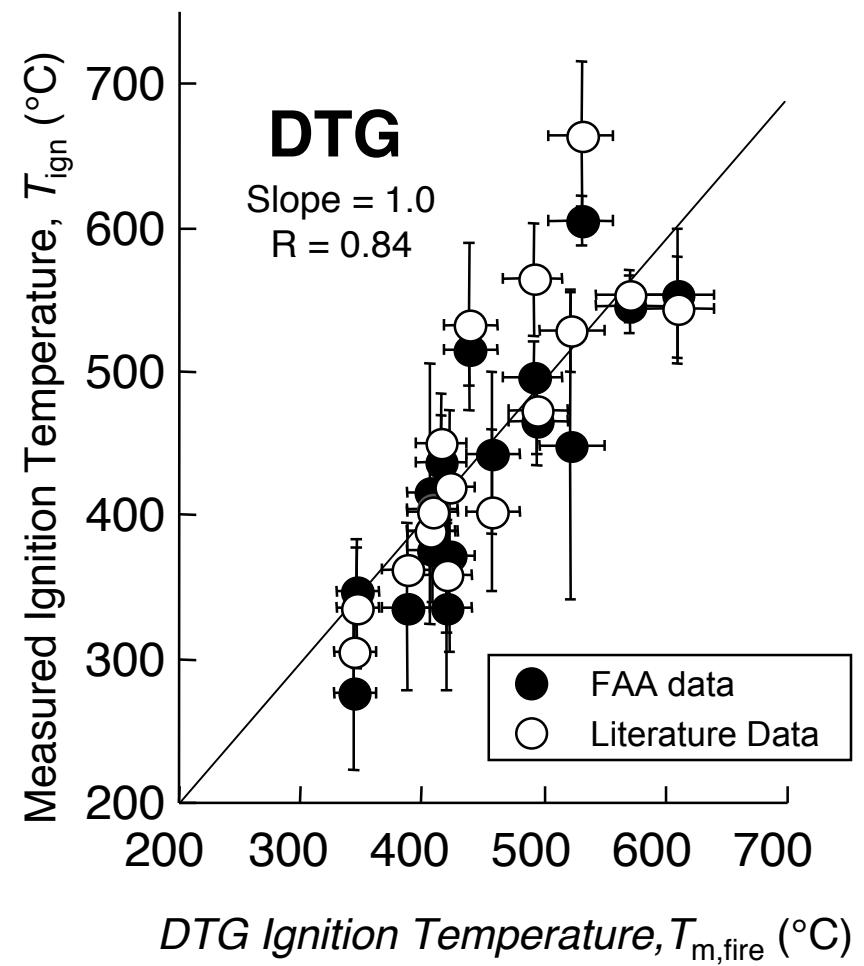
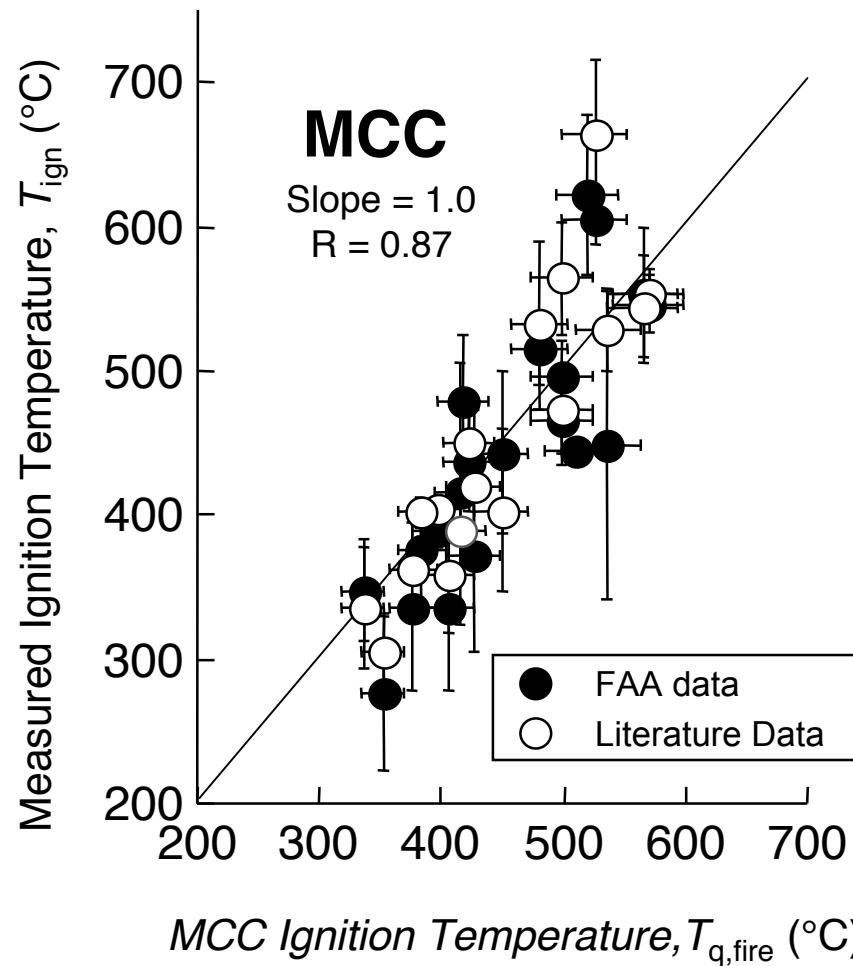


## Thermal Decomposition Kinetic Parameters\*

Polymers	$Q_{\infty}$ (kJ/g)	$E_a$ (kJ/mole)	$\ln[A]$ , ( $\text{s}^{-1}$ )
PP	46.1	347	51.67
PA66	30.4	251	36.46
PE	45.6	469	69.20
PS	40.5	304	48.31
PMMA	25.5	191	31.01
HIPS	40.4	269	40.90
PET	22.2	266	39.97
ABS	39.3	187	27.32
PC	21.7	422	58.78
PEEK	12.6	510	65.68
PEI	11.1	319	42.37
POM	14.9	144	21.66
PPSU	13.4	295	36.51
PPS	15.8	226	29.79
PVC rigid	12.3	168	23.54
PVDF	29.9	613	88.72
FEP	4.5	304	38.49
PEN	13.0	353	54.97
PSU	17.7	315	43.30
PAI	5.3	100	9.63

\*Principles and Practice of Microscale Combustion Calorimetry, R.E. Lyon, R.N. Walters, S.I. Stoliarov and N. Safronava, Final Report DOT/FAA/TC-12/53, Revision 1, April 2013

# Qualitative Agreement Between Fire Test and TA Ignition Temperatures



# Thermal Decomposition Kinetics of Solid Fuels in Nonisothermal Analysis (TA)

$$\text{Rate of conversion of solid to gaseous fuel} = \frac{d\alpha}{dt} = k(T)f(\alpha)$$

$\alpha$  = Extent of conversion of solid to gas  $\longrightarrow$

$$\left\{ \begin{array}{l} \frac{m_0 - m}{m_0 - m_{\text{final}}} \\ Q/Q_{\infty} \end{array} \right. \quad \begin{array}{l} \text{DTG} \\ \text{MCC} \end{array}$$

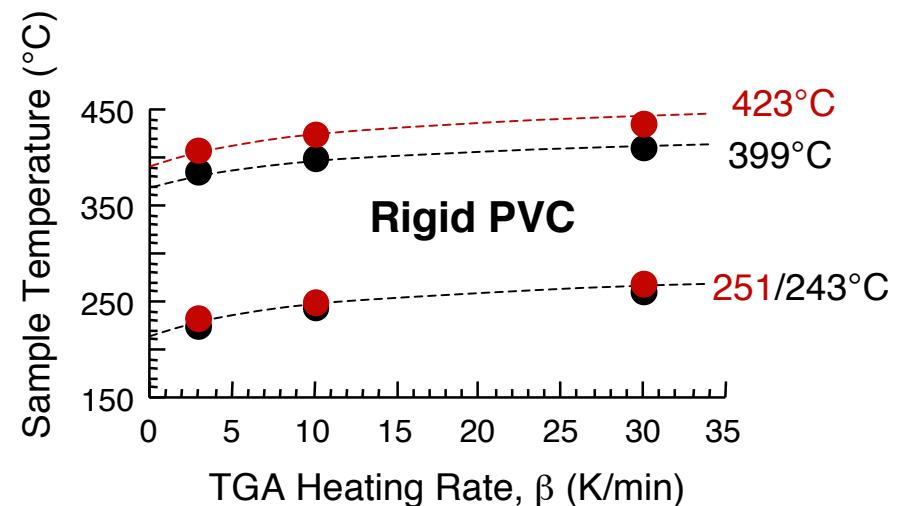
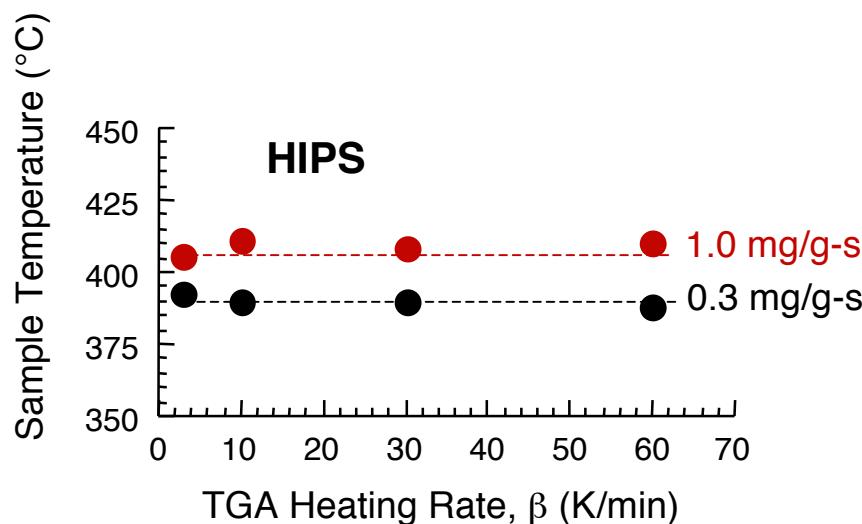
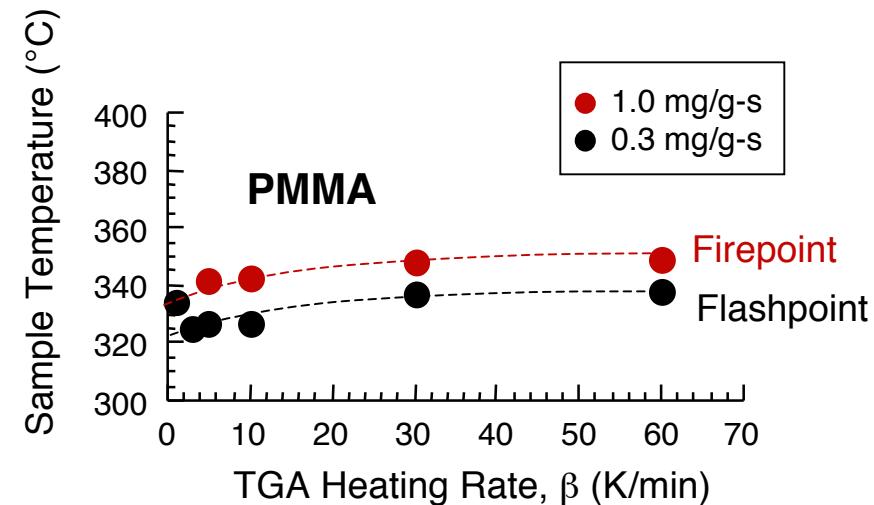
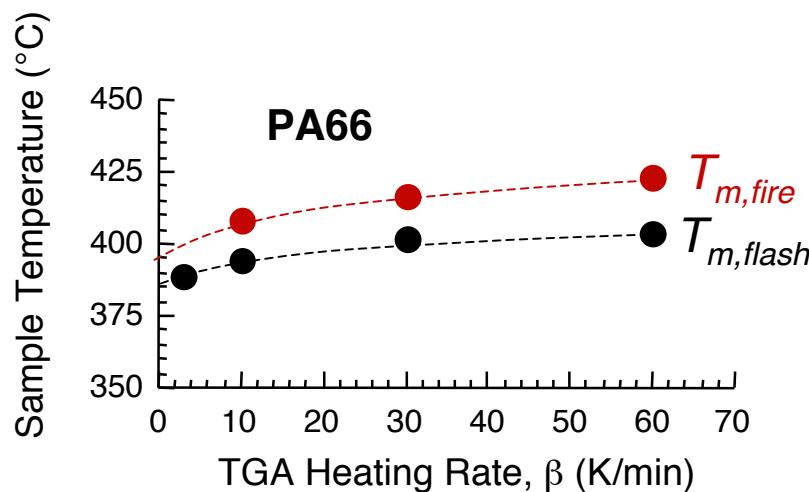
$f(\alpha) = (1-\alpha)^n$  = Reaction Model (typically)

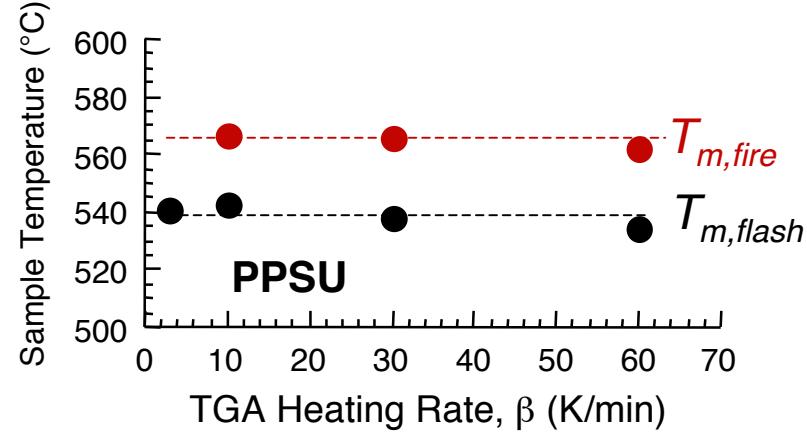
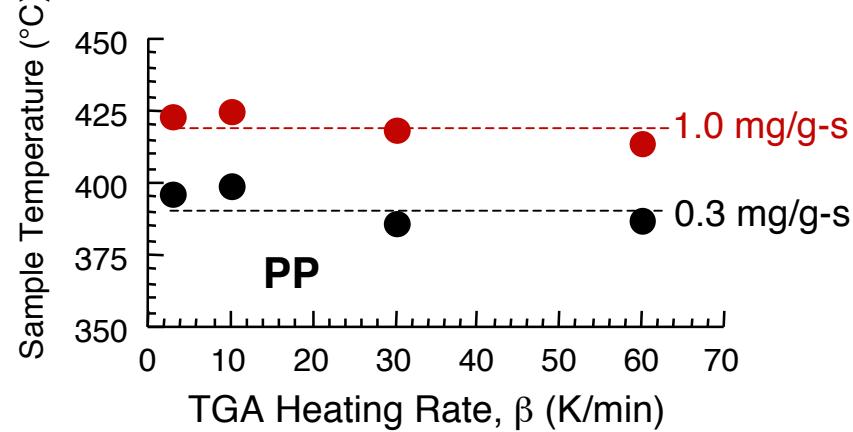
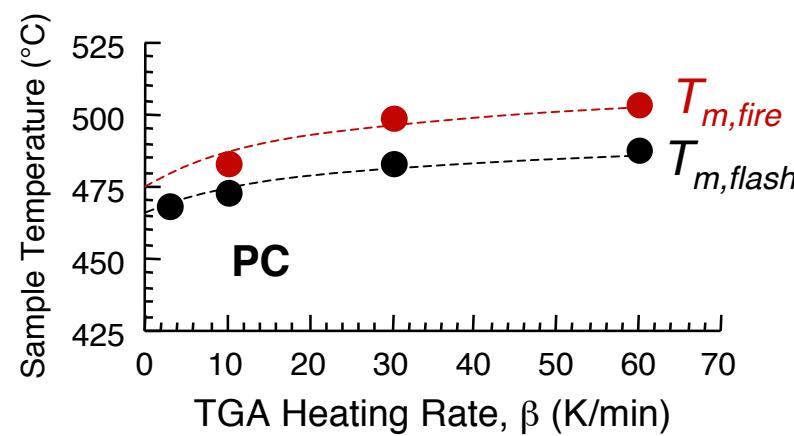
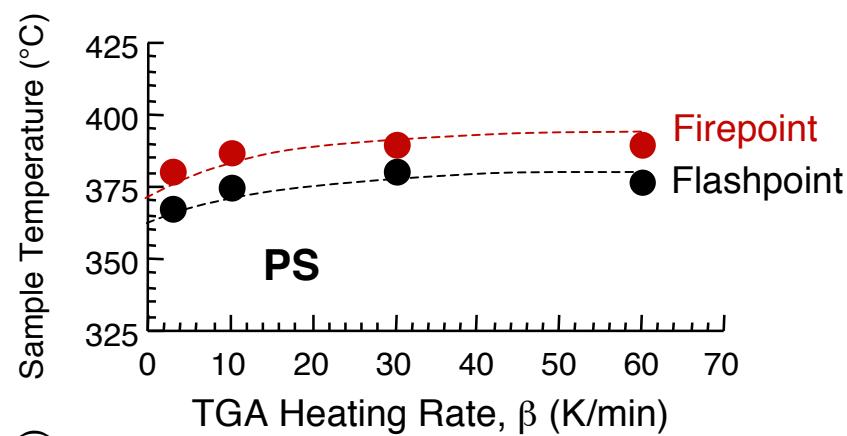
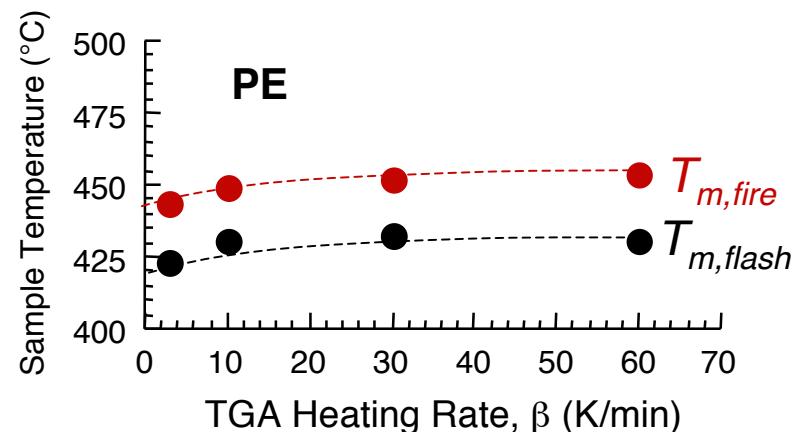
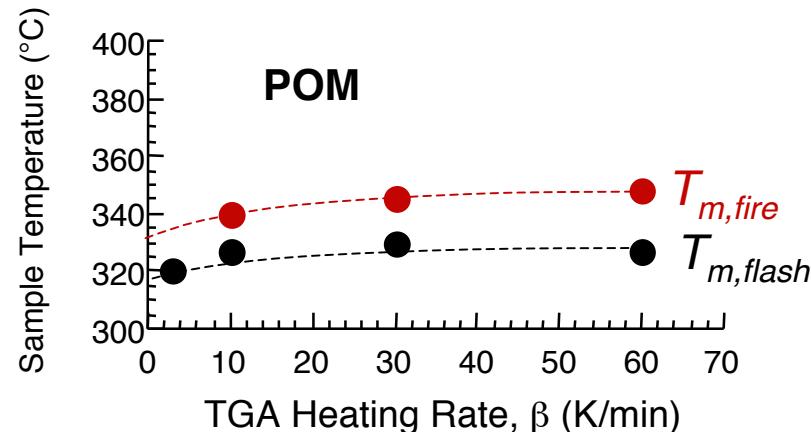
$k(T) = A \exp[-E_a/RT]$  = Rate Constant

At constant heating rate,  $dT/dt = \beta$  in TA with  $f(\alpha)=1-\alpha$ ,

$$\frac{d\alpha}{dt} = k(T) \exp \left[ -\frac{A}{\beta} \int_{T_0}^T \exp \left[ -\frac{E_a}{RT'} \right] dT' \right] = k(T)(1-\alpha)$$

# DTG Sample Temperatures $T_{m,flash}$ and $T_{m,fire}$ Become Constant at $\beta \geq 30$ K/min





# Thermal Stability and Ignition Temperature

$$\frac{d\alpha}{dt} \approx k(T) = A \exp\left[-\frac{E_a}{RT}\right] = \begin{cases} TA \text{ kinetics as } \\ \alpha \rightarrow 0 \text{ or as } \beta \rightarrow \infty \end{cases} \quad \begin{cases} Gas \text{ phase} \\ criteria \text{ for} \\ ignition \end{cases}$$

*Material properties*                    *Test Conditions*

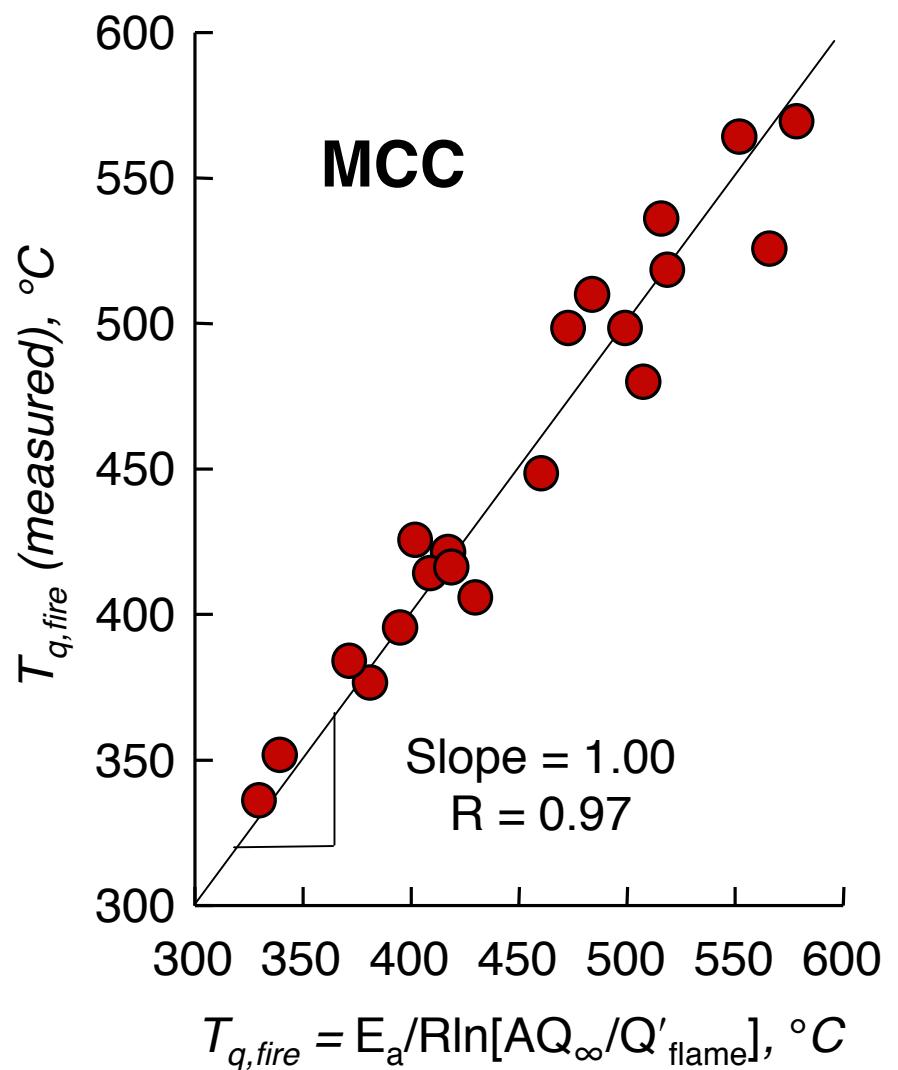
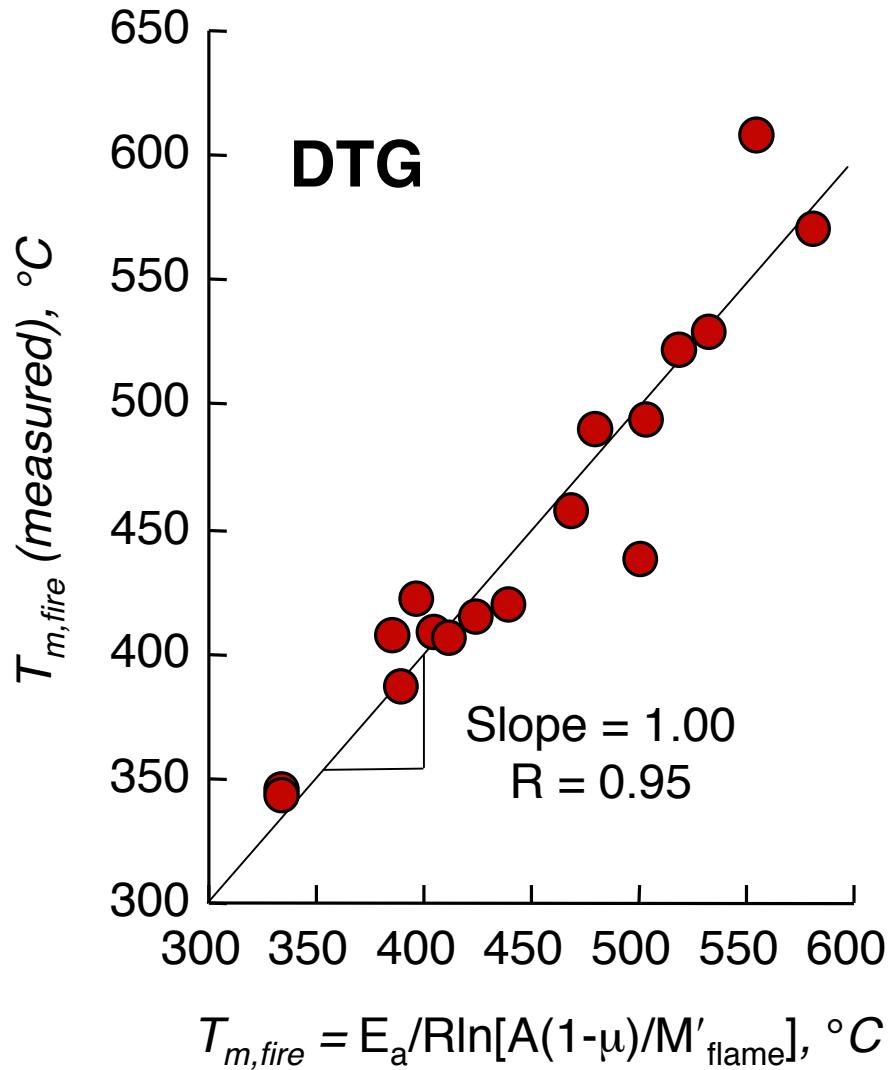
$$DTG: \quad T_{m,i} = \frac{E_a}{R \ln[A(1-\mu)/M_i]}.$$

$$MCC: \quad T_{q,i} = \frac{E_a}{R \ln[AQ_\infty/Q'_i]}$$

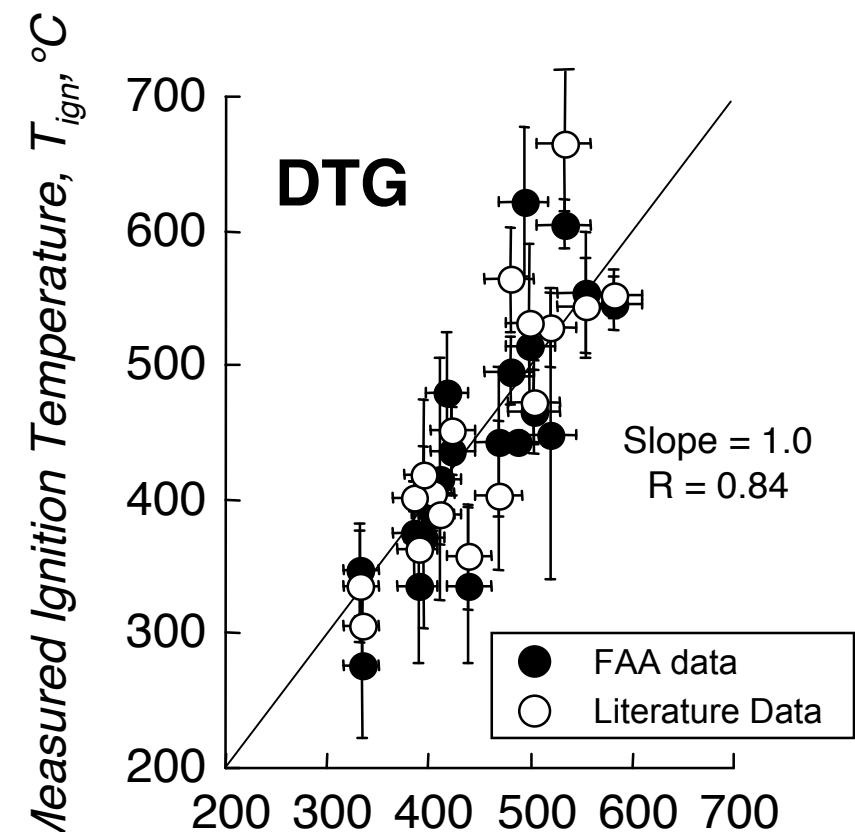
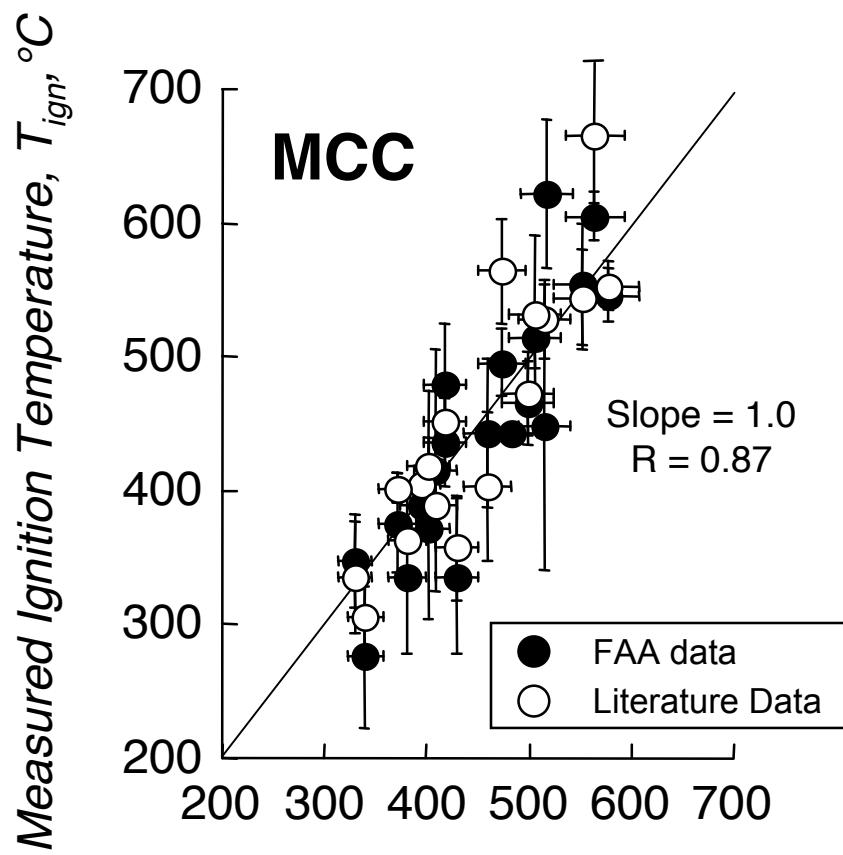
$i = \begin{cases} Transient \ Ignition \\ Sustained \ Ignition \end{cases}$

# TA Temperatures for Sustained Ignition

## *Measured Versus Calculated*



# Qualitative Agreement Between Fire Test and Calculated Ignition Temperatures



$$T_{q,fire} = \frac{E_a}{R \ln \left[ \frac{AQ_\infty}{Q'_{flame}} \right]} , \text{°C}$$

$$T_{m,fire} = \frac{E_a}{R \ln \left[ \frac{A(1-\mu)}{M'_{flame}} \right]} , \text{°C}$$

# Conclusions

Critical fluxes of mass ( $\text{MLR}_i^*$ ) and energy ( $\text{HRR}_i^*$ ) at piloted ignition in fire tests are related to specific (scalar) release rates of mass ( $M'_i$ ) and energy ( $Q'_i$ ) in TA by the requirement for controlled heating.

$i$  = Transient ignition (flash point) or Sustained Ignition (fire point).

TA temperatures at  $M'_i$  ( $T_{m,i}$ ) and  $Q'_i$  ( $T_{q,i}$ ) Correlate reasonably well with ignition temperatures ( $T_{ign}$ ) at  $\text{MLR}^*$  and  $\text{HRR}^*$  in fire tests.

Difference between TA and  $T_{ign}$  in fire test ( $\Delta T_{ign} \approx 40^\circ\text{C}$ ) is due to 25% uncertainty in  $\text{MLR}^*$  and  $\text{HRR}^*$ . This difference is the same as the average standard deviation of  $T_{ign}$  in fire test.

Thermal decomposition kinetics at small  $\alpha$  shows that  $T_{ign}$  is related to thermal stability by kinetic parameters  $E_a$  and  $A$ .