Material Change Similarity Task Group

Microscale Combustion Calorimetry

IAMFTWG

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Daniel Slaton, Boeing, Technical Fellow

Richard E. Lyon, Ph.D. and Natallia Safronava, FAATC

bccResearch

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Using the Microscale Combustion Calorimeter to Compare Materials

Richard E. Lyon, Natallia Safronava*, Richard N. Walters, Sean Crowley

Fire Safety Branch
Federal Aviation Administration
William J. Hughes Technical Center
Atlantic City, New Jersey 08405

*Technology and Management International
Toms River, NJ

Motivation

Code of Federal Regulations 14 (FAA)
Part 21 (Certification Procedures)

§ 21.93 Classification of changes in type design (paraphrased)

(a) Changes in type design (e.g., B737-100, -200, -300, -400, -500 and A340-200, -300, -500, -600) are classified as minor and major. A “minor change” is one that has no appreciable effect on the weight, balance, structural strength, reliability, operational characteristics, or other characteristics affecting the airworthiness of the product. All other changes are “major changes” and require re-certification of the airplane.

§ 21.95 Approval of minor changes in type design.

(a) Minor changes in a type design may be approved under a method acceptable to the FAA before submitting to the FAA any substantiating or descriptive data.

A change to the Type Design includes any change to a chemical formulation of a specific qualified/certified material listed on the specification or engineering drawings.

Pass / Fail FAA Flammability Tests

(≥ 2-Parameters)

OSU Rate of Heat Release Apparatus (Large Area Materials)

- Peak HR
- 2-min Total HR

Radiant Panel (Thermo-acoustic Insulation)

- Flame Propagation
- After Flame time

Vertical Bunsen Burner (All other materials)

- Burn length
- After Flame time
- Flame Drip time

Proposed Method to Determine Small Change

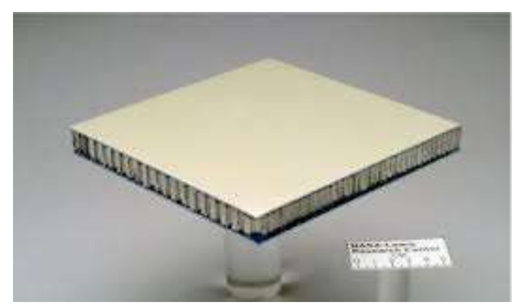
ASTM D7309 (MCC) Test and Criterion

- **Similar** → **MCC sufficient**
- **Different** → **FAR Test of coupon**
  - **Similar** → **Coupon sufficient**
  - **Different** → **FAR Test of construction (fabricated part)**

Components (mg)

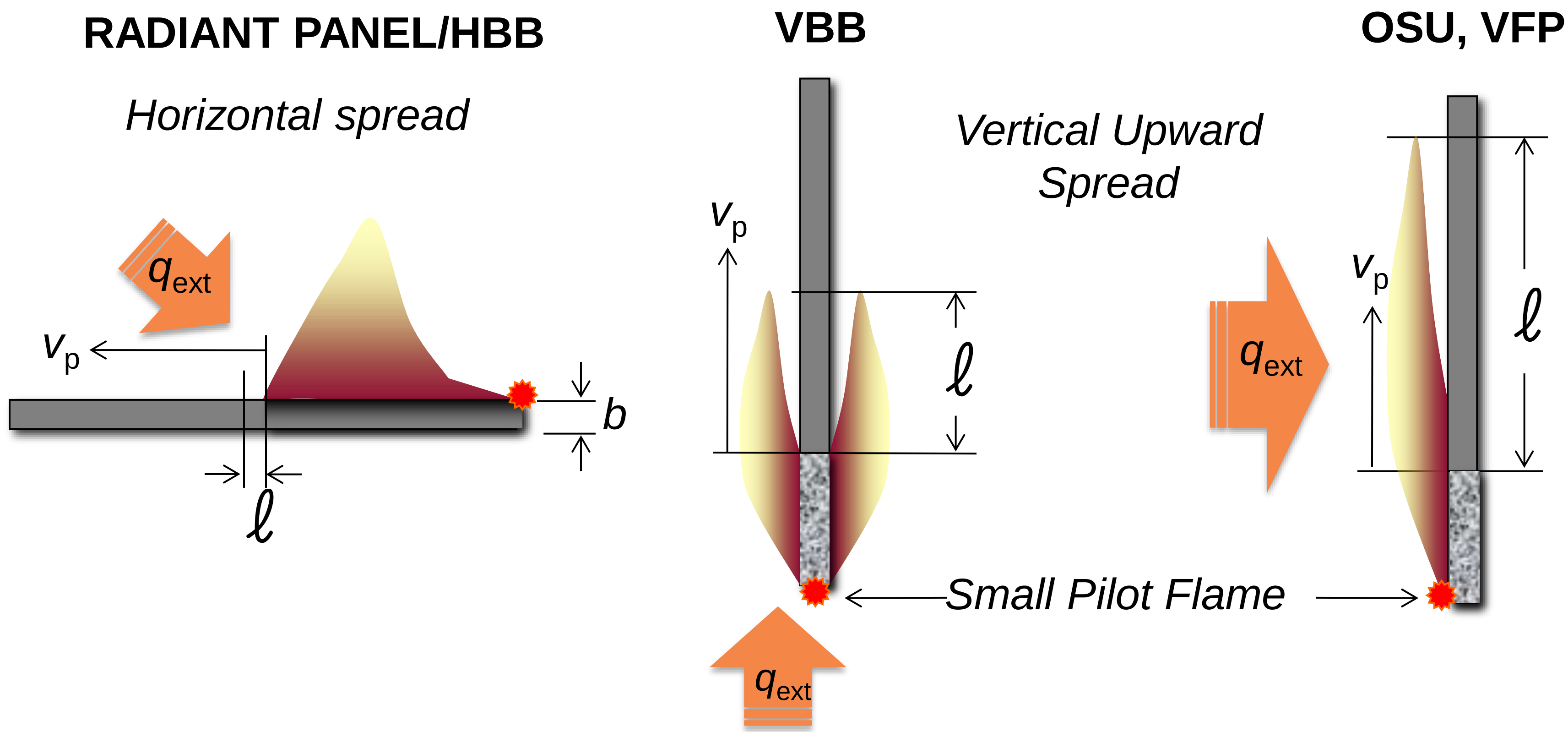
Coupons (g)
(self supporting components)

Constructions (kg)



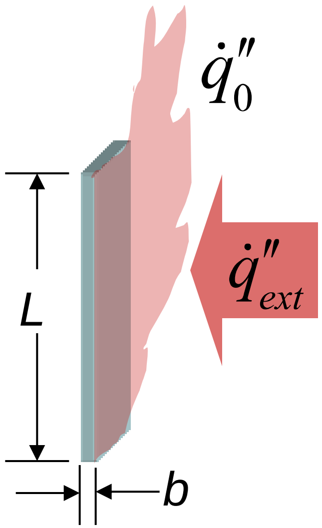
FAA Fire Tests Measure Flame Spread

✔ Thin Sample ✔ Piloted Ignition ✔ Radiant Heating



Flame Spread Velocity, $v_p = \frac{\text{Heated Length}}{\text{Time to Ignition}} = \frac{\ell}{t_{ign}} \propto \frac{HRR}{\Delta T_{ign}}$

Flame Spread And Fire Size



Fire Size (W) = $\dot{Q} = \dot{q}''A = \dot{q}''_0 L^2$ ($\dot{q}''_0$= peak HRR, W/m^2)

Flame Spread Theory and Empirical Correlations Give Fire Growth Rate, $$\frac{d\dot{Q}}{dt} = \frac{\dot{Q}}{\tau} \qquad (1)$$

Solution of (1) for $\dot{Q}(0) = \dot{Q}_0$ ⇨ $$\dot{Q}(t) = \dot{Q}_0 \exp\left[\frac{t}{\tau}\right] \qquad (2)$$

$$\tau = \frac{\rho c b (T_{ign} - T_0)}{2\dot{q}''_{in}}$$

Characteristic time for fire growth (s)

$$\beta = \frac{dT}{dt} = \frac{(T_{ign} - T_0)}{\tau} = \frac{2\dot{q}''_{in}}{\rho c b}$$

Heating rate in fire (K/s)

At early stages of fire when $t << \tau$, Equation 2 becomes

$$\dot{Q}(t) = \dot{Q}_0\left(1 + \frac{t}{\tau}\right) = \dot{Q}_0 + \frac{Q}{\tau} = \dot{Q}_0 + \beta\frac{Q}{(T_{ign} - T_0)} \qquad (3)$$

Normalizing for mass (m) and fire environment (β)

$$\underbrace{\frac{\dot{Q}}{m\beta}} = \frac{\dot{Q}_0 / m}{\beta} + \frac{Q / m}{(T_{ign} - T_0)} = \underbrace{\eta_c + \frac{Q_\infty}{\Delta T_{ign}}} \qquad (4)$$

Fire Response Parameter (FRP)

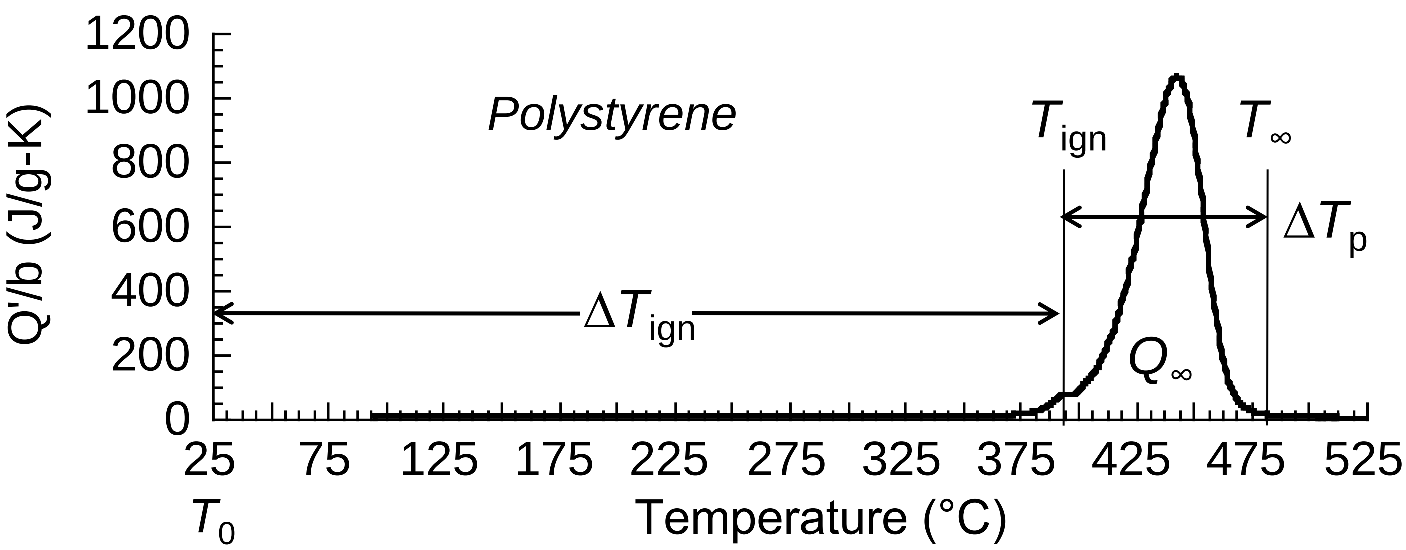
Measured in MCC (HRC + IGC)

MCC Combined Properties

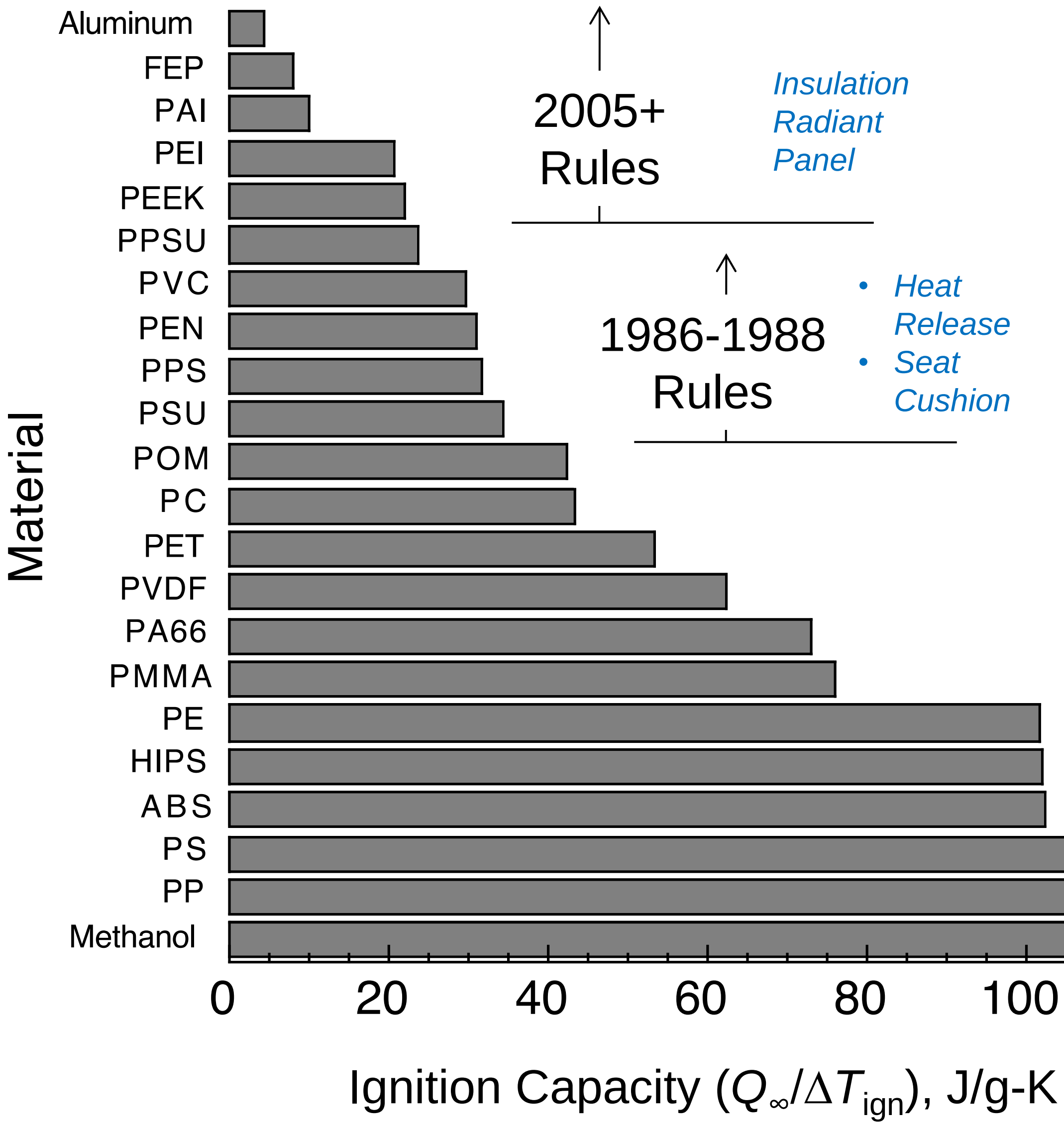
(*Flammability Parameters*)

Ignition Capacity (IGC) $= \dfrac{\text{Heat Released}}{\text{Heat to Ignite}} = \dfrac{Q_\infty}{c_p(T_{ign}-T_0)} \propto \dfrac{Q_\infty}{\Delta T_{ign}}$

Heat Release Capacity (HRC) $= \dfrac{\text{Heat Released}}{\text{Heat of Pyrolysis}} = \dfrac{Q_\infty}{c_p(T_{ign}-T_\infty)} \propto \dfrac{Q_\infty}{\Delta T_p}$



Ignition Capacity Scales with Post-Crash Fire Performance of Cabin Materials



737-500
Denver (2008)

767
Chicago (2016)

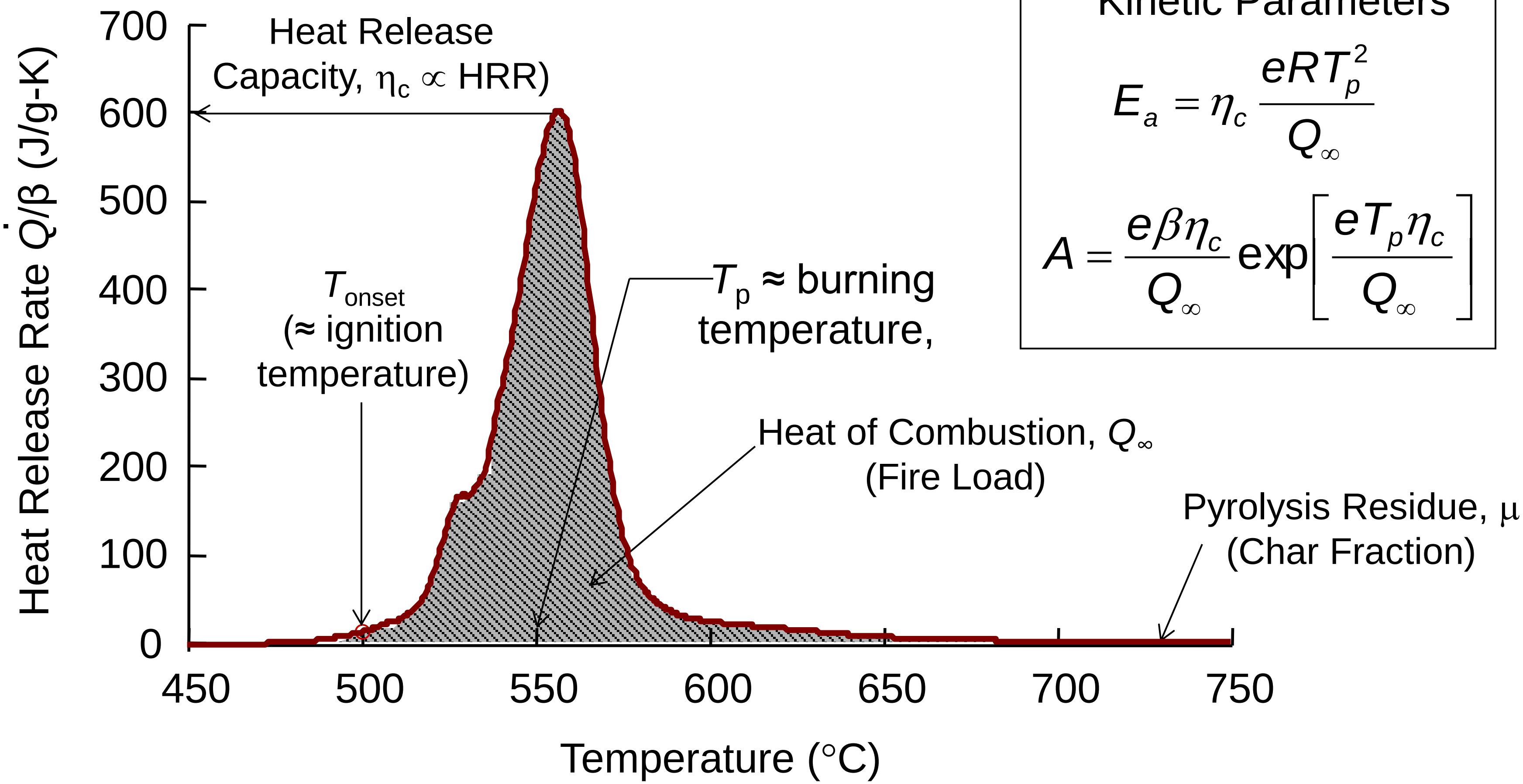
737-300
Manchester (1985)

March 2018 FTWG Presentation:
https://www.fire.tc.faa.gov/pdf/materials/March18Meeting/Slaton-0318-MCC.pdf

Regulatory Approach

1) Parameterize MCC data to obtain relevant micro-scale fire properties of materials for comparison.
2) Develop simple, reliable method to compute flammability parameters from MCC data
3) Compare materials in MCC and in FAA fire test to demonstrate acceptable “small change” method.
4) Define guidance document.

MCC Individual Fire Properties



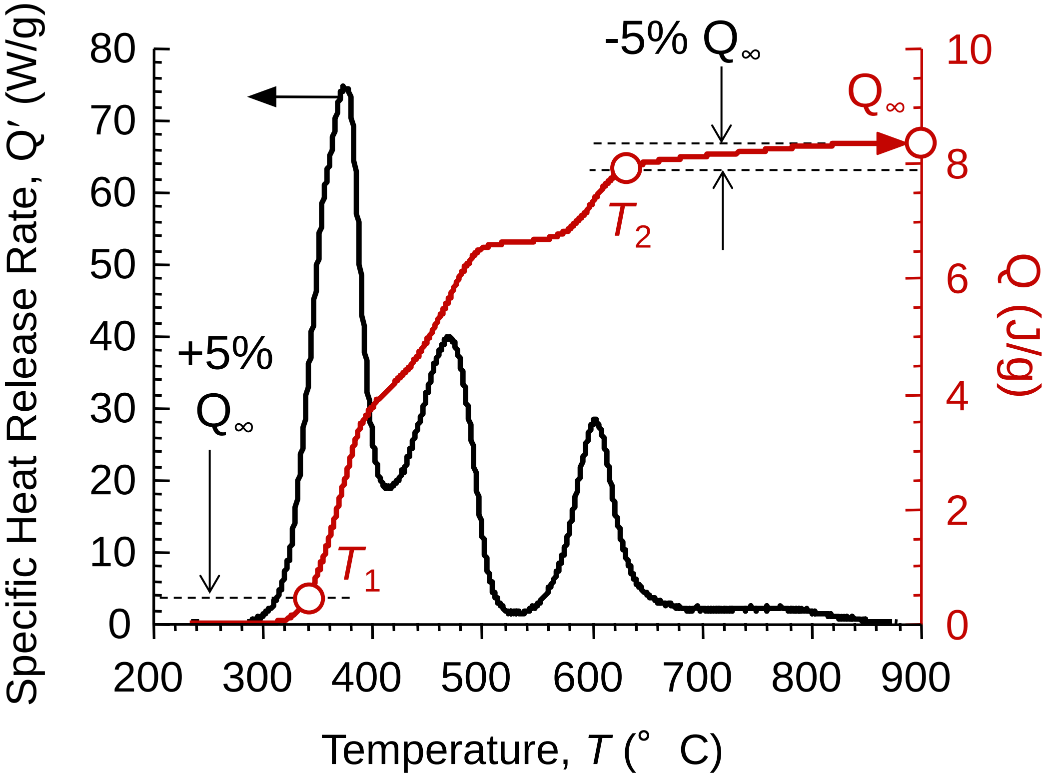
Decomposition Kinetic Parameters

$$E_a = \eta_c \frac{eRT_p^2}{Q_\infty}$$

$$A = \frac{e\beta\eta_c}{Q_\infty} \exp\left[\frac{eT_p\eta_c}{Q_\infty}\right]$$

β = Heating Rate (K/s)

MCC PROCEDURE



T_0 = *Standard Temperature = 25° C*
T_1 ≈ *Ignition temperature*
T_∞ = *900° C (typically)*

1. Measure specific heat release rate Q′ versus temperature *T* as per ASTM D7309
2. Integrate Q′/β versus *T* to obtain Q versus *T*, i.e., Q(*T*).
3. Obtain total heat release $Q(T_\infty) = Q_\infty$(J/g)
4. Obtain T_1 at 5% deflection from Q(T) baseline, i.e., at $0.05Q_\infty$
5. Obtain T_2 at $0.95Q_\infty$.
6. Calculate 2 Flammability Parameters
   - HRC (J/g-K) = $h_c/(T_2-T_1)$
   - IGC (J/g-K) = $h_c/(T_1-T_0)$

HRC + IGC = *FRP*

Summary

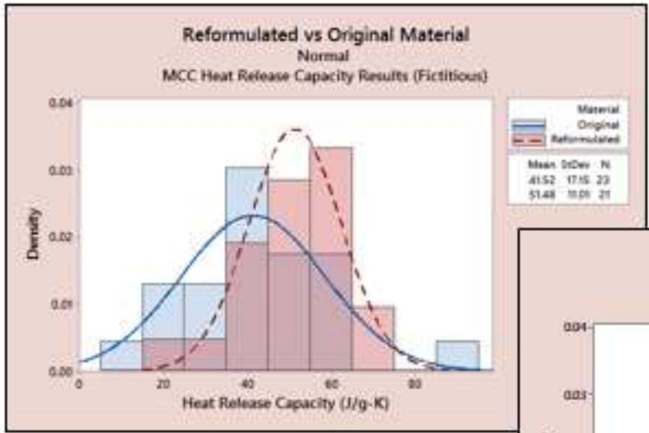
- FAA-Industry Fire Test Working Group is developing a regulatory process for certifying small changes in material formulations by comparing fire properties:
  - Milligram scale (MCC)
  - Kilogram scale (FAA coupon tests)
- Statistical criteria for comparing materials
- So far, materials that are **Similar** in the MCC are **Similar** in FAA coupon tests for statistically valid samples.
- Materials that are **Different** in the MCC can be **Similar** or **Different** in the FAA test depending on physical behavior, sample configuration, etc.

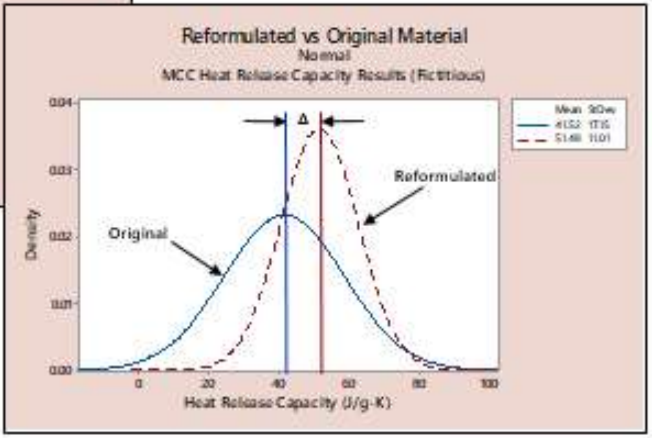
➢ **MCC Task Group using case studies to validate methodology.**

Statistical Analysis Methodology

Material Change Similarity

- **Proposed Statistical Methodology--EXAMPLE**
  - Example: *Fictitious* Heat Release Capacity (HRC) results from "original" and "reformulated" material
  - Intended to demonstrate statistical procedure only….not intended to be representative of any true material HRC





- Δ = (41.52 – 51.48) = -9.9545 J/g-K
- Pooled std dev (s_p) = 14.5512 J/g-K
- t-statistic = -2.27
- p-value = 0.014
- Significance level = 0.050
- -> Reject hypothesis that "reformulated" = "original"

Original Data

Heat Release Capacity (J/g-K)	
Original Material	Reformulated Material
42	24
43	43
55	58
26	71
62	43
37	49
33	61
41	44
19	67
54	49
20	53
85	56
46	59
10	52
17	62
60	54
53	57
42	33
37	46
42	43
55	57
28	
48	

https://www.fire.tc.faa.gov/pdf/materials/March18Meeting/Slaton-0318-MCC.pdf

Invitation to Submit

Indexed in: WEB OF SCIENCE

Impact Factor 3.364

Flammability of Polymers
—Special issue in *Polymers* (MDPI)

Special Issue Information:

Guest Editor: Dr. Richard E. Lyon

Deadline: 1 December 2018

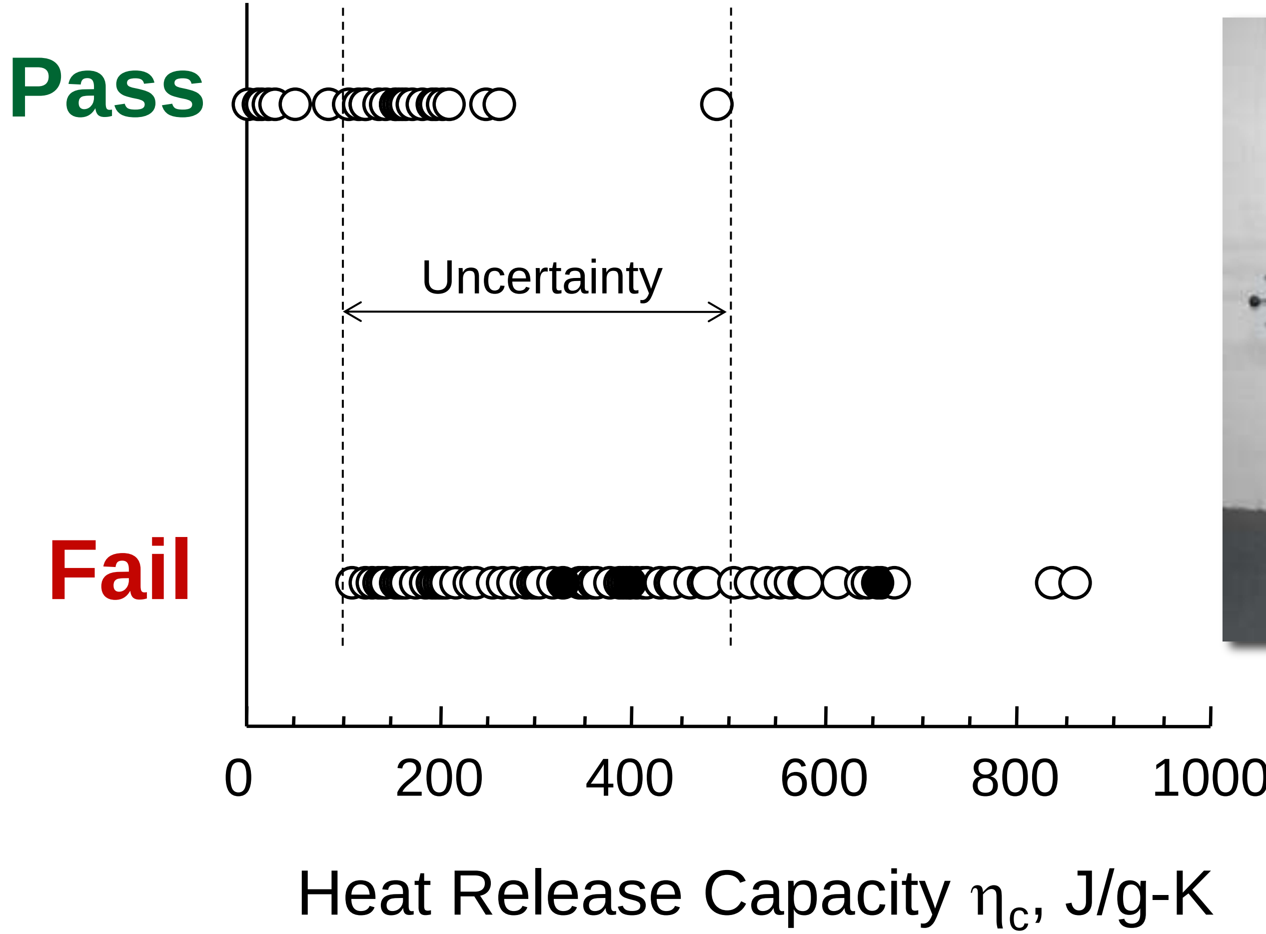
Keywords: polymer, flammability, fire test, thermal analysis, synthesis

polymers

an open access journal by MDPI

Additional Slides from the full BCC presentation by Dr. Richard Lyon

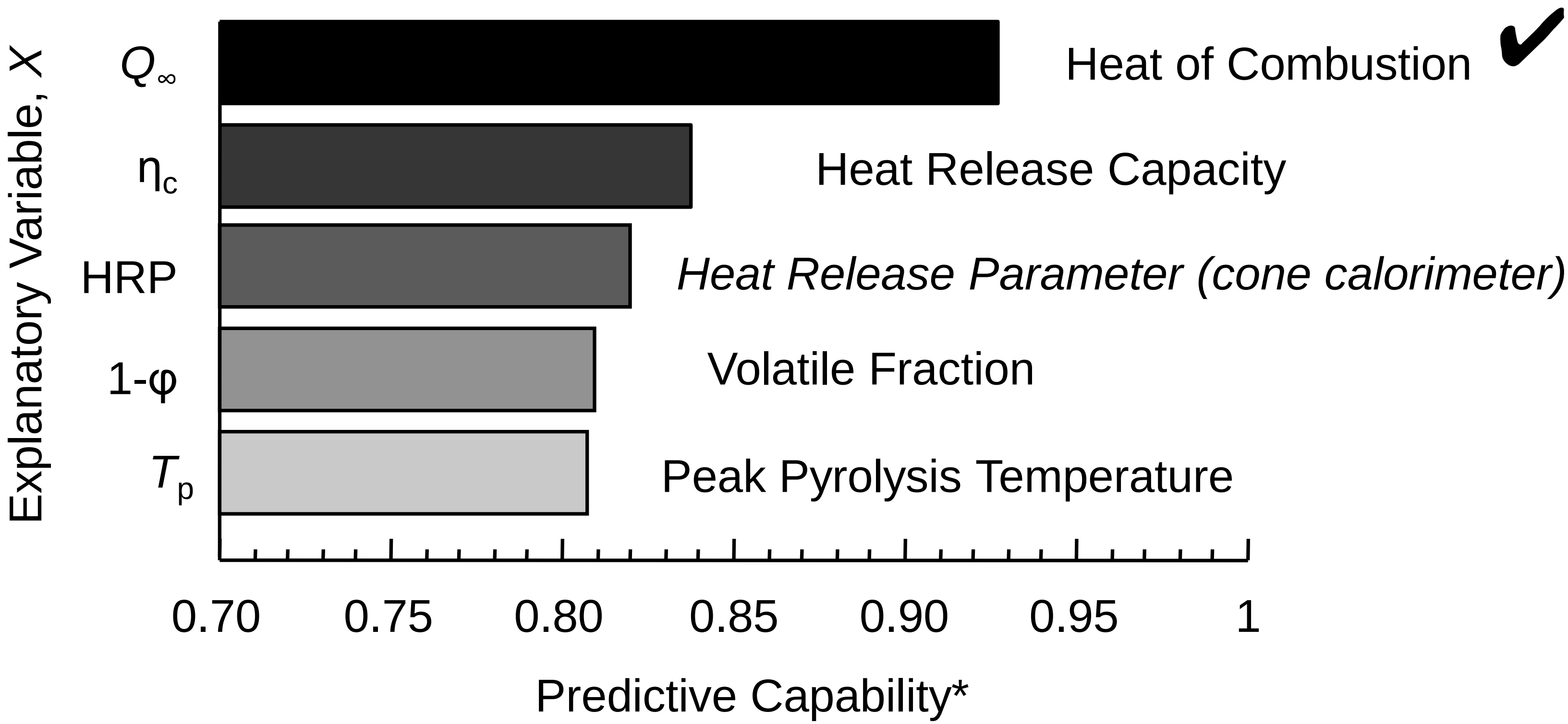
Large Uncertainty Using Single MCC Property to Predict Pass/Fail Results (Peak HRR) in OSU



Predictive Capability of Individual MCC Fire Properties on Pass / Fail Test Results

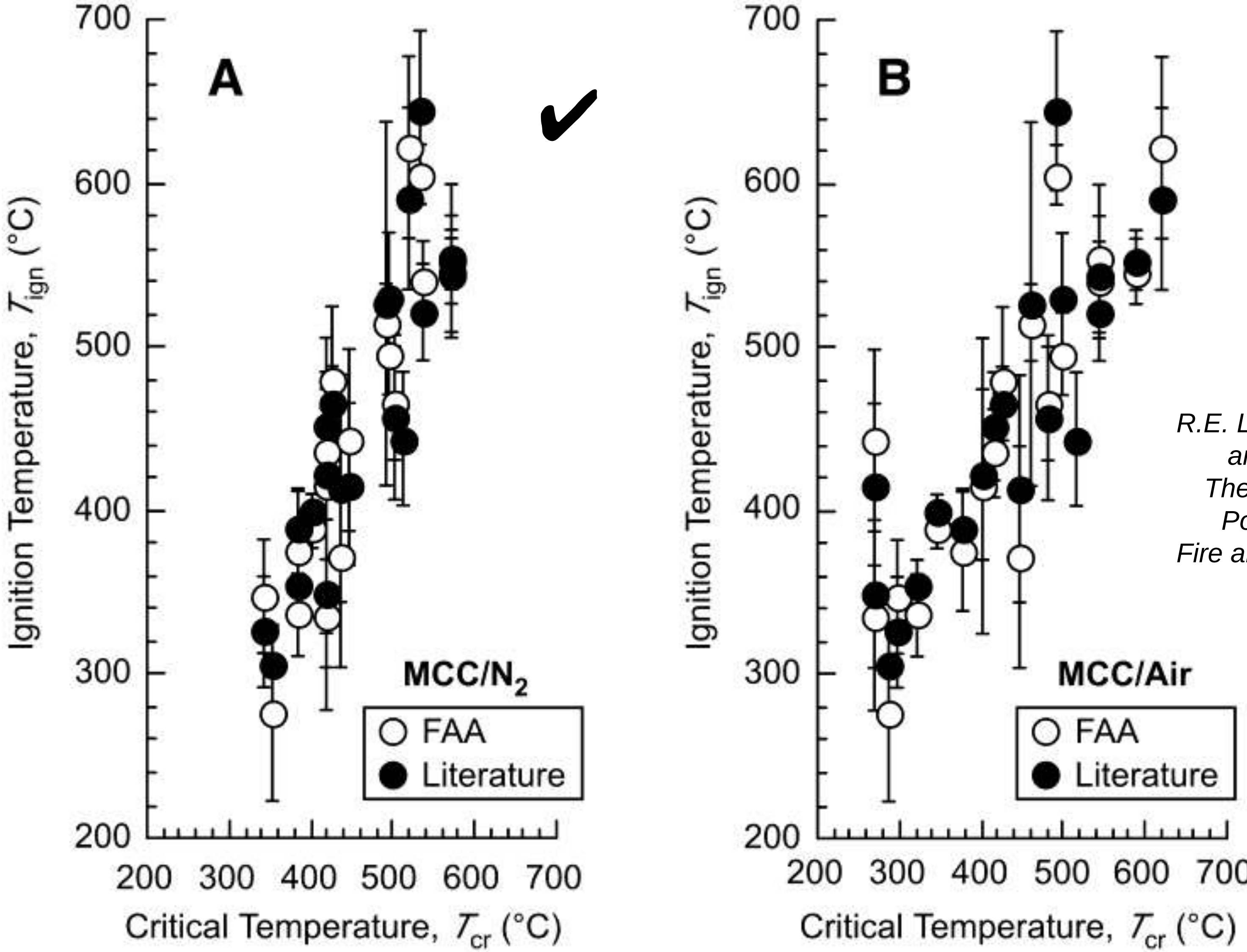
R.E. Lyon, N. Safronava, J.G. Quintiere, S.I. Stoliarov, R.N. Walters and S. Crowley, Material Properties and Fire Test Results *Fire and Materials*, 38, 264-278 (2014).

- UL 94 V-0
- FAA Heat Release of Aircraft Cabin Materials
- FAA Vertical Bunsen Burner Test (12s /60s)



**Predictive Capability = Predicted/Observed Frequency of Passing Test at Particular X*

MCC Critical Temperature (T_{onset}) is Good Predictor of Ignition Temperature (T_{ign})

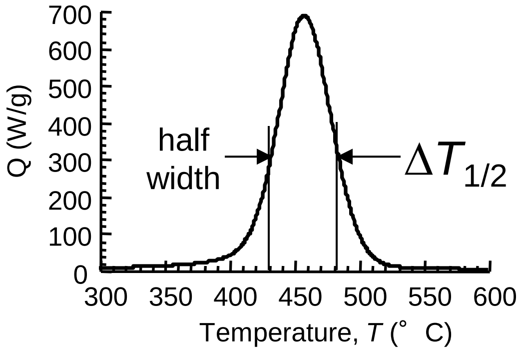


R.E. Lyon, N. Safronava and S. Crowley, Thermal Analysis of Polymer Ignition, Fire and Materials, 2018

Heat Release Capacity For Multi-Component Aircraft Materials

$$\eta_c = \frac{\dot{Q}_{\max}}{\beta} = \frac{Q_\infty}{\Delta T_{1/2}}$$

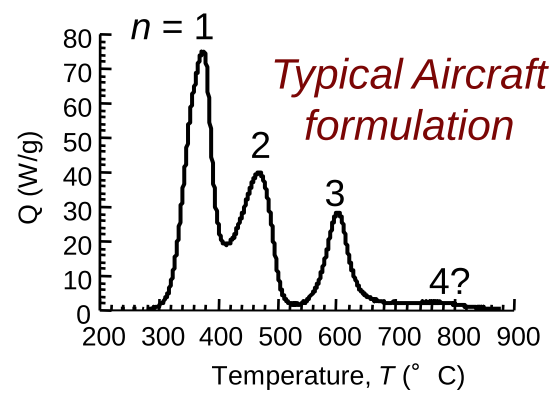
Single component (peak)
ASTM D 7309



$$\eta_c = \frac{1}{\beta}\sum_{i=1}^{n} \dot{Q}_{\max,i} = \sum_{i=1}^{n} \frac{Q_{\infty,i}}{\Delta T_{p,i}}$$

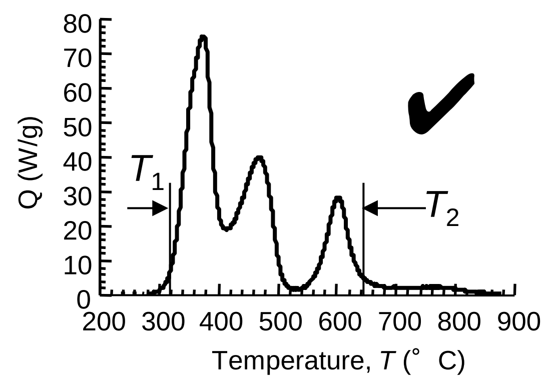
Multiple (n) peaks
DOT/FAA/TC-12/53, R1 (2013)

(*Requires peak deconvolution*)

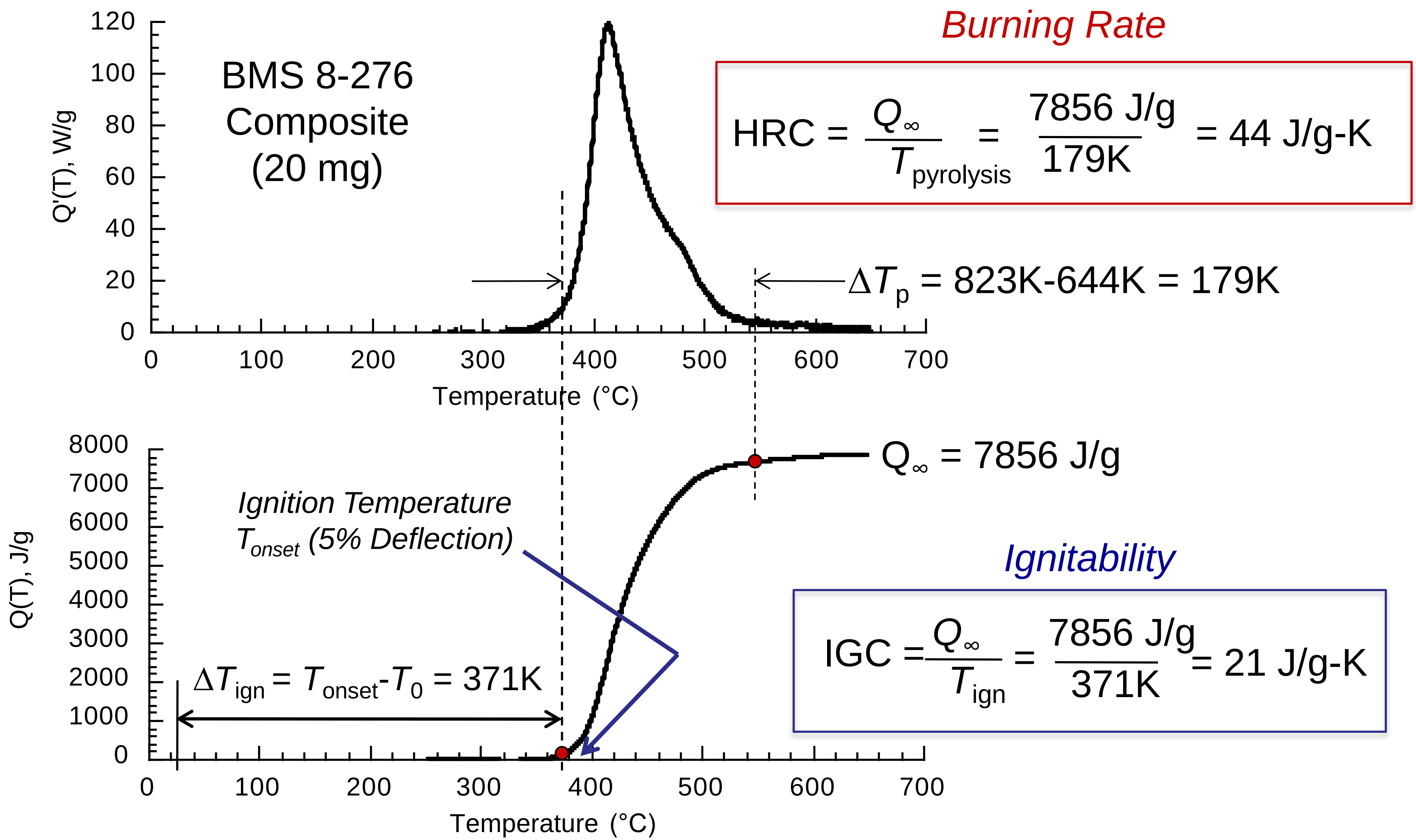


$$\langle h_c \rangle = HRC = \frac{Q_{\yen}}{(T_2 - T_1)}$$

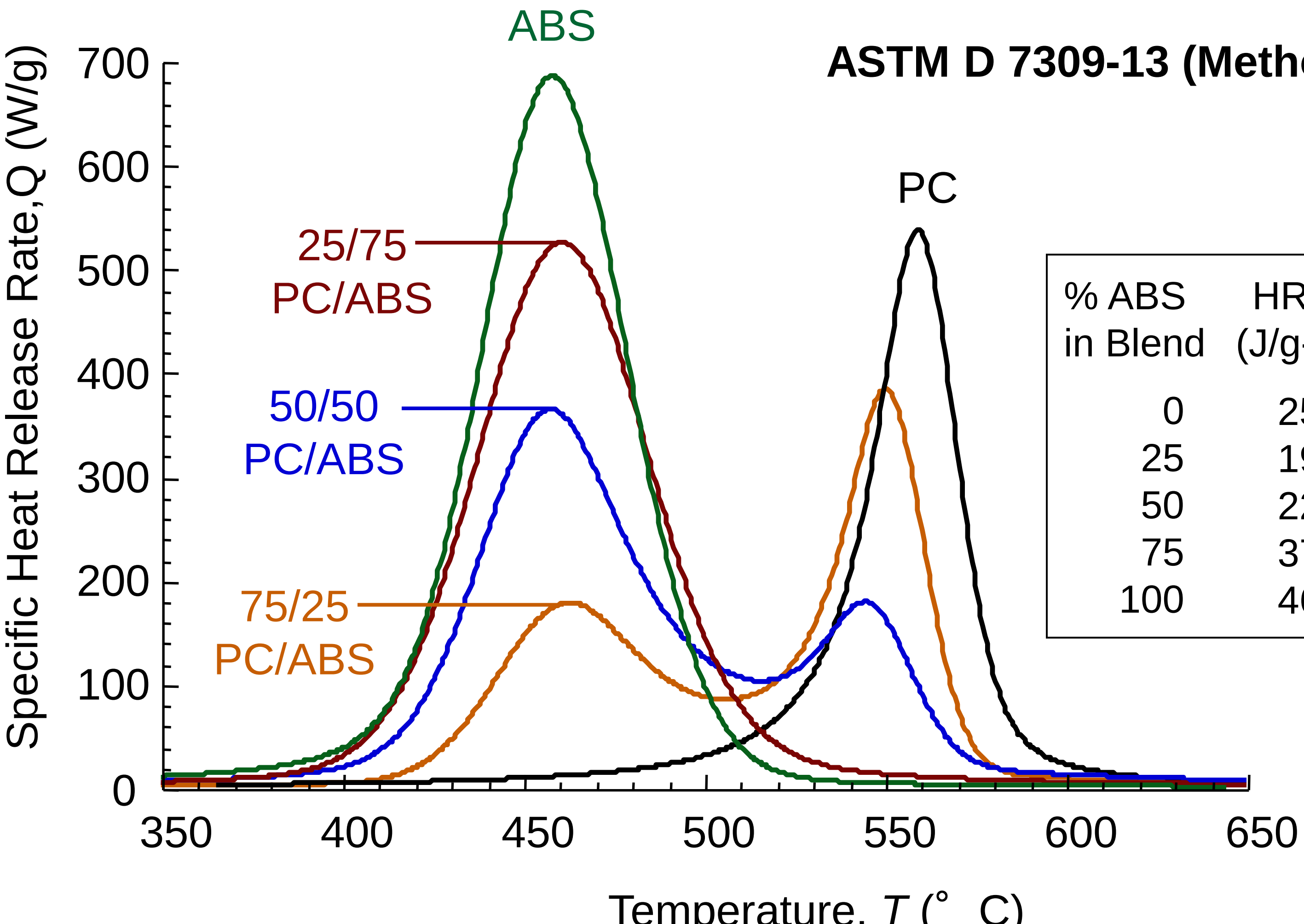
- Multiple peaks OK
- Simple integral method
- $T_1 \approx$ Ignition temperature



MCC Parameters for Burning Rate (HRC) and Ignitability (IGC)

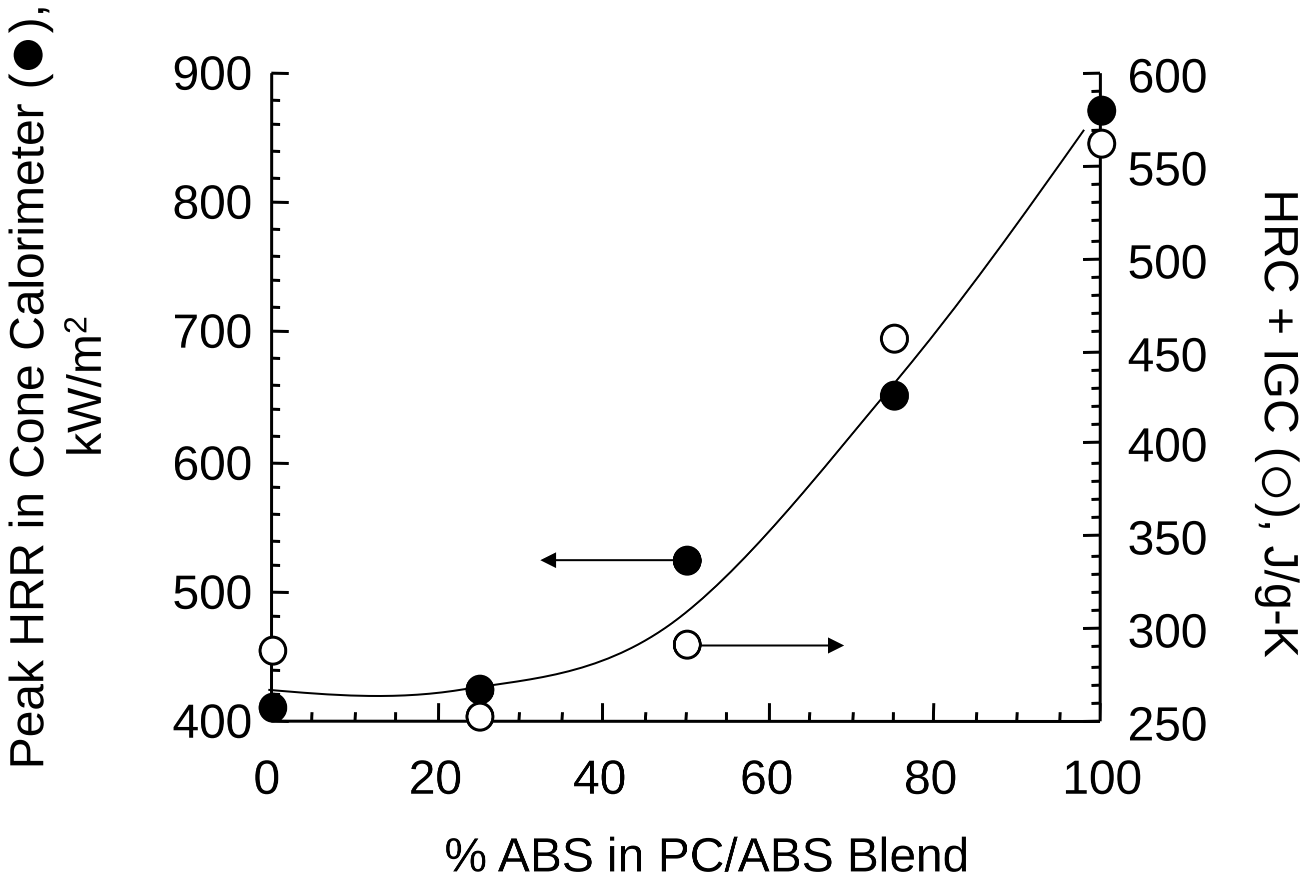


MCC and Cone Calorimeter Data for PC/ABS Blends: *2-component series*



% ABS in Blend	HRC (J/g-K)	IGC (J/g-K)
0	250	39
25	195	58
50	220	73
75	374	84
100	469	93

(HRC + IGC) from MCC* Correlates Peak HRR** of PC/ABS Blends



**MCC @ 1 K/s, 3-mg samples*

***Cone calorimeter @ 50 kW/m², 3-mm samples*

Criterion for No Significant Change in Flammability (MCC or FAR)

Fire Response Parameter of Sample A $(X+Y)_A$

$$X_A + Y_A = (X+Y)_A \pm \sigma_A$$

Fire Response Parameter of Sample B $(X+Y)_B$

$$X_B + Y_B = (X+Y)_B \pm \sigma_B$$

*Are the materials *__Significantly__ Different w/rt flammability?*

$$(X+Y)_A - (X+Y)_B = \Delta(X+Y)_{A,B} \pm \sigma_{A,B}$$

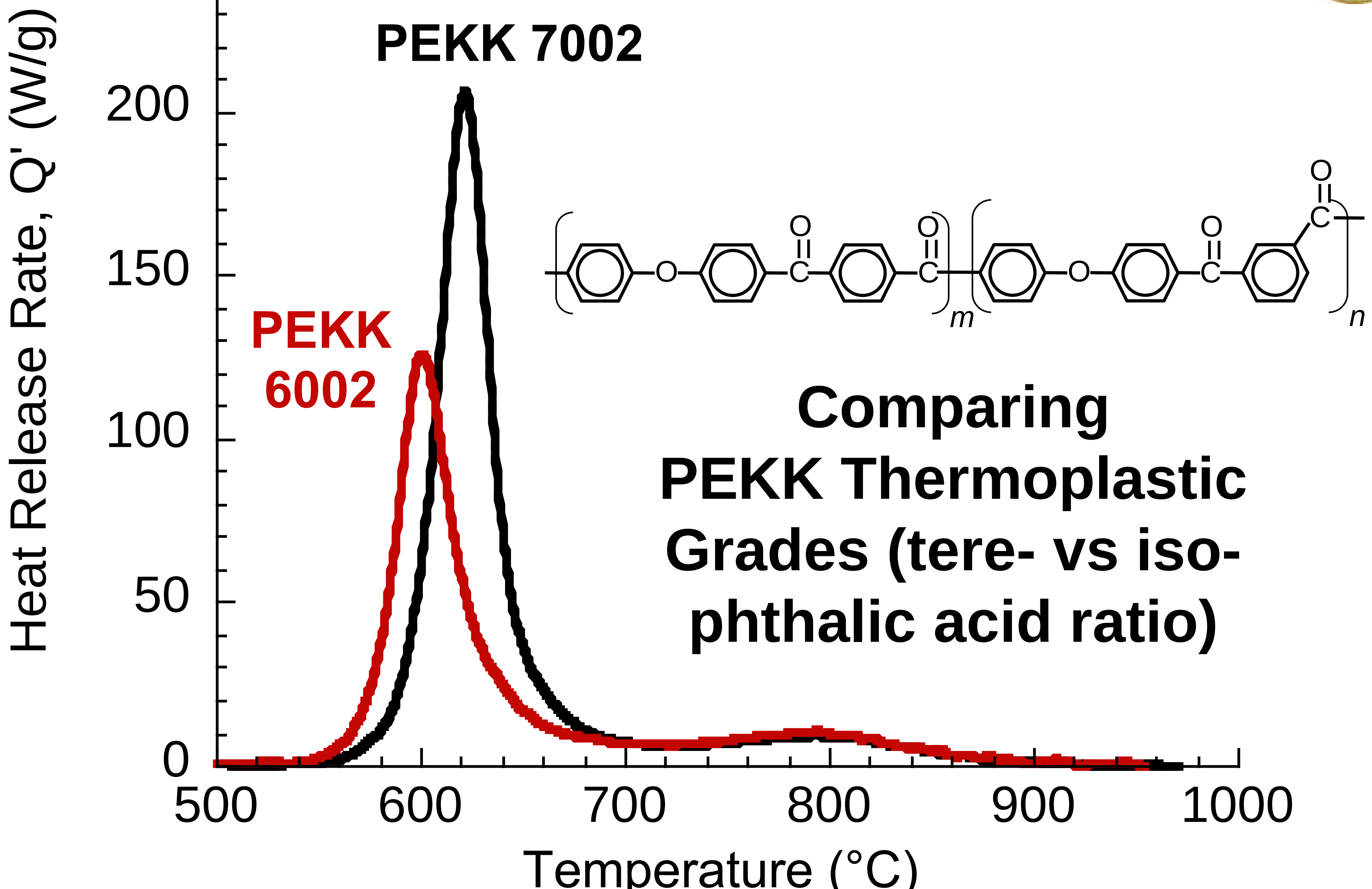
Is this difference… <u>significantly</u> different from zero?

Uncertainty of Differences

$$\sigma_{A,B} = (\sigma_A^2 + \sigma_B^2)^{1/2}$$

*TBD

Example of Method



Comparing PEKK Thermoplastic Grades (tere- vs iso-phthalic acid ratio)

PEKK **6002**	PHRR (5-min)	THR (2-min)	PHRR +THR
1	72	6	78
2	81	17	98
3	78	32	110
4	102	9	110
5	78	0	78
1.5 mm/50g Average:			95 ± 16

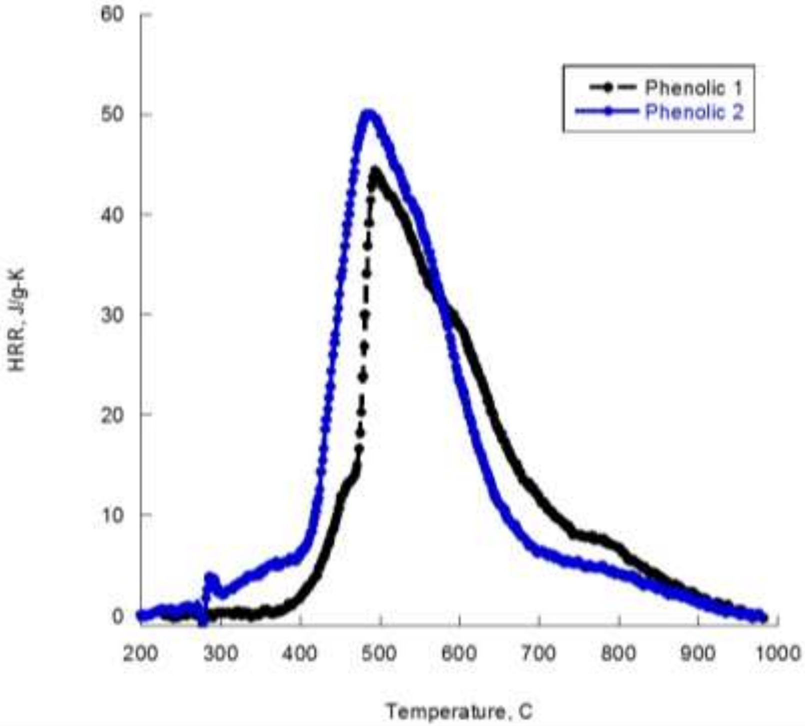
PEKK **7002**	PHRR (5-min)	THR (2-min)	PHRR +THR
1	84	4	88
2	79	5	84
3	71	8	79
4	61	5	66
5	68	0	68
1.5 mm/50g Average:			77 ± 10

$\Delta(\text{PHRR+THR}) = (95-77) \pm (16^2+10^2)^{1/2} = 18 \pm 18$ **Different** (from zero)

PEKK **6002**	IGC (J/g-K)	HRC (J/g-K)	IGC + HRC
1	14	31	45
2	13	28	41
3	14	30	44
5 mg Average:			43 ± 2

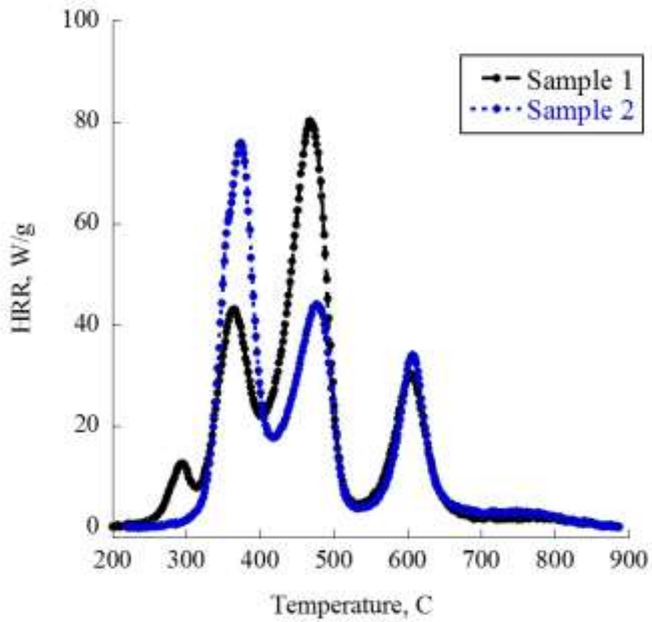
PEKK **7002**	IGC (J/g-K)	HRC (J/g-K)	IGC + HRC
1	16	45	61
2	16	42	58
3	16	41	57
5 mg Average:			59 ± 2

$\Delta(\text{IGC+HRC}) = (59-43) \pm (2^2 + 2^2)^{1/2} = 16 \pm 3$ **Different** (from zero)



Comparing Neat Phenolic Resins

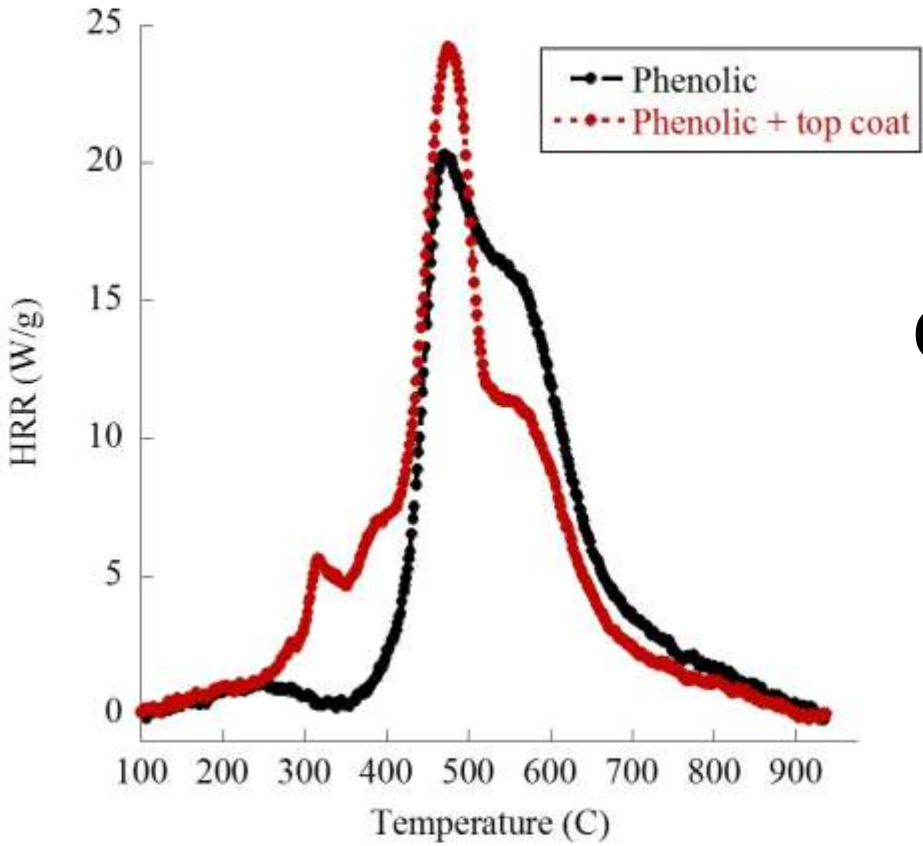
Phenolic	HRC (J/g-K)	IGC (J/g-K)	HRC + IGC	MCC result	OSU PHRR (kW/m^2)	OSU 2-min HR (kW-min/m^2)	PHR+ THR	FAR Result
1	24 ±1	20±1	44±1	Similar	14±9	8±5	22±10	Similar
2	25±1	24±1	49±1		13±1	15±3	28±3	



Comparing Thermoplastic Films

Film	HRC	IGC	HRC+IGC	MCC result	FAR Result *
1	31 ± 1	38 ± 3	69 ± 3	Different	Different
2	29 ± 2	28 ± 2	57 ± 3		

- FAR 25.856 Thermal/Acoustic Insulation Flame Propagation Test Method
- Failure probably due to configuration of the blankets

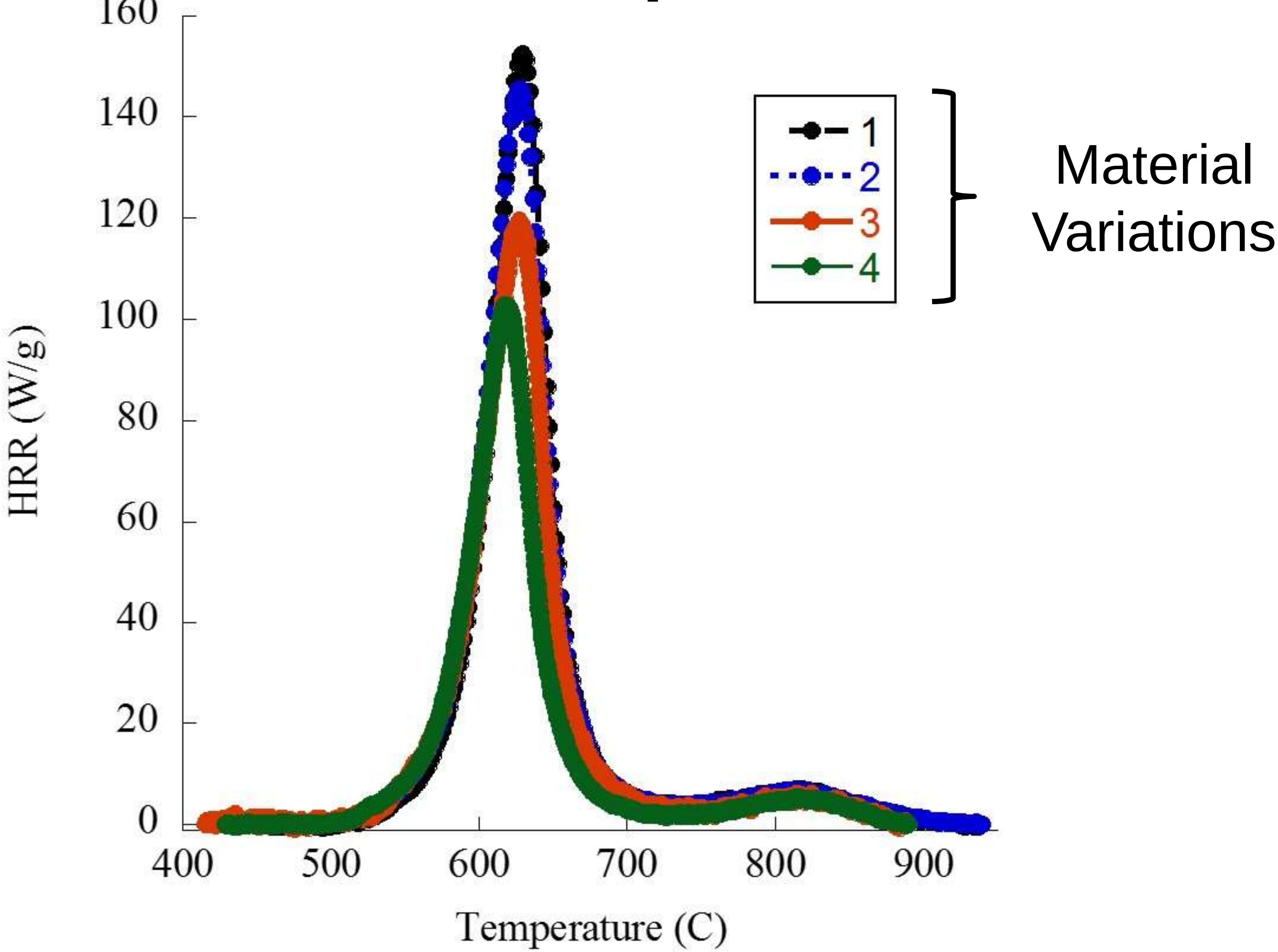


Comparing Phenolic Fiberglass Lamina
(w/ and w/o Topcoat)

Sample	HRC	IGC	HRC+ IGC	MCC result	Peak HRR	2 min HR	OSU result
Lamina	11 ± 1	12 ± 3	23 ± 3	Similar	68 ± 6	44 ± 6	Different*
Lamina + top coat	10 ± 1	16 ± 2	26 ± 2		72 ± 3	60 ± 6	

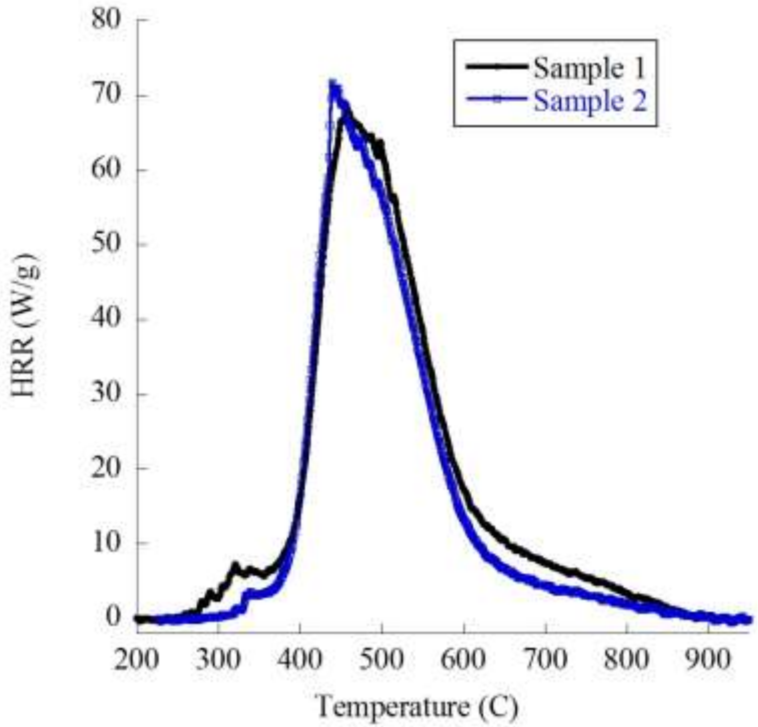
*insufficient sample size, n < 5

Polyphenylsulfone (PPSU) Thermoplastic



PPSU Pair-wise Comparison of 4 Samples

Sample	HRC	IGC	HRC+ IGC	MCC result	PHRR	HR 2-min	OSU result
1 **2**	42 ± 2 40 ± 1	17 ± 1 17 ± 0	59 ± 2 57 ± 1	**Similar**	34 ± 3 43 ± 14	4 ± 2 4 ± 1	**Similar**
1 **3**	42 ± 2 36 ± 1	17 ± 1 14 ± 1	59 ± 2 50 ± 1	**Different**	34 ± 3 40 ± 6	4 ± 2 9 ± 5	**Different**
1 **4**	42 ± 2 32 ± 4	17 ± 1 12 ± 1	59 ± 2 44 ± 4	**Different**	34 ± 3 48 ± 9	4 ± 2 6 ± 3	**Different**
2 **3**	40 ± 1 36 ± 1	17 ± 0 14 ± 1	57 ± 1 50 ± 1	**Different**	43 ± 14 40 ± 6	4 ± 1 9 ± 5	**Similar**
2 **4**	40 ± 1 32 ± 4	17 ± 0 12 ± 1	57 ± 1 44 ± 4	**Different**	43 ± 14 48 ± 9	4 ± 1 6 ± 3	**Similar**
3 **4**	36 ± 1 32 ± 4	14 ± 1 12 ± 1	50 ± 1 44 ± 4	**Different**	40 ± 6 48± 9	9 ± 5 6 ± 3	**Similar**

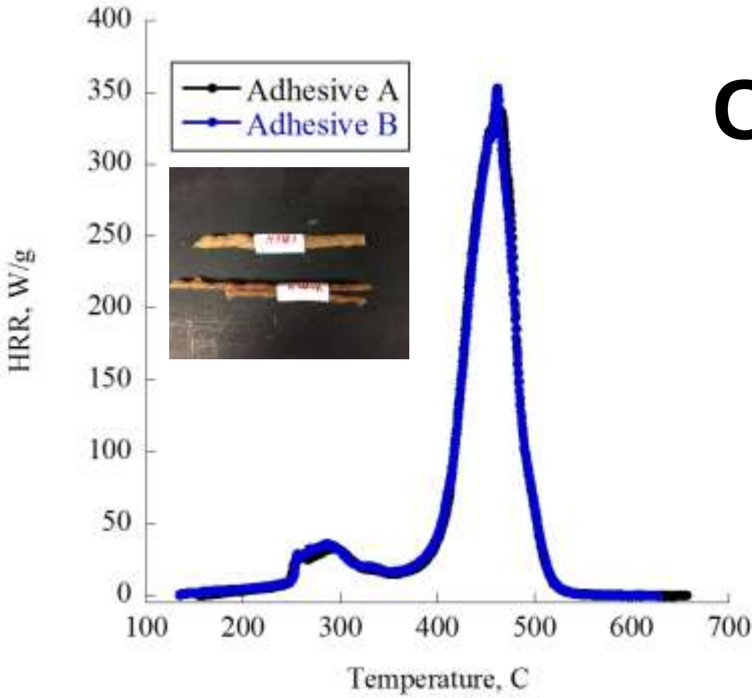


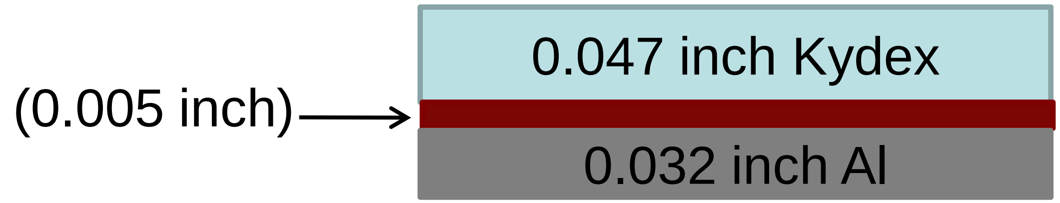
Comparing Phenolic Resins
(fiberglass lamina)

Sample	HRC	IGC	HRC+ IGC	MCC result	Peak HRR	2 min HR	OSU result
1	33 ± 2	36 ± 5	69 ± 5	Similar	20 ± 6	12 ± 3	Similar
2	40 ± 4	26 ± 2	66 ± 5		17 ± 7	12 ± 4	

Comparing Adhesives

(formulation change)





OSU Specimen

Adhesive	HRC	IGC	HRC+ IGC	MCC result	Peak HRR	2 min HR	OSU result
A	113 ± 1	98 ± 6	211 ± 6	**Similar**	52 ± 2	64 ± 4	**Different***
B	109 ± 1	101 ± 4	210 ± 4		54 ± 2	72 ± 3	

*invalid comparison-*combustible substrate*