Department of Fire Protection Engineering

History of the Milligram-scale Flame Calorimeter

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Timeline

- 2011 Development begins
- 2013 Proof of concept
- 2015 Sensitivity to Brominated and Phosphorus-based FRs
- 2016 Radiative fraction of solid fuel flames
- 2018 Screening methodology developed
- 2020 Emulation of Cone Calorimetry

Polymers + **Flame Retardants**

Motivation

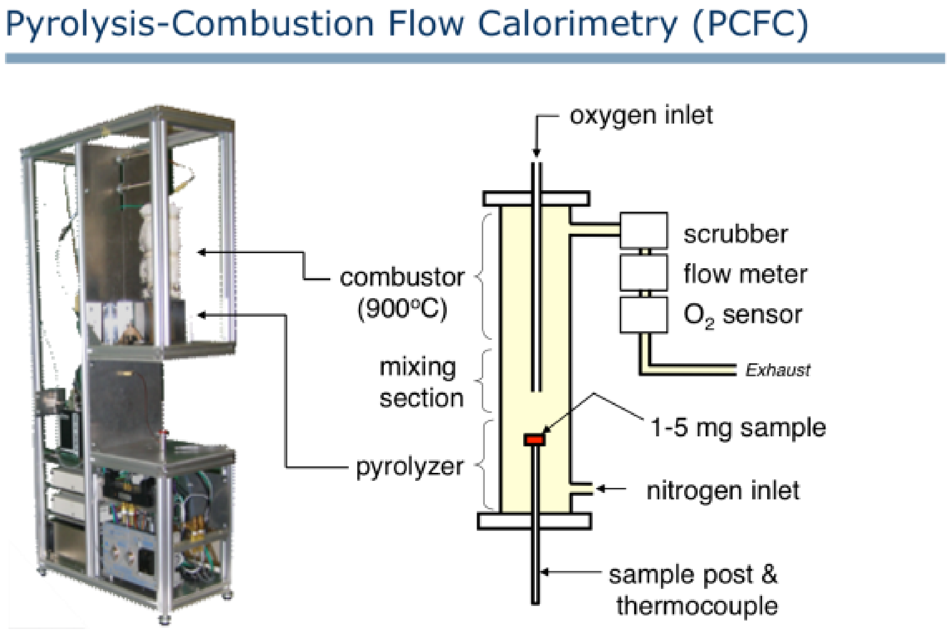
- Brominated flame retardants are highly effective at reducing polymer flammability.
- Environmental concerns (bioaccumulation).
- Desire for alternatives, but costly testing due to multiple factors.

Objective: Design a novel test method that can capture flame retardant activity in a cost-effective manner.

Cone Calorimetry

- Developed at NIST by Babrauskas and colleagues.
- Conical heater, constant incident heat flux.
- Coupled pyrolysis/combustion.
- Transitional/turbulent diffusion flame.
- Sample mass on the order of 10s of grams.
- O_2 consumption calorimetry based HRR, THR.

PCFC (MCC)



- Developed at the FAA.
- Uncoupled pyrolysis/combustion, linear heating rate.
- Laminar premixed reactor, complete combustion by design.
- Not very sensitive to flame retardants at on-design operation.
- mg-sized samples (1-5 mg).
- O_2 consumption calorimetry based HRR, THR.

Milligram-scale Flame Calorimeter

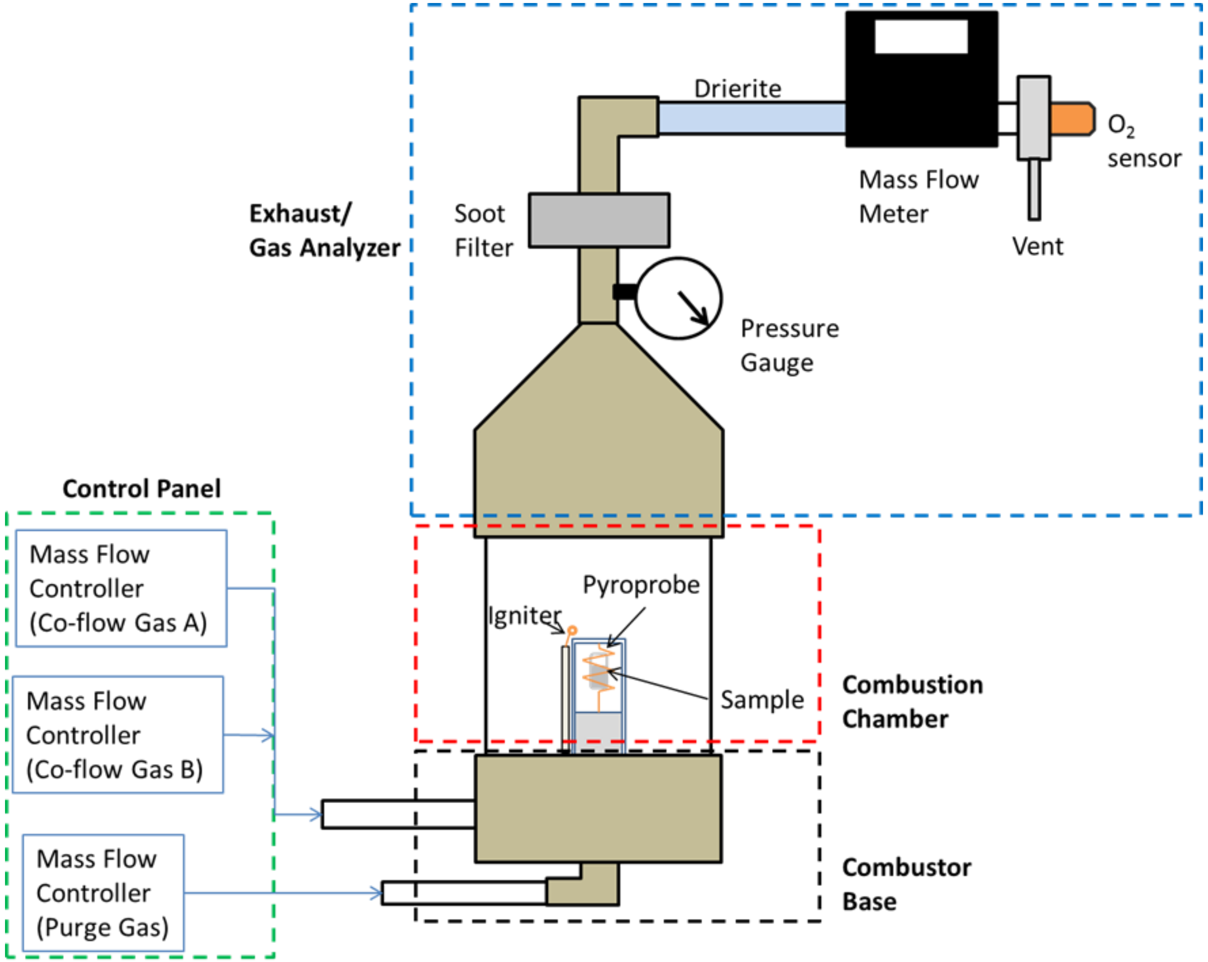
- Uncoupled pyrolysis/combustion, linear heating rate.
- Flaming combustion (laminar, axisymmetric, diffusion flame).
- Milligram-sized samples (25-35 mg).
- O_2 consumption calorimetry based HRR, THR.
- Solid product and solid residue yields (gravimetric measurements).

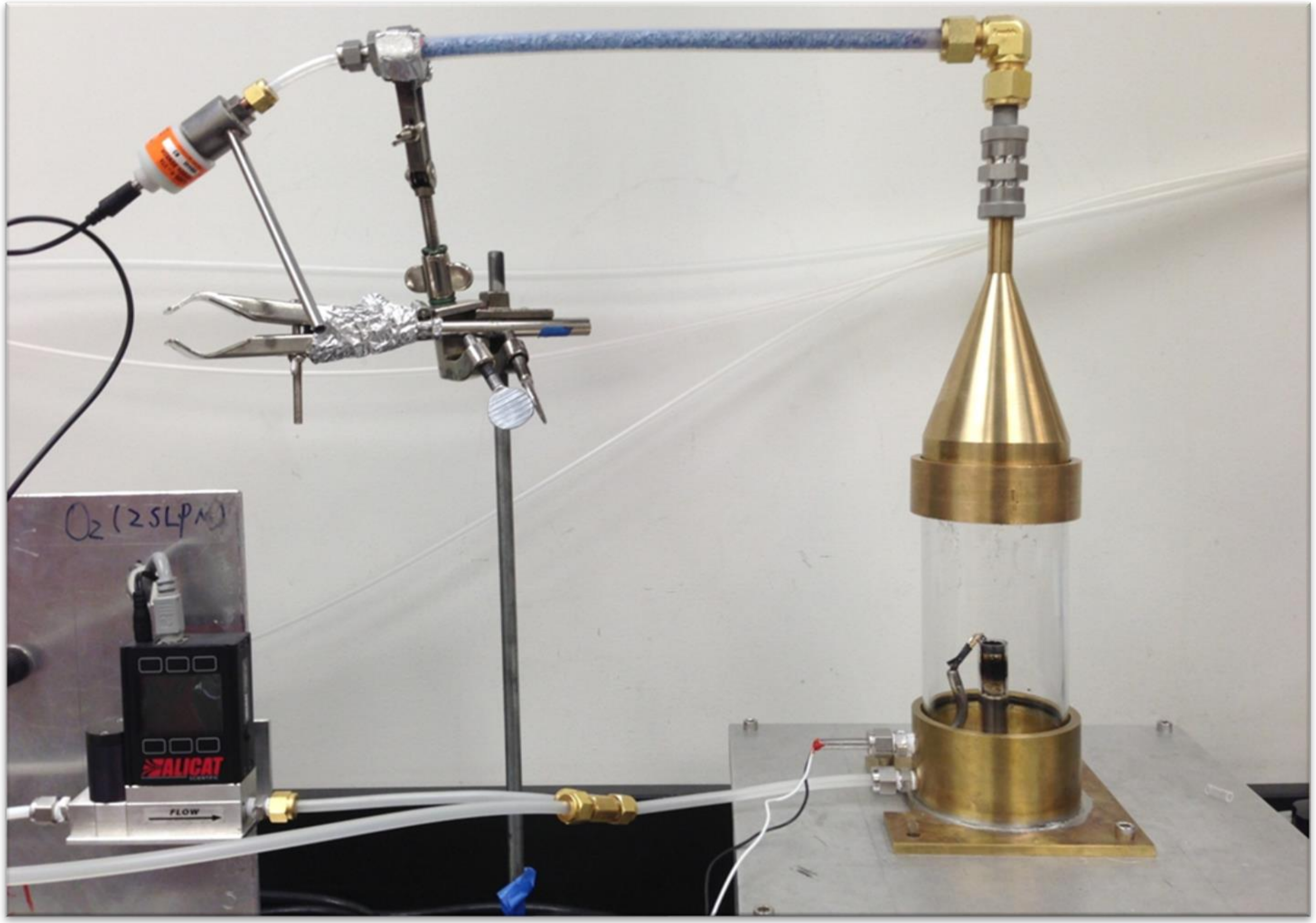
Initial Development

- Design and build apparatus.
- Parametric investigation (flowrates, O_2 concentration, heating rates, etc.).
- Test brominated flame retardant + polymer matrix and benchmark against PCFC and Cone.
- Test phosphorus-based flame retardant + polymer matrix and benchmark against PCFC and Cone.

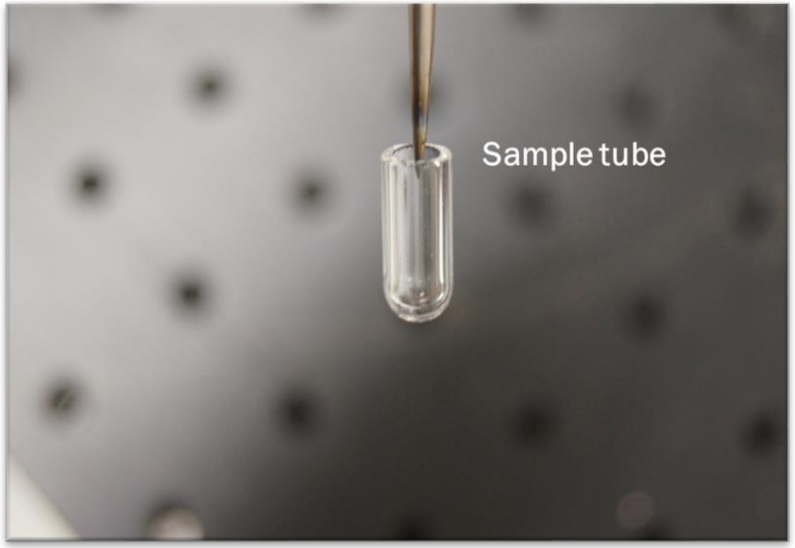
Graduate student: Xi Ding
Sponsor: BASF-FAA

Initial Design

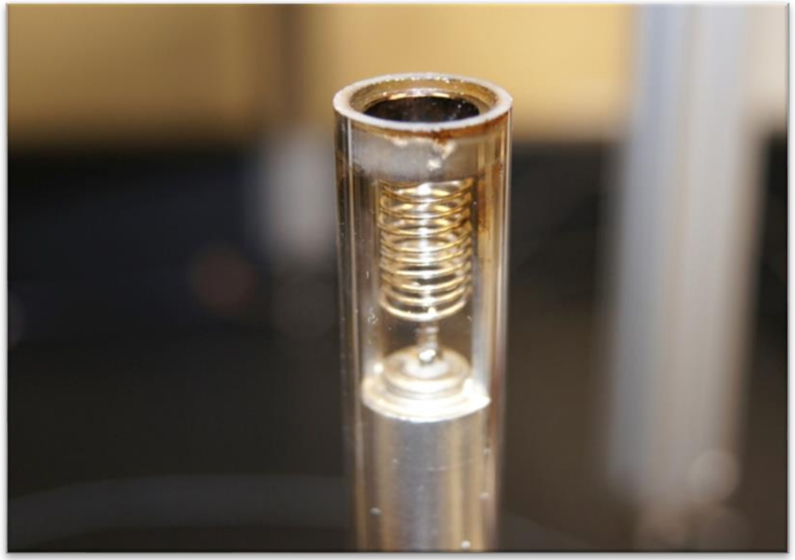




O2 (25LPM)
ALICAT
FLOW



Sample tube

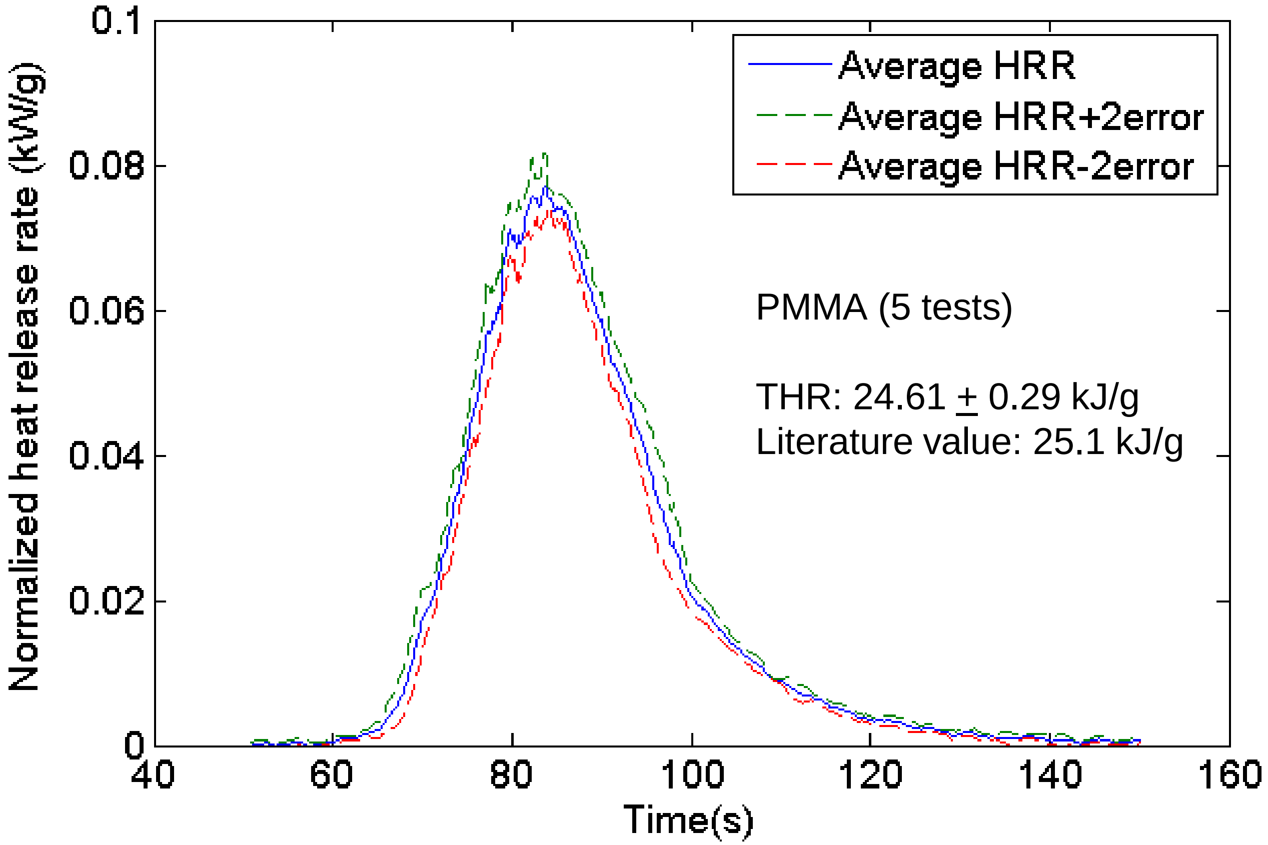


Parameterization & Optimization

- Co-flow and purge gas flow rates
- O_2 concentration
- Pyroprobe location, coil height, tube length
- Igniter size and power
- Heating rate

Operating Parameter	Range	Optimum Value
Co-flow (SLPM)	0.5 – 6	4
O_2 in co-flow (vol.%)	5 – 40	21
Purge gas (SCCM)	5 – 100	100
Heating rate (°C/s)	2 – 32	10

Repeatability



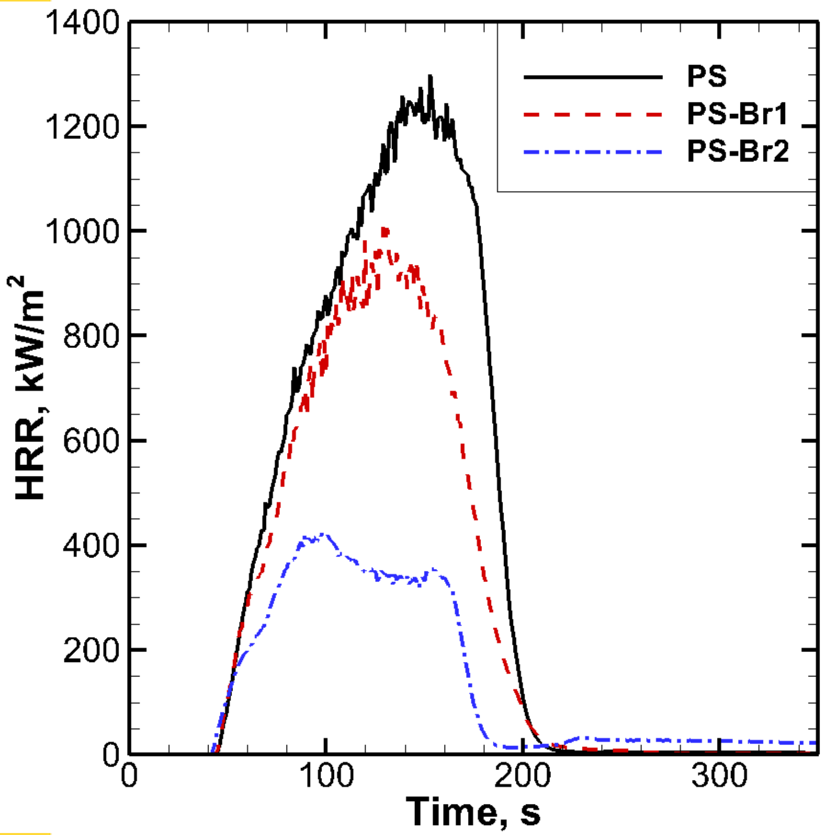
PBT (pure)

Initial benchmarking: sensitivity to gas-phase FRs (bromine and phosphorus based)

- PS +PSBr (Bromine)
- PBT + DEPAL (Phosphorus)
- Measurements: HRR, HOC, GPCE

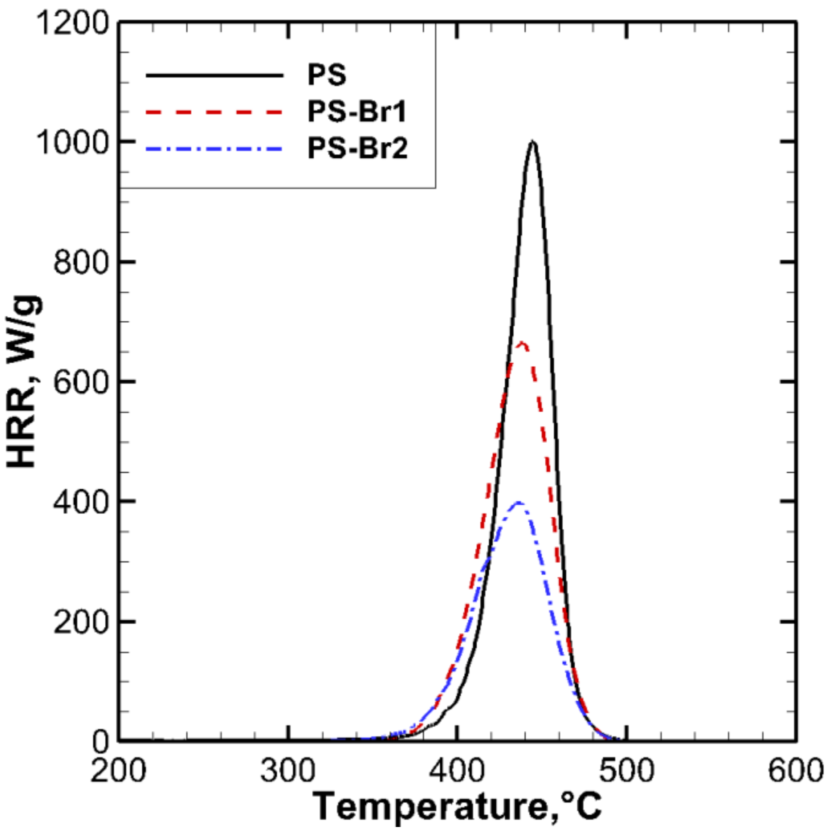
Material Name	Composition (by mass)	Cone Tests	MCC Tests	MFC Tests
PS	100 % PS	4	3	5
PS-Br1	90 % PS, 10 % PS_{Br}	4	3	5
PS-Br2	60 % PS, 40 % PS_{Br}	4	3	5

Material Name	Composition (by mass)	Cone Tests	MCC Tests	MFC Tests
PBT	75 % PBT, 25 % Glass,	4	3	5
PBT-P1	63 % PBT, 25 % Glass, 12 % DEPAL	4	3	5
PBT-P2	55 % PBT, 25 % Glass 20 % DEPAL	4	3	7



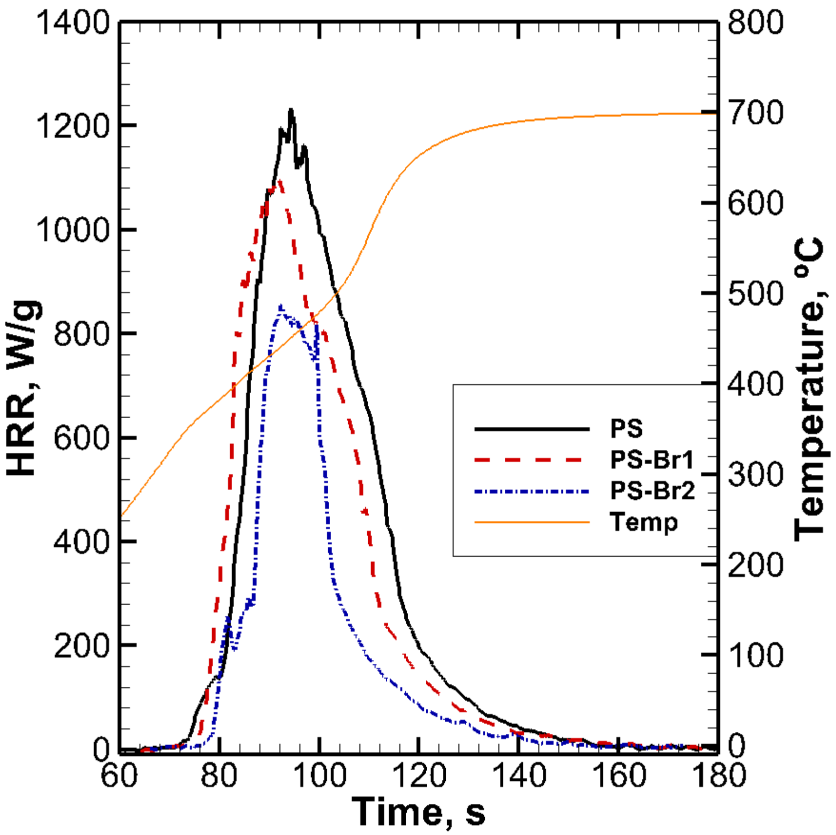
PS
PS-Br1
PS-Br2
HRR, kW/m2
Time, s
1400
1200
1000
800
600
400
200
0
0
100
200
300

Cone



PS
PS-Br1
PS-Br2
HRR, W/g
Temperature,°C
1200
1000
800
600
400
200
0
200
300
400
500
600

MCC

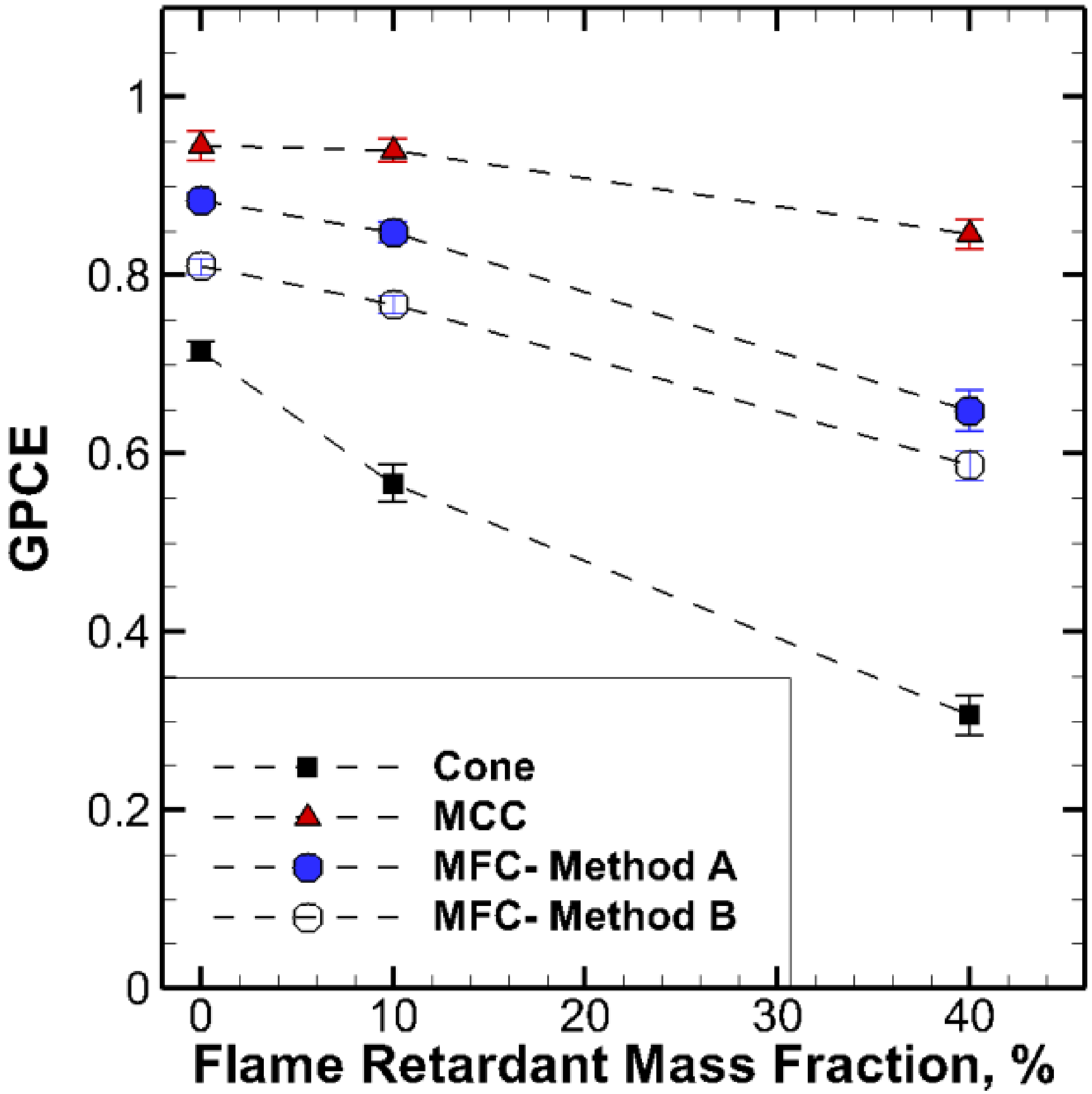


PS
PS-Br1
PS-Br2
Temp
HRR, W/g
Temperature, °C
Time, s
1400
1200
1000
800
600
400
200
0
800
700
600
500
400
300
200
100
0
60
80
100
120
140
160
180

MFC

PS + PSBr

- Gas phase combustion efficiency
- Ratio of measured total energy release to theoretical energy release of volatilized fuel (calculated using O_2 calorimetry principles)



Conclusions

- Successfully designed and built a novel apparatus for measuring flammability parameters in an axisymmetric, laminar diffusion flame using mg-sized samples
- MFC shown to be sensitive to gas-phase flame retardants (Bromine and Phosphorus based)
- MFC captures trends seen in Cone Calorimeter
- Gained insight into behavior of PSBr and DEPAL as flame retardants

Raffan-Montoya, F., Ding, Xi, Stoliarov, Stanislav I., Kraemer, Roland H., Measurement of heat release in laminar diffusion flames fueled by controlled pyrolysis of milligram-sized solid samples: Impact of bromine- and phosphorus-based flame retardants, Combustion and Flame, Volume 162, Issue 12, 2015, Pages 4660-4670.

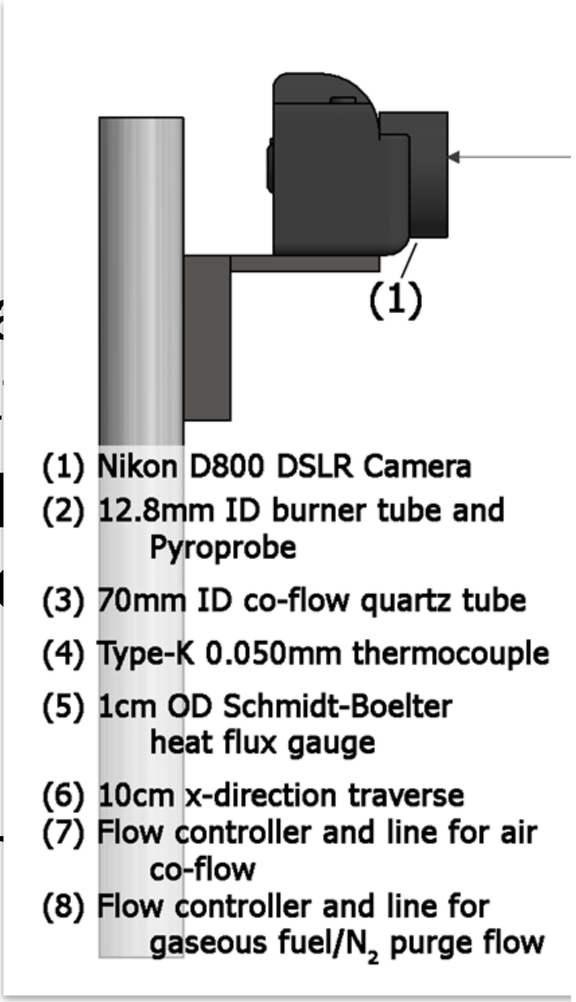
Evolution

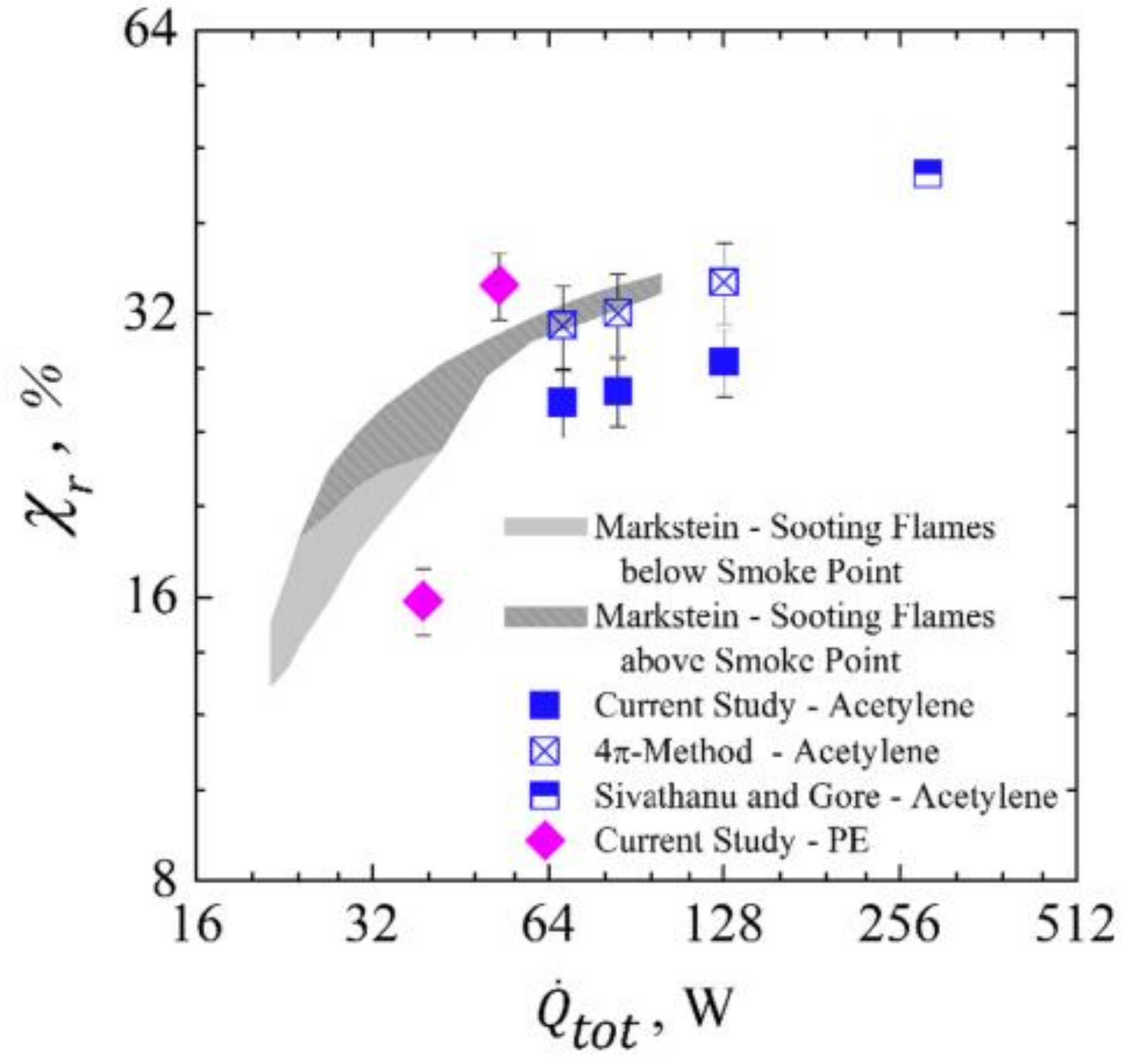
- Added CO and CO_2 sensors for improved detection of gas phase activity and characterization of actual exhaust composition (corrected outflow flowrate)
- Improved control panel
- Redesigned combustor base
- Explored radiative fraction of solid fuels and sensitivity to synergistic activity of additives

Graduate student: Catherine Hamel
Sponsor: FAA

Radiative fraction

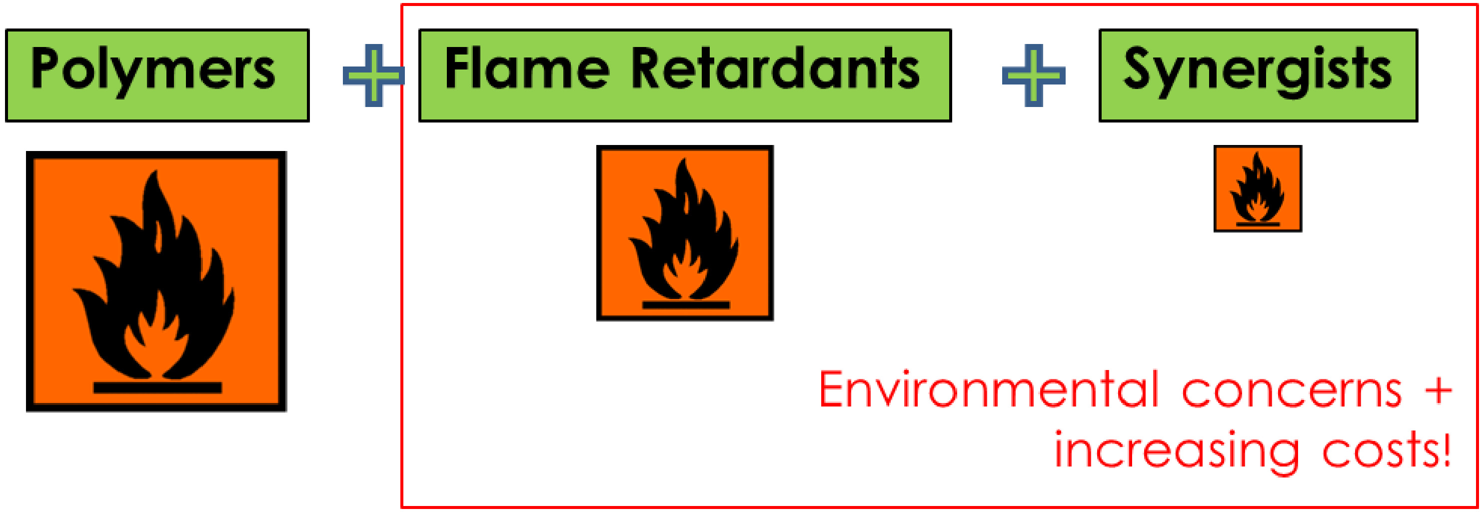
- MFC pyrolizer a used to genera
- Camera + singl flame sheet and sheet.
- Combined with heat release, th estimated.





Hamel, C., Raffan-Montoya, F., Stoliarov, S.I., *"A Method for Measurement of Spatially Resolved Radiation Intensity and Radiative Fraction of Laminar Flames of Gaseous and Solid Fuels,"* Experimental Thermal and Fluid Science 104, June 2019.

Screening of flame retardants + synergists



- Design and implement a methodology for screening flame retardant + synergist combinations using MFC
- Compare results between formulations mixed in-situ to industrially processed formulations

Sponsor: ICL-IP

Approach

PBT + FR-1025 (3 loading levels)

ATO (3 loading levels)
9 formulations
1 compounded formulation

Al-HYPO (3 loading levels)
9 formulations
1 compounded formulation

MPP+SOL-DP (3 loading levels each)
17 formulations
(Redundant binary interactions removed)

Hand mix formulations
- No compounding
- 4g per composition

Weigh samples

Test in duplicates (20 min/test)

Analyze results

Analysis

$$F(x,y) = a + bx + cy + dxy + ex^2 + fy^2$$

Primary Indicators (HOC, Mean HRR, Temp to Ignition)

Secondary Indicators (Residue and Particulate Yields, CO/CO2)

Model as a function of FR and synergist mass fractions

- Analyze trends
- Predict behavior
- Reveal interactions

HOC vs. Secondary Indicators

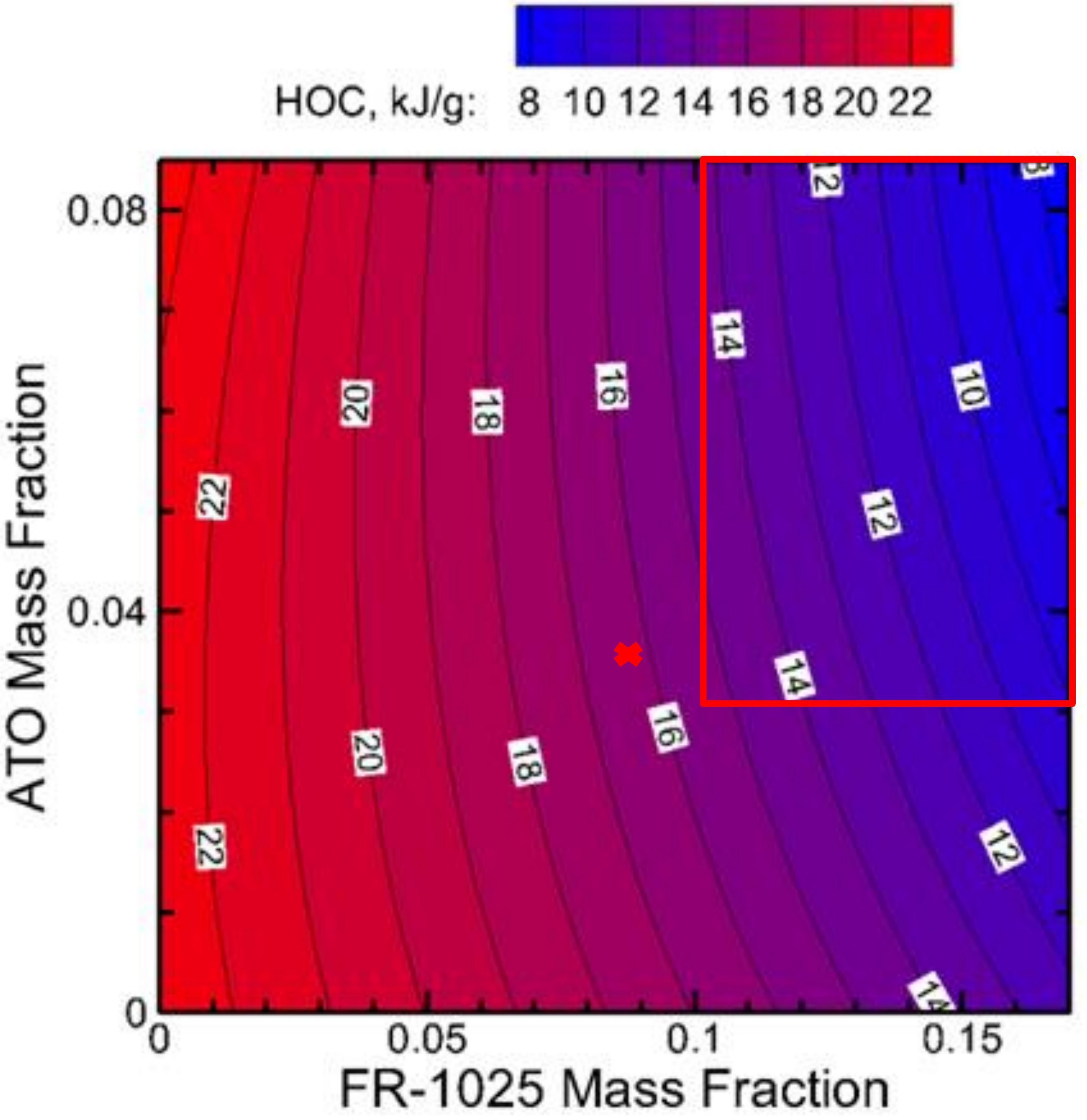
- Differentiate between gas-phase and condensed phase activity

Results
ATO

Coefficients (kJ/g)	
a	22.73
b	-52.73
c	-14.93
d	**-405.50**
e	-48.86
f	293.80

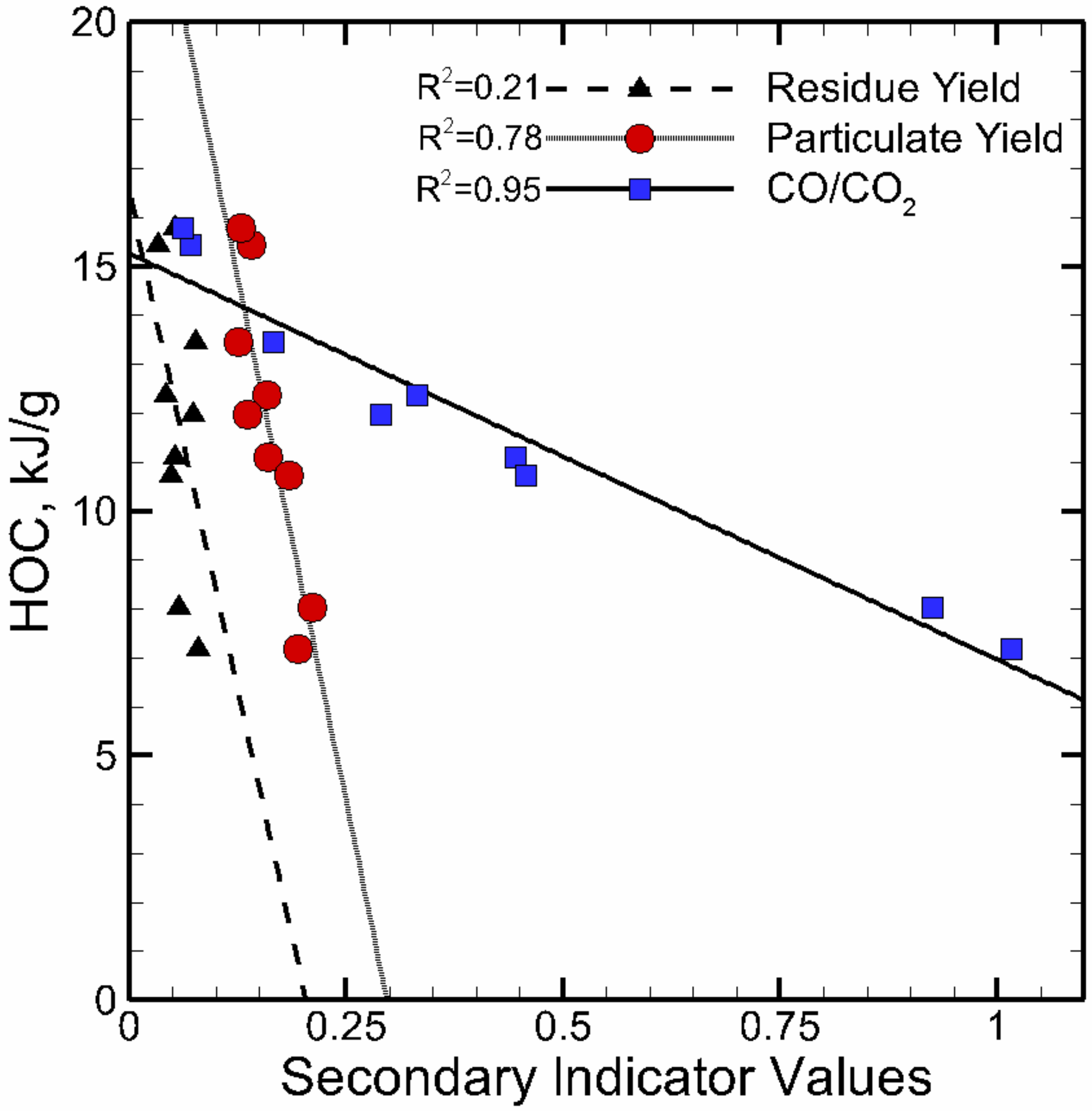
$R^2 = 0.98$

Compounded HOC (kJ/g)
Predicted: 16.8
Measured: 15.1
10% error



Results
ATO

- Strong correlation of HOC with CO/CO2. Also good correlation with particulate yield. Consistent with gas phase activity.

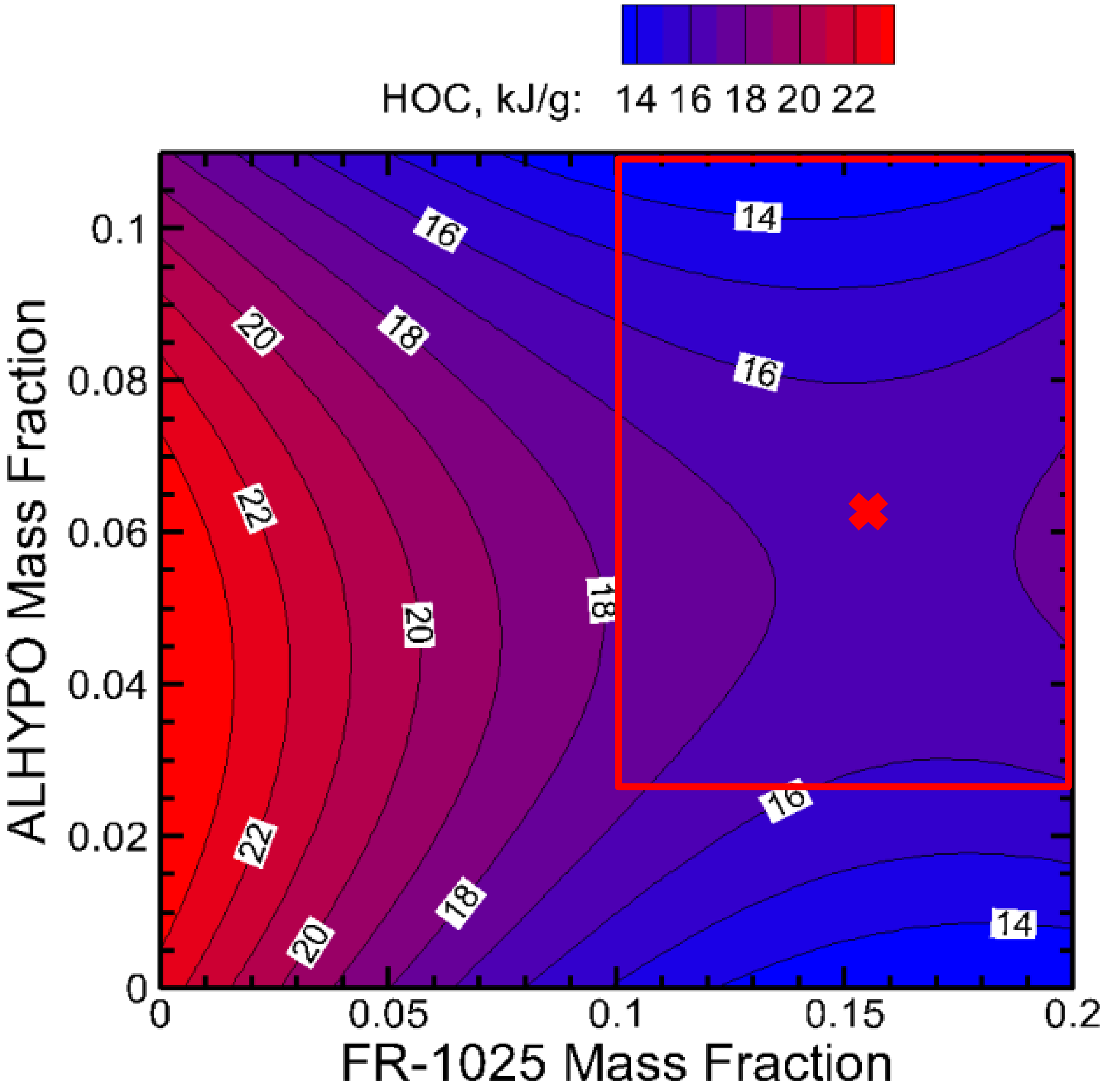


Results Al-Hypo

Coefficients (kJ/g)	
a	22.53
b	-104.27
c	96.83
d	**245.81**
e	281.91
f	-1241.20

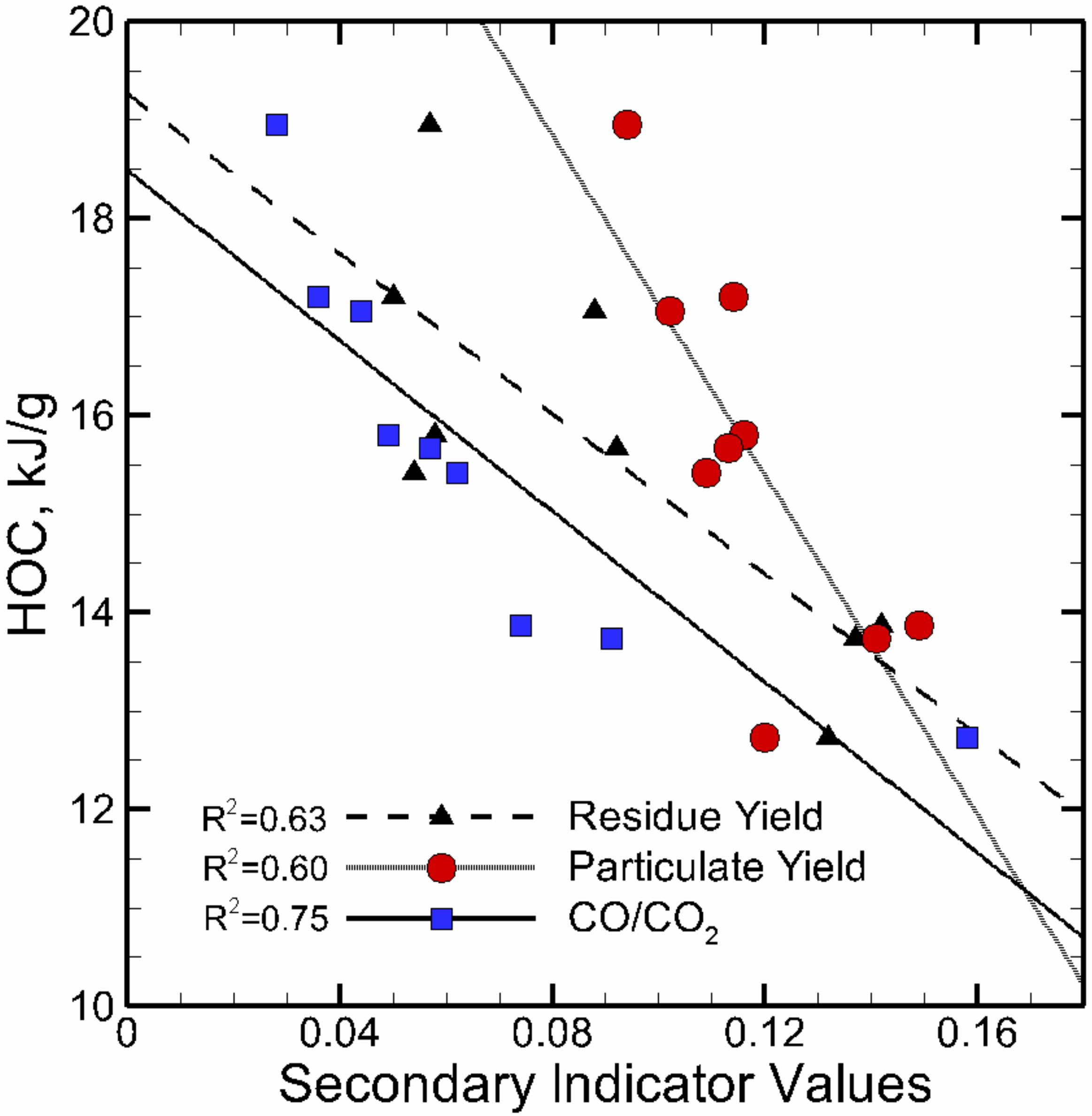
$R^2 = 0.91$

Compounded HOC (kJ/g)
Predicted: 16.4
Measured: 14.9
10% error



Results
Al-Hypo

- Highest correlation with CO/CO2. Nearly equal correlation with particulate and residue yield.
- Combined gas phase and condensed phase activity.



Conclusions

- MFC based methodology for screening multiple flame retardant/synergist combinations was developed and implemented.
- Methodology can quickly and cost-effectively screen formulations due to dry-blending of components in situ. Observed trends correlate well with compounded formulations.
- Beyond simply screening, methodology also provides insight into mode of action of additives (gas phase vs. condensed phase, particulate vs. CO) and synergistic/antagonistic effects can be quantified.
- The methodology should be readily applicable to any polymer matrix, any gas-phase active (and/or moderately condensed-phase active) flame retardant and any number of additives.

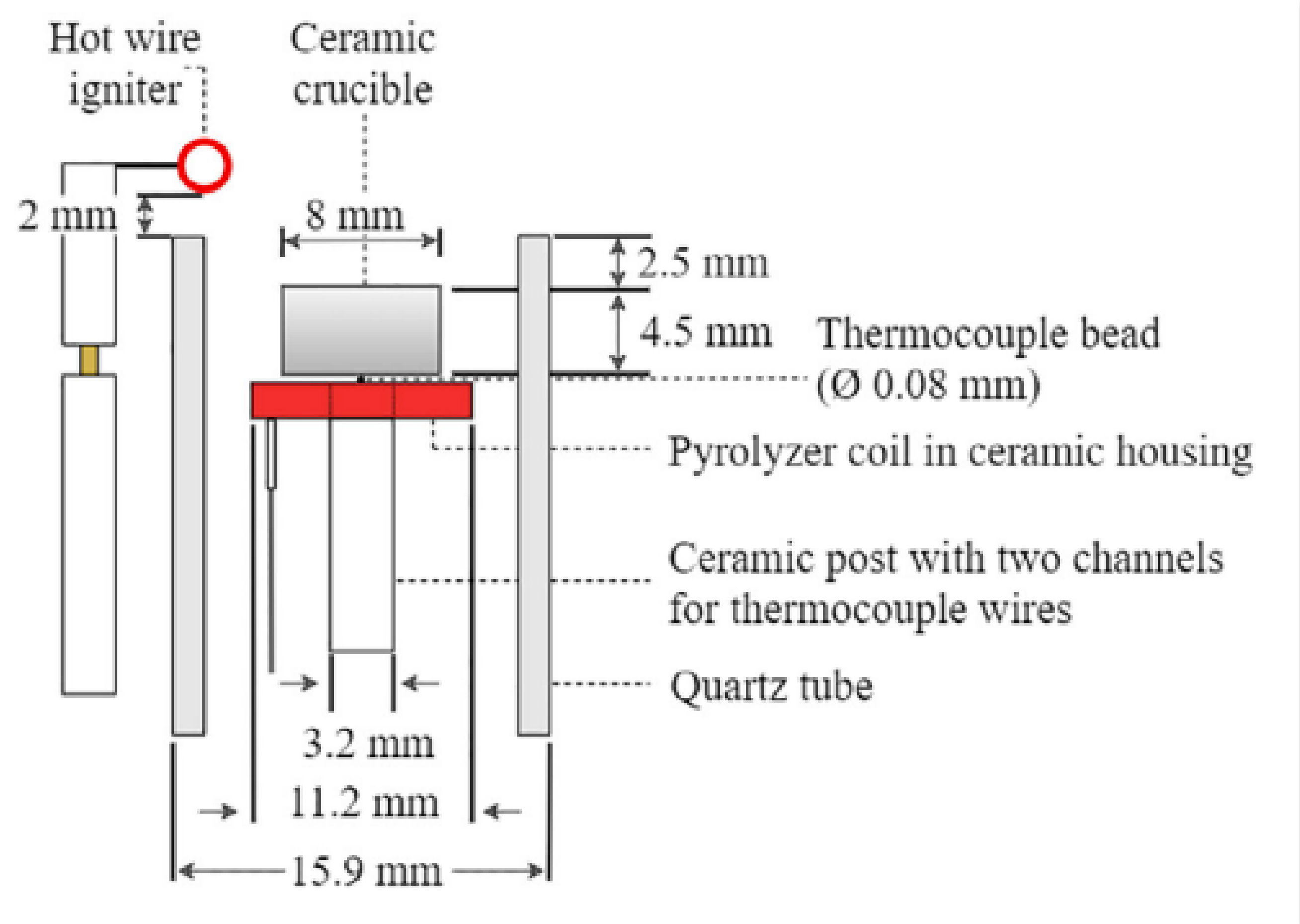
Raffan-Montoya, F., Stoliarov, S.I., Levchik, S., Eden, E., "*Screening Flame Retardants Using Milligram-scale Flame Calorimetry*," Polymer Degradation and Stability 151, May 2018.

Evolution

- Condensed phase effects such as intumescence constrict flow of volatiles, inducing unwanted hydrodynamic effects.
- Pyrolyzer component is expensive ~ $30,000
- Temperature measurement of sample heating process is desirable.
- Pyrolyzer redesign from scratch. Fabricated in-house to address all issues above.

Emulating heating of non-thermally thin samples

- Build new pyrolyzer based on prototype.
- Reoptimize parameters (heating rate, N2 purge flow)
- Benchmark MFC with new pyrolyzer against MCC and Cone for a wide range of pure polymers



Student: Jacques DeBeer

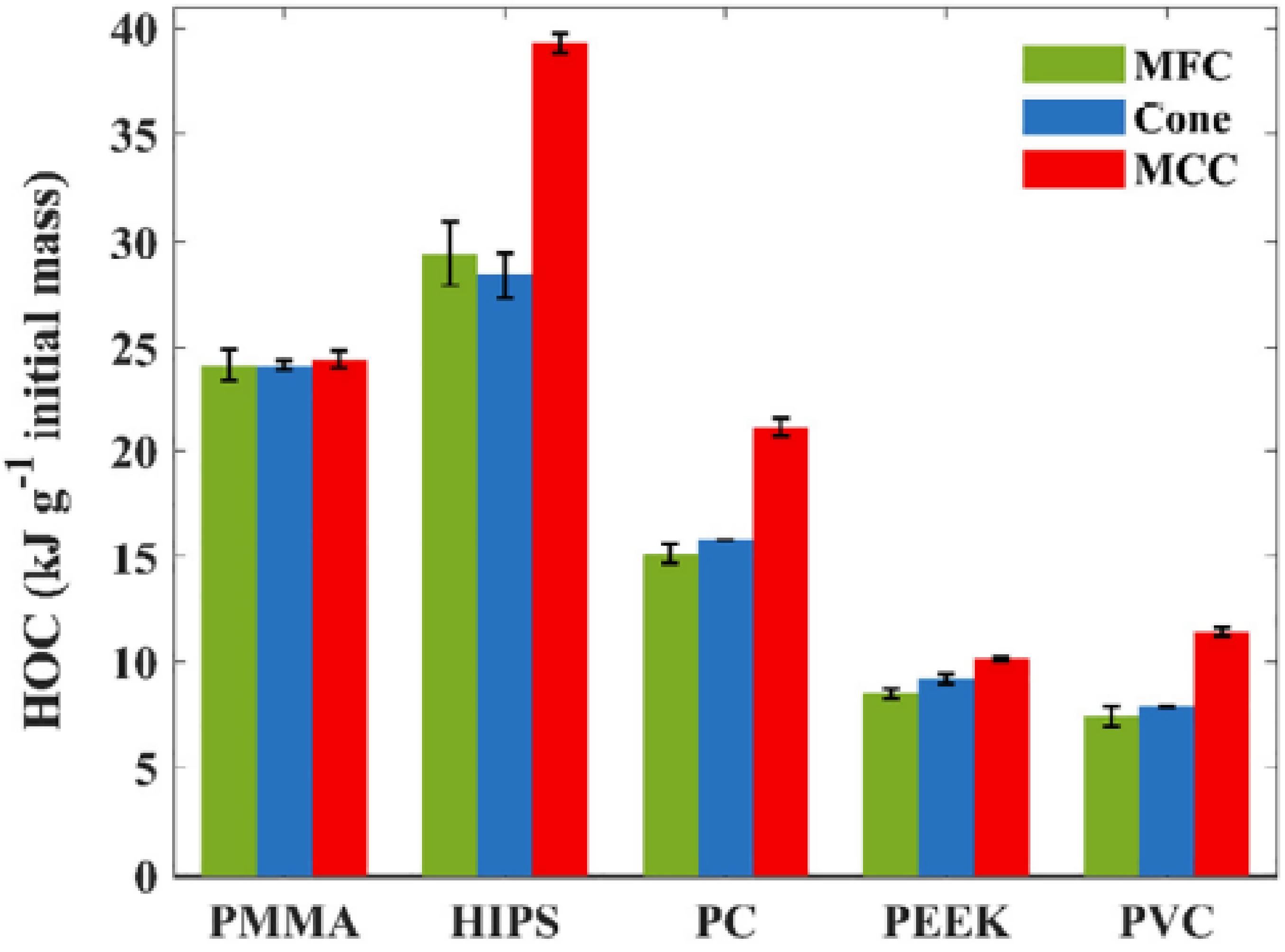
New pyrolyzer design

Emulating heating of non-thermally thin samples

- 5 pure polymers: PMMA, HIPS, PC, PEEK, and PVC.
- 2 ramp heating profile: conditioning + constant power.
- End pyrolyzer temperature equivalent to 50 kW/m^2 heat flux.

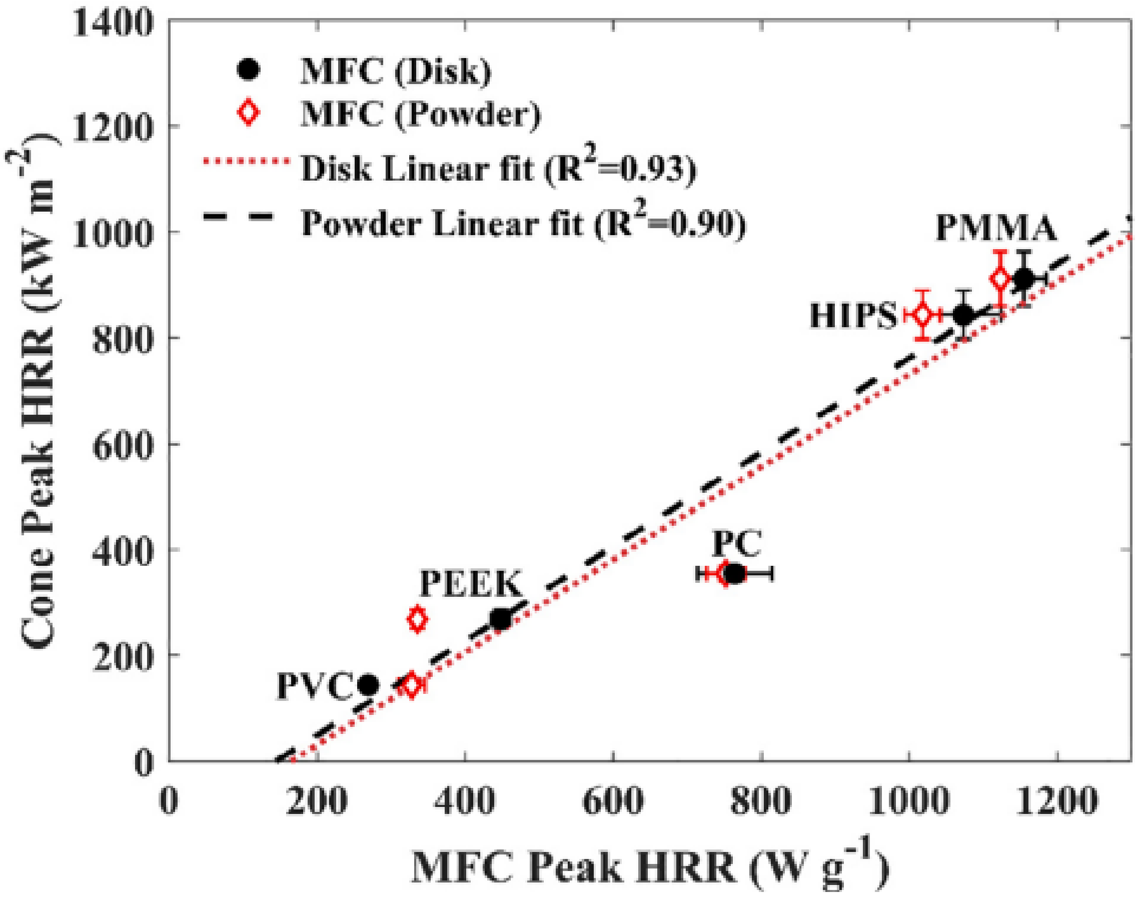
Results

- HOC comparison
- MFC and Cone are nearly identical
- MCC values $\geq$ other techniques (high combustion efficiency by design)



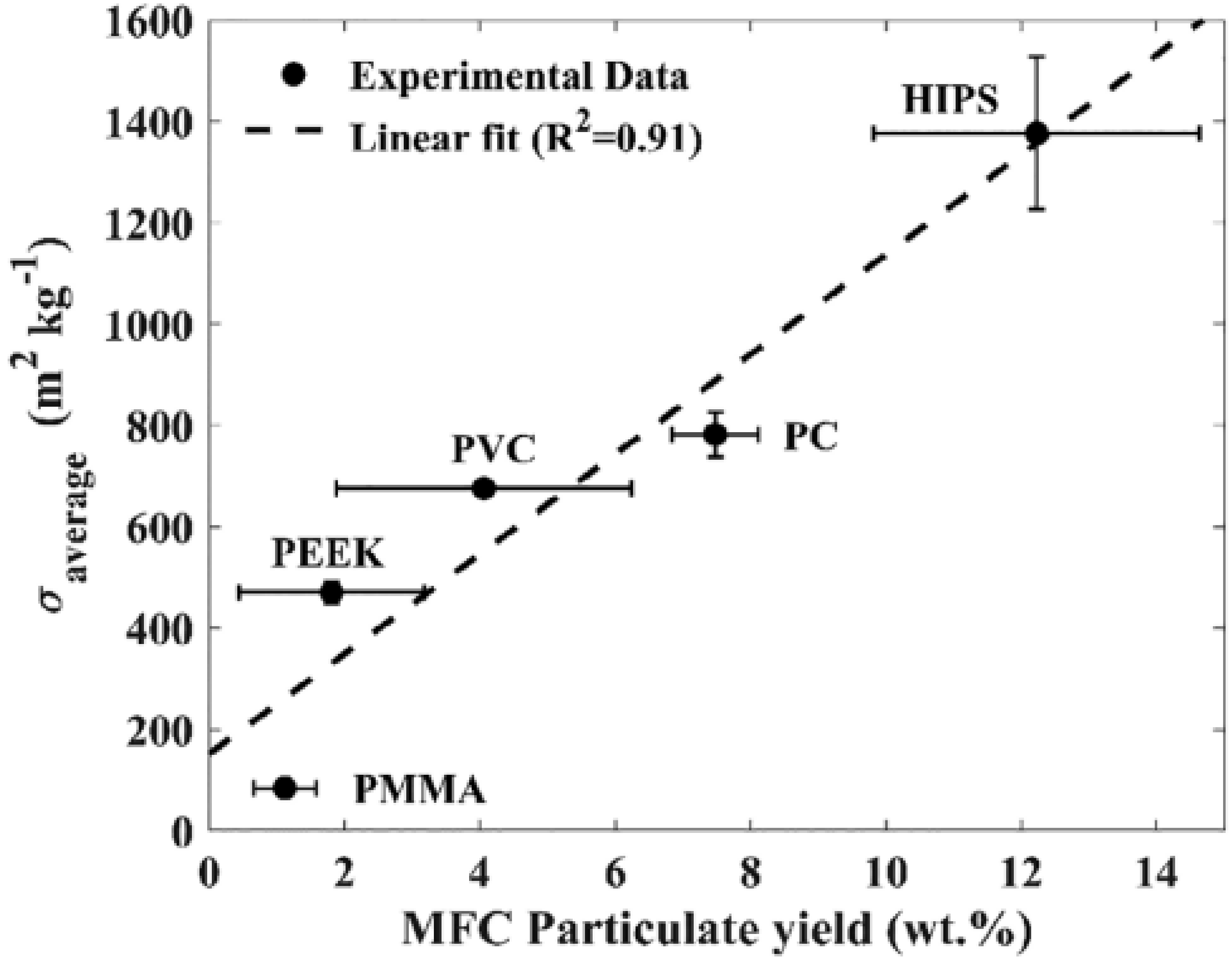
Results

- Explored effect of MFC sample form (powder vs. disk).
- Peak HRR correlates well with Cone Calorimeter in either sample presentation.



Results

- MFC Soot yield vs. Cone obscuration data



Conclusions

- A new pyrolyzer system was developed and implemented for the MFC to address some deficiencies of the previous version of this instrument.
- The relationship between the MFC and Cone peak HRR was found to be nearly perfectly linear. The MCC peak HRR exhibited a relatively poor correlation with the corresponding cone data.
- The MFC and Cone HOC values normalized by the initial sample mass were found to be nearly identical. The MCC produced notably higher HOC values for the majority of the studied materials.
- The airborne particulate yield measured in the MFC was found to correlate well with the average specific extinction area measured in the cone tests.
- MFC is capable of capturing all essential features of material behavior in gram-scale flammability tests and thus is an effective alternative for relative material flammability assessments.

DeBeer, J., Raffan-Montoya, F., Stoliarov, S.I., “A Milligram-scale Flame Calorimeter Pyrolyzer System Used to Emulate Burning of Non-thermally-thin Solid Samples,” Fire and Materials, 2021.

Future

- Screening of textiles.
- Fire toxicity measurements and benchmarking against FPA.
- Series of tests + machine learning for optimizing new formulations.
- Commercialization of MFC is possible.
- Round robin with independent labs, potential for a new standard.

Summary

- A novel apparatus has been built for the measurement of key flammability parameters of solid fuel samples, the MFC
  - Flaming combustion
  - Milligram-sized samples
- Sensitivity to gas phase flame retardants (bromine and phosphorus based)
- Sensitivity to gas-phase synergists
  - Developed a thorough methodology for screening any polymer matrix + FR + synergist formulation
  - Mixed in situ, no compounding required
  - Insight into synergistic/antagonistic activity as well as correlating flammability parameters with gas-phase or condensed phase activity
- Improved pyrolyzer (reduced cost, improved sensitivity to condensed phase activity (intumescence), temperature measurements of sample). Great correlation of measured parameters with those from Cone Calorimeter.

Acknowledgments

- Past students: Xi Ding, Colleen Frances, Catherine Hamel, Jacques DeBeer
- Sponsors (Roland Kraemer-BASF, Richard Lyon-FAA, Sergei Levchik-ICL-IP)

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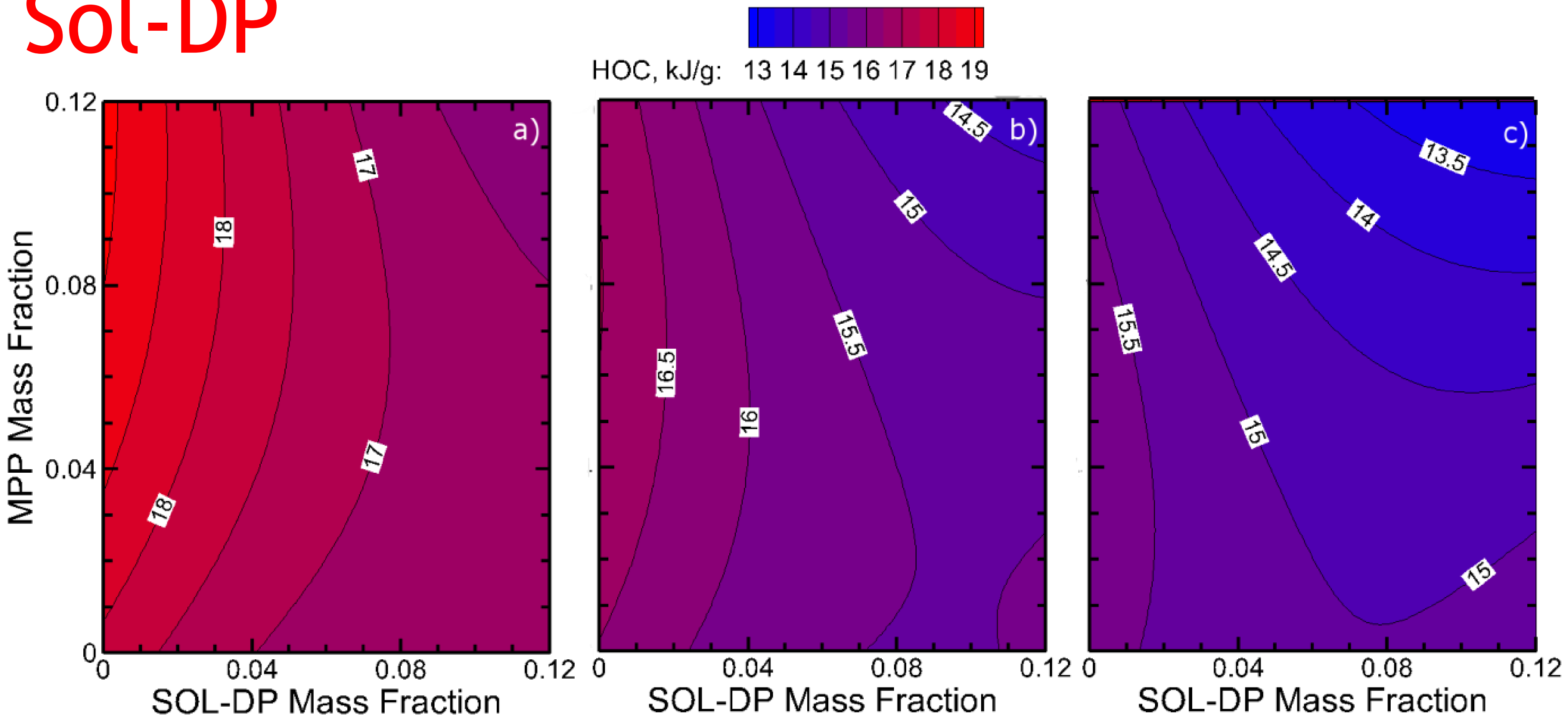
Questions?

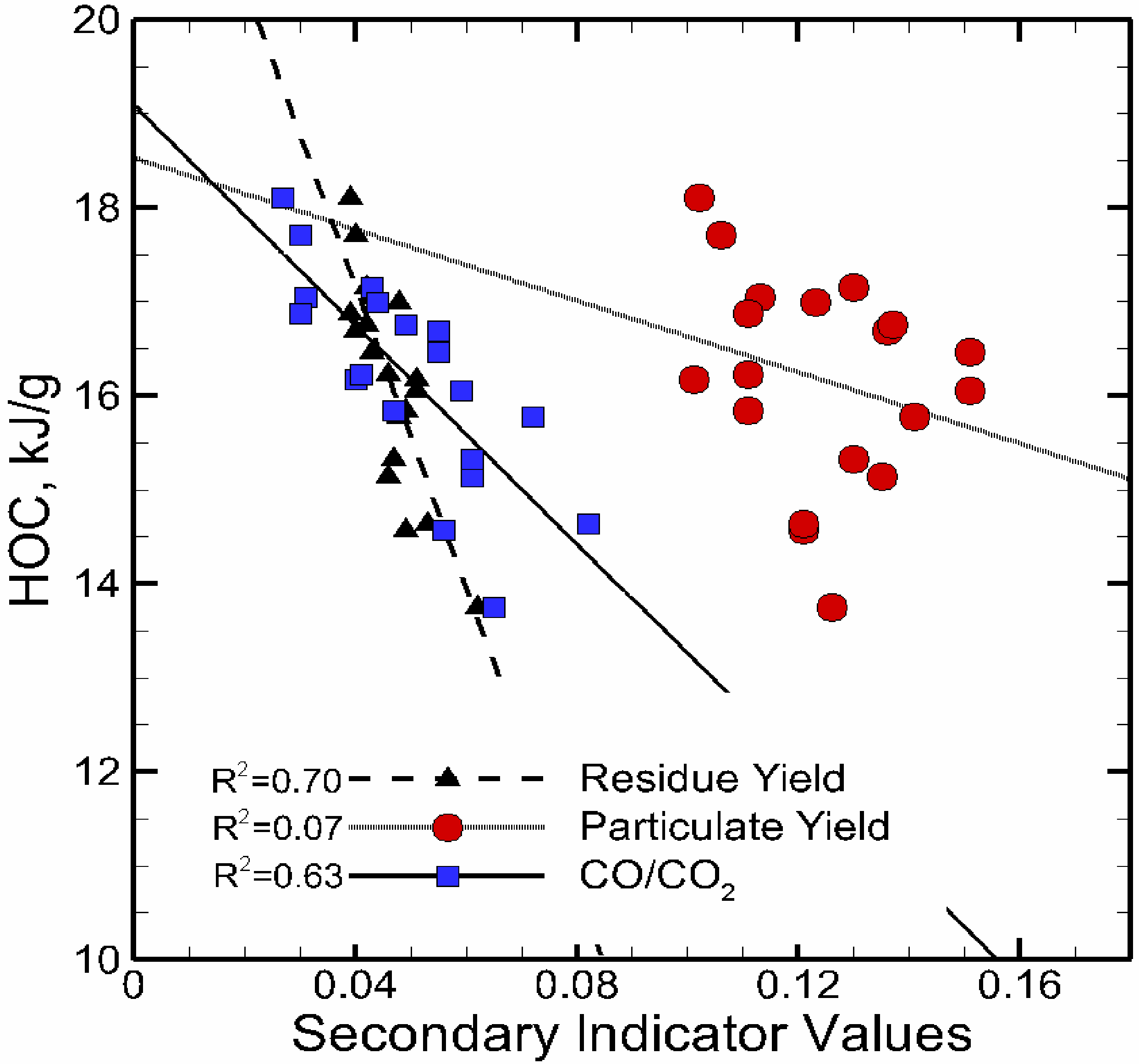
Results
MPP + Sol-DP

Coefficients (kJ/g)	
a	22.60
b	-60.57
c	-33.14
d	36.28
e	**71.08**
f	**-147.03**
g	**-123.58**
h	131.12
i	125.65
j	-89.77



Results
MPP + Sol-DP

- Best correlation with residue yield suggests condensed phase activity.
- Moderate correlation with CO/CO2 suggests some gas phase activity.



Prototype

Additional MFC applications

- Screening of metal oxides and bromides as synergists
- Screening of additional FR+synergist formulations
- Soot ratio pyrometry of laminar solid fuel samples