FAA Fire Safety Research Grants Update

Polymer Science & Engineering Department,
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Dept. of Fire Protection Engineering
University of Maryland, College Park

FAA-supported Research at UMass Amherst: Non-Halogenated Polymers and Additives with Low Flammability and High Char Yields

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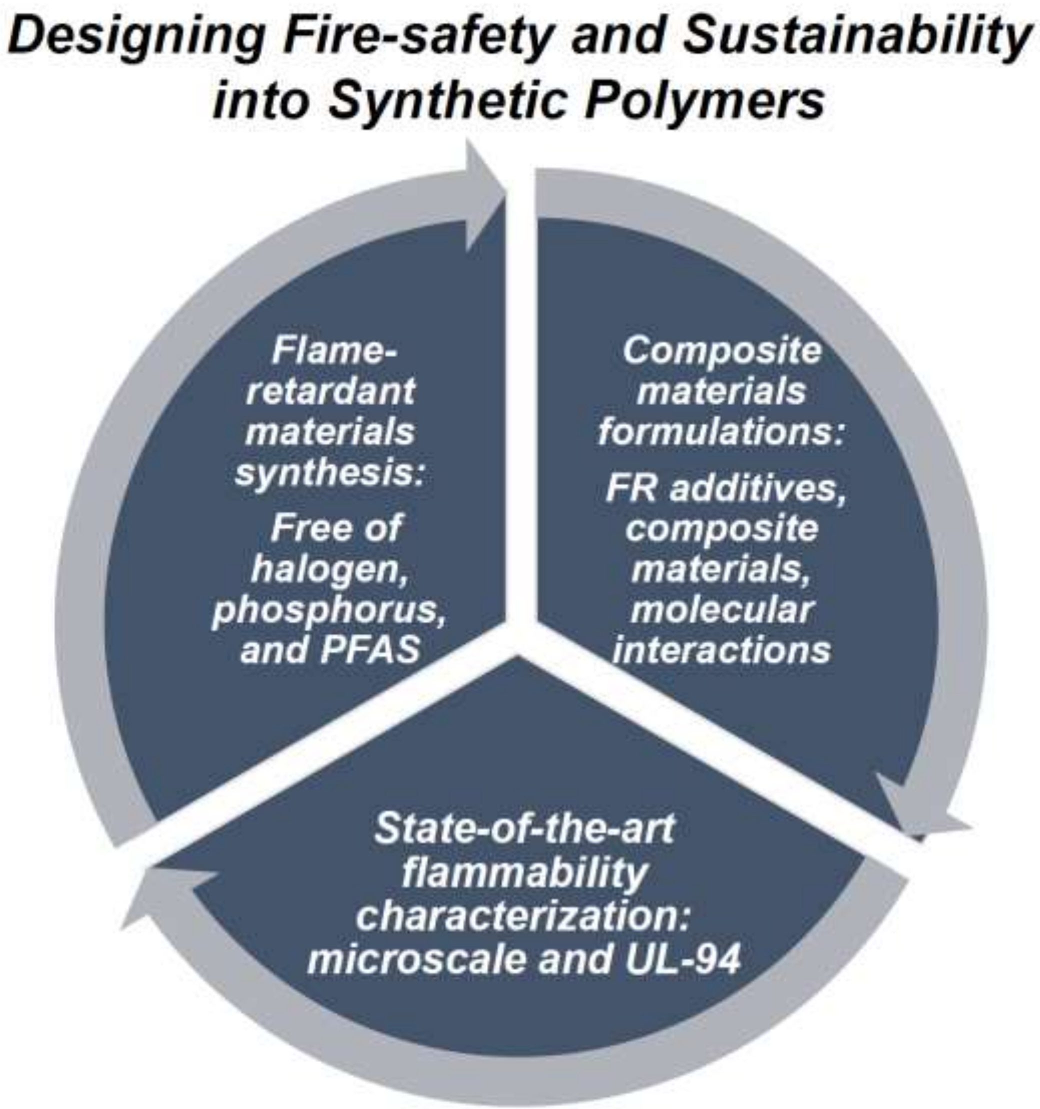
Project Objectives: from Materials Discovery to Workforce Development

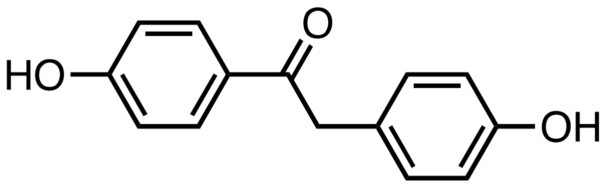


→ ***Materials Discovery***: create advanced synthetic methods to yield new polymer materials that satisfy stringent flammability requirements.

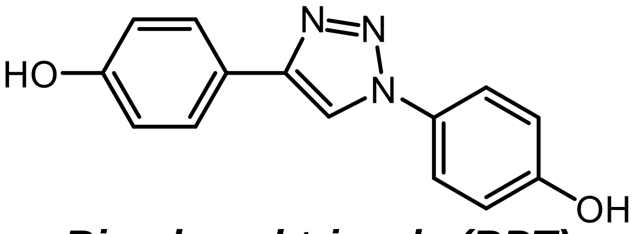
→ ***Heat Release Evaluation at the MIcroscale***: utilize state-of-the-art characterization techniques developed by FAA researchers, *i.e.,* microscale combustion calorimetry (MCC). Participate in round-robin analyses to reinforce fidelity of MCC data.

→ ***Human Resource Development***: train top-notch Ph.D. and postdoctoral researchers for impactful careers. Interface with industry to disseminate FR results and motivate collaboration.

Bottom-up Approaches:
Monomer Designs Yield Ultra-low Flammability Polymers



Bis-hydroxydeoxybenzoin (BHDB)



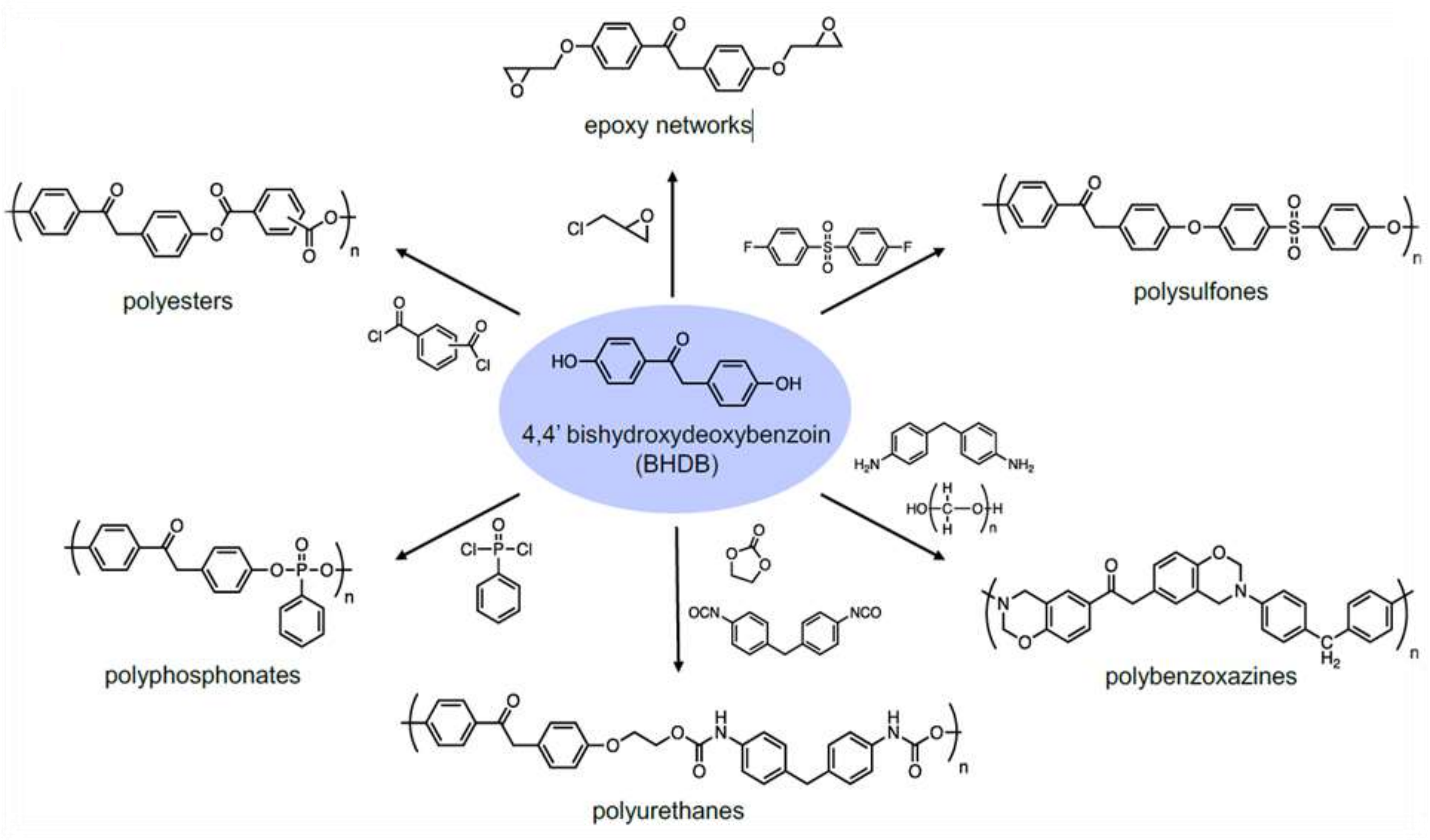
Bis-phenol triazole (BPT)

Polymers from BHDB generate char via cyclization of phenylacetylene intermediates

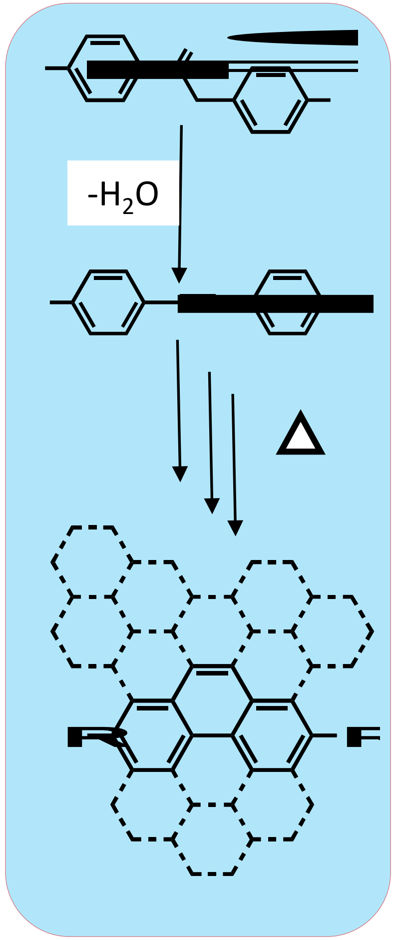
Polymers from BPT generate C,H,N-containing char and release nitrogen gas

Polymers from BHDB and BPT:
- High char and low heat release
- Bis-phenol A (BPA) alternatives
- Useful as comonomers for a large variety of polymers

Deoxybenzoin as a Versatile Starting Material in FR Materials

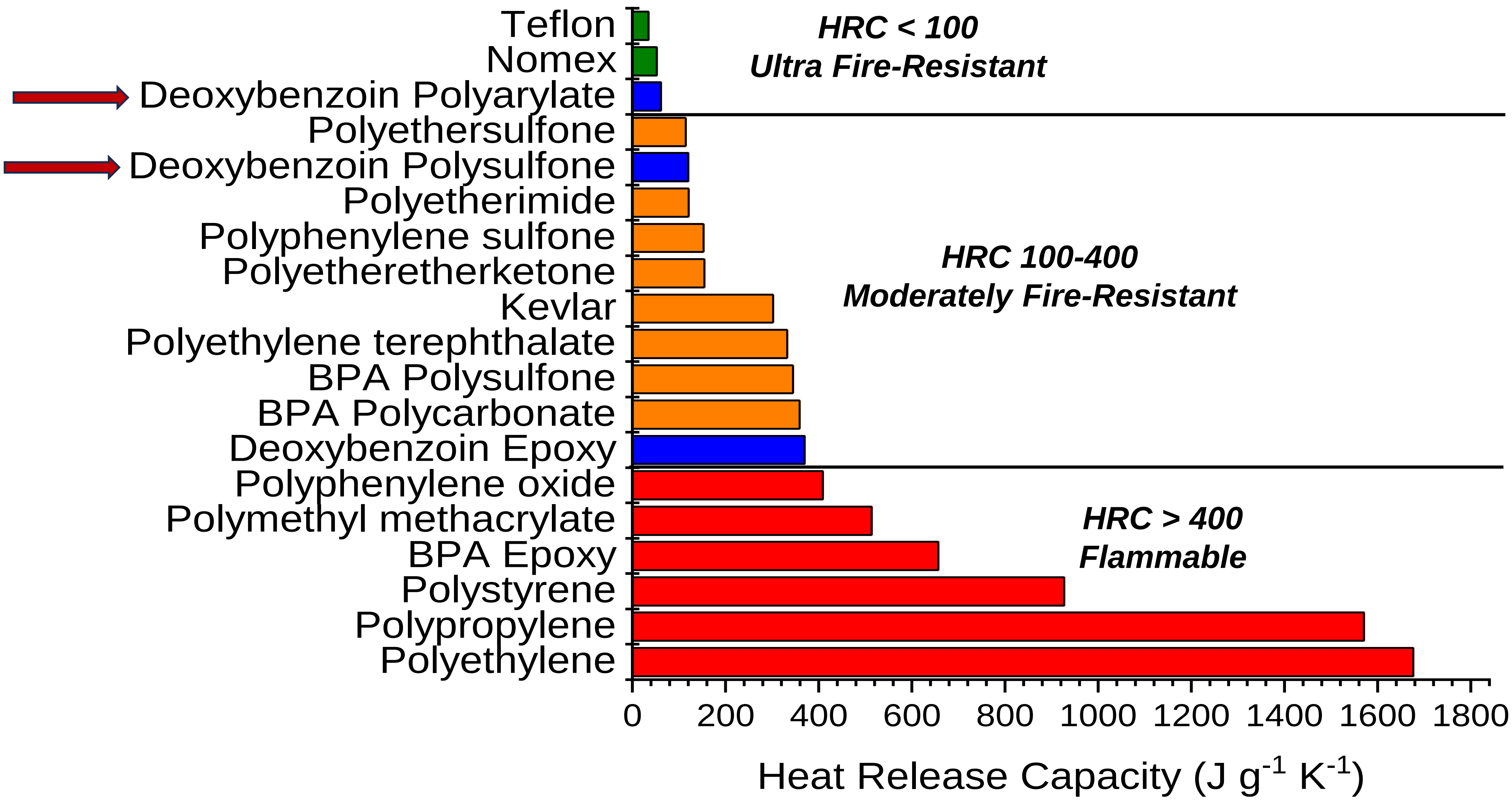


Char-forming mechanism



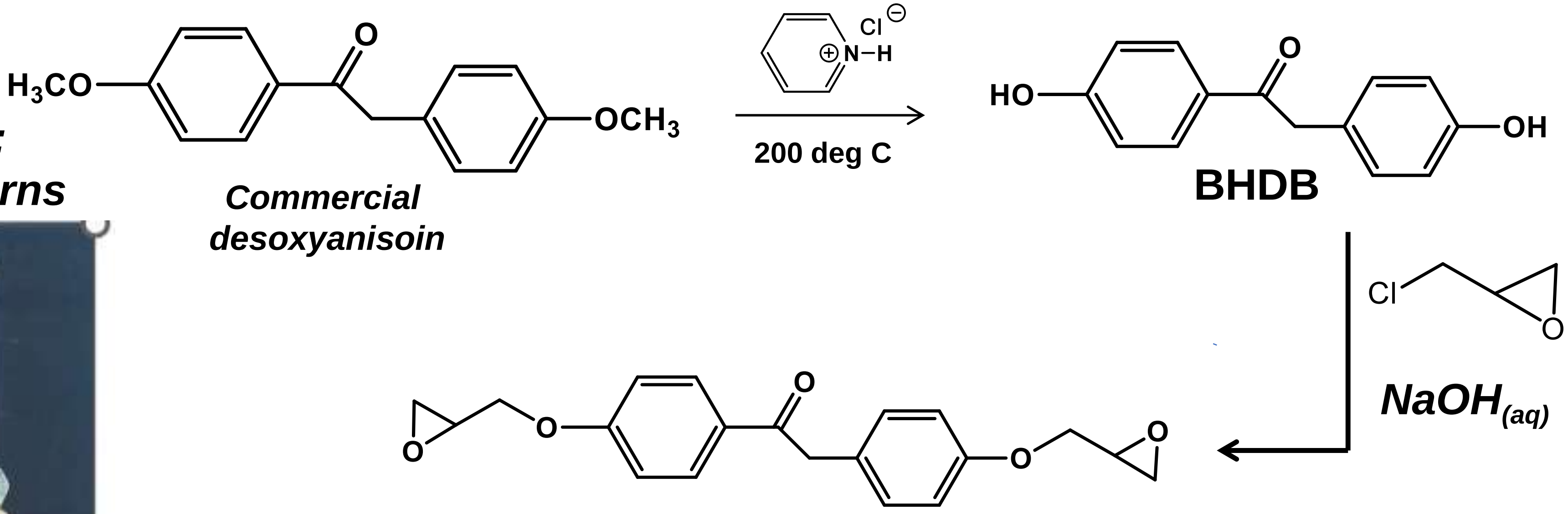
Inherent FR Characteristics of Deoxybenzoin Polymers

Principles underlying deoxybenzoin FR properties place it deep into FR category



Bis-epoxy deoxybenzoin (BEDB) simple synthesis → excellent FR properties

BPA-epoxy: Ignites and burns



BEDB-epoxy: self-extinguishes

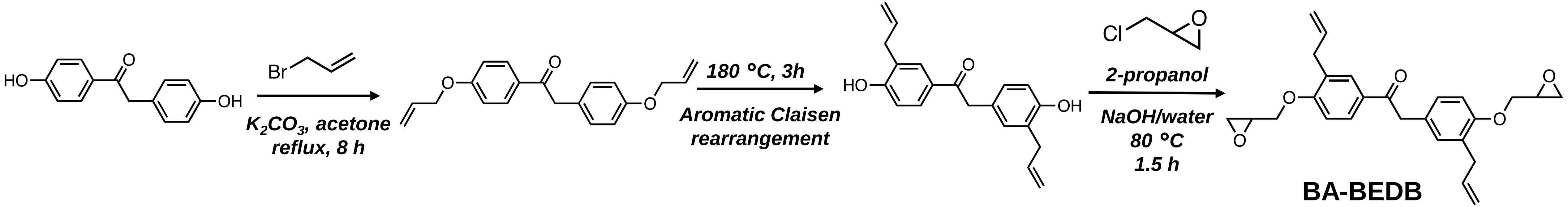
Readily scalable to kilo levels

Epoxy networks from BEDB:
Heat release is ~1/2 that of BPA-epoxies;
mechanical properties (lap shear evaluation) similar/better than BPA

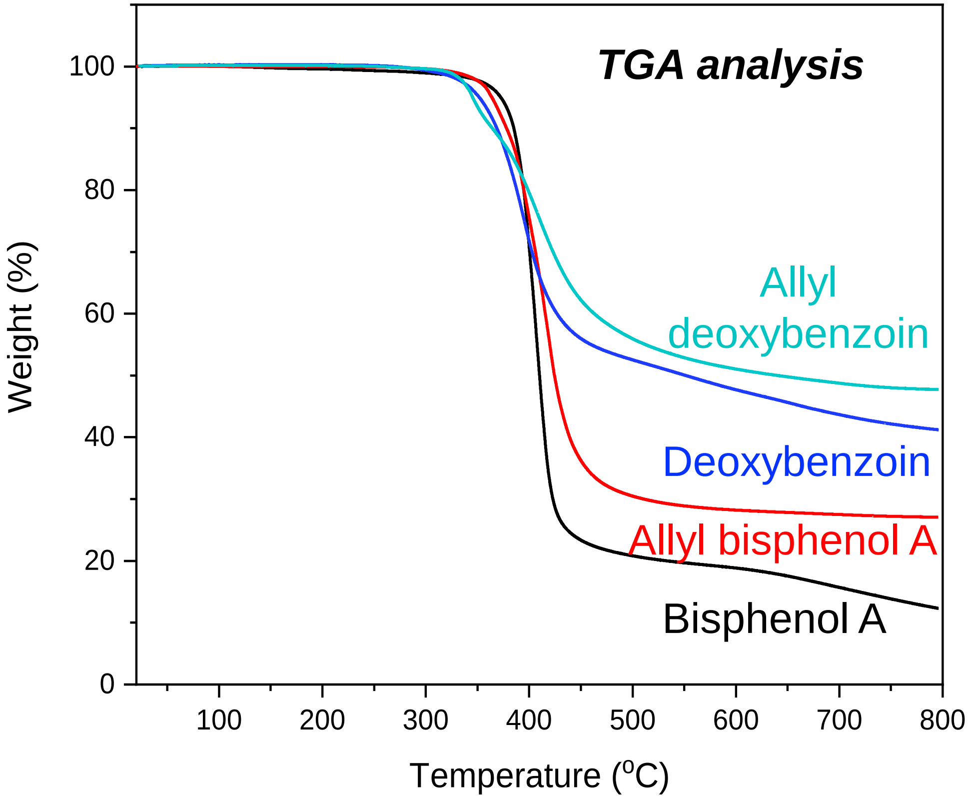
Macromolecular Materials and Engineering, 2020

A Framework for Multifunctional and Orthogonal Crosslinking Mechanisms

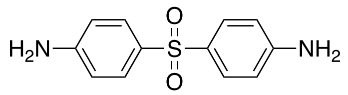
Simultaneously tailor chemical, mechanical, and FR properties (published in Polymer, 2023)



Allyl groups boost char yield!

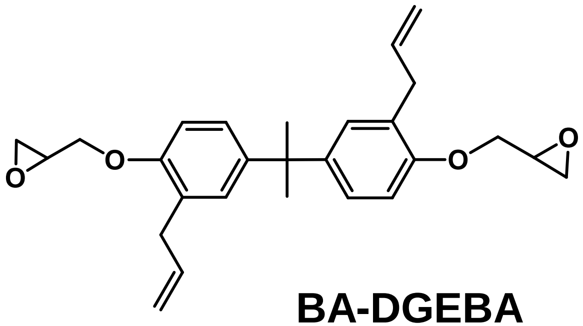


Curing conditions



Diphenyldiamino sulfone

190 °C
8 h



BA-DGEBA

Epoxide	**T_g** (°C)	**HRC** (J/g-K)	**peak HRR** (W/g)
DGEBA	215	602 ± 79	373 ± 25
BA-DGEBA	**119**	**240 ± 40**	**220 ± 16**
BEDB	177	232 ± 8	217 ± 2
BA-BEDB	**152**	**185 ± 6**	**146 ± 5**

Dissemination: Recent Publications, Patents, Presentations, etc…

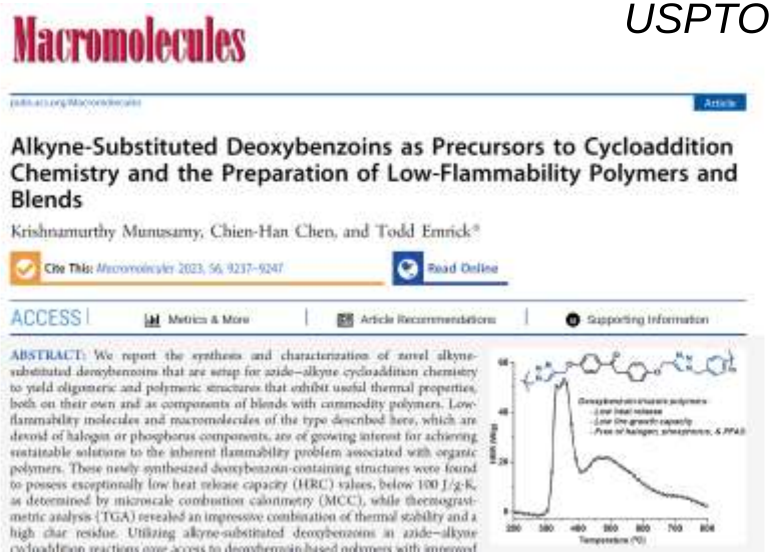
Stubbs, E.,…Emrick, T. Multifunctional Deoxybenzoins: Preparation of Low Heat Release Polymer Networks by Orthogonal Crosslinking. Polymer, ***2023****, 284, 126288. DOI 10.1016/j.polymer.2023.126288.*

Munusamy, K.; Chen, C-H.; Emrick, T. Alkyne-substituted Deoxybenzoins as Precursors to Cycloaddition Chemistry and the Preparation of Low-Flammability Polymers and Blends Macromolecules, ***2023****, 56, 9237-9247.*

Saraf, C., et al. Combining Mechanical Fortification and Ultralow Flammability in Epoxy Networks. Macromolecular Materials and Engineering ***2020****, Article 2000567 DOI: 10.1002/mame.202000567.*

Stubbs, E.; Brown, M.; Steele, A.; Song, C.; Emrick, T. Designing branched deoxybenzoin polyesters and polymeric flame retardants. Journal of Polymer Science Part A-Polymer Chemistry ***2019****, 57(16), 17645-1770. DOI: 10.1002/pola.29446*

Brown, M.C.; Stubbs, E.G.; Emrick, T. Deoxybenzoin Monomers and Branched Polymers Prepared Therefrom. USPTO patent number 11174214. Issued November 16, 2021.



Macromolecules

Alkyne-Substituted Deoxybenzoins as Precursors to Cycloaddition Chemistry and the Preparation of Low-Flammability Polymers and Blends

Krishnamurthy Munusamy, Chien-Han Chen, and Todd Emrick

Cite This: Macromolecules 2023, 56, 9237−9247 | Read Online

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ABSTRACT: We report the synthesis and characterization of novel alkyne-substituted deoxybenzoins that are setup for azide−alkyne cycloaddition chemistry to yield oligomeric and polymeric structures that exhibit useful thermal properties, both on their own and as components of blends with commodity polymers. Low-flammability molecules and macromolecules of the type described here, which are devoid of halogen or phosphorus components, are of growing interest for achieving sustainable solutions to the inherent flammability problem associated with organic polymers. These newly synthesized deoxybenzoin-containing structures were found to possess exceptionally low heat release capacity (HRC) values, below 100 J/g·K, as determined by microscale combustion calorimetry (MCC), while thermogravimetric analysis (TGA) revealed an impressive combination of thermal stability and a high char residue. Utilizing alkyne-substituted deoxybenzoins in azide−alkyne cycloaddition reactions gave access to deoxybenzoin-based polymers with improved

Recent FAA-supported alumni:
Elizabeth Stubbs (now DuPont), Chinmay Saraf (now PPG), Anna Steele (now Virginia Tech), Moira Brown (now Cyclopure, Inc.)

Project update for FAA Fire Safety Branch Meeting

Measurement and Modeling of Hazardous Substances Produced in Fires Fueled by Polymeric Materials

Prepared by:

- Farnaz Beygi Khosroshahi
- Dr. Fernando Raffan-Montoya
- Dr. Stanislav I. Stoliarov

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Modified Fire Propagation Apparatus (FPA) Research Phases

Standard bench scale test that facilitates controlled studies on solid fuel combustion

Modifications expand the FPA's capabilities to measure CO_2,CO, O_2, and particulate matter, HCN, HCl, HBr, and unburned hydrocarbons

1. Apparatus Enhancement (Complete):

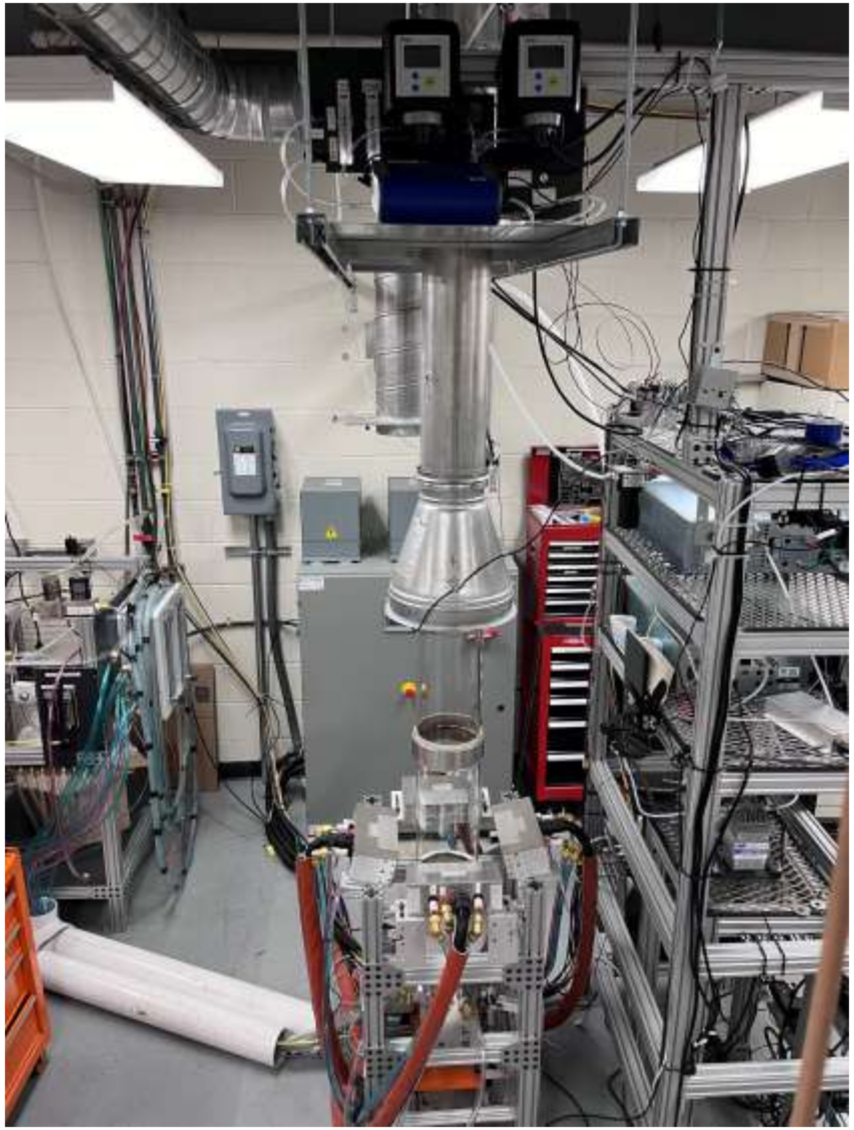
Redesigned the construction of the FPA, improving measurement capabilities

2. Instruments Precision and Accuracy Validation (Ongoing):

Examination of each sensor to validate functionality and accuracy, ensuring the precision of the measurements

3. Constant Ventilation Condition Tests (Ongoing):

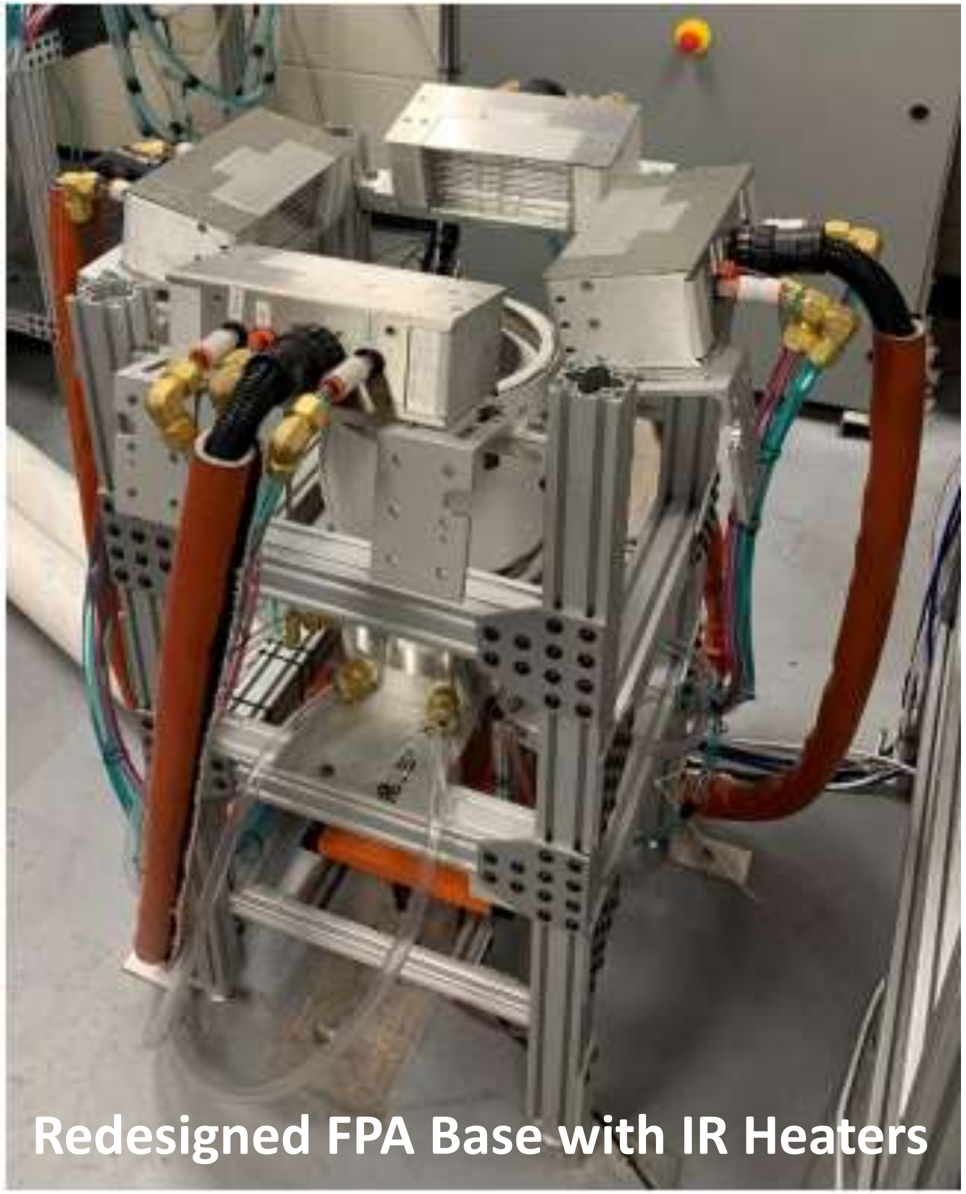
Maintain constant ventilation conditions throughout combustion, achieving a uniform equivalence (fuel:oxygen) ratio



Fire Propagation Apparatus Enhancements

FPA Design and Modifications

- Frame structure
- Combustion air distribution chamber
- Water-cooled outer shield
- Load cell
- Sample support assembly



Redesigned FPA Base with IR Heaters

Fire Propagation Apparatus Enhancements

Exhaust System Design and Modifications

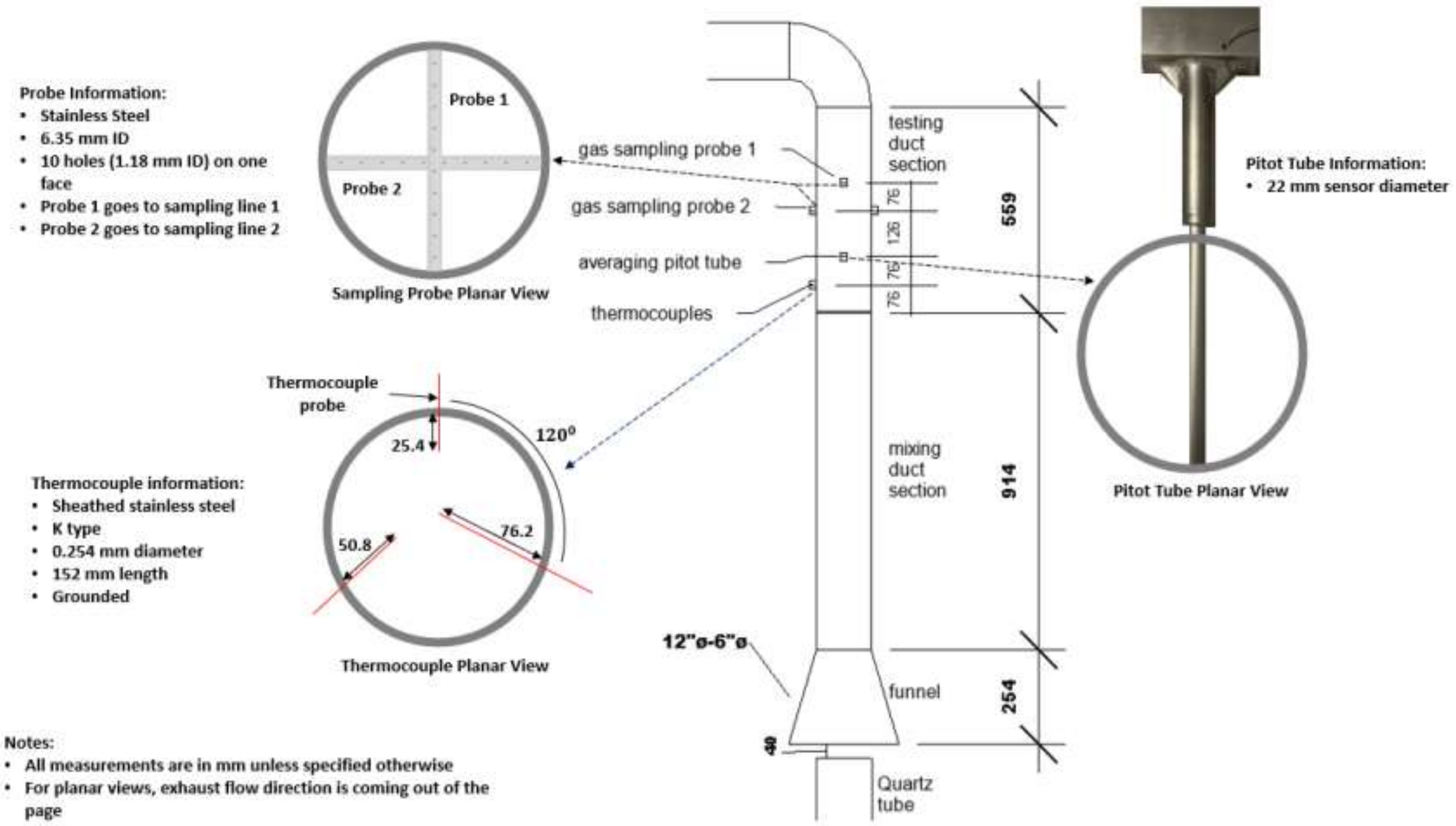
-Follows same configuration specified in ASTM E2058-19

An intake funnel

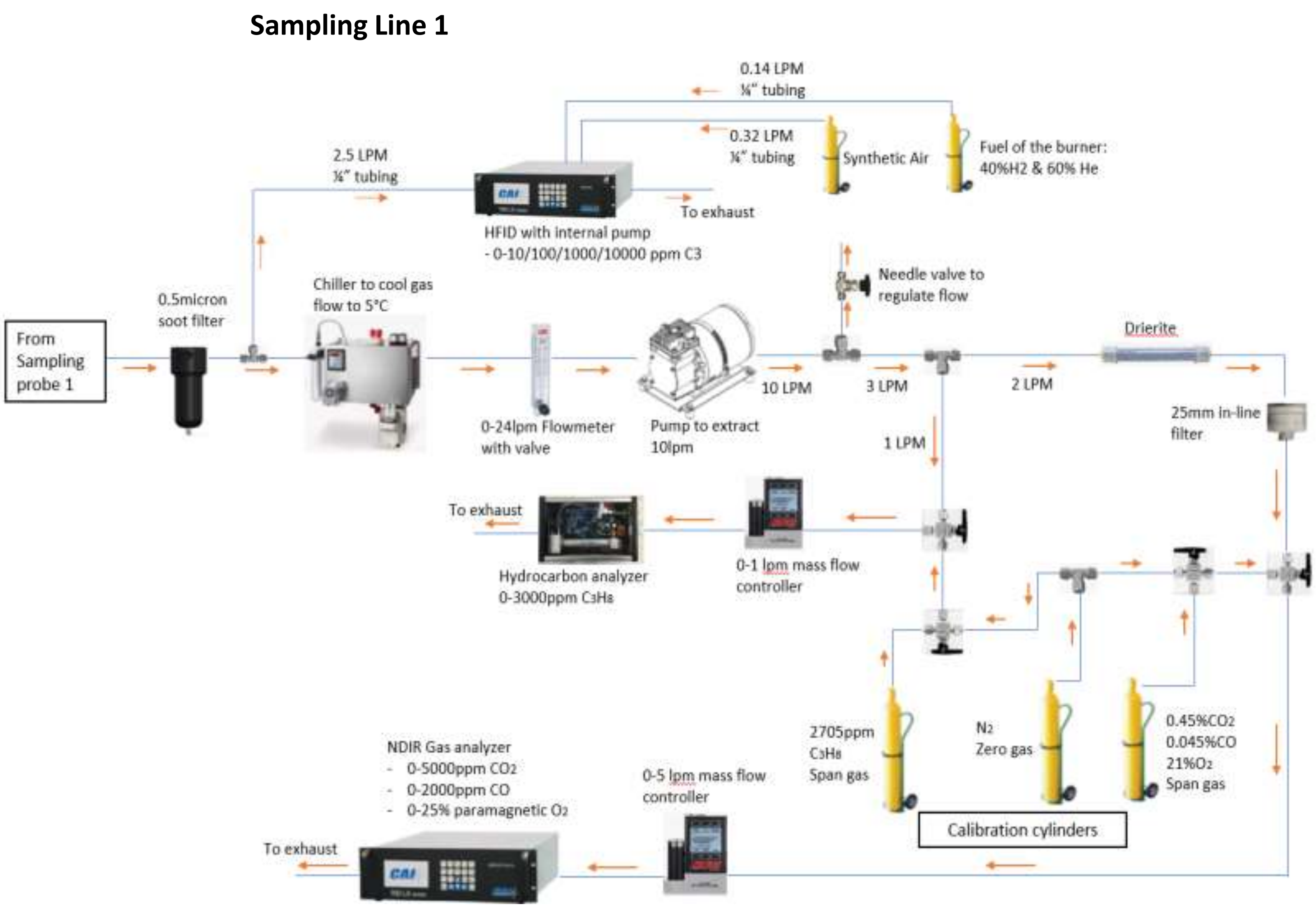
Mixing section

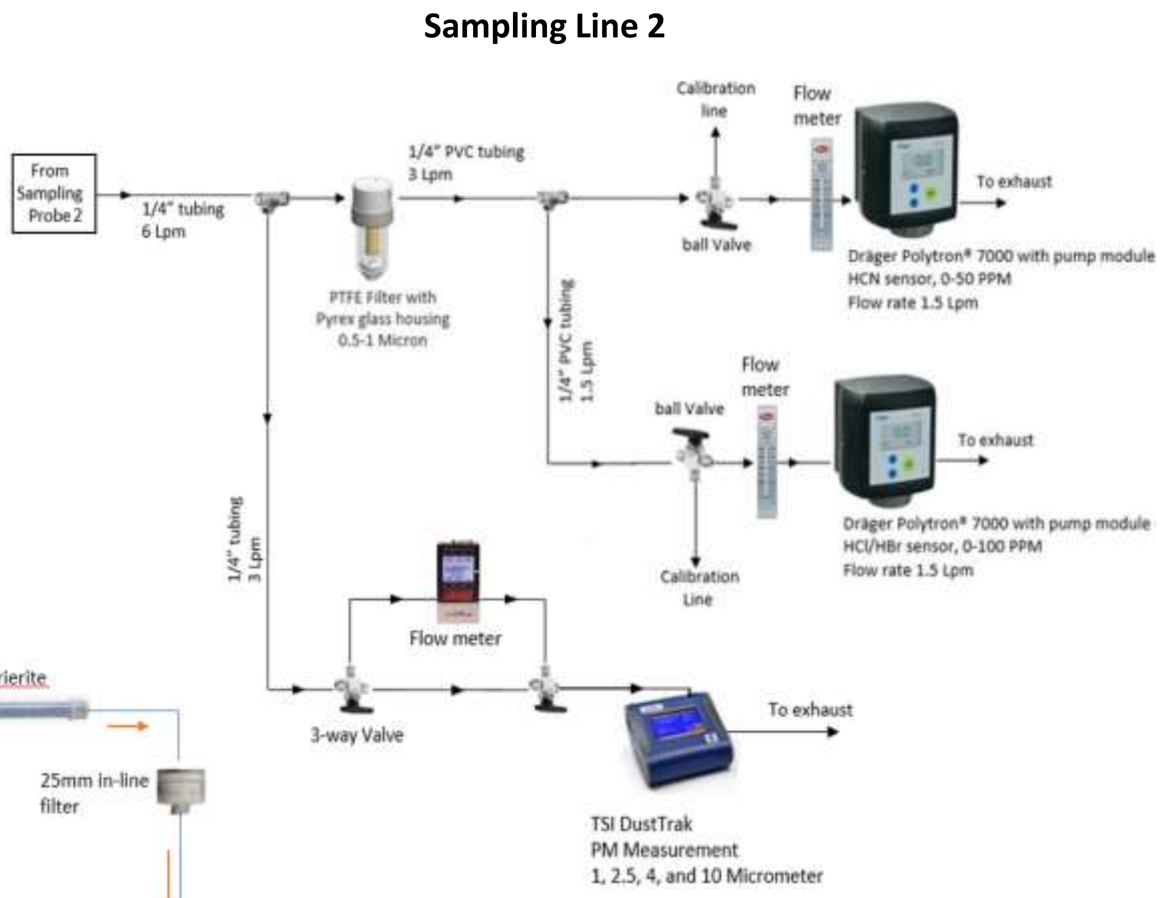
Test section

Blast gate section



Gas Sampling System





The final design of the sampling system is capable of measuring **CO2**, **CO**, **O2**, **total hydrocarbons**, **solid particles**, and acid gases including **HCN**, **HBr**, and **HCl**.

Instruments Precision and Accuracy Validation Preliminary Tests and Verification of Results

Carbon Mass Balance

Test materials of known composition to get carbon

Calculate carbon yield from measured values

$$C\% = \frac{Mass\ of\ carbon\ in\ the\ products}{Mass\ of\ carbon\ in\ the\ fuel}$$

Yields (gram species/ gram of fuel) for PMMA @ 50kW/m2

	Y_{CO2}	Y_{CO}	Y_{soot}	Y_{THC}	C%	Y_{O2}	Y_{O2} based on C%
Test 1	1.88	0.0166	0.0123	Not detected	89%	1.84	1.66
Test 2	1.88	0.0185	0.0120	Not detected	89%	1.85	1.66
Test 3	1.85	0.0157	0.0111	Not detected	87%	1.84	1.63
Average	1.87 ± 0.02	0.0169 ± 0.0017	0.0118 ± 0.0007	-	88.3%	1.84 ± 0.01	1.65 ± 0.02

Steps To Solve Carbon Balance Issue

- Recalibration of pitot tube & gas analyzers using multi-point calibration
- Reduction of orifice diameter in duct to improve mixing
- Implementation of Flame Ionization Detector (FID) for more accurate measurement of unburned hydrocarbons

The implementation of these steps led to an overall improvement in the carbon balance within the system, with the C% of PMMA tests achieving 99%.

Integral yields (gram species/ gram of fuel) of PMMA @ 50kW/m2 after carbon balance discrepancy

Test No.	Y_{CO2}	Y_{CO}	Y_{soot}	Y_{THC}	C%	Y_{O2}	Y_{O2} based on C%
1	2.07	0.0237	0.0131	0.0183	99.7	2.06	1.83
2	2.05	0.0220	0.0130	0.0164	98.3	2.02	1.81
3	2.06	0.0201	0.0129	0.0145	98.7	2.04	1.82
Average	2.06 ±0.01	0.0219±0.002	0.0130±0.0001	0.0164±0.0021	98.9 ±0.8	2.04±0.02	1.82±0.01

*While the carbon balance is acceptable and satisfactory, the oxygen consumption yield exceeds the reference value by approximately 10%.

Constant Equivalence Ratio Tests

- In FPA, the global equivalence ratio can be defined as $\phi = \frac{(\frac{\dot{m}_{fuel}}{\dot{m}_{O2}})_{actual}}{(\frac{\dot{m}_{fuel}}{\dot{m}_{O2}})_{Ref}}$

- The average mass loss rate of these three tests is used as $\dot{m}_{fuel}$ in $(\frac{\dot{m}_{fuel}}{\dot{m}_{O2}})_{actual}$. Then, $\dot{m}_{O2}$ is calculated for each target ϕ.

- Air flow rate is controlled to maintain a constant fuel to oxygen ratio

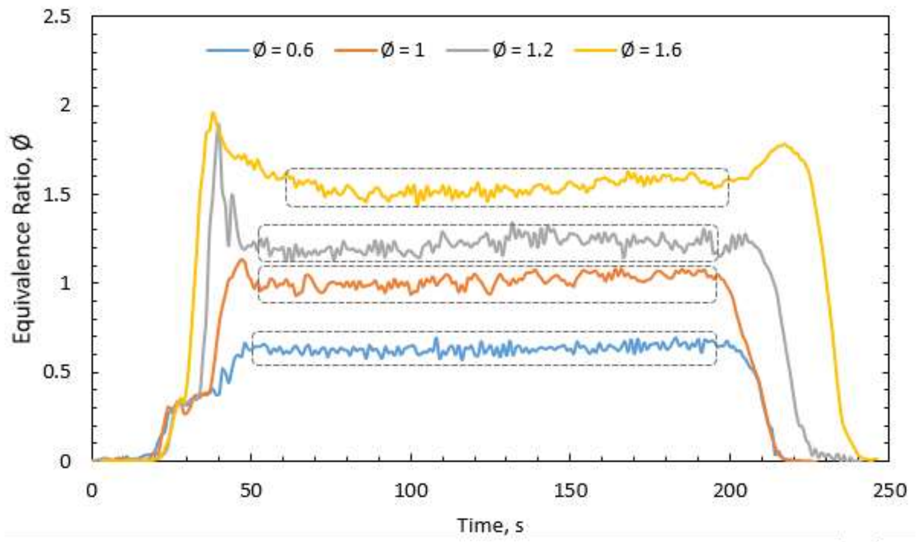


Fig. 5. Global equivalence ratio during controlled tests. Notice the nearly constant range highlighted for each case.

$$\phi = \frac{(\frac{\dot{m}_{fuel}}{\dot{m}_{O2}})_{actual}}{(\frac{\dot{m}_{fuel}}{\dot{m}_{O2}})_{Ref}}$$

Is measured from the spec tests ($\dot{m}_{fuel}$)

Is measured from well-ventilated tests. For PMMA: 0.54 ($(\frac{\dot{m}_{fuel}}{\dot{m}_{O2}})_{Ref}$)

It should be noted that these tests were conducted before addressing the carbon balance issue

Integral yields (g species/ g fuel) for combustion products and consumed oxygen for PMMA under controlled ϕ.

	Y_{CO2}	Y_{CO}	Y_{soot}	Y_{THC}	C %	Y_{O2}	Y_{O2} Based on C%
Ø=0.6	1.76±0.06	0.0158±0.005	0.0119±0.006	Not Detected	83%	1.76±0.05	1.55±0.05
Ø=1	1.53±0.05	0.0765±0.007	0.0177±0.002	Not Detected	78%	1.64±0.11	1.41± 0.07
Ø=1.2	1.35±0.03	0.1320±0.004	0.0258±0.0005	Not Detected	75%	1.46±0.02	1.30±0.03
Ø=1.6	1.18±0.03	0.1679±0.002	0.0397±0.0002	Not Detected	73%	1.29±0.03	1.20±0.03

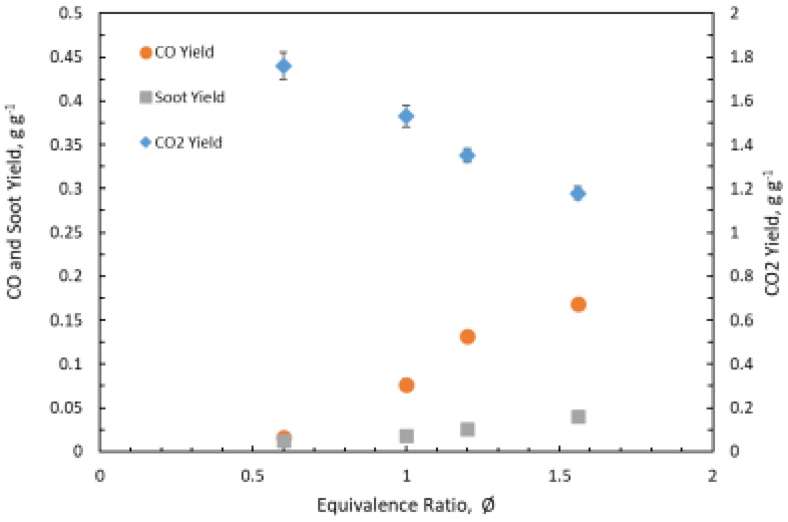
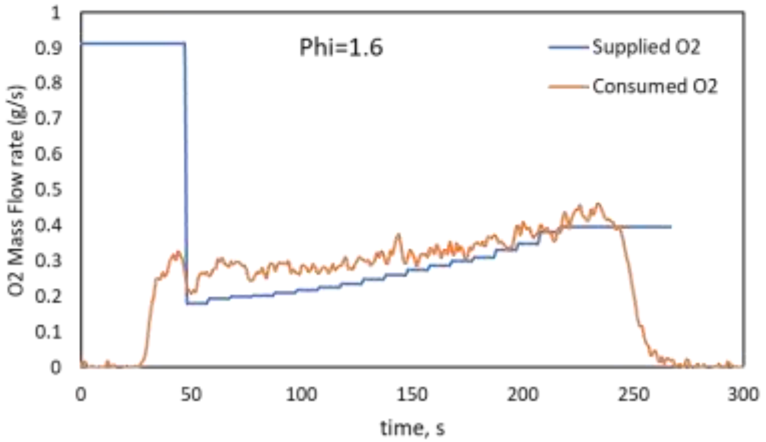


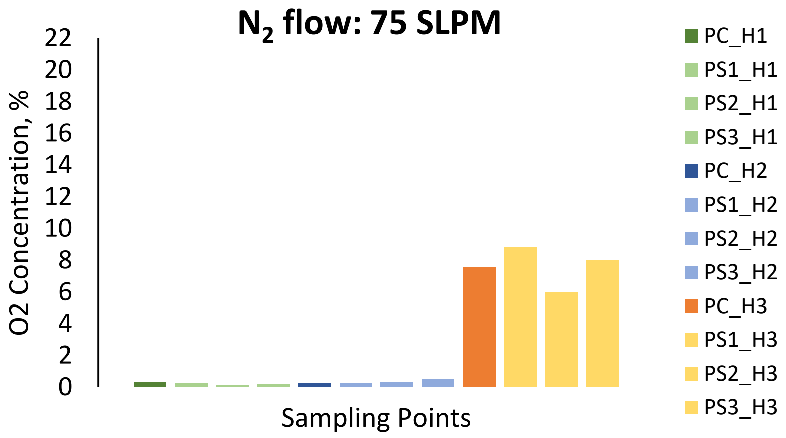
Fig. 6. Integrated yields for products of combustion of PMMA under controlled ϕ.

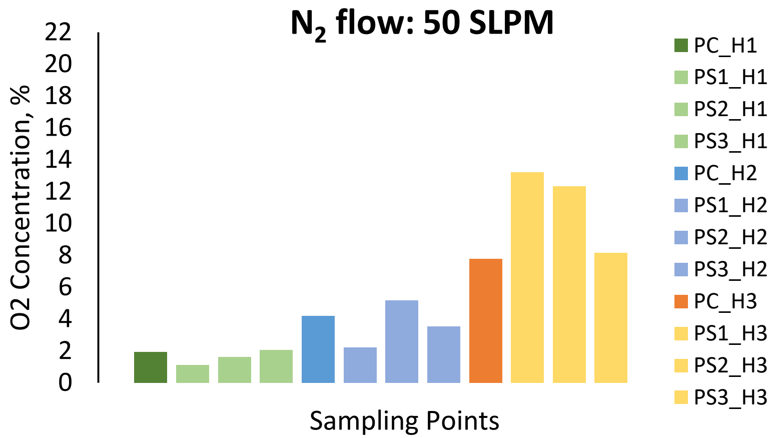
Addressing Air Entrainment Challenges in Constant ϕ Tests: Proposed Solutions

- Observation of air entrainment into the quartz tube from the top
- air entrainment from the bottom is initially low during the test
- Solution approach involves substituting nitrogen for air at various flow rates
- The absence of air backflow into the quartz tube should result in O_2 readings of zero

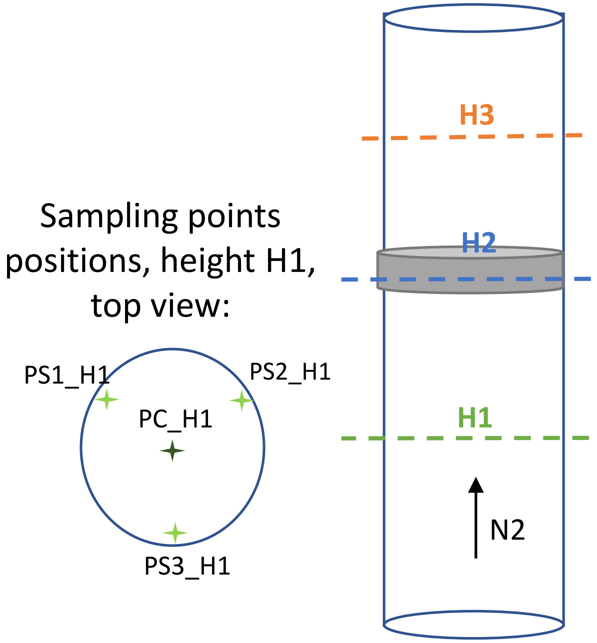


Comparison of supplied & consumed O2 at constant ϕ





O2 concentration measurement at different positions and nitrogen flow rate of 50 and 75SLPM. At 50 SLPM there is noticeable air backflow into the quartz tube at different heights, while at 75 SLPM air cannot reach the lower heights (H2 and H1)



Positions of sampling in the quartz tube at three heights

Summary & Future Plans

- Corrected issues of air entrainment, carbon balance errors and inaccurate hydrocarbon measurements
- Hydrocarbons were not detected in preliminary tests. A new, more sensitive, FID analyzer was added to address this.
- Experiments across a wider range of equivalence ratios will be conducted for different types of polymers.
- Results will be compared with the FAA ANG E-21 microscale combustion calorimeter data.
- Study effects of reducing oxygen by adding nitrogen to the system & compare to results from controlling the oxygen by varying the flow rates

Presentation of Preliminary Research Findings:
Preliminary results of this research were showcased as a poster presentation at FRPM 2023 (Switzerland) and IAFSS 2023 (Japan).