Current Lithium-ion battery fire research at Texas A&M University

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TEXAS A&M UNIVERSITY

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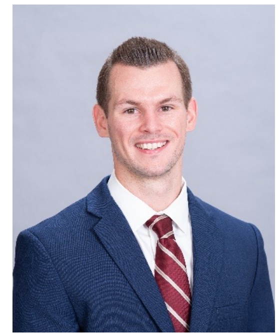

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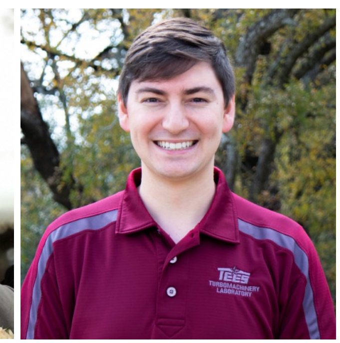

Mattias Turner

Outline

1. Introduction/Context
2. Fundamental Combustion properties of Li-ion battery electrolyte components
3. Fire suppressants for Li-ion battery electrolyte
4. Flammable thermal runaway gas (TRG)
   - Chemical equilibrium analysis (CEA) method for composition prediction
   - Experimental study of combustion properties

Introduction

Flammability of Li-ion batteries' electrolyte is a safety hazard

Electrolyte flammability

- Many fire incidents (cell phones, cars, cargo planes...)
- Need for a thermal control unit (weight addition for aerospace industry) or…
- Reduce/suppress flammability of electrolyte (fire suppressant agent(s) addition)

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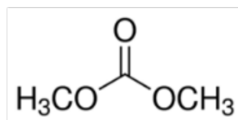
- Shock tubes (ignition delay time, CO and H_2O laser absorption) and closed vessels (laminar flame speed, lower flammability limit) to study combustion properties of:
  - Electrolyte's components
  - Battery thermal runaway gases (TRG)
  - Effect of fire suppressants

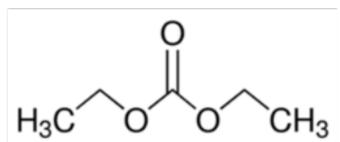
Outline

1. Introduction/Context
2. **Fundamental Combustion properties of Li-ion battery electrolyte components**

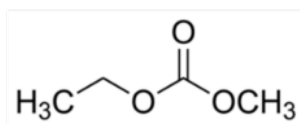
Linear Carbonates



DiMethyl Carbonate (DMC)

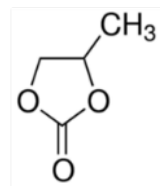


DiEthyl Carbonate (DEC)

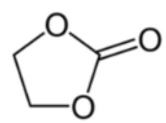


EthylMethyl Carbonate (EMC)

Cyclic Carbonates



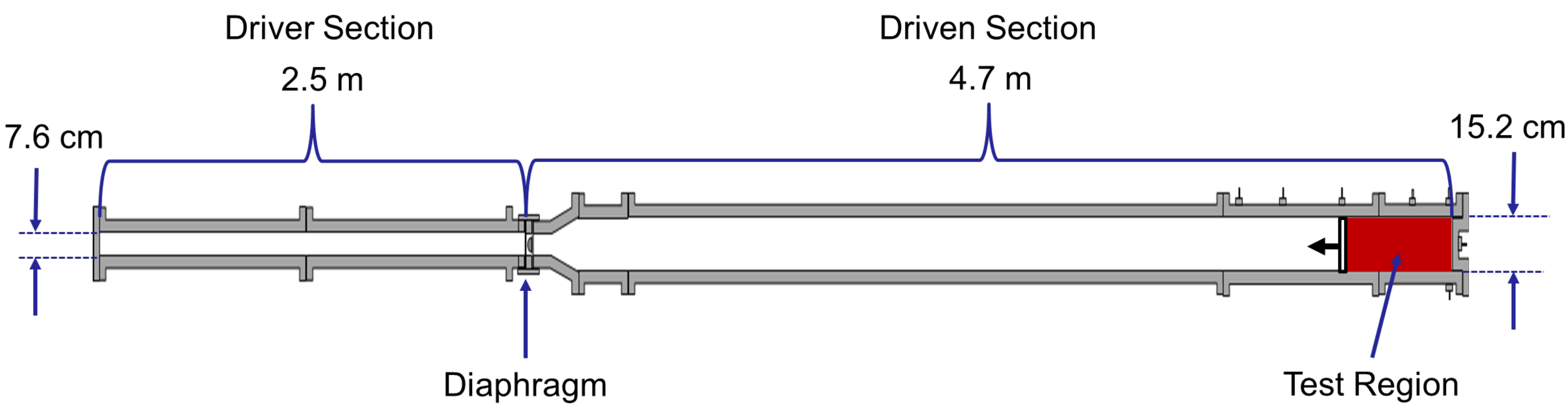
Propylene Carbonate (PC)



Ethylene Carbonate (EC)

Experimental Setup

Shock Tube

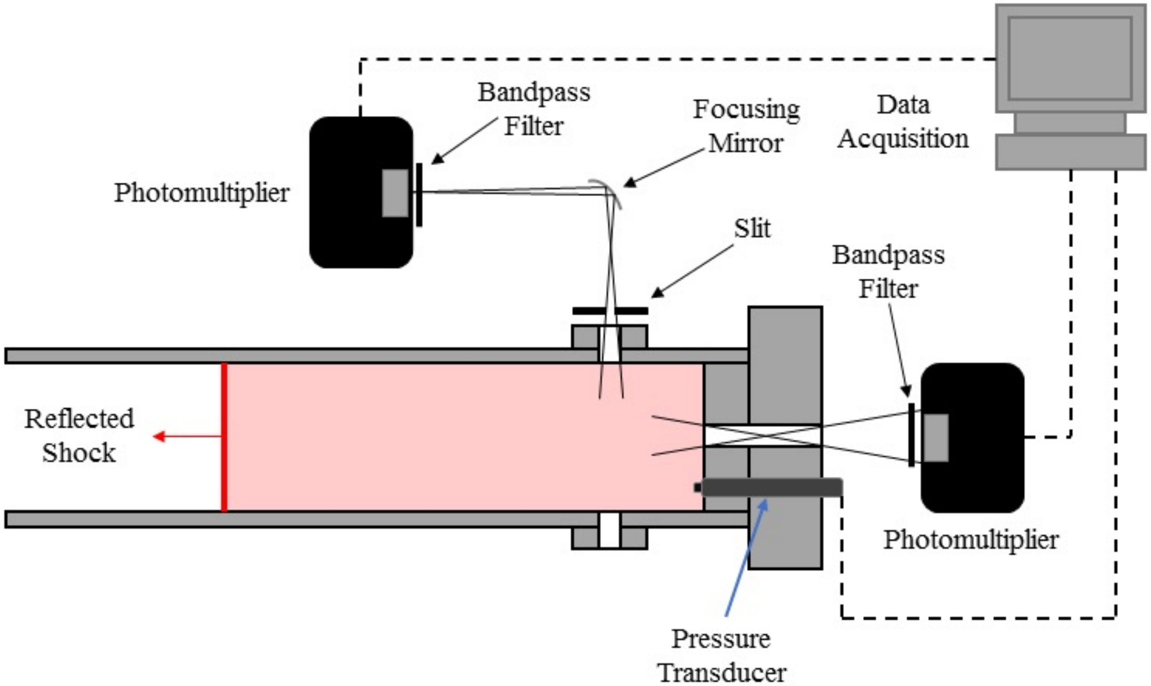


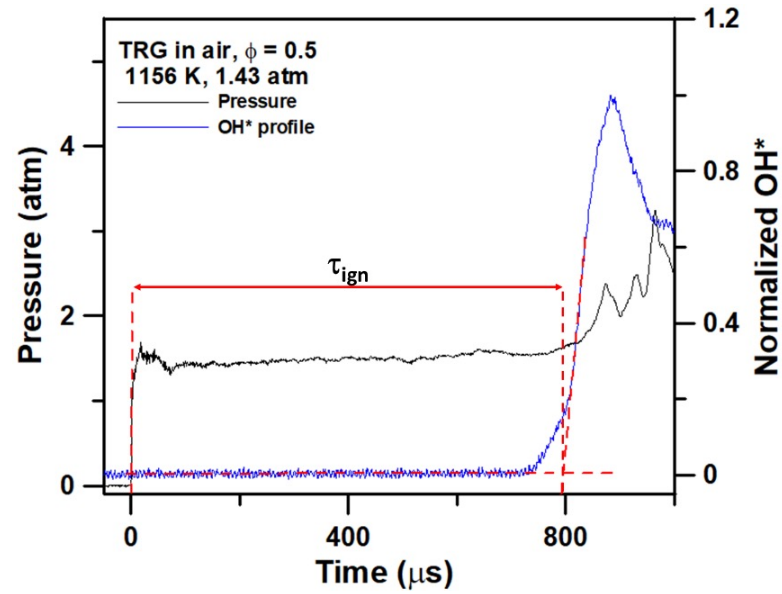
Driven section evacuated to 10^{-5} torr
(Turbomolecular pump)

Experimental Setup

Ignition Diagnostic

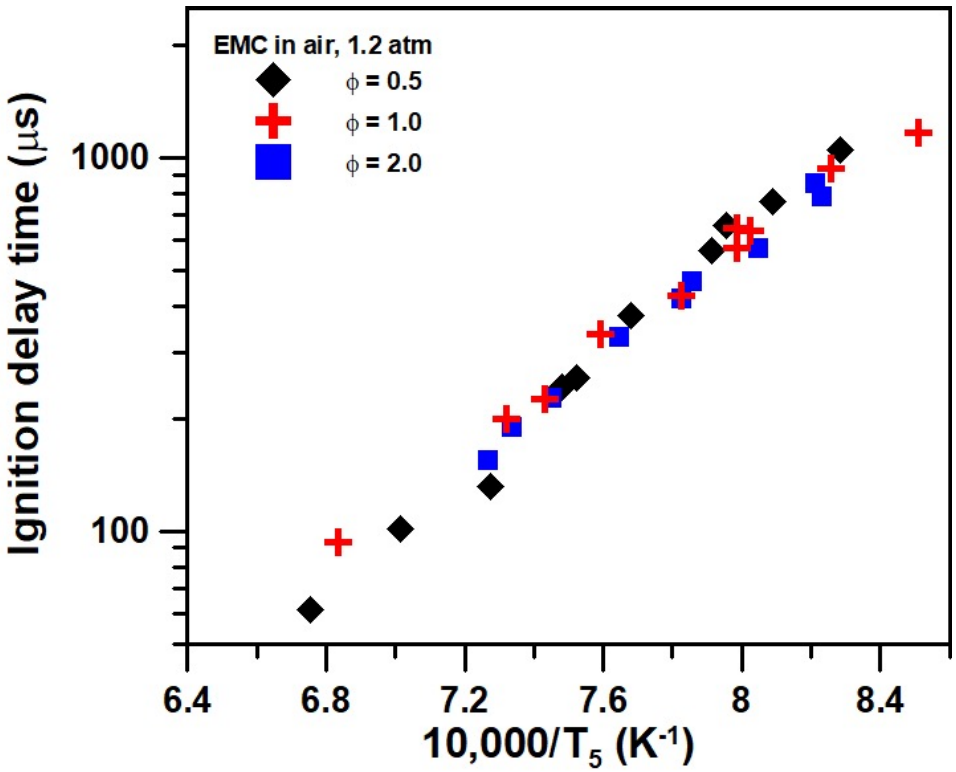
Endwall Region of the Shock Tube

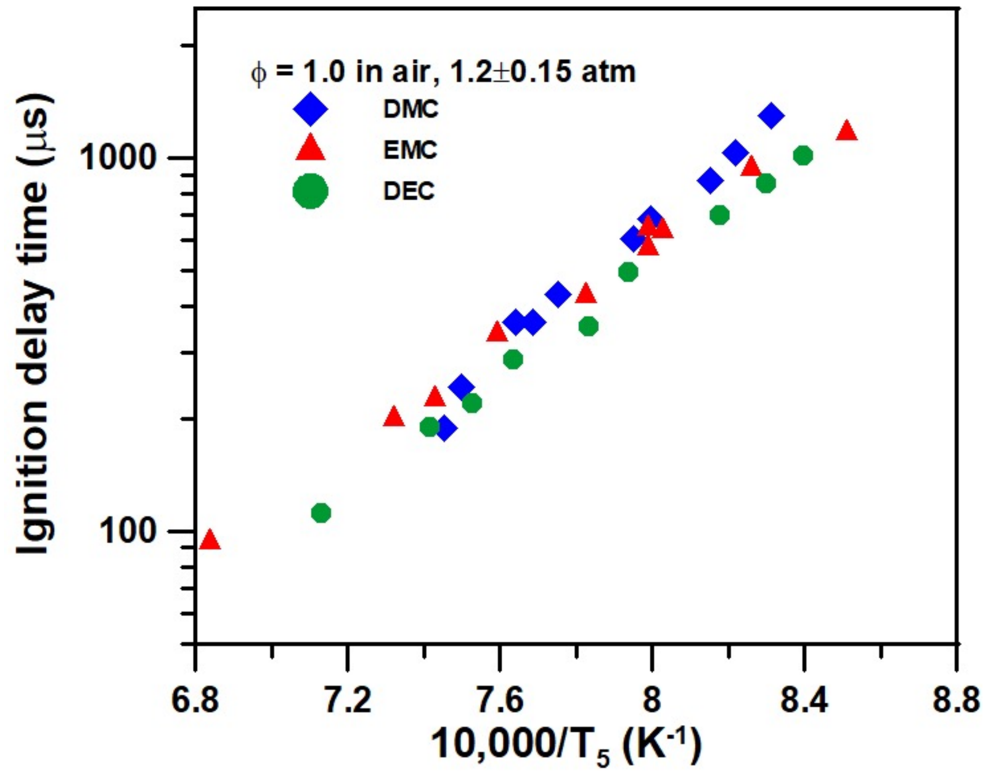




Results – Ignition delay time for linear carbonates

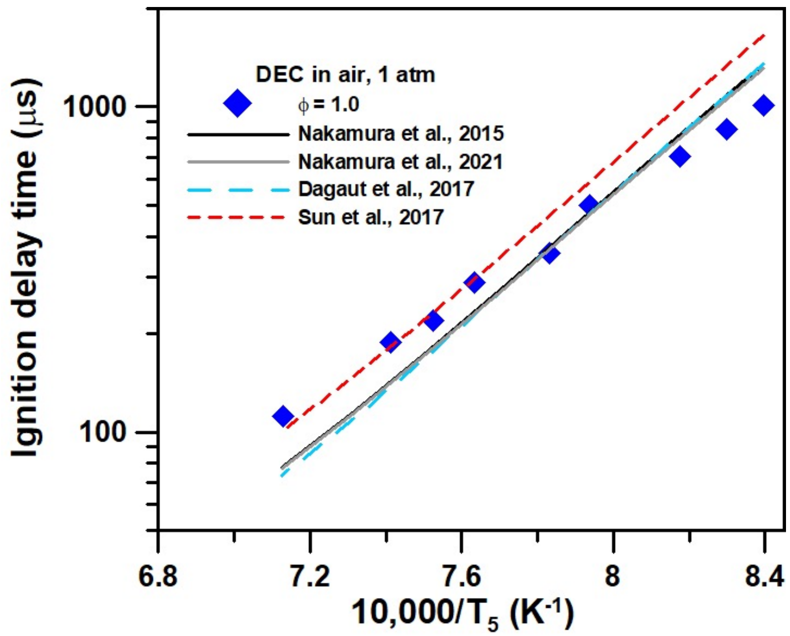
Lack of effect of equivalence ratio and molecular structure

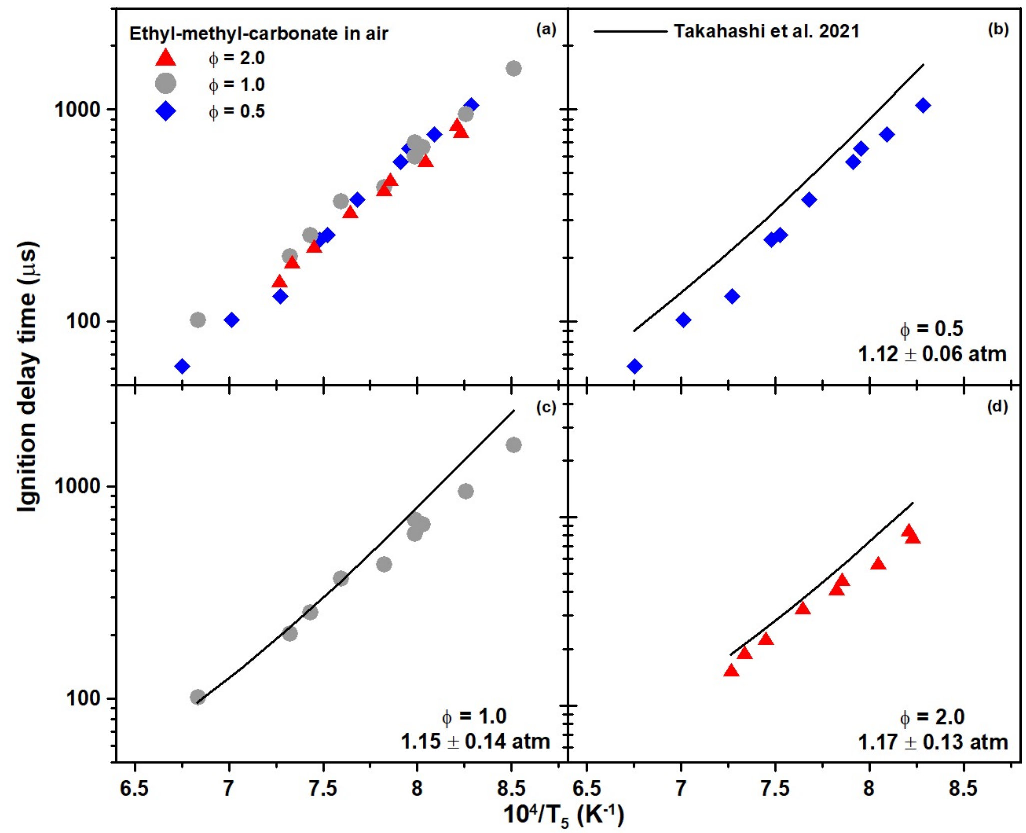




Results – Ignition delay time for linear carbonates

Models in good agreement with the new data but still could be improved



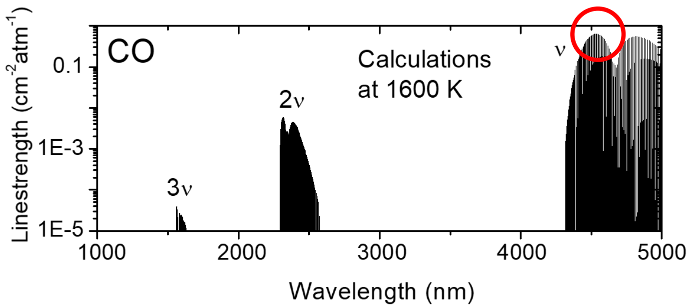


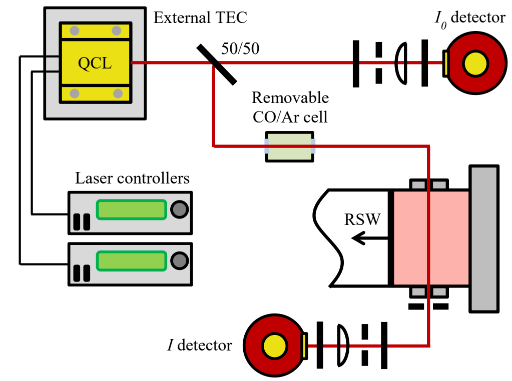
Experimental Setup – Laser Diagnostics

CO and H_2O laser diagnostics implemented on the TAMU shock tubes

CO Laser Diagnostic

- Quantum cascade laser (QCL)
- Matched InSb photodetectors
- Removable CO/Ar cell
- Fundamental ($\Delta\nu = 1$) CO band
- R(12), $\nu'' = 0$ transition (4566.17 nm)

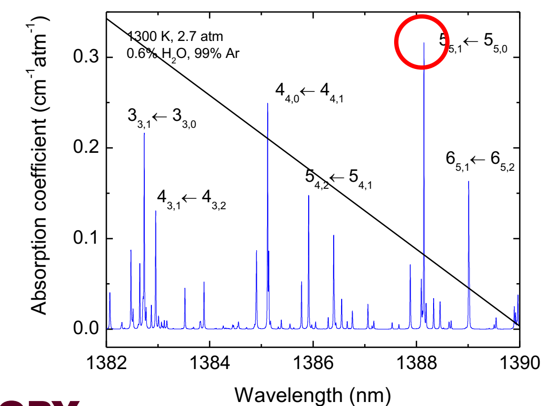


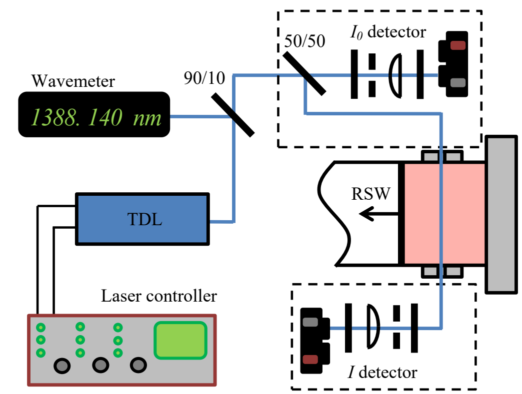


$$\frac{I}{I_0} = \exp(-k_\nu LPX_i)$$

H_2O Laser Diagnostic

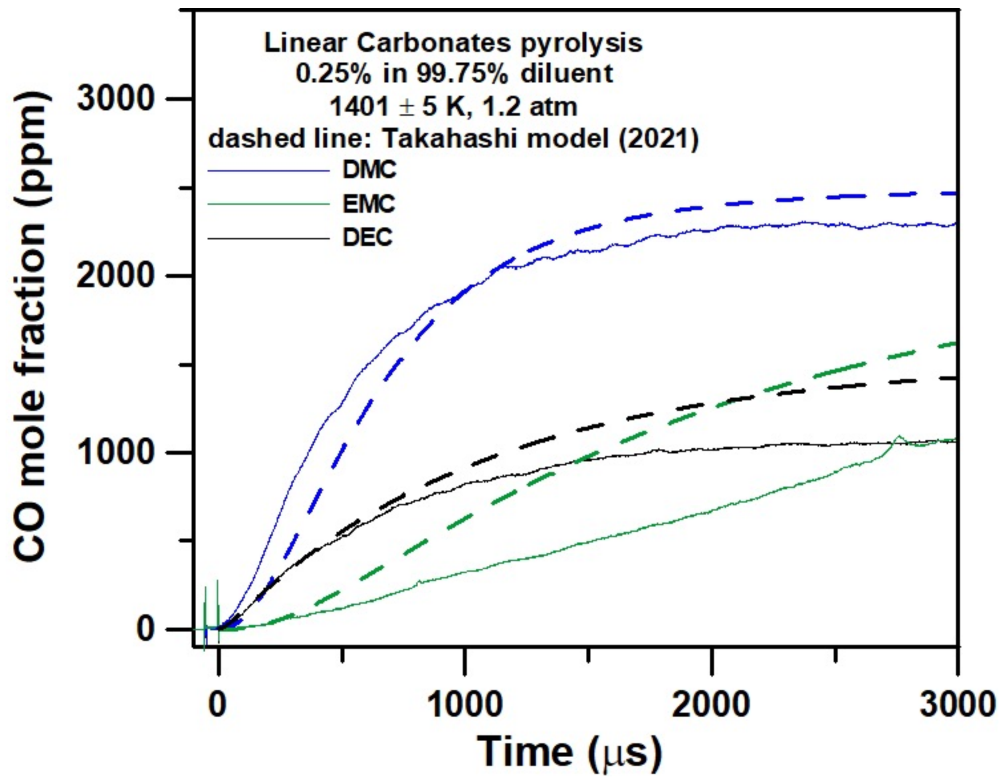
- Tunable diode laser (TDL)
- InGaAs photodetectors
- Lexan enclosures (N_2, < 0.1% RH)
- The $\nu_1 + \nu_3$ combination band
- $5_{5,1} \leftarrow 5_{5,0}$ transition (1388.139 nm)
- No interference from CO or CO_2

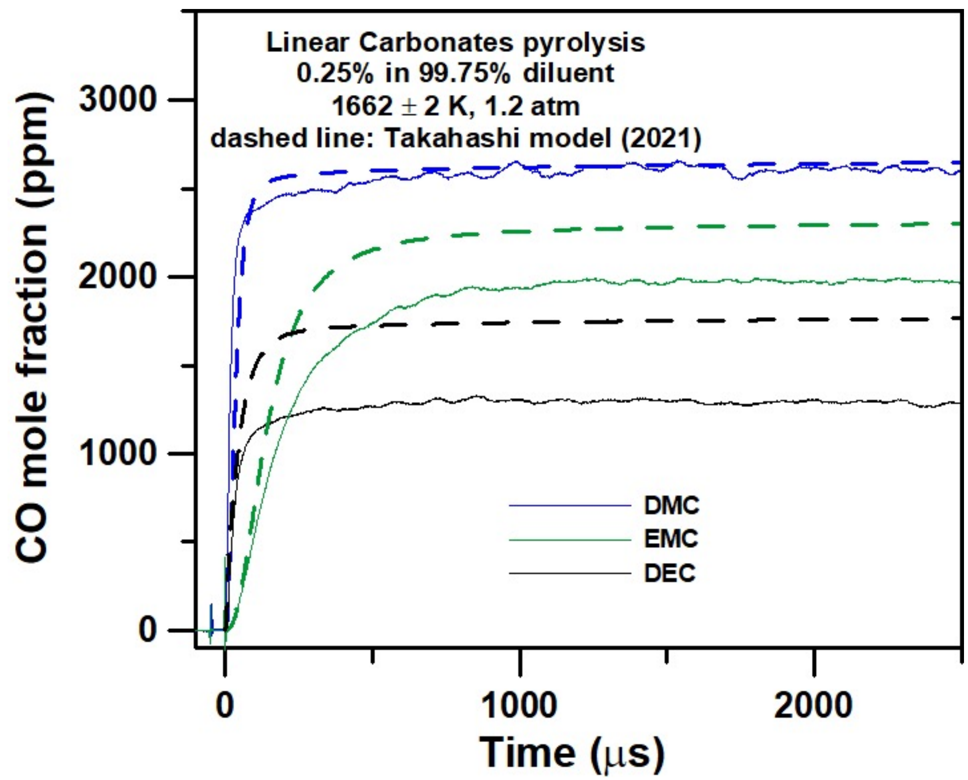




Results – Ignition delay timen for linear carbonates

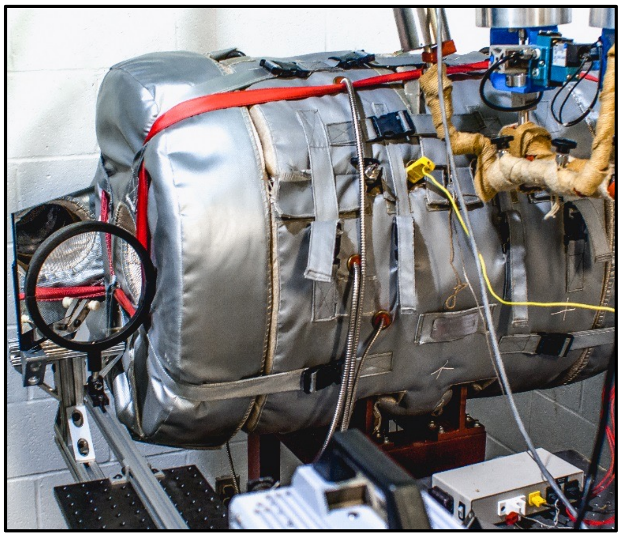
Model needs large improvements





Experimental Setup – Laminar Flame Speed

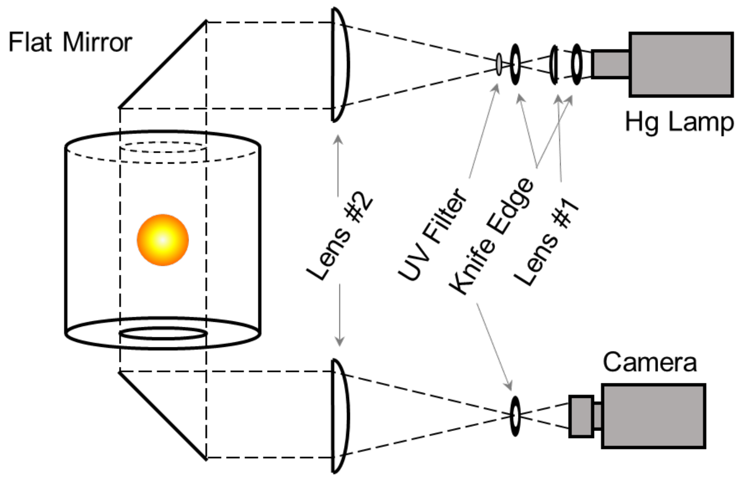
HTHP test vessel used for performing laminar flame speed experiments



- 17-4PH Stainless Steel
- 31.8 cm ID, 27.9 cm length
- Ø**12.7 cm** windows
- Maximum T_0, P_0: **475 K, 10 atm**

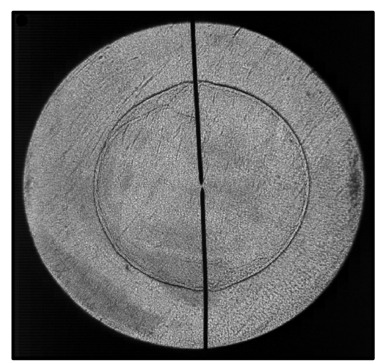
Experimental Setup – Laminar Flame Speed

Schlieren setup is used to monitor flame



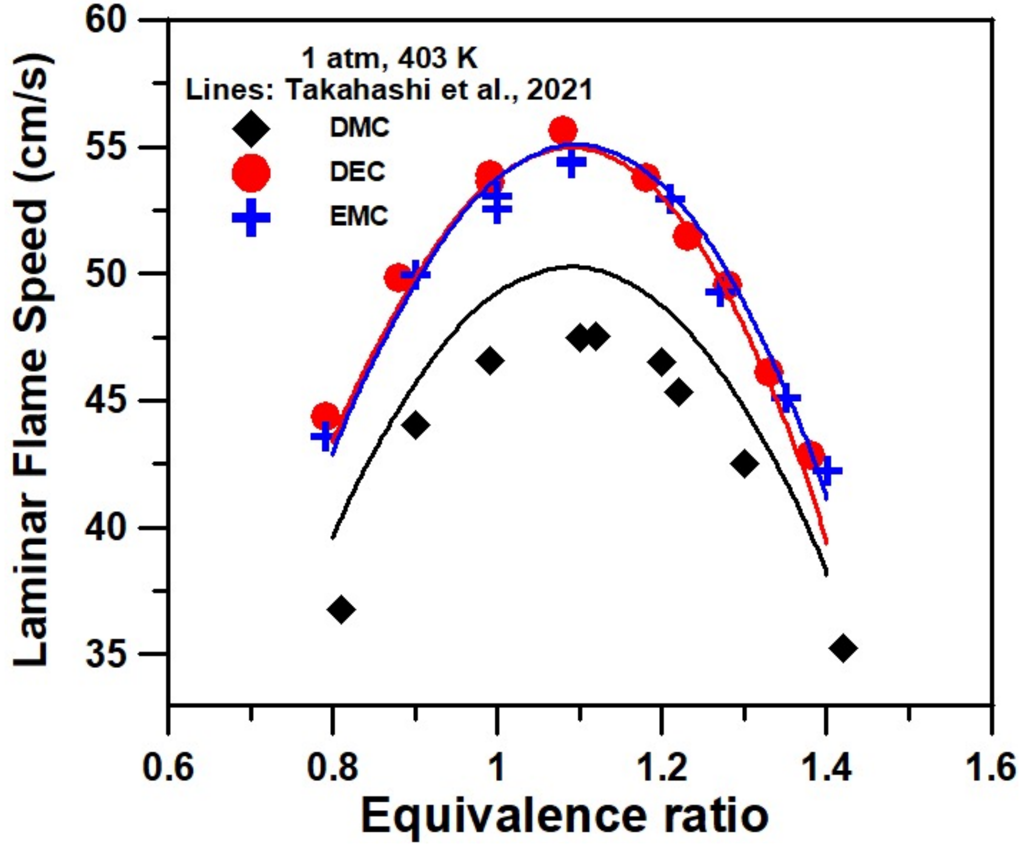
Lens #1: Plano-convex lens, Ø50.8 mm, f = 100 mm
Lens #2: Plano-convex lens, Ø200 mm, f = 800 mm

- Mercury arc lamp
- Circular knife edge
- Photron FastCam SA1.1 (8000 – 22,500 fps)



Results – Laminar Flame Speed for linear carbonates

Experimental trends captured by modern detailed kinetics mechanisms



DMC predictions improved in recent TAMU model (Atherley et al., 2021)

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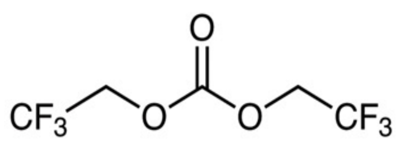
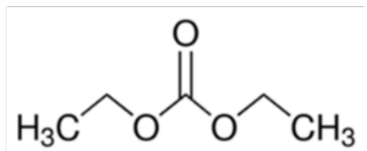
Fire suppressants for Li-ion battery electrolyte

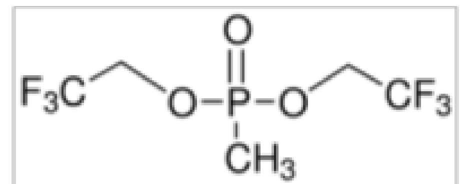
Several kinds of fire suppressants considered



Di (2,2,2 trifluoroethyl) Carbonate (DtFEC)



DiEthyl Carbonate (DEC)



Bis (2,2,2 trifluoroethyl) Phosphonate

Similar structure w/ electrolyte components

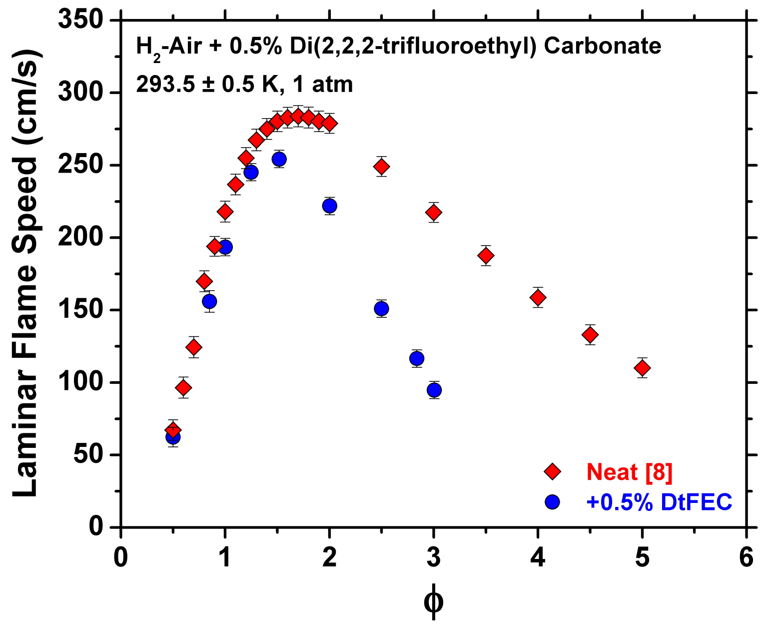
Fire suppressants for Li-ion battery electrolyte

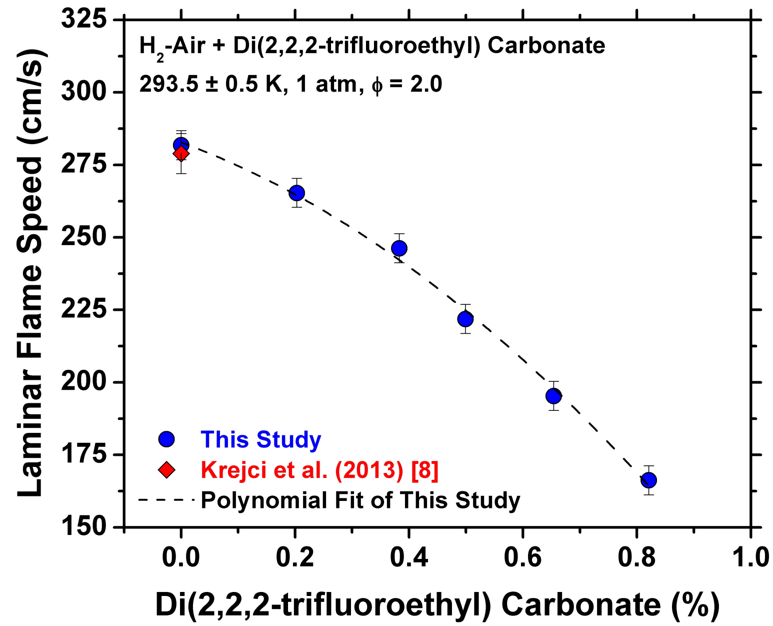
Way to assess the fire suppressant effectiveness

- Add a small proportion of fire suppressant to well-known fuels (H_2, CH_4)
- Fundamental combustion properties => comparison between neat and seeded mixtures
  - Ignition delay time
  - Laminar flame speed
- Method used with Halons (CF_3Br, CF_3I, CF_2BrCl, C_2HF_5…), and Organophosphorus (DMMP, DEMP, DIMP, TEP...)

Results – Di(2,2,2 trifluoroethyl)Carbonate (DtFEC)

LFS Results: Large effect of 0.5% DtFEC addition with H_2 (ϕ >1.5)

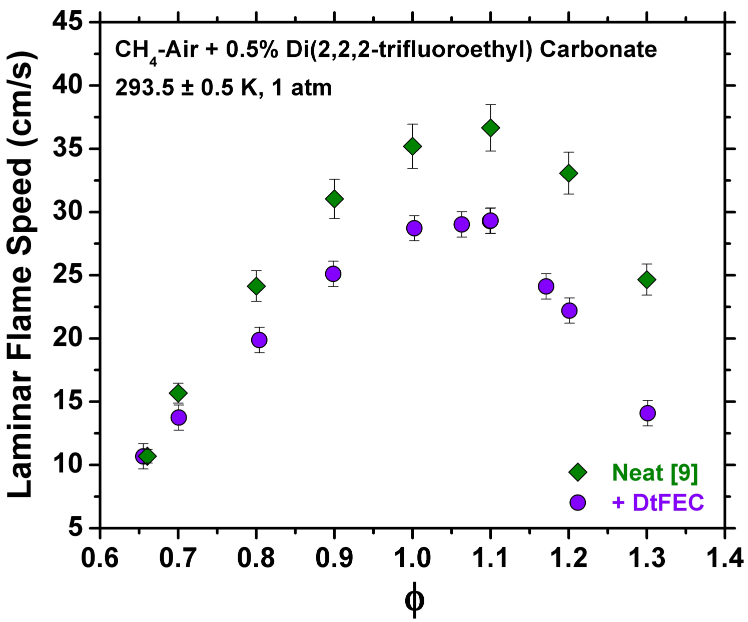


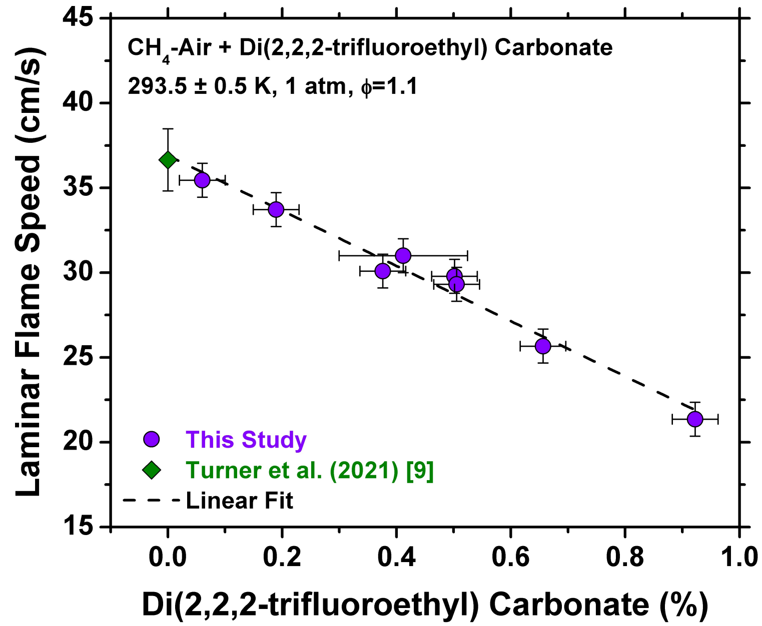


Fire suppressant effect proportional to DtFEC concentration

Results – Di(2,2,2 trifluoroethyl)Carbonate (DtFEC)

LFS Results: Large effect of 0.5% DtFEC addition with CH_4

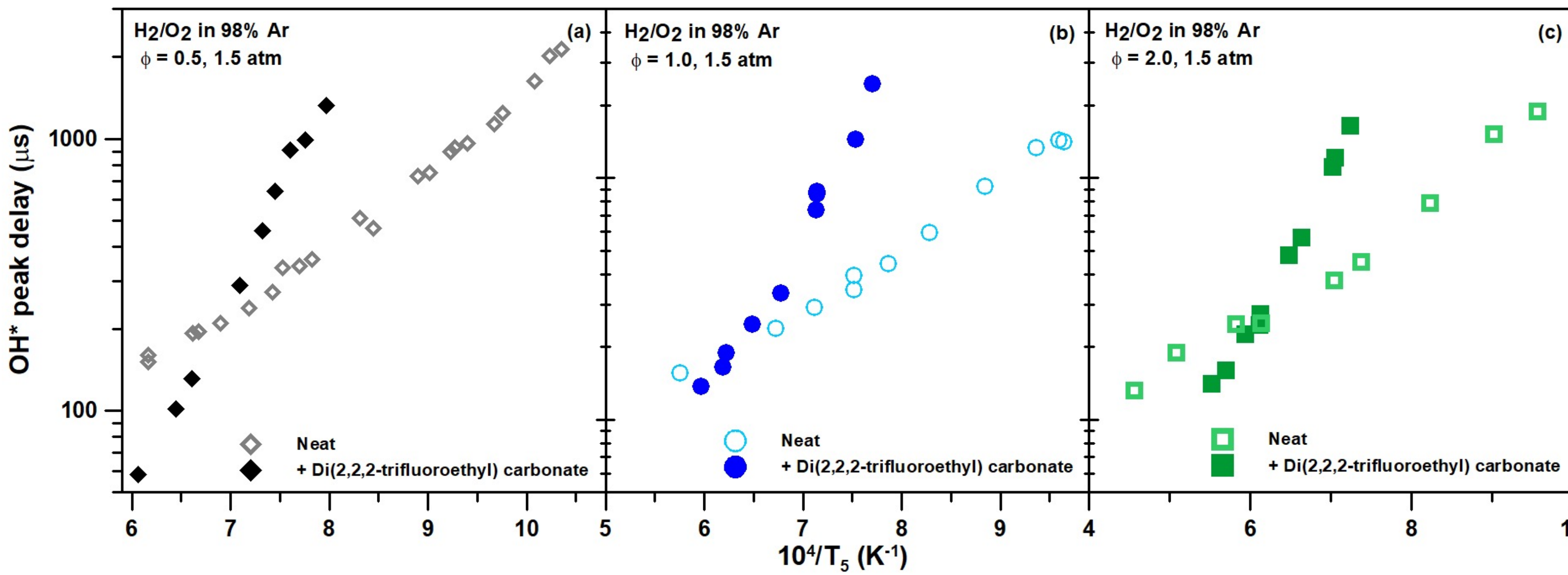




Fire suppressant effect proportional to DtFEC concentration

Results – Di(2,2,2 trifluoroethyl)Carbonate (DtFEC)

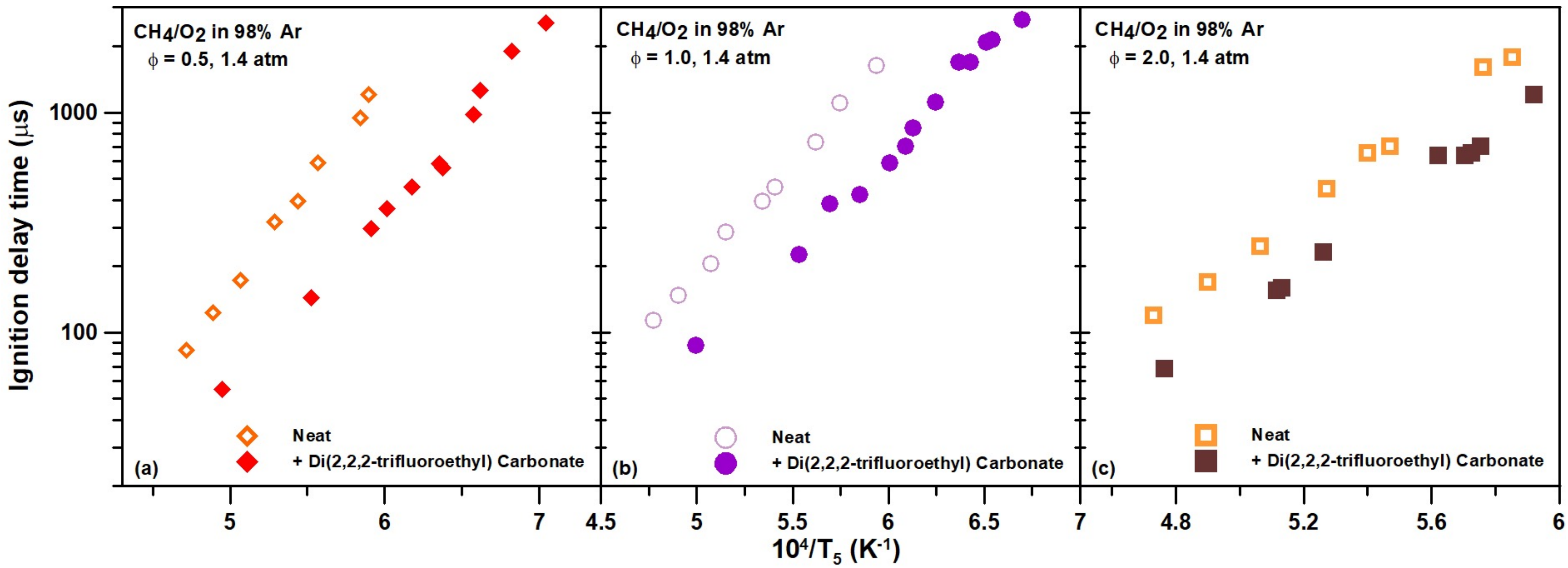
Shock Tube results: 10% of Fuel as DtFEC



Large change in the slope (global activation energy)

Results – Di(2,2,2 trifluoroethyl)Carbonate (DtFEC)

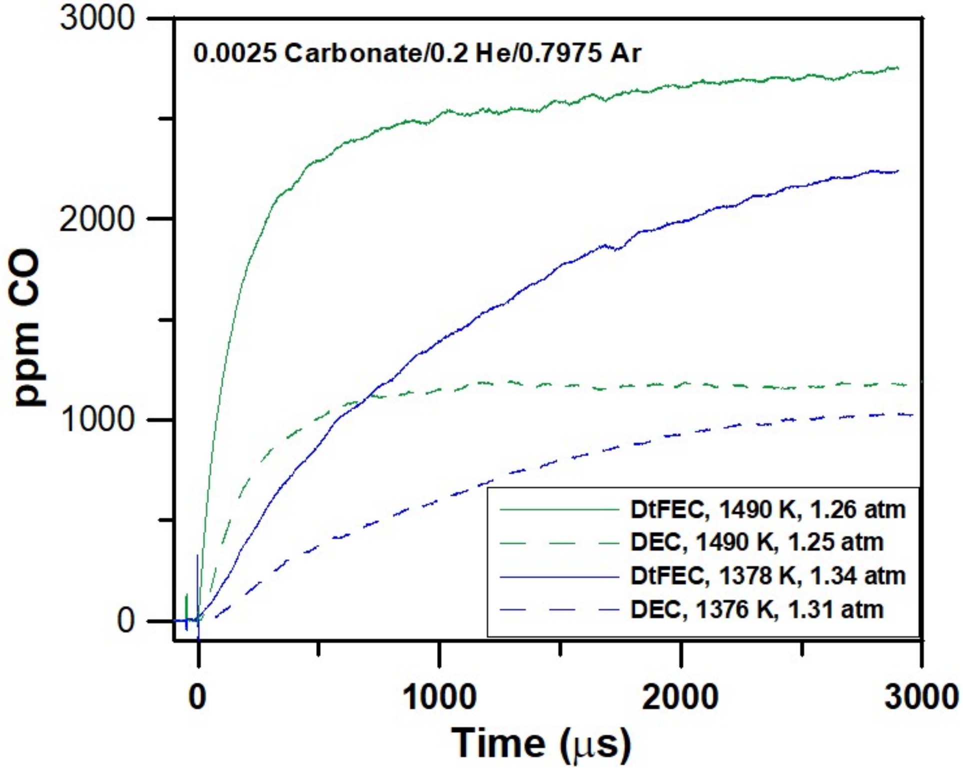
Shock Tube results: 10% of Fuel as DtFEC

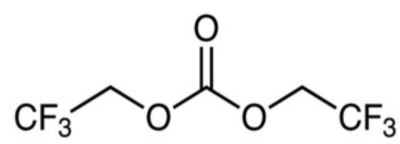


Significant difference of fire suppressant effect compared to H_2

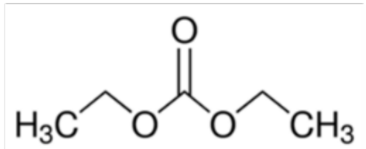
Results – Di(2,2,2 trifluoroethyl)Carbonate (DtFEC)

CO profile during pyrolysis – Comparison with DEC





DtFEC



DEC

Similar structure but F atoms (DtFEC) instead of H atoms (DEC)

=> radically changes the pyrolysis chemistry.

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4. **Flammable thermal runaway gas (TRG)**
    - **Chemical equilibrium analysis (CEA) method for composition prediction**
    - **Experimental study of combustion properties**

LIB CEA Motivation

The current approach to LIB TR hazard analysis is not a priori and can be expensive

- **Problem Statement:** Significant energy, toxic gases, and potentially combustible gases are released during thermal runaway of LIBs, which all represent potential hazards

- **Current Approach:** Evaluation of these hazards by inducing electrolyte decomposition or LIB thermal runaway in abuse experiments

- **Objective:** 1) Develop an a priori modeling approach
  2) Validate against existing experimental data
  3) Apply to various LIB chemistries, designs, conditions, etc.

Overview of Chemical Equilibrium Analysis (CEA)

CEA is utilized to predict reaction equilibrium conditions

Input Parameters:

1) Cell Composition
- Anode, Cathode, Electrolyte, etc.
- Mass concentration and ΔH_f^0

2) Ambient Conditions
- Pressure (ambient vs. vacuum)
- Gas Composition (air, ISS, or vacuum)

Conservation of Elements

Thermodynamic Libraries

Potential Product Properties: $C_p(T)$, $H(T)$, $S(T)$

Minimization of Gibbs Free Energy (G):

$$\Delta G = \Delta H - T\Delta S$$

CEA Software:

LIB Thermal Runaway

Commercial or free software:

NASA CEA
Praqsys CEQUEL
LLNL Cheetah

Various modeling systems:

T, P | H, P | T, V | U, V

Computation Output(s):

1) Reaction Product Chemistry
- Relative product concentrations
- Product phase (condensed vs. gaseous)

2) System Temperature

3) Total Heat Release

Equilibrium Constants:

$$\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$$

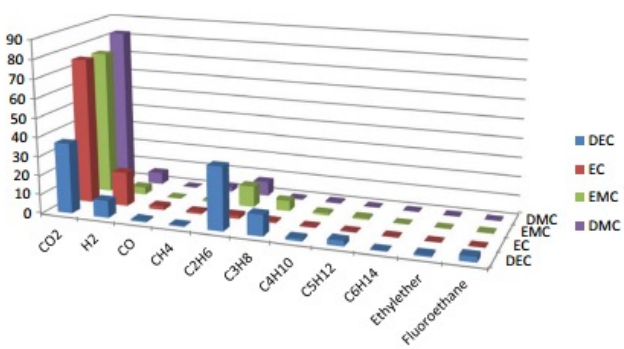
$$K = \frac{[C]^{\gamma}[D]^{\delta}}{[A]^{\alpha}[B]^{\beta}}$$

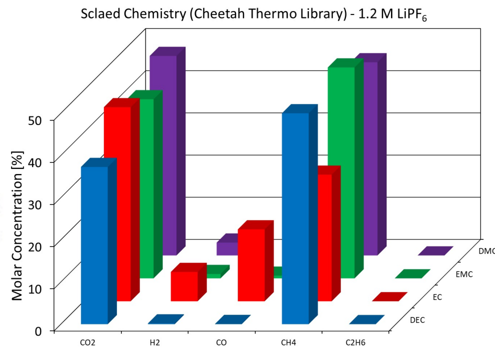
$$K = e^{-\Delta G^0 / RT}$$

CEA Modeling – Results and Trends

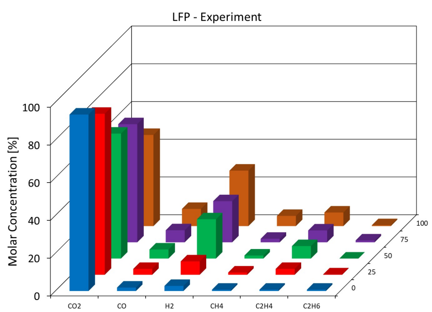
Good agreement for plain electrolyte experiments, discrepancies for full LIB

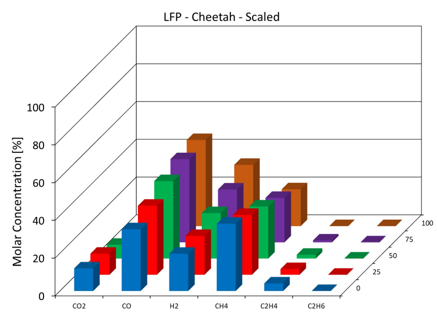
Example Results: Electrolyte Decomposition (ARC Experiments)





Example Results: LFP Battery Thermal Runaway (CV Bomb TR)





Key Findings:

- Moderate agreement observed between computations and experiments
- Modeling refinements:
  - Missing products (electrolytes, etc.)
  - Restrictive cathode decomposition
- Experiments can be improved
  - Pre-experiment characterization
  - Detect condensable gases (electrolytes, water, etc.)
- CEA has the potential be fully predictive for LIB thermal runaway hazards

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TRG mixture composition determination

Averaged from 40 detailed compositions from the literature

TRG composition varies greatly with:

- **Electrolyte composition**
- **Nature of the electrode**
- **State of charge**
- **Failure environment (air, N_2, Vacuum…)**
- **Etc.**

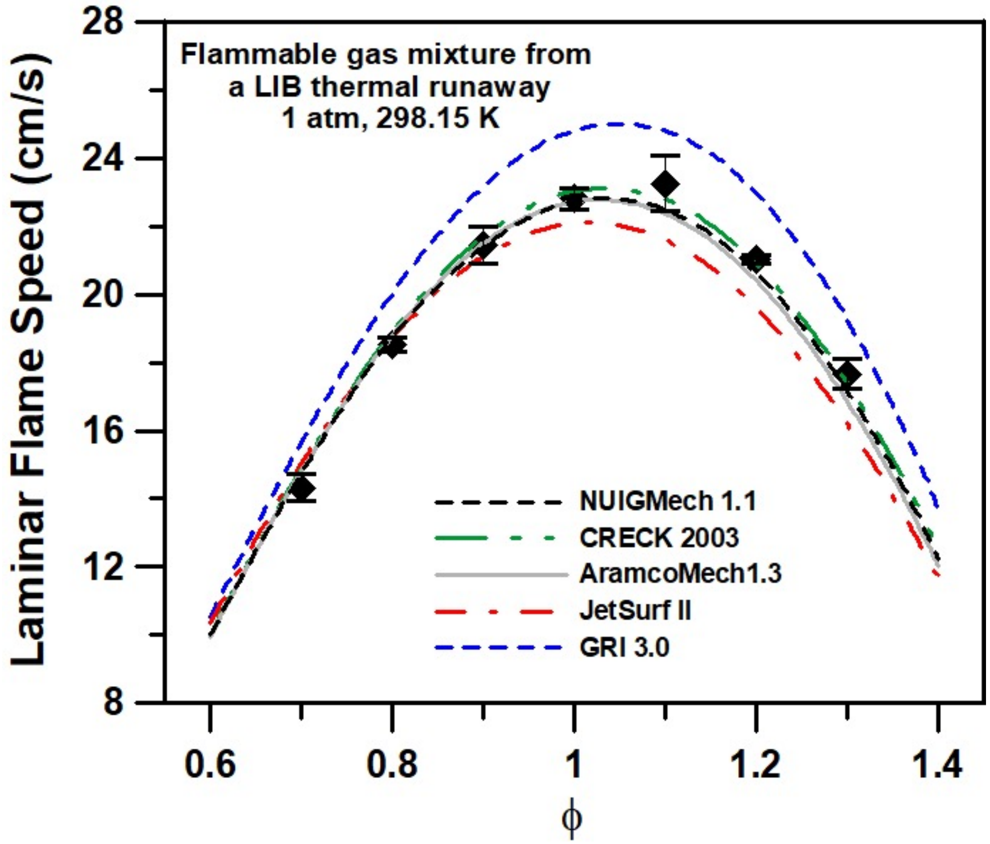
⇒ **Average mixture determined to see if models able to capture combustions properties**

⇒ **If models are accurate, the assumption is that models are good (enough) for any TRG mixture variation**

Fuel	C_3H_8	C_2H_6	C_2H_4	CH_4	H_2	CO	CO_2
Mole fraction	0.007	0.019	0.027	0.119	0.144	0.168	0.516

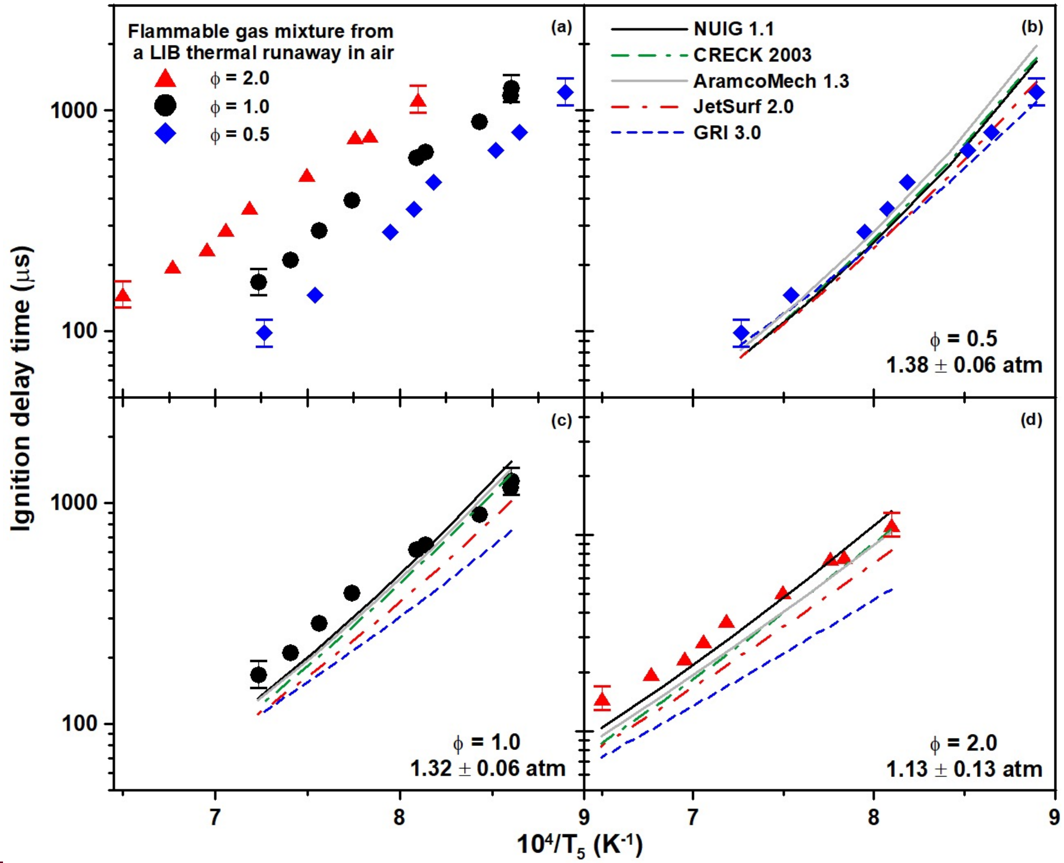
Results – TRG laminar flame speed

Experimental trends captured by modern detailed kinetics mechanisms



Results – TRG Ignition delay time

Experimental trends captured by modern detailed kinetics mechanisms



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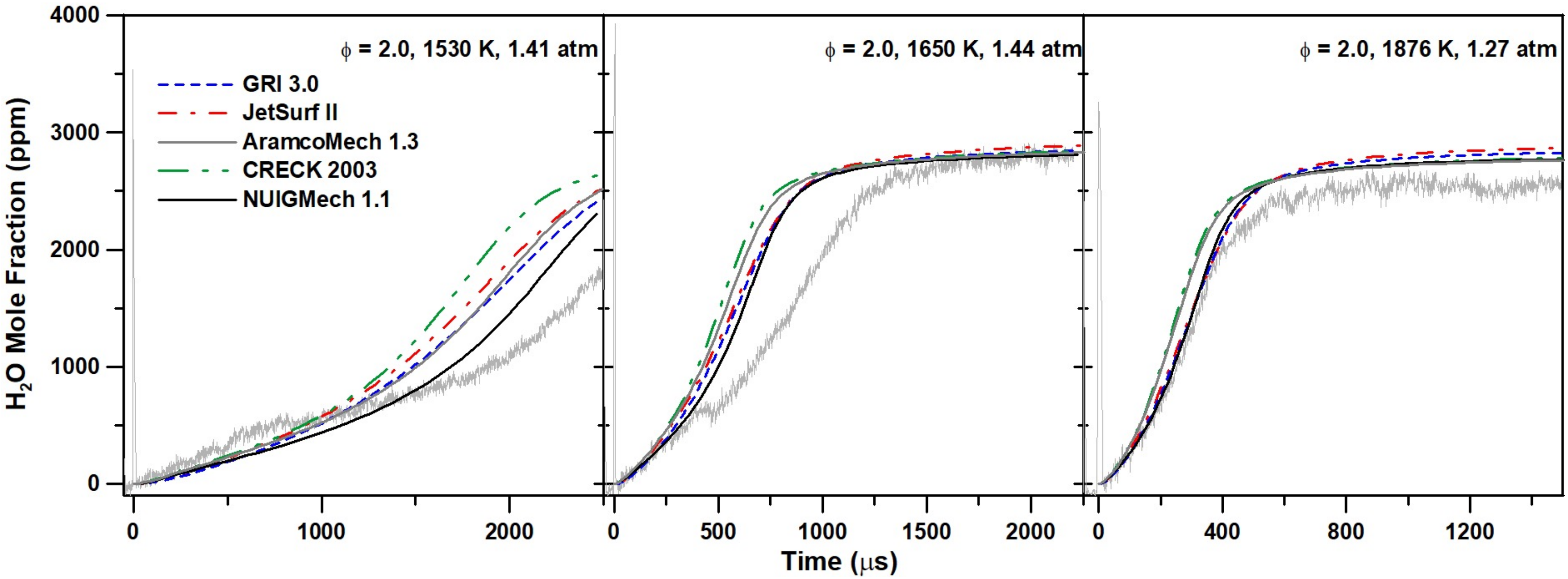
Results – H_2O profiles

Modern detailed kinetics mechanisms can still be improved



Results – Lower Flammability Limit

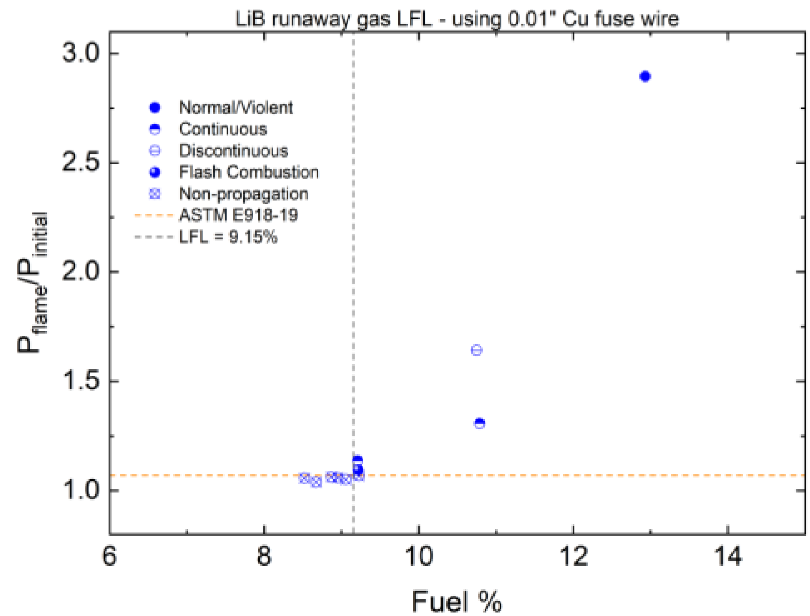
Critical parameter for fire safety in case of thermal runaway + venting

100% – 0% Combustion

100%

0%

- Violent Flame
  - Maximum flame pressure is at least 3 times the initial pressure.
- Continuous
  - Smooth increase in temperature and pressure readings.
- Discontinuous
  - Flame does not reach the top of the vessel, not all thermocouples capture the flame (typically TC3-TC4).
- Flash combustion
  - Flame only reaches the thermocouple closest to the ignitor ($\Delta T_{TC1} < 10$ deg.), $\Delta P \leq 1\ psi$. Observed with Mix 4.
- Non-propagation
  - Negligible temperature and pressure increase after ignition. $\Delta T < 5\ deg., \Delta P < 0.1\ psi$



LFL = 9.15% fuel in air (ϕ = 0.277)

Conclusions

- **New experimental data for Li-ion battery electrolyte combustion**
  - Wide array of techniques, ranging from global kinetics data to laser speciation profiles
  - Effects of fire suppressant candidates on combustion properties
- **Comparison with modern detailed kinetics models**
  - Current models for linear carbonates still need improvement (ongoing)
  - No models available for fire suppressants
    - Models under development in collaboration with ENSTA Paris (Dr. L. Catoire)
- **TRG combustion properties studied**
  - Modern detailed kinetics models capable of predicting satisfactorily the data => may eliminate the need for experiments w/ TRG flammable mixtures
- **Future work on cyclic carbonates (experiments + model) and ultimately unified model for TRG, linear + cyclic carbonates, and fire suppressants**

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