DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

Rapid Construction of Validated Chemistry Models for Advanced Biofuels (EE0007982)

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Co-Optimization of Fuels and Engines

Principal Investigator: William Green
Massachusetts Institute of Technology (MIT)
Co-PI: Subith Vasu, University of Central Florida (UCF)

Goal Statement

- Goal: **Demonstrate capability to rapidly generate accurate combustion chemistry computer models for advanced biofuels**
- Outcomes*:*
  - **Rapid simulation of proposed biofuels in future engines, including fuel effects on performance.**
  - **Faster, more reliable selection of proposed fuels.**
  - **Computer models for each promising biofuel available to engine & fuel designers, accelerating tuning of engines to new fuels and vice-versa.**

Quad Chart Overview

Timeline

- Official Start 1/15/17 (funded 8/1/17)
- Project End Date 3/30/20
- 30% Percent complete

		FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded		4k	263k	626k
Project Cost Share*		3k	40k	56k

•Partners:

MIT (60%)

Univ. Central Florida (40%)

Lab Contact: Bill Pitz (LLNL)

Barriers addressed

ADO-E.
Co-Development of Fuels and Engines

Objective

Develop computer methods for generating computer models for advanced biofuel combustion. Test accuracy of models with laser/shock tube experiments.

End of Project Goal

Demonstrate capability to rapidly generate accurate combustion chemistry computer models for advanced biofuels

1 - Project Overview

- **Many biofuels proposed, but few have been successful.**
  - Significant performance risk as well as economic risk.
- **Various biofuel + future engine combinations have significantly different performance, costs, and societal benefits**
  - Which biofuel + engine combination is best?
  - Much less expensive to explore on computer than by experiment
  - ….but ***need fuel chemistry computer model for each biofuel***
- **Building biofuel models by hand is tedious and challenging**
  - PI expert in ***computer-construction of chemistry models***
- **How to Test Accuracy? A few data on ignition delays, little else**
  - Need measurements at conditions relevant to future engines
  - ***Pre-ignition species time-profiles*** are most useful
  - Co-PI expert in high-sensitivity species measurements

2 – Approach (Management)

- Prof. Green (MIT) is PI, Prof. Vasu (UCF) is the co-PI
  - Green responsible for all the modeling, Vasu for all the experiments
- Project only involves ~6 people total, and we are modeling and measuring the exact same systems, so it is easy to keep in good communication and collaborate
- Broader Co-Optima team involves many people at many institutions, is challenging to stay well-connected with everyone
  - We participate in the Co-Optima meetings and teleconferences
- We have received excellent advice from and collaborate with Bill Pitz (the lead chemistry modeler on Co-Optima team), Mark Nimlos and others at NREL, and Scott Goldsborough (ANL).

2 – Approach (Technical)

- **Computer-constructed models**: Need computer to correctly identify the important species and reactions as model is being constructed
  - If computer misses an important reaction the model will not be accurate
  - If computer includes many unimportant reactions, process is not rapid
  - Often mis-identifications are due to poor thermo or rate estimates
- **Experimental Test of Model Accuracy**: Reliably measure species time profiles
  - Extremely low concentrations pre-ignition, need high sensitivity!
  - Measure absolute T-dependent line-strengths and pressure broadening
- **Some biofuels and intermediates have intramolecular H-bonds**: Develop methods to compute their thermo & rates
  - Developing high-accuracy method and also fast estimation method
- **Some fuel mixtures too complicated for computer modeling alone**: Correctly combine modeling with a few lab experiments

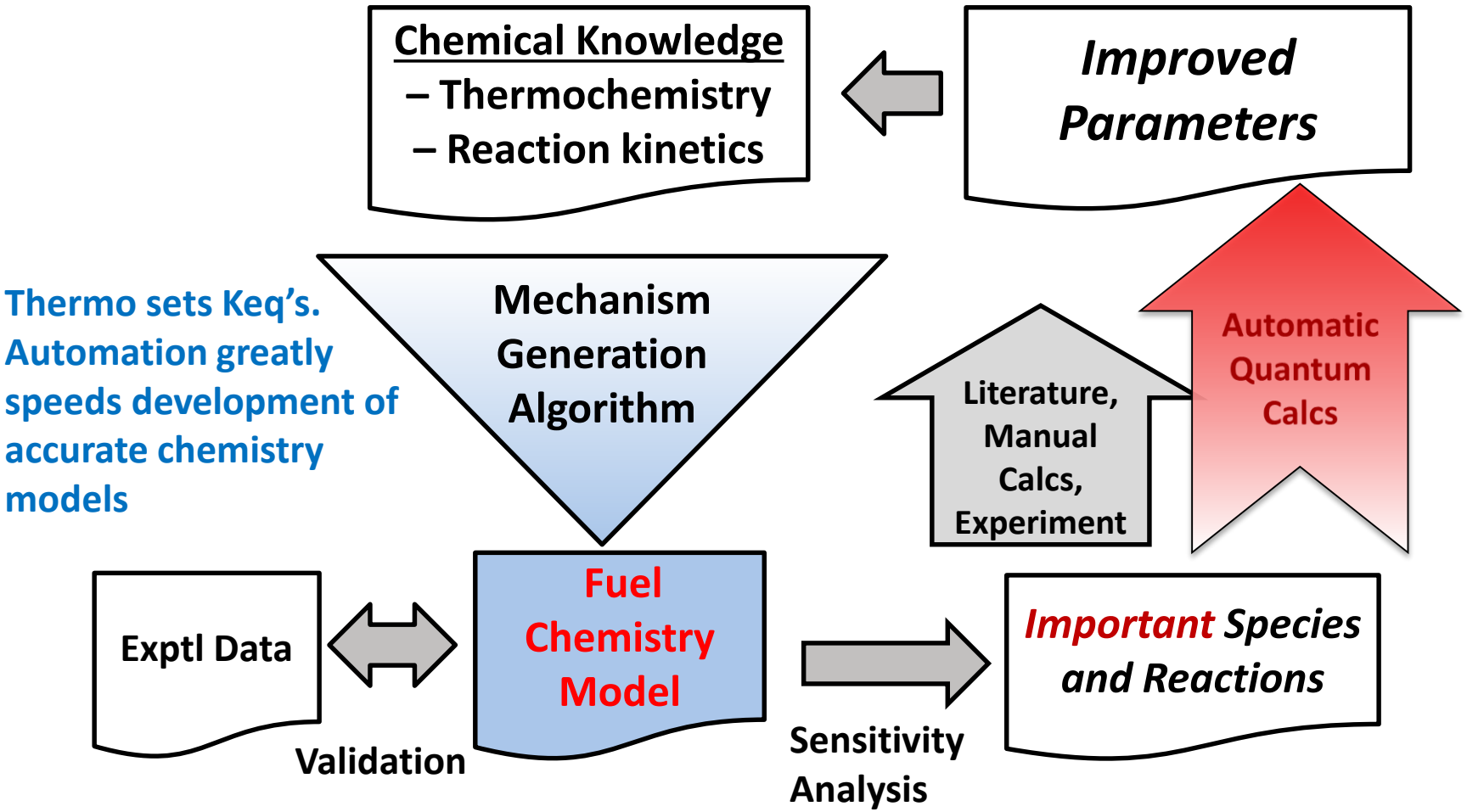
3 – Technical Progress

Methods for Constructing Biofuel Models

- **Milestone 4.5:** Implement and document an improved model construction workflow.
  - Software developed for automating quantum calculations for thermodynamic properties to reduce time spent on calculations
  - Machine learning based higher accuracy rate estimator used to reduce time wasted on unimportant reactions

3 – Technical Progress

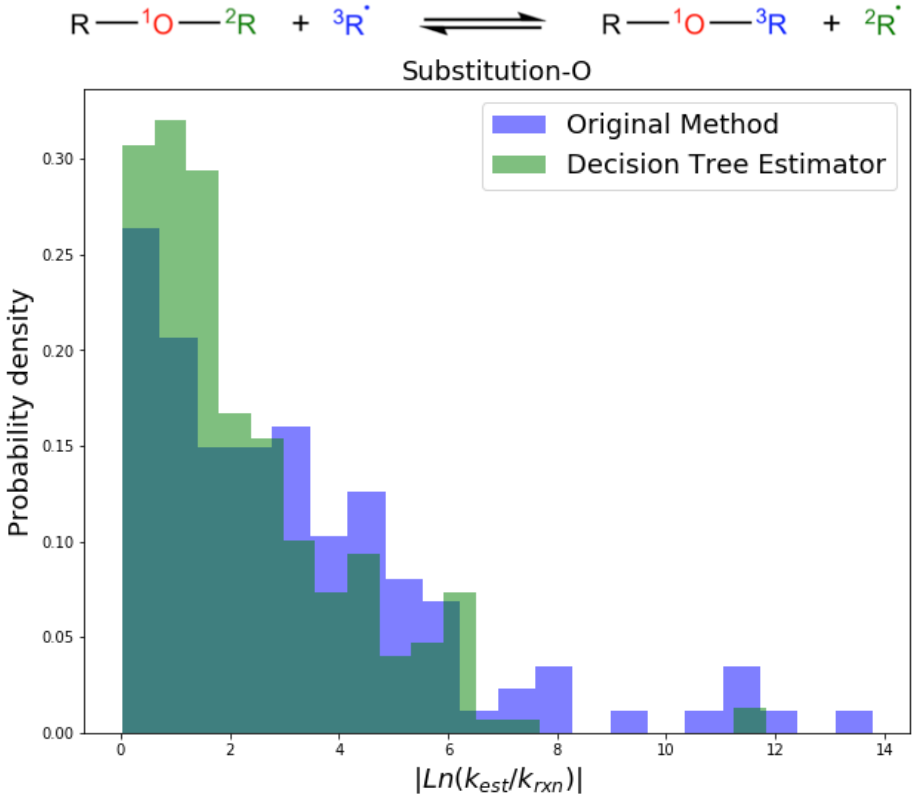
Integrated Accurate Thermo from Automated Quantum Calcs into Model-Building Workflow



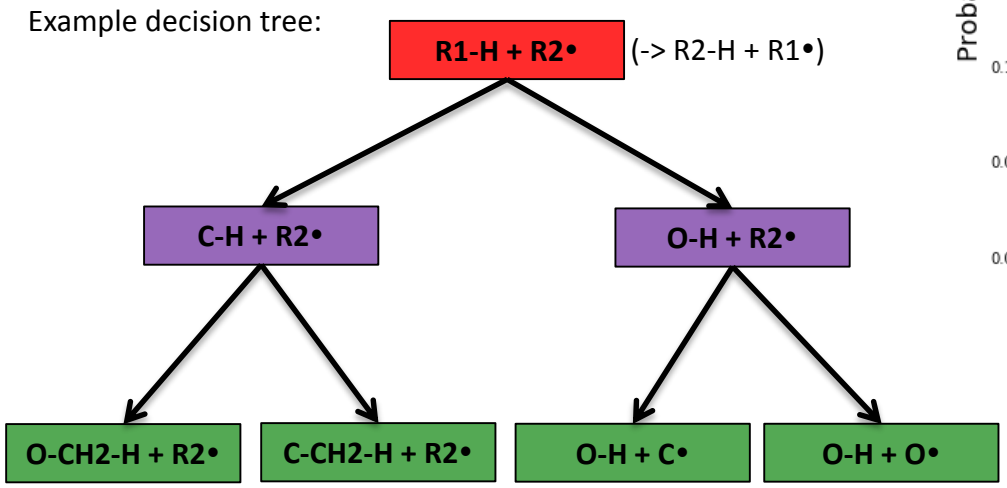
3 – Technical Progress

Improved k(T) Estimation reduces time wasted on unimportant reactions

Importance of reaction depends on k(T). Initial k(T) estimates from classifying new reaction as similar to known reactions. New Machine Learning Decision Tree method improves accuracy of classifications, cuts k(T) error bar 18x



Example decision tree:



3 – Technical Progress
Measurements of Species Time-Profiles

- **Milestone 2.1:** Measure **CO time-histories** during biofuel combustion for pressures **up to 10 atm**.
  - Measurements have been taken during cyclopentanone oxidation and pyrolysis, methyl propyl ether oxidation and pyrolysis, and 2,4,4-trimethyl-1-pentene oxidation

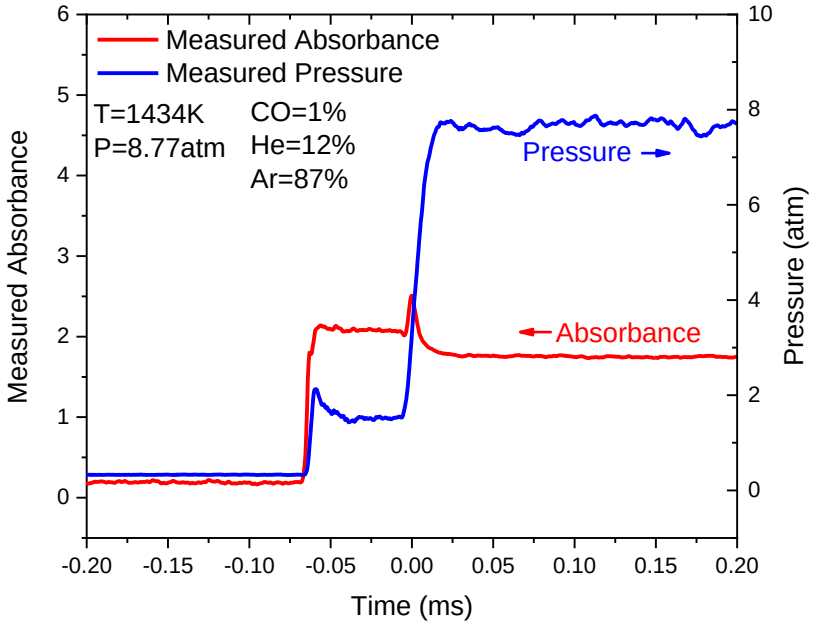
- **Milestone 2.2:** Measure **CO time-histories** during biofuel combustion for pressures **up to 30 atm**.
  - Diagnostics have been configured and tested. Measurements ongoing for ethanol oxidation

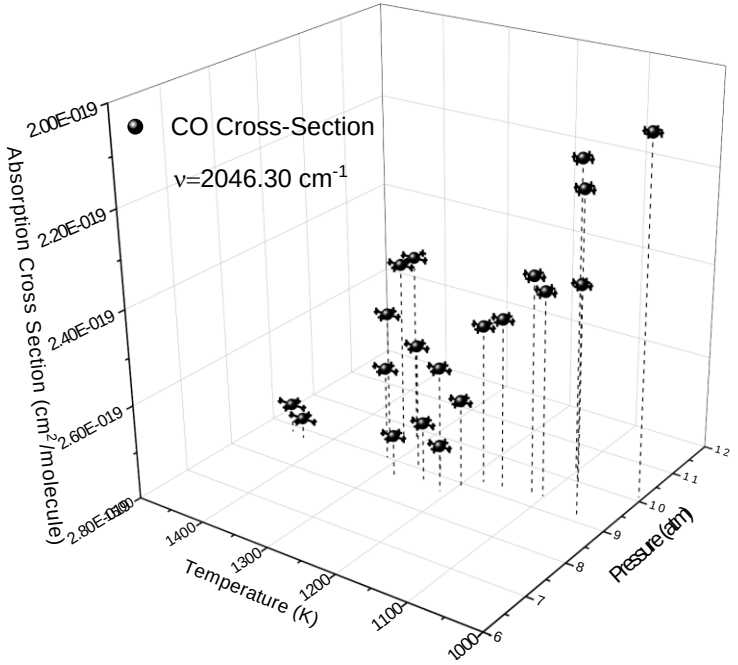
- **Milestone 3.1:** Measure **HCHO time-histories** during biofuel combustion for pressures up to 10 atm.
  - A sensor has been developed and measurements have been taken during the pyrolysis of methyl propyl ether

3 – Technical Progress

Measured absolute CO cross-sections at high T and P

Measured CO absorption cross-section behind reflected shockwaves at 10 and 20 atm over a temperature range of 900-1500 K. This data is used to extract concentrations of CO during combustion of the Co-Optima biofuels

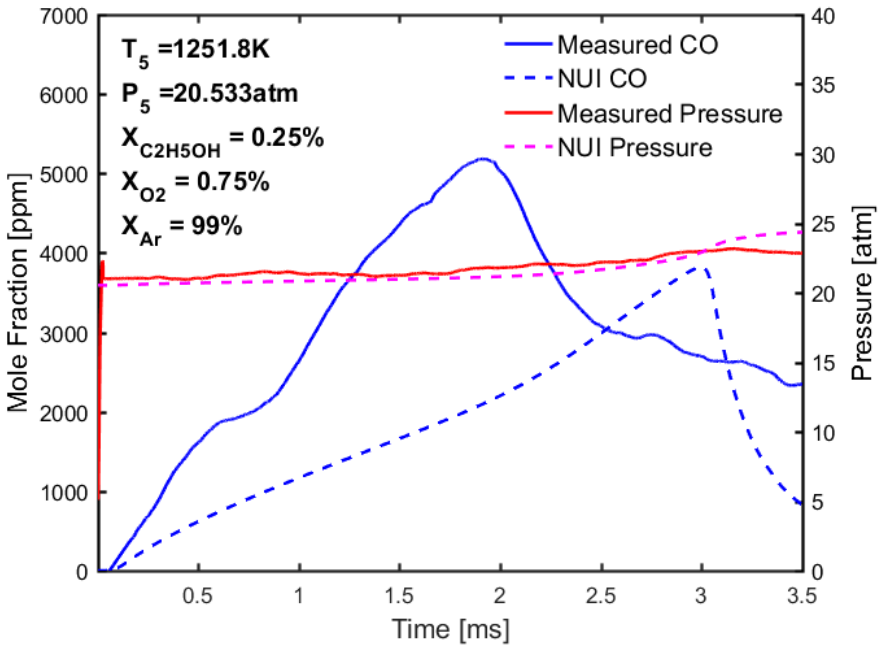


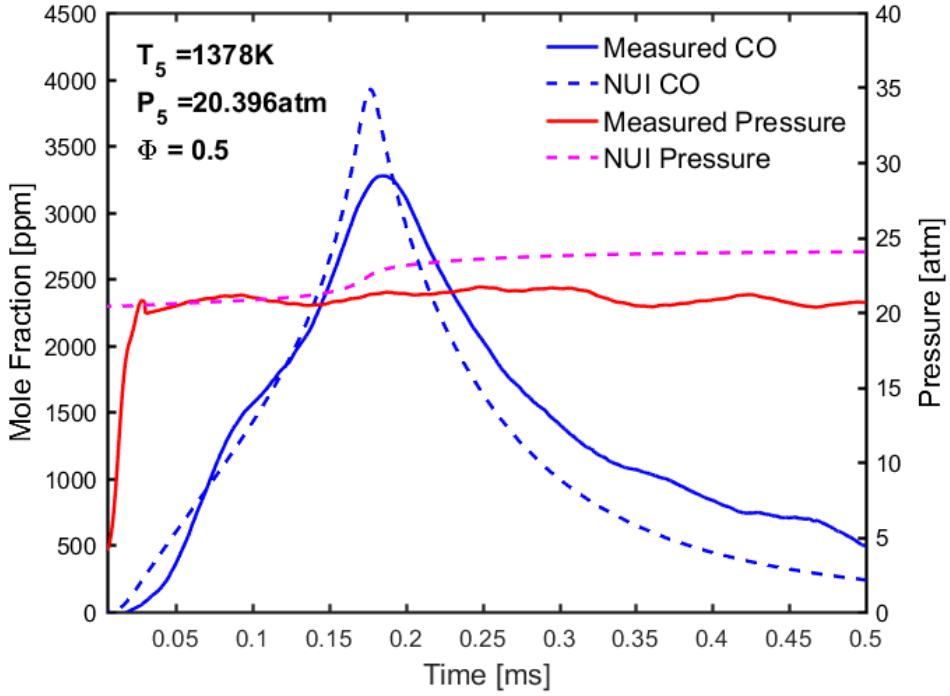


3 – Technical Progress

Measured CO time profiles up to 20 atm

As one example, time-histories of CO have been measured up to 20 atm in the Co-Optima fuel candidate, ethanol.





3 – Technical Progress

Tests of Models with Experiment

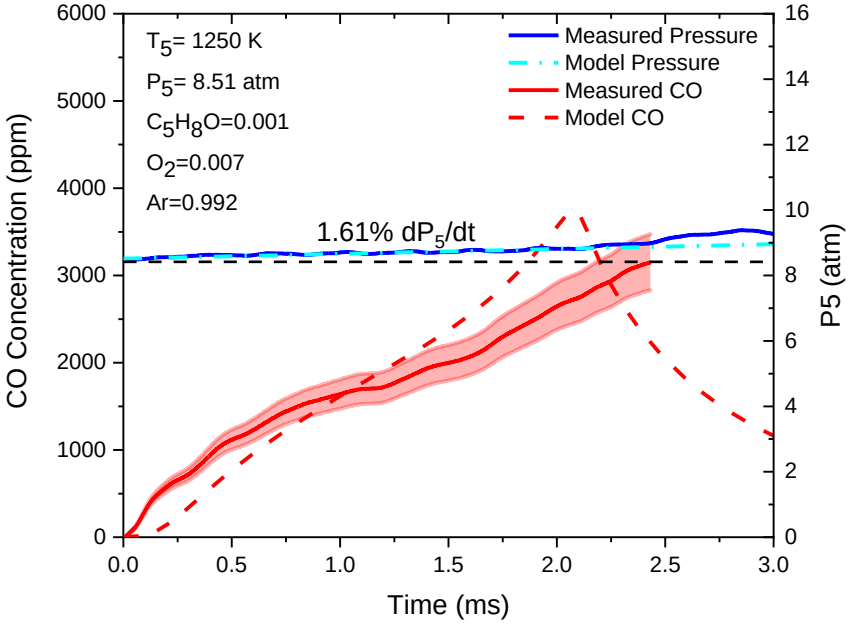
- **Milestone 4.1.1:** Develop models for first 2 biofuels
  - Combustion models developed for methyl-propyl ether and cyclopentanone. Cyclopentanone model was developed in collaboration with Bill Pitz and other Co-Optima team members.

- **Milestone 5.1:** Validate year one models against experiment
  - Both models validated against our shock tube data and additional data from experimental groups, some in Co-Optima team.

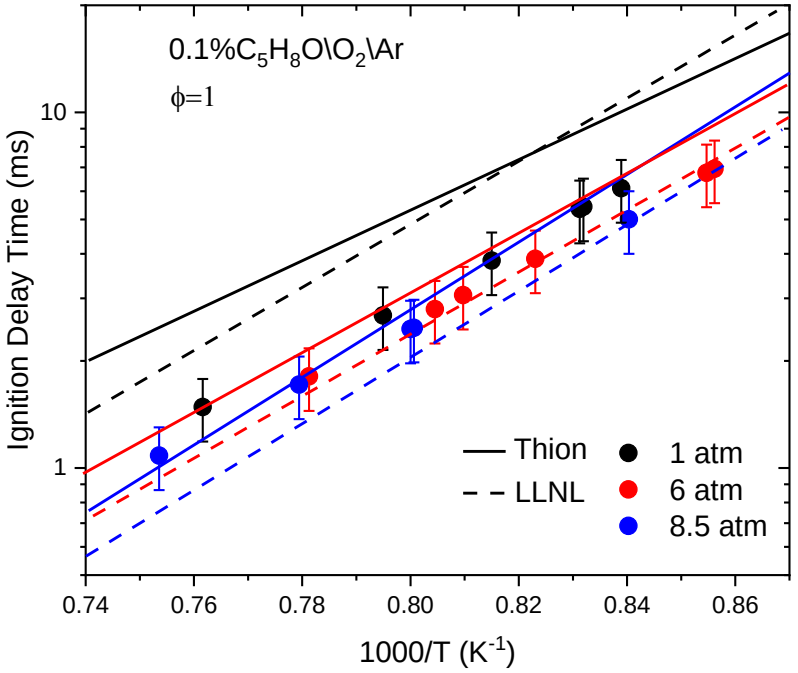
3 – Technical Results

Cyclopentanone Data vs. Models

Time-histories of CO have been measured up to 10 atm in three Co-Optima fuel candidates: cyclopentanone, methyl propyl ether, and 2,4,4-trimethyl-1-pentene. Here we show our measurements for cyclopentanone vs. models



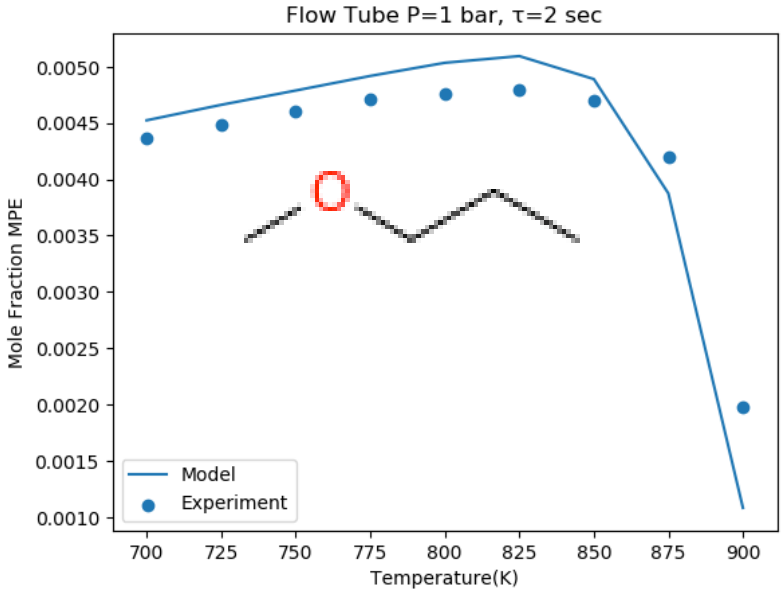
Co-Optima Team Model: Zhang et al. (2018) includes rates, thermo computed by Green's group at MIT



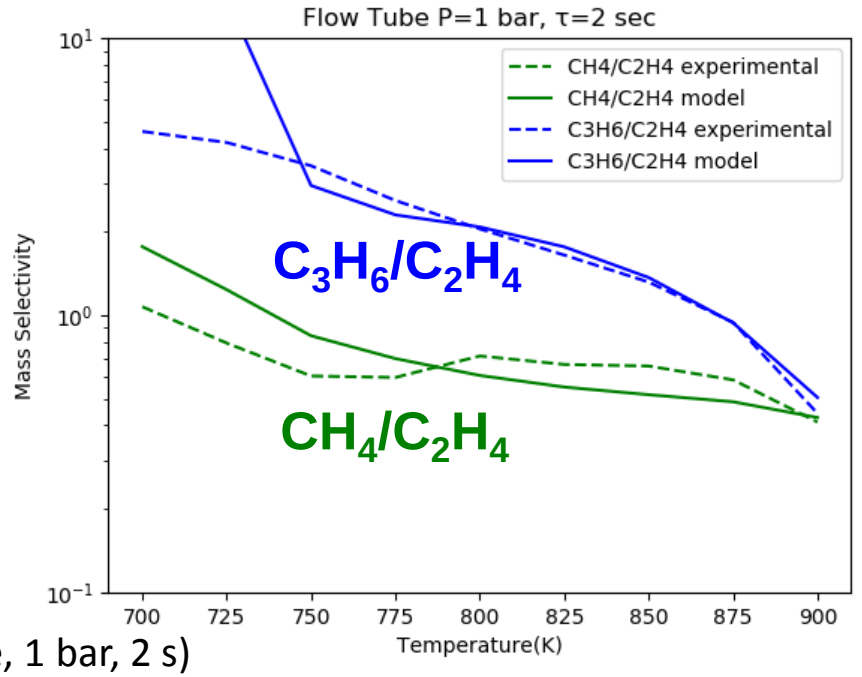
LLNL = Co-Optima team model Zhang et al. (2018)
Thion = model of Thion et al. (2017)

3 – Technical Results

Methyl Propyl Ether Model vs. Data



Experimental flow reactor data from G. Fiorina & R. McCormick (NREL). Computer generated model by MIT. Some important k(T) computed by M. Nimlos, B. Lintao, S. Kim (NREL)

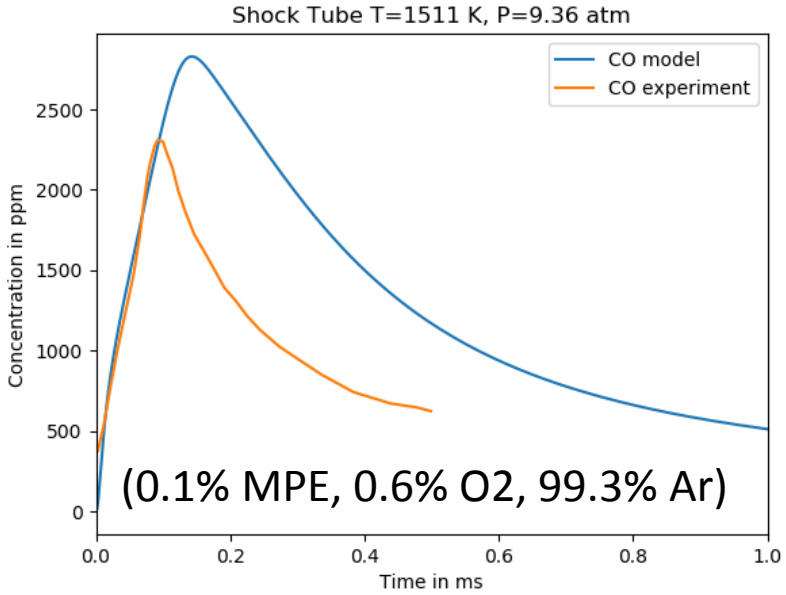


Model predicts Fuel conversion and major product ratios accurately for T>750 K.

(Conditions: ~8% O2, ~0.5% MPE, ~91.5% He, 1 bar, 2 s)

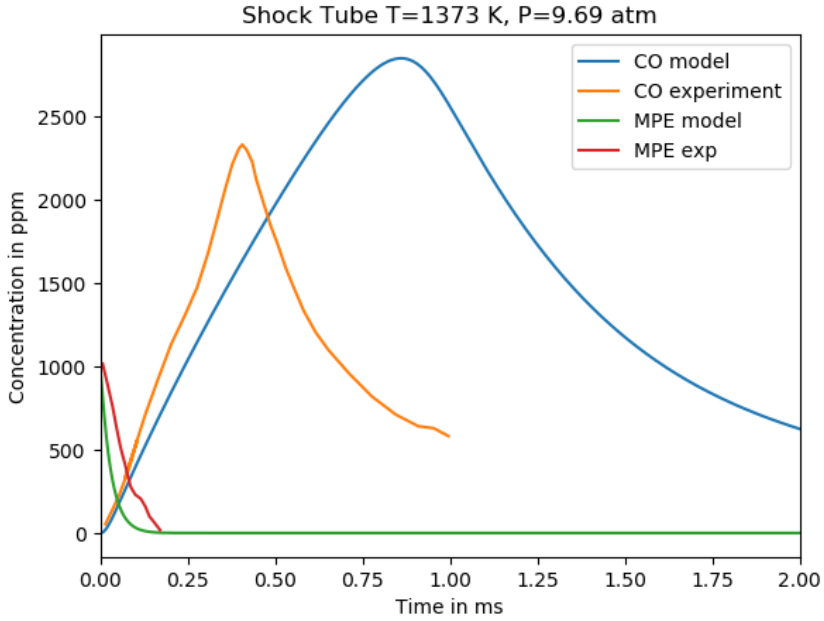
3 – Technical Results

Methyl Propyl Ether Combustion: UCF CO Time Profiles vs. Computer-Generated Model



Peak CO yields predicted within 20%, MPE decay time and CO rise & fall times all within factor of 2. This is close to exptl uncertainties in all quantities.

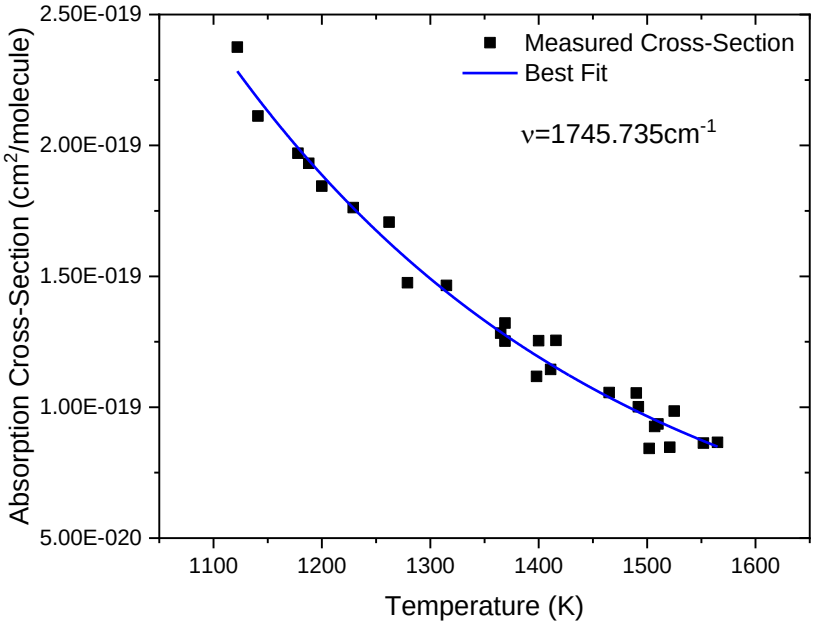
Without any tweaking to force a fit, computer-generated model predicts biofuel chemistry with fairly high fidelity –
Our method appears to work!

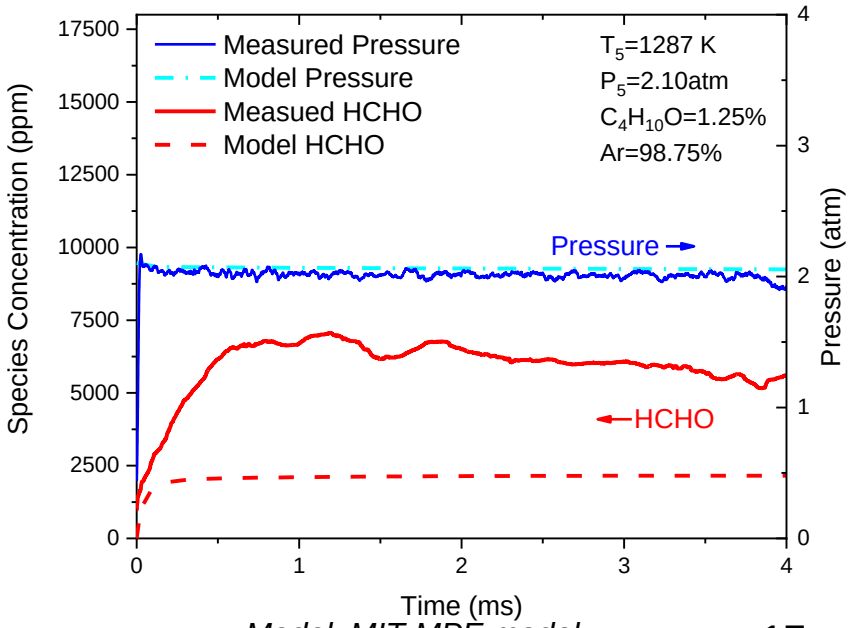


3 – Technical Progress

HCHO measurement scheme developed, first time-profiles measured

- Sensor has been designed and setup to measure HCHO time-histories up to 10 atm during combustion of Co-Optima fuel candidates.
  - Absorption cross-sections of HCHO have been measured behind reflected shockwaves to accurately extract HCHO time-histories
  - First demonstration: Methyl Propyl Ether pyrolysis





Model: MIT MPE model

4 – Relevance

Rapid Construction of Validated Accurate Biofuel Combustion Models

- *Part of BETO's mission: "develop… technologies to enable… biofuels"*
- *Directly addresses BETO's Advanced Development and Optimization Challenge E: Co-Development of Fuels and Engines*
- *Too many possible future fuel + future engine combinations to test them all experimentally.*
    - *Pre-screen on computer using Biofuel Combustion Models.*
    - *Focus experiments on biofuels most likely to succeed.*
- *Computer-aided design is used to develop future engines; to pick up fuel effects it needs fuel-specific combustion chemistry sub-models*
- *Automakers are big consumers of biofuel combustion models – they want their engines to work with whatever fuels will be commercialized*
- *Current methods for building fuel combustion models are slow and unreliable – our new approach can change that.*

5 – Future Work

More fuels and new methods

- **Milestones 4.2.1, 4.3.1:** Model six more biofuels.
  - Check robustness, efficiency of modeling methods.
- **Task 5.0:** Test new fuel models vs. experiment
- **Milestone 4.4.1:** Method for modeling intramolecular H-bonding (for oxygenated fuels)
- **Task 6.0:** Time-histories of other combustion species (e.g. CH_4, C_2H_4, CO_2, H_2O, H_2O_2)
  - More comprehensive test of fuel models
  - Requires development of probe methods for each.
- **Task 7.0:** Develop method for modeling fuels whose composition is known imperfectly
  - Some biofuels are complex mixtures, hard to analyze

Summary

Need fast reliable methods for assessing biofuels

Ideally, evaluate biofuels on computer.

Requires computer models for each fuel's chemistry…

…also useful for co-optimization of fuel with engines

Need models for many fuels: computer builds the models!

Can this really work? How accurate? Test with experiments!

Developed new experiments measuring CO, HCHO vs. time

Created models for 2 fuels and tested with experiments.

++++Looks promising so far!++++

Next: model more (and more complicated) fuels & measure more species, to see how accurate & robust new method is.

Additional Slides

Publications, Patents, Presentations, Awards, and Commercialization

- Zhang, K., et al., *An experimental, theoretical, and modeling study of the ignition behavior of cyclopentanone.* Proc. Combust. Inst. https://doi.org/10.1016/j.proci.2018.06.097
- Ninnemann et al. *Shock tube and CO laser-absorption measurements during cyclopentanone oxidation*. Eastern States Section of the Combustion Institute, 2018. Penn State University.
- Ninnemann, E., et al. *Pyrolysis of cyclopentanone: A shock tube and laser absorption study*. Joint Propulsion Conference, 2018. Cincinnati.
- Johnson, M.S. & Green, W.H. *Machine Learning Approach to Rate Estimation*. American Chemical Society National Meeting. 2018 Boston.
- Khanniche, S. & Green, W.H. *Chemical mechanism and kinetics of cylclopentanone combustion: A theoretical and RMG approach.* American Chemical Society National Meeting. 2018 Boston.
- Laich et al. *A shock tube and laser absorption study of CO time-histories during bio ether oxidation.* AIAA SciTech, 2019. San Diego, CA.
- Ninnemann et al*. Shock tube ignition study of prenol- a "hyperboosting" fuel relevant to the Co-Optima initiative.* 11th US National Combustion Meeting. 2019 Los Angeles, CA. (accepted)
- Nimlos, M.R. et al*. Low Temperature Oxidation of Methyl Propyl Ether.* 11th US National Combustion Meeting. 2019 Los Angeles, CA. (accepted)
- Green, W.H. *Automated Construction of High-Fidelity Fuel Chemistry Models: Status & Challenges*. 17th International Conference on Numerical Combustion. 2019. Aachen, Germany. (invited talk)