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)

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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)

<table>
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<th>DOE Funded</th>
<th>FY 17 Costs</th>
<th>FY 18 Costs</th>
<th>Total Planned Funding</th>
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<td>263k</td>
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<table>
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<th>Project Cost Share*</th>
<th>FY 17 Costs</th>
<th>FY 18 Costs</th>
<th>Total Planned Funding</th>
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<td>56k</td>
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### 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**

### Partners:
- MIT (60%)
- Univ. Central Florida (40%)
- Lab Contact: Bill Pitz (LLNL)
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

Chemical Knowledge
- Thermochemistry
- Reaction kinetics

Improved Parameters

Mechanism Generation Algorithm

Literature, Manual Calcs, Experiment

Automatic Quantum Calcs

Important Species and Reactions

Fuel Chemistry Model

Sensitivity Analysis

Validation

Exptl Data

Thermo sets $K_{eq}$’s. Automation greatly speeds development of accurate chemistry models.
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:

```
R - O^1 + R - O^2 + R^3 ^
```

```
R - O^1 + O^3 + R^2
```

```
R - O^1 + O + R^2
```

```
R - O^1 + O + O
```

```
R - O^1 + O + C
```

```
R - O^1 + C + C
```

```
R - O^1 + C
```

```
R - O^1 + O
```

```
R - O^1 + R
```

```
R - O^1 + R
```

```
R - O^1 + R
```

```
R - O^1 + R
```
• **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
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.
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)
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

![Graph showing absorption cross-sections and temperatures](image1.png)

![Graph showing species concentration and pressure over time](image2.png)

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. CH₄, C₂H₄, CO₂, H₂O, H₂O₂)
  – 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