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# Experimental and Modeling Studies of the Characteristics of Liquid Biofuels for Enhanced Combustion

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LEADING THE WAY TO CLEAN COMBUSTION DESIGN

# Outline

- Purpose of work
- Barriers
- Approach
- Performance Measures and Accomplishments
- Technology Transfer
- Publications
- Plans for Next Fiscal Year
- Summary

# Purpose of Work

- **Expand kinetics understanding for long-chain, surrogate biodiesel fuels**
  - Identify appropriate model-fuel mixtures
  - Perform fundamental flame experiments
  - Test and verify chemical kinetics descriptions of surrogate-fuel combustion through modeling
  - Predict combustion behavior and emissions
- **Identify chemical characteristics that differentiate the combustion behavior**
- **Enable simulation of engine combustion with biodiesel fuels**

# Barriers Being Addressed

- **Need models for biodiesel fuel to allow exploration of issues in engine & fuel design**
  - Models lack detailed kinetics information
- **Kinetics data must be validated**
  - Very little data is available for biodiesel-like molecules
  - Flame studies provide key kinetics validation data
- **Flame experiments are challenging**
  - Fuel must be uniformly vaporized but not cracked
- **Variability in biodiesel processing**
  - Difficult to draw conclusions about emissions
  - Not clear how processing can improve fuel behavior

# Technical Approach

- **Survey biodiesel fuels and production processes**
  - Procure samples, analyze & report on findings
- **Modify flame apparatus at USC**
  - Test & verify gasification and lack of partial oxidation for representative liquid fuels
  - Add emissions measurements capabilities
- **Assemble detailed kinetic models**
  - Build and improve models for methyl ester compounds
  - Consult with Dr. Westbrook and collaborate with LLNL
- **Extend flame models to predict soot**
  - Compare models to USC flame data
  - Enable CHEMKIN Particle Tracking Module in Flame models
  - Develop extinction-modeling capability

# Performance Measures for Phase 1

- **Are data from the biofuel survey useful in defining good biodiesel surrogates for modeling?**
- **Has USC successfully modified the flame apparatus to provide useful model-verification data for large-molecule fuels?**
  - Main milestone for Phase 1 is successful comparison between model and experiment for a representative model fuel
- **Has the RD flame-modeling software been extended to allow particle-size predictions?**

# Technical Accomplishments: Seven BQ9000-certified samples analyzed

- **Fuel sources and processes surveyed**
  - Samples obtained from 5 manufacturers that meet ASTM D 6751
- **Gas chromatography and mass spectrometry performed**
  - Solvent elution analysis with 4 different solvents
- **Results provide class and molecular composition**
  - Elution analysis shows dominance of esters (93-97 wt%)
  - Mass spectrometry shows molecular size & bond structure
    - Dominant molecule size is $C_{18}$
    - Largest % contains 2 double bonds (35-60 wt%)
    - Second largest % contains 1 double bond (20-40 wt%)
    - Other, lower-energy molecules are also present: $C_{16}$ and $C_{18}$ with no double-bonds
  - Results provide measure of fuel variability
- **Data key to fuel surrogate definition**

# Technical Accomplishments: Experimental facility successfully modified

- **Extended the flame facility to provide well characterized flame data**
  - Liquid biodiesel fuels and surrogates
- **Verified that:**
  - It operates under steady-state
  - There is no condensation
  - There is no thermal cracking or partial oxidation of the fuels before they enter the test section (GC analysis)
- **Determined laminar flame speeds for fuels**
  - Choose component that can be used to verify against other published data



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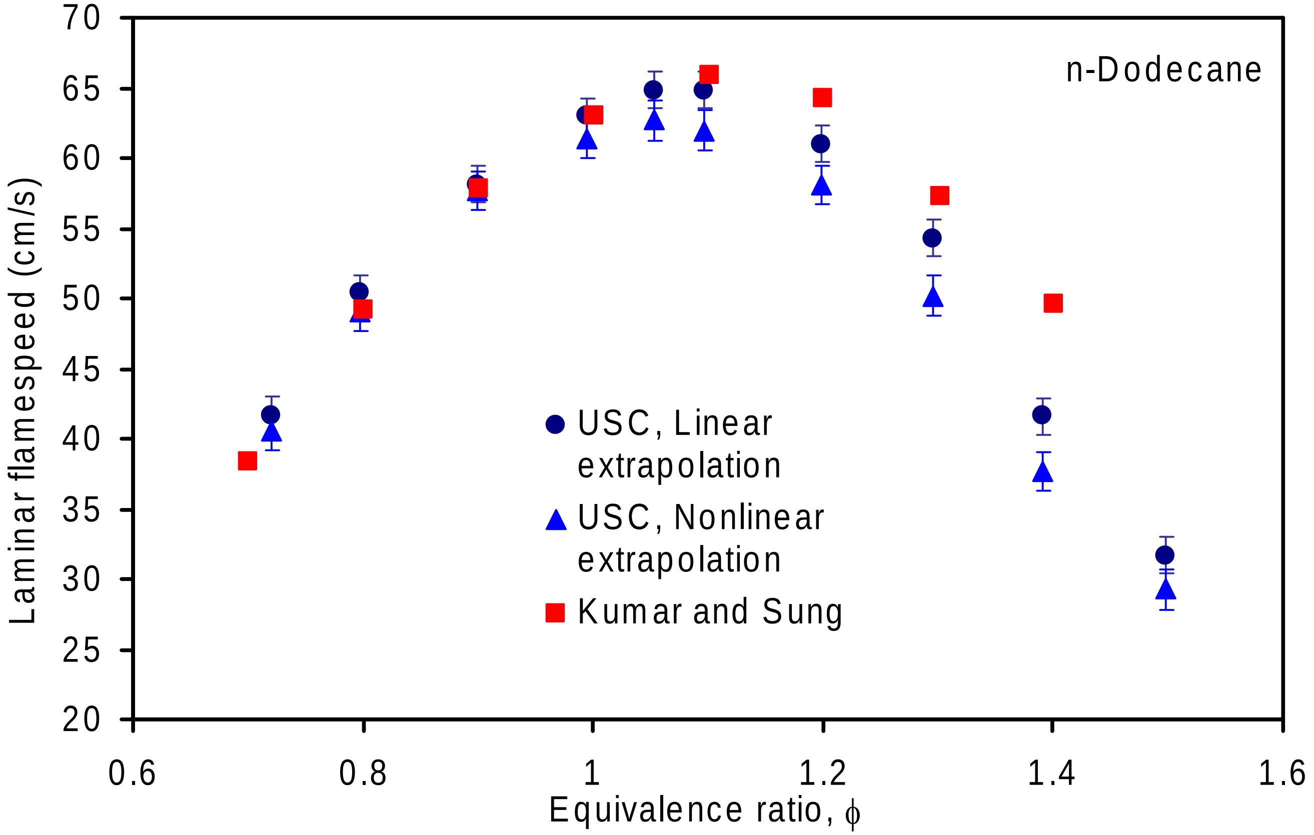
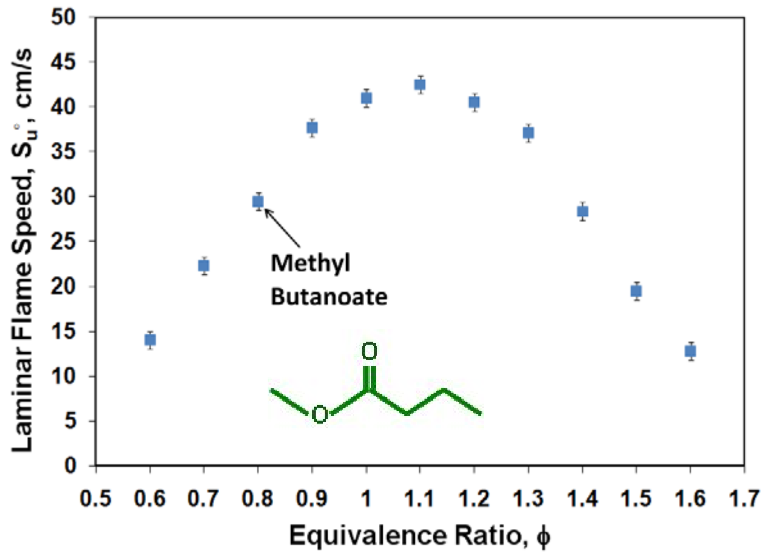
# Technical Accomplishments: Flame-speed measurements verified

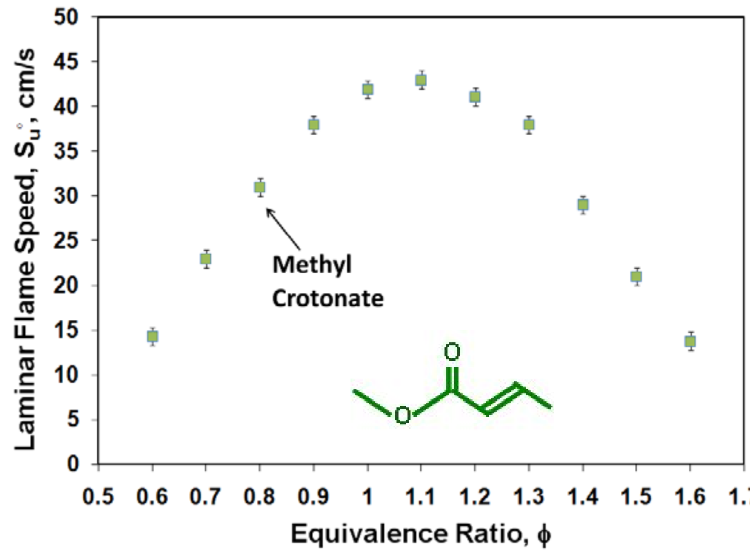
- **Demonstration compares well to data in literature**
  - n-$C_{12}H_{26}$ tests capability for large liquid hydrocarbon
  - Comparison made to n-$C_{12}H_{26}$ results from Case Western*
  - Two methods tested for data extrapolation

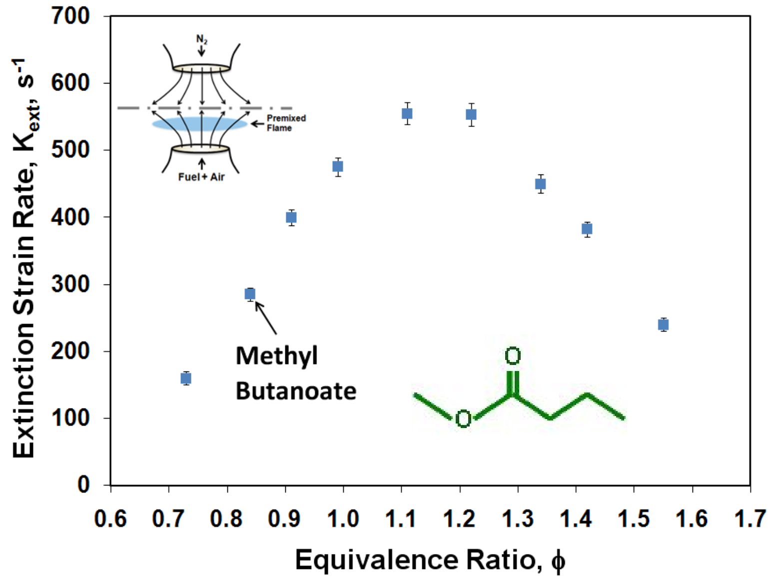


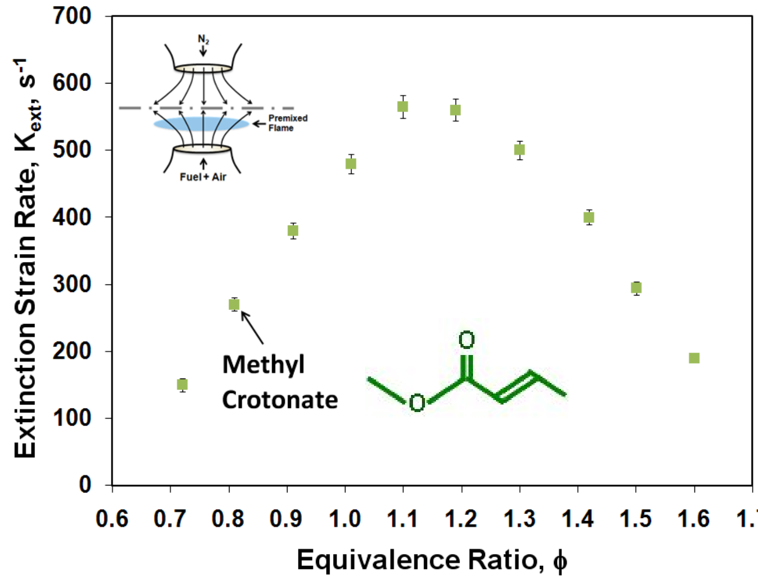

* Kumar and Sung, *Combust. and Flame*, **151,** 2007.

# Technical Accomplishments:
# Initial flame data for biodiesel surrogates

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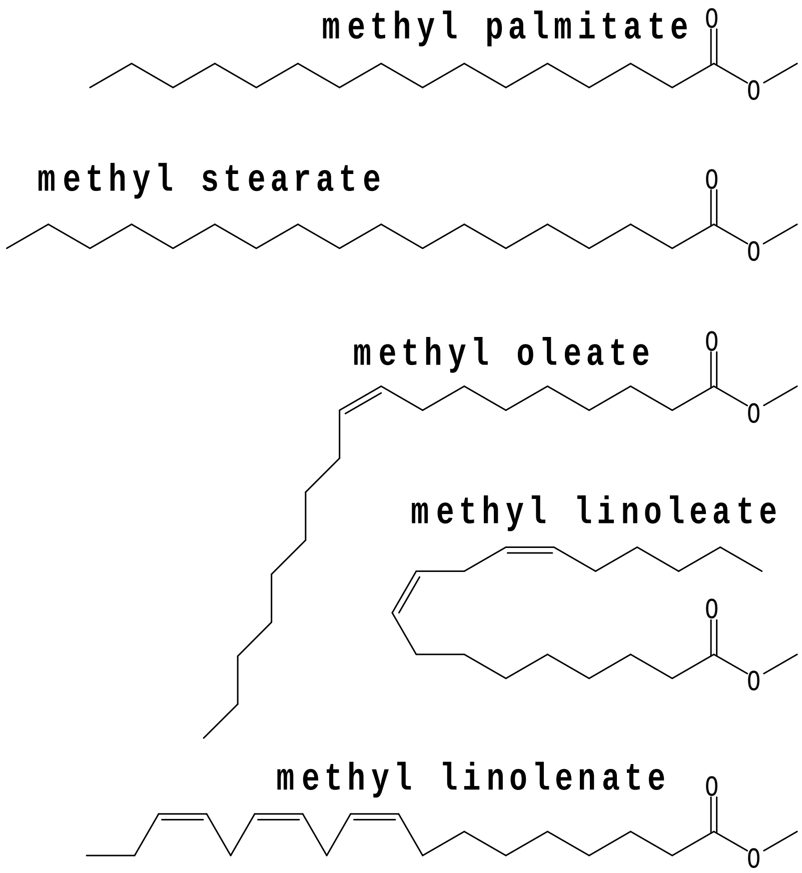
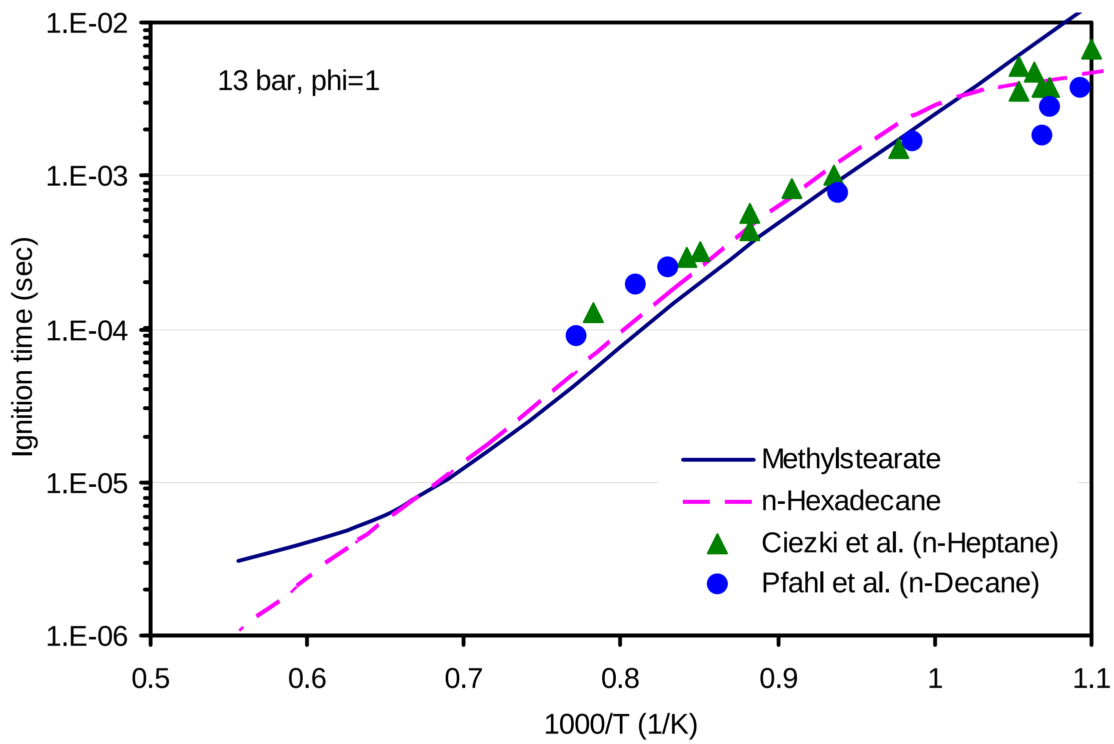
# Technical Accomplishments: Assembled and improved kinetics models

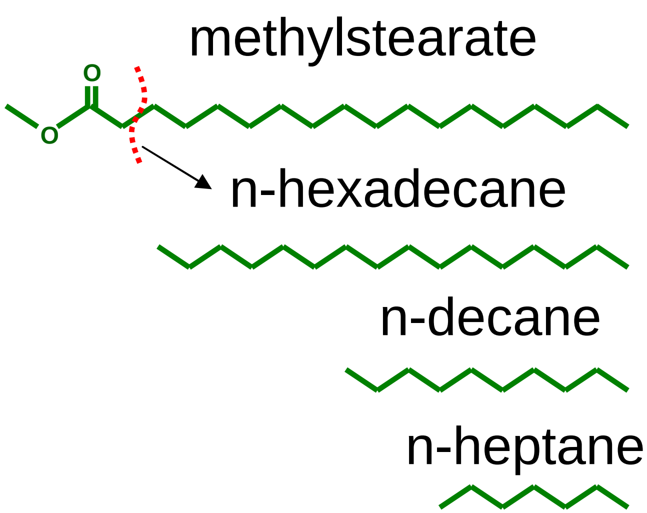
- **Collaboration with LLNL**
  - n-hexadecane, (Westbrook 2007)
  - Methylbutanoate, (Fisher 2000)
  - Methylcrotonate, (Fisher 2000)
  - Methyldecanoate, (Herbinet 2007)
- **Mechanism developed under the Reaction Design Model Fuels Consortium (MFC)**
  - Methylstearate
- **Improvements to mechanisms obtained from external sources**
  - Updated $C_0 – C_3$ sub-mechanisms
  - Improved transport-property data
  - Improved consistency in RO2 chemistry
  - Added missing reaction paths to methyl crotonate



# Technical Accomplishments: Observations regarding biodiesel surrogates

- **Methylstearate ignition characteristics are close to n-hexadecane and to n-decane**
  - n-hexadecane model from Westbrook, et al. (2007)
  - n-heptane shocktube data from Ciezki et al. (1993)
  - n-decane shocktube data from Pfahl et al. (1996)



# Technical Accomplishments: Initial conclusions on biodiesel surrogates

- **Long-chain alkanes may provide sufficient representation of the ignition behavior**
  - N-decane similar to methyldecanoate
  - N-hexadecane similar to methylstearate
- **Addition of smaller methyl-ester molecules may give sufficient representation of the methyl-ester group contribution**
  - Methylbutanoate may be sufficient
- **Could result in smaller mechanisms for same accuracy**
  - Less complexity needed for biodiesel/diesel blends



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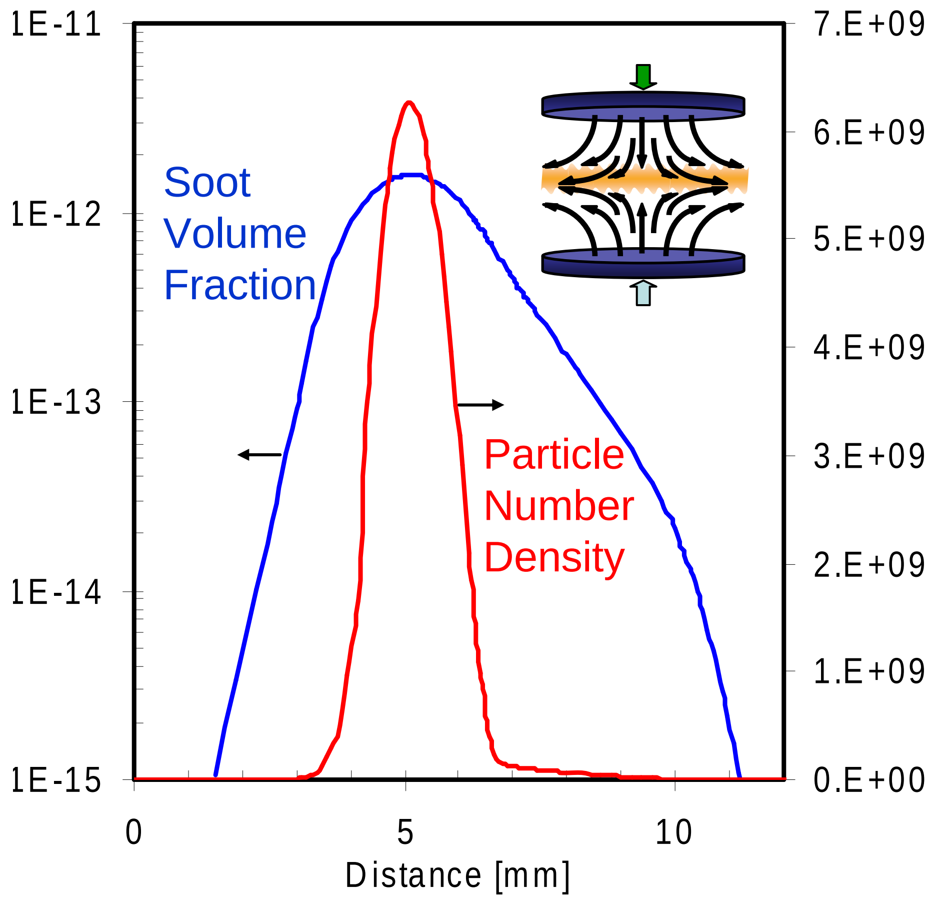
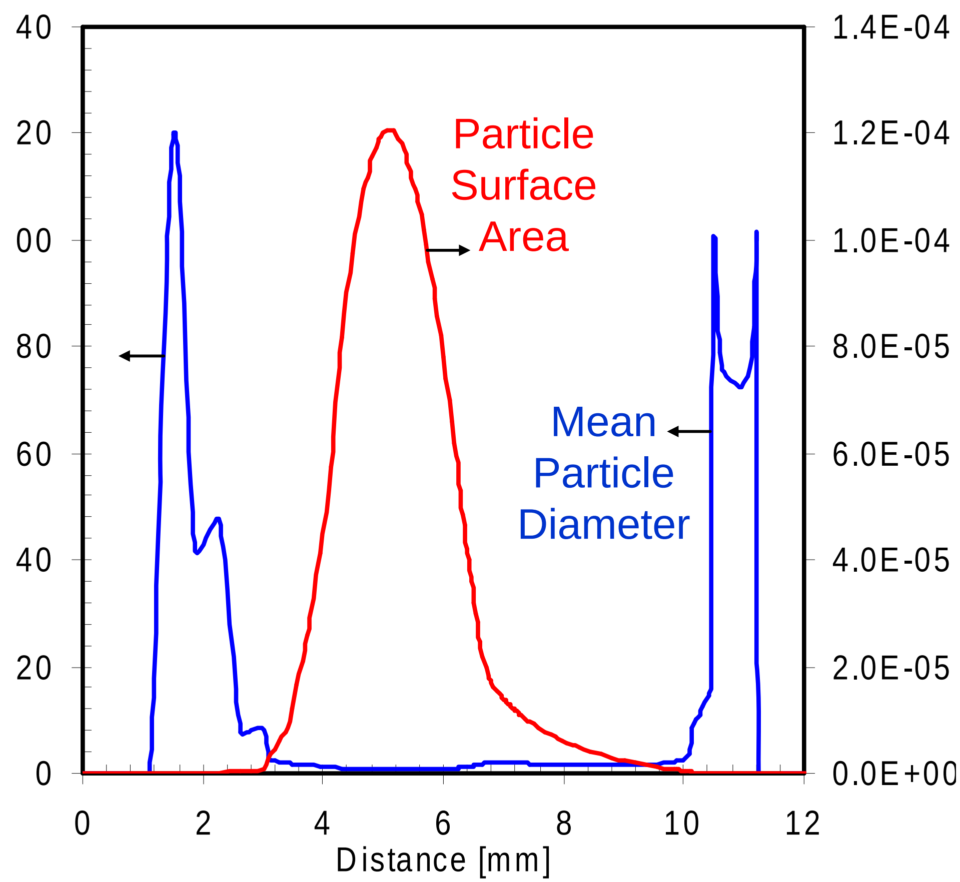
# Technical Accomplishments:
# Ability to predict particle formation in flames

- **Demonstrated for ethylene flame conditions:**




| **Fuel** | **Oxidizer** |
|---|---|
| 75%$C_2H_4$ + 25% Ar | 22% $O_2$ + 78% Ar |



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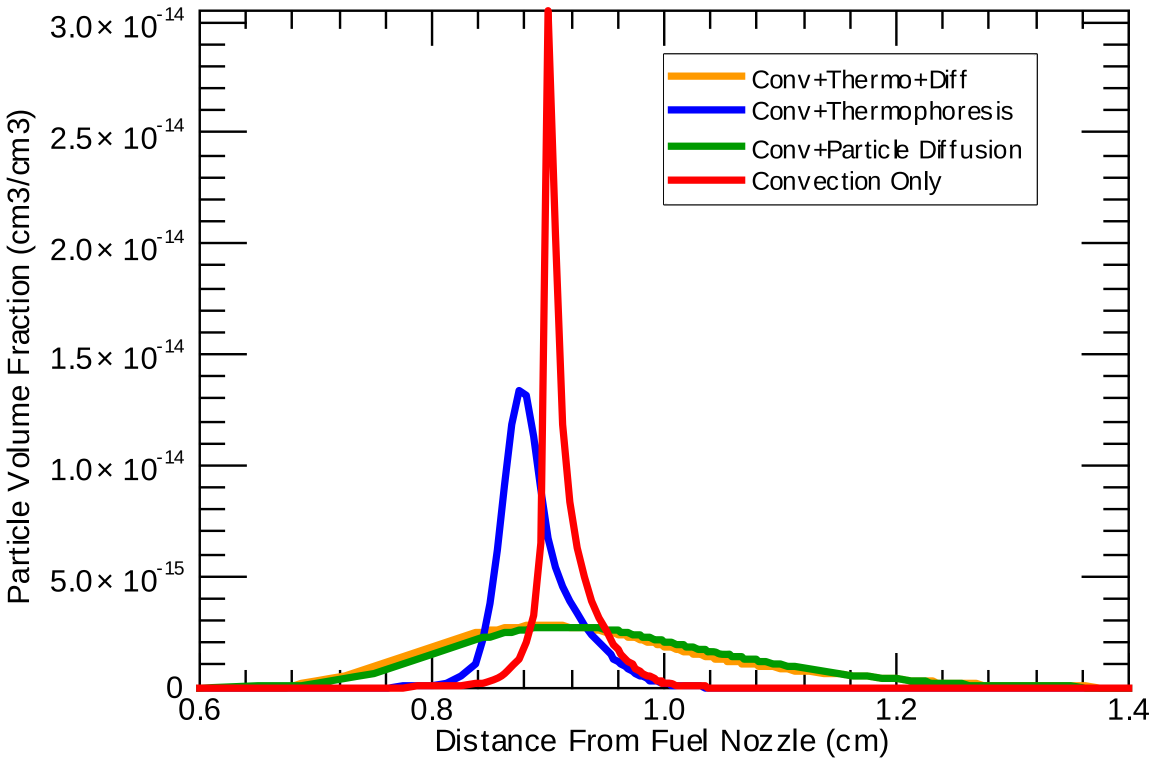
# Technical Accomplishments: Accounting of particle transport phenomena

- **Detailed particle transport is included in flame models**
  - Convection
  - Particle diffusion
  - Thermophoresis
- **Diffusion and thermophoresis significantly affect particle distribution in flame**



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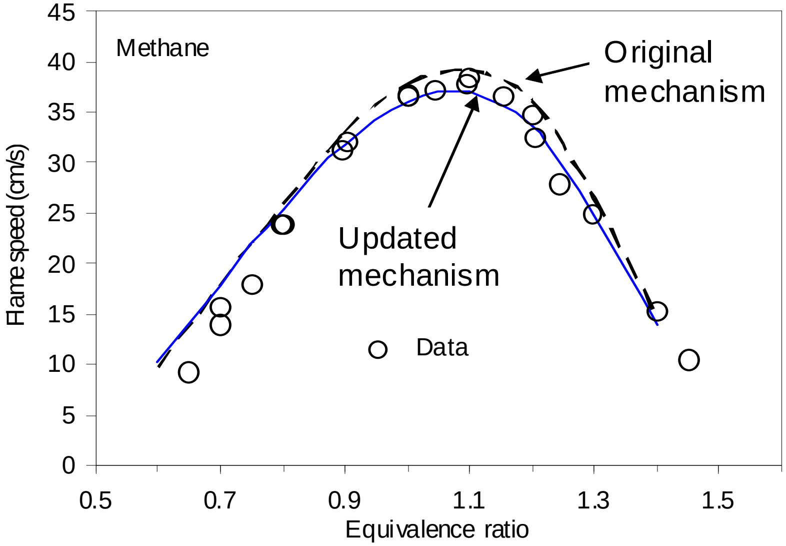
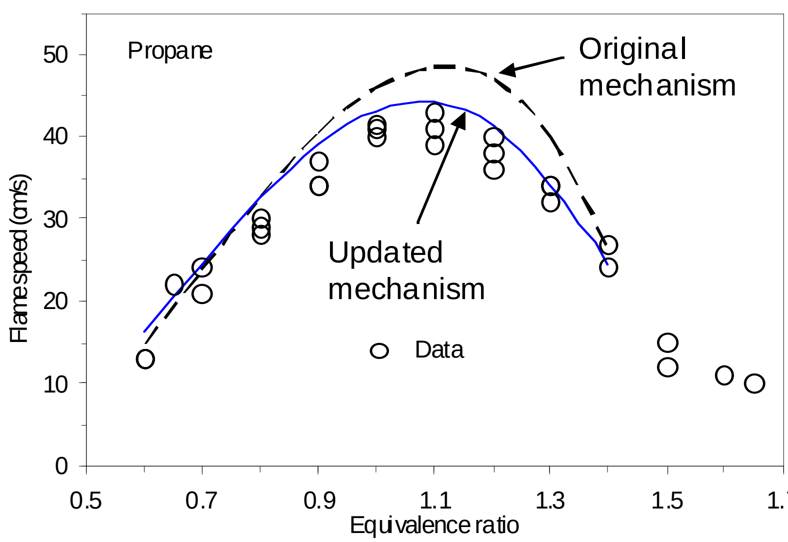
# Technical Accomplishments: Milestone met for modeling of flame data

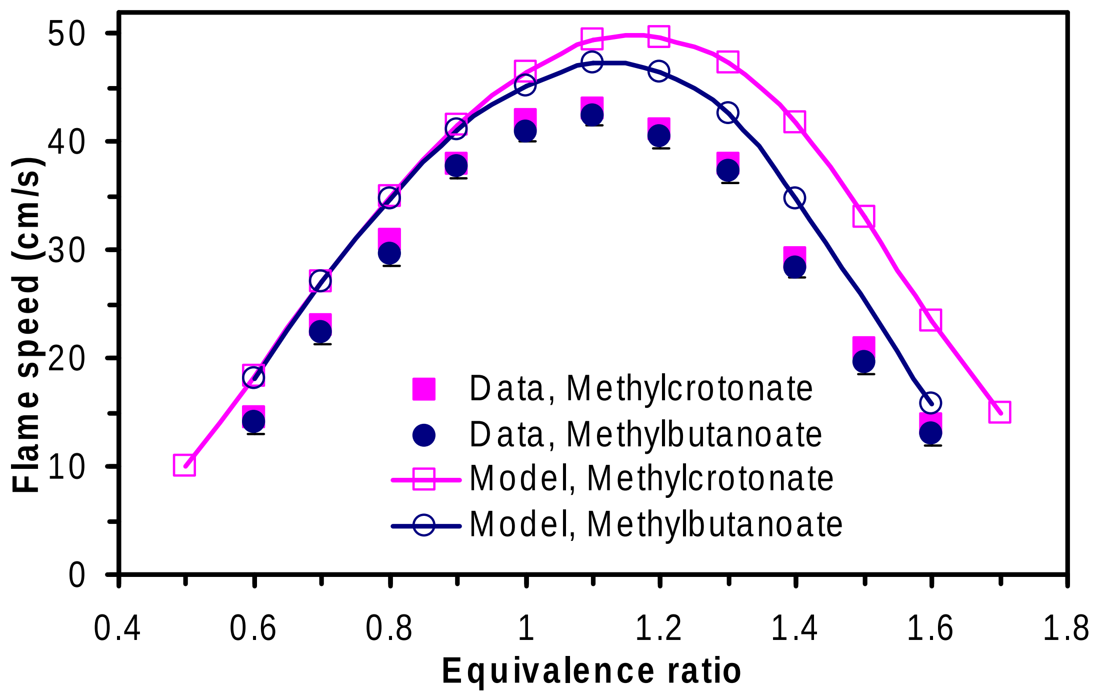
- **The flame model can predict USC data well**
- **Comparison led to improvement of chemistry models**
  - Methane and propane
  - $H_2/O_2$ sub-mechanism updated based on recent publications
  - More self-consistent transport-property data generated



# Technical Accomplishments: Preliminary comparisons for methyl esters

- **USC data from modified flame facility**
- **CHEMKIN flame-speed calculator**
  - Improved mechanisms for methyl-butanoate, methyl-crotonate
  - Mechanisms reduced for high-temperature only
  - Further improvements needed for methyl-crotonate mechanism



# Technology Transfer

- **Reaction Design provides commercial support for the use of detailed kinetics in industry**
- **We are closely engaged with key auto and fuels manufacturers in the Model Fuels Consortium**
  - Main goal is practical use of detailed kinetics in engineering simulations
    - Mechanism database management
    - Comprehensive validation studies
    - Automated mechanism-reduction
    - Automated match of model-fuel composition to real fuel
    - Multi-zone engine model
  - DOE project leverages this work
    - Provides critical biodiesel data
- **Chevron's in-kind contribution shows strong interest in result**

# Publications

- **"Studies of Combustion Characteristics of Biofuels in Premixed and Non-Premixed Flames," Y.L. Wang, C. Ji, A.T. Holley, F.N. Egolfopoulos, T.T. Tsotsis, and H.J. Curran, paper No. 07F-049 Fall Technical Meeting, Western States Section/Combustion Institute, Livermore, California, October 16-17, 2007**



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# Activities for Next Fiscal Year (Phase 2)

- **Continue characterization and analyses of biodiesel fuels and surrogates**
  - Flame experiments (at USC)
    - Extend focus onto $NO_x$ and soot measurements
  - Simulation & comparison to flame experiments
    - Test of particle-formation model
  - Kinetics model assembly, verification & reduction
    - Apply automated, accurate mechanism-reduction methods
  - Analysis and testing of biodiesels (at Chevron)
    - Match model-fuel surrogates to biodiesel fuel characteristics
  - Analysis of impact on production processes
- **Build on preparatory work from Phase 1**

# Summary

- **The project facilitates adoption of biodiesels**
  - Necessary for the simulation of biodiesels in engine combustion
  - Explores improvement of biodiesel fuel processing
- **Our approach employs detailed kinetics studies and carefully controlled experiments**
- **We have accomplished or exceeded all objectives for the Phase 1 project**
  - Successfully overcame challenges in flame experiments
- **There is a clear path for technology transfer**
  - The Model Fuels Consortium
  - Commercially supported software and services
- **We are well positioned for work planned next year**
  - Focus will turn towards emissions behavior of biodiesels



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