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

Ellen Meeks (PI), Chitral Naik, Karthik Puduppakkam, Abhijit Modak, Charlie Westbrook Fokion Egolfopoulos and Theo Tsotsis (USC)
Stephen Roby (Chevron)

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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
Technical Accomplishments: Flame-speed measurements verified

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

Technical Accomplishments:
Initial flame data for biodiesel surrogates

- Methyl Butanoate
- Methyl Crotonate

Equivalence Ratio, $\phi$

Laminar Flame Speed, $S_{\lambda,0}$, cm/s

Extinction Strain Rate, $K_{ext}$, s$^{-1}$
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
Technical Accomplishments: Ability to predict particle formation in flames

- Demonstrated for ethylene flame conditions:

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Oxidizer</th>
</tr>
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<tbody>
<tr>
<td>75% (\text{C}_2\text{H}_4) + 25% (\text{Ar})</td>
<td>22% (\text{O}_2) + 78% (\text{Ar})</td>
</tr>
</tbody>
</table>
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
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
  - H₂/O₂ 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

![Flame speed comparison graph](image)
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

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