Experimental and Modeling Studies of the Combustion Characteristics of F-T Fuels

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Collaborators on this project

- **NASA Glenn (Project oversight)**
  - M. Rabinowitz, D. Bulzan
  - Award # NNC07CB45C-Y1-Q1
  - 05-2007 through 04-2009

- **University of Southern California (Co-PIs)**
  - Profs. F. N. Egolfopoulos and T. Tsotsis

- **Reaction Design**
  - E. Meeks (PI)
  - C. V. Naik, K. V. Puduppakkam, A. Modak (Co-PIs)
  - Consultant: C. K. Westbrook (Co-PI)
Outline

● Project objectives
● Tasks and accomplishments to date
● Summary of Findings
● Future work
NASA Project Objectives

- Obtain fundamental data on combustion behavior of alternative jet fuels
  - Fischer-Tropsch and Bio-derived
  - Real fuels and associated model (surrogate) fuels

- Assemble fuel-chemistry models for simulation
  - Validate kinetics through comparison with experiment
  - Recommend surrogate blends
  - Provide accurate, reduced mechanisms

- Identify differentiating characteristics of molecular fuel components
  - Target design of optimal fuel processing
There are several tasks underway

● **Fuels survey and analysis**
  – F-T fuels
  – Bio-derived fuels

● **Surrogate-model assembly and testing**
  – Flame modeling, including NOₓ and soot formation
  – Mechanism reduction for targeted conditions

● **Flame experiments for liquid / heavy hydrocarbon fuels**
  – Laminar flame-speed and flame-extinction limits measurements
  – Augmentation of diagnostics with NOₓ and soot measurements
A fuels survey activity at USC has provided data on F-T and biojet fuels

● 2 F-T samples obtained from the Air Force
  – Courtesy of Tim Edwards, AFRL
  – Leveraged by other projects at USC
  – GC/MS data provides class/size composition of fuels

● Many biofuel suppliers surveyed
  – Only one identified that provides de-oxygenated fuel appropriate for jet applications

● De-oxygenated biodiesel fuel sample obtained from UOP
  – Currently undergoing fuel analysis
F-T Fuels analysis shows predominance of iso-alkanes with little branching

- Summary results for S-8 (Syntroleum) sample: (based on GCMS analysis courtesy of Tim Edwards of AFRL)

- Most of the iso-paraffins consist of only one methyl branch on a long and straight alkane chain
The AFRL analysis shows significant differences between F-T fuels

- Analysis (courtesy of Tim Edwards, AFRL):

![Graph showing mass percentage by hydrocarbon number for different fuels.

- Sasol IPK: ~4% n-paraffins
- Shell GTL: ~26% n-paraffins
- Sasol Oryx (GTL-1): ~72% n-paraffins
- Syntroleum S-8: ~22% n-paraffins
- Sasol Oryx isomerized (GTL-2): ~20% n-paraffins
Based on the S-8 sample data, we defined candidate surrogate blends for F-T fuels

Proposed surrogate mixtures for the F-T fuel (S-8)

<table>
<thead>
<tr>
<th>Model Fuel Component</th>
<th>With available mechanisms Mol %</th>
<th>With more components Mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-dodecane</td>
<td>24</td>
<td>15</td>
</tr>
<tr>
<td>n-decane</td>
<td>76</td>
<td>10</td>
</tr>
<tr>
<td>4-methyloctane</td>
<td>-</td>
<td>38</td>
</tr>
<tr>
<td>2-methyldodecane</td>
<td>-</td>
<td>37</td>
</tr>
</tbody>
</table>
Mechanism for F-T surrogate components is based on n-alkane work of Westbrook, et al.

- **n-decane and n-dodecane**
  - From Westbrook et al. (2008) mechanism of n-alkanes
  - Removed species > C12
  - Removed low-temperature kinetics to focus on flames
  - Added estimates of transport parameters
  - Updated the core mechanism for improved laminar flame-speed predictions

- **Resulting elementary reaction mechanism:**
  - 117 species
  - 795 reactions
Improvements were made to address under-prediction of laminar flame-speeds

- Sensitivity analysis pointed to C₀-C₃ chemistry and transport as source of systematic error
- Changes made to C₀-C₃ core chemistry
  - H₂ oxidation
    * Updated based on recent studies by Curran et al. (2004) and Dryer et al. (2007)
    * Updated ΔHᶠ₂⁹₈K for OH and HO₂
    * Significant effect on flame speeds
  - C₁ oxidation
    * Updated based on Petersen et al. (2007)
  - C₂ and C₃ oxidation
    * Updated based on Naik and Dean (2006)
    * Affects only low temperature oxidation of alkanes

- Transport properties calculated based on quantum chemistry for most sensitive species
  - N₂, H₂O, Ar, C₀ and C₁ species
Results provide improved predictions of laminar flame speeds for \( C_1 \) to \( C_{12} \) alkanes

- Data at 1 atm, 298K, from several sources in literature
- Almost equal contributions from updated chemistry and transport towards improved predictions
To test role of iso-alkanes, an iso-butane sub-mechanism was added to the F-T surrogate model

- Based on Curran et al. (2002) iso-octane mechanism
  - Removed low-temperature species
  - Removed C$_{5+}$ species

- Merged the C$_4$ sub-mechanism with the 2-component F-T surrogate mechanism
  - Based on unique identifiers for each species in system
  - Used thermodynamic data of F-T surrogate when different
  - Used reaction-rate data of F-T surrogate when different
A NO\textsubscript{x} sub-mechanism was also assembled, including pathways for low and mid temperatures

- Based on recent literature mechanisms
  - GRI 3.0 NO\textsubscript{x} sub-mechanism – High-T
  - Dagaut, Glarborg, et al. 2008 mechanism – Mid-T
    * Complete and up-to-date HCN chemistry, as well as N\textsubscript{2}O and NNH chemistry
  - Rasmussen, Glarborg, et al. 2008 mechanism – Low-T
    * NO\textsubscript{x}-HC interactions

- Mechanism to be tested against USC flame data
Modifications to the USC flame facility assure fuel vaporization without cracking

- 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)

- Tested laminar flame speeds for fuels where other data is available
Comparisons for n-dodecane demonstrate the capabilities of the USC facility

- Results compare well to data with literature
  - 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.
Comparisons for surrogate-fuel components test the kinetics mechanisms

- Model-fuel component mechanisms: $C_{12}H_{26}$

USC Non-linear Extrapolation, 403K

Non-linear extrapolation of data suggests model still overpredicts flame-speed by ~5 cm/s near phi=1
Some mechanism reduction was necessary even to do the flame studies

- High-temperature mechanisms routinely created based on chemistry logic
  - Remove species deemed to be only important for low-temperature chain-branching
    - Ketohydroperoxides and QOOH species
  - Remove reactions associated with removed species

- Method based on unique species identifiers
  - SMILES strings tag each species in system
  - Independent of any species naming convention
  - Allows full automation
Automated mechanism reduction methods can also provide skeletal mechanisms

- We have focused on use of Directed Relation Graph (DRG) for this work
  - Analyze a solution based on “master” mechanism
    1. Start with the Fuel & Oxidizer species
    2. Determine which production paths are below tolerance settings for each species
    3. Repeat as “tree” of species is descended
    4. Remove reactions that are below tolerance
    5. Remove species that no longer contribute

- Easily applied to range of conditions in CHEMKIN*
  - Super-position results of multiple cases
    * E.g., parameter study over range of equivalence ratios, $T_0$
  - Use all points in the solution (transient or 1-D)

*Product is not yet released to public
Skeletal reductions show good accuracy over a wide range of conditions

- Capability demonstrated for biodiesel surrogate:
  - 35% Methylcrotonate, 15% methylbutanoate, 50% dodecane
  - Master mechanism: 549 species, 3245 reactions
  - Skeletal mechanism (5% error target): 143 species, 969 reactions

70% Reduction in # Species
The USC Flame facility is also making measurements for real jet fuels

- Preliminary results suggest:
  - F-T similar to n-dodecane
  - F-T laminar flame speed is slightly faster than JP-8, JP-7

- Flames of 2 F-T samples propagate at same speed
  - Despite differences in chemical analysis

- Measurements are being evaluated now for reproducibility
Model comparisons with F-T samples test our candidate F-T surrogate blend

- Proposed surrogate agrees reasonably well for laminar flame-speed (preliminary measurements)
  - Other components may be needed to improve agreement
Flame extinction data provides further tests for the models

- JP fuels, F-T fuels, UOP bio-derived fuel and surrogates all behave similarly

- Different controlling phenomena than flame-speed

![Graph showing Extinction Strain Rate vs Fuel/Air Mass Ratio](image)

$T_u = 403K$
A new CHEMKIN-based Extinction Model is being tested against the USC data

- Based on CHEMKIN opposed-flow flame model
  - With modifications recommended by Egolfopoulos
- Preliminary results compared for methane data
  - First test of model against well characterized data
Summary of Findings (to date)

● Flame propagation is similar between F-T fuels,
  – Despite differences in chemical analysis

● Flame extinction behavior is very similar between all samples, including F-T, JP-8, JP-7, n-dodecane
  – Different behavior from flame propagation

● Improvements to chemistry mechanisms provide good agreement with flame-speed data for large alkanes
  – Updates to core C₀-C₃ mechanism were key

● Preliminary tests of flame-extinction model are promising
  – Need to investigate dependence on transport properties
Future work will continue to build knowledge of alternative jet-fuel combustion

- Evaluate surrogate model vs. data considering flame-model / flame-experiment uncertainties
  - Further refine mechanisms for alkanes if necessary
  - Identify other molecular components to include if necessary
  - Build mechanisms for (or test) most promising set of components

- Identify dominant reactions and transport data contributing to extinction behavior
  - Refine model / mechanisms as necessary

- Identify surrogate for de-oxygenated biodiesel, candidate for biojet fuel, from UOP

- Measure and test mechanisms for emissions data
  - Soot and NO\textsubscript{x}

- Apply systematic mechanism reduction to allow application of fuel models to jet-engine simulations