Use of Hydrocarbon-based Alternative Fuels in Gas Turbine Applications

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USAF SBIR Contract #

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Background and Motivation

- Alternatives to petroleum-based fuels are of interest to the aviation and power generation industry, adding another layer of complexity from a combustion behavior and fuel modeling standpoint.
- Alternative jet fuels need to be “drop-in” ready – i.e. function without modifications to the engine components while not affecting engine performance (emissions, stability etc.)
- Alternative fuels for power generation should not affect pollutant emissions (NOx, CO, particulates) while not greatly affecting engine maintenance schedules
- Examples of alternative jet fuels include:
  - Hydrotreated Renewable Jet Fuel (HRJ)
  - Fischer-Tropsch Fuels (F-T Fuels)
    - E.g. SPK, IPK, S-8
Background and Motivation

- A more complete method to test the combustion and ignition of alternative fuels is to examine the behavior of the fuels across a range of oxidizer conditions.
- Jet fuel injected into turbine exhaust of aircraft engines results in combustion at vitiated conditions which represent more complex combustion regimes compared to standard air.
- Exhaust gas recirculation (EGR) is being examined as a way to control emissions in power generation applications.
- Vitiated air in this study is defined as:
  - oxidizer stream with reduced O₂ concentrations typically due to EGR or operation as secondary combustion devices
  - O₂ concentrations as low as 12 – 18 vol% as well as the presence of combustion products including H₂O, CO₂, CO, and NOₓ
Background and Motivation

- Experimental work has shown that vitiation causes significant variations to combustion processes including:
  - flame propagation
  - ignition
  - extinction
  - emissions
- There are limited experimental data available for combustion of liquid hydrocarbon fuels under vitiated conditions.
- The focus of this effort is on the ignition behavior of petroleum based JP-8 and its alternatives at low-pressure vitiated conditions.
- The data obtained from this effort will be used to further develop kinetic models for surrogate fuels under normal air and vitiated combustion conditions.
Effect of Vitiation on Flame Speed

- Vitiation has been shown to have significant effects on flame propagation.
- Effects have been found to be based on the thermodynamics and the kinetics of the diluent species present in vitiated air.
- In the case of CO₂, its presence in propane/air flames reduced flame speed to a greater degree than would be expected based solely on its thermodynamic properties.

Figure adapted from Gokulakrishnan et al. 2014

Effect of Vitiation on Ignition

- Previous effort [Fuller et al. 2011] examined the effects of vitiation on ignition delay time of JP-8.
- Temperature, O₂ and NOₓ were found to have significant effect on the induction chemistry of jet fuels.
- Presence of NOₓ specifically reduces ignition delay time quite significantly when it is introduced to the oxidizer stream in relatively small quantities (50 - 1000 ppm).
Alternative Jet Fuels: FT-SPK and HRJ

Petroleum → Treating → Hydrocracking → Fractionation → JP-8

Natural Gas → Synthesis Gas / Purification → Fischer-Tropsch Synthesis → Conversion and Upgrading → FT-SPK

Coal → Gasification

Biomass

Waste Fats & Oils → Treating → Hydrocracking → Fractionation → HRJ

Plant / Algae Oils
Alternative Jet Fuels

- Current study examined 5 separate fuels:
  - JP-8 6169
  - F-T: Sasol IPK 7629
  - Shell SPK 5729
  - HRJ: Camelina 7720
  - Tallow 6308

- Compositions and combustion characteristics of the fuel properties varied significantly.

- Alternative fuels lack aromatic and cyclo-paraffinic content found in JP-8 but are comprised of larger quantities of iso-paraffins

Fuel data provided by Tim Edwards (AFRL) and Won et al. (AIAA 2013-0156)
GC-MS Chromatography: JP8 vs FT Fuels

JP8-6169

nC_7  nC_8  nC_9  nC_{10}  nC_{11}  nC_{12}  nC_{13}  nC_{14}  nC_{15}  nC_{16}

FT-SPK

nC_7  nC_8  nC_9  nC_{10}  nC_{11}  nC_{12}  nC_{14}
GC-MS Chromatography: JP8 vs FT Fuels

JP8-6169

FT-IPK

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Jet Fuel Surrogate Kinetic Model

- CSE detailed surrogate kinetic model consists of four components to represent chemical groups found in jet fuels
  - n-paraffins: n-Dodecane/n-Decane
  - Iso-paraffins: iso-Octane
  - Aromatics: n-propyl-Benzene

- The surrogate model was validated for a wide range of conditions using kinetic experimental data for ignition delay time, flame speed and species profiles

- The kinetic mechanism also includes detailed nitrogen chemistry for vitiation and NOx emission predictions

- Surrogate mixture formulation is based on three target criteria:
  - Hydrogen-Carbon Ratio (H/C)
  - Derived Cetane Number (DCN)
  - Threshold Sooting Index (TSI)
### Alternative JP-8 Surrogate Mixtures

<table>
<thead>
<tr>
<th>Surrogate</th>
<th>JP-8 6169</th>
<th>IPK 7629</th>
<th>SPK 5729</th>
<th>Tal 6308</th>
<th>Cam 7720</th>
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<td>n-Dodecane</td>
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<td>propyl-Benzene</td>
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<td>0.193</td>
<td>0.087</td>
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**Surrogate Mixture Properties (CSE Calculations)**

<table>
<thead>
<tr>
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<th>DCN</th>
<th>TSI</th>
<th>H-C Ratio</th>
<th>MW</th>
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**Target Fuel Properties (Princeton Measurements)**

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<th>TSI</th>
<th>H-C Ratio</th>
<th>MW</th>
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<td>9.11</td>
<td>2.237</td>
<td>136.7</td>
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<td>11.58</td>
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<td>Cam 7720</td>
<td>58.9</td>
<td>11.99</td>
<td>2.202</td>
<td>165.0</td>
</tr>
</tbody>
</table>
Hydrocarbon Oxidation Pathways

Fuel
RH

H-atom abstraction

Products + OH

Propagation

O2

RO2

QOOH

Products + OH

O2

O2QOOH

OH + R’OOH

Branching

RO + OH

Low temperature oxidation

Intermediate temperature oxidation

RH

R + H2O2  \rightarrow  HO2 + Alkene

Branching

β-scission

Alkene + small alkyl radicals (C1, C2, C3)

Branching

OH + OH

OH + OH

OH + OH

OH + OH

Intermediate temperature oxidation

High temperature oxidation

H + Alkene

Branching

O2

O2

OH + O

OH + O
Experimental Conditions and Setup

- Pressure
  - 1 atm

- Temperature
  - 832 K, 875 K, & 917 K

- Equivalence Ratio
  - 0.5, 1.0, & 1.5

- Fuel:
  - JP-8, IPK, SPK, Camelina & Tallow

- Oxidizer Composition:
  - O₂: 17 mol% & 20 mol%
  - NOₓ: 0 ppmv – 755 ppmv
**Ignition Delay Time w/out Vitiation**

**FT Fuels**

**HRJ Fuels**

**Experimental Activation Energies (832 – 917 K)**

<table>
<thead>
<tr>
<th>Fuel</th>
<th>E [kcal/mol]</th>
<th>DCN</th>
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<tbody>
<tr>
<td>JP-8</td>
<td>30.90</td>
<td>47.3</td>
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<tr>
<td>Sasol IPK</td>
<td>40.40</td>
<td>31.3</td>
</tr>
<tr>
<td>Shell SPK</td>
<td>30.78</td>
<td>58.4</td>
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<tr>
<td>Camelina</td>
<td>31.49</td>
<td>58.9</td>
</tr>
<tr>
<td>Tallow</td>
<td>33.11</td>
<td>58.1</td>
</tr>
</tbody>
</table>
Variation in IDT between the fuels reduces with increased NO$_x$
Sasol IPK has shorter IDT despite having the lowest DCN
HRJ Tallow has longer IDT while DCN is higher than JP-8 and Sasol IPK
The marginal effect on IDT diminishes with an asymptotic behavior as NO$_x$ concentration approaches 800 ppm
Surrogate Model Development

- CSE jet fuel surrogate kinetic model is a four-component surrogate kinetic model validated for each individual component.
- n-Paraffins:
  - n-decane & n-dodecane
- iso-Paraffins:
  - iso-octane
- Aromatics:
  - n-propyl-benzene

For Jet-A and JP-8 mixtures the surrogate model predicts ignition delay time reasonably well but requires development for alternative fuels and vitiated combustion.
**Surrogate Model Composition**

- Surrogate mixture compositions are determined by matching the following target characteristics (Dooley et al., 2010):
  - hydrogen-to-carbon ratio (H/C)
  - derived cetane number (DCN)
  - threshold sooting index (TSI)
  - mean molecular weight (MW)

- Surrogate mixture compositions (mol %) for the fuels examined in this study are provided below:

<table>
<thead>
<tr>
<th>Surrogate</th>
<th>JP-8</th>
<th>Sasol IPK</th>
<th>Shell SPK</th>
<th>HRJ Camel.</th>
<th>HRJ Tallow</th>
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</thead>
<tbody>
<tr>
<td>n-decane</td>
<td>0.0</td>
<td>0.0</td>
<td>74.6</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>n-dodecane</td>
<td>38.2</td>
<td>16.0</td>
<td>4.5</td>
<td>61.1</td>
<td>59.5</td>
</tr>
<tr>
<td>iso-octane</td>
<td>37.2</td>
<td>64.7</td>
<td>12.2</td>
<td>29.2</td>
<td>31.5</td>
</tr>
<tr>
<td>propyl-benzene</td>
<td>24.6</td>
<td>19.3</td>
<td>8.7</td>
<td>9.6</td>
<td>9.0</td>
</tr>
</tbody>
</table>
Surrogate Component Experiments

Effect of Temperature

- n-Dodecane
  - Phi - 1.0
  - O₂ - 20 mol%
  - 832 K, 875 K, 917 K

- Iso-Octane
  - Phi - 1.0
  - O₂ - 20 mol%
  - 875 K, 917 K

Effect of Oxidizer O₂

- n-Dodecane
  - Phi - 1.0
  - Temp - 875 K
  - 14% O₂, 17% O₂, 20% O₂

- Iso-Octane
  - Phi - 1.0
  - Temp - 875 K
  - 14% O₂, 17% O₂, 20% O₂
Surrogate Model Comparison

- Overall the model predicts effect of NO\textsubscript{x} on IDT for JP-8, SPK and HRJ Tallow reasonably well.
- The model does not predict IDT well for the Sasol IPK fuel.
- Sasol IPK: ~95% iso-paraffins with the lowest DCN
- Current model uses highly-branched iso-octane to model iso-paraffinic fuel components
2-component surrogate for IPK, comprised of 82 mol % iso-octane and 18 mol % n-dodecane (DCN = 31), was tested in the flow reactor.

Model predicts IDT of the iC\textsubscript{8} / nC\textsubscript{12} mixture significantly better than the it does for the IPK fuel.

Work in progress to investigate weakly-branched iso-paraffinic fuels to improve the surrogate model.
Modeling of Jet Fuel-NO$_x$ Kinetics

- NO$_x$ promotes oxidation in the low- and intermediate-temperature regimes through fuel independent and fuel dependent pathways.

- Major fuel-independent reaction pathways of NO$_x$ on jet fuel oxidation promotes OH radical production:
  - $\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$

- Fuel dependent reactions involve NO$_2$ to form alkyl radicals and HONO/HNO$_2$ and eventually NO and OH:
  - $\text{C}_x\text{H}_y + \text{NO}_2 = \text{C}_x\text{H}_{y-1} + \text{HONO/HNO}_2$
  - $\text{HNO}_2 + \text{M} = \text{HONO} + \text{M}$
  - $\text{HONO} + \text{M} = \text{NO} + \text{OH} + \text{M}$

- Fuel dependent HC-NO$_x$ interaction is relatively better understood for natural gas surrogate fuels (Gokulakrishnan et al. CNF 2014) than gasoline or jet fuels.
Lean, Premixed Prevaporized Combustion

- Ground-based power production is highly regulated for pollution emissions (NOx, CO, particulates)
  - Lean, Premixed combustion allows for control of flame temperature
  - Lower flame temperature reduces NOx production and minimizes soot production
- Typical Lean, Premixed Gas Turbines burn natural gas
- Many locations do not have access to low-cost natural gas
  - Need pipeline infrastructure to move natural gas from wells to users
  - Liquified natural gas (LNG) requires significant processing, adding expense
  - Liquid fuels typically have higher energy density and are easier to transport
- Techniques for ‘clean’ combustion of liquid fuels are needed
LPP Combustion Concept

**LPP** = Lean, Premixed & Prevaporized

- LPP Skid converts liquid fuel into a substitute natural gas (LPP Gas) by vaporizing the liquid fuel into a reduced-oxygen background gas (diluent).
- LPP Gas properties adjusted with choice/quantity of diluent to match natural gas characteristics (heating value, Modified Wobbe Index, etc.)
- LPP Gas is burned with low emissions in place of natural gas in combustion device.
- Burning renewable liquid fuels (biodiesel, ethanol, etc.) creates a low-emissions, renewable energy power plant with no net CO₂ emissions.
Combustor Technology Review

Traditional Combustion of Liquid Fuels in a Spray (Diffusion) Flame Creates High Levels of NOx, CO and Particulate Matter, even with Significant Water Injection to Reduce Emissions.

Gaseous Fuel Combustion (with Natural Gas or LPP Gas) in a Lean, Premixed Burner Creates a Low-Emissions Combustion
Fuel Autoignition Characteristics

Autoignition becomes a problem for higher hydrocarbons, at higher inlet temperatures, where it is not a problem for natural gas.
Premixed Combustion of Liquid Fuels

NOx Emissions
Capstone C30

- Methane
- Gasoline
- Naphtha
- Biodiesel
- Kerosene
- JP-8
- S-8
- #2 Diesel Fuel
- Acetone
- Iso-Propyl Alcohol
- Ethanol
- Toluene
- Toluene
- Pentane
- Propane

DLE Mode
Premixed Combustion of Liquid Fuels

CO Emissions
Capstone C30

- Methane
- Gasoline
- Naphtha
- Biodiesel
- Kerosene
- JP-8
- S-8
- #2 Diesel Fuel
- Acetone
- Iso-Propyl Alcohol
- Ethanol
- Toluene
- Pentane
- Propane

DLE Mode

Load (kW)

CO (ppm, 15% O₂)
Conclusions

- Alternative fuels are viable ‘drop-in’ replacements for jet engines
- Differences in chemical composition can alter the combustion behavior of these fuels under both standard and vitiated conditions
- Current 4-component surrogate model predicts IDT for JP-8 and certain alternative fuels at the experimental conditions of this study with reasonable accuracy
- Vitiated combustion aspects of the model, specifically NO\textsubscript{x} chemistry, are found to predict the enhancement of ignition, accounting for the change of reaction pathways in the low- and intermediate-temperature regimes
- Lean, Premixed, Prevaporized combustion is a viable option for burning alternative liquid fuels in gas turbines
  - Emissions are similar to those found for natural gas combustion
  - Wide-range of liquid fuels have been tested
Future Work

- Future research will focus on improvement of the surrogate model at both standard air and vitiated conditions including:
  - Inclusion of additional surrogate component(s) to represent larger, less-branched iso-paraffins
  - Investigation of additional target criteria to improve surrogate formulation
Acknowledgements

- U.S. Air Force Research Laboratory
- Dr. Barry Kiel, Air Force Research Laboratory
- Bethany Huelskamp at ISSI
- Dr. Tim Edwards, Air Force Research Laboratory
Thank You

• Questions?

• Contact:
  ◦ mklassen@csefire.com
Extra Slides
Ignition Delay Time Measurement

- Absorption of infrared HeNe beam (3.39 μm) by H-C bonds in the fuel/oxidizer mixture used to determine time delay between solenoid activation and fuel injection into the reactor.
- OH* excitation measured by PMT equipped with 310 (± 5) nm band pass filter to determine ignition event.
- IDT ($\tau_{ig}$) measured as the time difference between initial PMT excitation and 50% reduction in the HeNe laser signal at the diffuser entrance.
Data provided by Tim Edwards (AFRL) 2014
JP-8 & Hydrotreated Fuel Comparisons

Data provided by Tim Edwards (AFRL) 2014
Jet Fuel Comparisons

- Five separate jet fuels were examined in this study:
  - Petroleum based: JP-8 6169
  - Fischer-Tropsch Fuels: Sasol IPK 7629 & Shell SPK 5729
  - Hydrotreated Renewable Jet Fuels: Camelina 7720 & Tallow 6308

<table>
<thead>
<tr>
<th>Jet Fuel Type</th>
<th>Air Force POSF #</th>
<th>Density (^{a}) [kg/m(^3)]</th>
<th>DCN(^{b})</th>
<th>TSI(^{b})</th>
<th>H/C Ratio(^{b})</th>
<th>MW(^{b}) [g/mol]</th>
<th>Molecular Formula(^{b})</th>
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<tbody>
<tr>
<td>JP-8</td>
<td>6169</td>
<td>785</td>
<td>47.3</td>
<td>19.28</td>
<td>2.02</td>
<td>153.9</td>
<td>C(<em>{11.0})H(</em>{22.1})</td>
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<td>F-T Sasol IPK</td>
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<td>2.20</td>
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\(^{a}\) – Edwards (2014); \(^{b}\) – Won et al. (2013)
Reaction Sensitivity for NO$_x$ Addition

**Normalized Sensitivity Coefficient w.r.t. Fuel Molecule**

- **NO = 500 ppmv (100% nC12)**
- **NO = 0 ppmv (100% nC12)**

Reactions:
- HONO($+M$) = NO + OH($+M$)
- NO + HO$_2$ = NO$_2$ + OH
- CH$_3$ + NO$_2$($+M$) = CH$_3$NO$_2$($+M$)
- CH$_3$ + NO$_2$ = CH$_3$O + NO
- RH + HO$_2$ = R + H$_2$O$_2$
- HO$_2$ + HO$_2$ = H$_2$O$_2$ + O$_2$
- H$_2$O$_2$($+M$) = OH + OH($+M$)
Jet Fuel Chemical Class Composition

Ref: Moses (2012)