Sustainable Aviation Fuel R&D at Sandia National Laboratories

Presented by

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Fuel Production

Ryan W. Davis
Principal Member of Technical Staff
- Sandia staff have engaged in biofuels R&D for over 3 decades
  o in-house collaboration between Combustion Research Facility (CRF) and Chemical and Biological Sciences.

- Examples of recent production process development and scale-up for heavy-duty ground transport

- Opportunities for utilizing new biomass feedstocks for SAF

- Lessons from sustainability and cost assessments
Demonstrated Capabilities – From feedstock to production for engine testing

- Upgrading fusel alcohols (AOA class)
- Rational design & Scale-up (AOA-7)
- Structure-property relationships

We are using computational modeling to identify promising SAF production targets for adherence to JetA specifications, and identifying opportunities for reduced sooting.
• Production process maximizes utilization of mixed substrates commonly found in algae, food waste, and distiller’s grains, e.g. roughly equal fractions of lipids, carbs, and proteins

• FAFEs provide improved LHV (+15%), cetane (+21%), and cold flow (-7°C cloud point) performance compared to FAME, without sacrificing viscosity, lubricity, or sooting metrics

• Production methods compatible with existing biodiesel production and distribution infrastructure

• Subsequent reduction of ester to ether, i.e. fatty alkyl ethers, provides additional MCCI fuel performance, including further improved cold flow (-15°C cloud point), LHV (+11%), and sooting (-7.4 YSI/MJ)

Klein et al Biomass Bioenergy 2021
Monroe et al Fuel 2020
Carlson et al Energy & Fuel 2020
Demonstrated Capability – Continuous flow chemistry

Proof-of-Concept (DAOA synthesis for Co-Optima)

\[ RCOOH \xrightarrow{\text{flow conditions}} RCOOR' \]

>90% conv.; >2 kg scale continuous operation >7 d

Potential Application for SAF (diacid synthesis)

\[ \text{flow ozonolysis} \rightarrow \text{HO}_2\text{C} \]

Myllenbeck et al. manuscript in preparation for Green Chemistry.

Myllenbeck N, Davis RW, Monroe E, Carlson J “Alkyl-di(alkoxyalkanoates as biodervied, high cetane diesel fuels” US Patent No. 11,492,565

We have facilities and expertise for lab-scale conversion testing and process integration using next generation biomass feedstocks
OPPORTUNITY: UNDERUTILIZED PROTEINACEOUS BIOMASS FEEDSTOCKS CAN INCREASE PRODUCTION CAPACITY BY 400% TO FULFILL THE SAF GRAND CHALLENGE

### 2030 Practical Feedstock Availability (Mt)

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Availability (Mt)</th>
<th>Protein Content</th>
<th>Capacity (BGal/yr)</th>
<th>Yield (Mbbl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste &amp; residue lipids</td>
<td>40</td>
<td>~10-25% protein</td>
<td>1100</td>
<td>195</td>
</tr>
<tr>
<td>Oil trees on degraded land</td>
<td>85</td>
<td>~0.2-5% protein</td>
<td>660</td>
<td>3815</td>
</tr>
<tr>
<td>Oil-cover crops</td>
<td>70</td>
<td>~0.2-5% protein</td>
<td>580</td>
<td>3815</td>
</tr>
<tr>
<td>Cellulosic cover crops</td>
<td></td>
<td>~10-25% protein</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agricultural residues</td>
<td></td>
<td>~1-2% protein</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forestry residues</td>
<td></td>
<td>~1-2% protein</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood-processing waste</td>
<td>320</td>
<td>~1-2% protein</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Municipal solid waste</td>
<td>960</td>
<td>~1-2% protein</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

195Mt Current SAF biomass feedstocks
HEFA, FRL = 9 (0.42 g/g SAF yield)
31.6 BGal/yr : 753 Mbbl
20% of 2030 global demand

Technologies are required that can maximize yield from variable proteinaceous biomass feeds

3815Mt Total biomass resource
FRL < 7 (0.256 g/g SAF yield)
158.3 BGal/yr : 3.77 Bbbl
100% of 2030 global demand

Guiding Principles:

• Current feedstocks for high TRL/FRL SAF production (HEFA, AtJ, Biomass gasification) can provide up to ~20% of the 2030 SAF demand.

• Physico-chemical and combustion properties of final products must adhere to tiered-screening req’s for SAF (JetA)

• Vetted pathways focus on those providing sufficiently low carbon intensity and cost-efficient production, with special attention to realizable yield, H₂ consumption, petroleum refinery integration, and feedback from SAF industry

Technology Concept: Mixed Proteinaceous Biomass to Fusel Alcohol SAF intermediates

• Current regulatory limits for fusel alcohol co-products of bioethanol would support ~4% of US SAF demand (18M bbl). By providing the capability to obtain >26% w/w conversion yield from cover crops, we can provide up to 38% of the total US SAF demand.
**Goal:** to de-risk bioconversion of proteinaceous biomass for fuels and co-products for GHG savings

Sandia seeks partners to intensify processes for new biomass feedstocks

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**Novel Fusel-SAF Blend for Net Zero Emissions**

- **Cover-crops**
- **Algae**
- **Distiller’s Grains**
- **Food Waste**

E. coli & C. glutamicum - catalyzed fusel alcohol biosynthesis

**Target:**
- T = 25 g/L
- R = 0.45 g/L/h
- Y = 55% g/g

Fusel alcohols (C4-C8)

Novel isoparaffin SAF (C8 – C16)

Fusel alcohol
Dehydration,
Oligomerization & Hydrogenation (AtJ).

>50% reduced energy req. than ethanol, predicted
LIFE CYCLE CO₂ EMISSIONS ESTIMATES SUGGEST THAT FEW SCENARIOS PROVIDE TARGET GHG REDUCTION COMPARED TO CRUDE OIL-DERIVED JETA

- LCA assuming energy and materials variation by +/- 20%, and H₂ consumption uncertainties,
- JP-10 can achieve life cycle CO₂eq emissions at or below 3.6 gCO₂eq MJ⁻¹ through process optimization, e.g., Lower H₂ consumption at 0.14 KgH₂ Gal⁻¹ Jet fuel
- Fusel alcohol AtJ can achieve life cycle CO₂eq emissions at or below 1.9 gCO₂eq MJ⁻¹ through process optimization, e.g., Lower H₂ consumption at 0.08 KgH₂ Gal⁻¹ Jet fuel

*Best cases for minimizing CO₂ emission correspond to reduced H₂ requirement*

Other authors
Conventional Jet fuel from crude oil: 11.1 gCO₂ MJ⁻¹
Corn oil-based renewable Jet fuel: 22.6 gCO₂ MJ⁻¹
Fischer-Tropsch Jet fuel from Biomass: 4.5 gCO₂ MJ⁻¹

Sandia POC: Carlos Quiroz-Arita
PRELIMINARY TEA OF SANDIA’S SAF CONCEPTS INDICATES COMPETITIVE COSTS COMPARED TO EXISTING METHODS

**Fuel cost at current 2.8$/kg H₂:**

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Cost ($/Gal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>corn stover</td>
<td>6.20</td>
</tr>
<tr>
<td>wheat straw</td>
<td>7.82</td>
</tr>
<tr>
<td>sugar cane</td>
<td>5.71</td>
</tr>
<tr>
<td>forestry residues</td>
<td>5.22</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hydrogenated esters and fatty acids:</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.70 to 11.83 $/Gal</td>
</tr>
</tbody>
</table>

**H₂ is a major driver of Jet fuel cost (e.g., Fusel alcohols in $/Gal):**

<table>
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<tr>
<td>forestry residues</td>
<td>5.22 $/Gal</td>
</tr>
</tbody>
</table>

**Assumptions**

- Electricity cost: 0.07$/KWh
- Feedstock costs:
  - 101 $/ton waste
  - 85 $/ton lignocellulosic biomass
  - 1.13 $/Gal methanol
  - 1225 $/ton toluene
  - 2.8-6.1 $/kg hydrogen

Sandia TEA/LCA POC: Carlos Quiroz-Arita
Fuel Identification

Alexander Landera
Member of Technical Staff
• SAF physical property values measure safety, and performance of a SAF
• A drop-in SAF is highly desirable
  • No changes to aircraft infrastructure needed
  • Cannot be drop-in if it does not meet ASTM standards
• Estimating physical properties of a SAF can
  • Help determine issues early
  • Identify promising SAF components
  • Establish blend limits
• Blend models are hard to develop
  • Large number of components
  • Sparse data parameters
  • Time to solution must be fast

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Constraint</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Energy, MJ/kg</td>
<td>&gt; 42.8</td>
</tr>
<tr>
<td>Energy Density, MJ/L</td>
<td>***</td>
</tr>
<tr>
<td>Density at 15°C, kg/m³</td>
<td>775-840</td>
</tr>
<tr>
<td>Flashpoint, °C</td>
<td>&gt; 38</td>
</tr>
<tr>
<td>Melting point, °C</td>
<td>&lt; -40</td>
</tr>
</tbody>
</table>

Physical property metrics, their constraints, and Jet-A median values
From ASTM D-7566
Approach: Employ modeling in place of time-consuming laboratory measurements for screening SAF components and blends.

Modeling methods employed:

• Equation of State
  • Group contribution theory

• Quantum chemistry
  • Structure energy
  • Reaction barriers
  • Optimized geometries
  • Enthalpies of reaction

Quantities predicted:

Solid-Liquid-Equilibrium

Energy density/Specific energy

Vapor pressure

Liquid densities

Flashpoint

Liquid viscosities

Reaction rates

Soot production

Polymer swelling (o-ring material)
Goal: Use GCxGC data to accurately estimate physical properties of reference aviation fuels

Method: Eliminate minor chemical species (those which are present < 1 wt%)
- Focus on chemical classes for which enough data is available
  - Branched alkanes => 2-methylalkanes
  - Alkyl benzene => linear alkyl benzenes
  - Alkyl monocycloalkanes => linear alkyl cycloalkanes
- These decisions are based on the availability of data, not on actual isomers present in the reference fuels

<table>
<thead>
<tr>
<th>Aromatics</th>
<th>Weight %</th>
<th>Volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkylbenzenes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>benzene (C06)</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>toluene (C07)</td>
<td>0.23</td>
<td>0.21</td>
</tr>
<tr>
<td>C2-benzene (C08)</td>
<td>1.98</td>
<td>1.77</td>
</tr>
<tr>
<td>C3-benzene (C09)</td>
<td>4.17</td>
<td>3.73</td>
</tr>
<tr>
<td>C4-benzene (C10)</td>
<td>2.33</td>
<td>2.09</td>
</tr>
<tr>
<td>C5-benzene (C11)</td>
<td>1.19</td>
<td>1.07</td>
</tr>
<tr>
<td>C6-benzene (C12)</td>
<td>0.66</td>
<td>0.59</td>
</tr>
<tr>
<td>C7-benzene (C13)</td>
<td>0.25</td>
<td>0.22</td>
</tr>
<tr>
<td>C8-benzene (C14)</td>
<td>0.12</td>
<td>0.11</td>
</tr>
<tr>
<td>C9-benzene (C15)</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>C10+-benzene (C16+)</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td><strong>Total Alkylbenzenes</strong></td>
<td><strong>11.00</strong></td>
<td><strong>9.85</strong></td>
</tr>
</tbody>
</table>
Accurate densities within ~ 1% are obtained
DENSITY PREDICTIONS ARE IN GOOD AGREEMENT WITH EXPERIMENTAL MEASUREMENTS

- Blend model shows that density can be accurately modeled. Largest error in validation is 1.4%
- Validated with C6-C15 cycloalkanes
- A select group of cycloalkanes were chosen
  - Based on not meeting density requirements
- Blend models show that density can be accurately modeled
- Blend model shows that even though these molecules can’t be used neat, they can be used as blends in about 35-60 wt.%
- Experimental measurements were performed in collaboration with Los Alamos National Laboratory
ACCURATE VISCOSITIES ARE OBTAINED USING A SIMPLE BLEND MODEL

Experimental viscosities are in good agreement with our modeled viscosities
This is a good initial validation step
SELECTED CYCLOALKANES MEET VISCOSITY REQUIREMENT AS A BLEND OF UP TO 40-80% BY WEIGHT

Viscosity of cycloalkane + POSF-10325 at -20°C

Viscosity of cycloalkane + POSF-10325 at -40°C

Meeting viscosity requirements at -20°C does not ensure you meet requirements at -40°C
Shows the blending limits of select, non-validated, alkanes in POSF-10325
Flashpoints are accurately predicted using a simple blend model.

- N-butylcyclopentane and n-propylcyclohexane were chosen as representative cycloalkanes for blend study.
- As neat molecules they do not meet the flashpoint requirements for jet-A fuel.
- Flashpoint decreases steadily as blends increase.
- n-butylcyclopentane and n-propylcyclohexane can be blended to at least 50% by wt.
U. Dayton analyzed complex jet fuels

- Viscosity and Density were measured.
- Temp from -40°C to 15°C
- Total of 63 fuels were measured
  - From 2020 to 2021
  - Less fuels at -40°C due to freezing
- Viscosity predictions => SUPERTRAPP
- Density predictions => Ratchet eq.
- Viscosity at -40°C is difficult to handle
- Other temperatures are much better
**The challenge:** aromatics promote seal swelling but have high sooting tendencies

**Approach:** conduct a modeling study and literature review to address the following question: Are cycloalkanes viable replacements for aromatics?

**Our findings:**
- Cycloalkanes with single substitutions generally have the best physical properties.
- Unsubstituted cycloalkanes suffer from high melting points.
- Monosubstituted cycloalkanes have beneficially low melting points.
- Poly-substitution typically leads to higher soot levels.
- Flat fused cycloalkanes (e.g., decalins) are good seal swelling agents.

*It depends!*

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**Melting point of monosubstituted 5 and 6 membered rings with linear alkane substitutions.**

**Flashpoint: monosubstituted 3,4, and 5 membered rings with linear alkane substitutions.**

SAF MODELS ENABLE OUR DEVELOPMENT PARTNERS

High performance fuel components:
• Strained ring structures for enhanced energy density and specific energy

Cycloalkane properties:
• Selecting suitable replacements for conventional aromatics

Development of new blend components:
• Sesquiterpenes
• Polycyclopropanated molecules

Blending models for fuel optimization:
• Accurate predictions of viscosity
End-Use

Isaac Ekoto
Manager, Applied Combustion Research
CURRENT SIMULATIONS WELL-PREDICT COMBUSTION AT CRUISE BUT STRUGGLE TO PREDICT MIXING, IGNITION, AND EMISSIONS FORMATION PROCESSES ACROSS THE OPERATING RANGE

Lean Blow-Out

- **Modeling Challenge:** Sub-models lack modularity and are missing relevant processes
- **Experimental Challenge:** Swirl stabilized combustors are resource intensive with complex physicochemical interactions and uncertain boundary conditions
- **Sandia Approach:** Interrogate relevant physics in bespoke experiments with advanced optical and sampling diagnostics used to obtain data needed for associated model development

<table>
<thead>
<tr>
<th>Code</th>
<th>LESLIE</th>
<th>OpenNCC</th>
<th>FLUENT</th>
<th>VIDA</th>
<th>CONVERGE (All with PDPA spray inject &amp; secondary breakup)</th>
<th>EXP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel</td>
<td>FR, PaSR, HyChem Reduced, PDPA w/ breakup</td>
<td>FR, Laminar, HyChem Reduced, PDPA no breakup</td>
<td>FR, EDM, 4-step tuned to HyChem, Rosin-R w/ breakup</td>
<td>FR, PPDF, HyChem Detailed, Rosin-R w/ BU</td>
<td>Zonal FR, Laminar, Dryer-Won Compact</td>
<td>Zonal FR, Laminar, HyChem Skeletal</td>
</tr>
<tr>
<td>A-2</td>
<td>0.070</td>
<td>0.078</td>
<td>0.085</td>
<td>.090</td>
<td>0.085</td>
<td>0.082</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.080</td>
<td></td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>0.090</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.082</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0806</td>
<td>0.0788 to 0.0824</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-1</td>
<td>0.074</td>
<td>0.087</td>
<td>0.094</td>
<td>.085</td>
<td>0.092</td>
<td>0.080</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.084</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.088</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.0869</td>
<td>0.0850 to 0.0884</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Rich, Quench, Lean (RQL) Combustor

1. **Liquid**: Spray breakup and atomization
2. **Flame**: Mixing and ignition
3. **Recirculation Zone**: Flame stabilization / soot formation
4. **Lean-Burn**: Soot aging and oxidation

Sandia Constant-Volume Spray Chamber

- Reproduces relevant CRZ conditions
  - 300 - 1800 K (by vitiation)
  - up to 350 bar
  - 0 – 21% O₂ (exhaust gas)

Single-Hole Atomizer

- Specialized injectors to produce relevant droplet sizes / velocities
AT TAKEOFF CONDITIONS WHERE COMBUSTOR PRESSURES AND TEMPERATURES ARE ELEVATED, TRANSCRITICAL MIXING PROCESSES CAN DOMINATE

- Transcritical liquids undergo faster “diffusive” mixing due to the lack of a liquid-vapor interface

Current modeling approaches only consider classic droplet breakup and evaporation and thus will incorrectly predict the mixing state
**FLAME STABILIZATION**

<table>
<thead>
<tr>
<th>Combustor Condition</th>
<th>Temperature [K]</th>
<th>Pressure [bar]</th>
<th>$O_2$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cruise</td>
<td>800</td>
<td>20</td>
<td>21</td>
</tr>
<tr>
<td>Cruise (CRZ)</td>
<td>1200</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>Take-off</td>
<td>900</td>
<td>60</td>
<td>21</td>
</tr>
<tr>
<td>Take-off (CRZ)</td>
<td>1200</td>
<td>60</td>
<td>15</td>
</tr>
<tr>
<td>DCN</td>
<td>817</td>
<td>21.37</td>
<td>21</td>
</tr>
</tbody>
</table>

- **ASTM D4054**: Derived cetane number (DCN) is the only fuel combustion metric specified.

Ignition behavior at non-cruise conditions deviates substantially relative to correlations with DCN.
• **Electron Energy Loss Spectroscopy**: Soot particle density & bond structure

Soot sampling and high-resolution transmission electron microscopy (HR-TEM) used to characterize particle nanostructure and aggregate morphology
BEYOND SOOT PARTICLE MASS AND NUMBER, SURFACE PROPERTIES RELEVANT TO CONTRAILS FORMATION CAN ALSO BE CHARACTERIZED

• **Energy Dispersive X-ray Spectroscopy:** Soot surface atomic composition (e.g., sulfates)

• Companion project seeks to clarify water nucleation processes as a function of soot surface chemistry and morphology in a newly developed atmospheric chamber

Sandia approach complements existing gas turbine combustor research by leveraging well-controlled facilities that replicate relevant conditions to support development of physics-based modeling methods
Emissions & Repercussions

Shruti Mishra
• The benefits of sustainable aviation fuel include co-benefits such as health benefits.

• Blending SAF into jet fuel could reduce the air pollutants due to lower sulfur and aromatics content in SAF (Benosa et al., 2018).

• Reduction in air pollutants lead to reduction in mortalities and morbidities related to the air pollutants (Arter et al., 2022).

• SNL are quantifying the health benefits of SAF including those to disadvantaged communities.
1. Air pollutants from Jet fuel Vs. Blended SAF/Jetfuel
2. Identify the area of influence (AoI)
3. Quantify the change in morbidity and mortalities due to increased use of SAF
4. Quantify the SAF led reduction in the number of mortalities among target disadvantaged communities (DAC).
The benefits of SAF to disadvantaged communities in other major airports in the U.S. should be significant.

skhadka@sandia.gov
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