Energy & Homeland Security

Sustainable Aviation Fuel R&D at Sandia National Laboratories

Presented by

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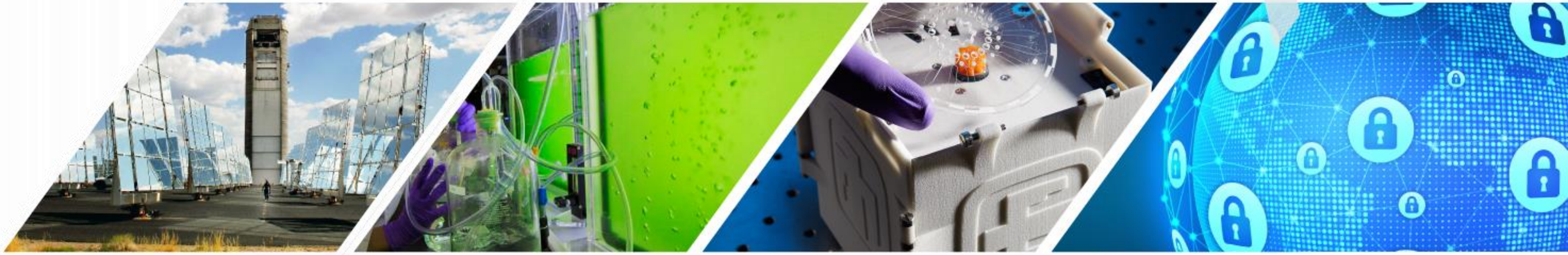
SAND2023-12144C

Introduction → Fuel Production → Fuel Identification → End-Use → Emissions & Repercussions



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Fuel Production

Ryan W. Davis

Principal Member of Technical Staff

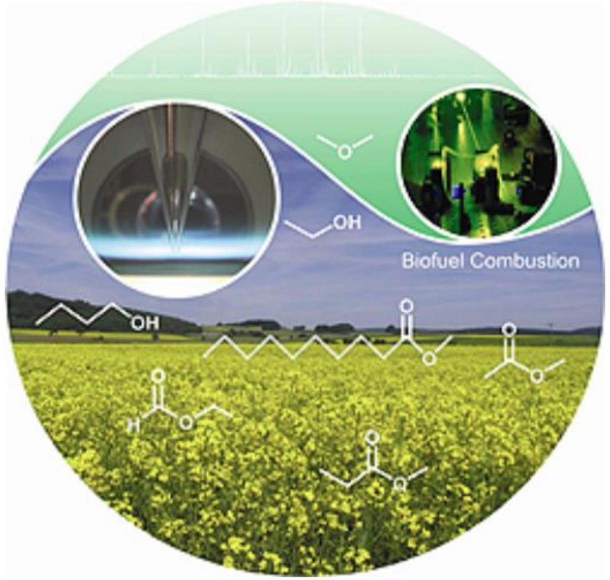
SANDIA'S LEGACY IN ADVANCED BIOFUELS PRODUCTION

- Sandia staff have engaged in biofuels R&D for over 3 decades
  - 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

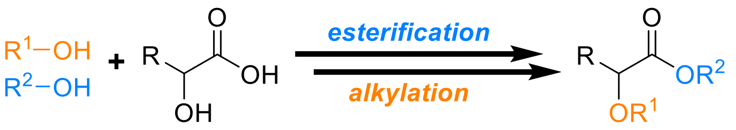
- Opportunities for utilizing new biomass feedstocks for SAF

- Lessons from sustainability and cost assessments

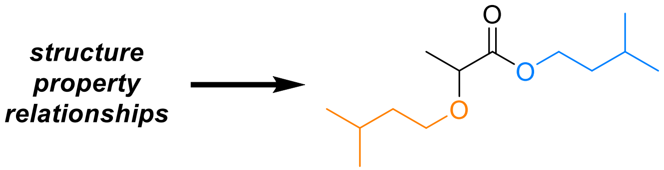


Demonstrated Capabilities – From feedstock to production for engine testing

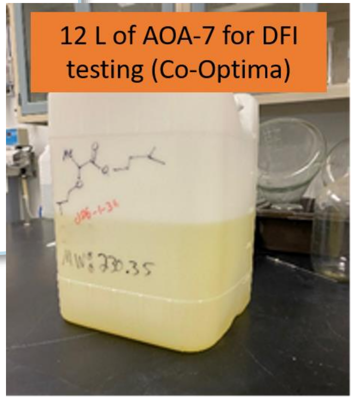
Upgrading fusel alcohols (AOA class)

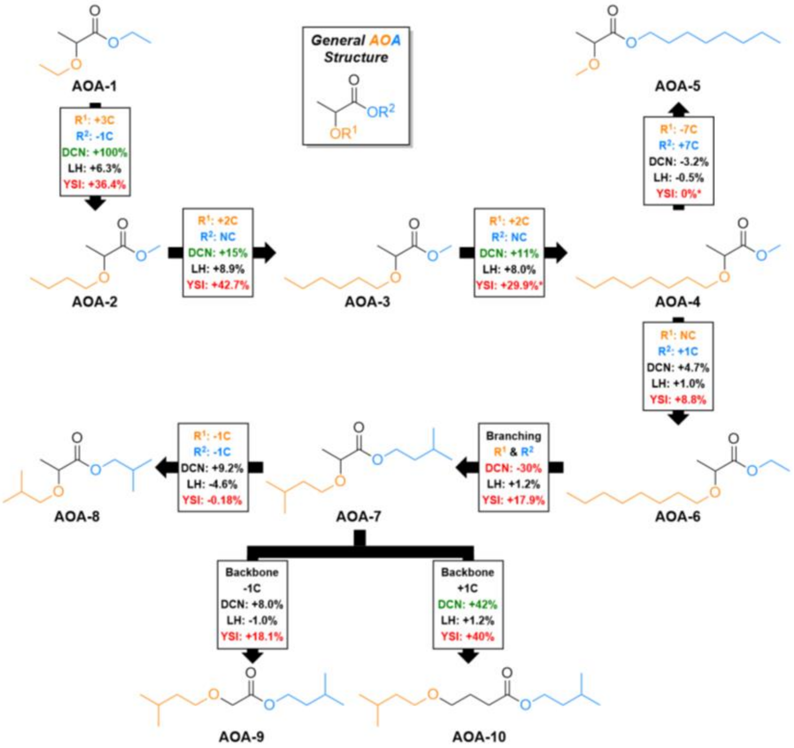


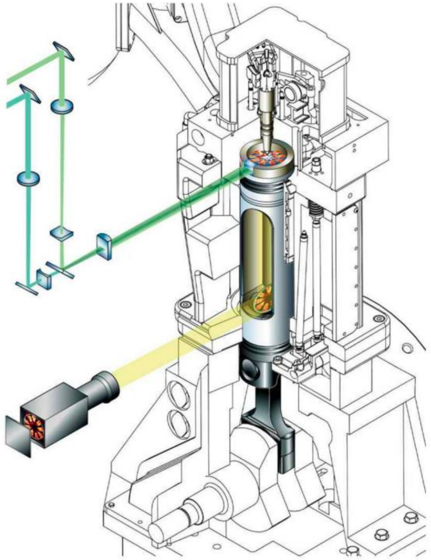
Rational design & Scale-up (AOA-7)



Monroe et al *Energy & Fuels* 2022







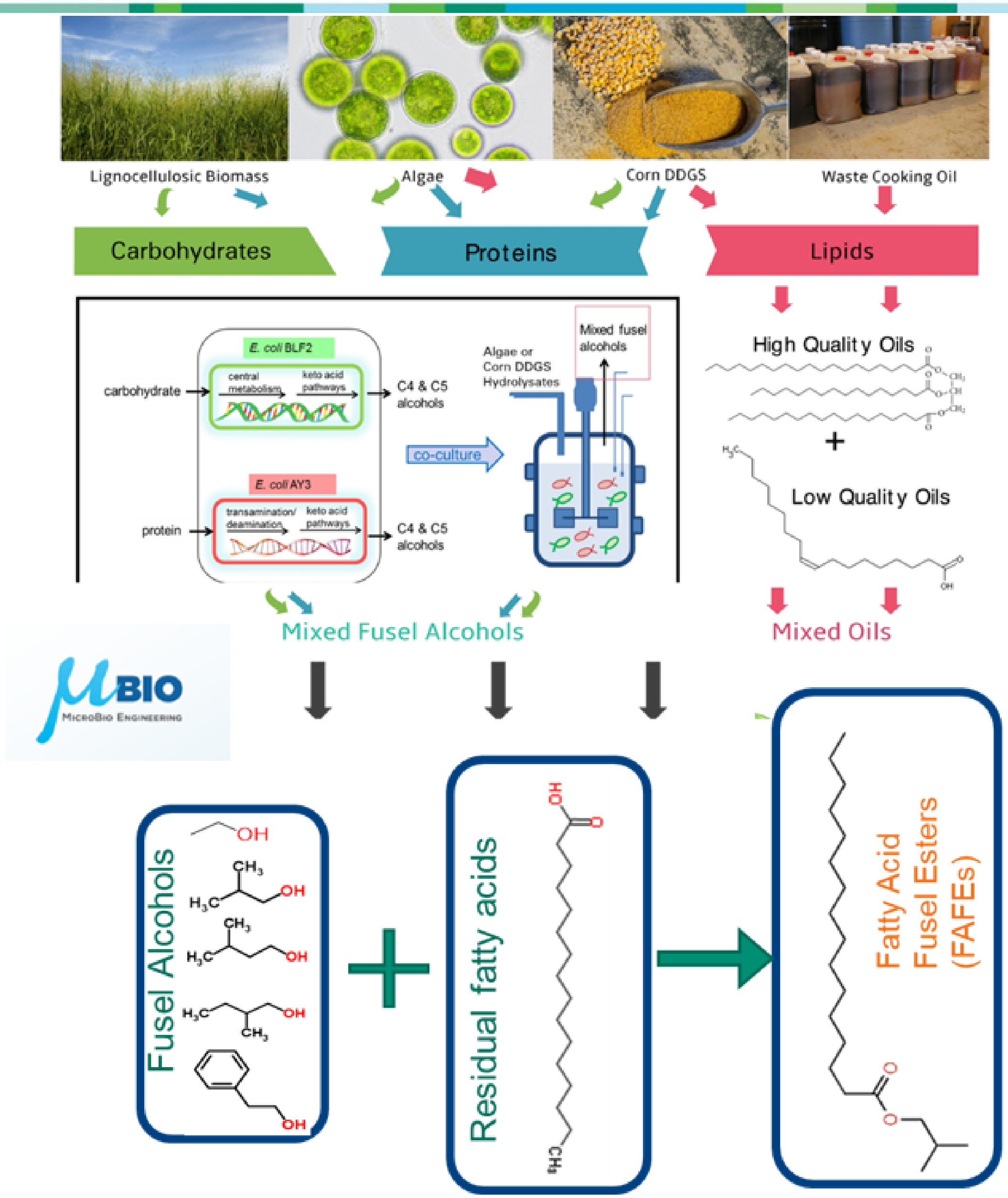
Nilsen et al *SAE Intl* 2019

We are using computational modeling to identify promising SAF production targets for adherence to JetA specifications, and identifying opportunities for reduced sooting

Co-Optimization of Fuels & Engines

SUPERIOR PERFORMANCE BIODIESEL FROM WHOLE BIOMASS PROCESSING

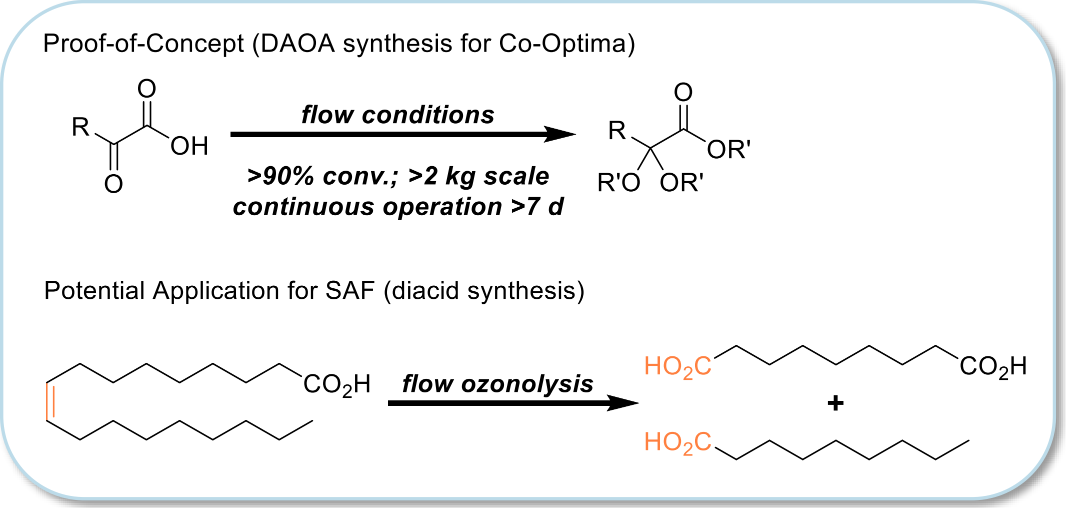
- Production process maximizes utilization of mixed substrates commonly found in algae, food waste, and distiller's grains, e.g. roughly equal fractions of lipids, carbs, and proteins
- FAFEs provide *improved LHV (+15%), cetane (+21%), and cold flow (-7°C cloud point) performance* compared to FAME, 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

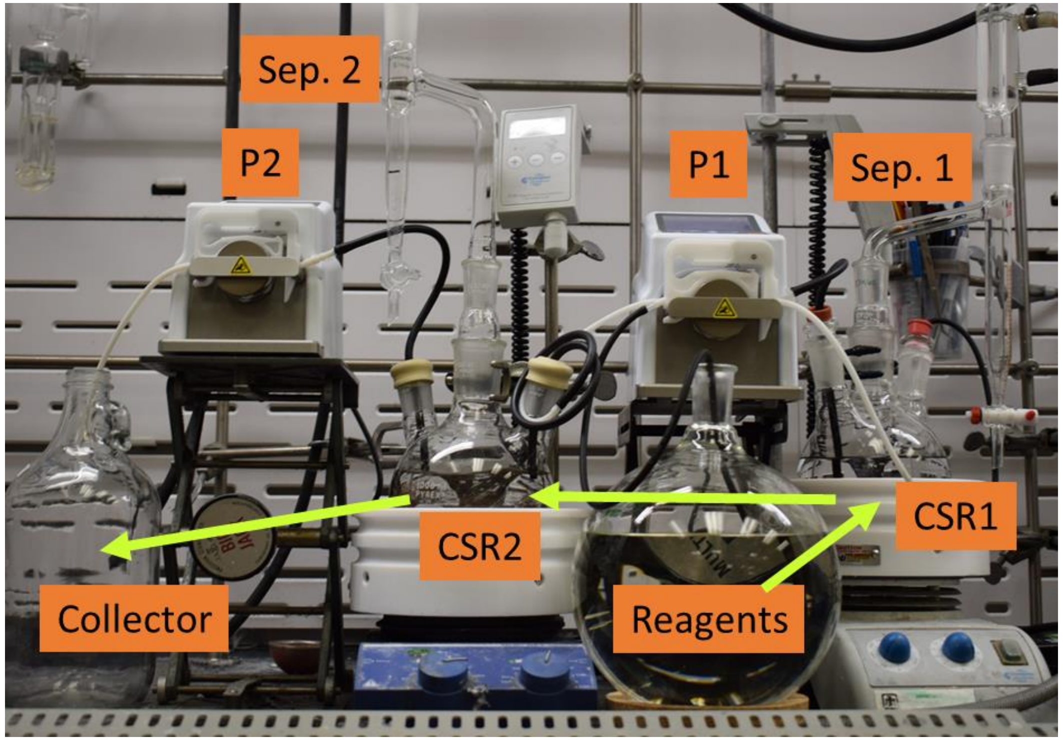
PROCESS DEVELOPMENT: FROM BIO-INTERMEDIATES TO BIO-BLENDSTOCKS

Demonstrated Capability – Continuous flow chemistry



Myllenbeck et al. manuscript in preparation for *Green Chemistry*.

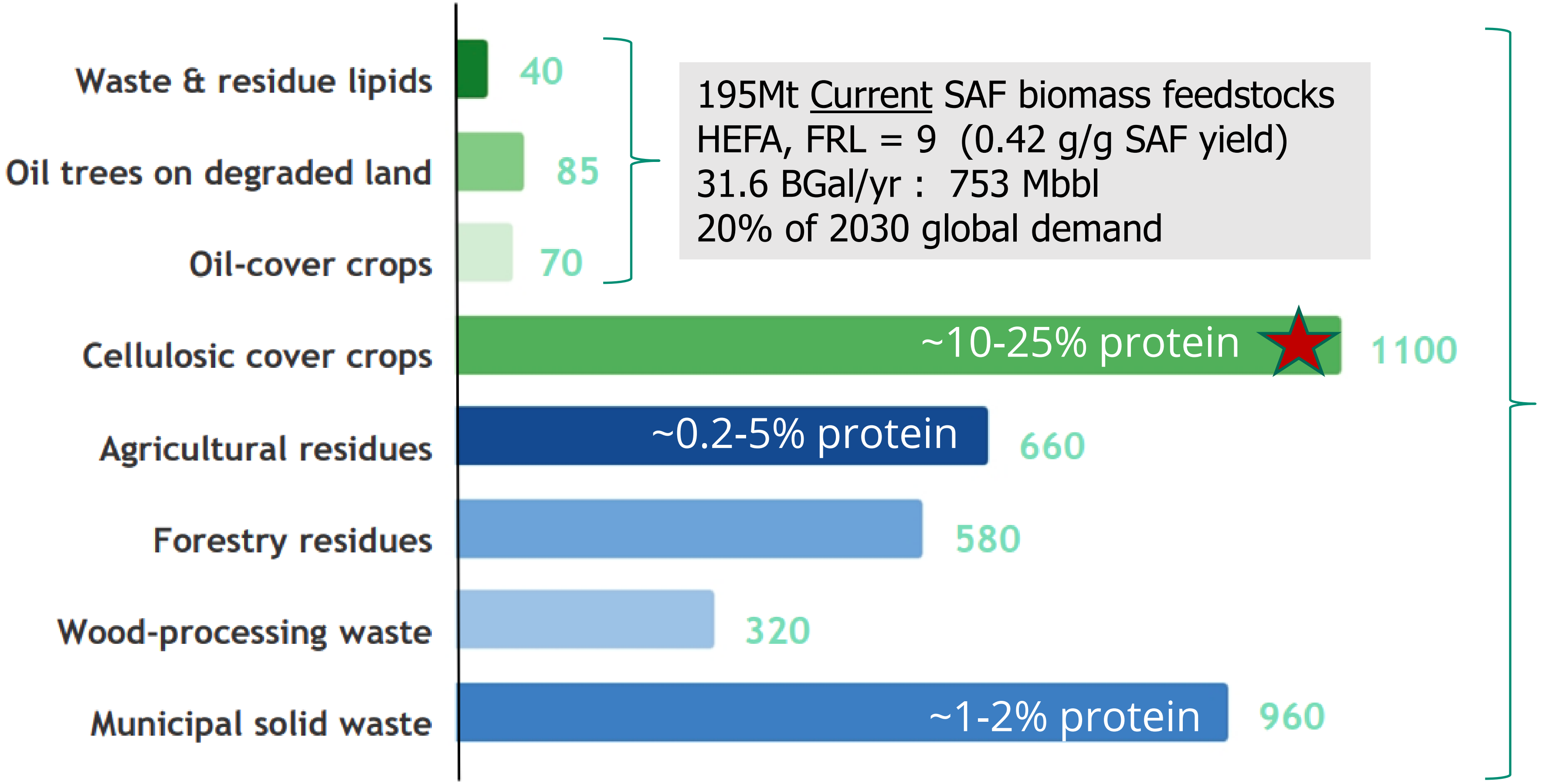
Myllenbeck N, Davis RW, Monroe E, Carlson J "Alkyl-dialkoxyalkanoates as biodervied, high cetane diesel fuels" US Patent No. 11,492,565



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)



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

World Economic Forum & McKinsey & Company, Clean Skies for Tomorrow Insight report, November 2020

CORE COMPETENCIES IN PRE-TREATMENT AND CONVERSION OF VARIED PROTEINACEOUS BIOMASS SUPPORTS SAF TECHNOLOGY MATURATION

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, H_2 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.*

Novel Fusel-SAF Blend for Net Zero Emissions

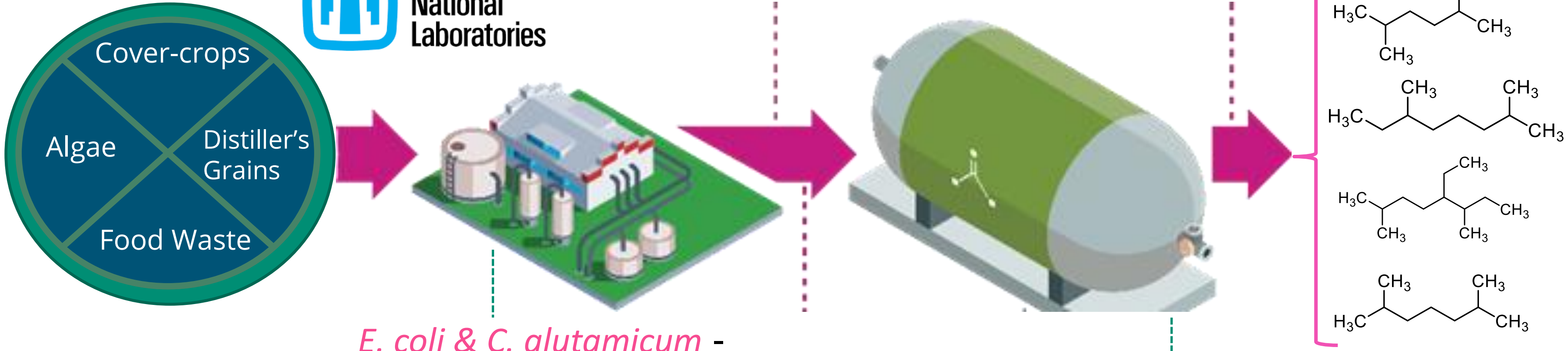
Goal: to de-risk bioconversion of proteinaceous biomass for fuels and co-products for GHG savings

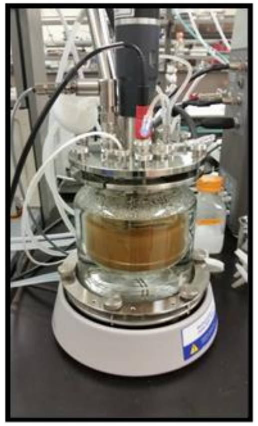
Sandia seeks partners to intensify processes for new biomass feedstocks

Sandia National Laboratories

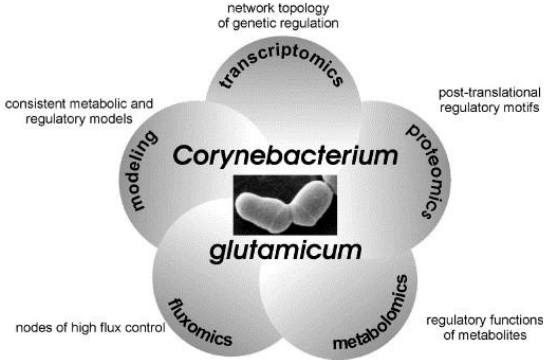
Fusel alcohols (C4-C8)

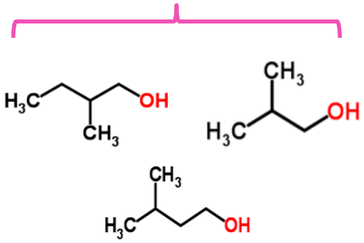
Novel isoparaffin SAF (C8 – C16)





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

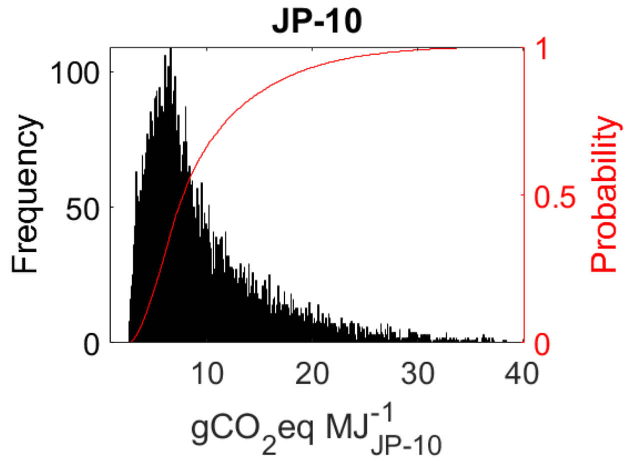


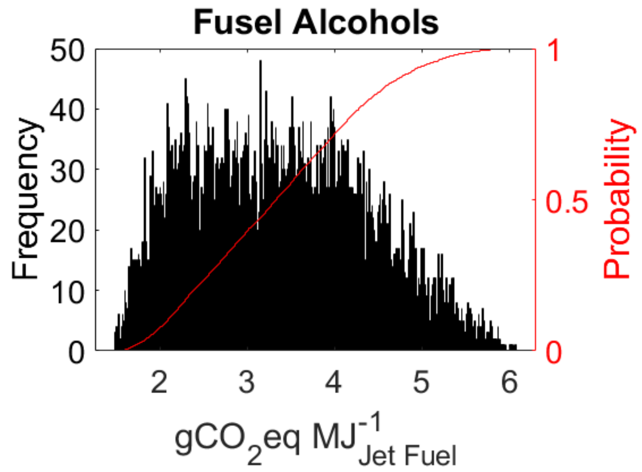


Target:
T = 25 g/L
R = 0.45 g/L/h
Y = 55% g/g

Fusel alcohol Dehydration, Oligomerization & Hydrogenation (AtJ). >50% reduced energy req. than ethanol, predicted

LIFE CYCLE CO_2 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 H_2 consumption uncertainties,***
- ***JP-10*** can achieve life cycle ***CO_2eq emissions at or below 3.6 $gCO_2eq\ MJ^{-1}{}_{JP-10}$*** through process optimization, e.g., Lower H_2 consumption at 0.14 $KgH_2\ Gal_{Jet\ fuel}$
- ***Fusel alcohol AtJ*** can achieve life cycle ***CO_2eq emissions at or below 1.9 $gCO_2eq\ MJ^{-1}{}_{Fusel\ alcohol}$*** through process optimization, e.g., Lower H_2 consumption at 0.08 $KgH_2\ Gal_{Jet\ fuel}$

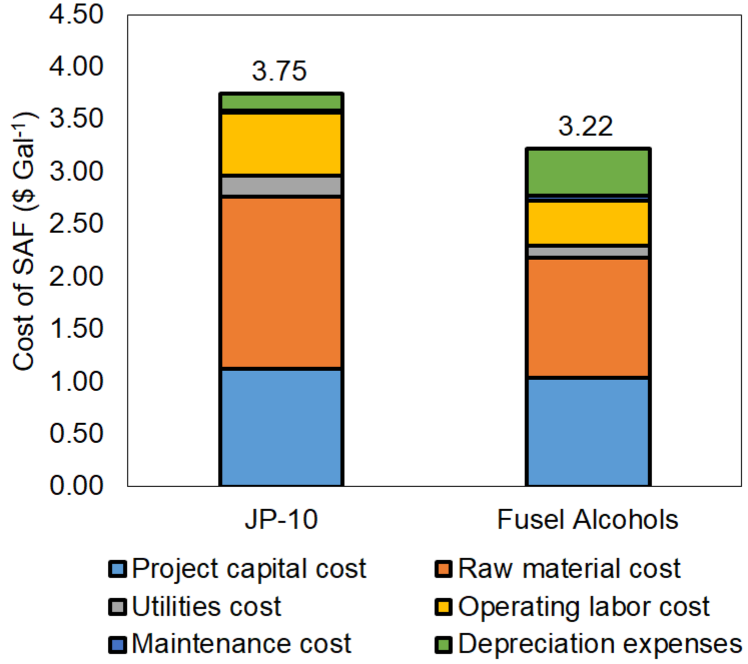
Best cases for minimizing CO_2 emission correspond to reduced H_2 requirement

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 H_2:



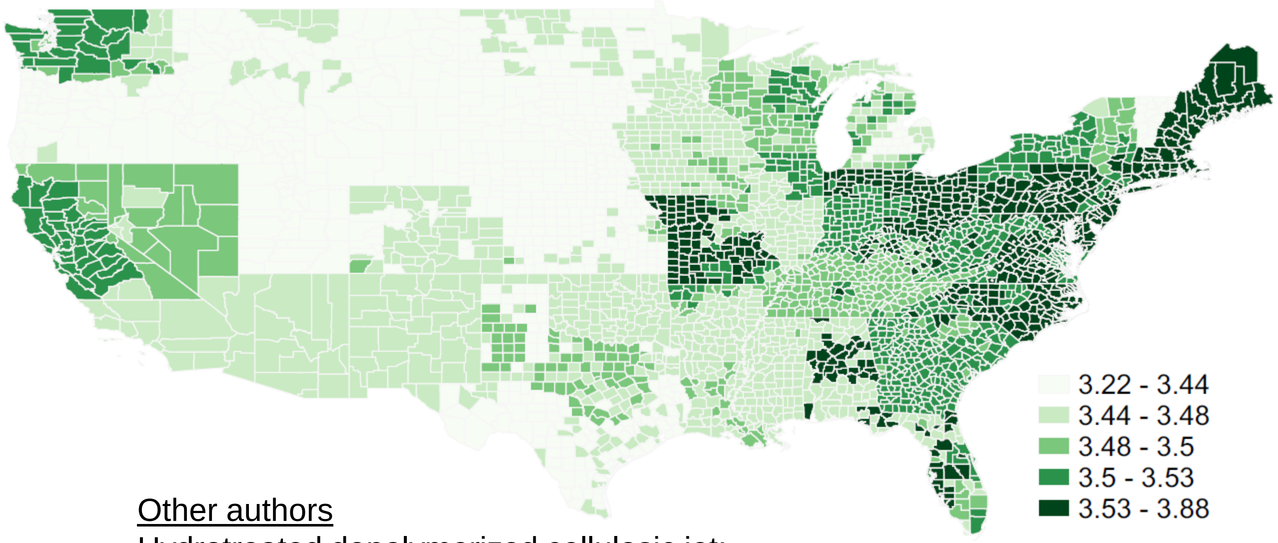
Assumptions

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***

H_2 is a major driver of Jet fuel cost (*e.g.*, Fusel alcohols in $\$/Gal_{Jet\ Fuel}$):



Other authors

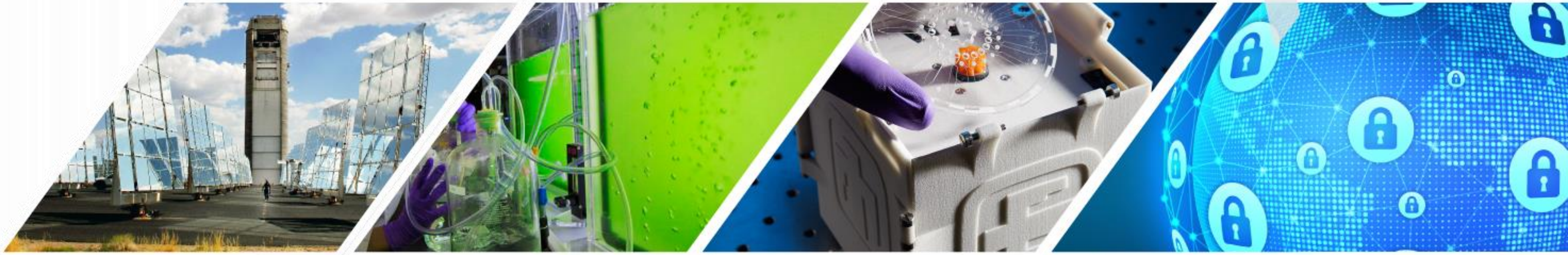
Hydrotreated depolymerized cellulosic jet:

- Corn stover: **6.20 $/Gal**
- Wheat straw: **7.82**
- Sugar cane: **5.71**
- Forestry residues: **5.22**

Hydrogenated esters and fatty acids:

- **3.70 to 11.83 $/Gal**

Sandia TEA/LCA POC: Carlos Quiroz-Arita



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Fuel Identification

Alexander Landera
Member of Technical Staff

PHYSICAL PROPERTY PREDICTIONS HELP SCREEN FOR DROP-IN FUELS

- 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

Physical property	Constraint
Specific Energy, MJ/kg	> 42.8
Energy Density, MJ/L	***
Density at 15°C, kg/m³	775-840
Flashpoint, °C	> 38
Melting point, °C	< -40

Physical property metrics, their constraints, and Jet-A median values
From ASTM D-7566

ACCELERATING SAF DEVELOPMENT BY PREDICTING PROPERTIES OF NEW BIOJET COMPONENTS AND BLENDS

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

Tier α pred.
Important for
cold flow and safe handli

Reaction rates

Soot production

Polymer swelling (o-ring material)

A SIMPLE MODEL FOR COMPLEX MIXTURES

Goal: Use GCxGC data to accurately estimate physical properties of reference aviation fuels

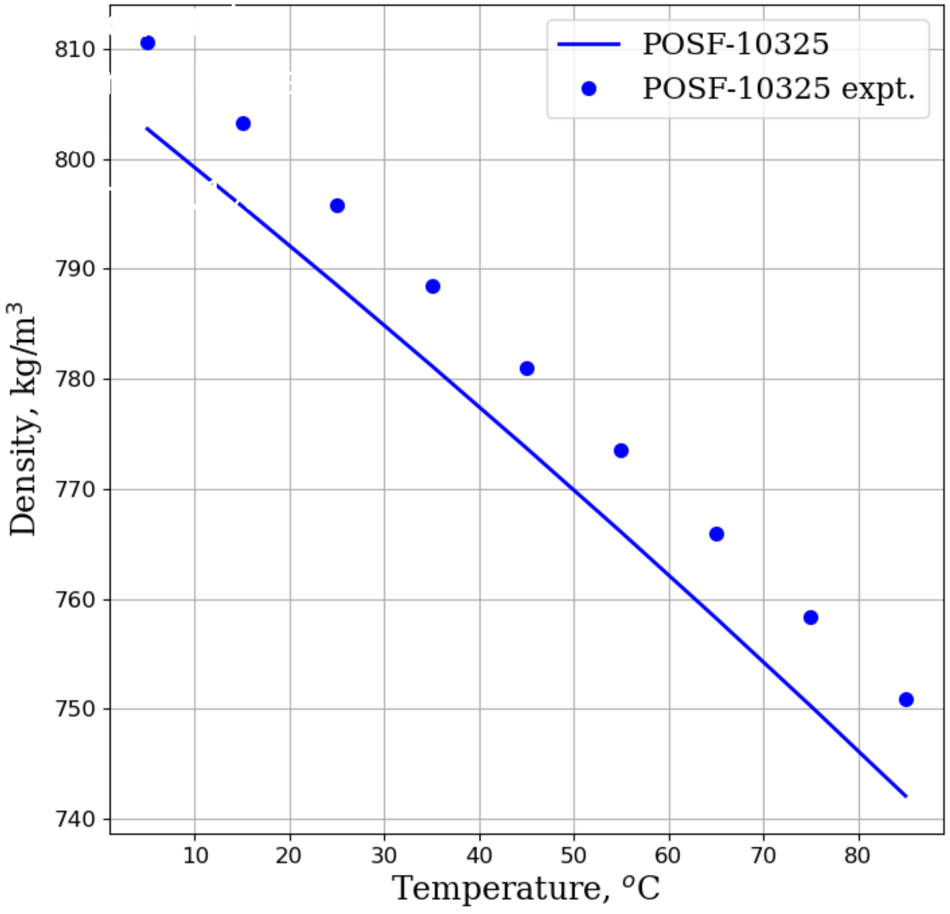
Method: Eliminate minor chemical species (those which are present < 1 wt%)

- 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

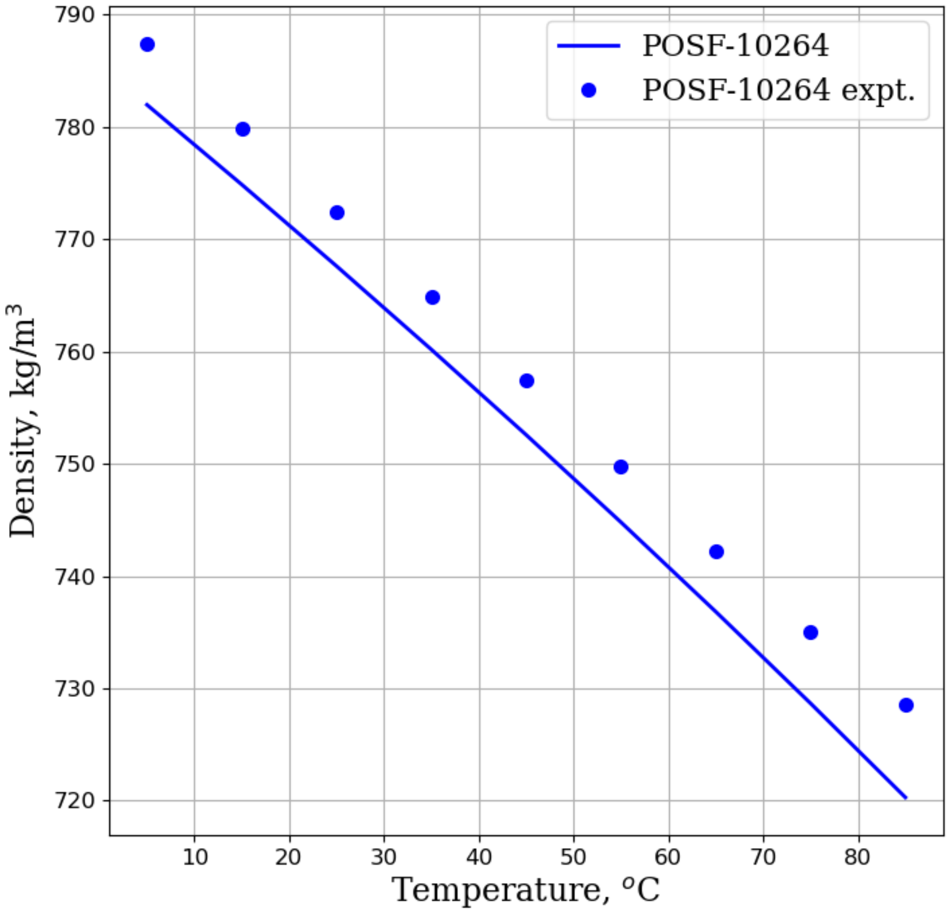
	Weight %	Volume %
Aromatics		
Alkylbenzenes		
benzene (C06)	0.01	0.01
toluene (C07)	0.23	0.21
C2-benzene (C08)	1.98	1.77
C3-benzene (C09)	4.17	3.73
C4-benzene (C10)	2.33	2.09
C5-benzene (C11)	1.19	1.07
C6-benzene (C12)	0.66	0.59
C7-benzene (C13)	0.25	0.22
C8-benzene (C14)	0.12	0.11
C9-benzene (C15)	0.06	0.05
C10+-benzene (C16+)	<0.01	<0.01
Total Alkylbenzenes	**11.00**	9.85

- Ethylbenzene
- Propylbenzene
- Butylbenzene
- Pentylbenzene

ACCURATE DENSITIES ARE OBTAINED USING A SIMPLE BLEND MODEL



Density of POSF-10325

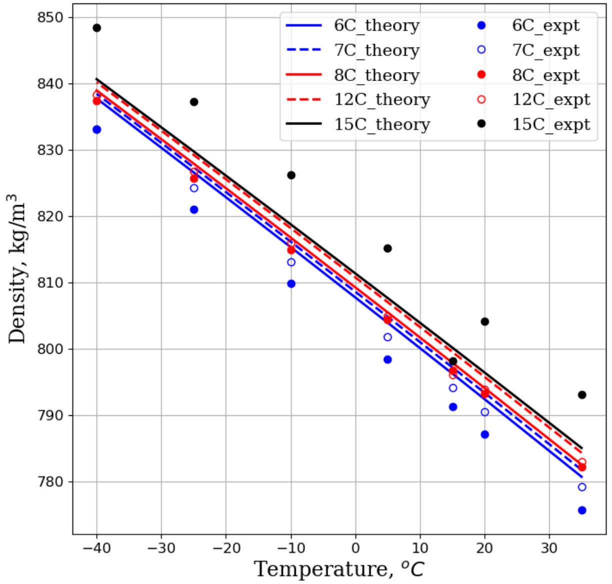


Density of POSF-10264

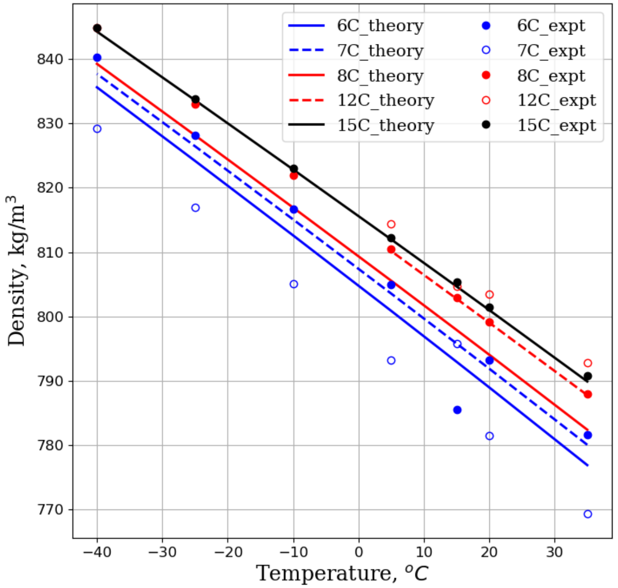
Accurate densities within ~ 1% are obtained

DENSITY PREDICTIONS ARE IN GOOD AGREEMENT WITH EXPERIMENTAL MEASUREMENTS

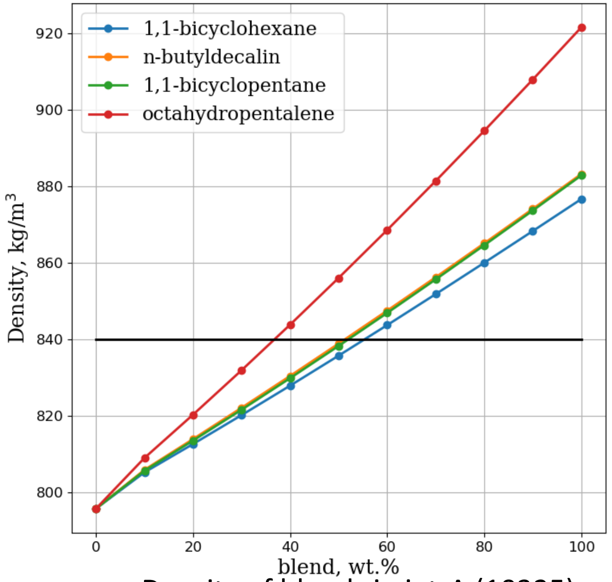
- Blend model shows that density can be accurately modeled. Largest error in validation is 1.4%
- Validated with **C6-C15** cycloalkanes
- A select group of cycloalkanes were chosen
  - Based on not meeting density requirements
- Blend models show that density can be accurately modeled
- Blend model 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



Density of 10 wt.% blends in jet-A (10325)



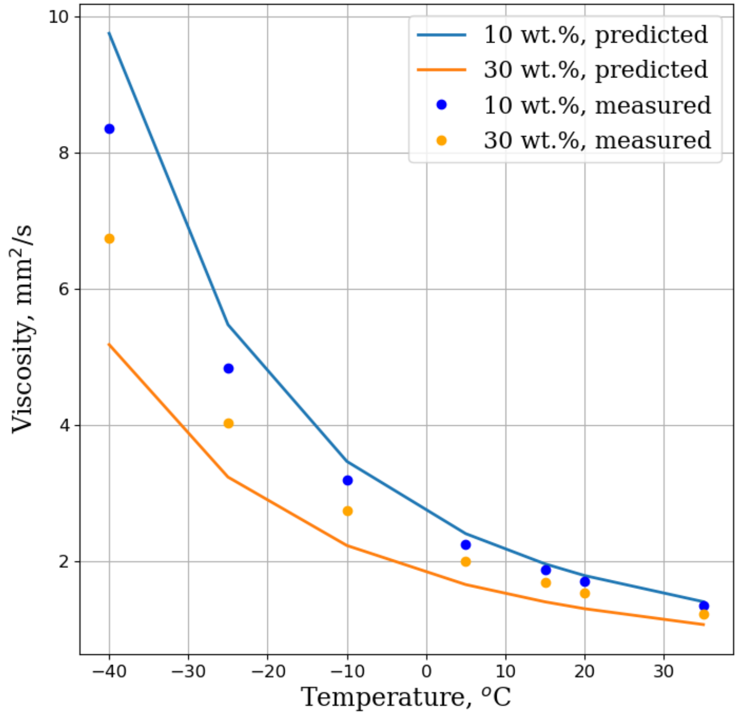
Density of 30 wt.% blends in jet-A (10325)



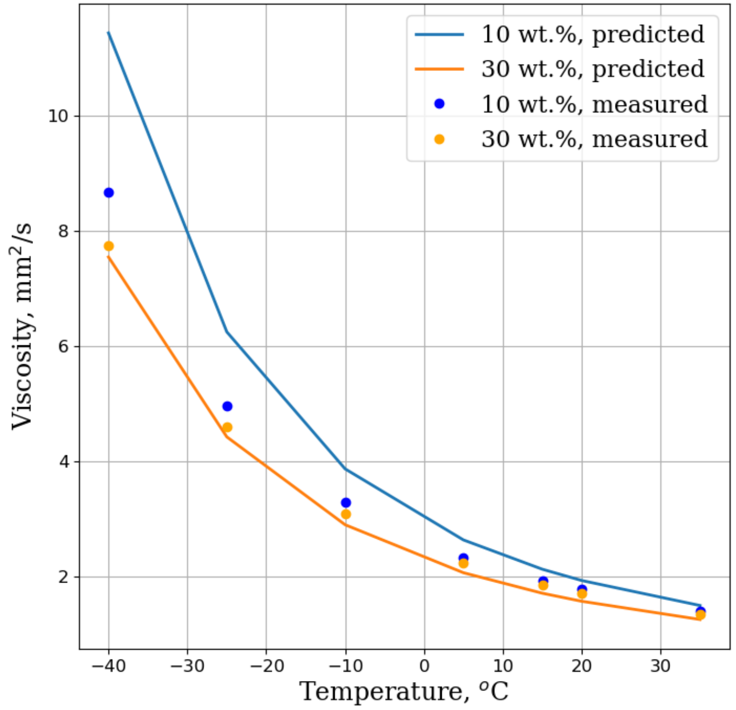
Density of blends in jet-A (10325)

Molecules can be blended in 35-60 wt.% in Jet-A

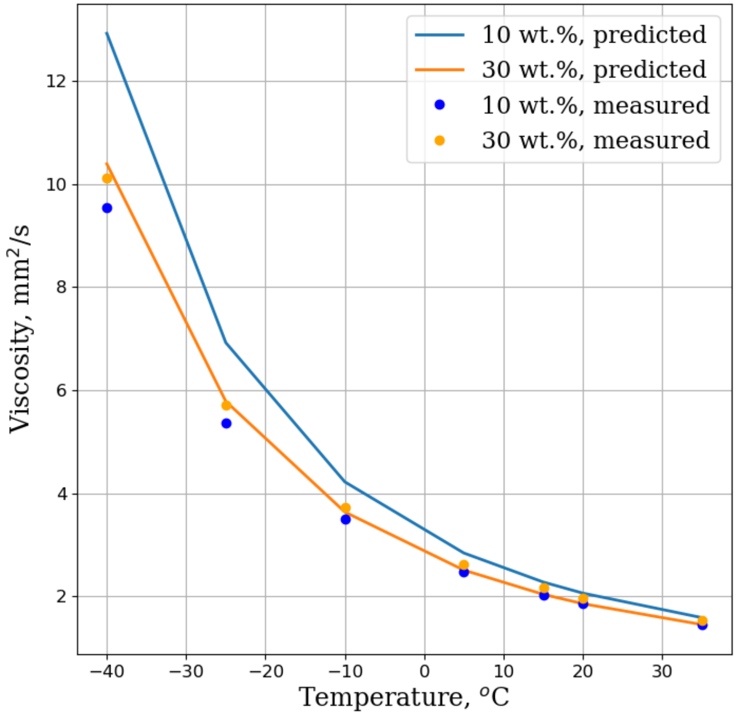
ACCURATE VISCOSITIES ARE OBTAINED USING A SIMPLE BLEND MODEL



POSF-10325 + cyclohexane



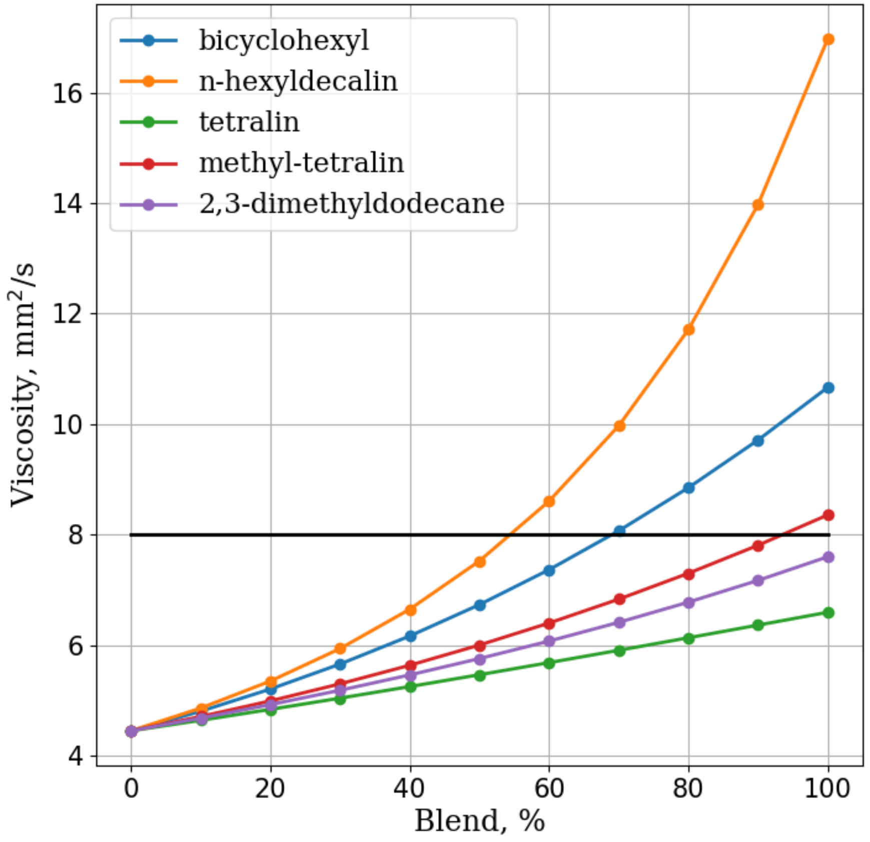
POSF-10325 + cycloheptane



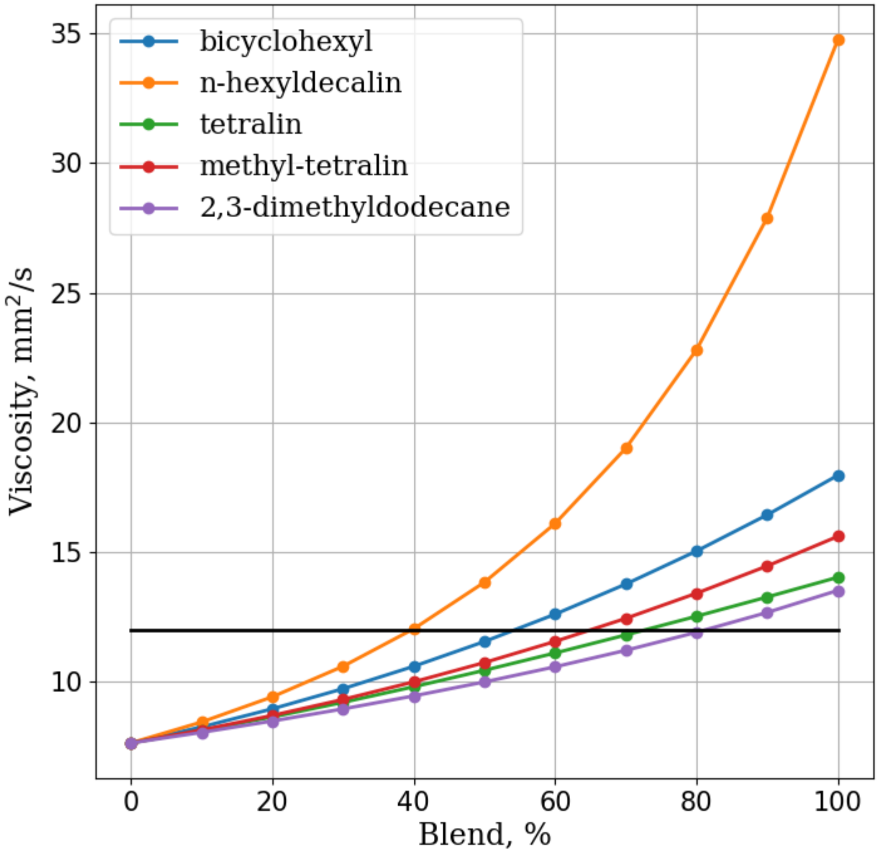
POSF-10325 + cyclooctane

Experimental viscosities are in good agreement with our modeled viscosities
This is a good initial validation step

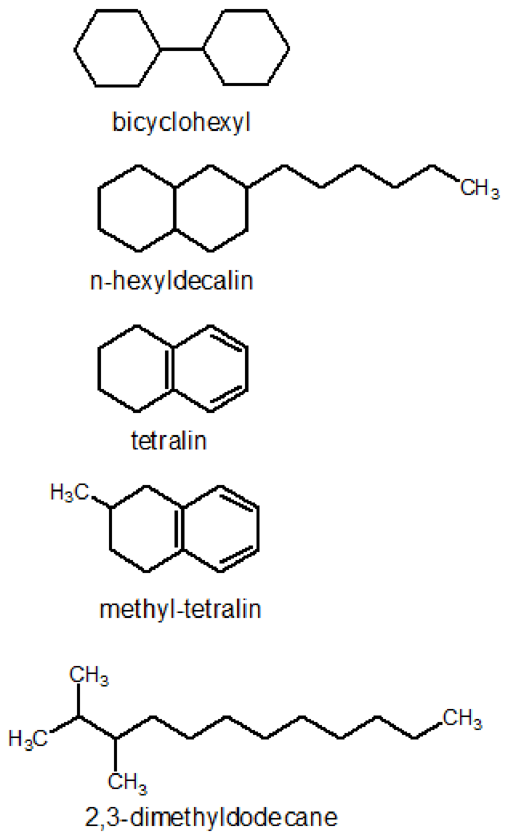
SELECTED CYCLOALKANES MEET VISCOSITY REQUIREMENT AS A BLEND OF UP TO 40-80% BY WEIGHT



Viscosity of cycloalkane + POSF-10325 at -20^{o}C



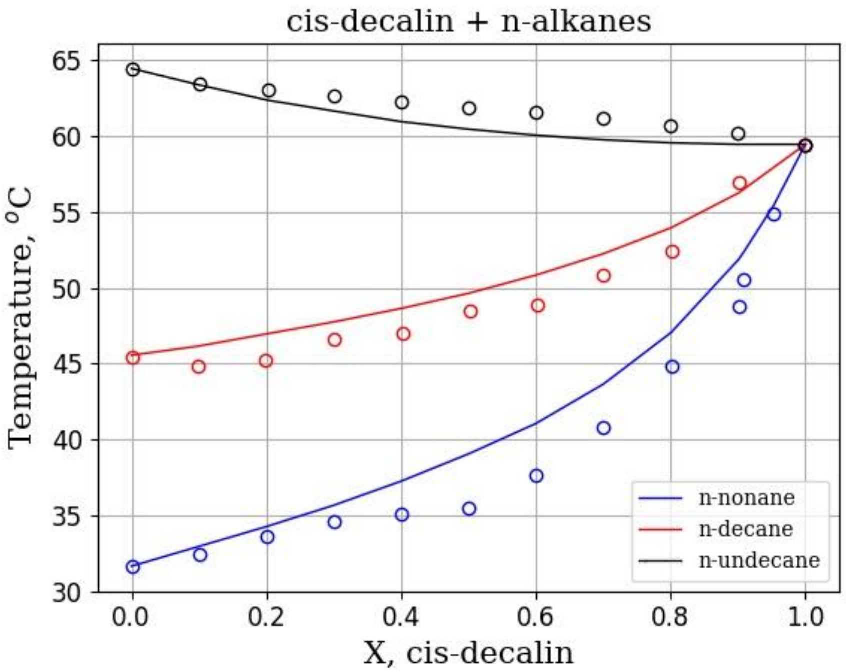
Viscosity of cycloalkane + POSF-10325 at -40^{o}C

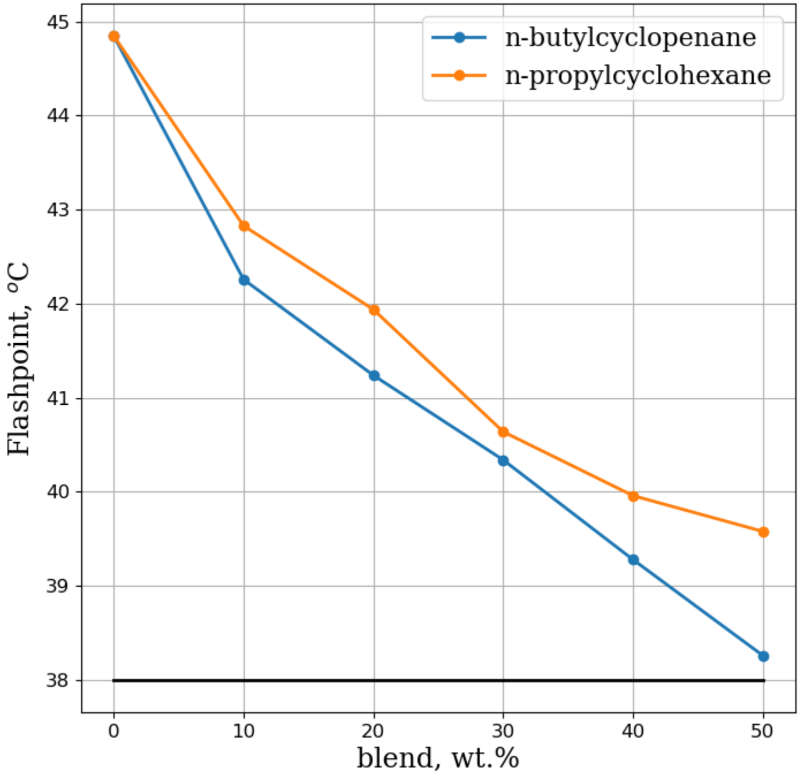


Meeting viscosity requirements at -20^{o}C does not ensure you meet requirements at –40^{o}C
Shows the blending limits of select, non-validated, alkanes in POSF-10325

FLASHPOINT IS ACCURATELY PREDICTED USING A SIMPLE BLEND MODEL

- 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.



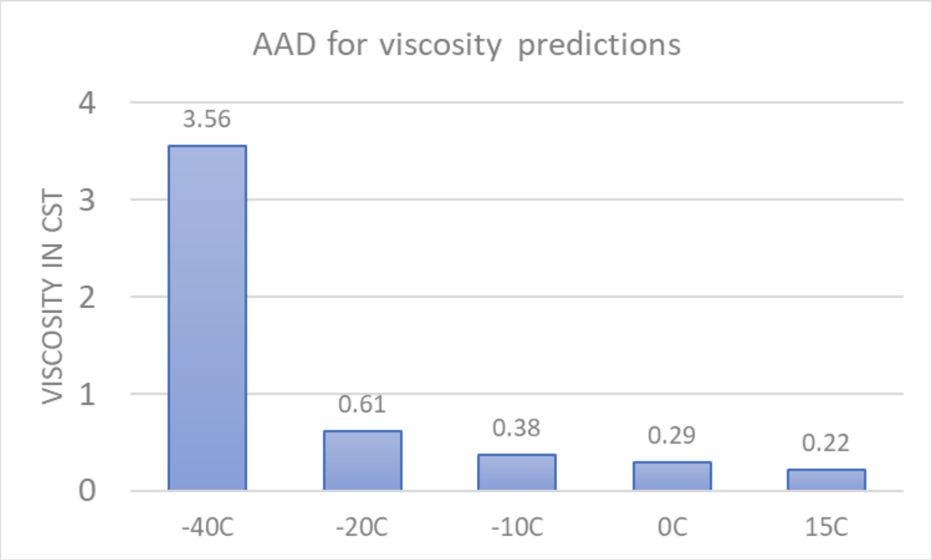


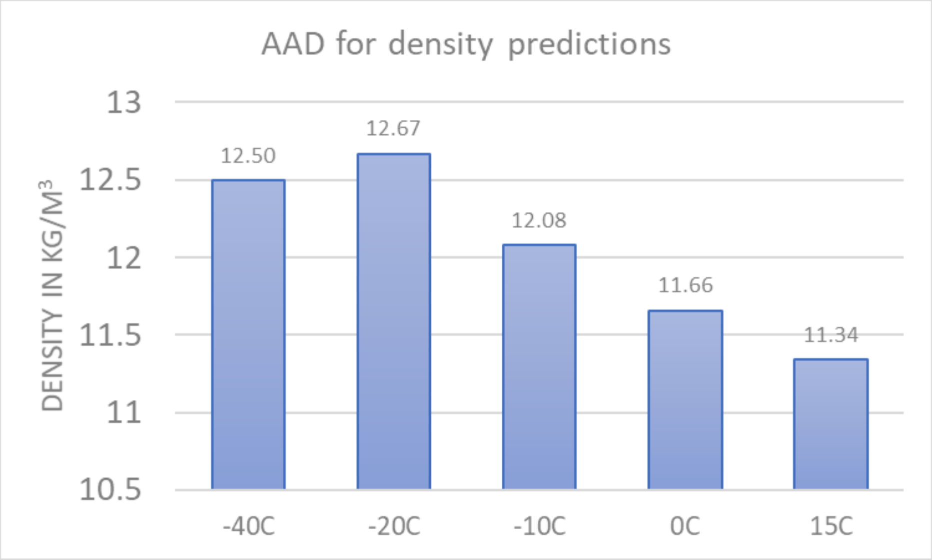
VISCOSITY OF COMPLEX FUELS (WITH U. DAYTON)

U.Dayton analyzed complex jet fuels

- Viscosity and Density were meas.
- Temp from -40C to 15C
- Total of 63 fuels were measured
    - From 2020 to 2021
- Less fuels at -40C due to freezing

- Viscosity predictions => SUPERTRAPP
- Density predictions => Ratchet eq.
- Viscosity at -40C is difficult to handle
- Other temperatures are much better





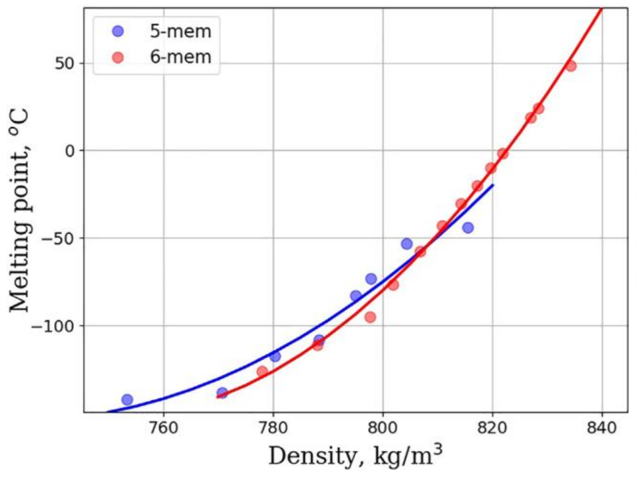
CAN CYCLOALKANES REPLACE AROMATICS?

The challenge: aromatics promote seal swelling but have high sooting tendencies

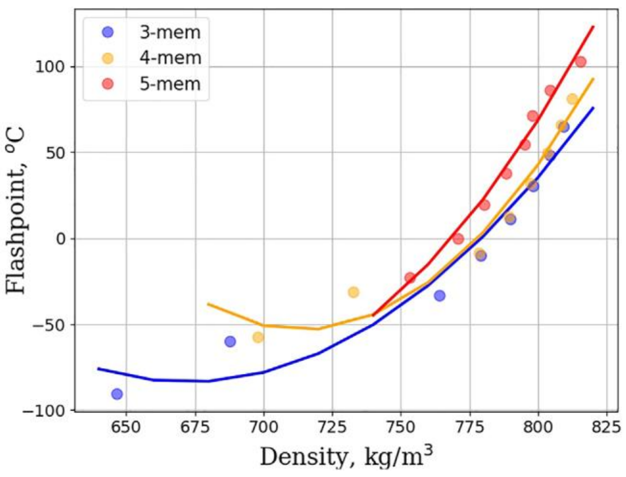
Approach: conduct a modeling study and literature review to address the following question:
Are cycloalkanes viable replacements for aromatics?

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!



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.

Landera A., et al "Building Structure-Property Relationships of Cycloalkanes in Support of Their Use in Sustainable Aviation Fuels". *Front. Energy Res.,* 2022, 9:771697. doi: 10.3389/fenrg.2021.771697

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

frontiers in Energy Research
ORIGINAL RESEARCH
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Building Structure-Property Relationships of Cycloalkanes in Support of Their Use in Sustainable Aviation Fuels

Alexander Landera[1], Ray P. Bambha[1], Naijia Hao[2], Sai Puneet Desai[2], Cameron M. Moore[2], Andrew D. Sutton[2†] and Anthe George[1]*

Geiselman et al. Microb Cell Fact (2020) 19:208
https://doi.org/10.1186/s12934-020-01456-4
Microbial Cell Factories
RESEARCH Open Access

Conversion of poplar biomass into high-energy density tricyclic sesquiterpene jet fuel blendstocks

Gina M. Geiselman[1,2], James Kirby[1,2], Alexander Landera[2], Peter Otoupal[1,2], Gabriella Papa[3,4], Carolina Barcelos[3,4], Eric R. Sundstrom[3,4], ...
Alberto Rodriguez[1,2], Blake A. Simmons[1] ...
Anthe George[1,2] and John M. Gladden[1*] ...

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Volume 6, Issue 7, 20 July 2022, Pages 1590-1605
Article

Biosynthesis of polycyclopropanated high energy biofuels

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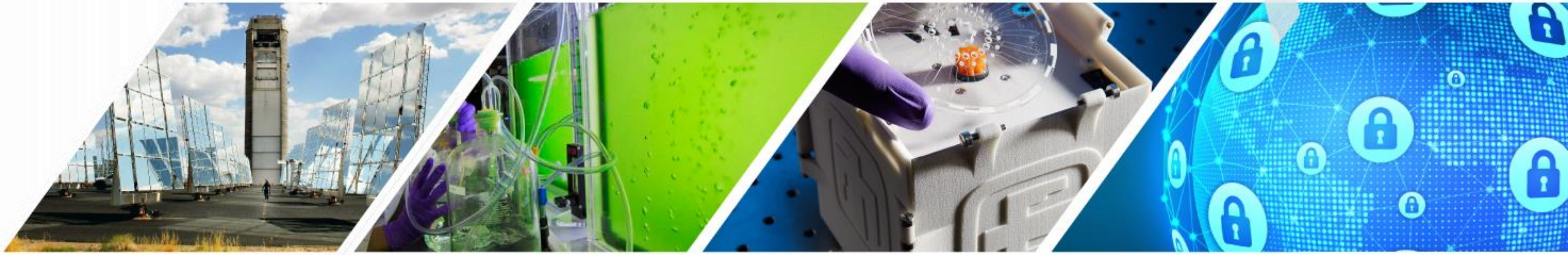

Energy & Homeland Security

End-Use

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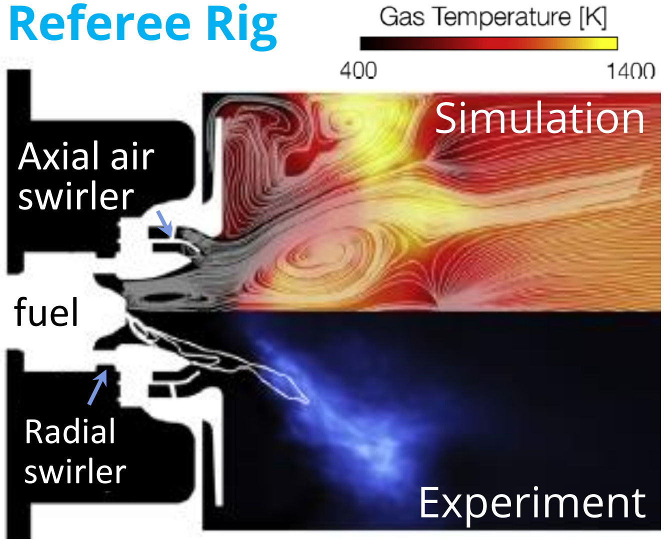
CURRENT SIMULATIONS WELL-PREDICT COMBUSTION AT CRUISE BUT STRUGGLE TO PREDICT MIXING, IGNITION, AND EMISSIONS FORMATION PROCESSES ACROSS THE OPERATING RANGE

AFRL Referee Rig



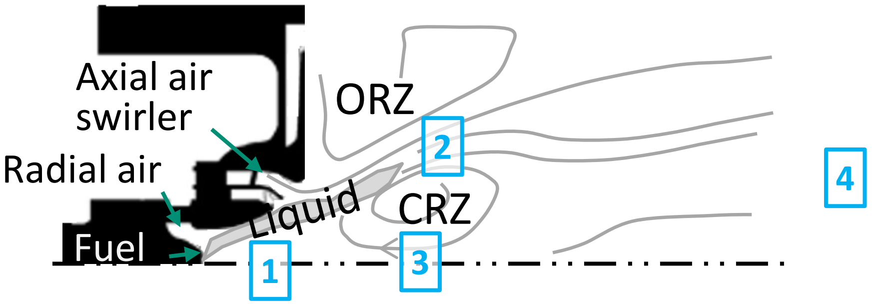
Lean Blow-Out

code → / Fuel ↓	LESLIE	OpenNCC	FLUENT	VIDA	CONVERGE (All with PDPA spray inject & secondary breakup)					EXP
	FR, PaSR, HyChem Reduced, PDPA w/ breakup	FR, Laminar, HyChem Reduced, PDPA no breakup	FR, EDM, 4-step tuned to HyChem, Rosin-R w/ breakup	FPV, PPDF, HyChem Detailed, Rosin-R w/ BU	Zonal FR, Laminar, Dryer-Won Compact	Zonal FR, Laminar, HyChem Skeletal	FR, Laminar, HyChem Detailed	Zonal FR, Laminar, HyChem Reduced	FGM Flamlet, PPDF, Dryer-Won Compact,	Average value, and +/- 2 st-dev
A-2	0.070	0.078	0.0885	.090	0.085	0.080	0.090	0.082	0.082	**0.0806** 0.0788 to 0.0824
C-1	0.074	0.087	0.094	.085	0.092	0.084	0.088	0.080	0.084	**0.0869** 0.08535 to 0.0884

Book Chapter in "Fuel Effects on Operability of Aircraft Gas Turbine Combustors", Eds. M. Colket, J. Heyne, AIAA, 2021; ISBN 978-1-62410-603-3

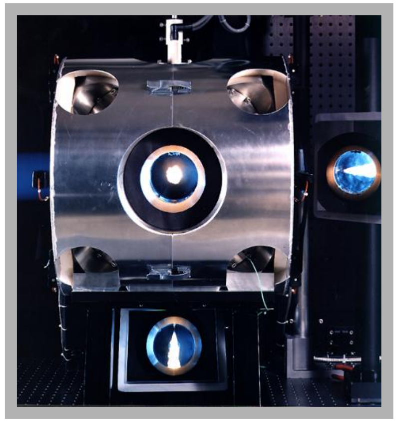
- **Modeling Challenge:** Sub-models ***lack modularity*** and are ***missing relevant processes***
- **Experimental Challenge:** Swirl stabilized combustors are ***resource intensive*** with ***complex physicochemical interactions*** and ***uncertain boundary conditions***
- **Sandia Approach:** Interrogate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

RELEVANT PROCESSES CAN BE ISOLATED IN SPECIALIZED OPTICALLY ACCESSIBLE SPRAY COMBUSTION CHAMBERS WITH WELL-CONTROLLED BOUNDARY CONDITIONS



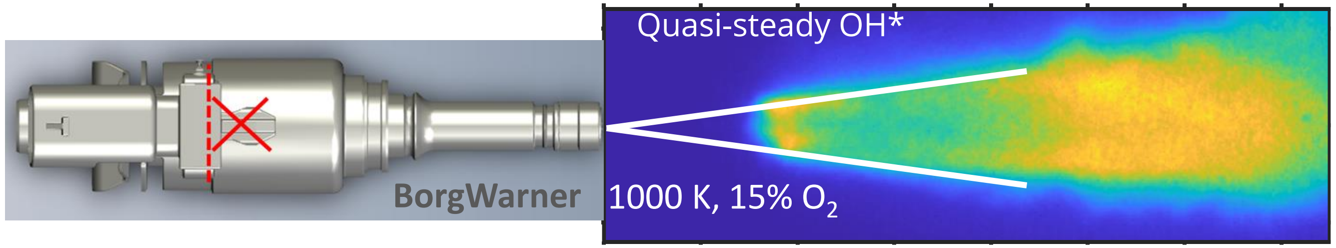
Rich, Quench, Lean (RQL) Combustor

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

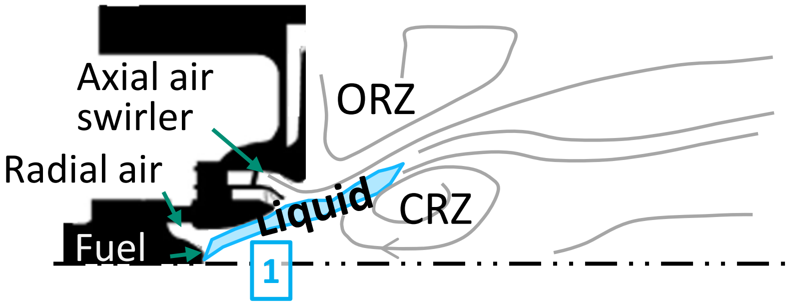
- Reproduces relevant CRZ conditions
  - 300 - 1800 K (by vitiation)
  - up to 350 bar
  - 0 – 21% O_2 (exhaust gas)



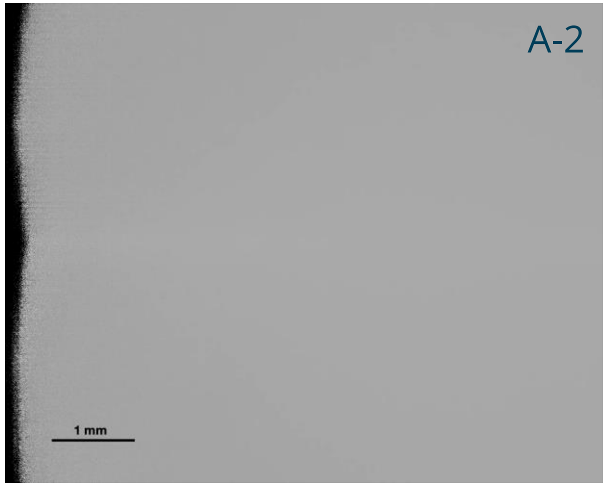
Single-Hole Atomizer

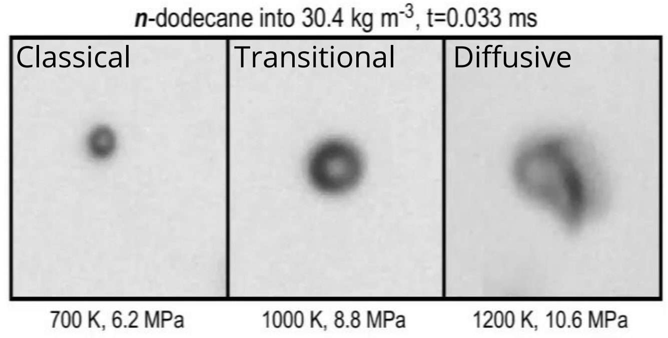
- Specialized injectors to produce relevant droplet sizes / velocities

AT TAKEOFF CONDITIONS WHERE COMBUSTOR PRESSURES AND TEMPERATURES ARE ELEVATED, TRANSCRITICAL MIXING PROCESSES CAN DOMINATE



Fuel	Distillation
n-dodecane	Single component (216°C)
A-2 (Jet A)	Standard boiling
C-1	Narrow boiling
C-4	Wide boiling
Bicyclohexyl (BCH)	High boiling (227°C)

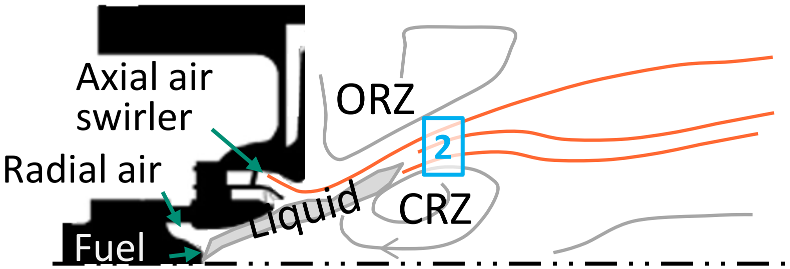




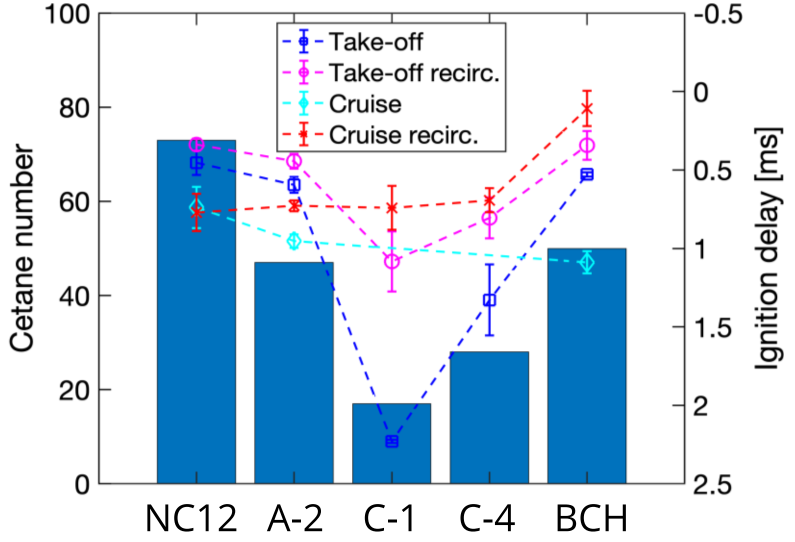
- Transcritical liquids undergo faster “diffusive” mixing due to the lack of a liquid-vapor interface

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

FLAME STABILIZATION

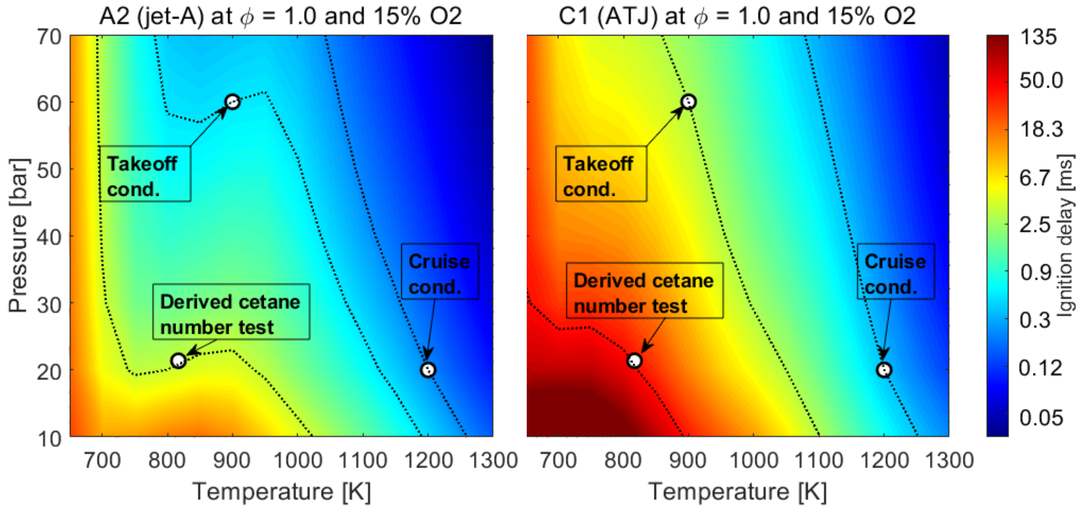


Combustor Condition	Temperature [K]	Pressure [bar]	O_2 [%]
Cruise	800	20	21
Cruise (CRZ)	1200	20	15
Take-off	900	60	21
Take-off (CRZ)	1200	60	15
DCN	817	21.37	21



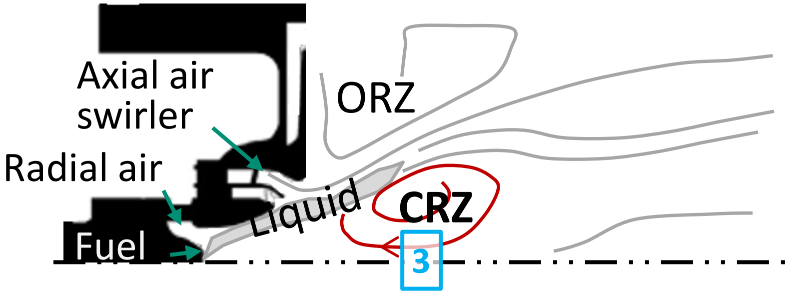
- **ASTM D4054**: Derived cetane number (DCN) is the only fuel combustion metric specified

Ignition behavior at non-cruise conditions deviates substantially relative to correlations with DCN

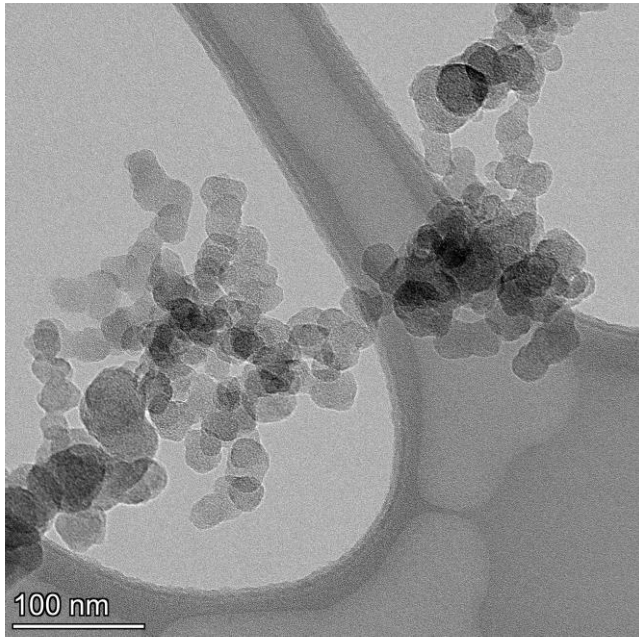


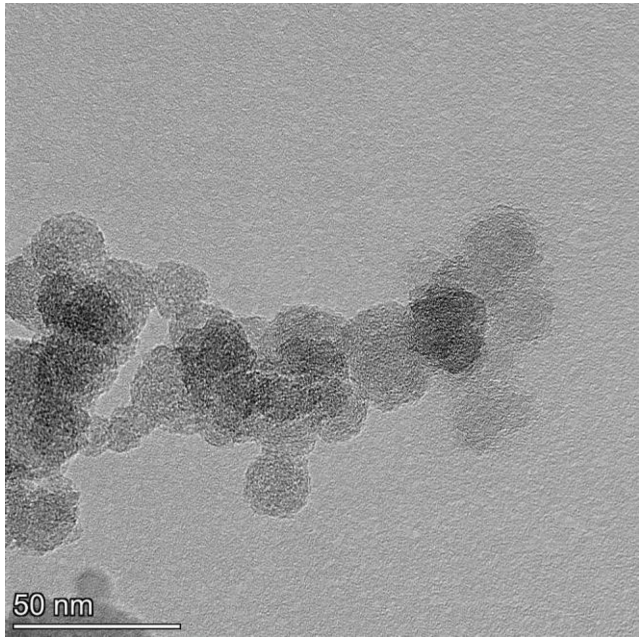
Courtesy of Dario Lopez-Pintor

SOOT PROPERTIES CAN BE SAMPLED AND DIFFERENT FORMATION AND OXIDATION STAGES TO PROVIDE RICH DATA NEEDED FOR COMPANION MODEL DEVELOPMENT



HR TEM

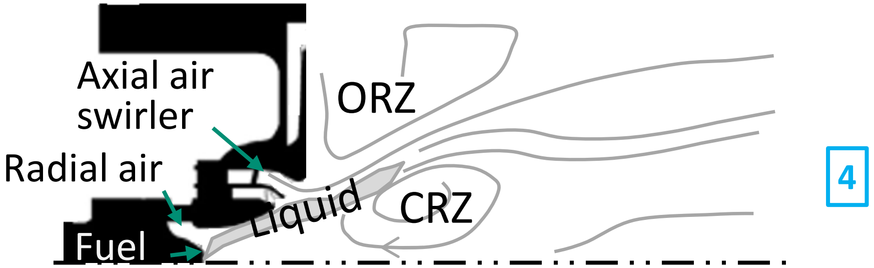


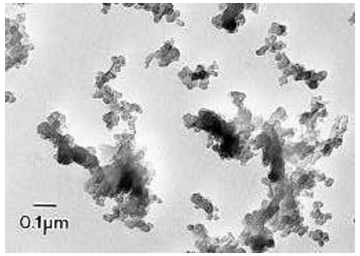


- **Electron Energy Loss Spectroscopy:** Soot particle density & bond structure

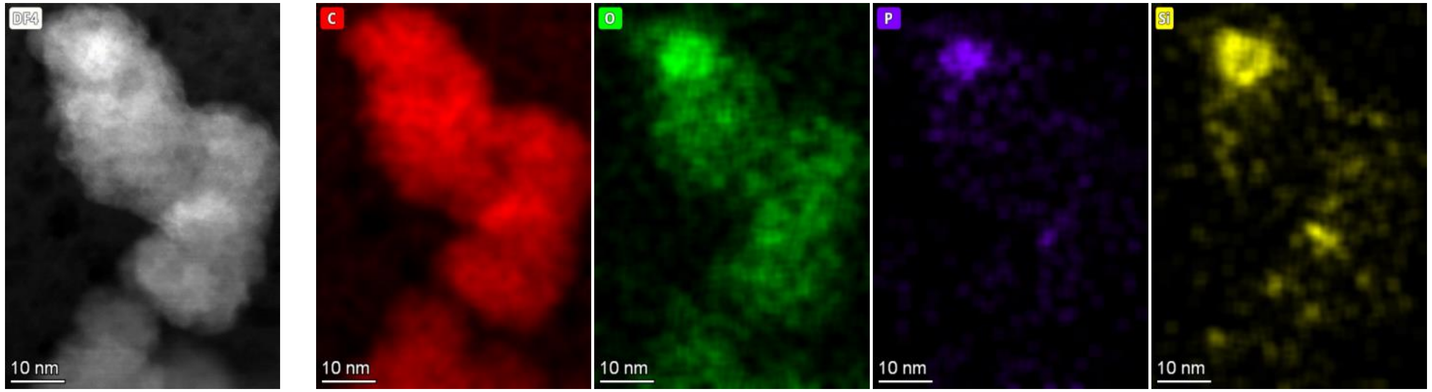
Soot sampling and high-resolution transmission electron microscopy (HR-TEM) used to characterize particle nanostructure and aggregate morphology

BEYOND SOOT PARTICLE MASS AND NUMBER, SURFACE PROPERTIES RELEVANT TO CONTRAILS FORMATION CAN ALSO BE CHARACTERIZED



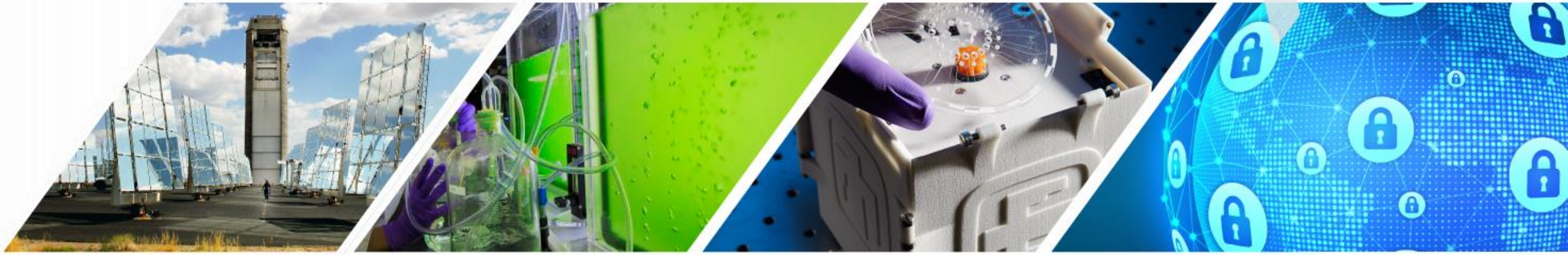


- **Energy Dispersive X-ray Spectroscopy:** Soot surface atomic composition (e.g., sulfates)



- 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



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Emissions & Repercussions

Shruti Mishra

BENEFITS OF SUSTAINABLE AVIATION FUEL EXTEND BEYOND LOW CARBON

- 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

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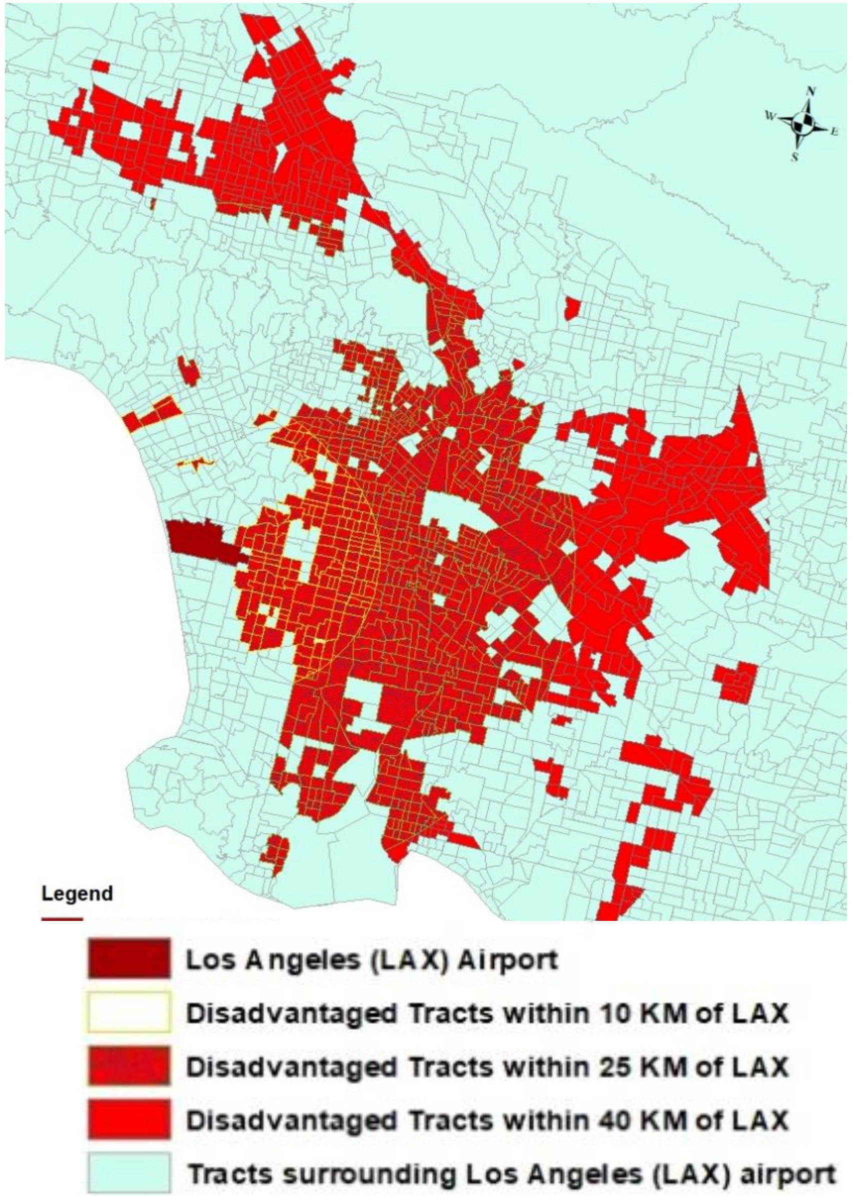
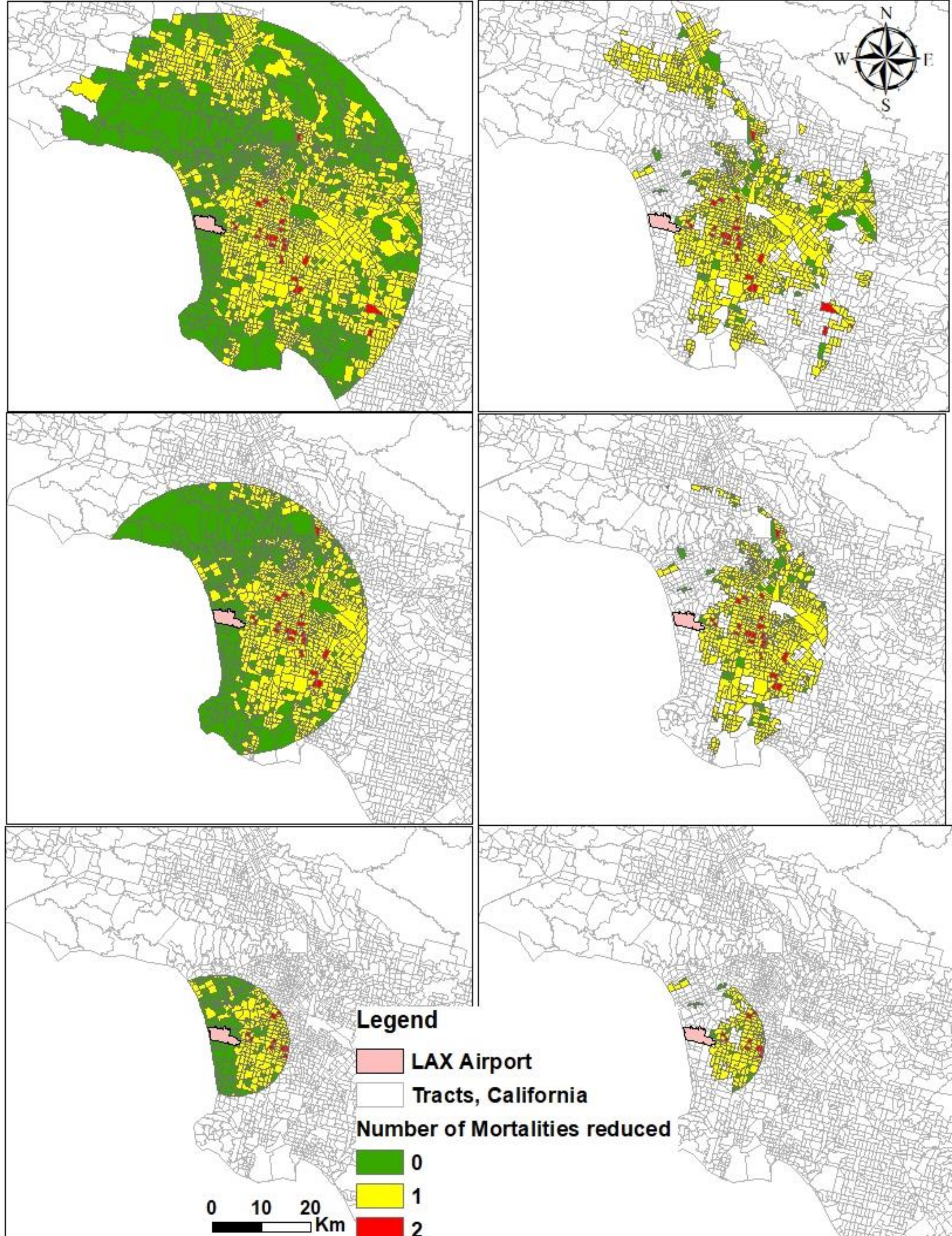
APPROACH - PRELIMINARY

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).

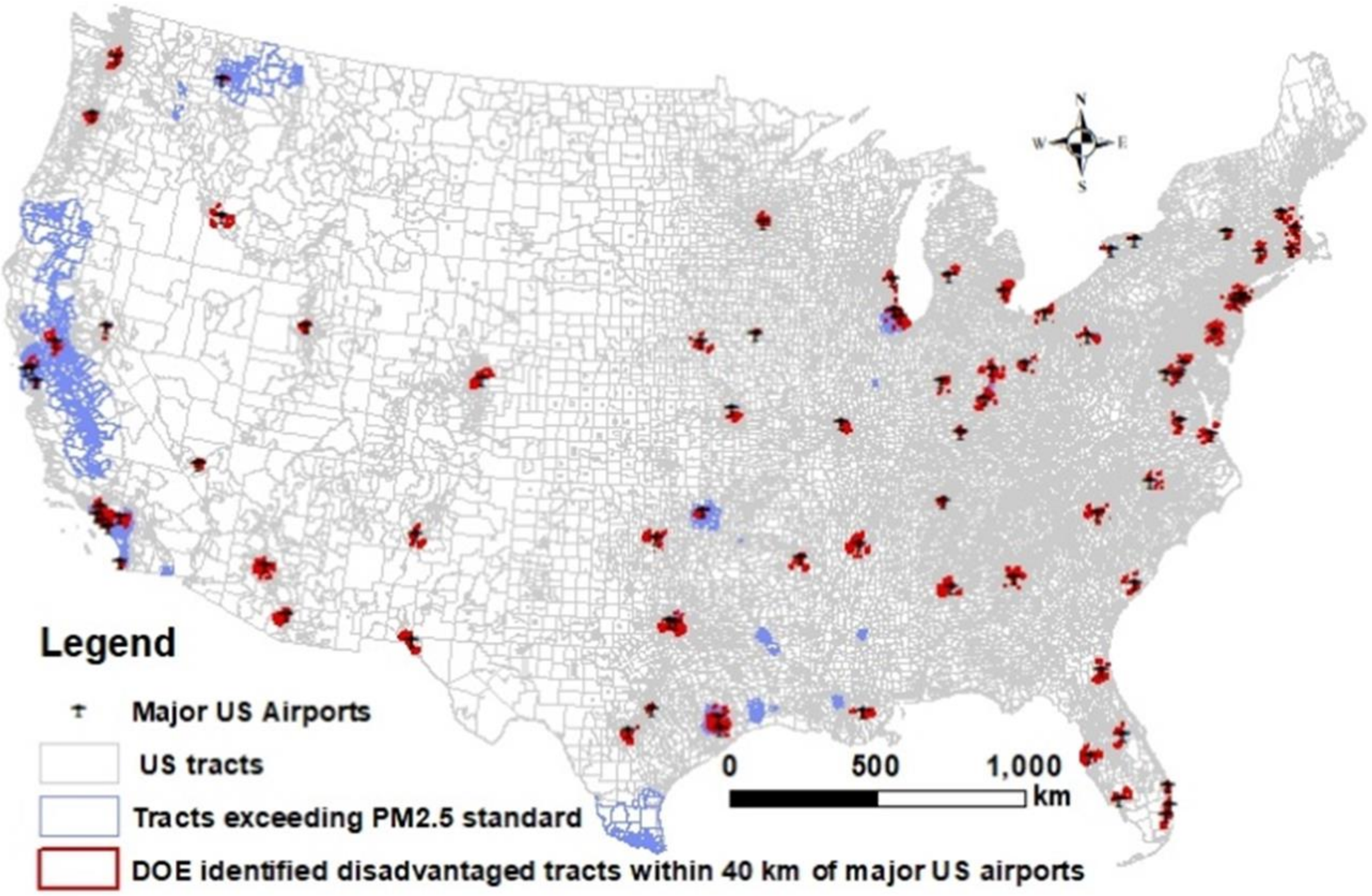
RESULTS (preliminary)





WAY FORWARD

The benefits of SAF to disadvantaged communities in other major airports in the U.S. should be significant.



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