

ASCENT Project 065a

Fuel Testing Approaches for Rapid Jet Fuel Prescreening



University of Dayton

PI: Joshua Heyne

PM: Anna Oldani

Cost Share Partner: VUV Analytics, Greenfield Global, and DLR Germany

Objective:

To develop early-stage low volume evaluations of novel Sustainable Aviation Fuel (SAF) candidates via ASTM property tests and internal predictions

Project Benefits:

Rapid feedback to novel fuel producers on the blend ratios, compatibility, and combustor operability impacts of SAF candidates

Research Approach:

Evaluation methodologies are developed around a two-tiered prescreening process

Tier α focuses on predictions; Tier β focuses on measurements (*increase since F21 ASCENT*)

Tier	Measured Property	Predicted Property	Vol. (mL)	No. tested
α	GCxGC	LHV, Density, Surface tension, Freeze point, Viscosity, DCN, Flash point	1	90 (17)
	Distillation			
β	Density	LHV	10	57 (15)
	Viscosity			
	Surface ten.			
	Freeze point			
	Flash point			
	DCN		140	12 (2)

Major Accomplishments (to date):

Tools developed in P65a have been used to evaluate total **90 SAF candidate samples**

Distillation cuts for particular feedstock-pathway are in standard practices; variance across candidate compositions is substantial and requires some tailoring.

Publications total: 8 / 2 are in review (1 on Virent's SAK) / 2 are nearing submission

Invited talks total/since Fall '21: 16 / 3

Future Work / Schedule:

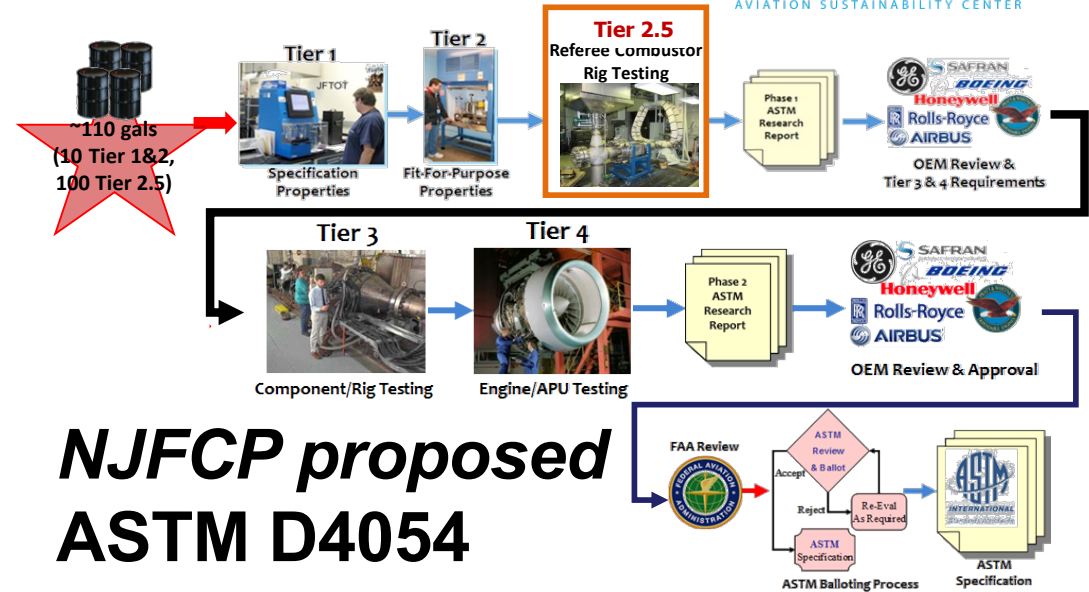
Development of additional Tier α methods

April '22: Submission of two papers in regards on VUV identification and usage

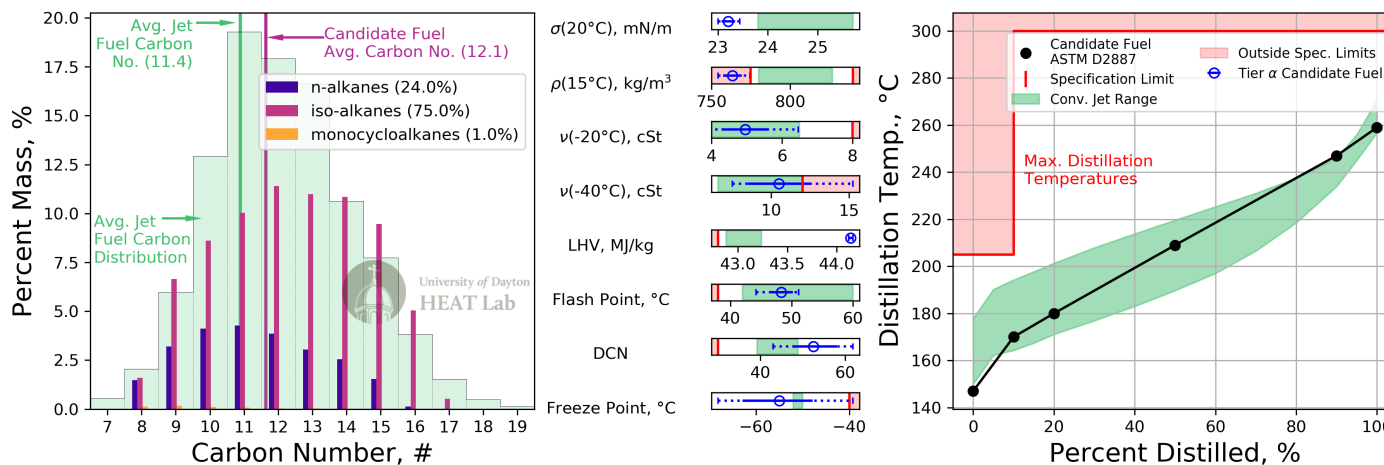
July '22: Development of more automated algorithms for complex mixtures.

Background and Motivation

- Bulk properties accounted for the majority of combustor operability variance in the NJFCP
- ASTM D4054 is volume intensive
- Measure or predict key properties (and others) before the ASTM evaluation process



Exemplar prescreening evaluation

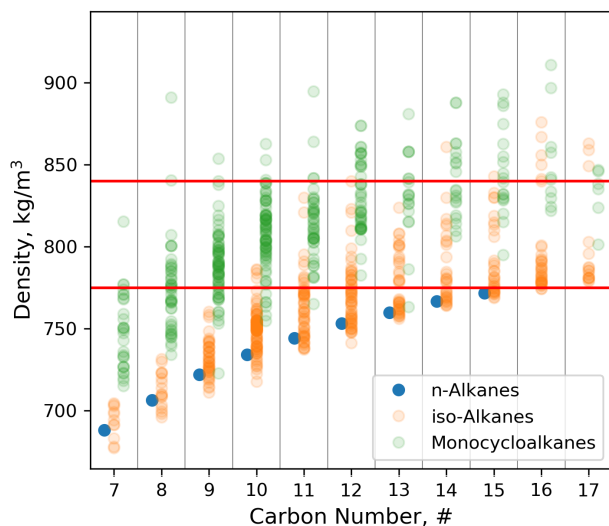


Volumes needed for various testing Tiers

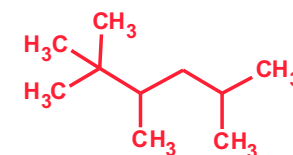
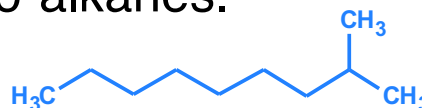
Tier	ϕ (gal)	
α	$\sim 10^{-6}$	P65a prescreening
β	$\sim 10^{-1}$	
γ	~ 10	P65b prescreening
1 & 2	$\sim 10^2$	Referee Rig
2.5	$\sim 10^2$	
3 & 4	$\sim 10^3$	

Isomeric structure has a significant impact on properties

Significant variance within a hydrocarbon group and carbon number

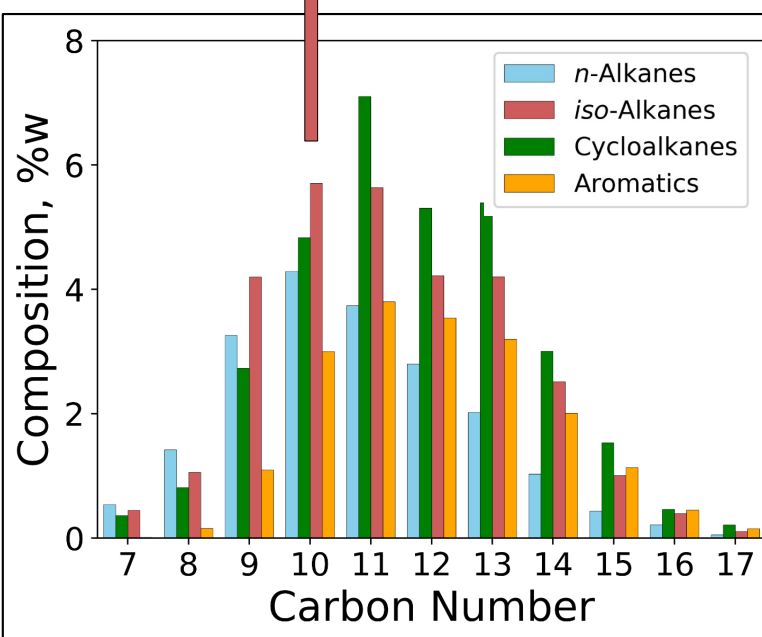


Hydrocarbon properties can vary substantially within a hydrocarbon type bin, e.g., ten carbon iso-alkanes.



2-methyl nonane has a higher DCN than **2,2,3,5-tetramethyl hexane**.

C10 iso-alkanes



$\sigma(22^\circ\text{C}), \text{mN/m}$

$\rho(15^\circ\text{C}), \text{kg/m}^3$

Flash Point, $^\circ\text{C}$

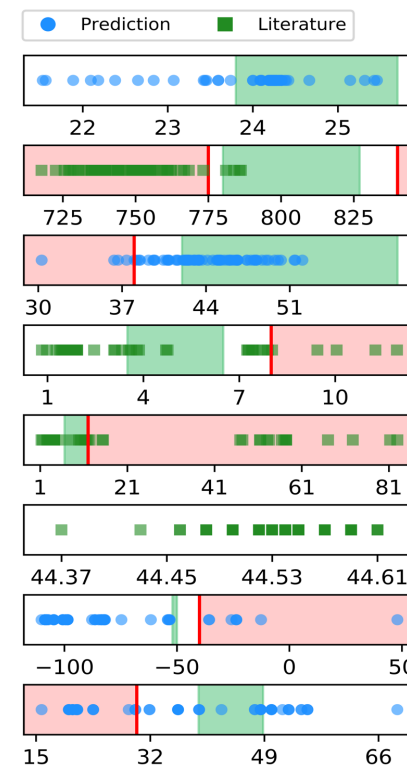
$\nu(-20^\circ\text{C}), \text{cSt}$

$\nu(-40^\circ\text{C}), \text{cSt}$

HOC, MJ/kg

Freeze Point, $^\circ\text{C}$

DCN

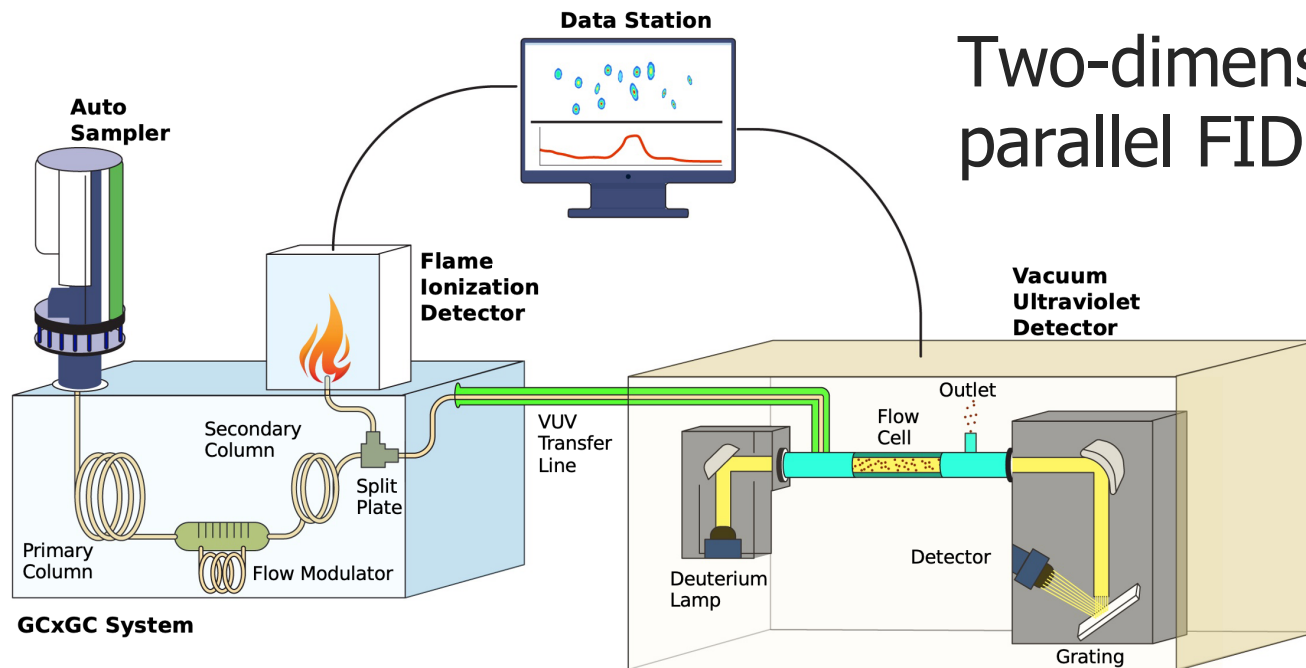


Heyne, et al., "Sustainable aviation fuel prescreening tools and procedures," *FUEL*, 2021.

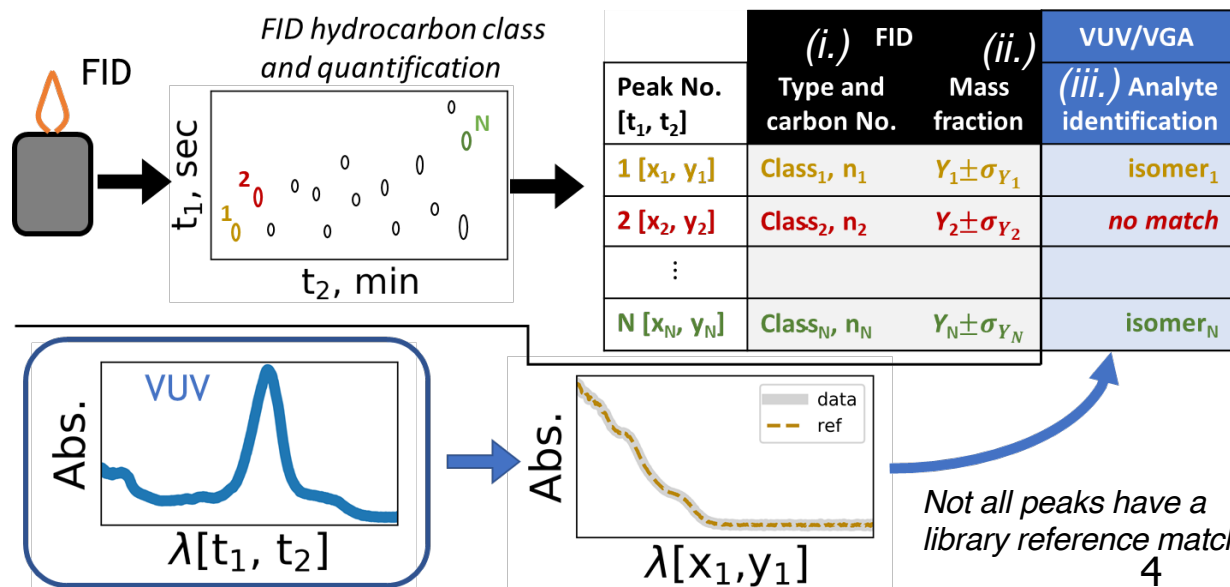
<https://doi.org/10.1016/j.fuel.2020.120004>

Approach Experimental

Two-dimensional separation with parallel FID and VUV sensing



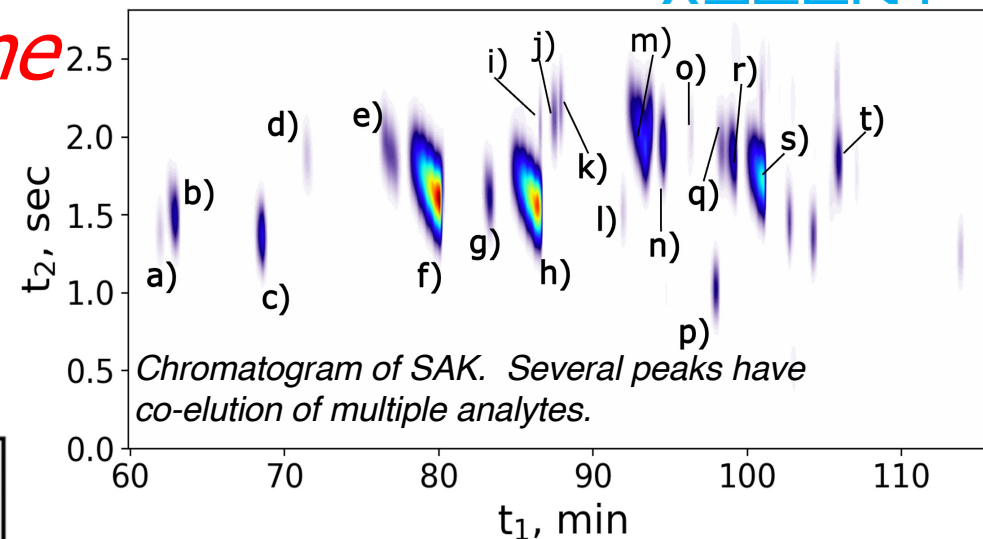
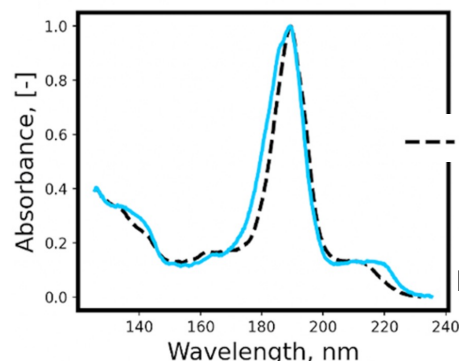
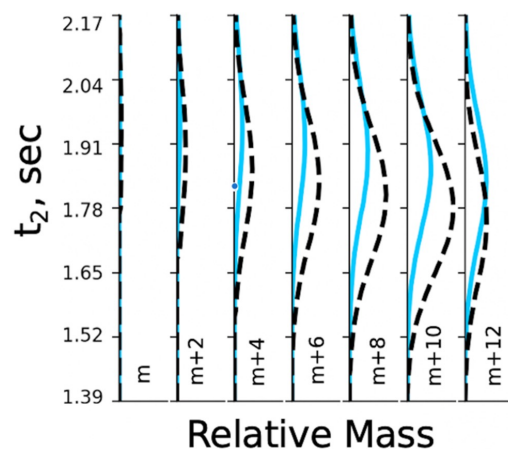
Analytes are assigned to a hydrocarbon class and carbon number (i.), quantified (ii.), and identified (iii.)



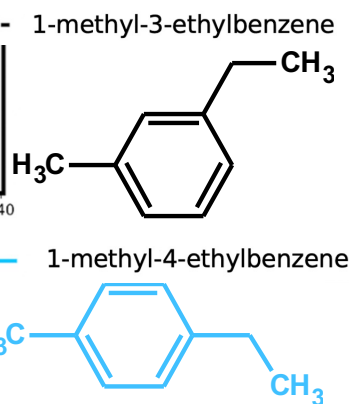
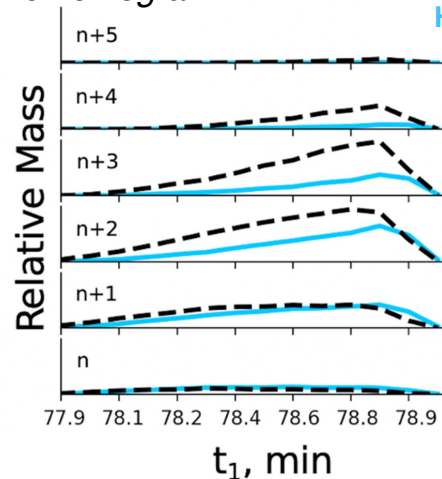
Example characterization of SAF candidate

synthetic aromatic kerosene

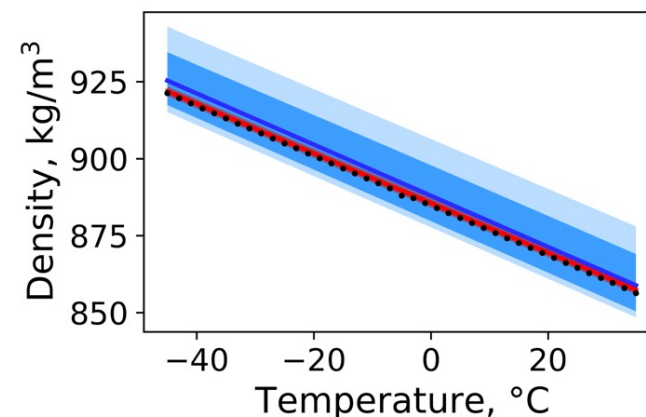
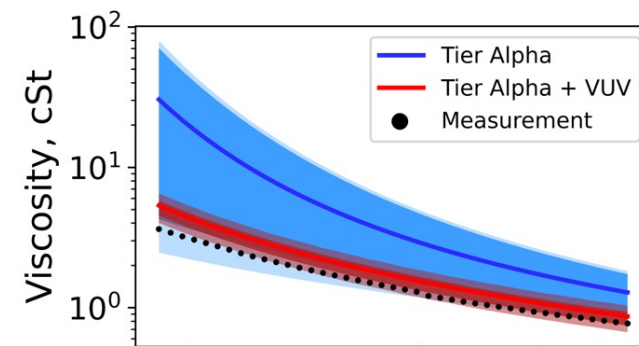
- 26 specific isomers accounts for >94%*m*
 - Limit of identification <0.15%*m*
- Submitted to Fuel SAF special issue



Magnification of 'f' peak in chromatogram.



The utilization of specific identification information reduces uncertainties significantly.



VUV Analyte Identification

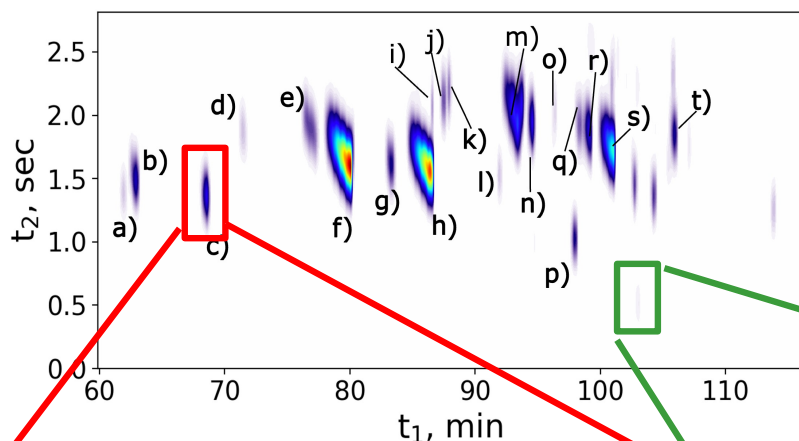
Spectra matching or hypothesis testing

We have observed:

- a) non-matches with $R^2 > 0.997$ (high S/N)
- b) matches with $R^2 < 0.97$ (low S/N)

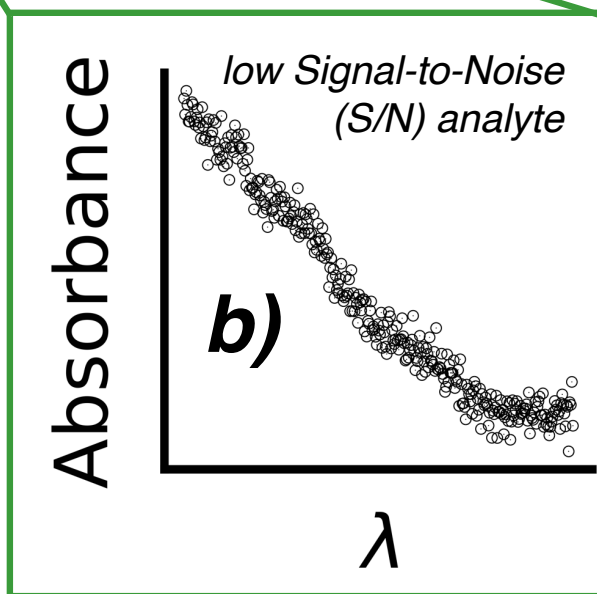
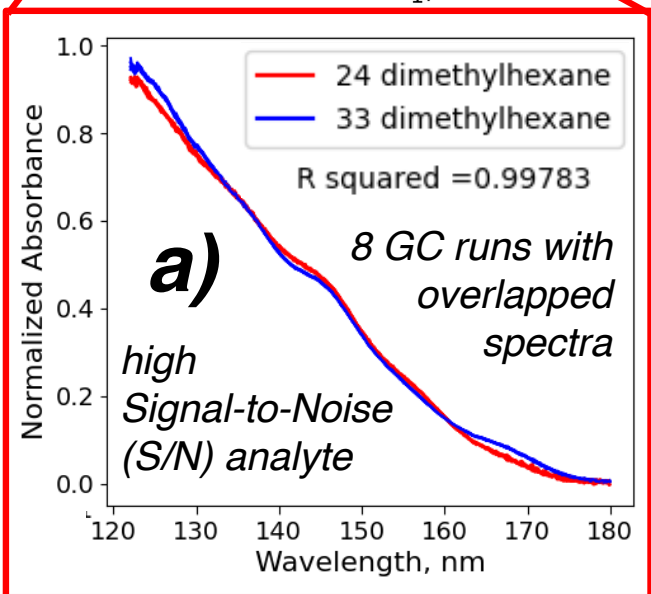
Goodness-of-fit methods (such as R^2):

- a) mask variance with similar spectra
- b) ignore noise for comparisons, so noisy spectra are 'penalized'



Impact:

Results are faster! *Less 'human' (\$) in the loop
Excellent *true-negative* detection
Deconvoluting peaks is very rigorous.
The method can be applied to many other problems.



Literature methods typically attempt to 'clean' data with fitting.

Current method compares expected variance (i.e., noise) to observed variance.

Conclusions and next steps



- Significant progress on signal processing or matching spectra
- Several properties are predicted very well:
 - LHV, density, surface tension, and flash point
- 17 new candidate fuels have been tested and properties predicted
 - Processes have been altered and improved as a result of tests
- Next steps:
 - Finalizing experimental method for generic evaluation of complex mixtures
 - Further software and numerical method development
 - Pareto fronts for %blend versus %original carbon

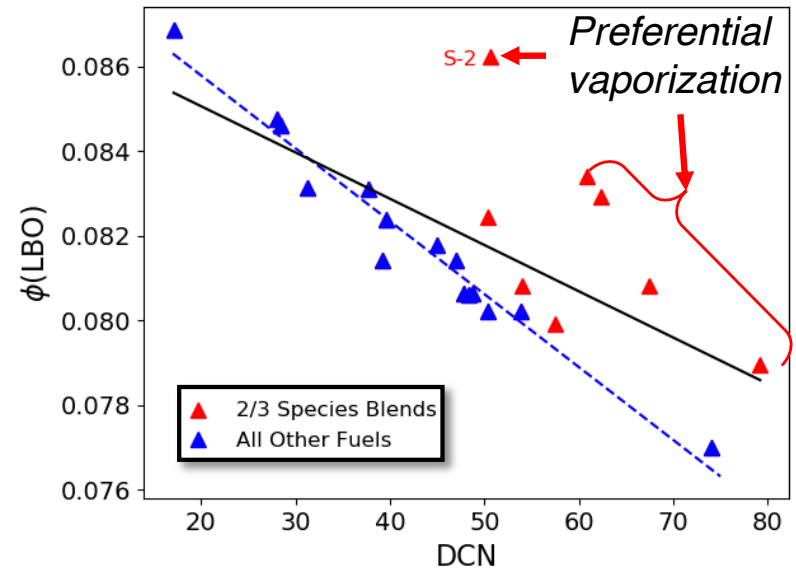
Back-up



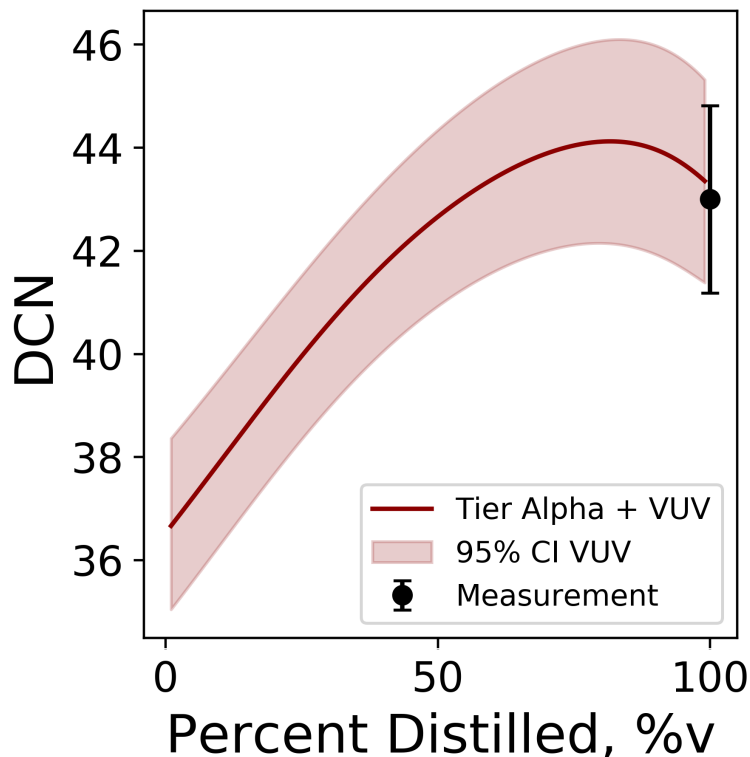
Property predictions with VUV



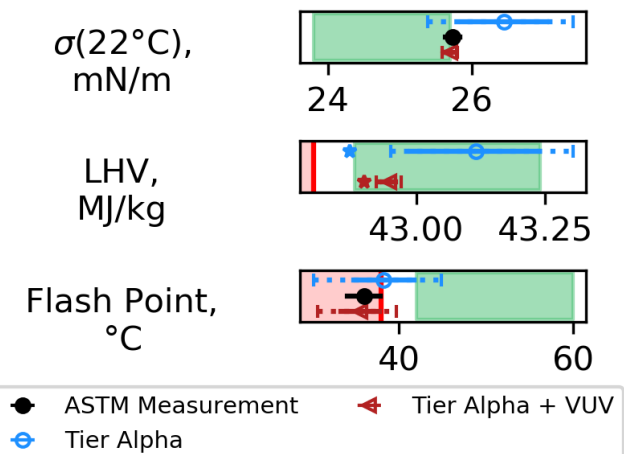
- Preferential vaporization was important in the NJFCP for LBO for fuels with only a few species
 - Example below illustrates predicted dynamic behavior of candidate fuel's DCN across the distillation curve



Bell, Heyne, Won, Dryer, ASME PowerEnergy (7432) 2018.



- VUV reduces uncertainty and increases the accuracy of predictions versus measurements
- Sparsity in the database leads to another uncertainty 'bottle-neck'



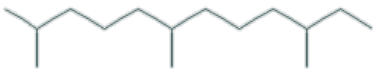
From the molecular perspective, **SAFs are *not* conventional fuels** *compositions can be very selective AND diverse*

Theoretical and experimental observations

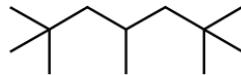
- Selective: existing ASTM D7566

Annexes

Farnesane (A3)



iso-Dodecane (A5)



- Gibb's energy over geological time scales biases conventional fuel compositions
 - $dG = d(H - TS)$
 - Diverse: Future, approved fuel...?

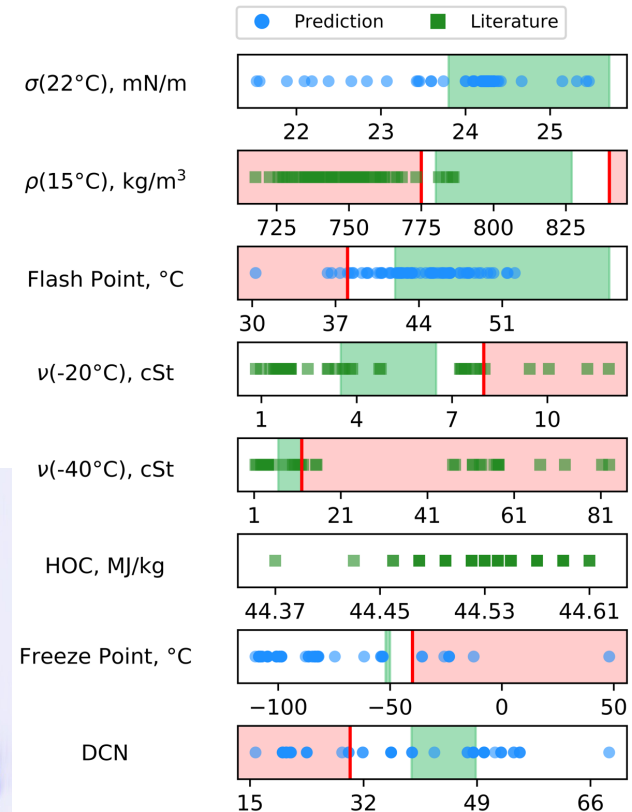
SAF candidate:
Every modulation has at least one isomer elute.

Avg. Jet A
analyte separation between modulations

➤ Implication

- **Top-down** methods trained on conventional fuels are insufficient for predicting properties that have significant variance within a sub-class
- **Bottom-up** approaches enable more physics and straightforward uncertainty quantification

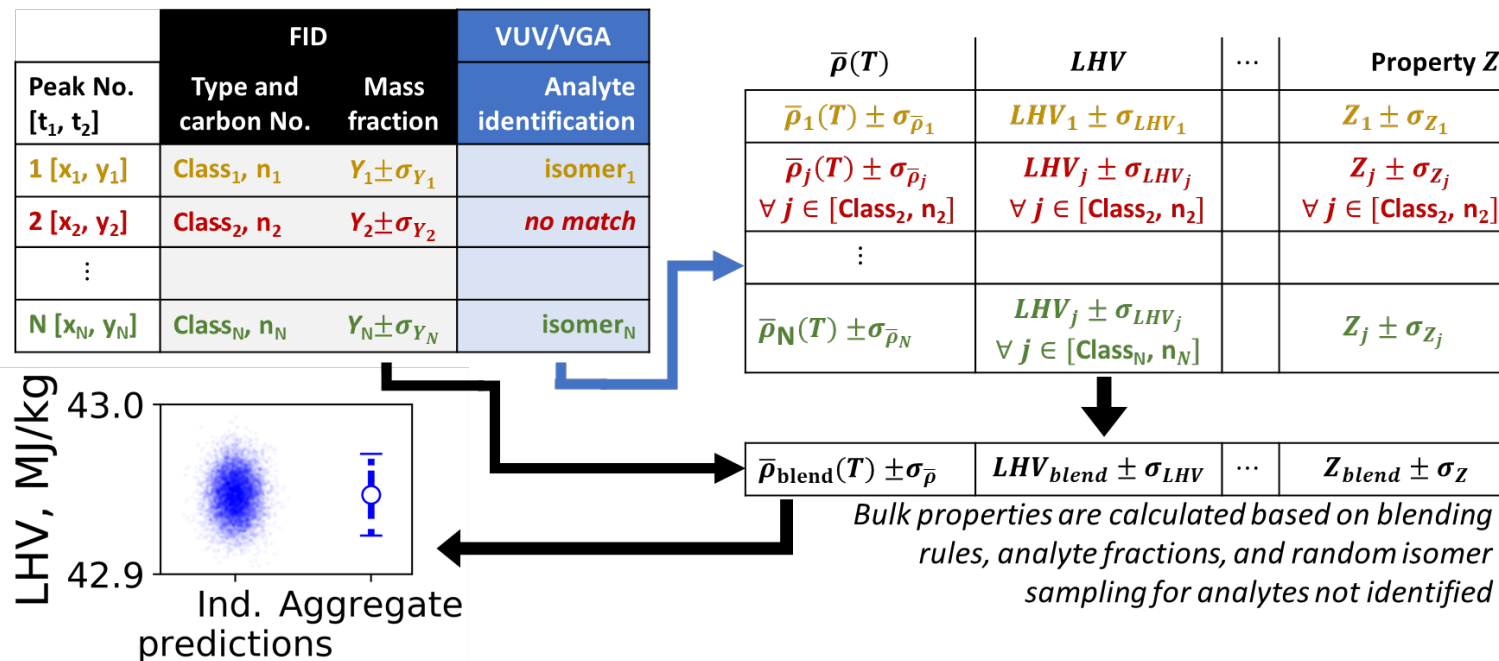
C10 iso-alkanes



- Three types of uncertainty are considered:
 - Mass quantification (σ_{Y_i}); normal distribution
 - Property in reference library (σ_{Z_j}); normal distribution
 - Isomeric identification (σ_{isomer}); uniform distribution

$$\sigma_{isomer} = f(Z_i \pm \sigma_{Z_i} \forall i \in [Class_j, n_j])$$

- Distributions are sampled until convergence

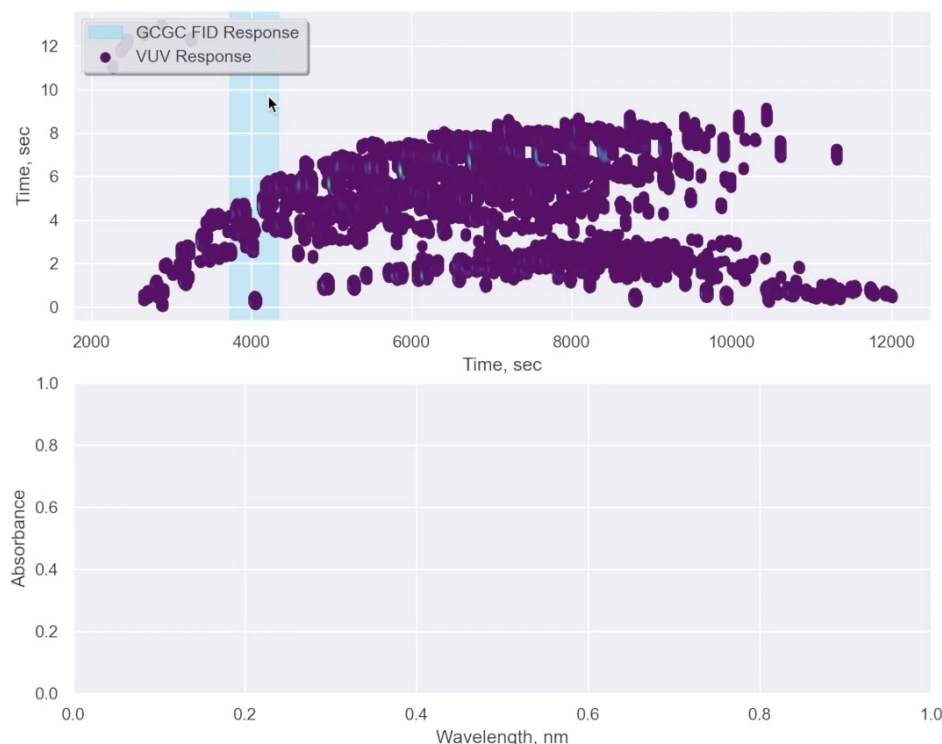


Database consists of 3k molecules in the jet range

Identification Methods

Manual Method

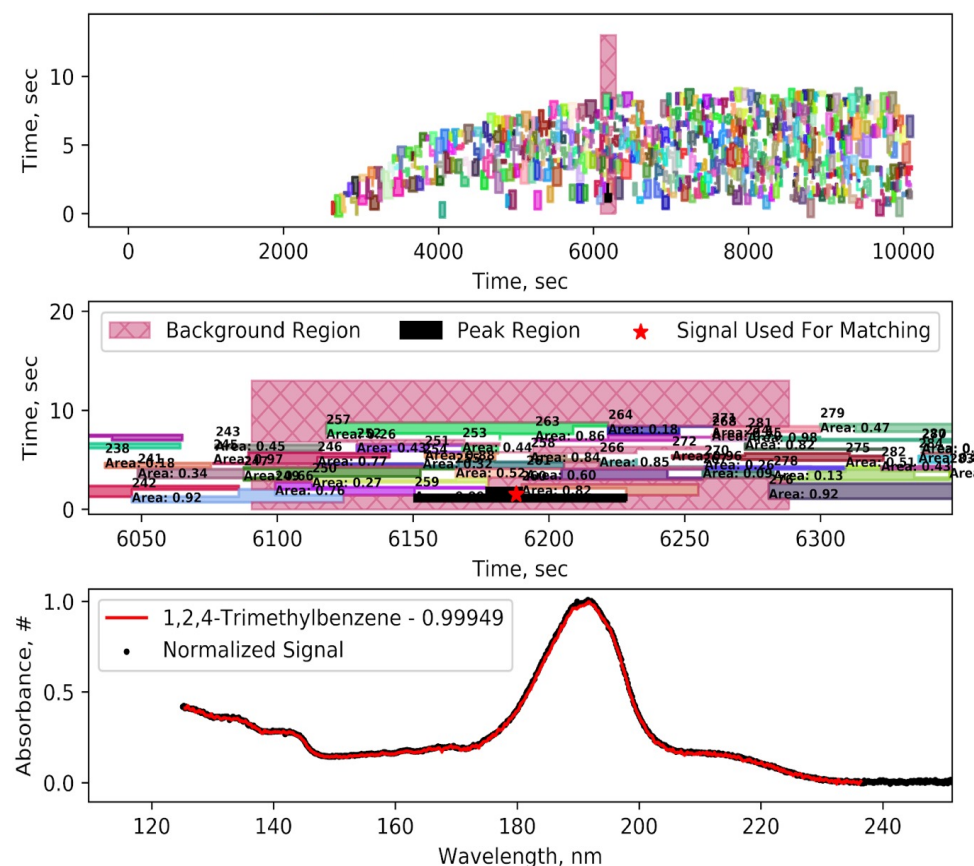
Select background region



Steps Taken In Video:

- 1.) Select a local background region near our peak of interest
- 2.) Select the peak region
- 3.) Process the peak by normalizing and removing background noise
- 3.) Run matching to resolve highest R^2 match for the peak of interest

Automated Method



Future work:

- Most of the identified carbon will be identified with an automated method.
- Remaining carbon for smaller peaks will likely need to be manually selected.