University of Dayton Research Institute

FAA CENTER OF EXCELLENCE FOR ALTERNATIVE JET FUELS & ENVIRONMENT

Alternative Jet Fuel Test and Evaluation

Project 31a

Lead investigator: S. Zabarnick, University of Dayton Research Institute
Project manager: C. Shaw, FAA

April 18-19
Atlanta, GA

ASCENT
AVIATION SUSTAINABILITY CENTER

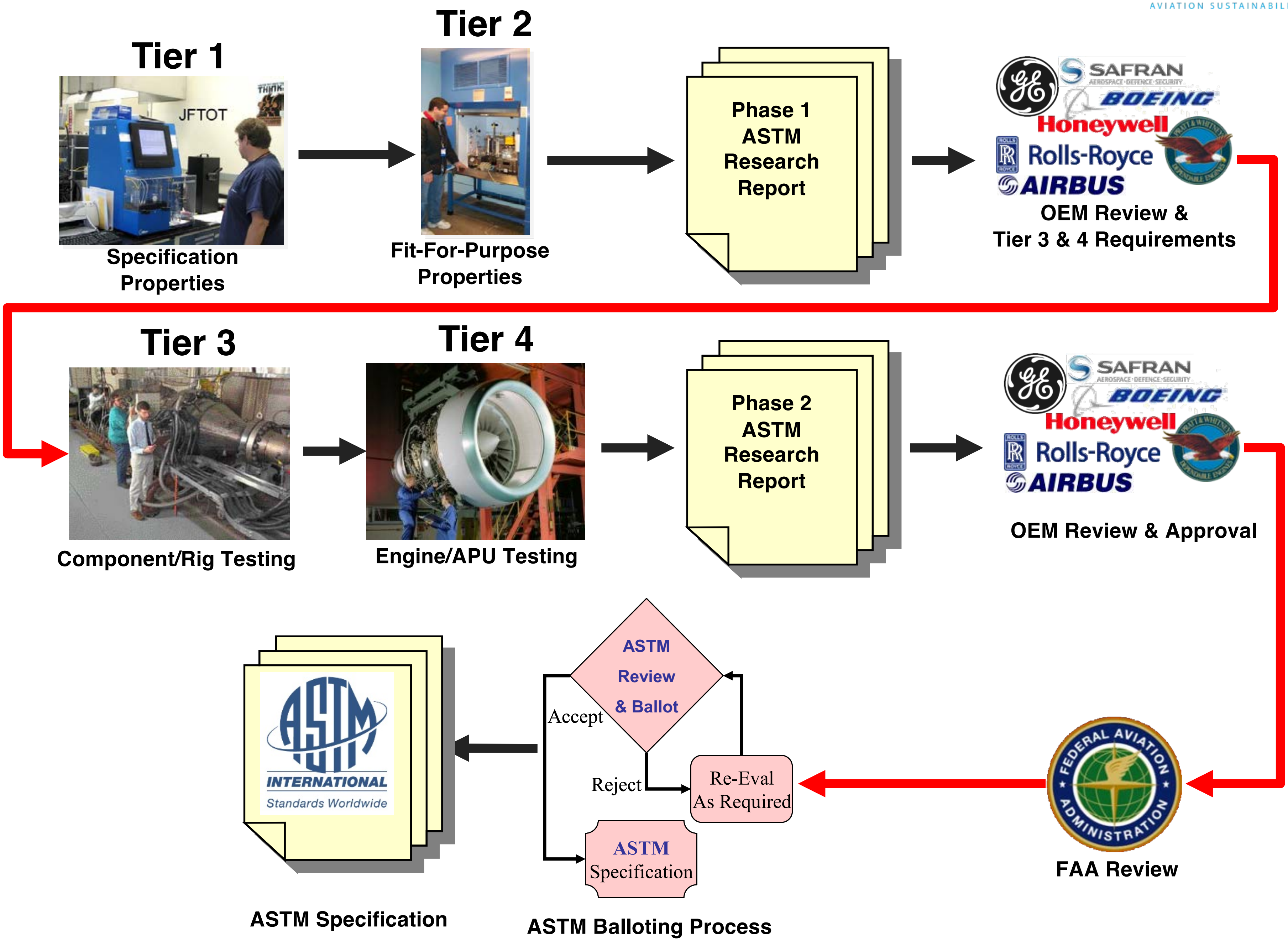
Introduction

- Motivation – Establish a centralized facility to support continued approval/certification of candidate alternative jet fuels through the ASTM process
- Objectives
  - Fuel property and composition testing
  - Support for rig/engine evaluations
  - Coordination of OEM approval process
- Outcomes and practical applications
  - ASTM research reports for OEM approval
  - Creation of D7566 annex
  - Recognized focal point for management of D4054 qualifications process
  - Increased supply of secure, safe alternative aviation fuels

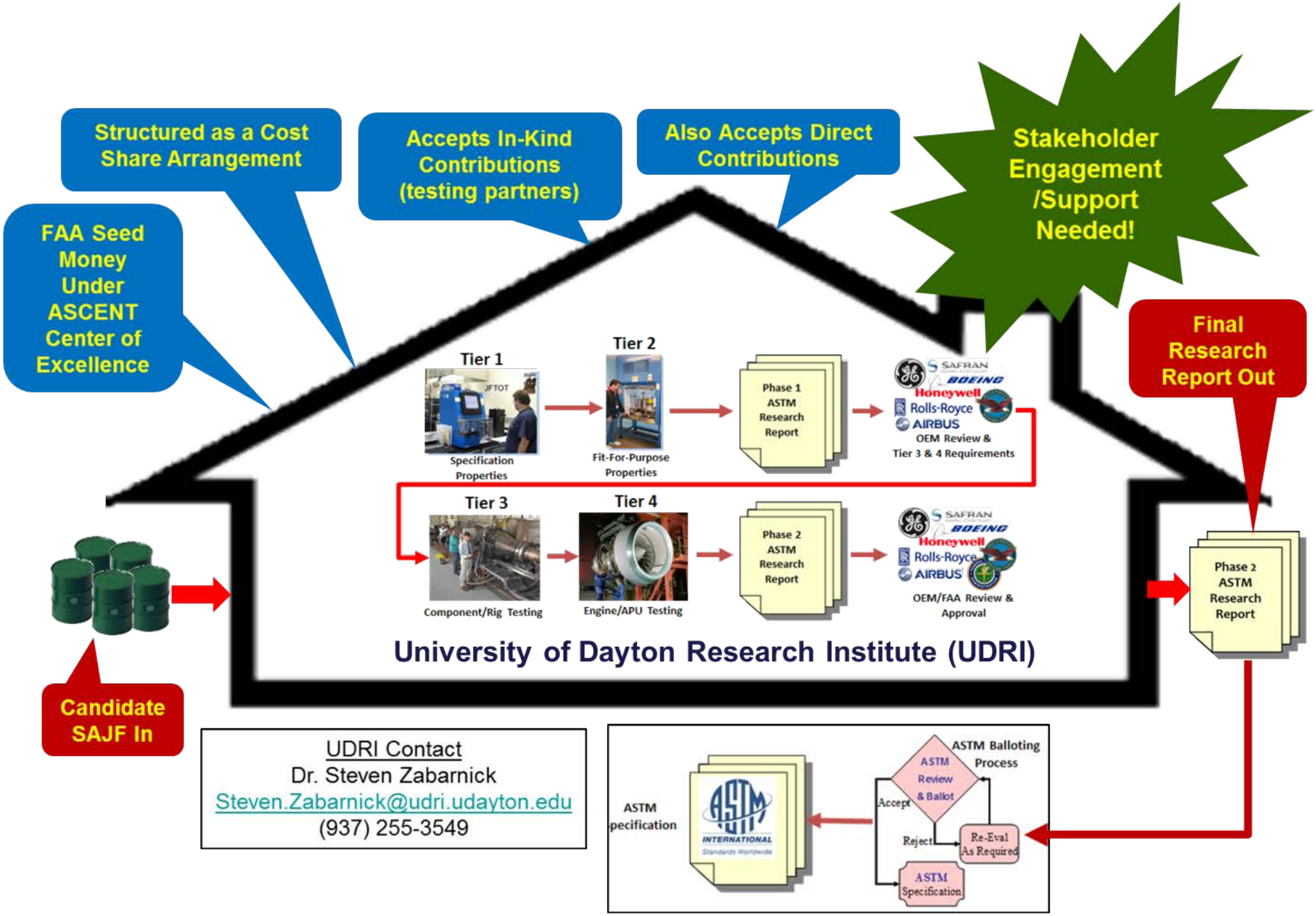
Primary Tasks

- Alternative Fuel Candidate Evaluation
  - LanzaTech ATJ approved, Shell IH2, IHI Bb-oil being tested
- Coordination of Research Report Review Process
  - LanzaTech ATJ, Boeing HFP-HEFA, ARA CHJ, Virent SAK, Shell IH2, IHI Bb-oil
- Development of ~~Generic Annex~~ Fast Track Process
  - D4054 Annex with stringent requirements/fast approval
  - Chemical composition – GCxGC methods
- GCxGC Method Development – hydrocarbon type and trace polars methods
  - Replace D2425 mass spec method
  - Method documentation, precision determination, comparison with other labs/columns/modulators

D4054 Certification Process



D4054 Clearinghouse Concept



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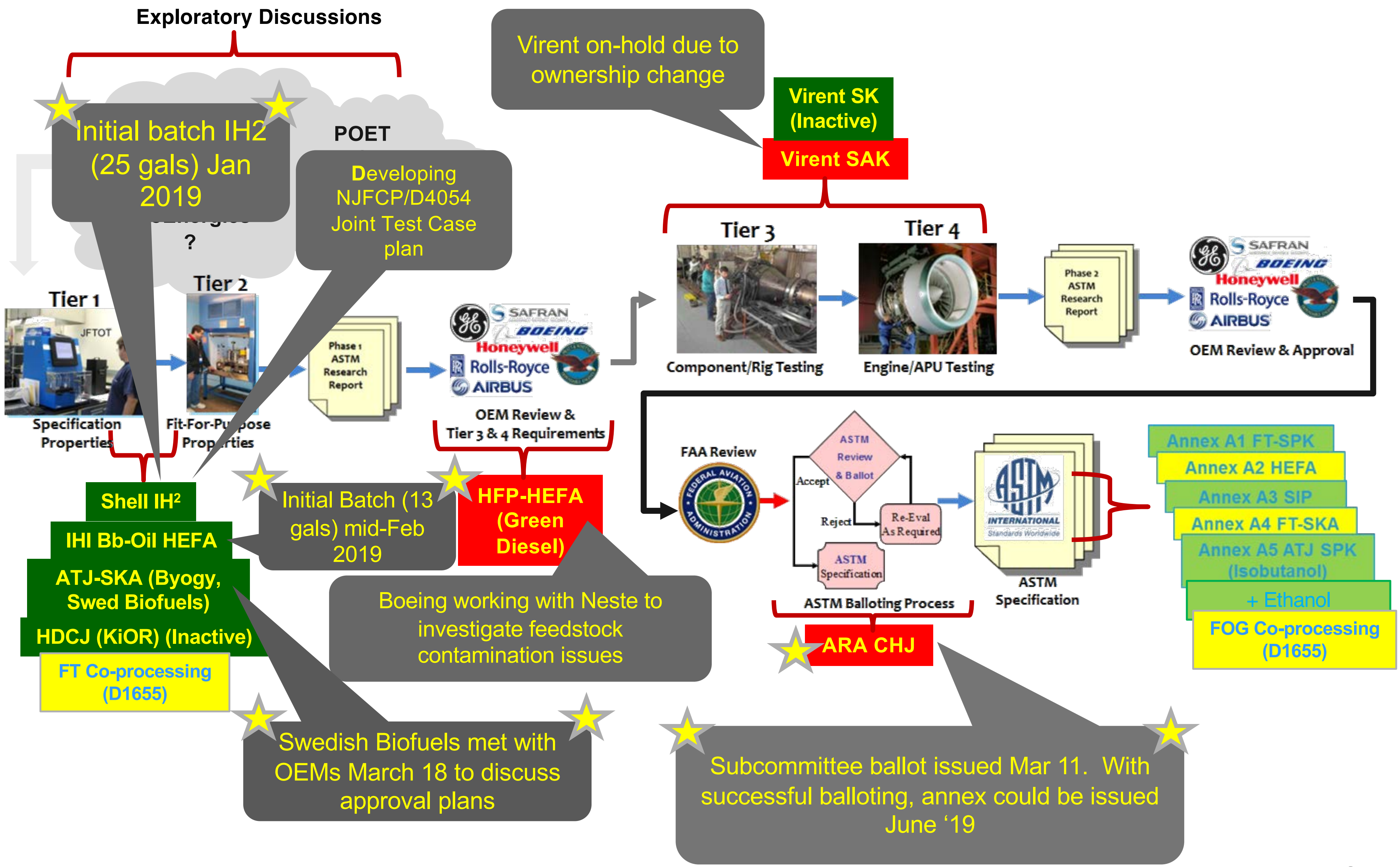
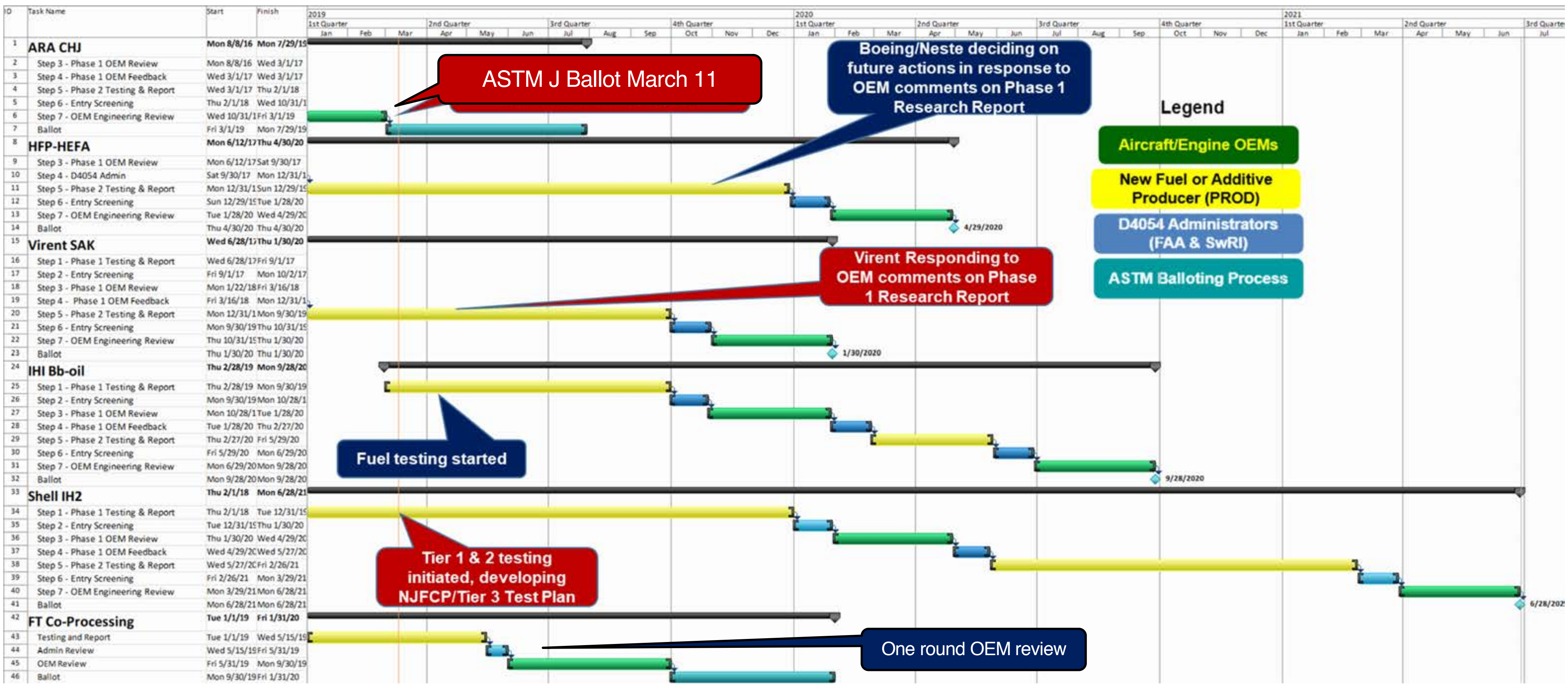
Candidate Fuels in Queue



Gantt Schedule for Current Fuels



Status of Subcontracts for ASTM Research Report Review

- SwRI – coordination of ASTM approval & research report review (also Tier 2 testing)
- Honeywell –
- Rolls Royce –
- GE Aviation –
- Pratt & Whitney
- Boeing –

Research report review

Additional Funding Needed to Continue the ASTM Approval Process

Generic Annex → Fast Track Annex

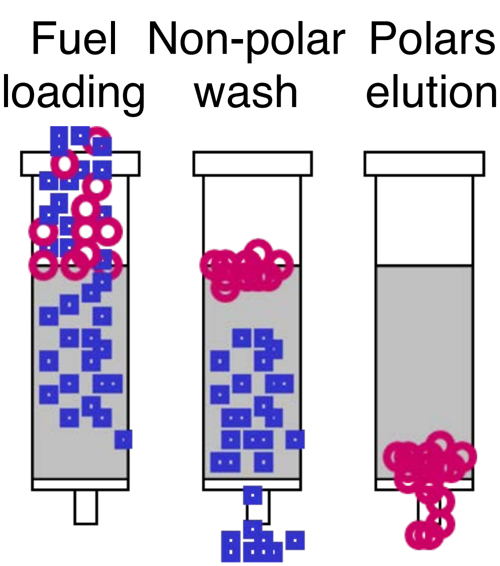
- Generic Annex D7566 – no OEM review process
  - Stringent property requirements
  - Feedstock and process not defined
  - Push back from OEMs on approval without OEM review
  - Abandoned in Spring/Summer 2018
- Fast Track Annex for D4054 – defines new streamlined approval process
  - *Stringent property requirements*
  - *More detailed Table 1 (composition, C# distribution, etc.)*
  - *Feedstock and process defined*
  - Includes OEM review requirement
  - D7566 annex produced – 10% blend limit?

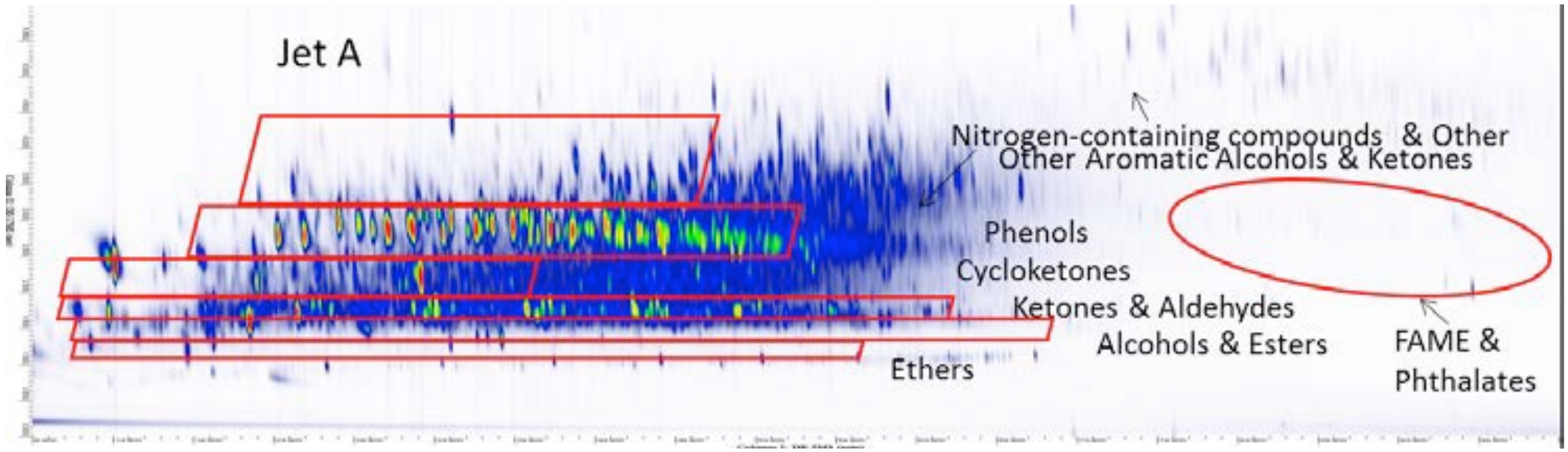
Research report

ASTM Ballots
-approved J ballot
-one negative March D02 ballot

Chemical Composition for the Fast Track Annex

- Need to limit non-hydrocarbon species & select limits
- Sulfur, nitrogen, oxygen, and metals
- ASTM methods exist for S, N, and metals
- GCxGC with SPE for polar oxygenates/N





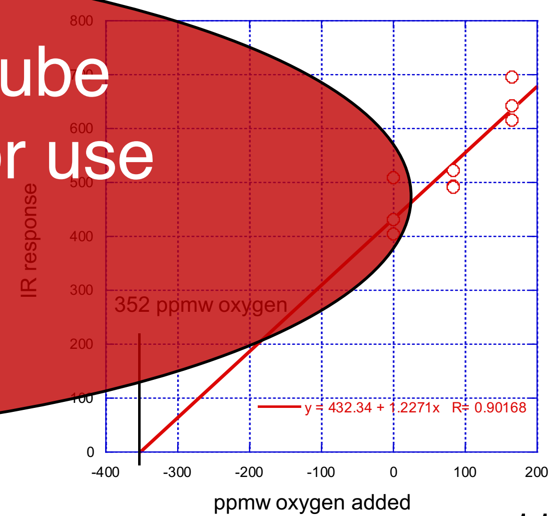
Trace Oxygen Analysis

- OEM's concerned with unknown trace oxygenate contaminants
  - No current ASTM method to measure total oxygen at ppm levels
- Evaluation of Elementar Oxycube with IR detector
  - Reductive pyrolysis of O to CO
  - Address interferences
    - O_2 from air – N_2 sparge
    - Dissolved/free H_2O in fuel – mol sieve
  - Evaluate sensitivity, LOQ in fuel
- 10 ppm limit currently not promising
- Determine usefulness and need for in Generic Annex
  - May no longer be needed for Fast Track Annex

We determined that the Oxycube does not have the sensitivity for use in jet fuel specifications – interferences

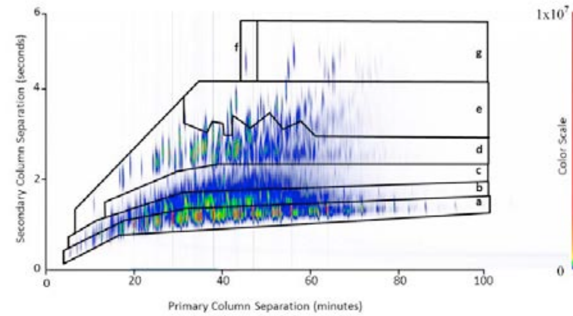
+ IR

rapid OXY cube + IR detector
10 ppm
±0.001 - 0.1%

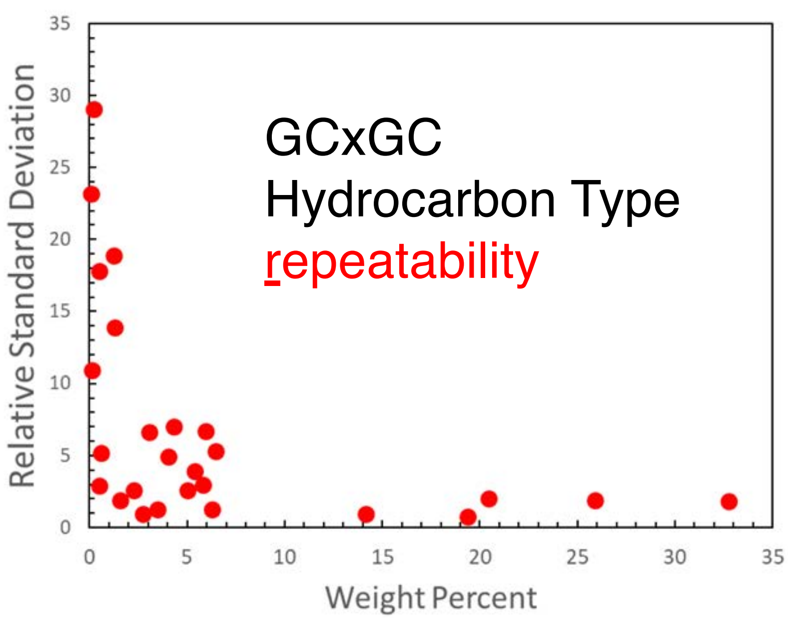


GCxGC Method Documentation & Analysis

- Two phase project – Funding received Sept 2018
  - Phase I progress
    - Document hydrocarbon type and polars methods (Completed)
    - Precision of GCxGC method (repeatability – "little r"
      - One fuel measured 5 times over 8 years (2011 - 2018)

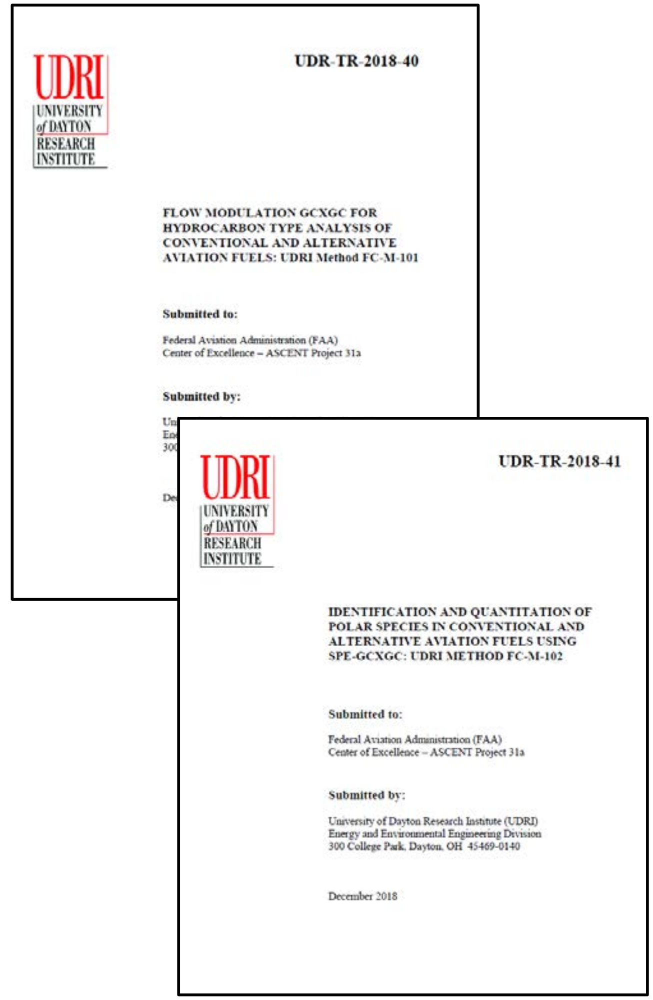


	Mean (n=5), (wt%)	Standard deviation	RSD, %
benzene	<0.01	-	-
toluene	0.10	0.01	11
C2 - benzene	0.58	0.03	5.2
C3 - benzene	2.25	0.06	2.6
C4 - benzene	3.46	0.04	1.3
C5 - benzene	2.74	0.03	1.0
C6+ benzenes	5.00	0.13	2.6
Total Alkylbenzenes	14.13	0.14	1.0
Total Alkylnaphthalenes	1.55	0.03	1.9
indans and tetralins	6.28	0.08	1.3
C07 and lower-iso	0.21	0.06	29
C08-iso-	0.51	0.09	18
C09-iso-	1.28	0.18	14
C10-iso-	4.05	0.20	4.9
C11-iso-	6.46	0.34	5.3
C12-iso-	5.93	0.40	6.7
C13-iso-	5.83	0.17	3.0
C14-iso-	4.30	0.30	7.0
C15-iso-	3.08	0.20	6.6
C16-iso-	1.22	0.23	19
C17 and greater	0.48	0.01	2.9
Total iso-Paraffins	32.77	0.61	1.9
Total n-Paraffins	19.36	0.15	0.8
Monocycloparaffins	20.44	0.41	2.0
Dicycloparaffins	5.40	0.21	3.9
Tricycloparaffins	0.05	0.01	23
Total Cycloparaffins	25.9	0.49	1.9



GCxGC Method Development & Documentation

- Phase I progress (continued)
- UDRI Method FC-M-101, "Flow Modulation GCxGC for Hydrocarbon Type Analysis of Conventional and Alternative Aviation Fuels," UDR-TR-2018-40
- UDRI Method FC-M-102, "Identification and Quantification of Polar Species in Conventional and Alternative Aviation Fuel Using SPE-GCxGC," UDR-TR-2018-41
- These are included in Fast Track Annex (D4054) – replace in D7566 annexes?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UDR-TR-2018-40

FLOW MODULATION GCXGC FOR HYDROCARBON TYPE ANALYSIS OF CONVENTIONAL AND ALTERNATIVE AVIATION FUELS: UDRI Method FC-M-101

Submitted to:

Federal Aviation Administration (FAA)
Center of Excellence – ASCENT Project 31a

Submitted by:

UDRI UNIVERSITY of DAYTON RESEARCH INSTITUTE

UDR-TR-2018-41

IDENTIFICATION AND QUANTITATION OF POLAR SPECIES IN CONVENTIONAL AND ALTERNATIVE AVIATION FUELS USING SPE-GCXGC: UDRI METHOD FC-M-102

Submitted to:

Federal Aviation Administration (FAA)
Center of Excellence – ASCENT Project 31a

Submitted by:

University of Dayton Research Institute (UDRI)
Energy and Environmental Engineering Division
300 College Park, Dayton, OH 45469-0140

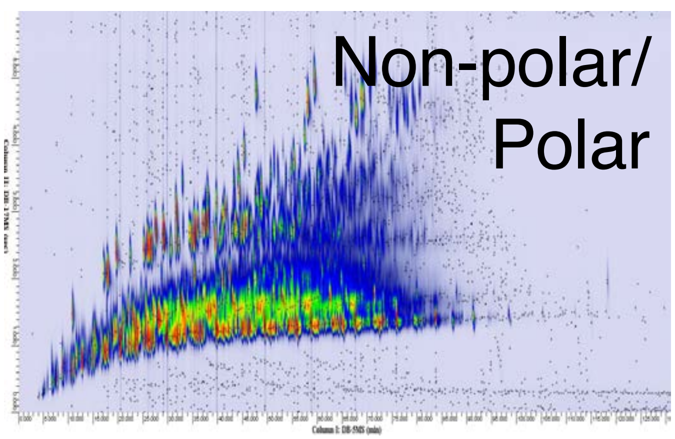
December 2018

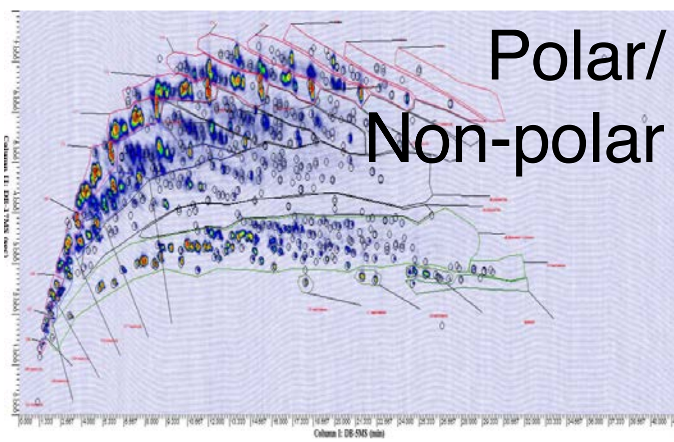
GCxGC Method Documentation & Analysis (Phase II progress)

- Reproducibility – "big R"
- Comparison with external lab
  - Identical GCxGC system
    - Columns, modulator, chrom condx, template, etc.
  - RSD usually <2%, except low levels

	Weight %			Relative Difference, %		
	JP-8	HEFA	diesel	JP-8	HEFA	diesel
Alkylbenzenes	14.0	<0.01	8.50	0.91	-	10
Diaromatics	1.55	<0.01	2.92	1.9	-	5.4
Cycloaromatics	6.23	<0.01	13.6	0.60	-	15
Total Aromatics	21.8	<0.01	25.1	0.89	-	3.3
iso-Paraffins	32.3	85.5	23.5	2.0	0.68	0.12
n-Paraffins	18.8	12.2	13.7	1.2	2.0	1.4
Total Paraffins	51.1	97.6	37.2	0.81	0.33	0.58
Monocycloparaffins	21.4	2.35	24.1	1.2	12	1.9
Dicycloparaffins	5.60	0.038	11.9	7.9	58	0.05
Tricycloparaffins	0.094	<0.01	1.45	13	-	11
Total Cycloparaffins	27.1	2.38	37.5	0.82	13	0.82

- Comparison with four external labs
  - Various GCxGC systems – modulators (flow and thermal), column sets (P/NP vs NP/P), chrom condx, templates, etc.
  - Currently coordinating reporting methods, templates
  - Beginning results comparison





Shell IH² Technology

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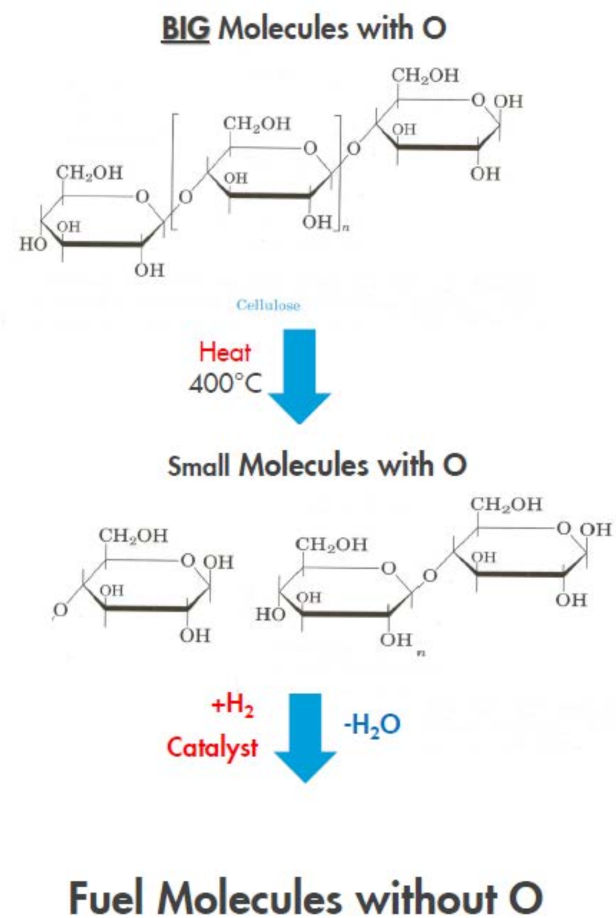
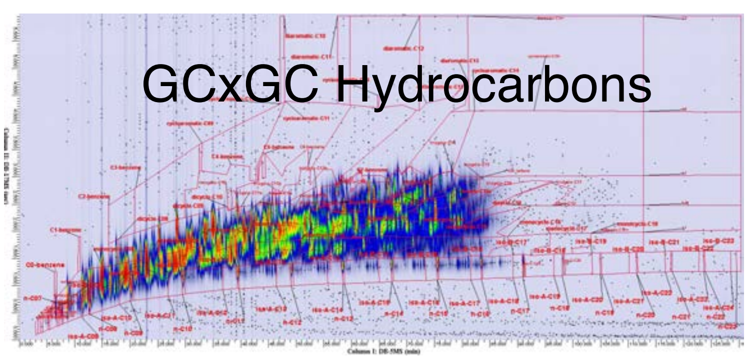
- Hydropyrolysis & hydrotreating of biomass
- Woody biomass, MSW, Ag residue, etc.
- ~95% cycloparaffins (5% other paraffins)
- Original sample showed storage degradation
- New sample being evaluated – received Jan 2019
- High cycloparaffin content – likely requires Tier 3/4 evaluations – combustor rig/APU
  - NJFCP plan being developed



Shell IH²

- Unusual composition
  - Very high cycloparaffin content (95.7%)
  - Very high density (0.832 kg/m³)
- All other properties look good to date
  - Seal swell much improved over iso/normal paraffinic fuel
- 50/50 blend meets all D1655 properties
- OEMs require Tier 3 combustion and extended material compat evaluations
  - NJFCP evaluation in the works
  - Additional funding needed to support



GCxGC Hydrocarbons

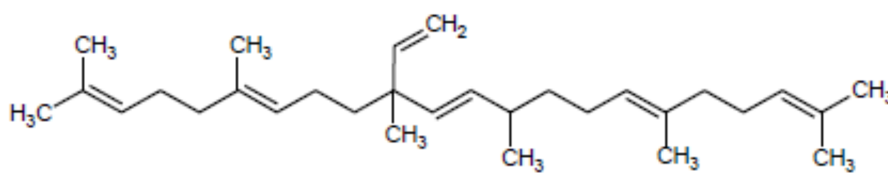
	POSF-10325 Jet A	POSF-13511 IH2-CPK-0	POSF-13512 50/50 Blend
Hydrogen Content (weight %)	14.0	13.8	13.9
Average Molecular Weight (g/mole)	159	148	153
Column1	**Weight %**	**Weight %3**	**Weight %6**
Total Alkylbenzenes	**12.89**	**0.05**	**6.04**
Total Alkylnaphthalenes	**2.28**	**<0.01**	**1.06**
Total Cycloaromatics	**3.24**	**0.04**	**1.51**
Total Aromatics	**18.41**	**0.08**	**8.60**
Total iso-Paraffins	**28.75**	**1.70**	**14.65**
Total n-Paraffins	**18.96**	**2.56**	**10.56**
Total Monocycloparaffins	**25.11**	**47.12**	**35.53**
Total Dicycloparaffins	**8.53**	**40.33**	**25.83**
Total Tricycloparaffins	**0.23**	**8.21**	**4.80**
Total Cycloparaffins	**33.88**	**95.66**	**66.15**

GCxGC-SPE Polars

Speciated Polars (mg/L)	Jet A POSF-10325	IH2-CPK-0 POSF-13511	50/50 Blend POSF-13512
Phenols	120	<1	64
Anilines	3	<1	1
Indoles	1	<1	<1
Quinolines	8	<1	4
Tetrahydro-quinolines	1	<1	<1
Pyridines	2	<1	1
Carbazoles	2	<1	1
Ketones	54	<1	28
Cycloketones	19	<1	10
Alcohols	20	1	11
Aldehydes	6	<1	3
Ethers	1	1	1
Esters	1	1	1
Phthalates	<1	<1	<1
Other	99	1	52
Total	**336**	**4**	**176**

IHI Bb-oil Technology

- Open pond algae cultivation – algae strain selected and bred to maximize hydrocarbon production
- Typical algal processing:
  - Cultivation, dewatering, drying, extraction, conversion
- 80-90% hydrocarbon, 10-20% free fatty acids



- Deoxygenation, hydroisomerization/ hydrocracking similar to HEFA processes
- Composition similar to HEFA except for high cycloparaffins – ~30-50%
  - high density 0.778, above HEFA SPK limit
- Candidate for Fast Track procedure?

IHI Bb-SPK Results

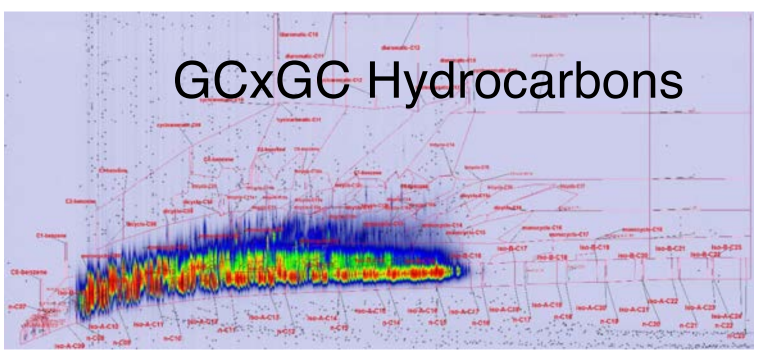
- Cycloparaffin content (40.0%) is higher than other D7566 approved SPK's (15%) and Fast Track limit (30%)
  - Cycloparaffins are now understood to be highly desirable fuel components
- Density is high for SPK due to high cycloparaffin content
  - Annex would have higher lower limit
  - Higher density is desirable – more "fuel-like"
- All other properties look good to date
- 50/50 blend meets all D1655 properties

GCxGC Hydrocarbons

Column1	POSF-10325	POSF-13516	POSF-13517
	Jet A	IHI-Bio-SPK	50/50 Blend
	Weight %	Weight %	Weight %
Total Alkylbenzenes	12.89	<0.03	6.59
Total Alkylnaphthalenes	2.28	<0.01	1.10
Total Cycloaromatics	3.24	<0.01	1.64
Total Aromatics	18.41	<0.03	9.33
Total iso-Paraffins	28.75	56.00	41.99
Total n-Paraffins	18.96	4.01	12.14
Total Monocycloparaffins	25.11	33.66	29.51
Total Dicycloparaffins	8.53	6.02	6.77
Total Tricycloparaffins	0.23	0.27	0.25
Total Cycloparaffins	33.88	39.95	36.53

GCxGC-SPE Polars

Speciated Polars (mg/L)	Jet A POSF-10325	IHI-Bio-SPK POSF-13516	50/50 Blend POSF-13517
Phenols	120	<1	57
Anilines	3	<1	1
Indoles	1	<1	<1
Quinolines	8	<1	4
Tetrahydro-quinolines	1	<1	1
Pyridines	2	<1	<1
Carbazoles	2	<1	1
Ketones	54	<1	26
Cycloketones	19	<1	9
Alcohols	20	<1	11
Aldehydes	6	<1	3
Ethers	1	<1	1
Esters	1	1	<2
Phthalates	<1	1	<2
Other	99	1	50
Total	**336**	**<5**	**165**



2019 FY New Tasks

- Combustion rig & APU evaluations of Shell IH^2 – not yet funded
- Database (Project 33) support – not yet funded
- Continued OEM research report review support – need additional funds to continue after summer 2019
- GCxGC method development/documentation – continuing

Acknowledgements

- We ❤ our cost share partners:

- Thanks to FAA AEE Team: Cecilia Shaw, Levent Ileri, Jim Hileman, and Mark Rumizen
- Thanks to the AFRL Fuels Branch (Tim Edwards, Paul Wrzesinski, Milissa Griesenbrock) for use of their facilities
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