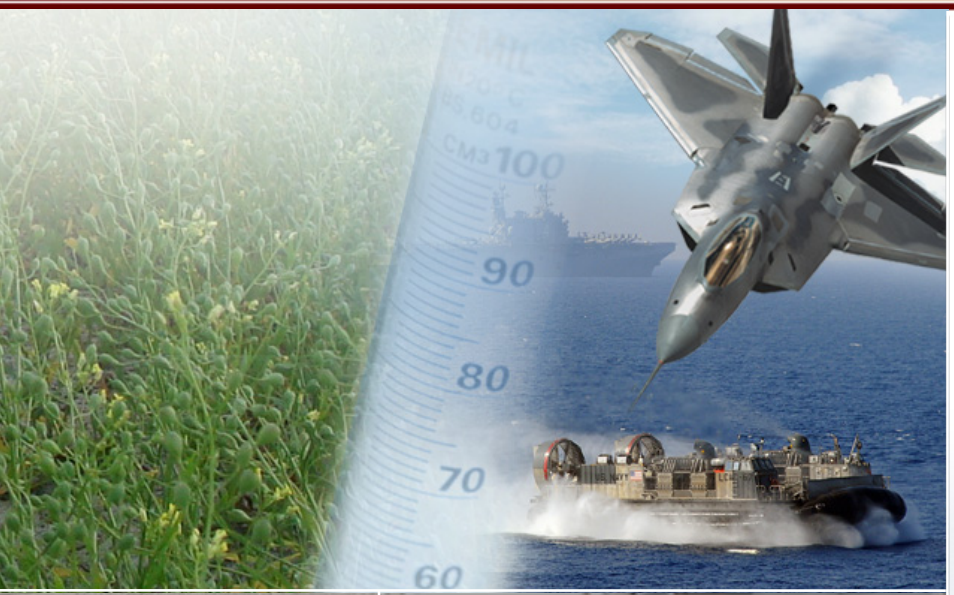
expanding the realm of POSSIBILITY®



"Drop-In" Renewable Jet Fuel Containing Aromatics and Cycloparaffins

Edward N. Coppola

14 November 2012

4th ICBS, NIST, Gaithersburg, MD

ReadiJet™

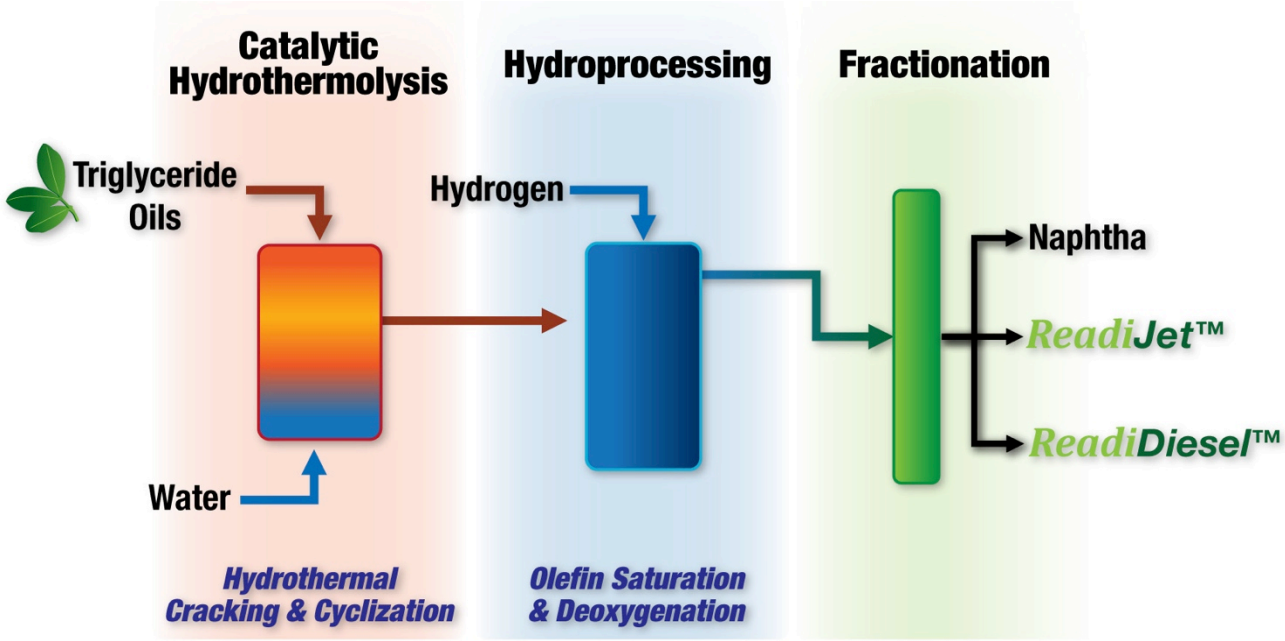
ReadiDiesel™

ARA®

Overview

- Process
  - Process Background
  - Process Chemistry
- Jet Fuel Quality
- Certification Challenges
- Test Activities
- Summary

ARA Hydrothermal Process *(patented)*



- CH uses water to convert triglycerides, esters, and fatty acids directly into cracked and cyclized hydrocarbons
  - Same hydrocarbon types as petroleum – distributed over entire boiling range
- Hydrotreating saturates residual olefins and removes residual oxygen
  - Aromatics and cycloparaffins are preserved
  - Hydrogen consumption & GHG generation are much less than SPK from HEFA
- Fuel gas, naphtha, jet, and diesel products

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CH Process Background

- ARA developed "Catalytic Hydrothermolysis" (CH) in 2006
  - A hydrothermal process where water mediates the CH reactions
  - U.S. patent 7,691,159 was awarded April 6, 2010
- Goals of the CH process:
  - Produce a true "drop-in" fuel containing aromatics and cycloparaffins
  - *Re*newable *a*romatic *d*rop-*i*n Jet fuel – *Readi* Jet®
  - *Re*newable *a*romatic *d*rop-*i*n diesel fuel – *Readi* Diesel®
- Commercial benefits
  - Eliminates hydrocracking, hydroisomerization and catalysts consumption
  - Reduces hydrogen consumption and carbon footprint
  - Provides energy equivalent to petroleum fuels on both weight and volume bases
  - Avoids blending and infrastructure modifications
  - Reduces logistics costs – able to ship neat, without petroleum
  - Eliminates concerns regarding petroleum quality if/when comingled
  - Results in higher-quality, lower-cost, renewable fuels – blended or un-blended

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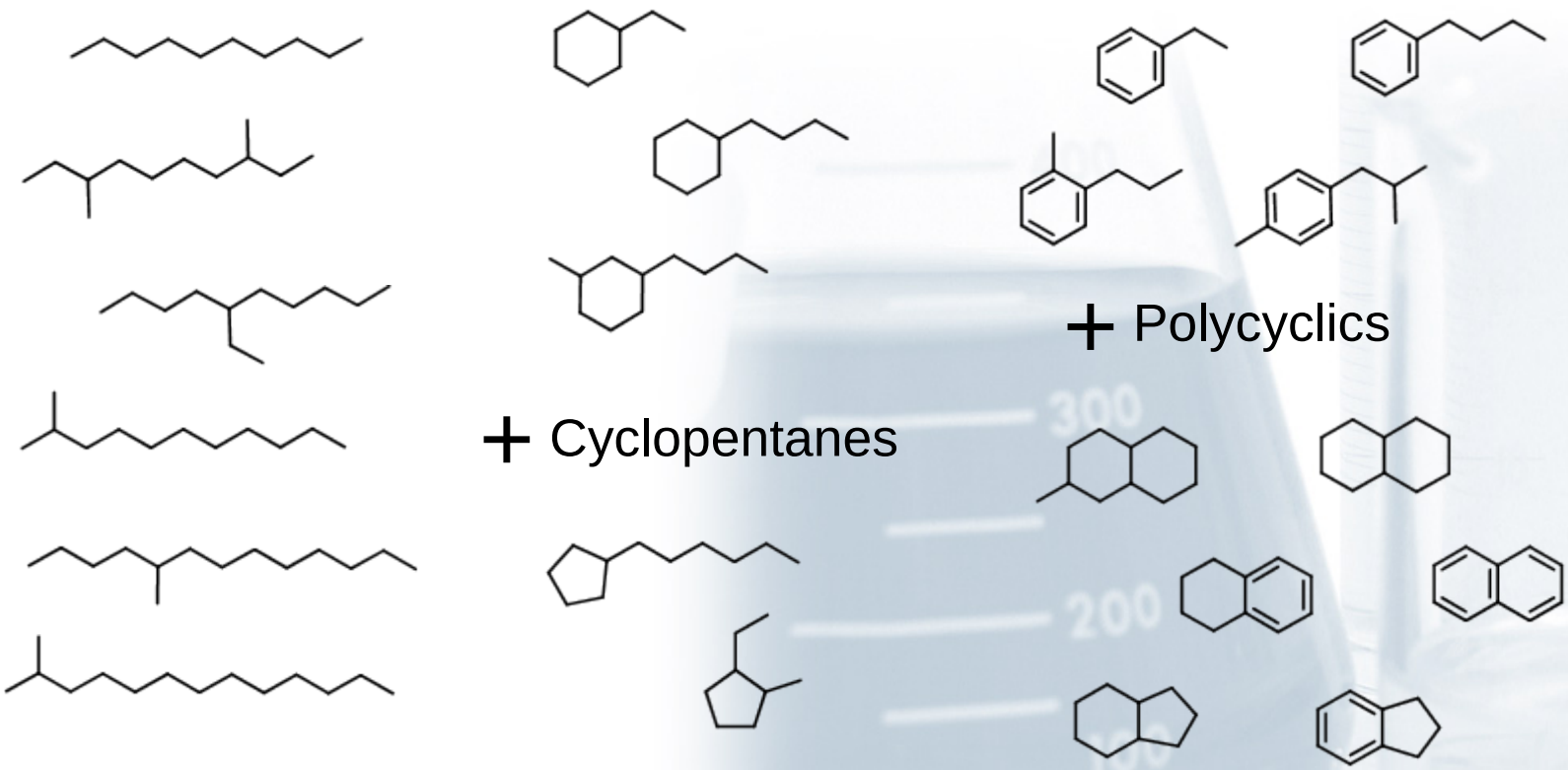
Typical Alternate Fuel Hydrocarbons

SPK from FT & HEFA

Catalytic Hydrothermolysis (CH)

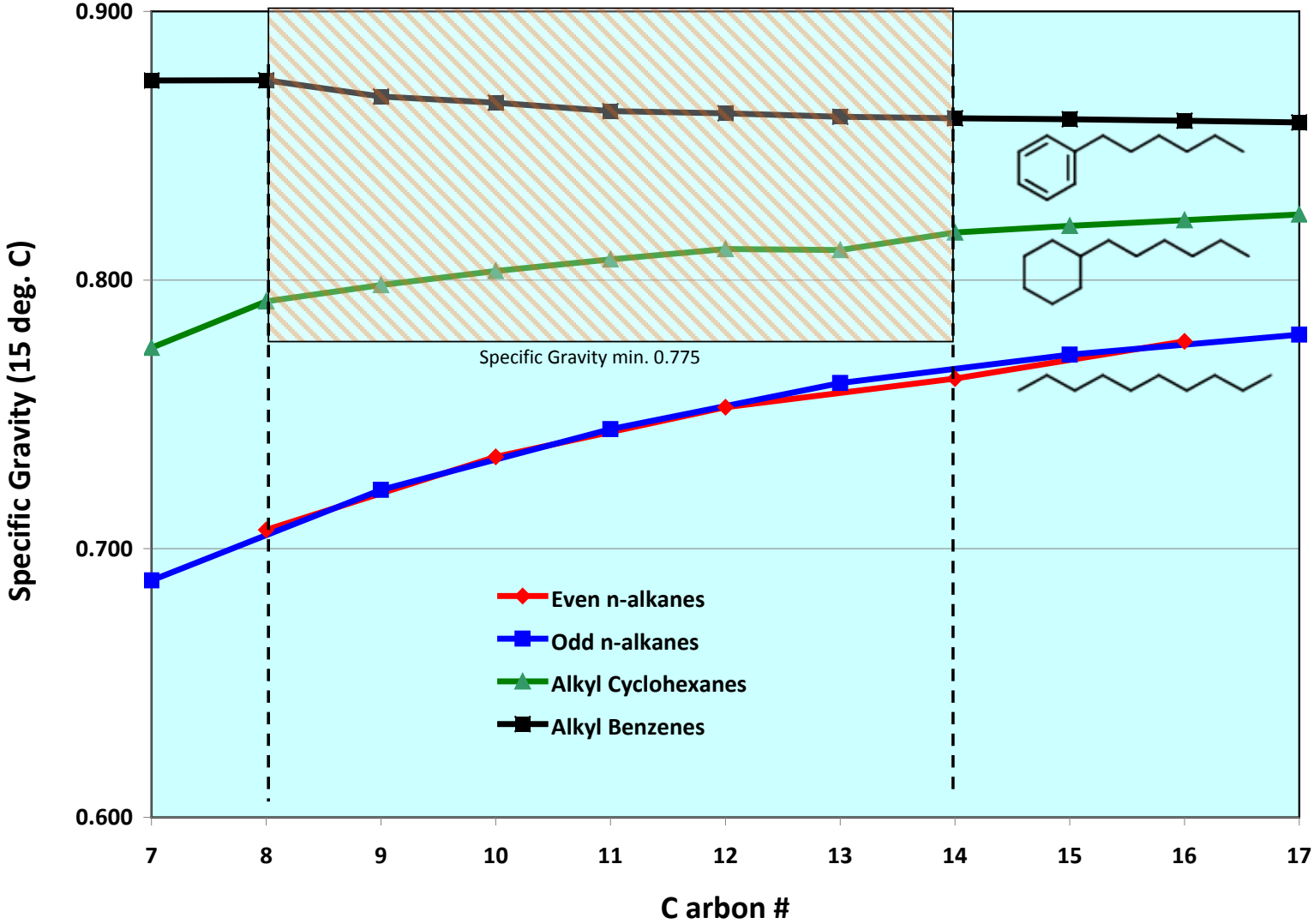
Paraffins + Cyclohexanes + Alkylbenzenes



+ Polycyclics

+ Cyclopentanes

Hydrocarbon Type – Specific Gravity Effect



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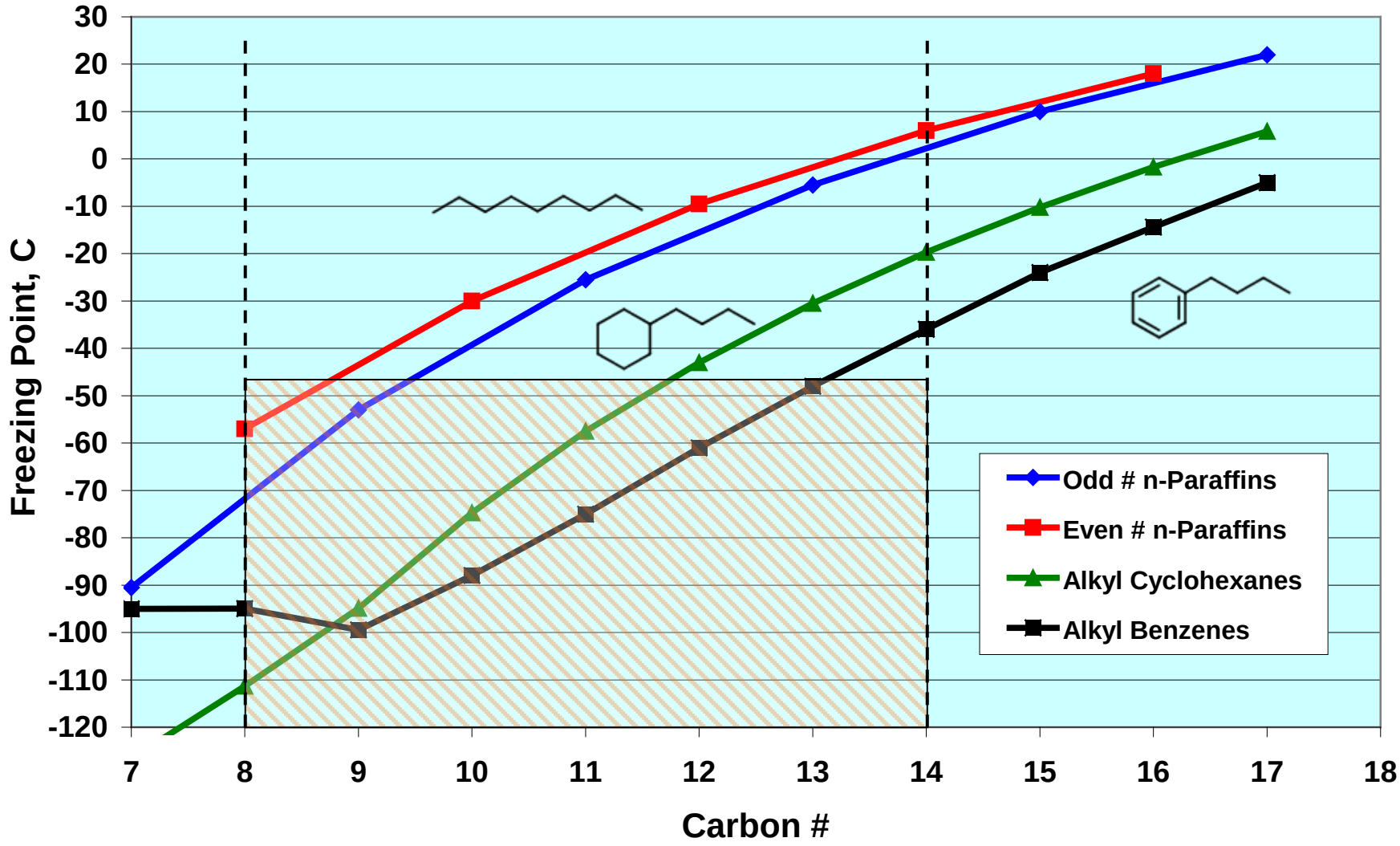
Hydrocarbon Type – Freezing Point Effect



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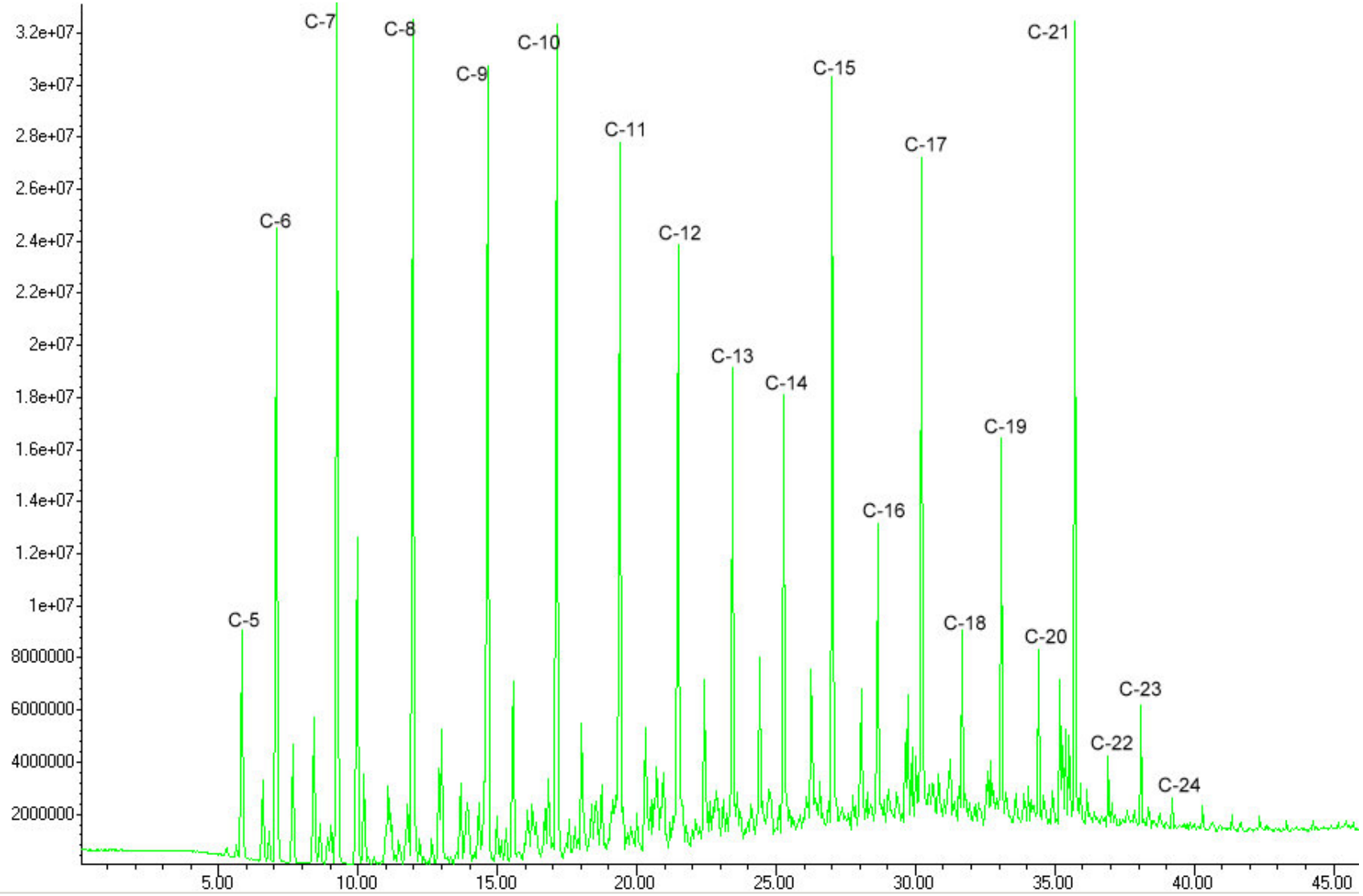
GC of Hydrotreated CH Crude Carinata Oil



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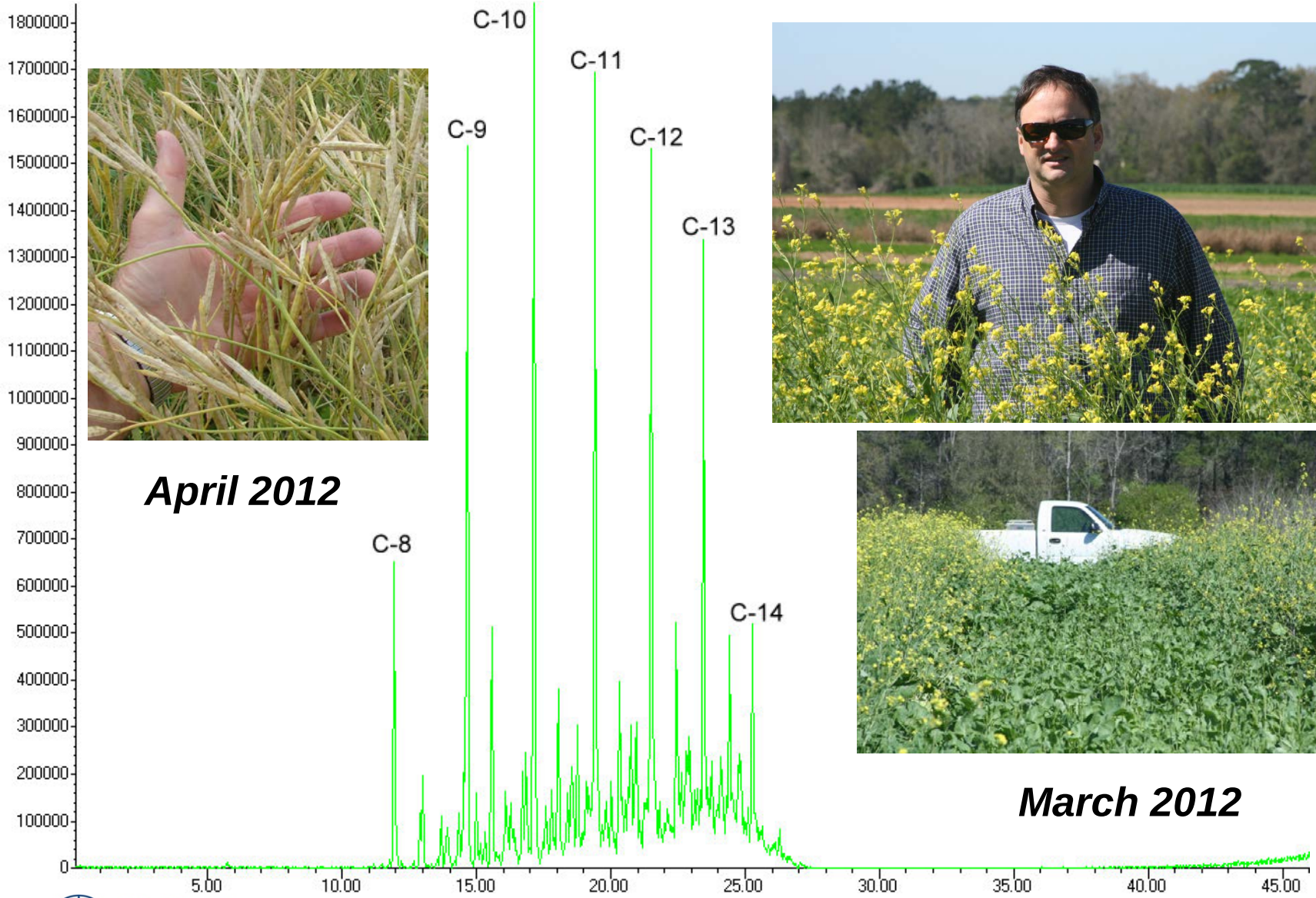
ReadiJet® from Carinata Oil via the ARA CH Process



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ReadiJet® from Carinata via ARA CH Process

Specification Test Results (Provided by AFRL & AFPET)

Specification Test	MIL-DTL-83133H Spec Requirement	ReadiJet™ from Camelina	ReadiJet™ from Carinata	Petroleum JP-8 Reference
Total Acid Number, mg KOH/g	≤0.015	0.011	0.012	0.003
Aromatics, vol %	≤25	24.2	16.8	18.8
Olefins, vol %	≤5	1.3	1.8	0.8
Heat of Combustion (m), MJ/kg	≥42.8	42.9	43.2	43.3
Hydrogen Content, % mass	≥13.4	13.3*	13.8	13.8
Smoke Point, mm	≥19	22	26	22
Thermal Stability @ 260°C:				
Tube Deposit Rating	≤3	1	1	1
Change in Pressure, mm Hg	≤25	0	0	2
Flash point, °C	≥38	48	46	51
Freeze Point, °C	≤-47	-54	-57	-51
Viscosity @ -20°C, cSt	≤8.0	3.9	3.5	4.9
Viscosity @ -40°C, cSt	≤12.0	7.4	6.5	9.9
Density, kg/L @ 15°C	0.775 - 0.840	0.818	0.802	0.804
Lubricity (BOCLE), wear scar mm	≤0.85	0.59	0.57	0.53

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ReadiJet® from Carinata via ARA CH Process

Hydrocarbon Type Analysis – GC x GC Results

	ReadiJet™ from Camelina	ReadiJet™ from Carinata	Petroleum JP-8 Reference
GCxGC (mass %)			
n-Paraffins	24.0	30.3	18.8
iso-Paraffins	5.9	8.2	31.4
Monocycloparaffins	29.8	31.1	20.8
Dicycloparaffins	14.6	10.4	5.7
Alkylbenzenes	16.2	11.8	15.1
Indans and Tetralins	8.0	7.8	6.5
Naphthalene	0.4	0.1	0.1
Naphthalenes	1.0	0.4	1.6
Total	100	100	100

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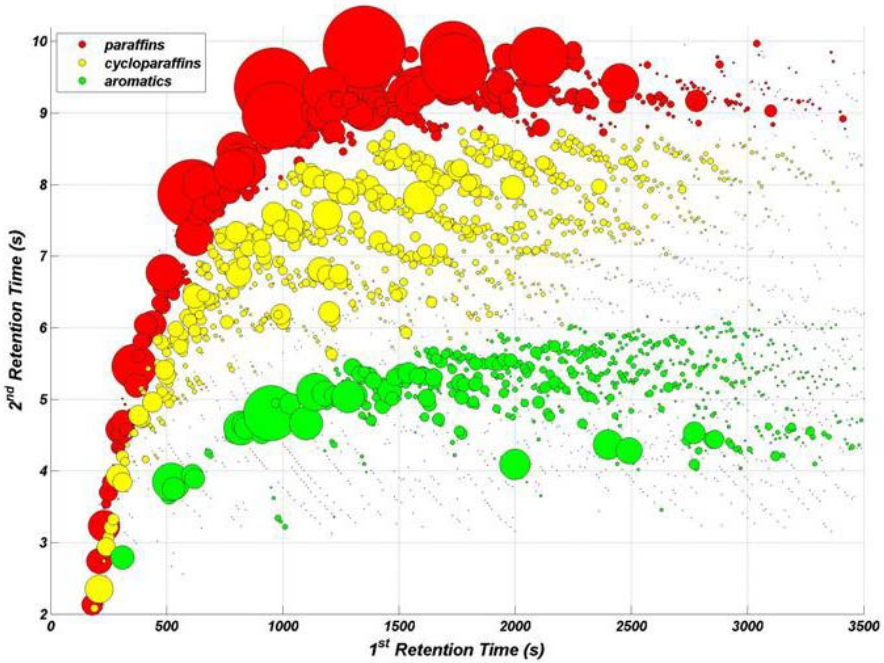
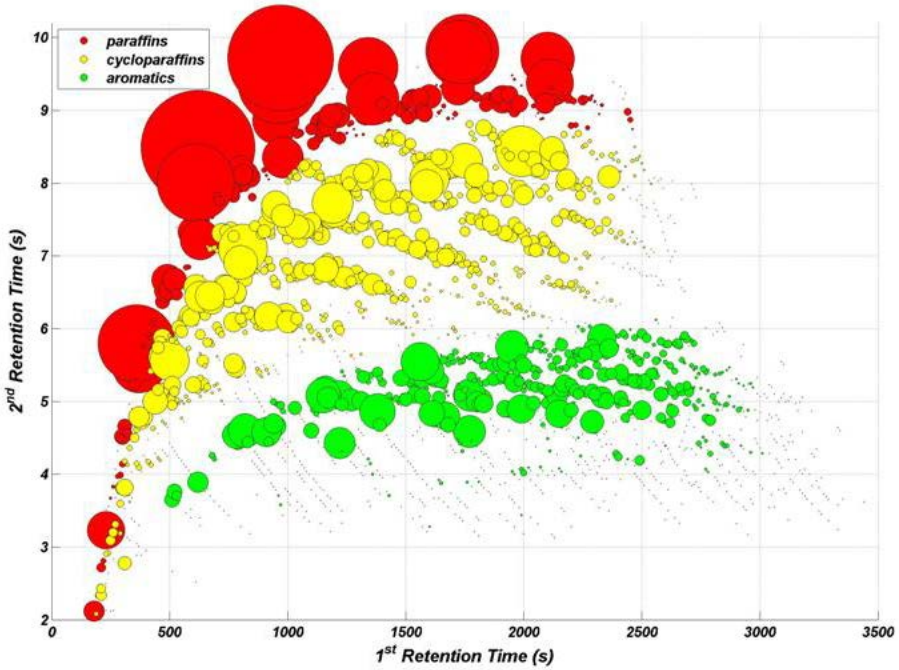
GC x GC Reversed Column, Bubble Chromatograph

Canmet Energy, Natural Resources Canada

Petroleum JP-8



Carinata ReadiJet®



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ReadiJet® from Carinata via ARA CH Process

Metals Analysis by ICP-MS

	Concentration (ppb wt)		
	ReadiJet™ from Camelina	ReadiJet™ from Carinata	Petroleum JP-8 Reference
Aluminum	134	189	306
Calcium	8	7	7
Chromium	<5	<5	<5
Cobalt	<5	<5	<5
Iron	<5	<5	<5
Magnesium	7	5	7
Molybdenum	<5	<5	<5
Nickel	<5	<5	<5
Phosphorus	<500	<500	<500
Potassium	23	28	<5
Selenium	<2	<5	<5
Sodium	8	27	49
Titanium	8	41	<5
Vanadium	28	<5	10
Zinc	<5	<5	6

As, Ba, Be, Cd, Cu, Pb, Mn, Hg, Ag, Sr, Sn < 5 ppb wt

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ReadiJet® from Carinata via ARA CH Process

Volume Swell of Selected O-ring Elastomers Compared to Average Values for JP-8

Material ID	Material	JP-8 - 90% Prediction Interval			ReadiJet™ from Camelina %v/v	ReadiJet™ from Carinata %v/v
		LL %v/v	Mean %v/v	UL %v/v		
N0602e*	Nitrile Rubber	16.38	21.43	26.54	25.69	21.92
N0602	Nitrile Rubber	3.39	6.92	10.52	8.83	7.11
L1120	Fluorosilicone	5.01	5.95	6.92	5.93	6.14
V0747	Fluorocarbon	0.19	0.44	0.69	0.27	0.31

*Plasticer pre-extracted

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Certification Challenges

- ReadiJet® cannot be procured under ASTM D1655 or ASTM D7566
- Meets ASTM D1655 (and JP-8) spec requirements, but.....
  - Not petroleum derived
- Meets ASTM D7566 Annex 2 feed stock and conversion requirements
  - ReadiJet™ is Hydroprocessed Esters and Fatty Acids (HEFA), but…..
  - Does not meet synthetic blending component spec - Tables A2.1 & A2.2:
    - Limit aromatic content to <0.5 mass %
    - Limit cycloparaffin content to <15 mass %
    - Limit density range to 730-770 kg/m^3
- ReadiJet® Requires a New Annex – Relative to Annex 2:
  - No change to Table 1 requirements
  - Increase limit on aromatic content to 25 vol% - same as petroleum specs
  - Eliminate limit on cycloparaffins – same as petroleum specs
  - Change density range to 775-840 kg/m^3 – same as petroleum specs
- New ASTM Task Force established – "HEFA SKA"
- Additional tests are on-going

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First Flight Test conducted on 100% "Drop-in" ReadiJet®

- **National Research Council Canada**
  - 29 October 2012
  - Falcon 20 Aircraft
  - Ground tests on GE 700 2D2 Turbofan
  - Unblended fuel that meets D1655 spec
- **Operation on ReadiJet® at 30,000 ft**
  - 20 minutes of operations
  - Variable thrust settings
  - Both engines running at cruise
  - In-flight engine shutdown and relight
  - In-flight emissions measurements
- **Performed better than Jet A**
  - Specific fuel consumption was lower
  - Reduction in black carbon, oxides of nitrogen and aerosol emissions

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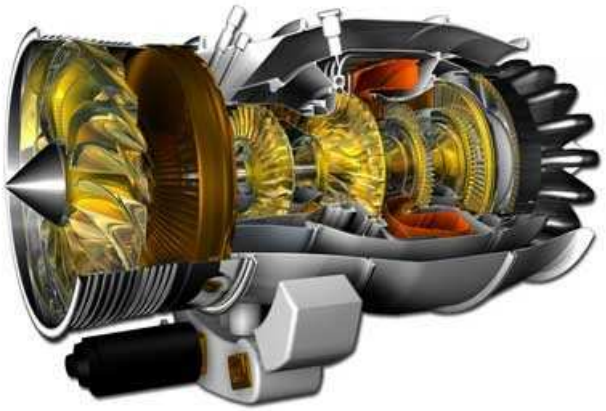
Testing Under the FAA CLEEN program

- **Pratt & Whitney – Feb 2013**
  - **PW615 Turbofan engine test**
  - **Tests to be performed by P&W Canada**
  - **400 gallons of ReadiJet® hydrotreated at AFRL**
  - **Fuel derived from Canola oil feed stock**
  - **Follow-on endurance test option**



- **Rolls-Royce – testing in progress**
  - **Thermal stability (JFTOT and HiRets)**
  - **Elastocon seal performance test**
  - **Altitude re-light/combustion/operability rig tests**
  - **Auxiliary Power Unit tests**
  - **Same fuel as NRC flight test**
  - **Follow-on larger engine performance test option**

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Production of Fuels for Certification Testing

- CH Pilot system – operational since 2010
  - 120 gal/day treatment capacity
  - Short residence time (<5 minutes)
  - Thousands of gallons of crude produced
- Evaluated many different feed stocks
  - Algal oil, Camelina, Canola, Carinata, Castor, Corn, Jatropha, Peanut, Shae Butter, Soybean, Tall oil fatty acids, Tung, WVO
- Conducted two hydrotreating campaigns
  - Chevron – at pilot plant in Richmond CA
  - Air Force Research Lab – WPAFB, Ohio
- Engineering 100 bbl/day pilot
  - Produce certification quantities of ReadiJet®
- Teamed with Chevron Lummus Global
  - Preformed preliminary engineering
  - 3500 and 5000 BPD commercial facilities

Summary

- **CH technology offers unique process advantages**
  - **Water is the primary conversion medium**
  - **Optimal conversion chemistry in a single step operation**
  - **Very short residence time**
  - **Adaptable to many renewable feed stocks**
- **ReadiJet® exhibits chemical, physical, and performance characteristics nearly identical to petroleum-derived jet in testing to date**
  - **True "drop-in" fuels containing aromatics and cycloparaffins**
  - **High density – same as petroleum**
  - **Excellent low-temperature and thermal/storage stability properties**
- **Commercial advantages relative to hydrocracking & isomerization**
  - **Smaller footprint, fewer unit operations, reduced hydrogen and catalyst consumption**
- **Certification challenges still exist**
  - **Test requirements, blending requirements, specification**

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