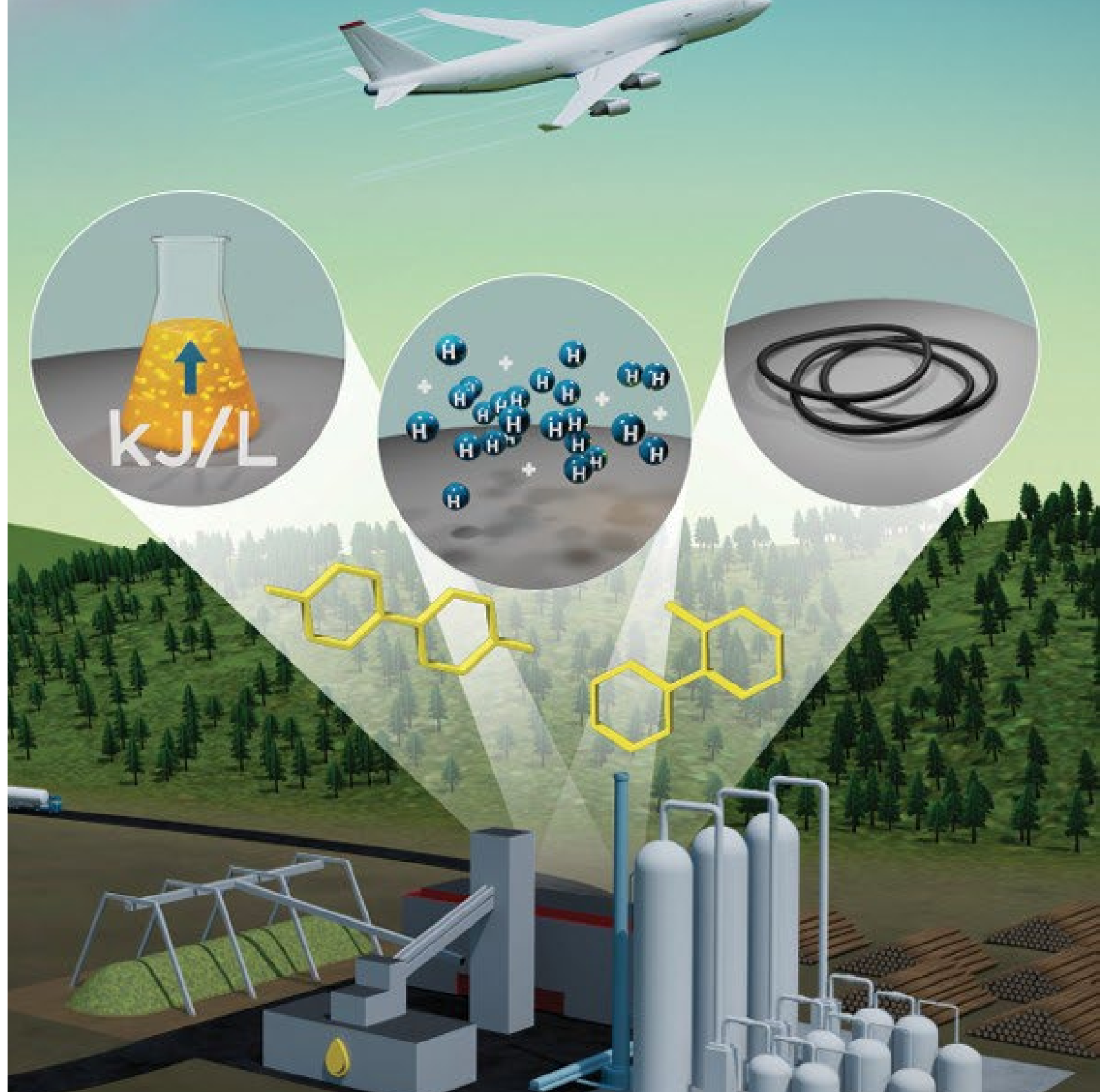


Upgrading Bio-Derived Aromatics via Hydroalkylation to Bicycloalkane-Rich Jet Blendstocks

Nickolas Riedel, Mike Hubbard, Johnny Saavedra Lopez, Bhanupriya Boruah, Vanessa Lebarbier Dagle, and Robert Dagle*

Pacific Northwest National Laboratory

TCBiomass 2026
August 27, 2026

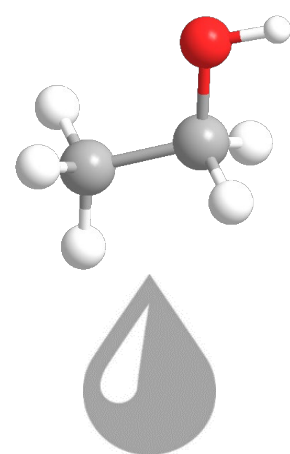


Catalytic conversion of biomass-derived alcohols to isoparaffinic jet fuels:

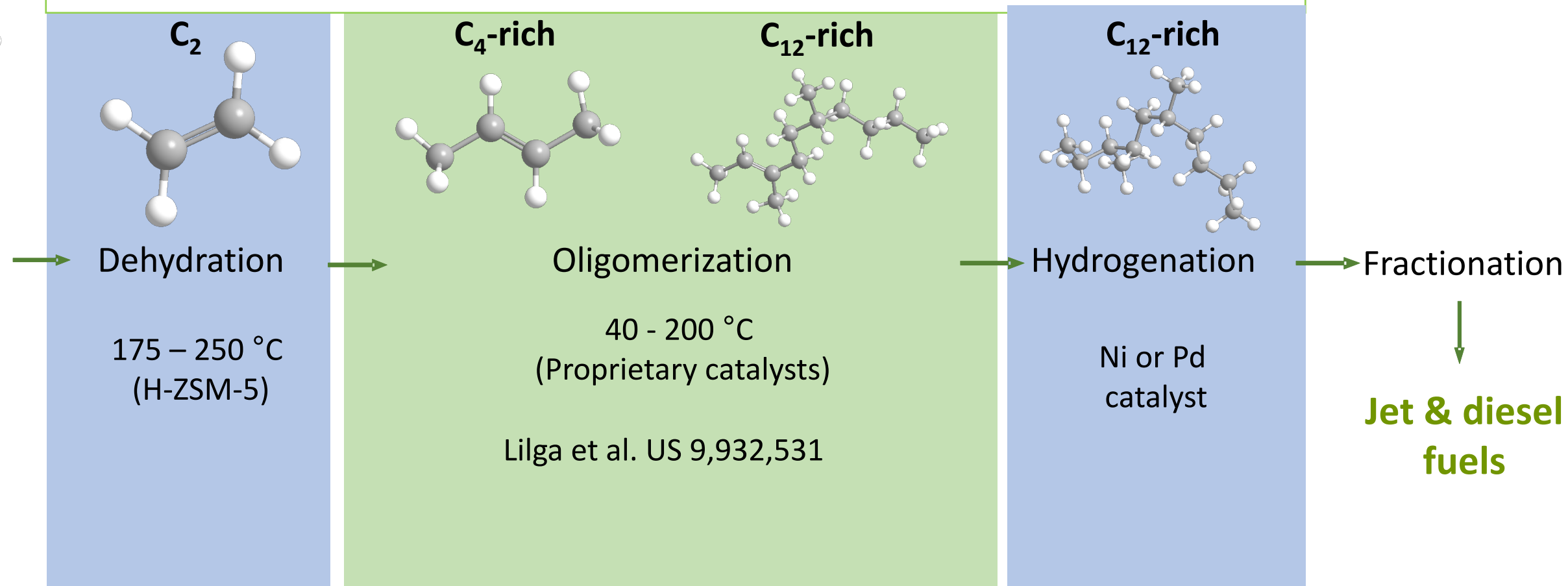
PNNL's ATJ technology enabling commercial deployment

Alcohol to jet (ATJ) ASTM D7566 Annex A5 for 50% blend

Alcohols → 1. Dehydration 2. Oligomerization 3. Hydrogenation 4. Fractionation → Isoparaffins

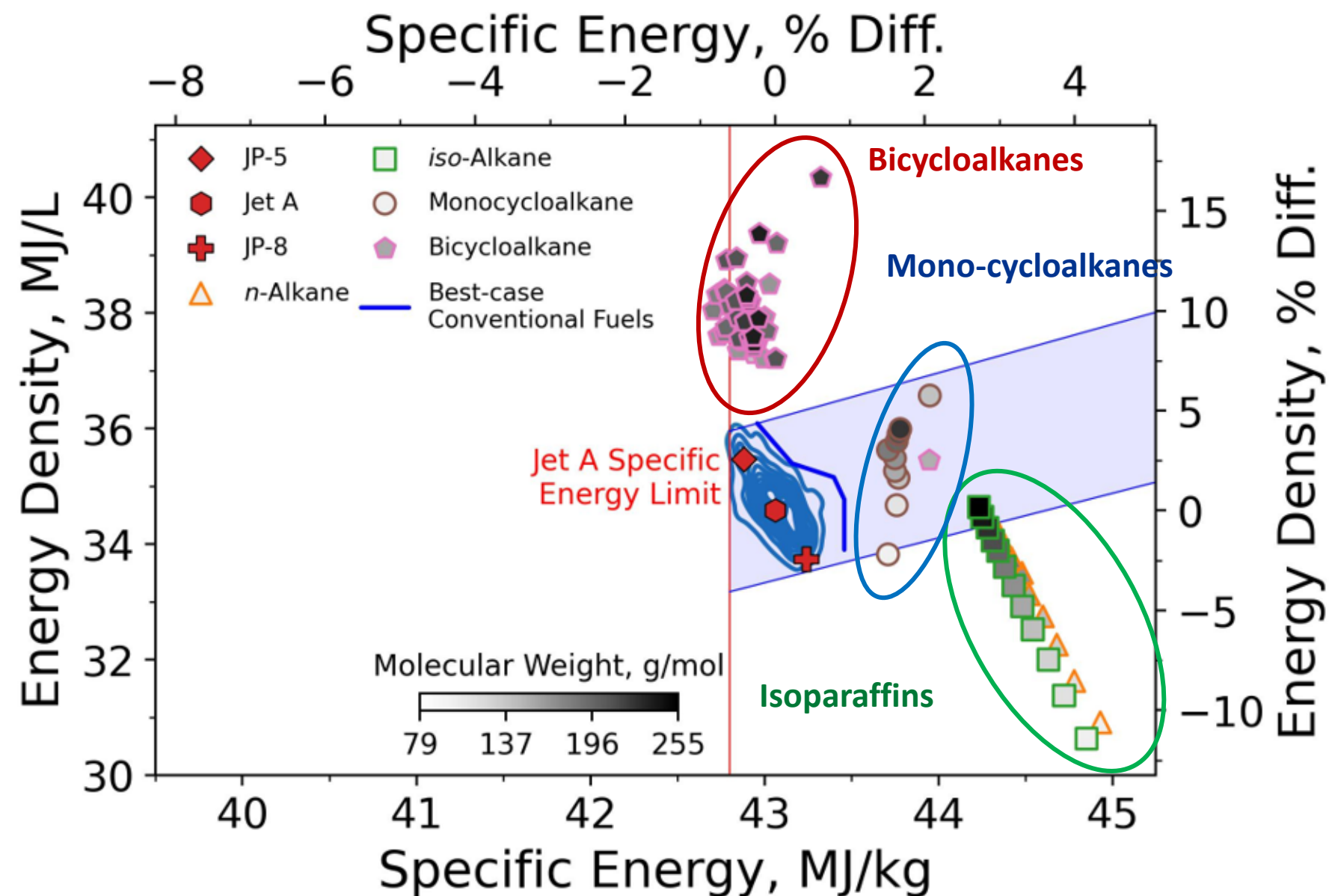


Ethanol



Synthetic Aviation Fuels (SAF) can enable improved performance over conventional jet fuel

- **Isoparaaffinic-rich** jet-range hydrocarbons meet ASTM jet blendstock standards
- **Monocycloalkanes** provides higher energy density, on par with Jet A
- **Bicycloalkanes** can offer superior energy density to Jet A



Producing Mono- and Bicycloalkane Jet Blendstocks from Ethanol

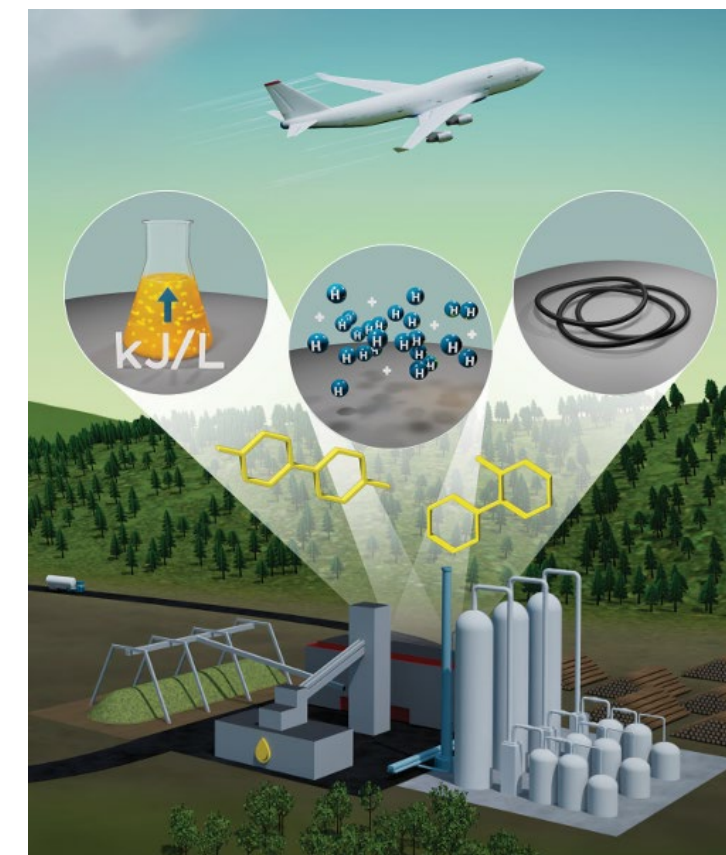
Objective: Evaluate two catalytic routes for **cycloalkane-rich jet blendstocks** from **ethanol-derived intermediates** and understand resulting fuel properties.

Approach:

- Convert (ethanol-derived) butene to BTX aromatics
- Upgrade aromatics via **alkylation** or **hydroalkylation**
- Hydrotreat and distill products and assess jet fuel properties

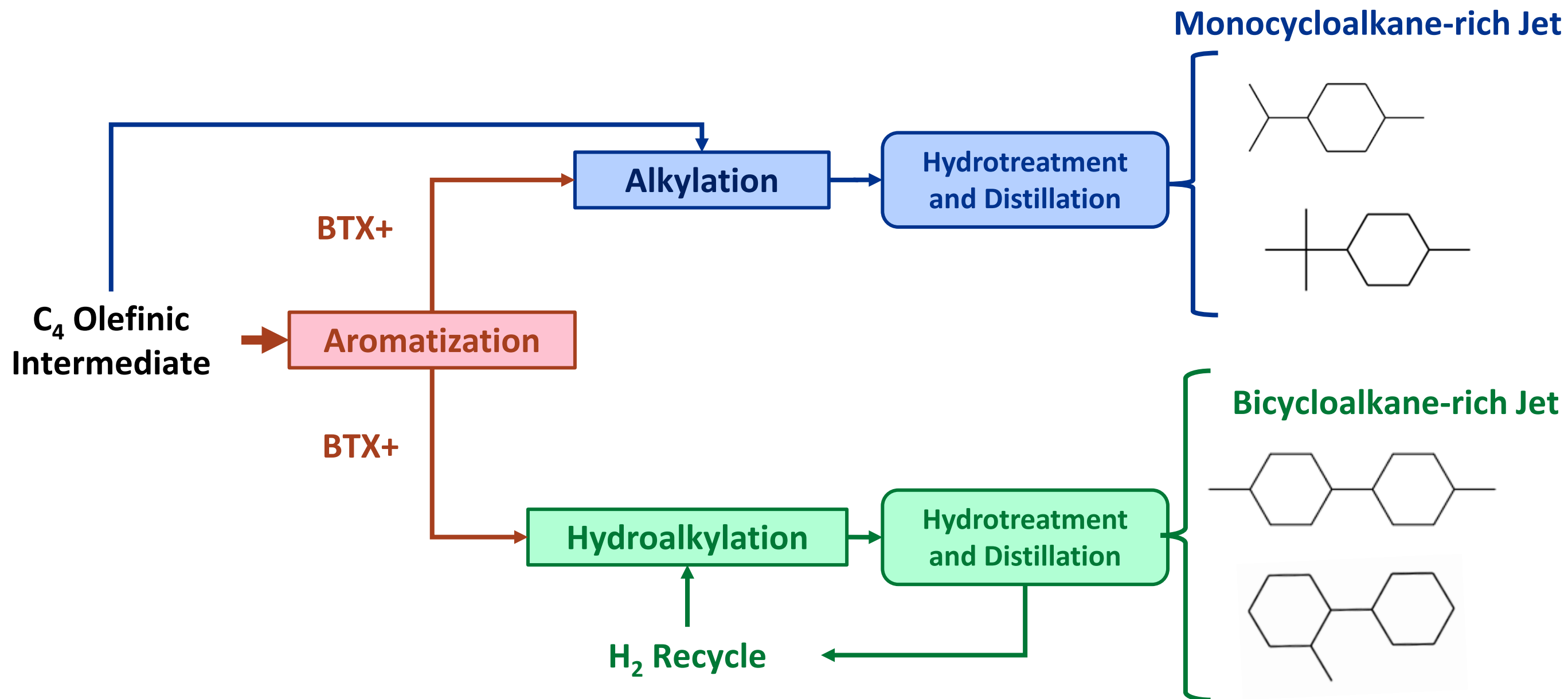
Key Results:

- Both fuels meet ASTM D7566 standard as jet blendstock
- Bicycloalkane-rich blendstock:
 - ✓ **+5% energy density** vs. Jet A
 - ✓ **>10% O-ring swell** with <3% aromatics (favorable seal swelling)
 - ✓ **Lower H₂ utilization** than conventional ATJ

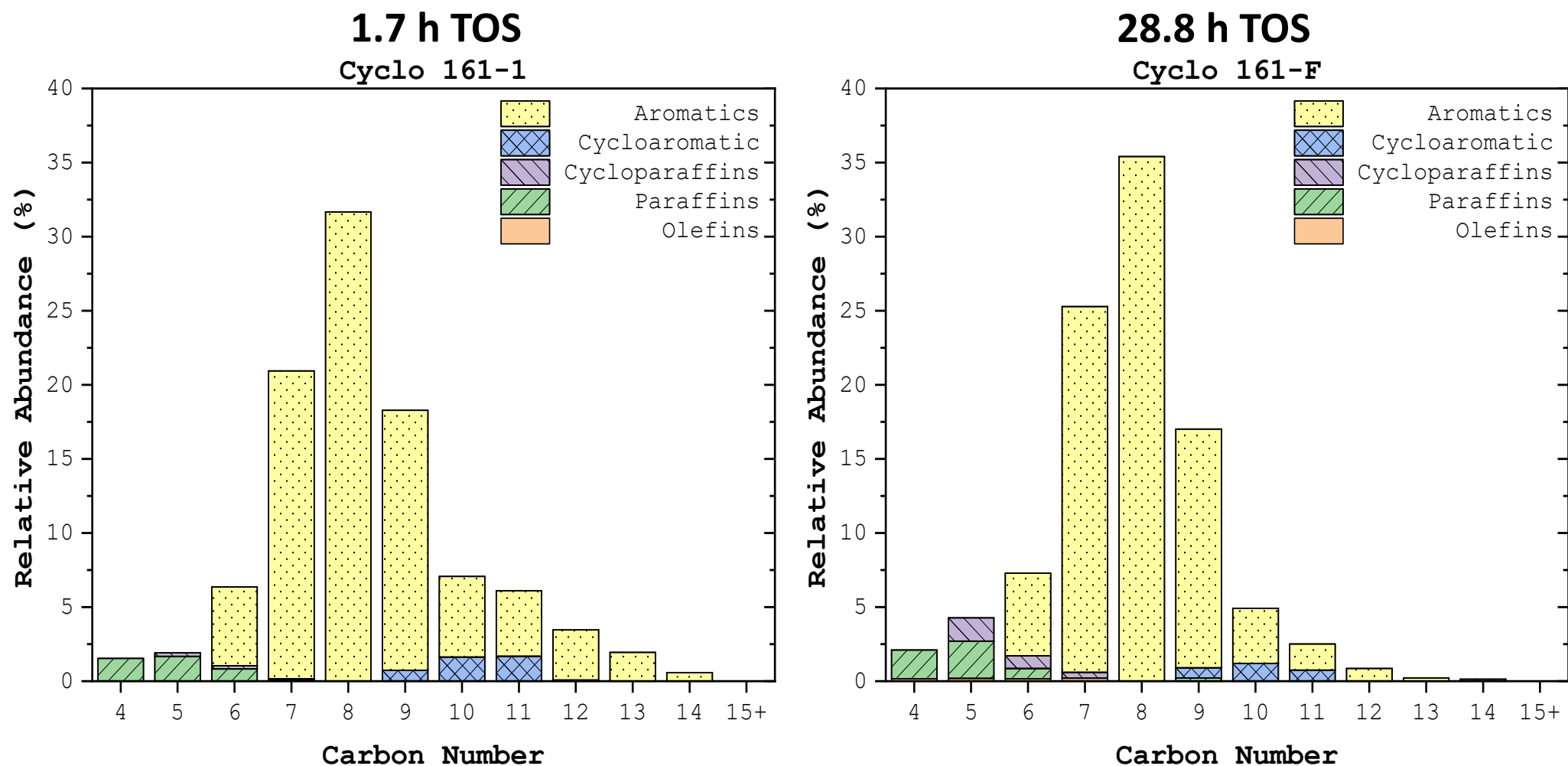


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Alkylation and hydroalkylation pathways to energy-dense cycloalkane jet blendstocks



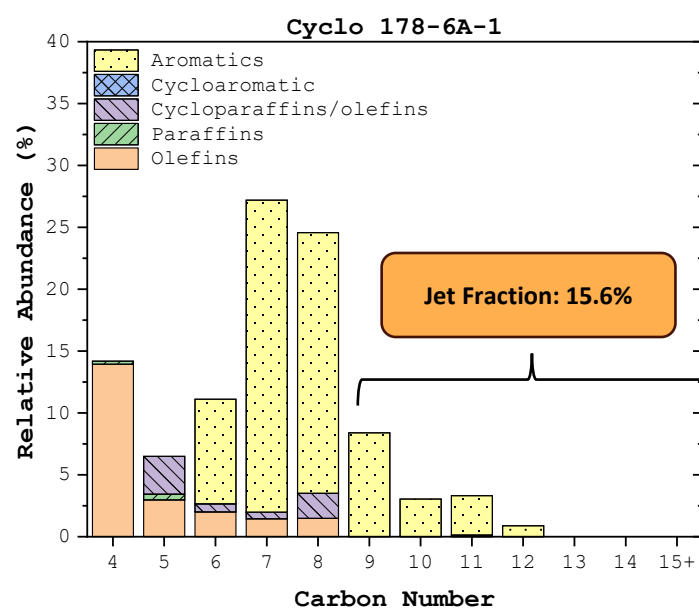
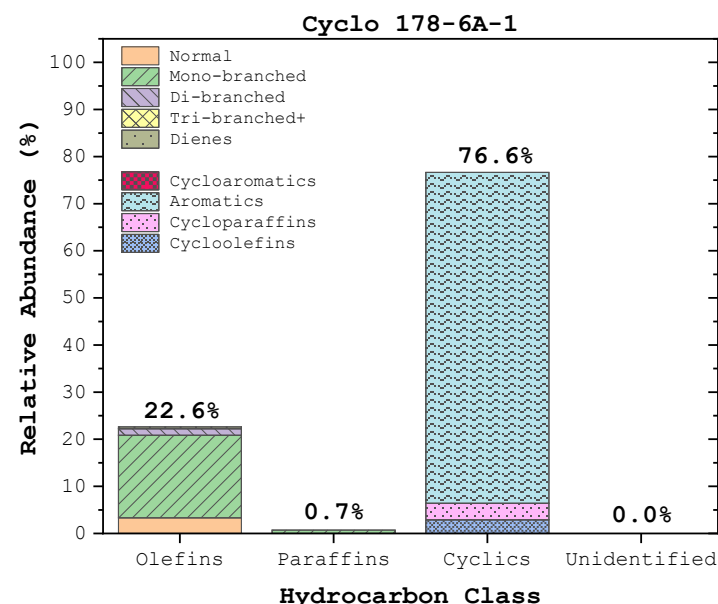
Aromatization of 1-butene using olefin-aromatization catalyst design principles



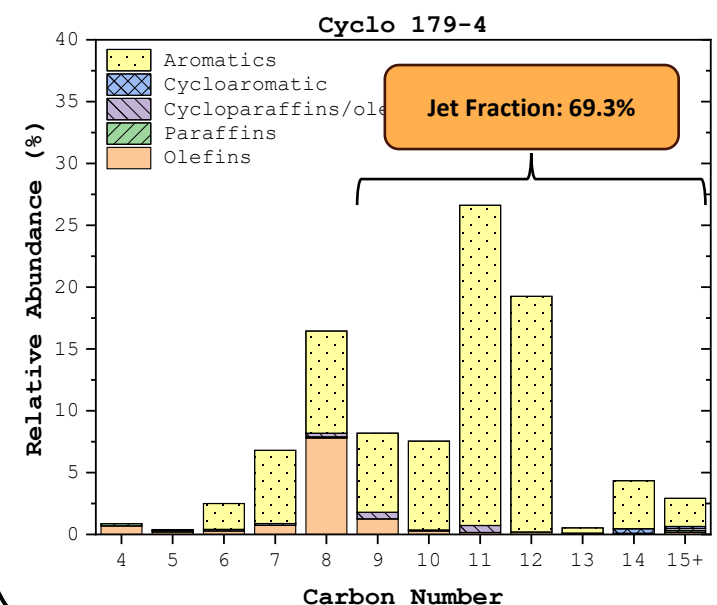
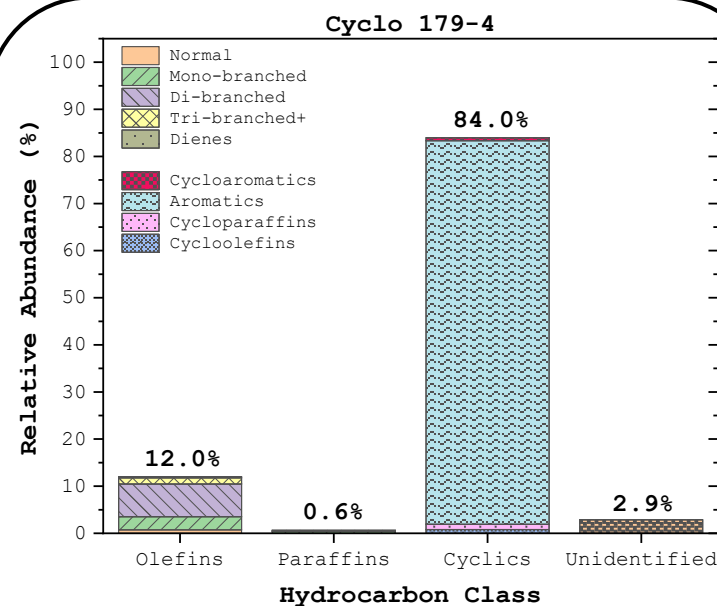
Hydrothermally-treated 1.5 wt.% Zn/ZSM-5 at 515 °C, 75 psig, WHSV = 2.8 h⁻¹

Alkylation of 1-butene to the mixed aromatics feed increases jet content by 4-fold

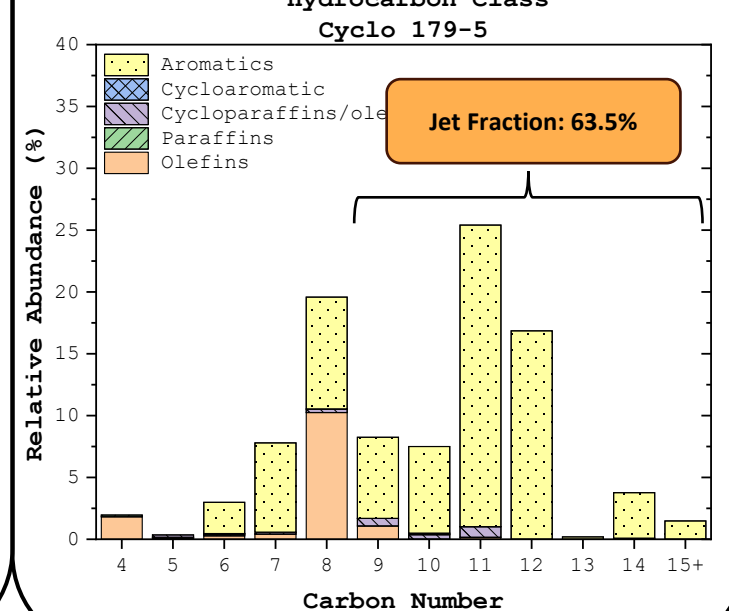
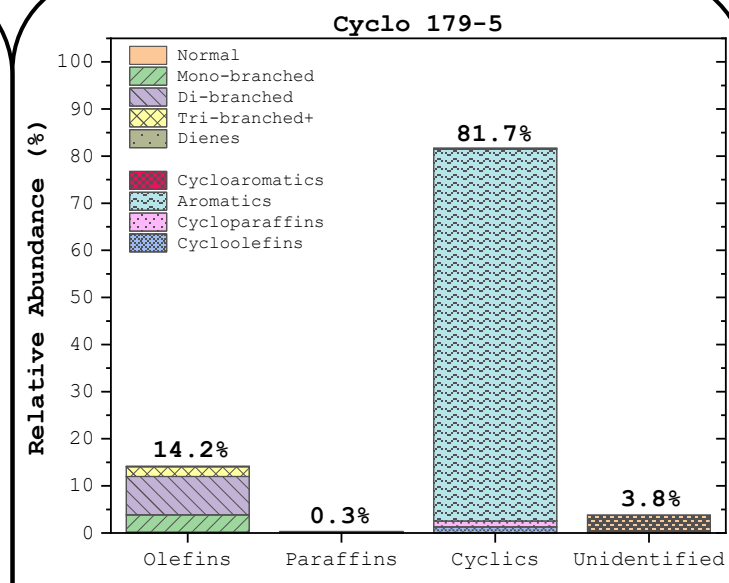
Feed



5.7 h TOS



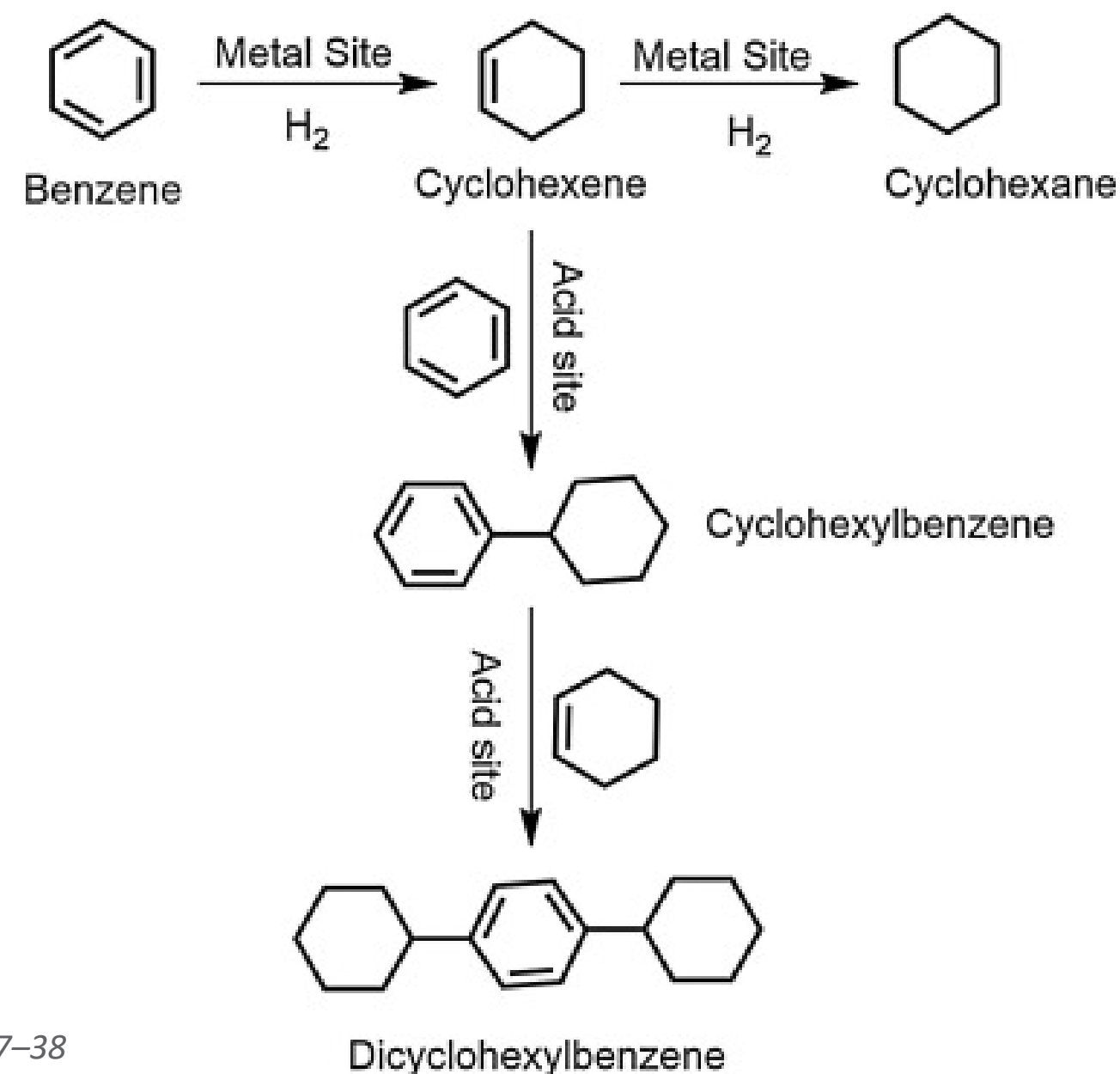
17.5 h TOS



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Hydroalkylation: Repurposing a chemical production technology for fuels

- Hydroalkylation was developed as an alternative route to **cyclohexanone** and **phenol** and/or **biphenyl esters**
- Hydroalkylation of **aromatics** to **cycloaromatics** requires:
 - ✓ Balanced acid (BEA) and metal (Pd) sites
 - ✓ Close proximity of the two sites
 - ✓ Micro/Mesoporous support (BEA)

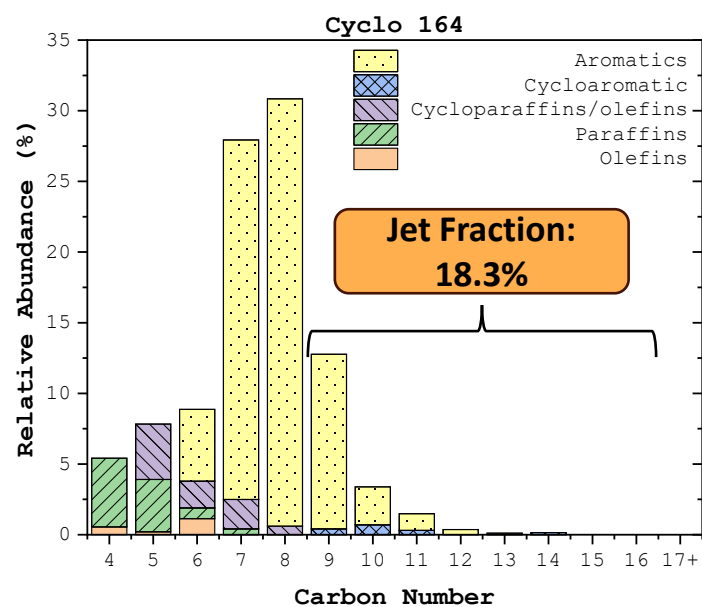
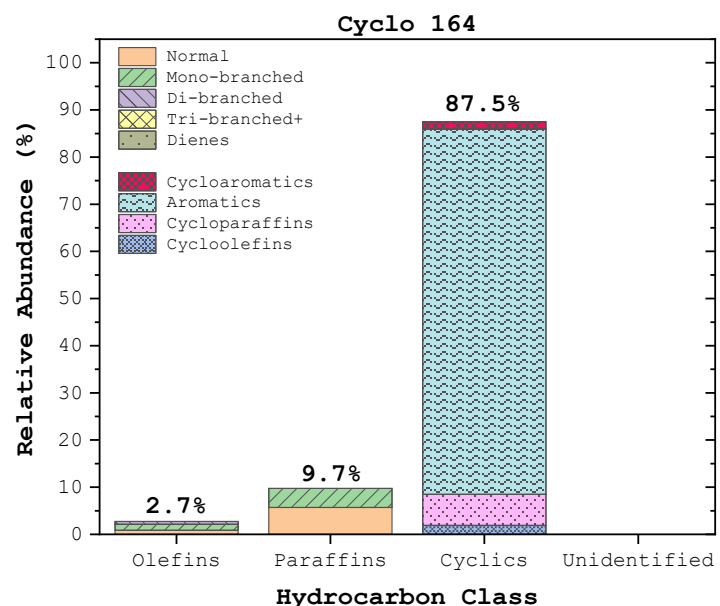


Mol Cat 442 (2017) 27–38

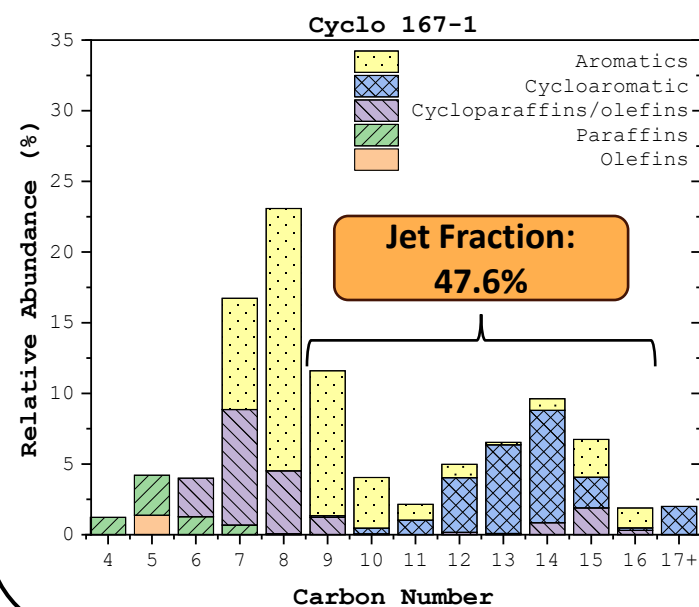
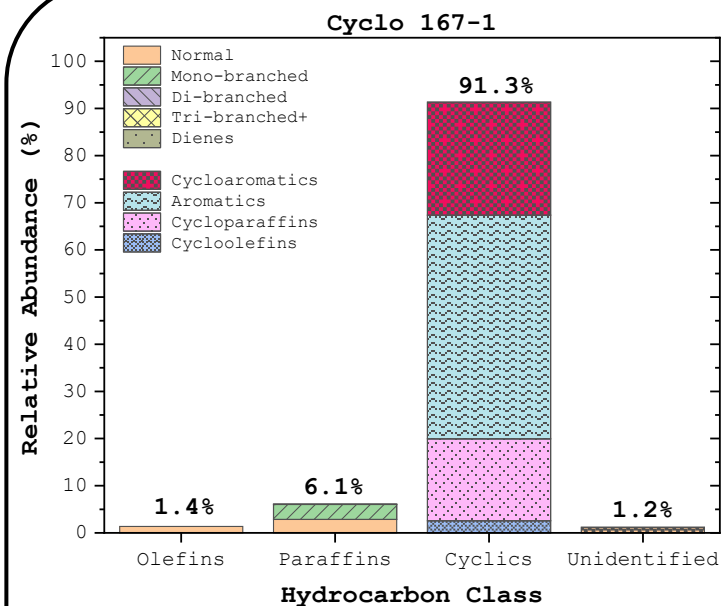
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Hydroalkylation of a mixed aromatic feed increases jet content by ~2.5 fold

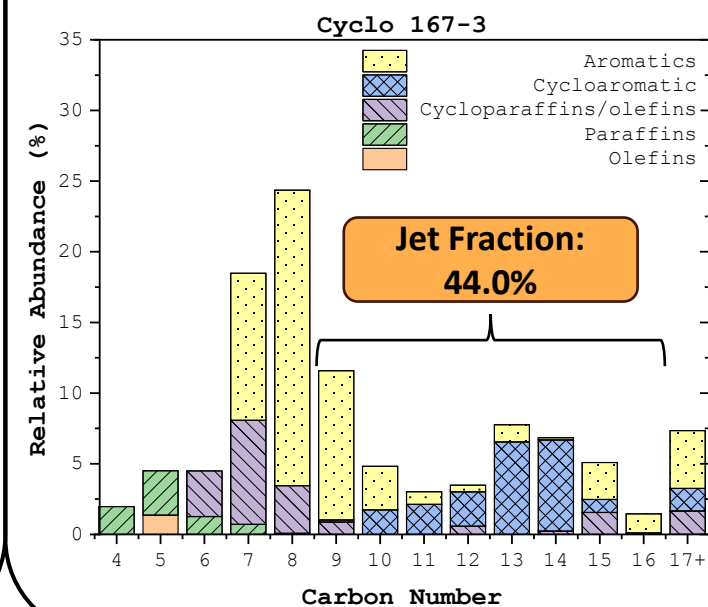
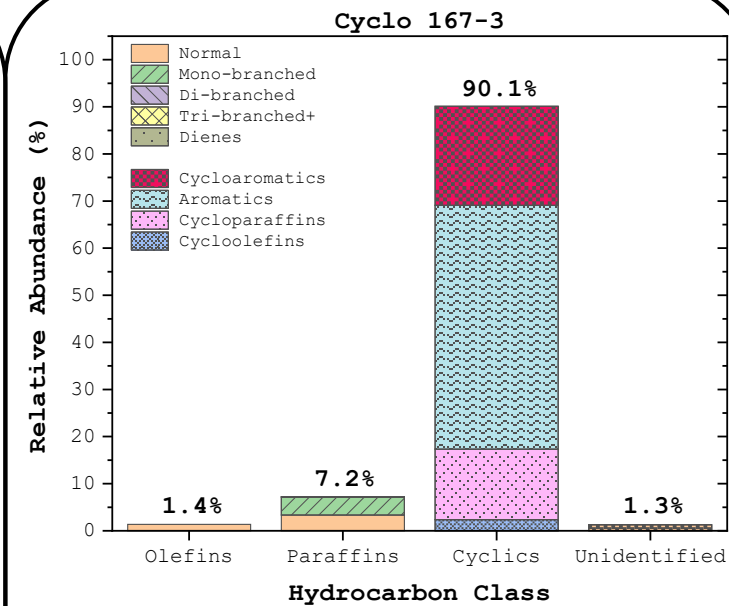
Aromatic Feed



2 h TOS

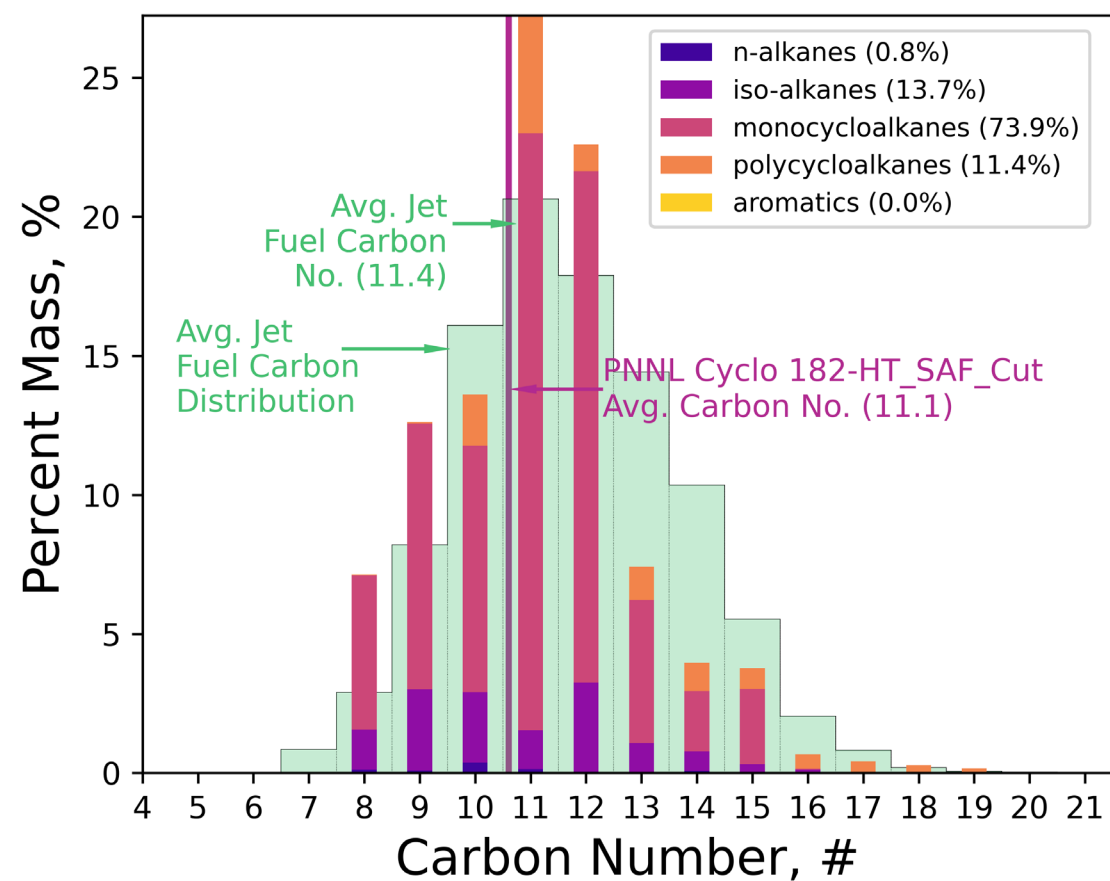


6 h TOS

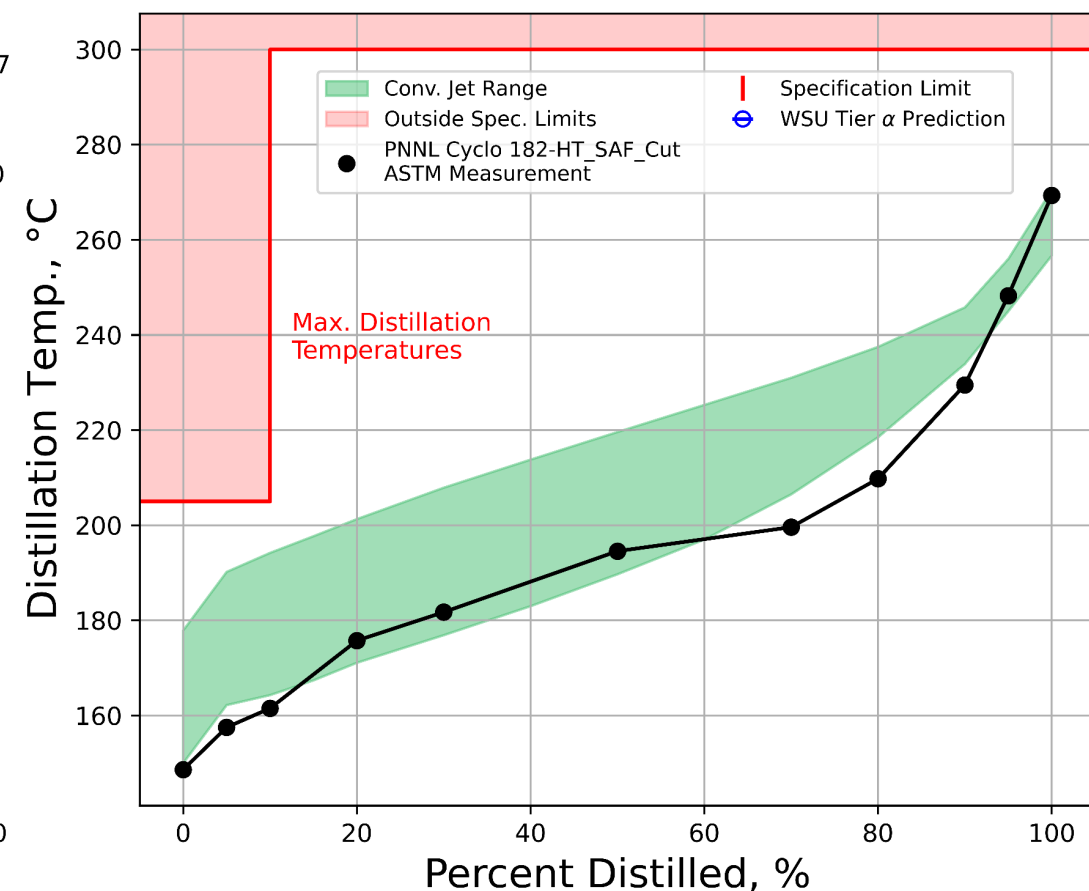
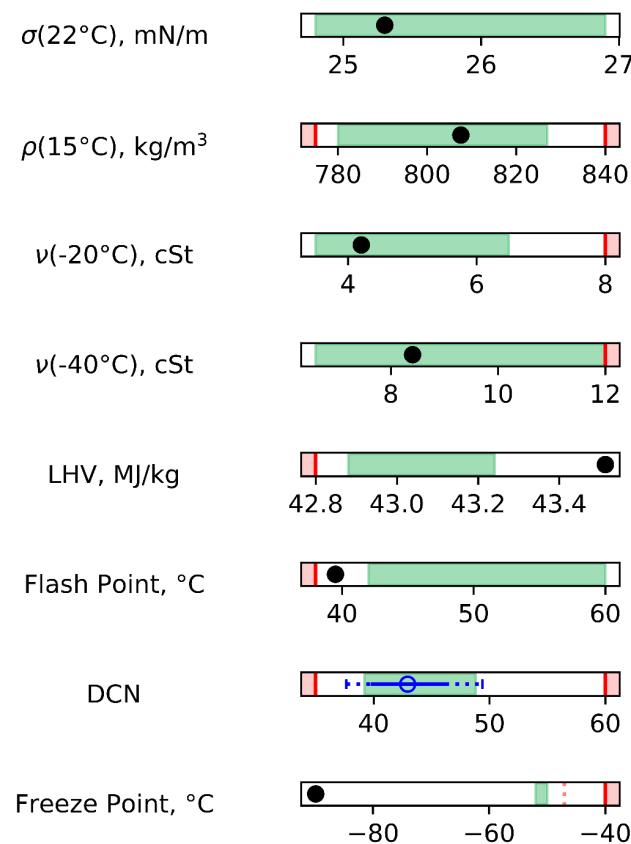


0.15 wt.% Pd/BEA (SiO₂/Al₂O₃ = 25); 140 °C; 270 psig; H₂/aromatic = 1/1; WHSV = 2 h⁻¹

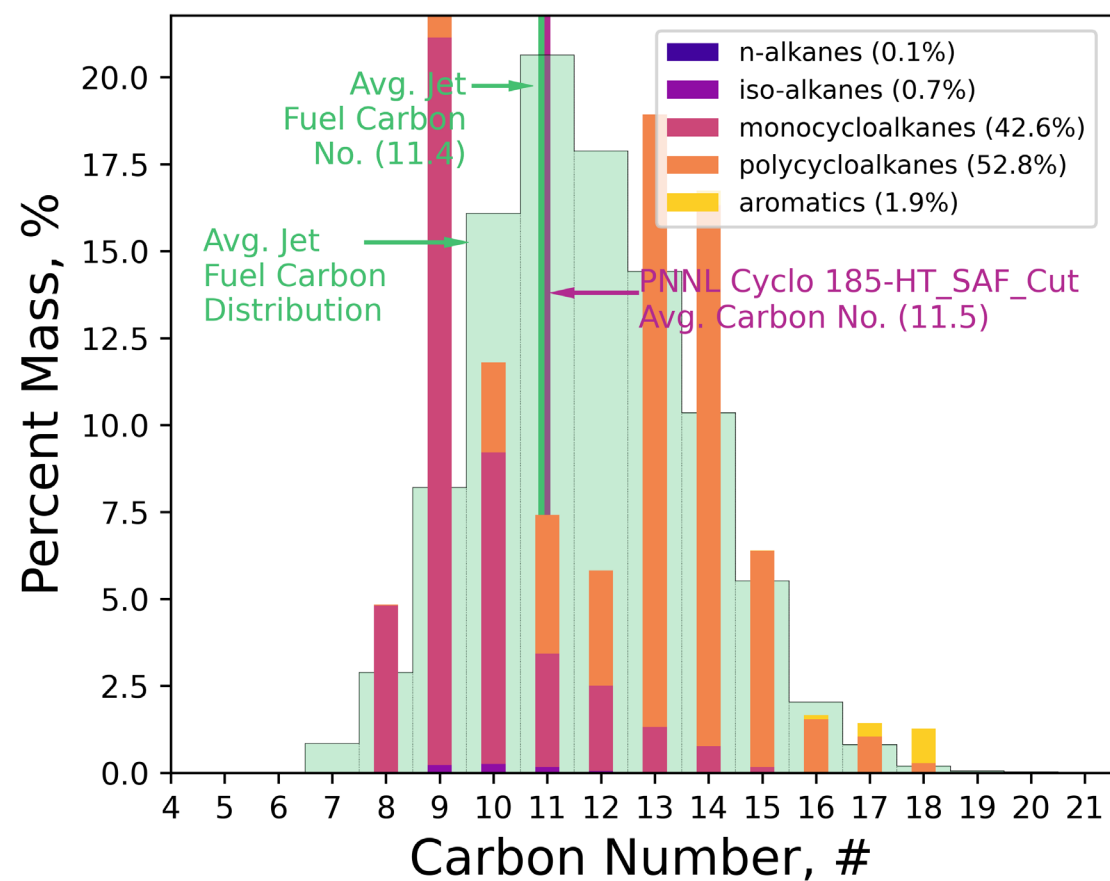
Monocycloalkane rich jet blendstock successfully met all ASTM D7566 specifications



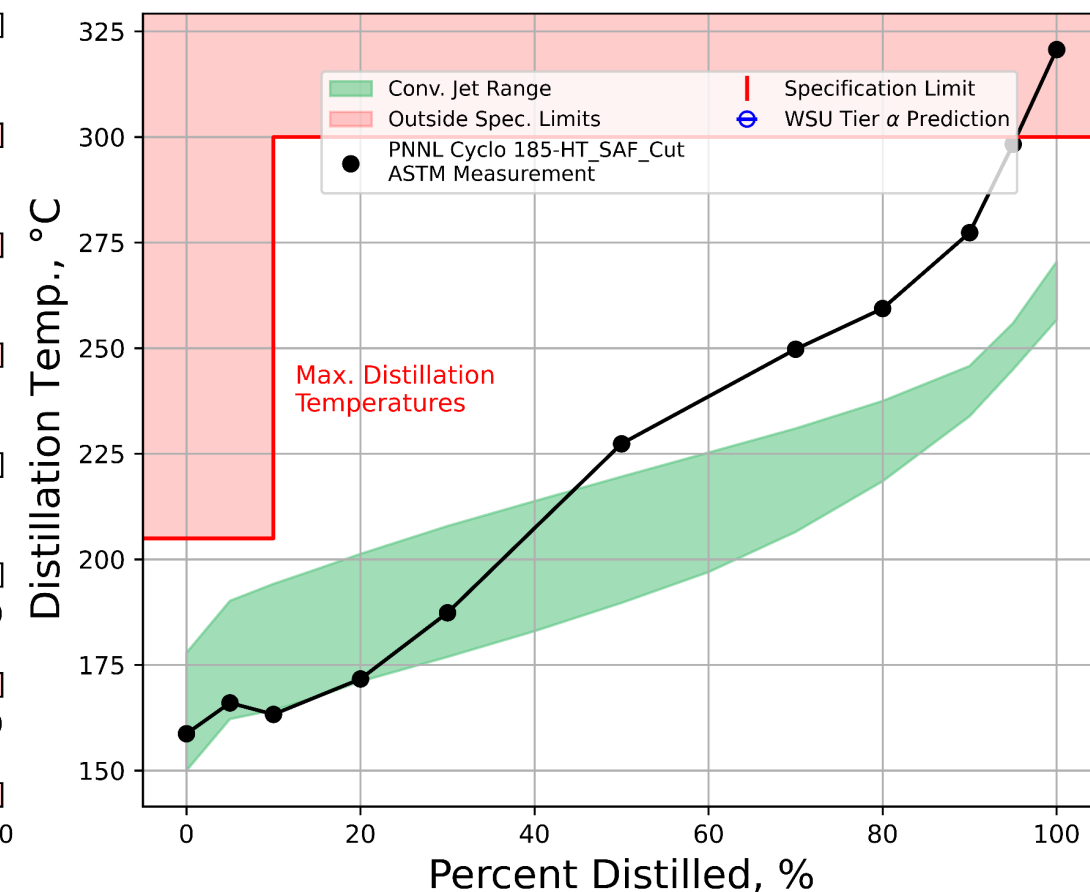
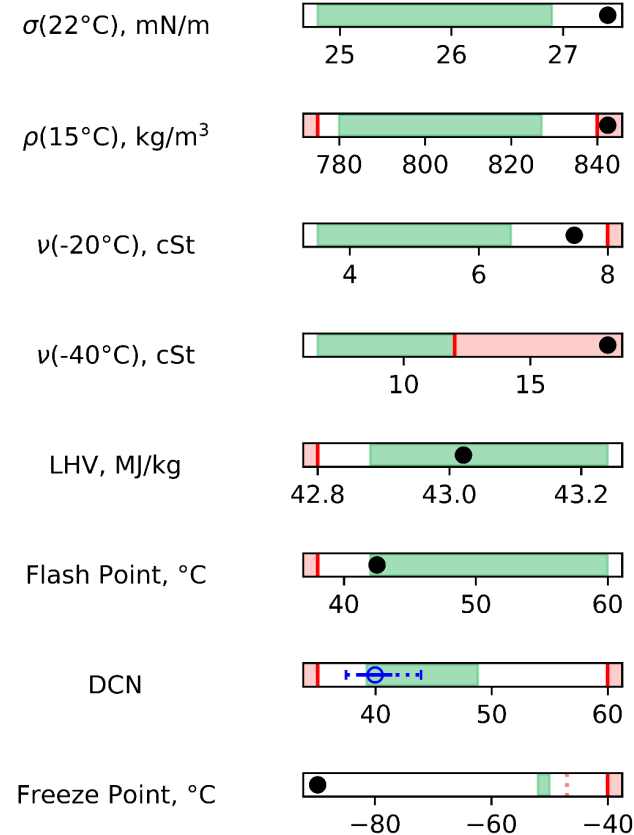
Hydrotreated and Distilled



Bicycloalkane rich jet blendstock also successfully met all ASTM D7566 specifications

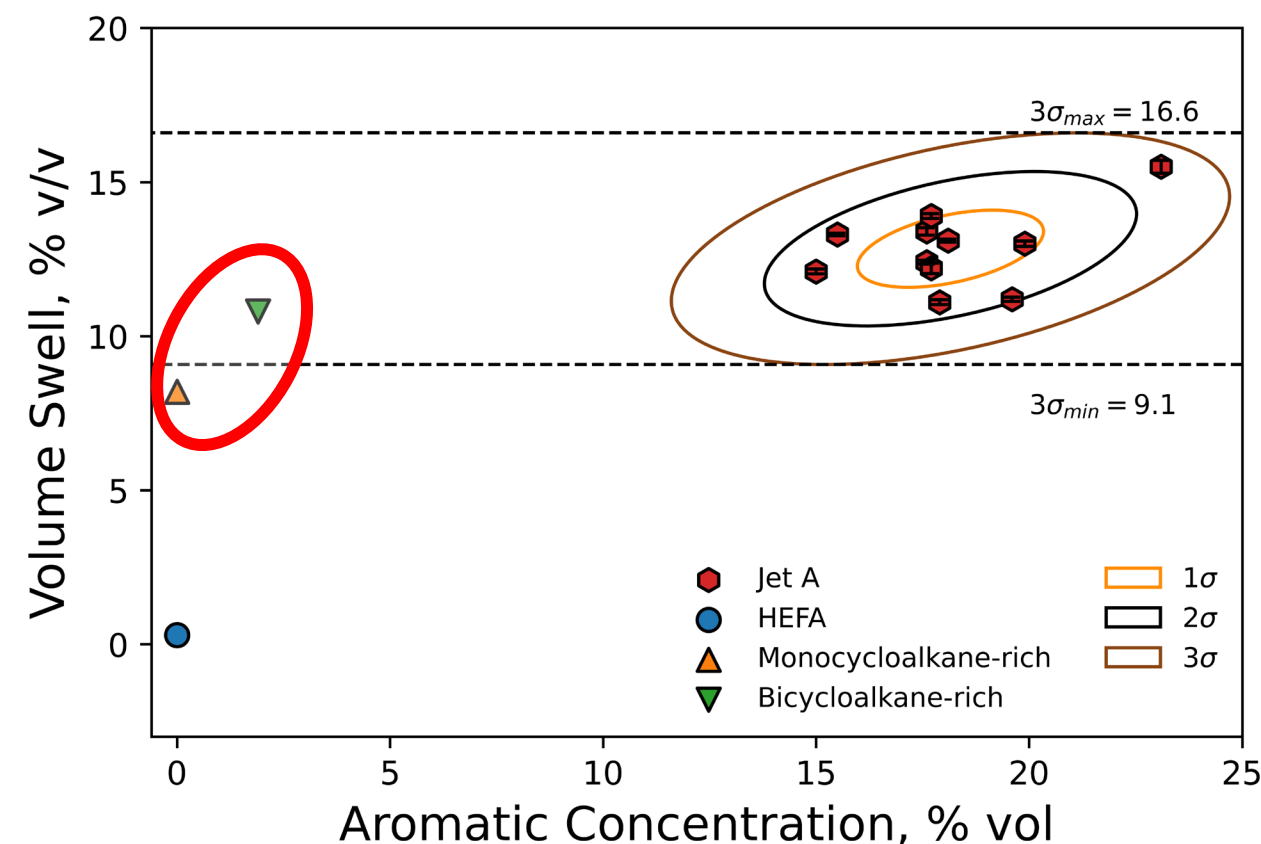


Hydrotreated and Distilled



Bicycloalkane-Rich Blendstock: +5% Energy Density & Favorable O-Ring Swell

Blendstock	Specific Energy (MJ/kg)	Energy Density (MJ/L)	Δ Energy Density vs. Jet A (%)
Jet A (reference)	43.06	34.58	0.0
Iso-alkanes	43.90	33.50	-3.1
Mono-cycloalkane-rich	43.51	35.11	+1.5
Bicycloalkane-rich	43.02	36.24	+4.8



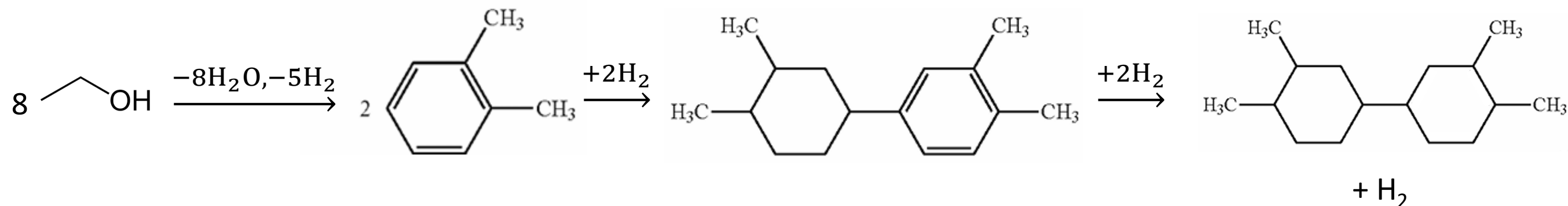
- 5% increase in energy density over Jet A
- At < 3% aromatic content, both products exhibited favorable volume swell behavior

Ethanol aromatization and hydroalkylation: key targets for improving carbon efficiency

Catalytic Step	Conversion (%)	Catalyst	Conditions	Carbon Efficiency (%)
1-Butene Aromatization	97	Hydrothermally Treated 1.5% Zn/ZSM-5	T = 515 °C P = 75 psig WHSV = 2.8 h ⁻¹	40
Conventional Alkylation with 1-Butene	~100	Solid Phosphoric Acid	T = 220 °C P = 550 psig WHSV _{1-butene} = 0.5 h ⁻¹ WHSV _{Aromatics} = 1 h ⁻¹	92
Hydroalkylation	48	0.15% Pd/BEA	T = 140 °C P = 270 psig H ₂ /Aromatic Ratio = 1/1 WHSV = 2 h ⁻¹	76
Hydrotreatment	100 ^e	Commercial Ni catalyst	T = 180 °C P = 700 psig WHSV _{feed} = 1 h ⁻¹	~100

Favorable H₂ utilization making bicycloalkanes

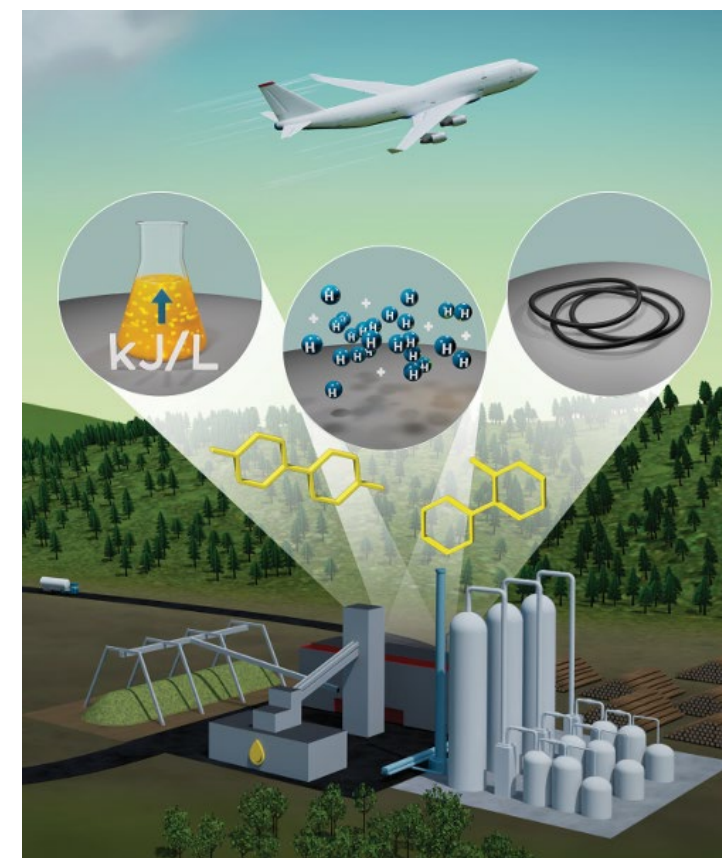
Target hydrocarbon type	Idealized net reaction	Net H ₂ balance per fuel mole (mol)
Linear/branched alkanes (C _n H _{2n+2})	$(n/2)\text{C}_2\text{H}_5\text{OH} + \text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + (n/2)\text{H}_2\text{O}$	+1 (H ₂ required)
Monocycloalkanes (C _n H _{2n})	$(n/2)\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_n\text{H}_{2n} + (n/2)\text{H}_2\text{O}$	0 (no H ₂ required or produced)
Bicycloalkanes (fused or non-fused, C _n H _{2n-2})	$(n/2)\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_n\text{H}_{2n-2} + (n/2)\text{H}_2\text{O} + \text{H}_2$	-1 (H ₂ produced)



- Targeting **bicycloalkanes** derived from ethanol can nominally lead to a **net production of H₂** rather than consumption

Summary

- 1-Butene used as a model olefin to generate BTX+ aromatics over hydrothermally treated Zn/ZSM-5.
- Aromatics upgraded to:
 - **Monocycloalkane-rich jet-range hydrocarbons** via SPA-catalyzed alkylation
 - **Bicycloalkane-rich jet-range hydrocarbons** via Pd/Beta-catalyzed hydroalkylation
- Both upgraded streams hydrogenated over commercial Ni catalyst to produce cycloalkane-rich jet blendstocks.
- **Patent pending:** Bicycloalkane-rich blendstock offers **lower theoretical H₂ demand**, demonstrated **~5% higher energy density** vs Jet A, and **favorable O-ring swell** (<3% aromatics).

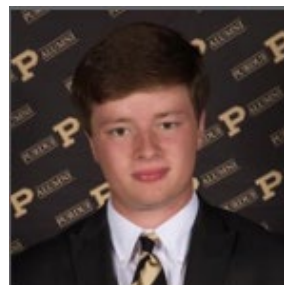


Green Chem., 2026, 28, 1935

Thank you!



DOE-AFFO Technology Managers:
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Nick Riedel

Catalyst Testing/
Development



Johnny
Saavedra Lopez

Materials and
Catalysis



Alia Cooper

Hydrotreatment/
Distillation



Michael
Thorson

Chemical
Processing



Rob Dagle

Co-PI
(Catalysis)



LanzaTech



Ralph
Gillespie

Co-PI



Joshua Heyne

Jet Blend Properties

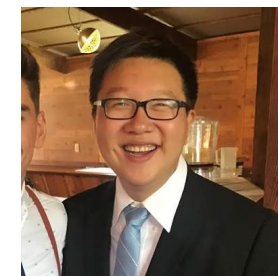


Zhibin Yang

Jet Bend Properties



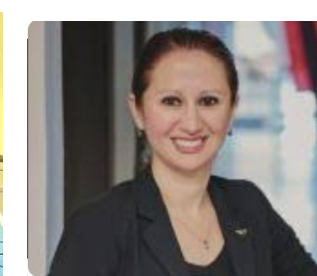
Louis Edwards
Caceres-Martinez



Wan Tang
Jeff Zhang



Hilkka I.
Kenttämää



Gozdem
Kilaz

Co-PI

Liquid Product Characterization



PNNL is operated by Battelle for the U.S. Department of Energy

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ENERGY

Energy Efficiency &
Renewable Energy

BIOENERGY TECHNOLOGIES OFFICE

Thank you

Questions?

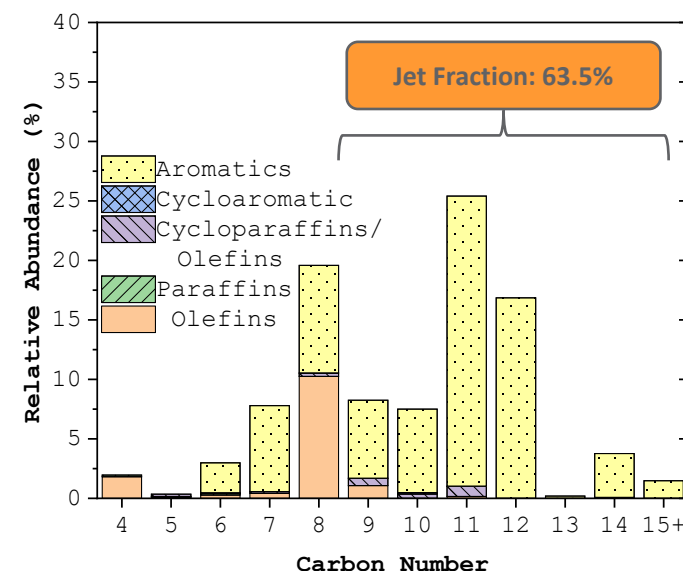
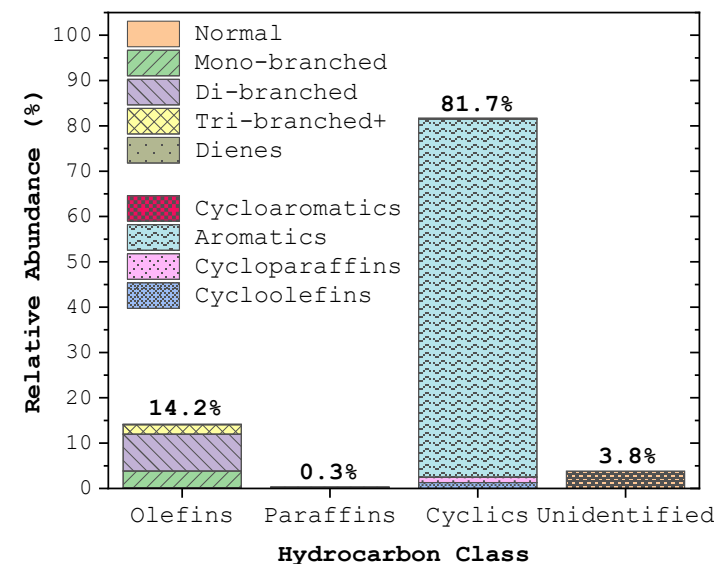
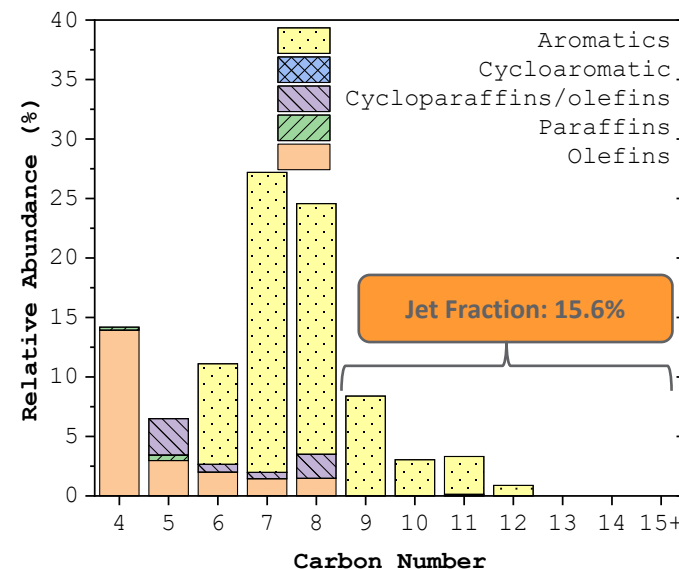
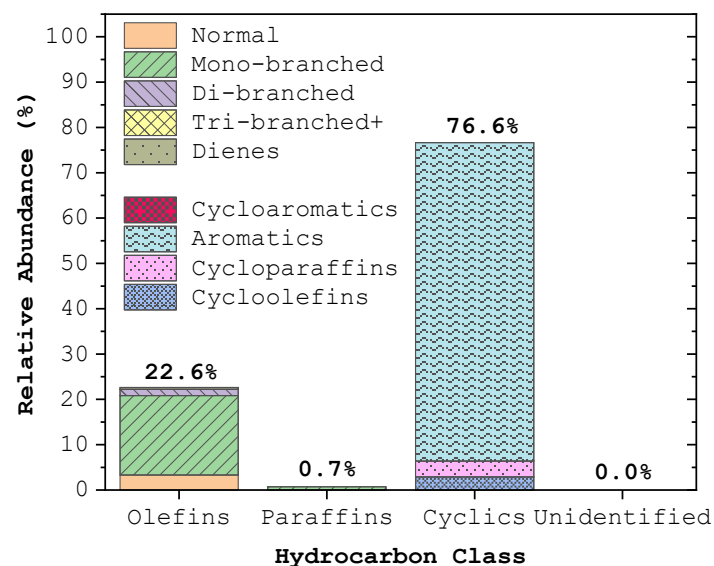
robert.dagle@pnnl.gov



Supplementary Slides

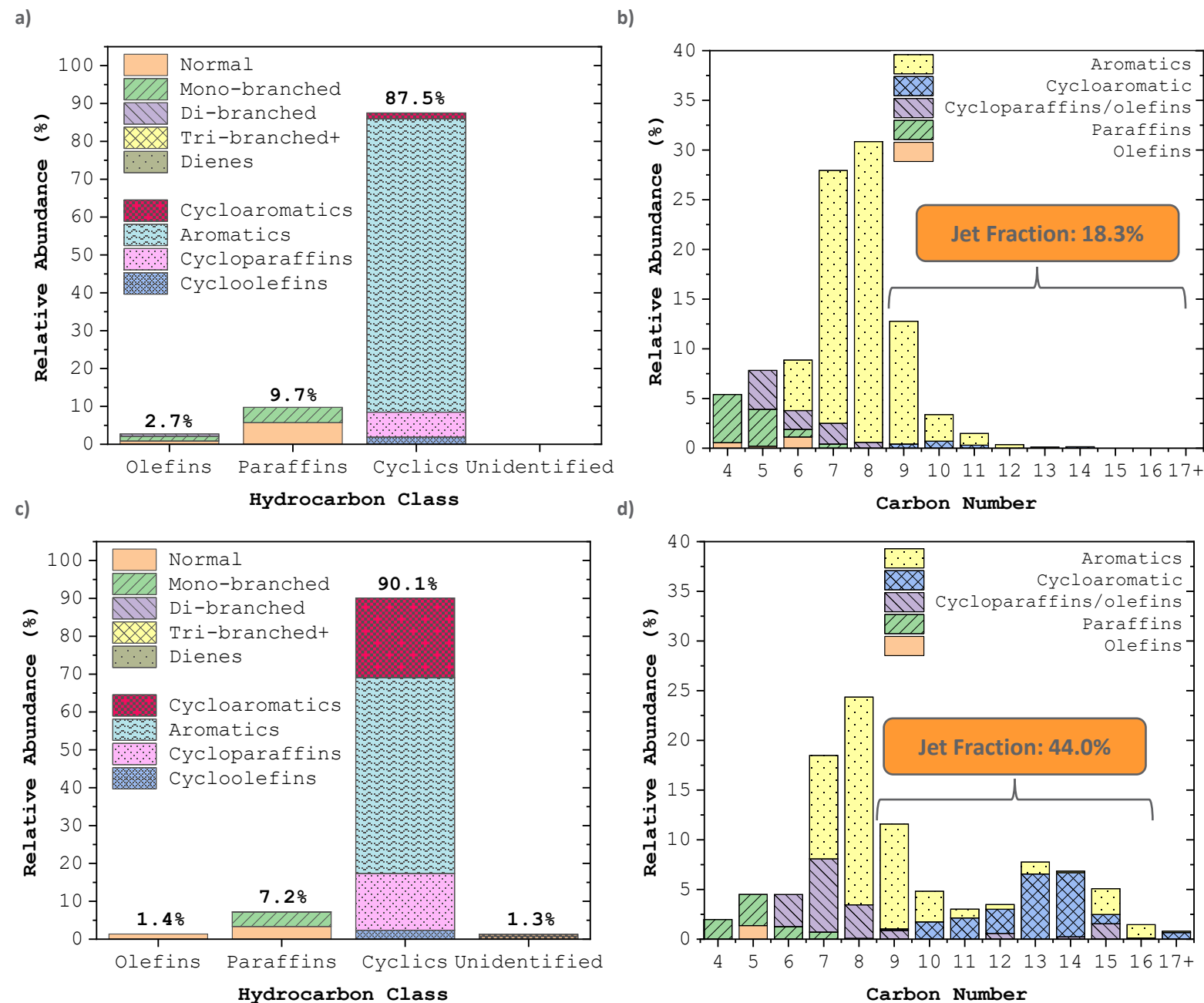


Abbreviated Conventional Alkylation Figure

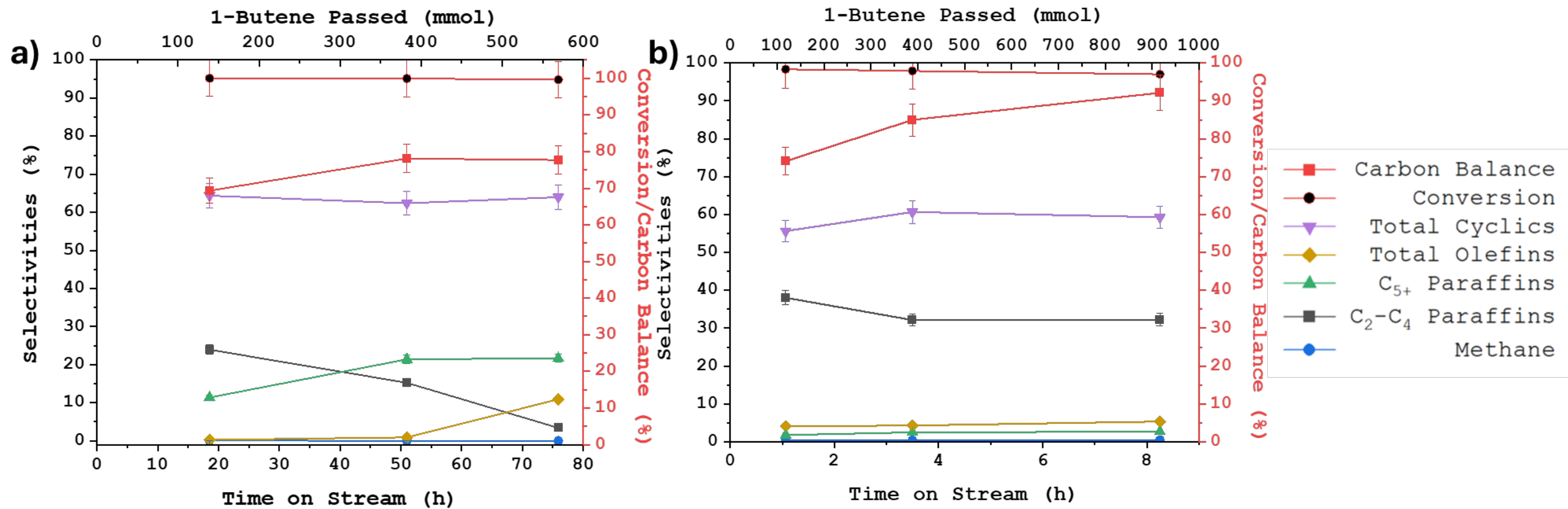


(a) Liquid product classification and (b) carbon number for the high aromatic content feed (as performed in Step i, Figure 2); and resulting (c) liquid product composition and (d) carbon number distribution after alkylating this feedstock with 1-butene after 17.5 hours' time-on-stream (Step ii; Feed: cyclic feed/ 1-butene = 1/1 mol; SPA catalyst; 220°C, 550 psig, 1.5 h⁻¹ WHSV).

Abbreviated Hydroalkylation Figure



(a) Liquid product classification and (b) carbon number for the high aromatic content feed (Step i, Figure 2); (c) liquid product composition and (d) carbon number distribution for the hydroalkylation product after 6 hours' time-on-stream (Step i; Feed: aromatic feed/ H₂ = 1/1 mol; 0.15%Pd/BEA catalyst; 140°C, 270 psig, 2.0 h⁻¹ WHSV).



Catalyst Characterization

Catalyst	Surface Area	Pore Size	Pore Volume	Weak Acid Sites, (< 250 °C)	Medium Acid Sites, (250 – 500°C)	Strong Acid Sites (> 500°C)
	m ² /g	Å	cm ³ /g	mmol NH ₃ /g	mmol NH ₃ /g	mmol NH ₃ /g
Clariant PolyMax 1000	5.2	34.7	0.33	-	-	-
1.5 Zn%/ZSM-5	233	14.0	0.20	0.207	0.238	0.403
1.5 Zn%/ZSM-5 (stream- treated)	267	34.2	0.20	0.044	0.073	0.037
0.15%Pd/BEA	517	9.1	1.12	0.581	0.356	Not detected

Tier α and β testing equipment and ASTM Standards

Property	Company/model	ASTM or other methods
Hydrocarbon type analysis	Agilent 8890 GC $\times$ GC-FID/VUV	Ref [8]
Simulated distillation	Agilent 8860 GC-FID	ASTM D2887
Surface tension	KRUSS – Force Tensiometer K20	ASTM D1331
Viscosity, density	Anton Paar – SVM 3001	ASTM D7042
Heat of combustion	IKA – C 3000	ASTM D4809
Hydrogen content	Bruker – minispec mq-one	ASTM D7171
Flash point	PAC – OptiFlash	ASTM D3828
Freezing point	PAC – Phase FPA-70Xi	ASTM D5972
O-ring volume swell	Optical dilatometry	Ref [9]