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Sustainable jet fuel production technologies: an overview

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U.S. DEPARTMENT OF ENERGY
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Three things from this talk

- We must reduce cost
- There are environmental benefits for lowering the aromatic and sulfur content of jet fuel
- Three jet fuel properties: “energy content, low temperature fluidity, thermal stability”

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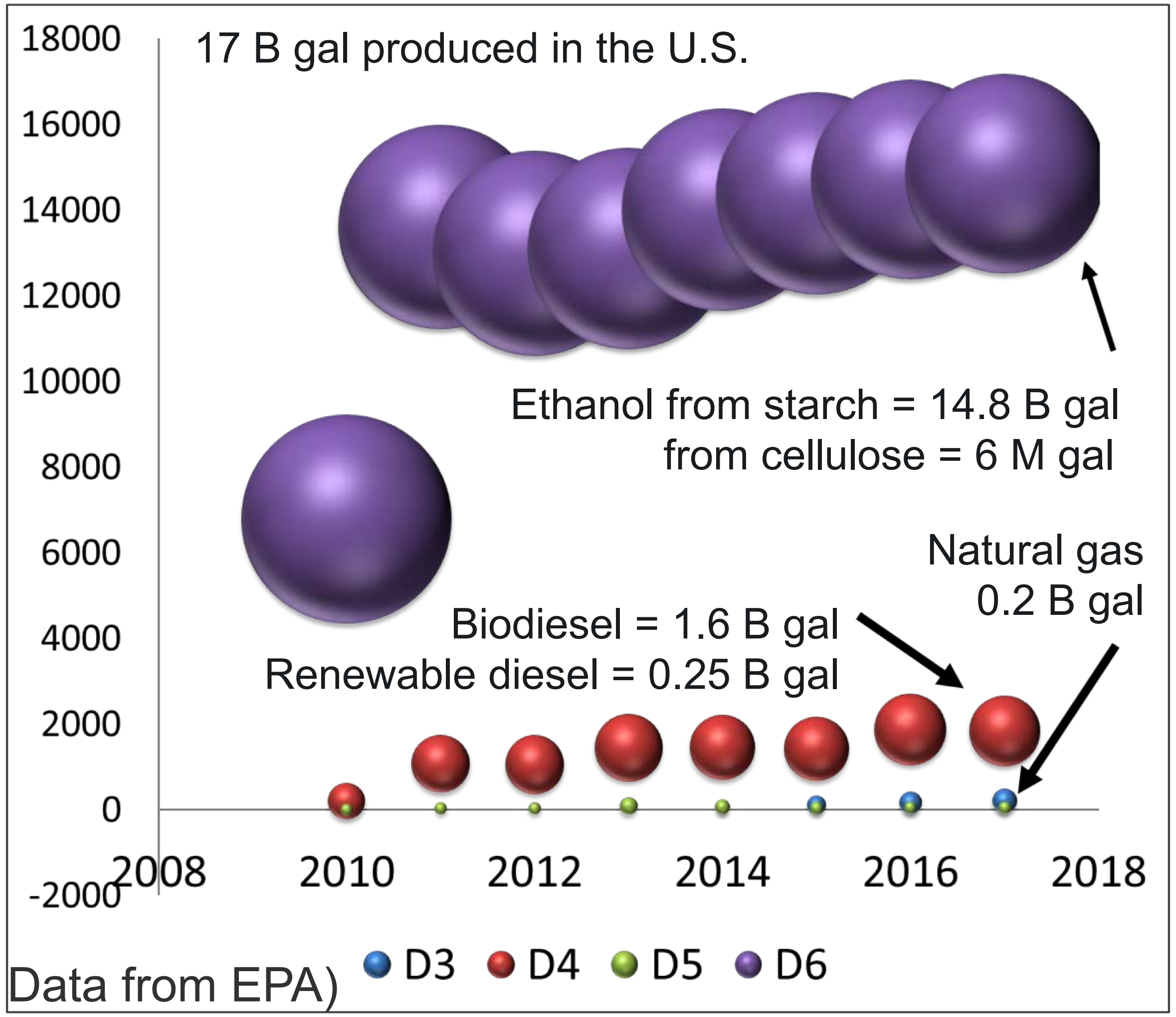
U.S. biofuels production in 2017 was 1.4 EJ, which includes 0.035 EJ of renewable diesel



U.S. production, 2017[1]

1.4 EJ fuel produced (5%)

13 Tg CO_2 abated[2] (0.04% of transportation)

3.5 PJ of renewable diesel produced (1% of U.S. jet demand)

A decade after the Energy Independence and Security Act (EISA 2007)

[1] ethanol energy content = 26.7 MJ/kg, density = 0.789 kg/L
[2] GREET 2018 was used in this calculation. Based on building a blended fuel with ethanol and biodiesel and compared the g CO_2 of petroleum fuel of same energy content

Overview

Energy – U.S. jet fuel is 3.4 EJ and growing

Emissions – need to keep U.S. airlines competitive (CORSIA)

- Lower soot and S, lower contrails (from reducing aromatics and S)
- Reducing CO_2 footprint

Science and Technology – Needs differ than for gasoline or diesel

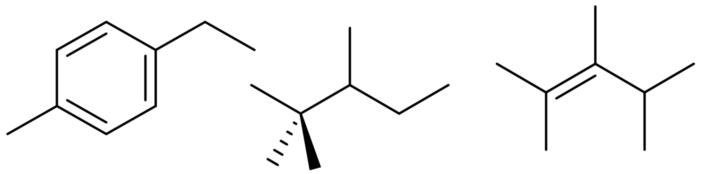
- Outline desired fuel properties
- High level overview of some routes under evaluation

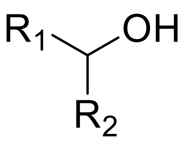
Jet fuel differs by both carbon number and molecule type from gasoline and diesel

Gasoline

Key property: octane

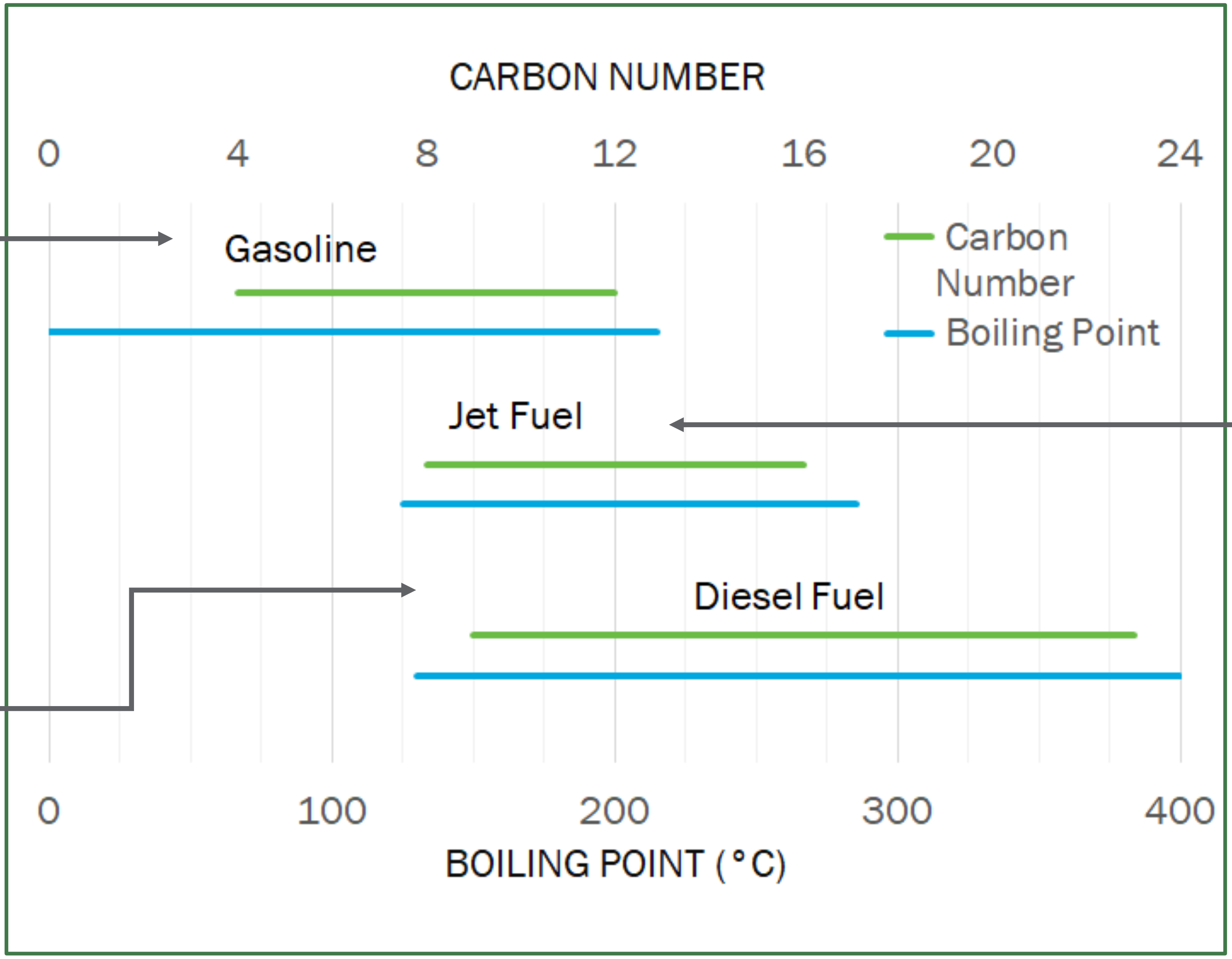
- Aromatics
- Highly branched alkanes or alkenes
- Small alcohols





R_1 = $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2CH_3$

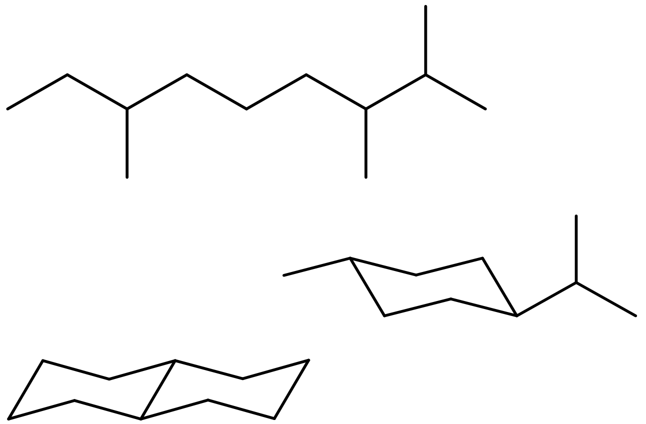
R_2 = H, CH_3



Jet fuel

Key properties: energy content, low temp fluidity, thermal stability

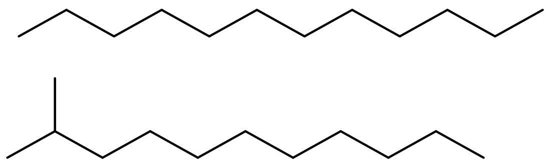
- Iso-alkanes (prefer low branching)
- Cycloalkanes
- No heteroatoms or alkenes!
- Fuel cleanliness (no metals or water)



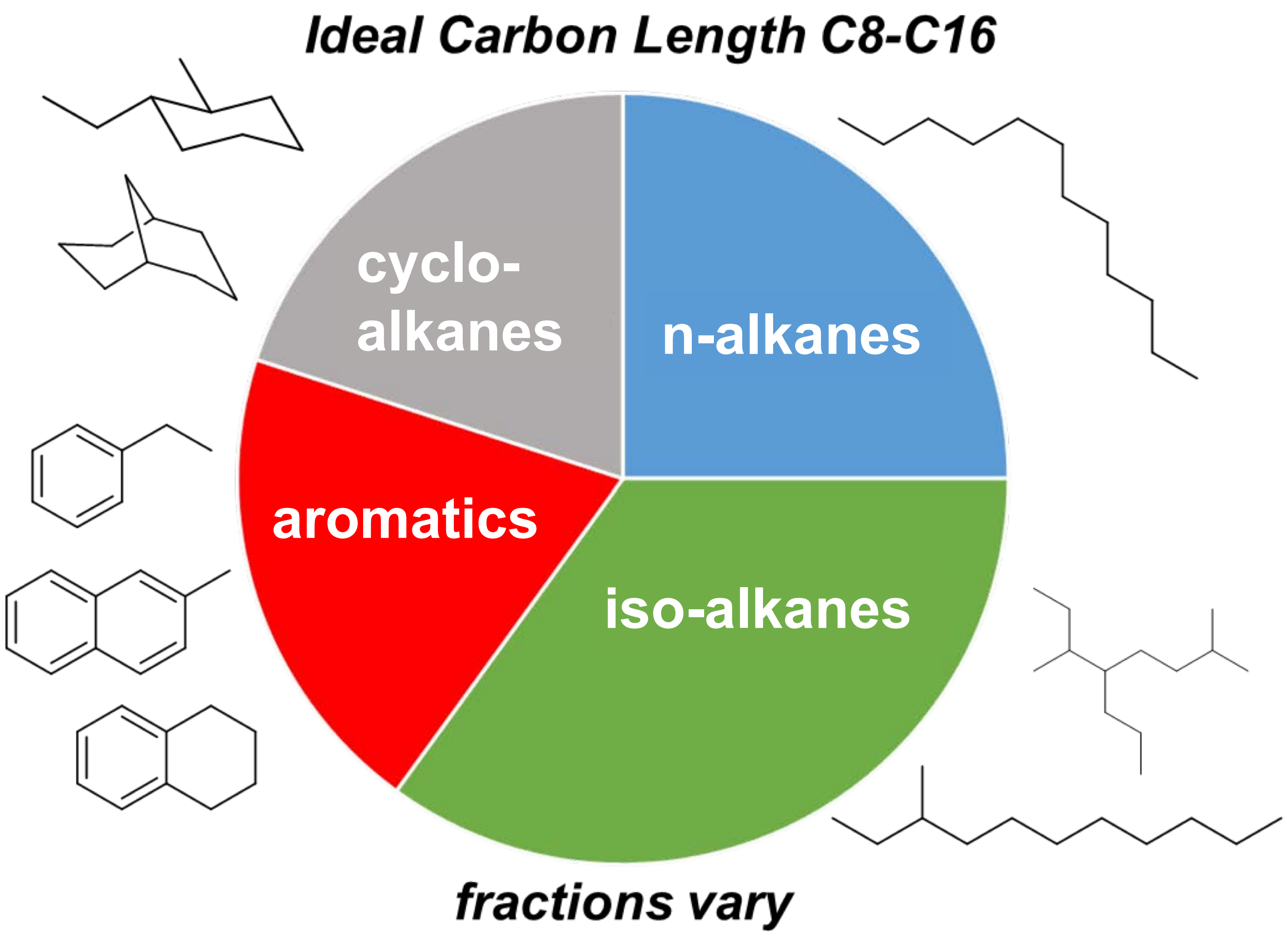
Diesel

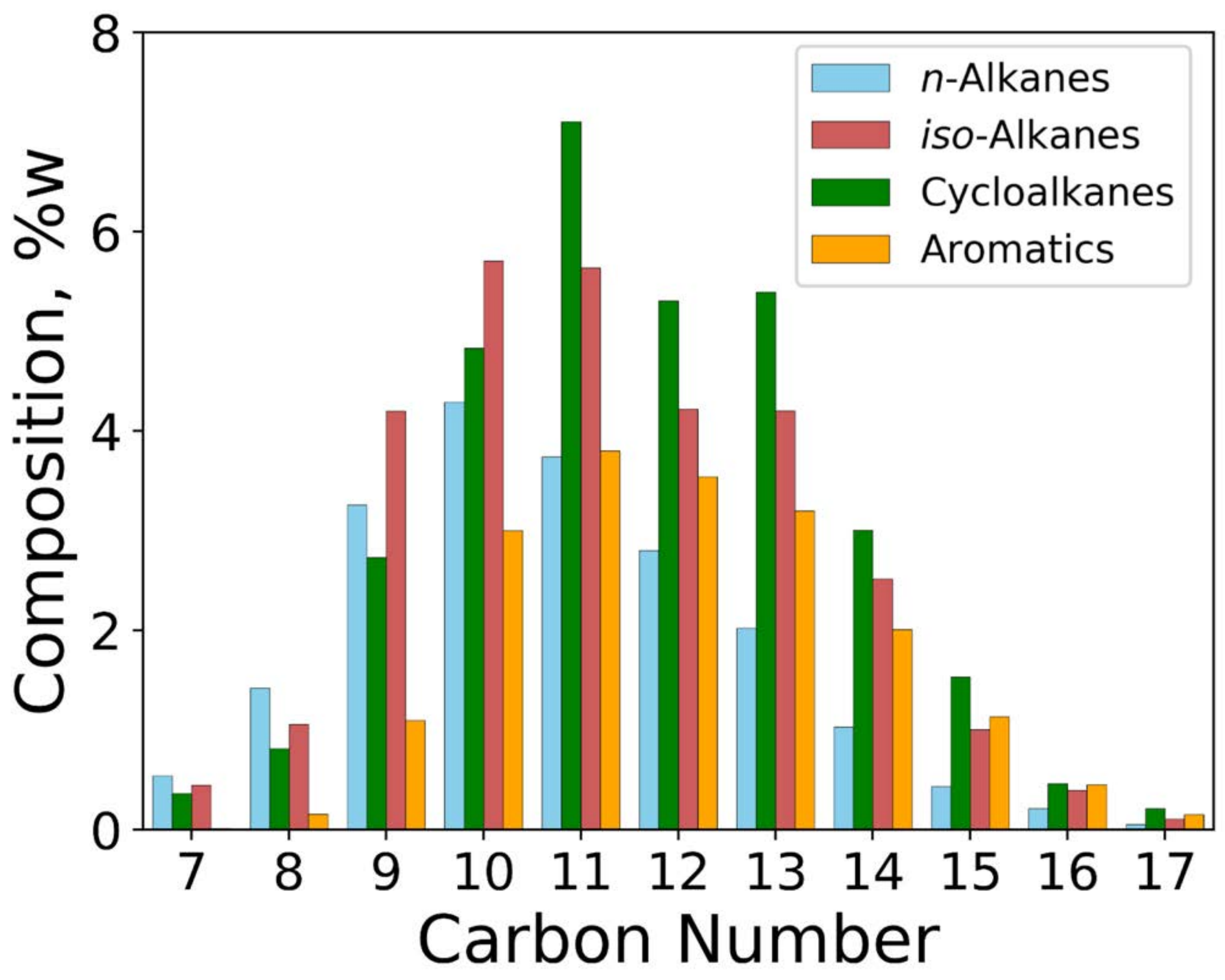
Key property: cetane

- n-Alkanes or very low branched iso-alkanes
- Some ethers



Jet fuel is composed of C8-C16 hydrocarbons





Aromatics are limited to 25%
Olefins and heteroatoms are limited (not allowed)
- Olefins (<1%) (gum formation)
- S, N, O containing (limited allowance)

Pie chart adapted from Tim Edwards
Composition from Josh Heyne

Both the bulk composition and the trace components are important

Bulk composition properties	Trace composition properties
Energy content	Lubricity
Combustion character	Stability
Distillation range	Corrosivity
Density	Cleanliness
Fluidity	Electrical conductivity

Trace property impact on maintenance can be at least as significant as bulk properties – and hard to control

Aviation Fuels Technical Review, Chevron Products Company, 2007
https://www.cgabusinessdesk.com/document/aviation_tech_review.pdf (accessed June 19, 2018)

There a number of fuel properties that jet fuel must meet

		n-Alkanes	iso-Alkanes Weakly branched	iso-Alkanes Strongly branched	Cycloalkanes Monocyclic	Cycloalkanes Fused bicyclic	Aromatics
Performance	Specific Energy	++	++	++	+	0	-
	Energy Density	-	-	-	+	++	++
	Thermal Stability	+	+	+	+	+	
Operability	DCN	++	+	-			-
	Density	-	-	-	+	++	+
	Freeze Point	-	+/-	+	+	+	+
	Sooting	++	++	++	+	+	--

- n-Alkanes do not have the low-temperature properties needed
- Aromatics have poor combustion behavior and are the primary cause for soot formation (which also contributes to engine corrosion)

Source: Abdullah, Heyne, and Holladay

Biojet does not need to mimic the composition of petroleum…but it still needs to be low cost

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Goal 1

Determine new platforms to reduce cost of iso- and cyclo- alkanes

Goal 2

Understand properties of current and new cycloalkanes

n-alkanes

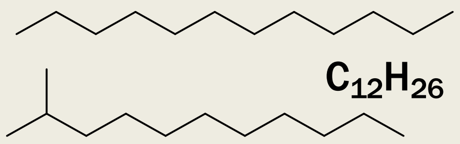
Jet A is 55-60% n- and iso-alkanes

iso-alkanes

FP

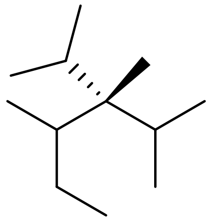
-10 °C

-46 °C

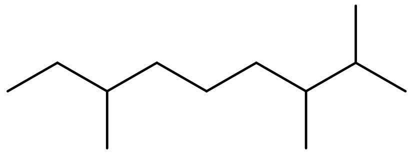


$C_{12}H_{26}$

Importance of substitution



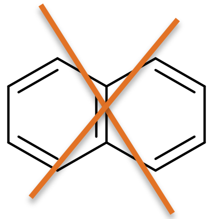
Heavy branching mixtures (50% blend)
low DCN i-butanol to jet



Light branching (50% blend)
higher DC, HEFA, ethanol to jet

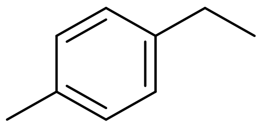
Prefer mixtures with broad coverage over boiling point and carbon number

Objective: reduce cost (feedstock and conversion)



Small (single ring) preferred over heavy (multi-ring)

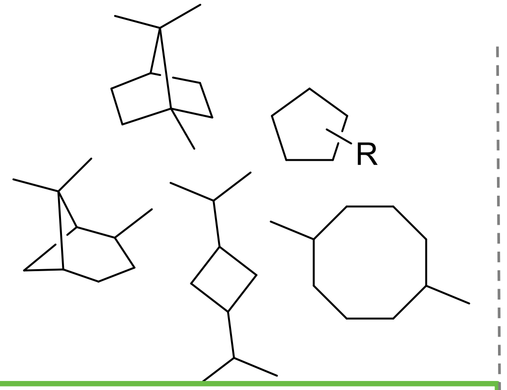
small amount (<8%) needed for nitrile seals subjected to high [aromatics]

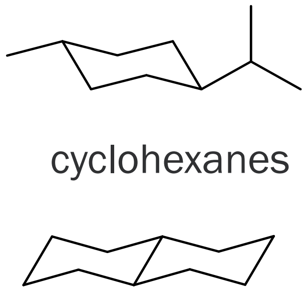


Objective: reduce aromatic content to minimum possible

aromatics

Specialty
Risks: high mp, thermal stability





cyclohexanes

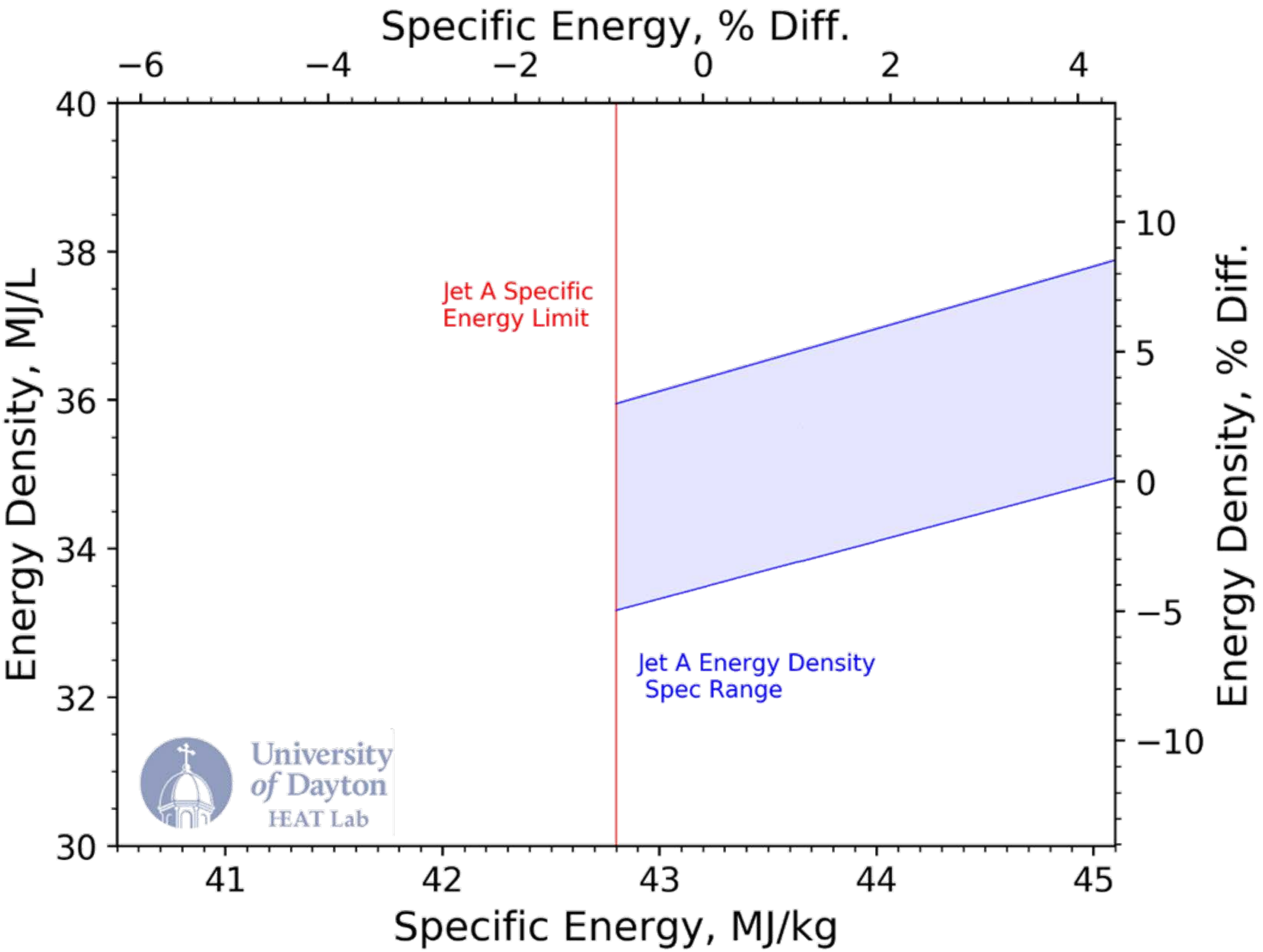
decalins (fused rings)

objective: understand properties, if "worth it" seek low cost routes

cyclo-alkanes

Energy content

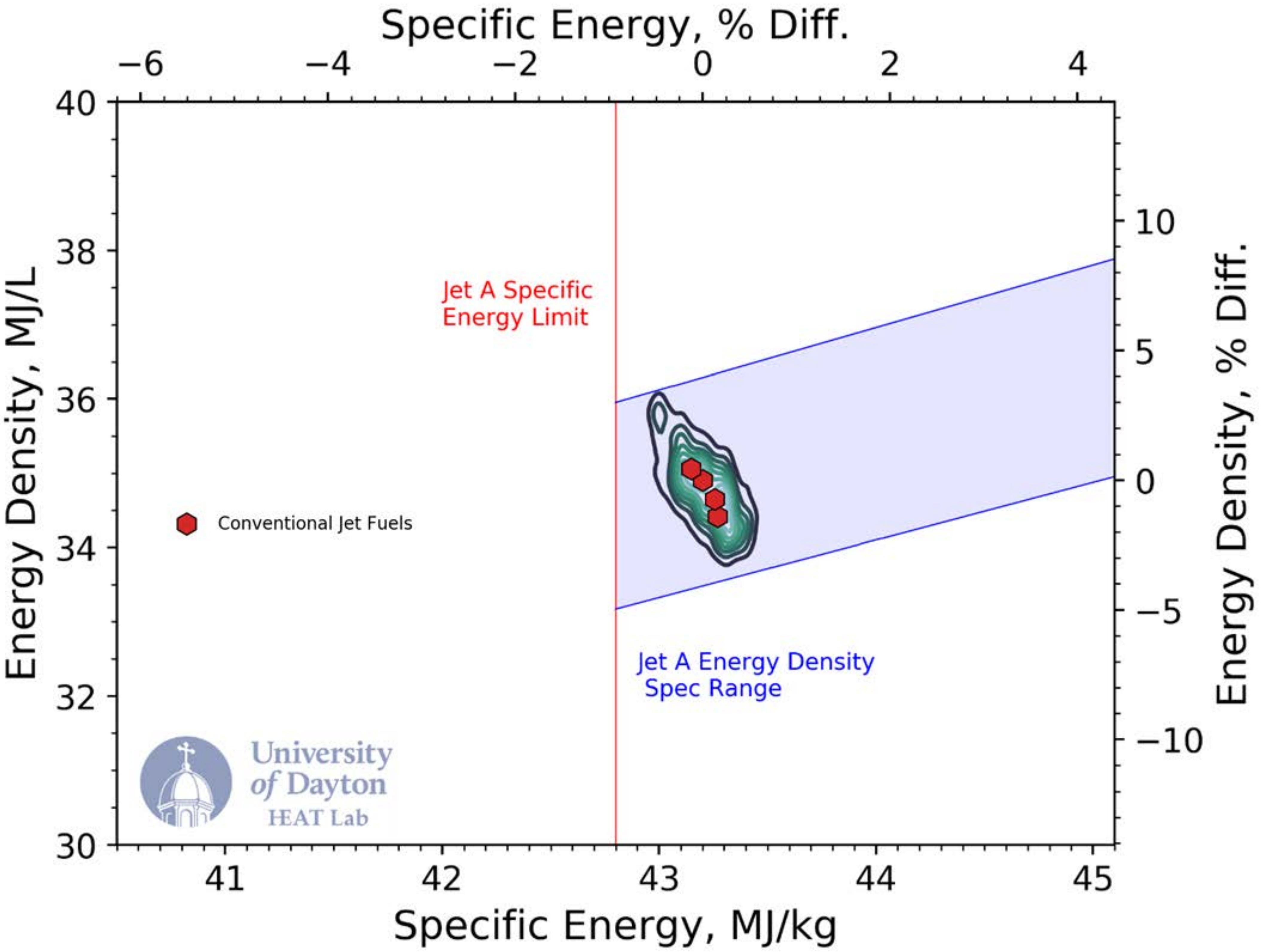
- The blue area shows the spec range for energy content



Energy content

Conventional jet fuel

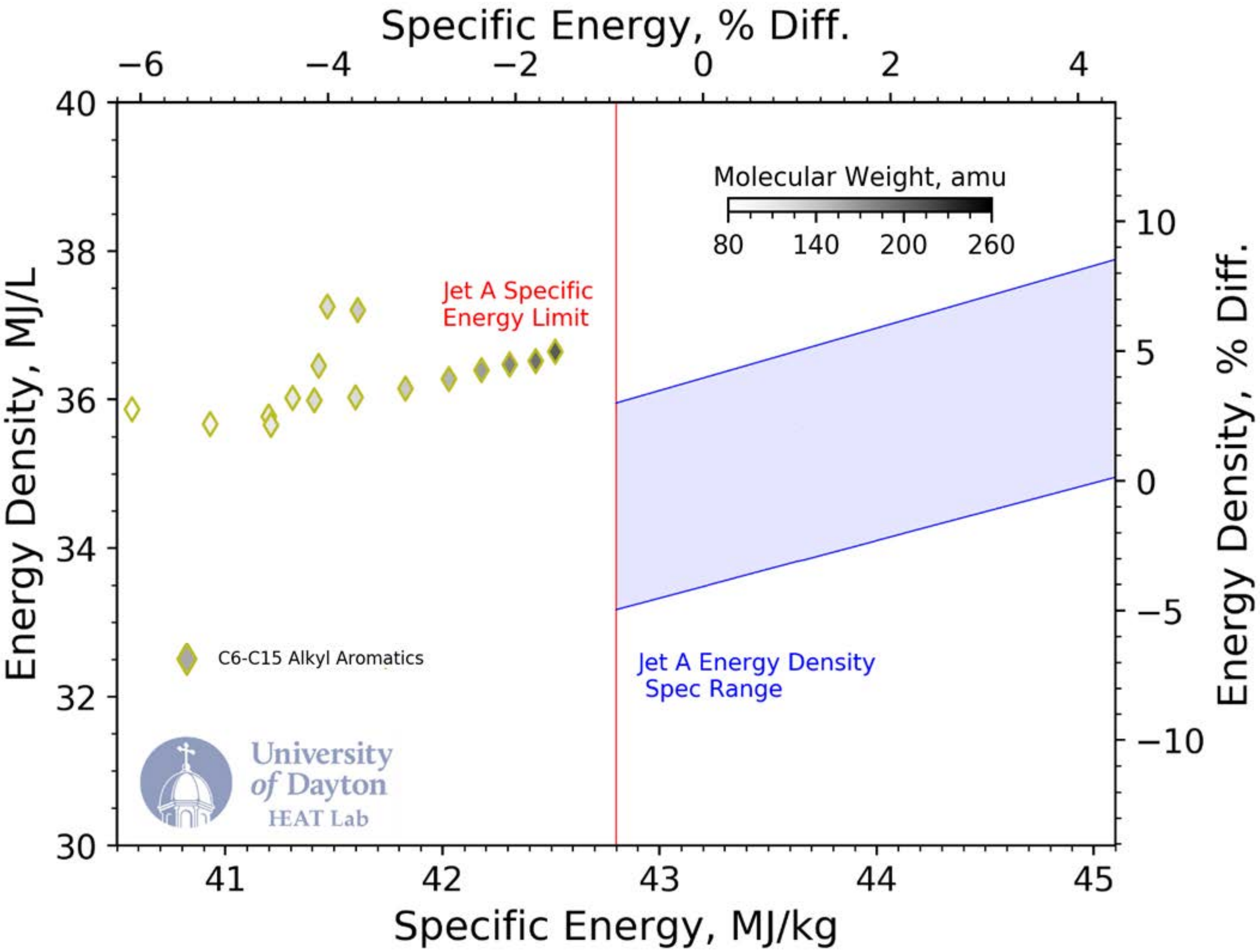
- Mixture of all four hydrocarbon classes



Energy content

Aromatics

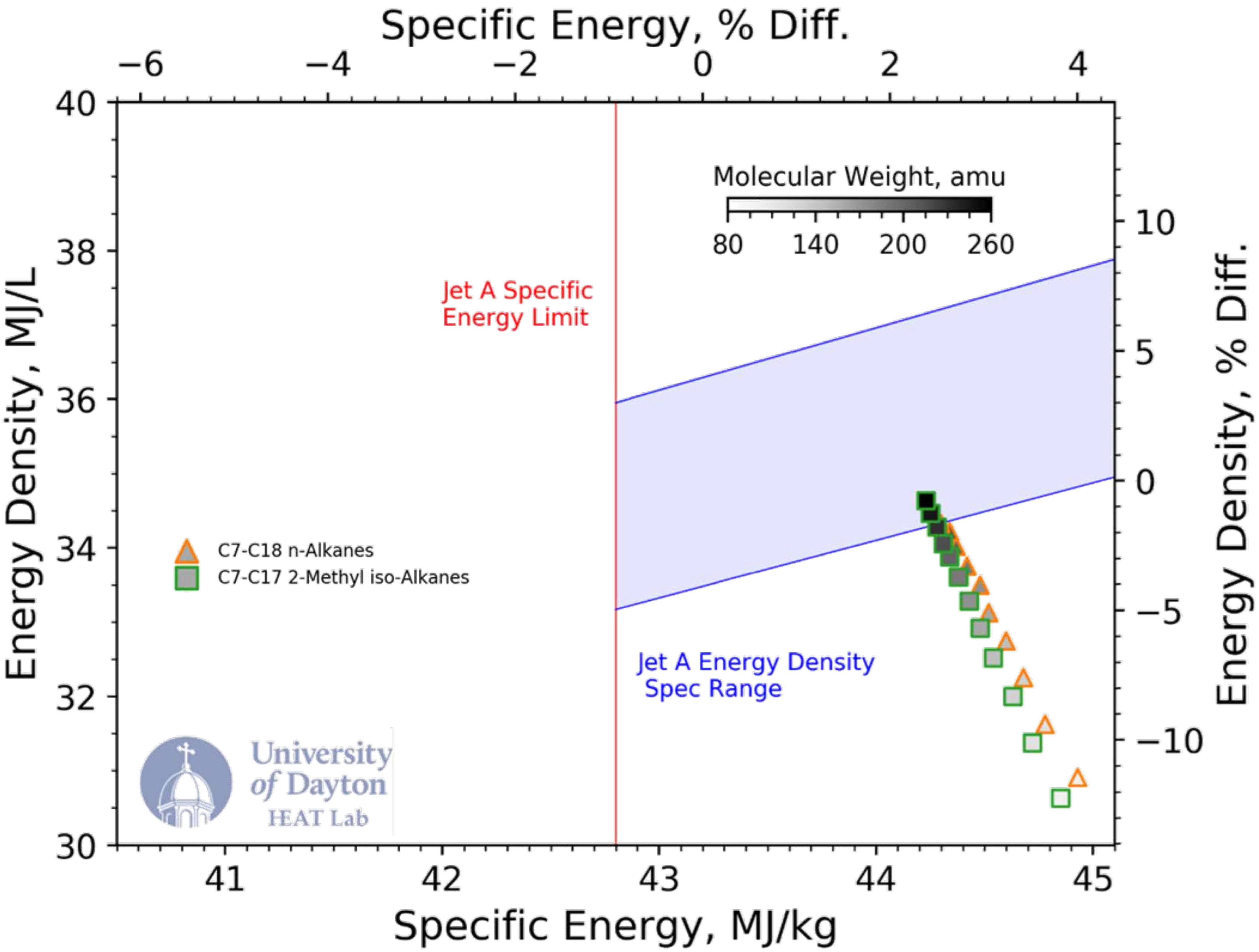
- low specific energy
- High energy density



Energy content

Isoalkanes

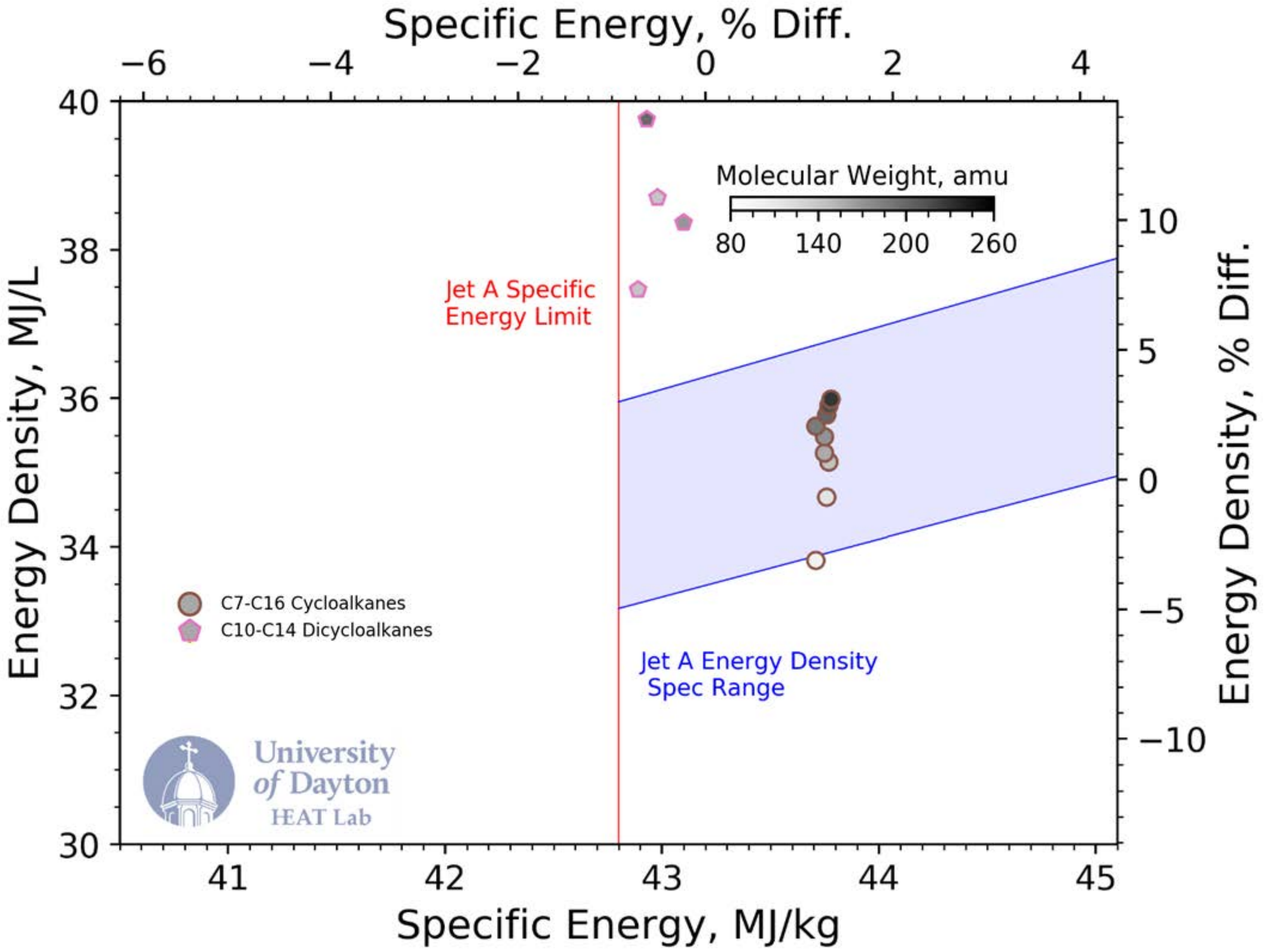
- High specific energy
- Low energy density



Energy content

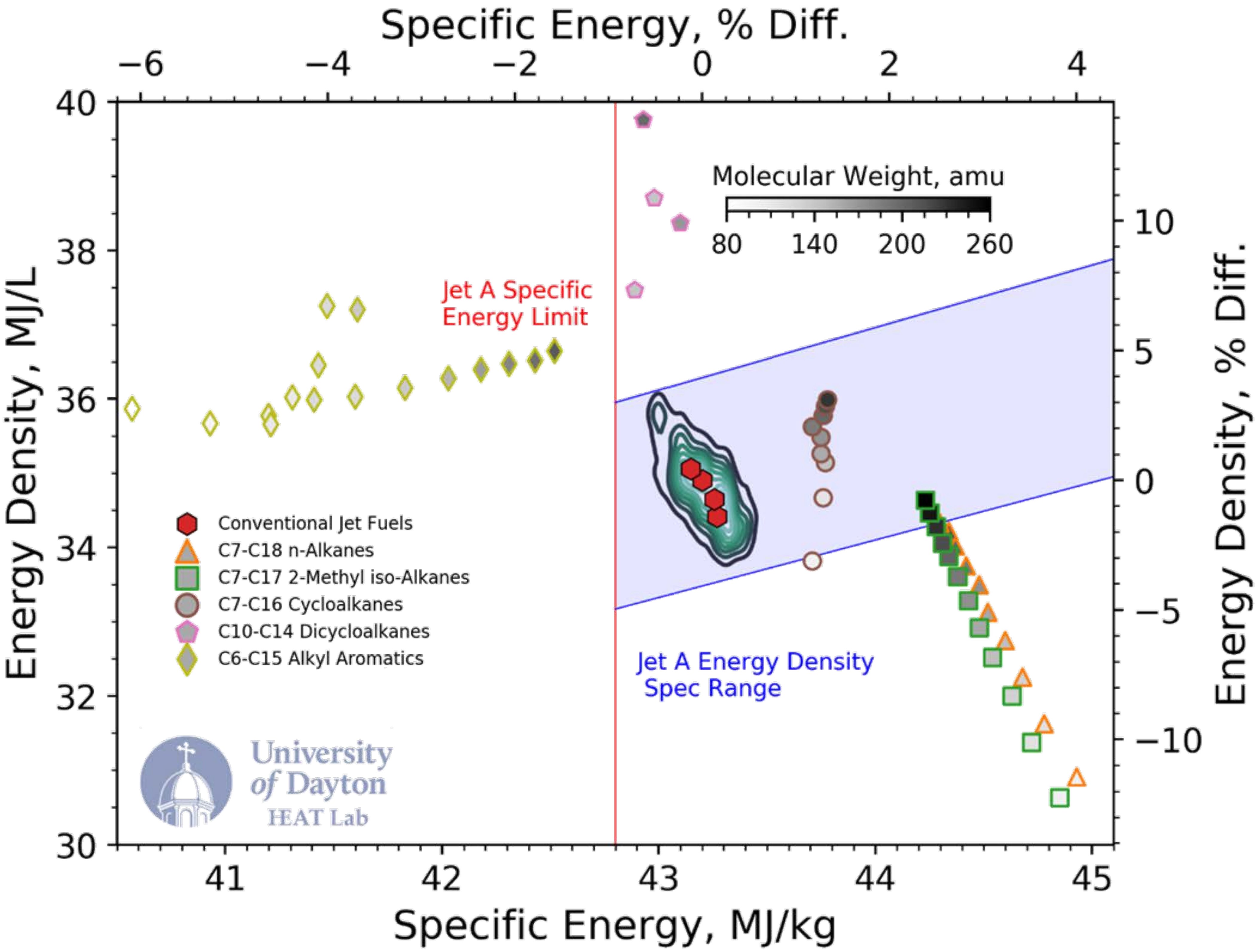
Cycloalkanes

- Intermediate specific energy
- High energy density



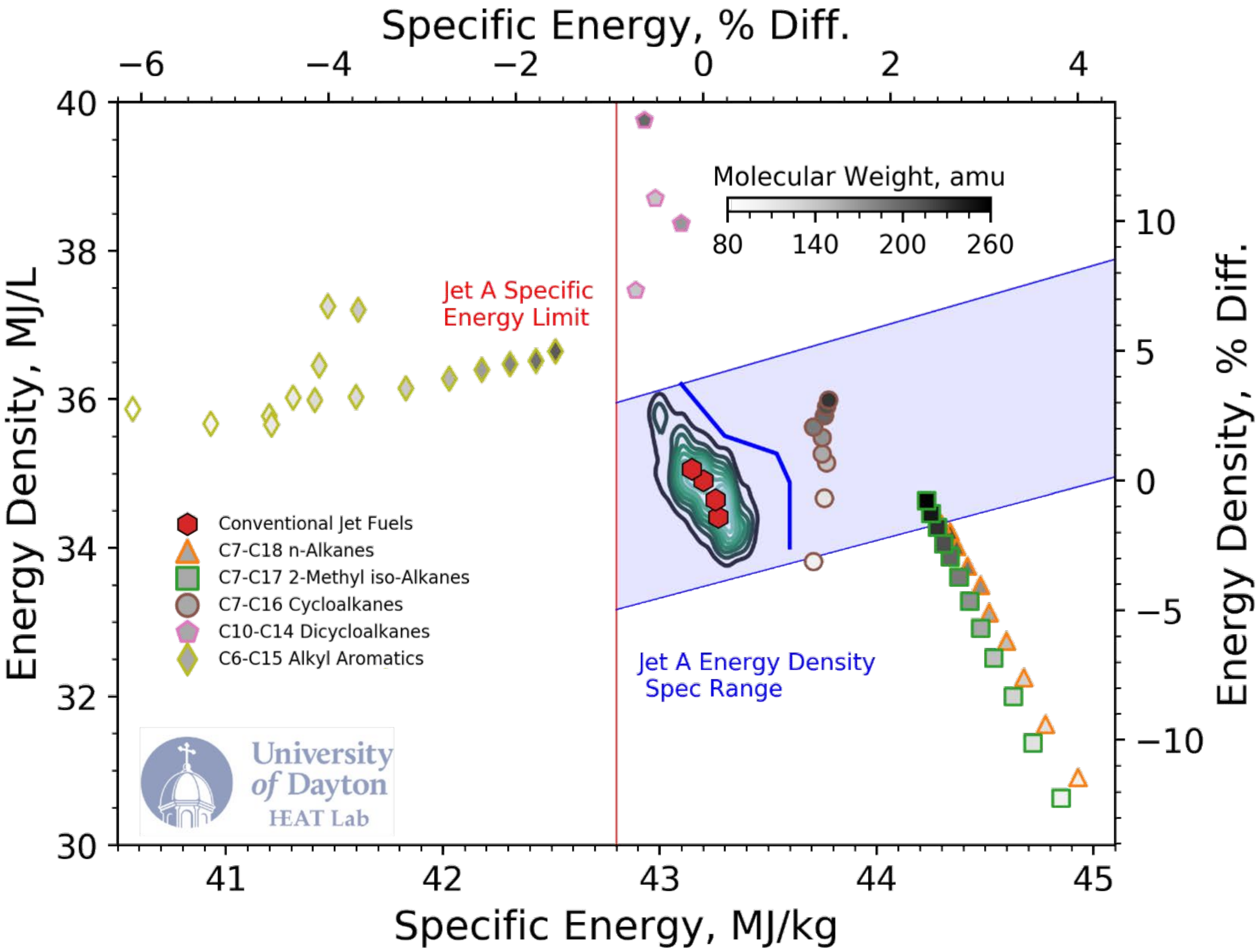
Jet fuel

- Combination of all four families



Jet fuel

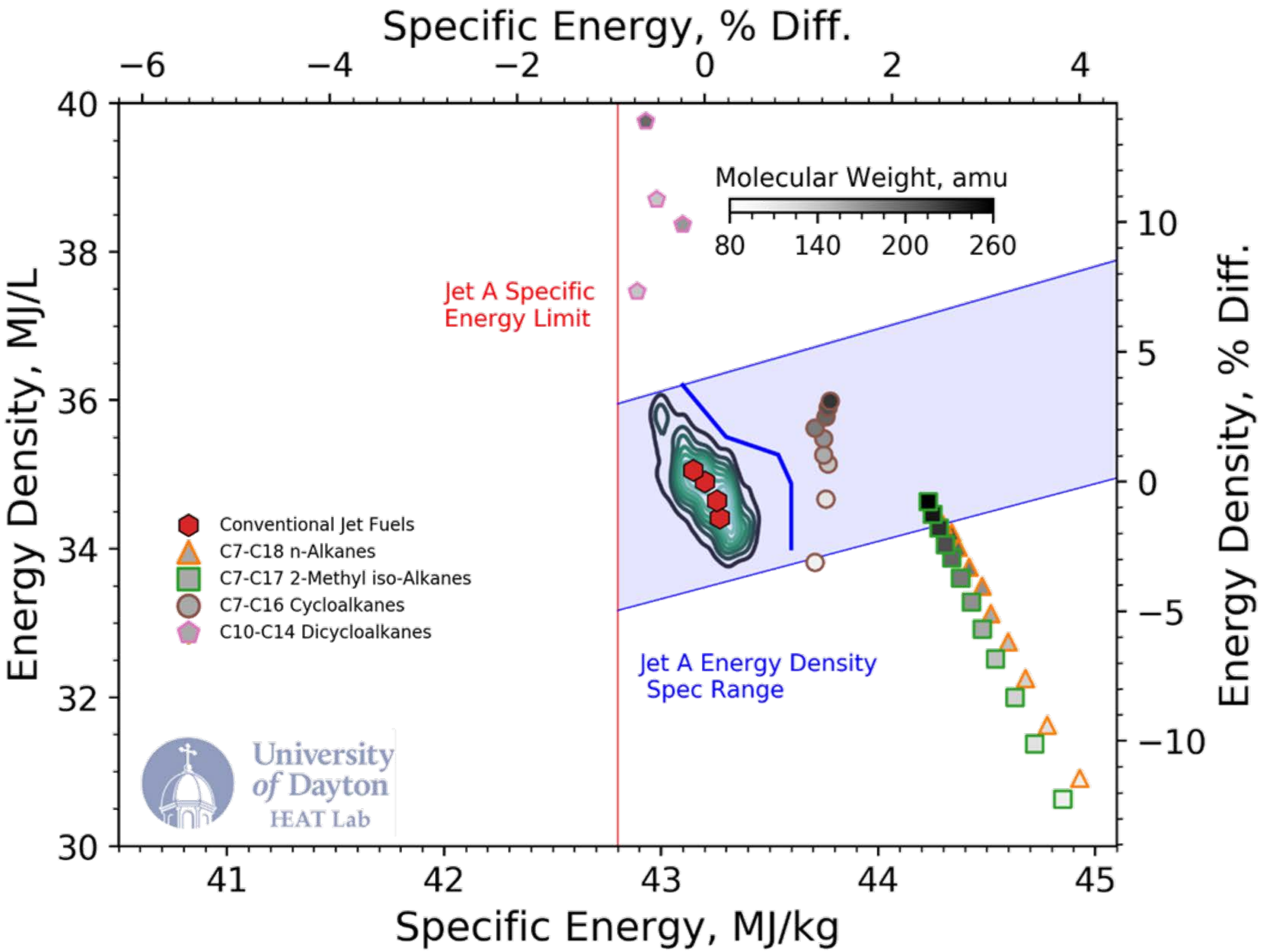
- With petroleum bulk specific energy does not surpass the blue line



Jet fuel tomorrow

By making fuels without aromatics

- Higher specific energy
- Retain energy density
- Cleaner burning



ASTM D4054 defines the steps needed for an alternative jet fuel to be approved

Amount of fuel needed in gallons (liters)

Tier 1 10 gallons
(40 L)

Tier 2 10-100 gallons
(40-400 L)

Tier 3 250-10,000 gallons
(1,000-40,000 L)

Tier 4 up to 225,000 gallons
(850,000 L)

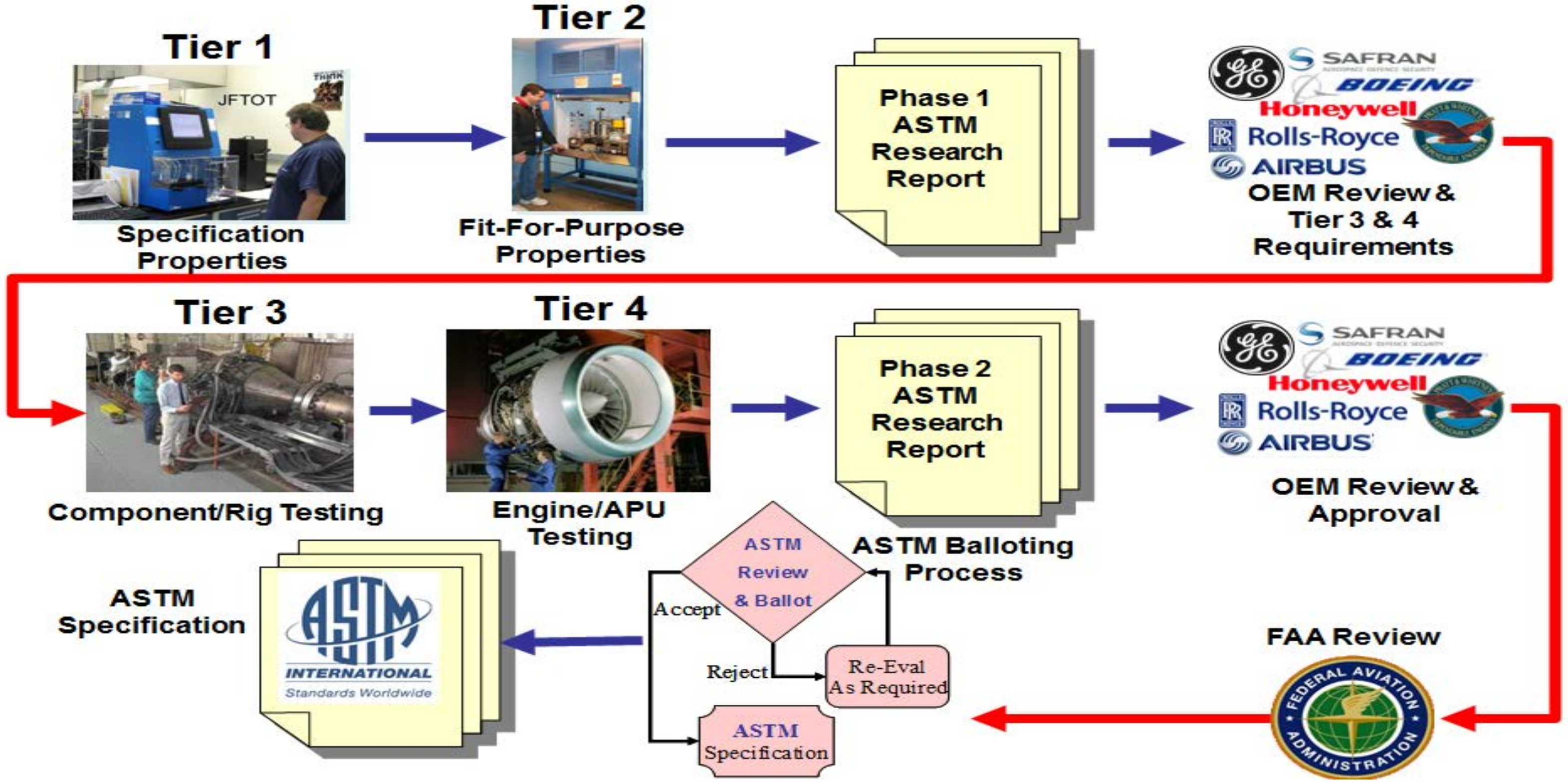


Figure from Mark Rumizen

ASTM D4054 process

- Two fuels collecting tier 3 and 4 data
- 1 fuel in Phase 1 review
- Several fuels collecting Tier 1 and 2 data

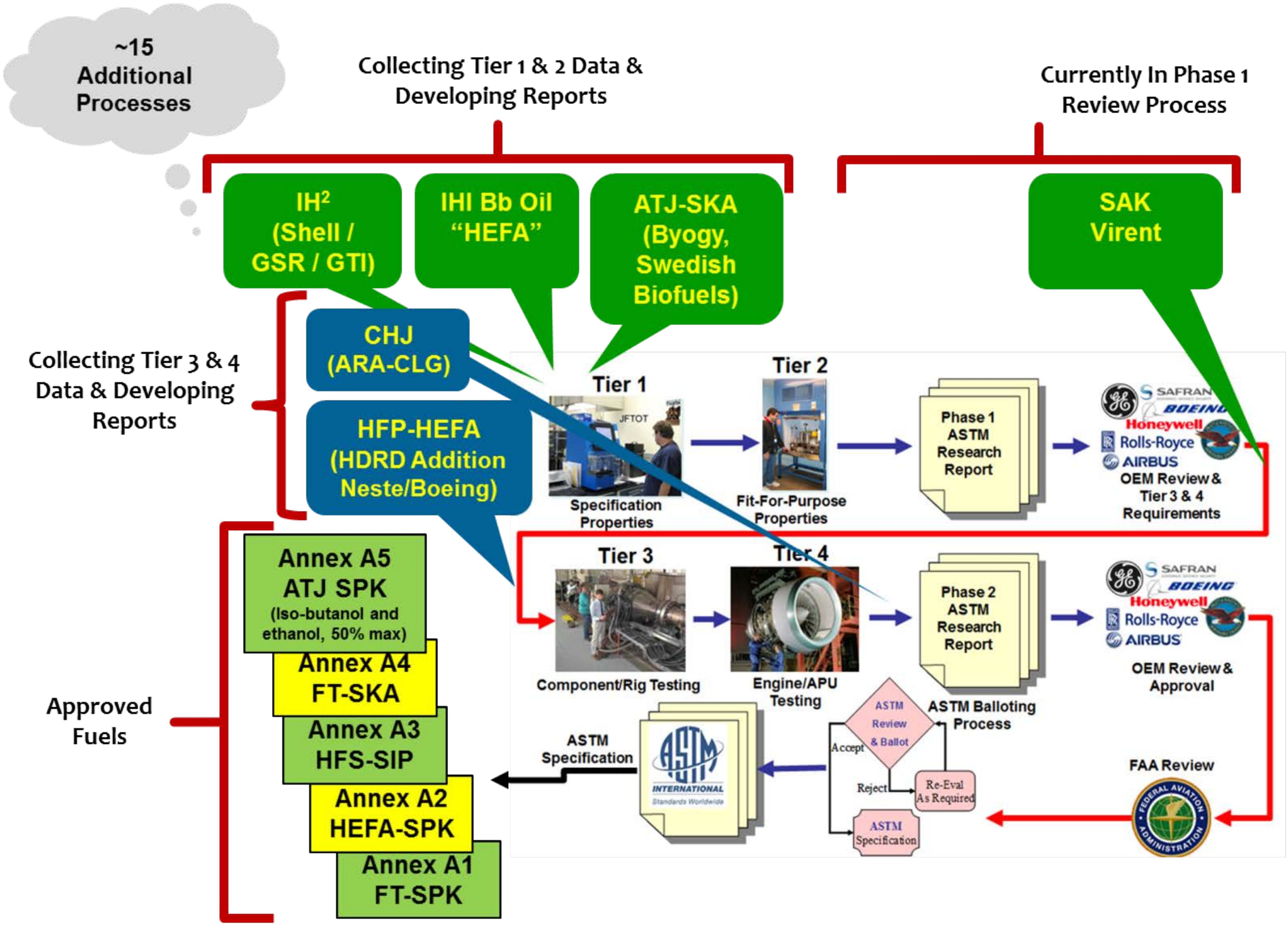
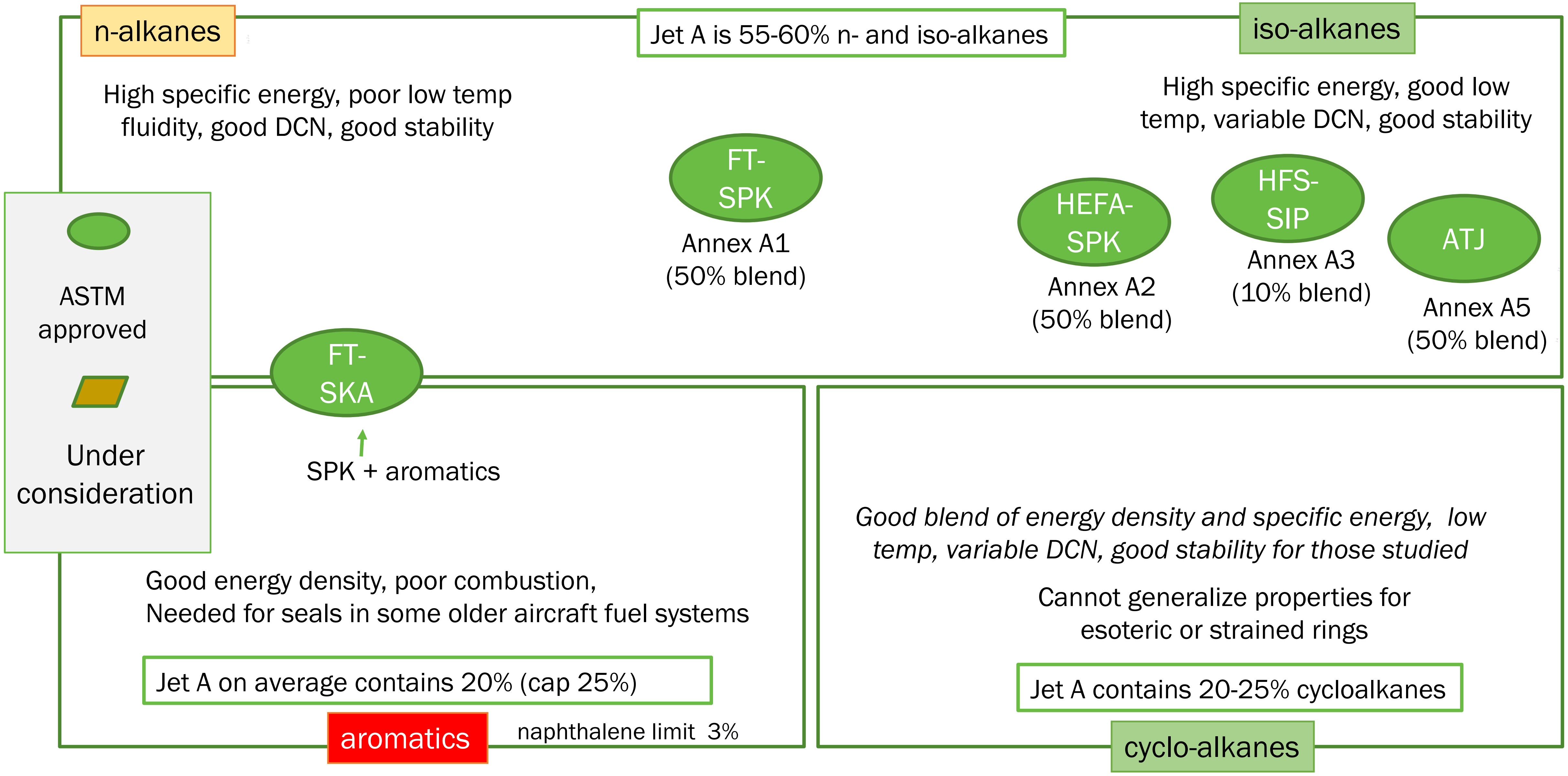


Figure from Mark Rumizen

Alternative jet fuels approved today are based on iso-alkanes and are approved as blends



Five fuels are part of D7566, when mixed with petroleum Jet-A are fully fungible

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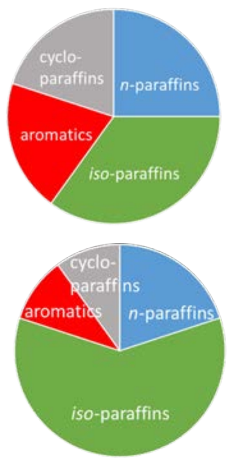
Standard	Pathway	Feedstock	Process	Product
D1655	**Petroleum**	Crude oil		
D7566 Annex A1* June 2009	Fischer-Tropsch (FT-SPK)	Coal / Natural gas / Biomass / MSW	Gasify, condition syn gas Fischer-Tropsch, isom	syn-crude oil
D7566 Annex A2 July 2011	Hydroprocessed esters & fatty acids (HEFA)	Oil seed crops	oil extraction and cleaning, hydroprocessing, isomerizing and cracking, fractionation	paraffins
D7566 Annex A3 June 2014	Synthesized iso-paraffins from hydroprocessed fermented sugars (SIP)	sugars	Fermentation, extraction, hydrogenation, distillation	Farnesane (C15 paraffin)
D7566 Annex A5 April 2016†	Alcohol to jet (ATJ)	alcohols	1. dehydration 2. oligomerization → 3. hydrogenation 4. fractionation	paraffins

Petroleum refinery operations

Distilling, reforming, fluid catalytic cracking, alkylating, isomerizing, hydrotreating, cracking, coking

blending



jet fuel

Airport hydrant system

* FT-SPK/A Annex A4 was approved Nov 2015 (FT + aromatics)

† Annex A5 was expanded in April 2018 to include ethanol and raised to 50%

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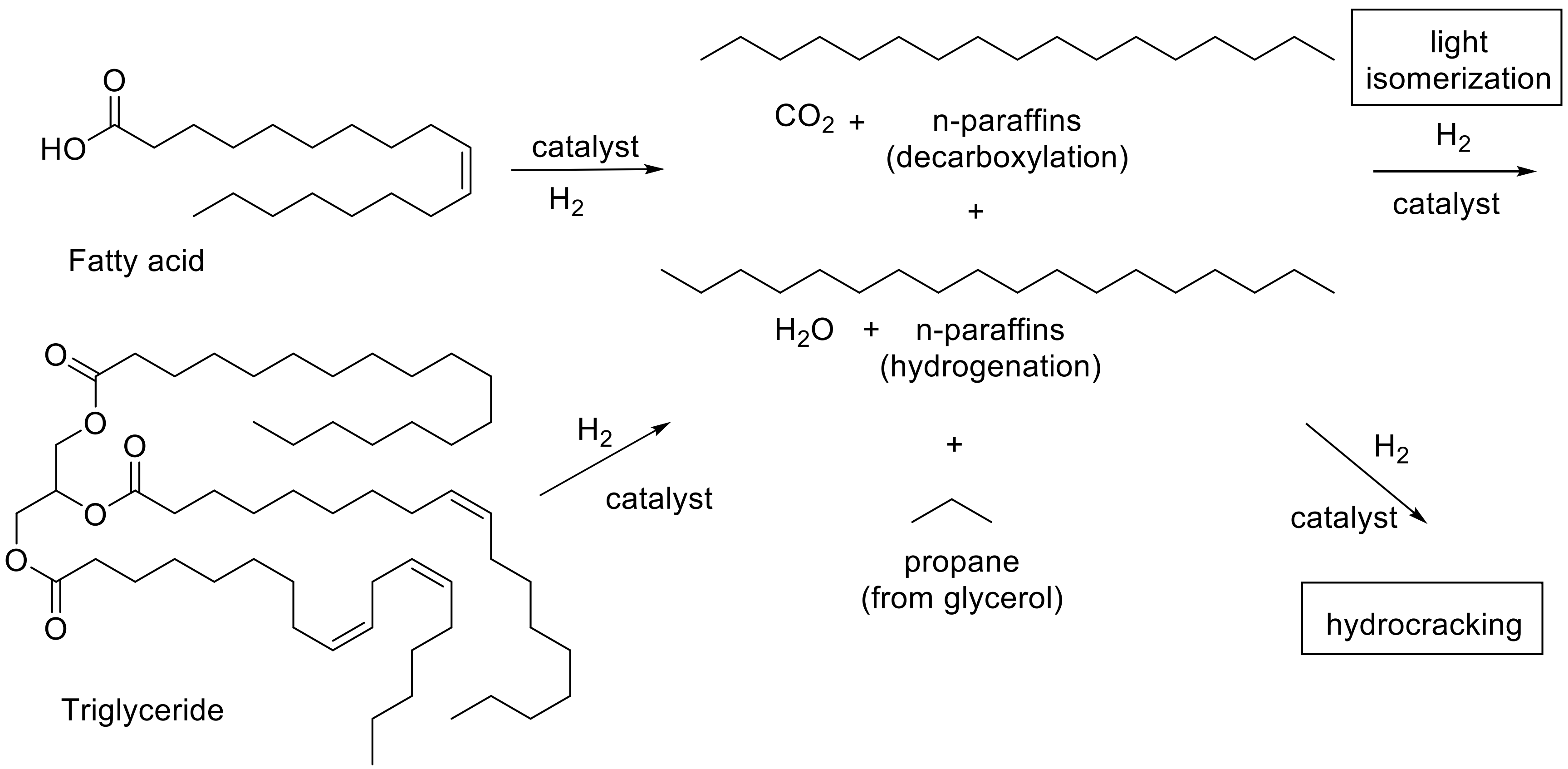
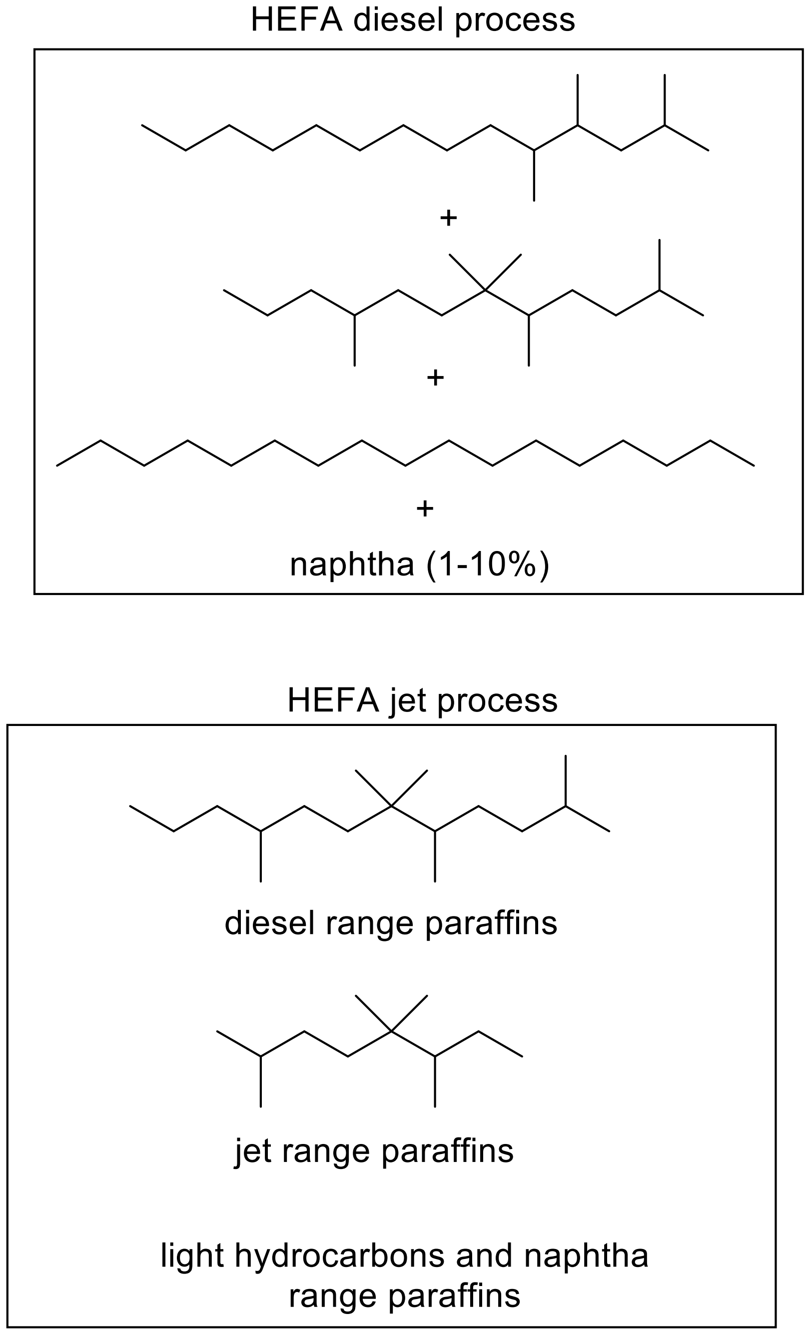
HEFA* fuel production, ASTM led by UOP





Challenge
Availability of low cost lipids

Challenge
Carbon chain to long

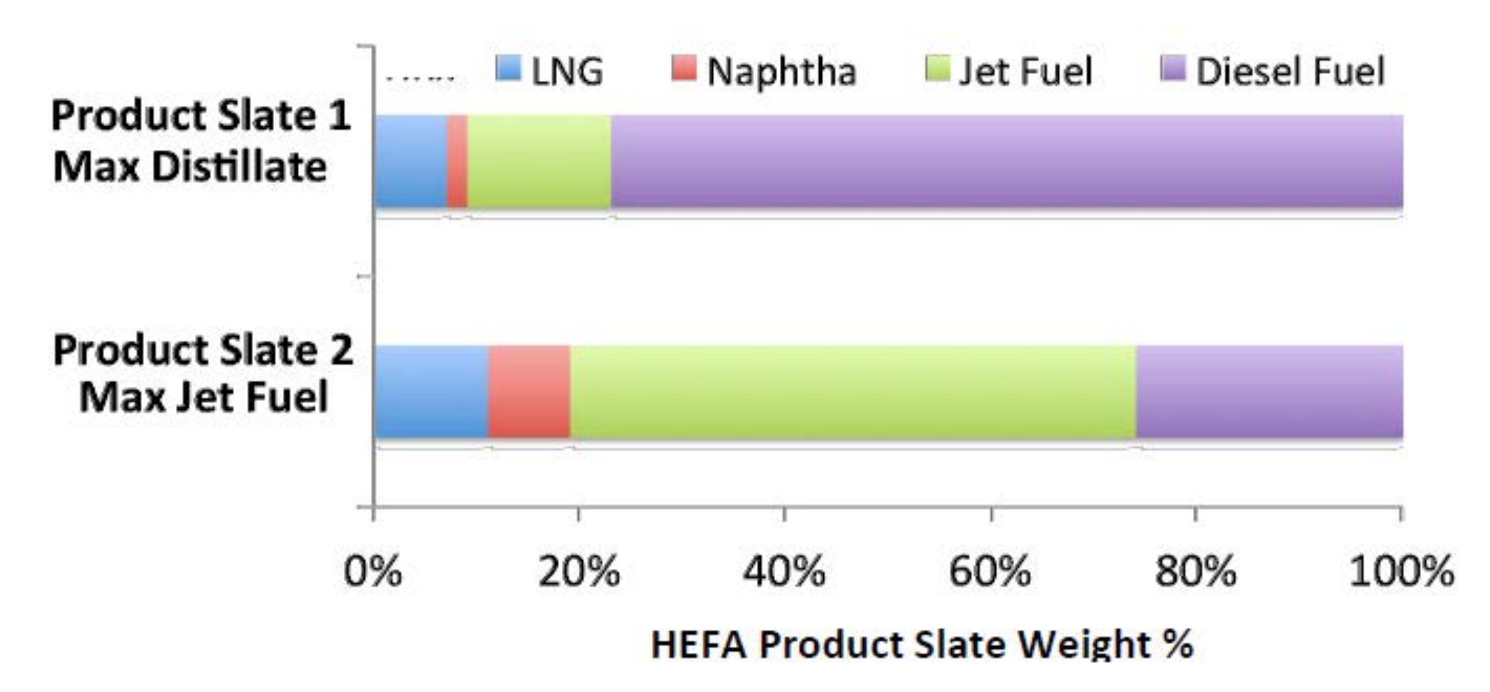
Challenge
Loss of carbon to low-value naphtha

HEFA is done in a 2-stage reactor (hydrogenation followed by isomerization)
diesel yield is 88 - 98 vol%, naphtha yield is 1 - 10 vol%

To produce jet fuel hydrocracking is required to bring the carbon number and boiling point into the jet range, resultin in loss of carbon to light gasses and a higher naphtha yield

*hydroprocessed esters and fatty acids

HEFA product slate from National Alliance for Advanced Biofuels and Bioproducts



Malina; Source: Pearlson (2011) and Pearlson et al. (2012)

Fractionation results via spinning-band distillation of hydrotreated and isomerized N. oceanica (low lipid) HTL bio-oil.		
Fraction	Boiling Range	Mass %
Noncondensable material (gas)	--	6%
Naphtha	IBP–150 °C	4%
Jet (SPK)	150–250 °C	26%
Diesel	250–350 °C	47%
Heavies	350+°C	17%

The technology is well demonstrated and commercially practiced

The product slate can be adjusted

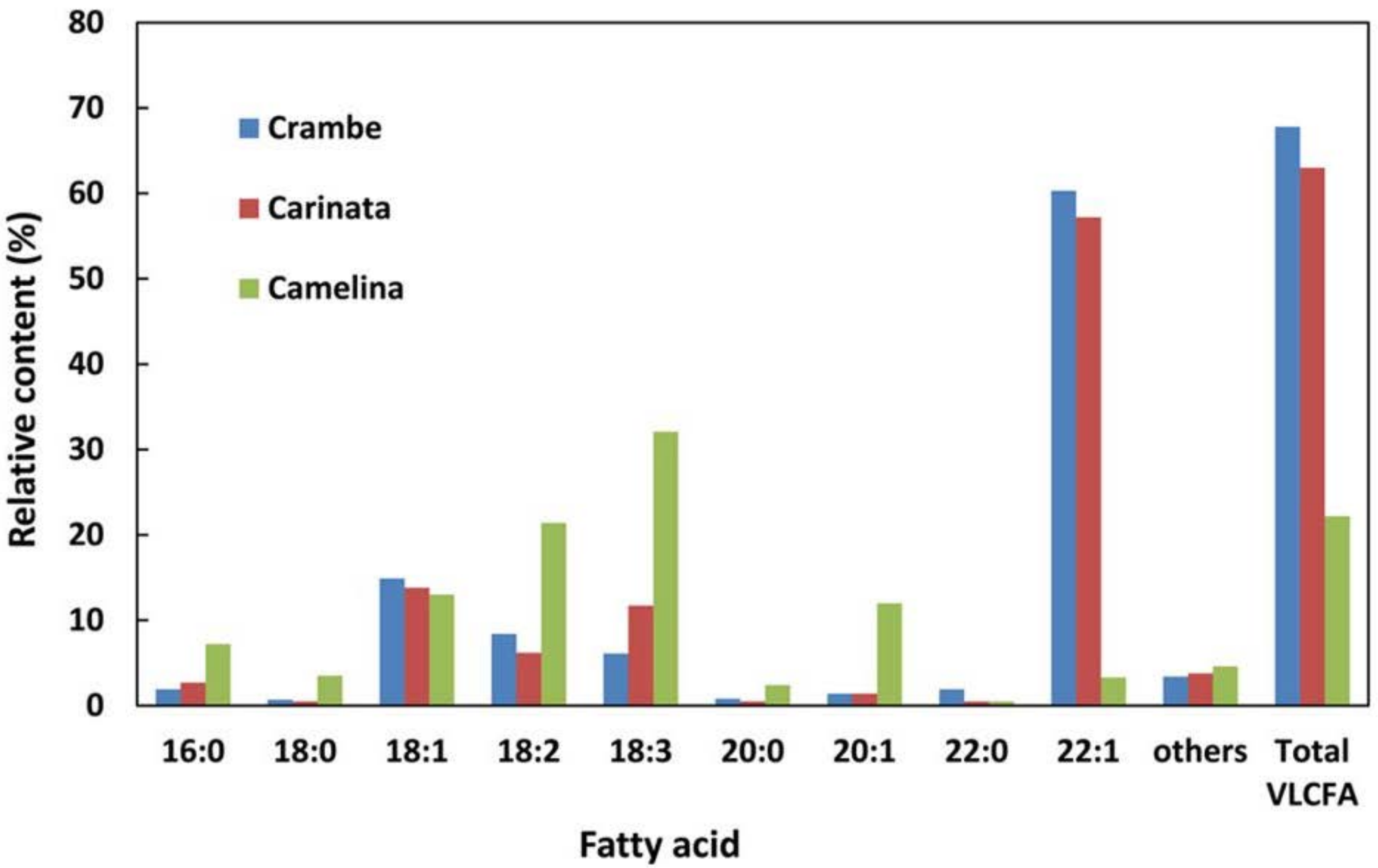
Challenge is the cost of the feedstock

Regional (niche) opportunities with fats, oils, greases (FOG)

NAABB data

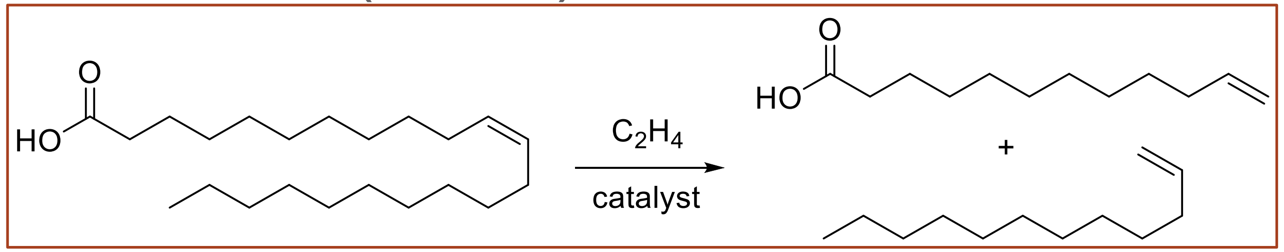
What can we learn from fuels produced today?

1. Diesel in direct competition for lipids
2. Producers look for higher lipid supply "as the world needs more protein oils come along for the ride and will need a home")
3. New feedstocks looked at by USDA – carinata – could change landscape
4. Feedstock cost is near the fuel cost
5. New chemistry to jet fuel possible



Soybean spot price = $2.12 / gal
jet fuel spot price $2.20 / gal

Larger chain length may be preferred when hydrocracking, or perhaps there is a role for metathesis (below)



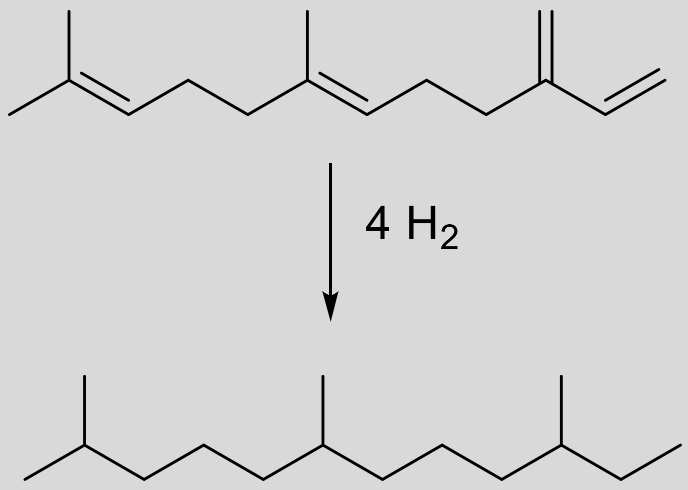
Farnesane, approved as a 10% blend, was led by Amyris and Total

hydrothermal pretreatment → soluble sugars → fermentation

H_2O_{SC}

Cane juice

Sesquiterpene



Farnesene

Farnesane

Renmatix

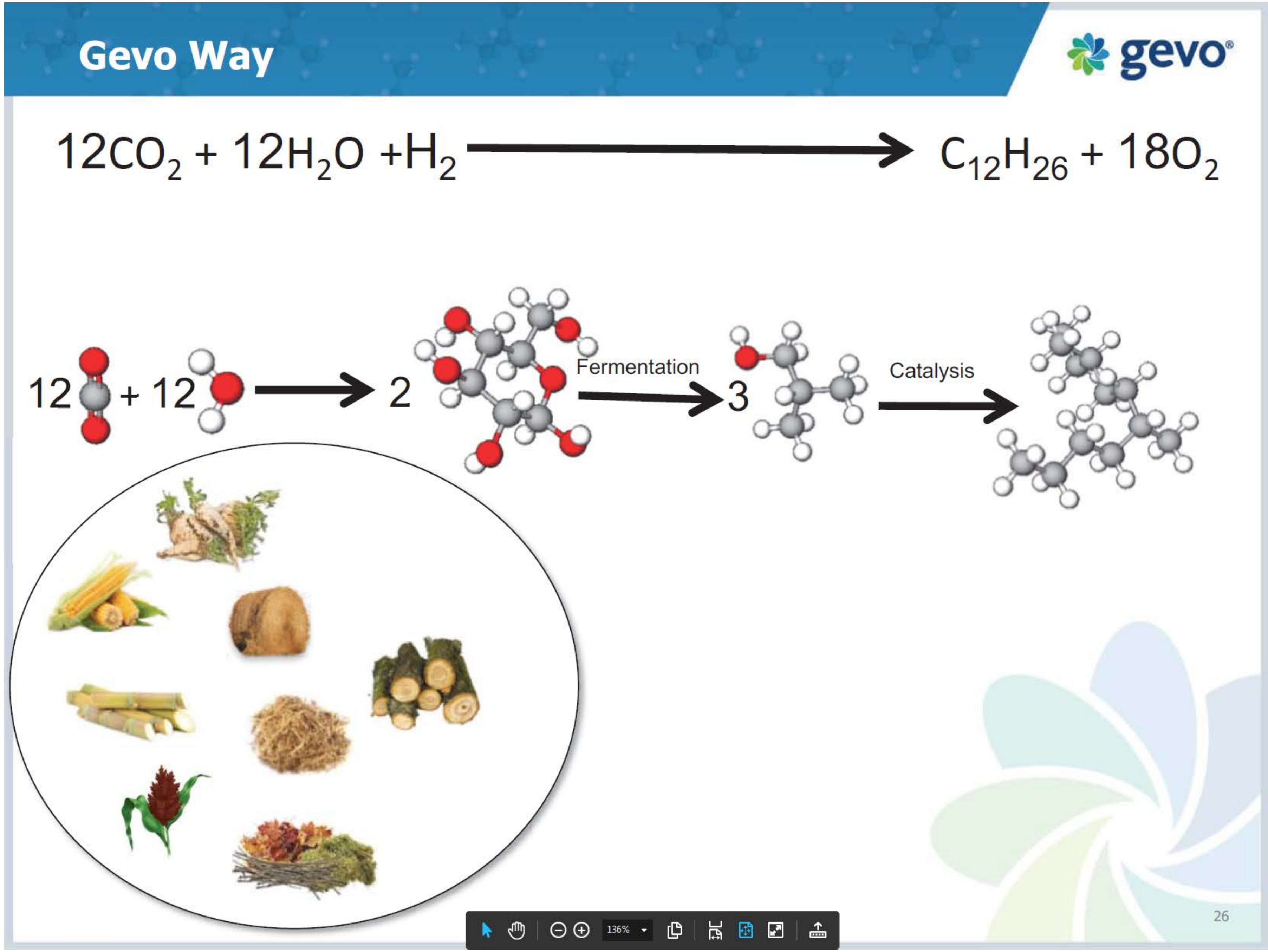
AMYRIS

TOTAL

Jet fuel state of technology – Total (refiner)
- Total stake in Amyris, Joint venture (75/25)
- Total stake in Renmatix (sugar source)

Cost: In 2015 Amyris stated farnesene production cost of \$1.75/L (\$6.62/gal)

Alcohol to jet, using iso-butanol, was led by Gevo and approved as a 30% blend

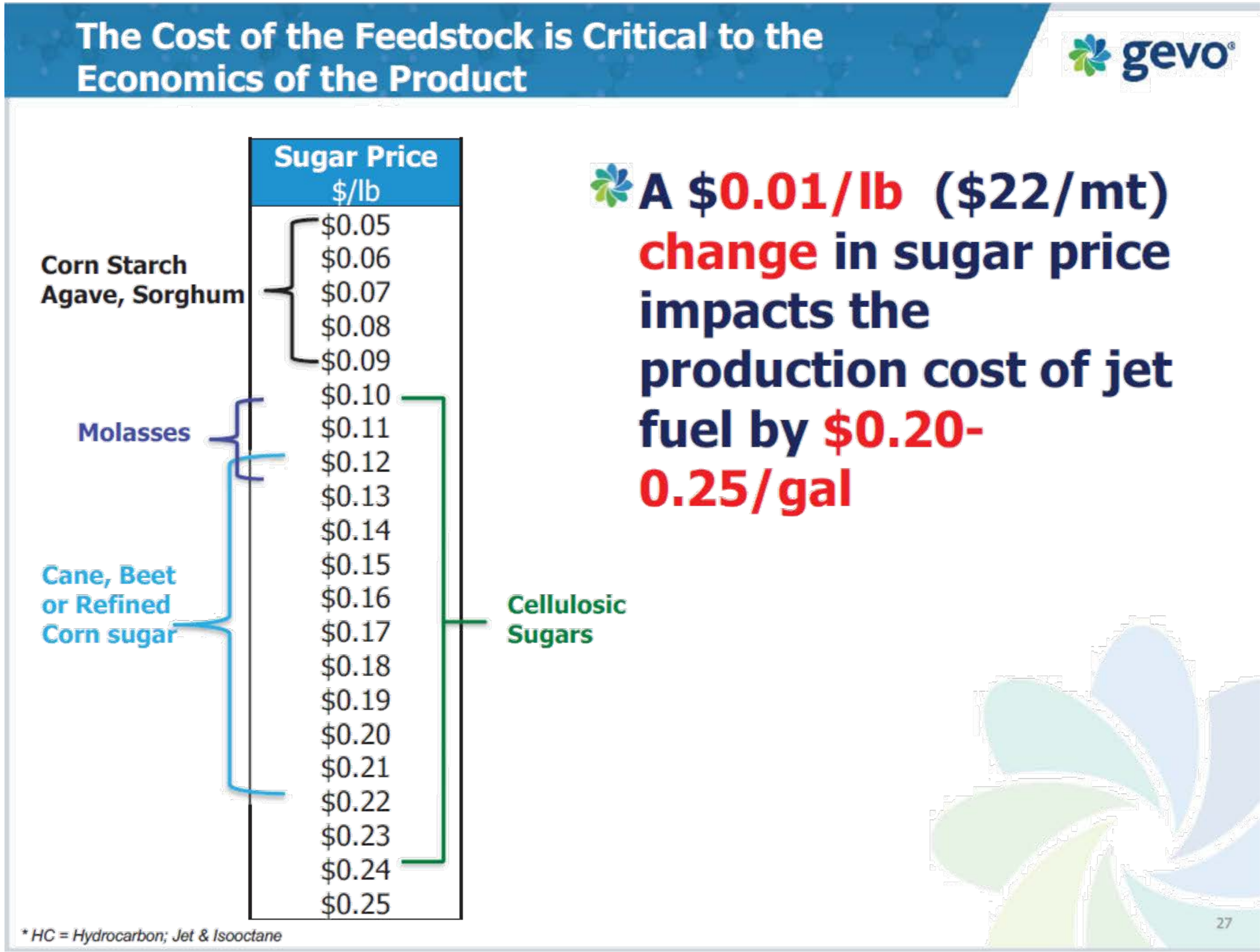


Carbon length
Starting with isobutanol, grow carbon chain by 4, 8, 12 carbon

Challenge
Availability of isobutanol

Unknown
Lower cetane than typical in kerosene

Sugar cost has large impact on fuel cost



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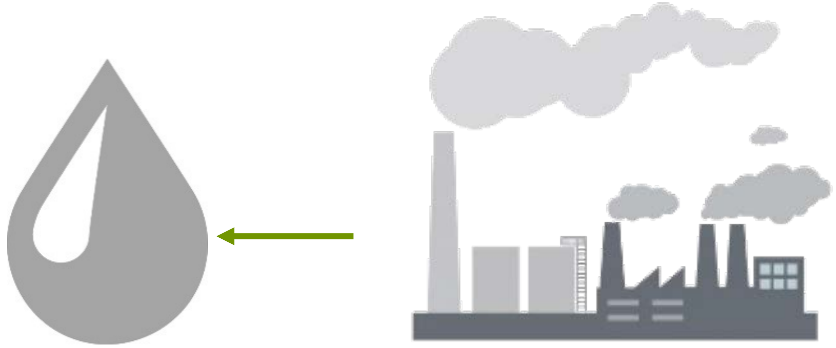
LanzaTech successfully extended alcohol to jet to include ethanol and increased the blend to 50%



Industrial waste gas provides a low cost route to ethanol

Ethanol

↓

Dehydration → Oligomerization → Hydrogenation → Fractionation

↓

Synthetic paraffinic kerosene (ATJ-SPK)

LanzaTech
首钢朗泽
Shougang LanzaTech
virgin atlantic
BOEING
HSBC
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
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Source: LanzaTech

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PNNL developed the catalyst technology for converting alcohols to targeted fuel molecules

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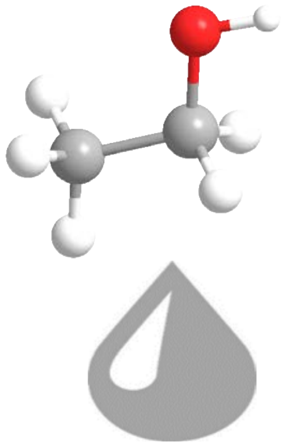
Alcohol to jet (ATJ) ASTM D7566 Annex A5 approved April 1, 2018 for 50% blend

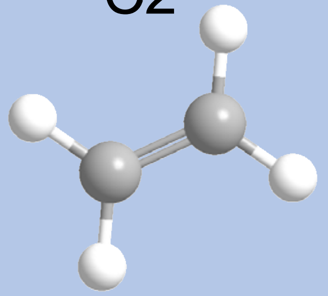
alcohols → 1. dehydration 2. oligomerization 3. hydrogenation 4. fractionation → Iso-paraffins



Ethanol

→

C2

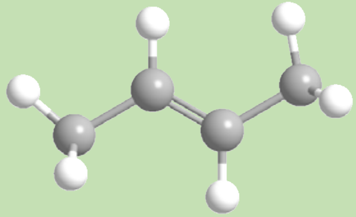


Dehydration

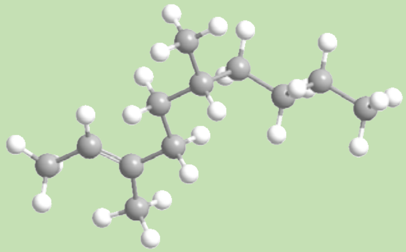
175 – 250 °C
(HZSM-5)

→

C4-rich



C12-rich



Oligomerization

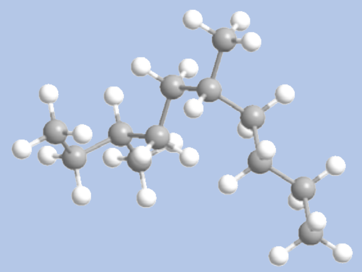
40 - 200 °C
(catalyst)

Lilga et al. US 9,932,531

Flexibility: up to 85% in jet range

→

C12-rich



Hydrogenation

Ni or Pd
catalyst

only 1 double bond in oligomer

→ Fractionation

↓

Jet & diesel fuels

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The fuel is exceptional high in quality and the technology is flexible to product output

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Ethanol to Gasoline (61666-113-D1H)

- RON = 85
- MON = 81
- Final Octane (R+M)/2 = 83

Ethanol to Jet (61666-107-ETJ-FIN)

- Highly energy dense (density 0.782, similar to Jet A)
- Safe to handle (Flash Point 56°C, ASTM D1655 requires > 38°C)
- Safe to use (Low Freeze (Point < -70°C, ASTM D1655 requires < -40°C)

Ethanol to Diesel* (61666-77-H7)

- High Cetane = 53.6 (Diesel fuels are typically in the 40-55 range)
- Can use in extreme environments like the arctic
  Cloud Point = -60.1°C Pour Point = -66.0°C

✓ 98% isoalkane

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Enough fuel could be made to replace all the jet fuel used globally

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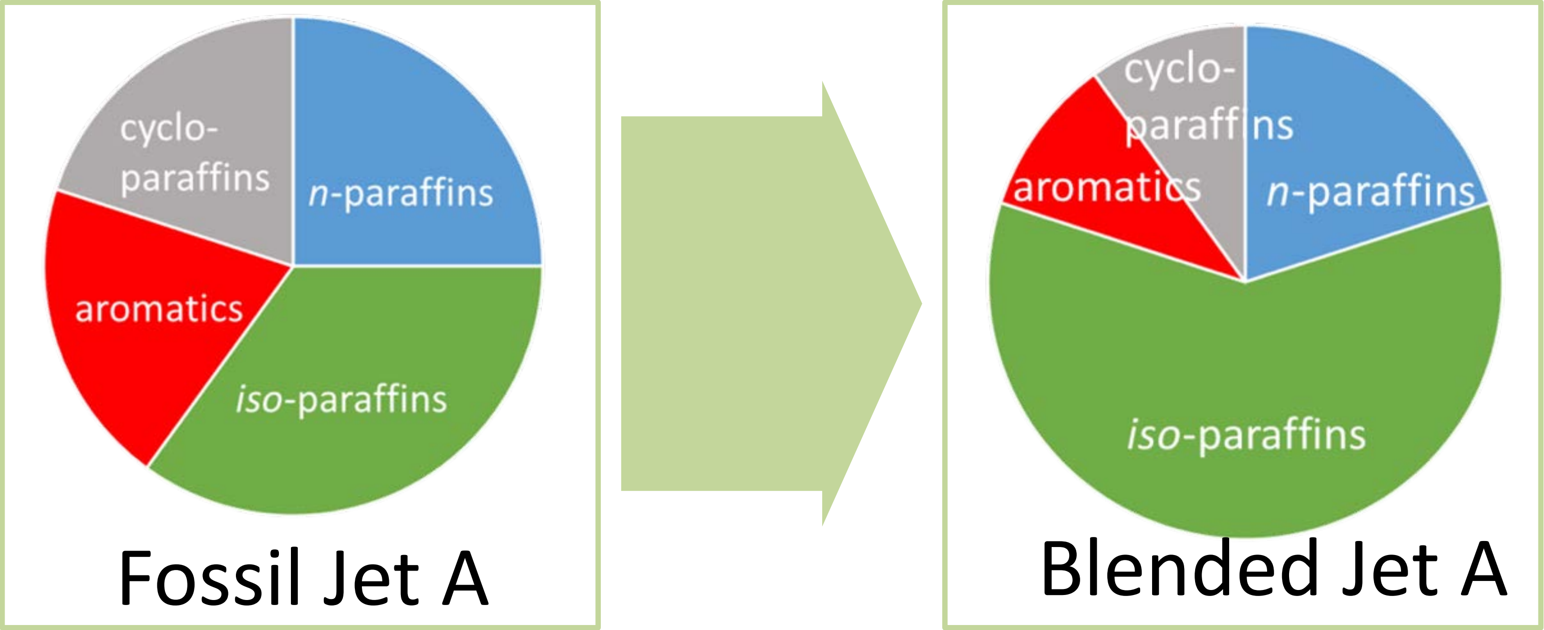
Fuel performance benefits extend to the environment

More efficient engines create more contrails

Mach 0.76 at 35,000 ft
2x engines
92% LanzaTech, 8% aromatics

LanzaTech

Common themes for iso-alkane fuels: (i) improve fuel by diluting aromatics (ii) source from waste C

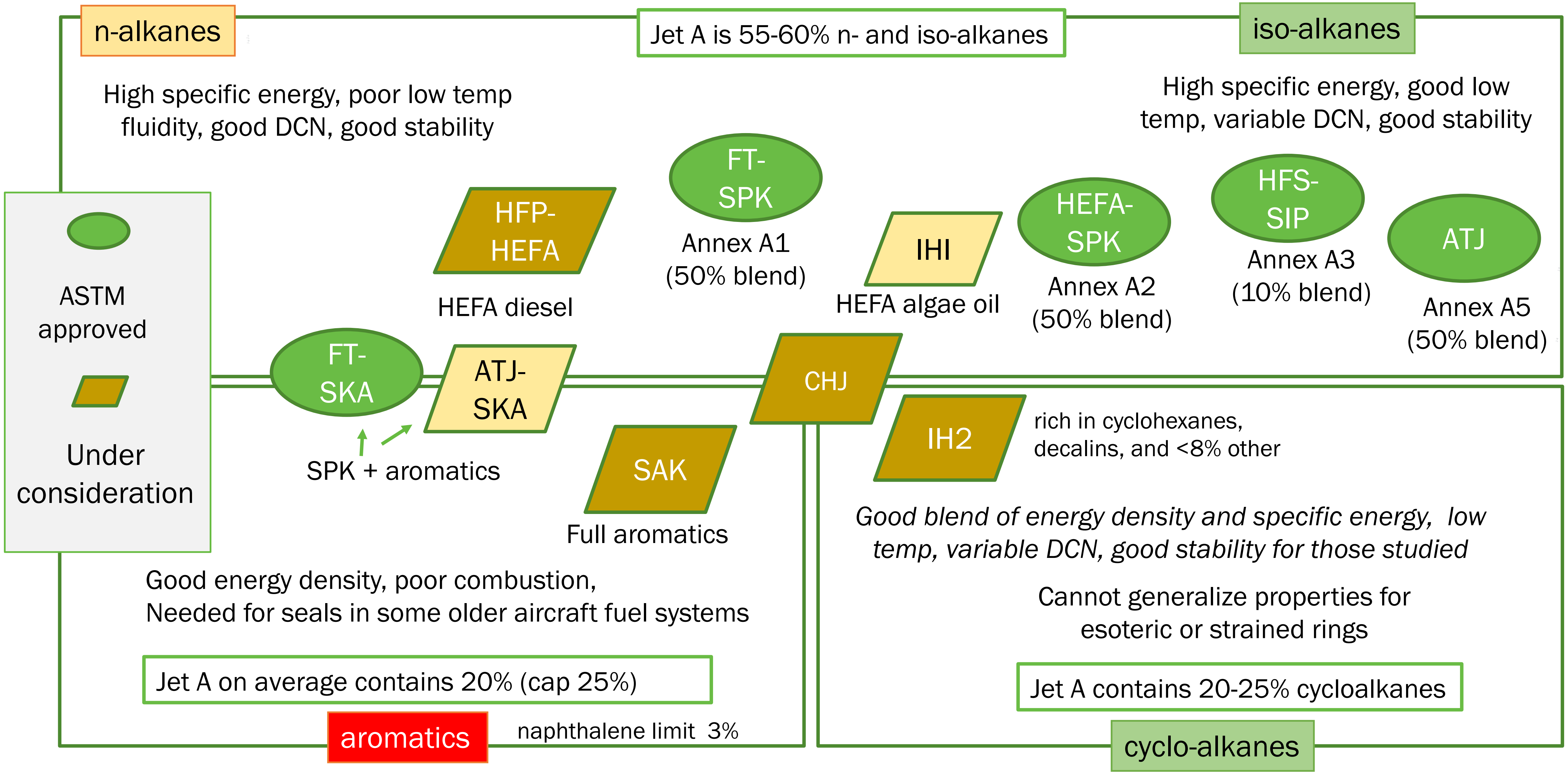


Make it better by only producing hydrocarbons that contribute to key fuel properties

Ethanol-jet reduces cost by recycling industrial gas

To reduce cost HEFA uses waste fats

Additional fuels are working through ASTM D4054 that have cycloalkanes and aromatics



Even if Tier 3 and 4 tests are limited the ASTM process takes money, material, and time

Jet Production	2014-PNNL Lab 2015-Lab & Demo 2016-Lab & Demo	Sep 2015 1 gallon Apr 2016 5 gallons Aug 2016 4000 gallons
ASTM D7566 Specification Testing	May 2014 - Sep 2016	Passed Tier 1 >30 properties
ASTM D4054 Fit for Purpose Testing	Mar 2016 - Sep 2016	Passed Tier 2 >2500 tests >100 properties
Phase 1 ASTM Research Report	Sep 2016	>90 pages >100 figures and graphs
OEM Review	Jan 2017 - July 2017	34 pages of comments NO TIER 3 & 4 REQUIRED!
Phase 2 ASTM Research Report	Sep 2017	>105 pages >120 figures and graphs
OEM & FAA Review	Sep - Oct 2017	Approved no changes
ASTM Aviation Ballot	D02.J0 Oct - Nov 2017	Passed with NO NEGATIVES
ASTM Fuel Ballot	D02 Feb - Mar 2018	Passed with NO NEGATIVES
ASTM D7566 Ethanol ATJ Annex A5	D7566 Publication Apr 2018	Published International Standard

- 2500 tests on >100 properties all put into context of current fuels
- Fuel broad boiling range similar to HEFA (rather than ATJ-isobutanol)
- 1.5 years after the research report was written

Jet fuel can burn cleaner and have higher energy content than what we get from petroleum

To reduce soot

- Limit aromatic content (and S)

To increase energy content

- Increase iso-alkanes (specific energy)
- Increase cycloalkanes (energy density)

To maintain low temperature fluidity

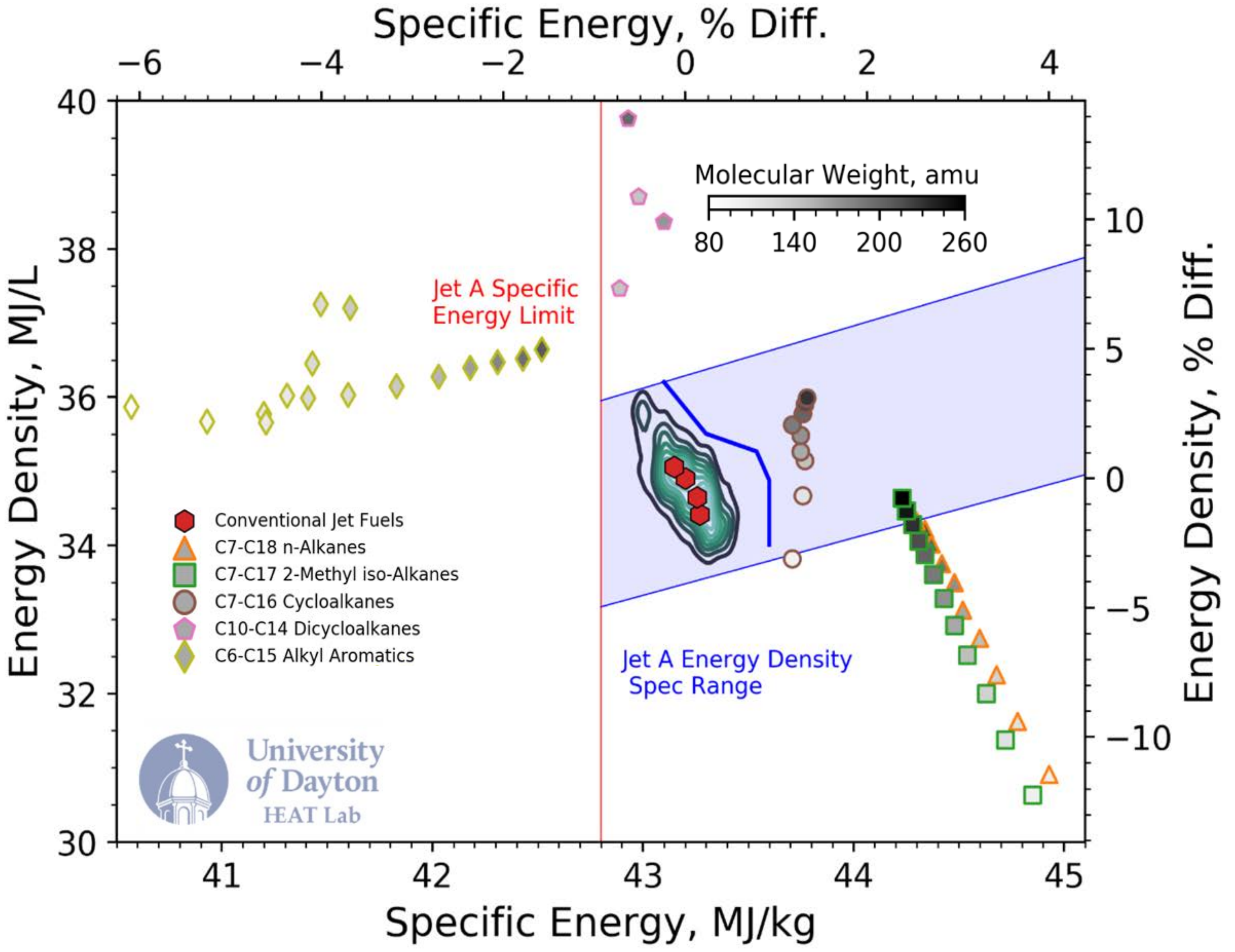
- control level of branching in alkanes

To achieve thermal stability

- No metals, no heteroatoms, no compounds that gum or break down (e.g., olefins)*

To maintain seal swelling in older planes

- Consider specific cycloalkanes**



*Research needs: will highly strained cycloalkanes have required thermal stability?

** Boeing has shown seal swelling from decalin, a 10 carbon fused cyclohexane

Three broad routes to iso-alkanes

Reducing cost

- Lowest cost feedstock
- Solve another societal problem
    - improve land quality carinata and other oil seeds (extra cropping)
- Use current infrastructure
    - Reduce capital
    - use current infrastructure
- Other costs
    - Sugar cost,
    - fermentation cost
    - New hybrid approaches

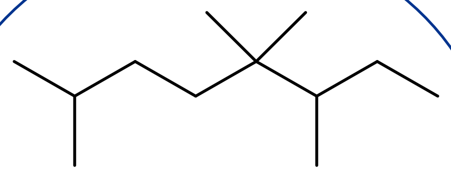
Isoalkane production

crack large molecules

HEFA
(hydrotreat and hydrocrack/ isom esters and fatty acids)

FT liquids
(hydrotreat residual oxygenations and hydrocrack/ isomerize liquids/waxes)

Other routs
hydrothermal processing
metathesis (on carinata)



control jet vs diesel
limit naphtha
control branching

build up small molecules

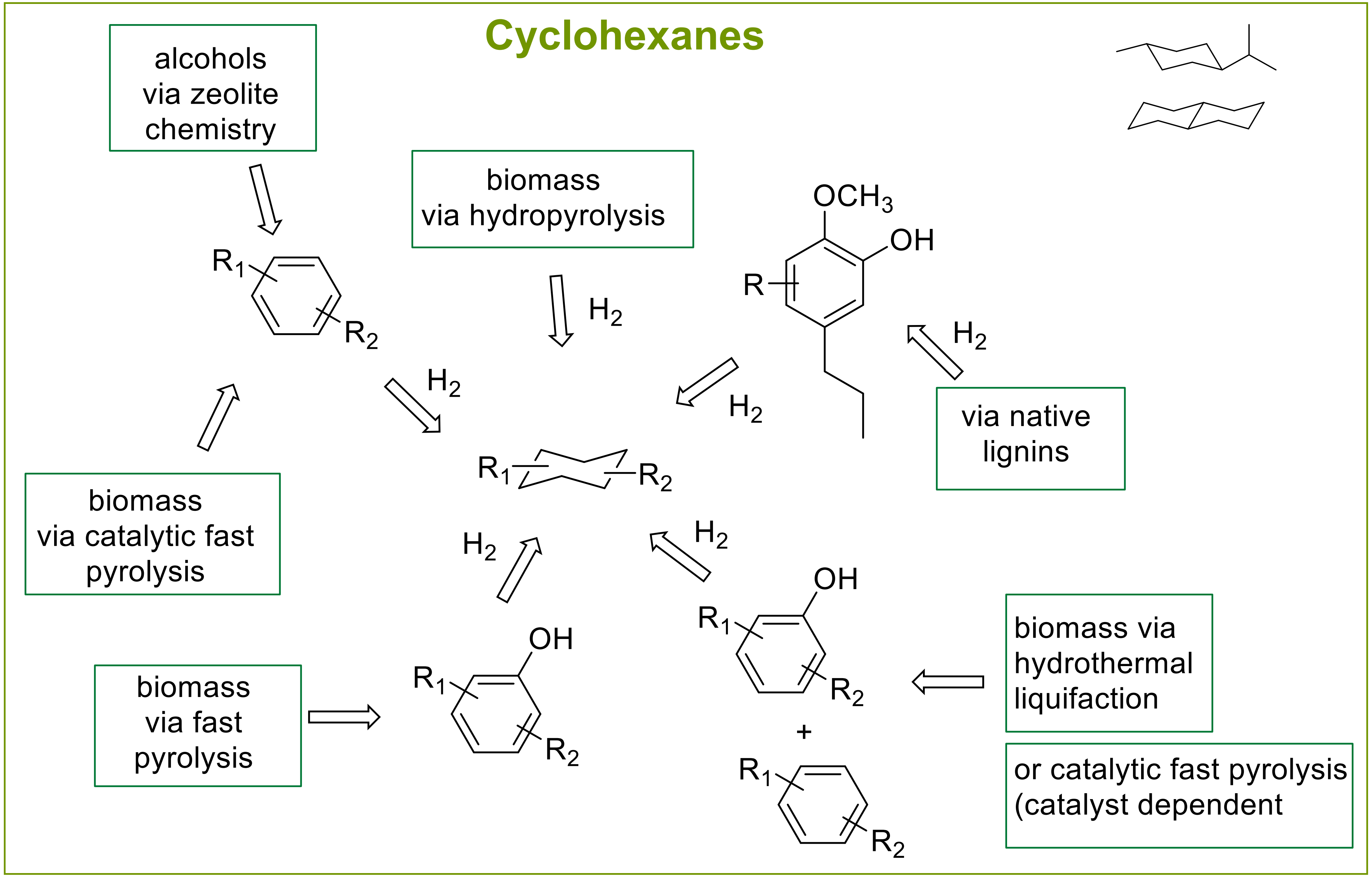
ATJ
(oligomerize alkenes, hydrotreat (1 mole H_2)
ethanol – light branching
i-butanol – heavier branching

potential routes
dimerize/hydrotreat isoprene
oliogomerize alcohols
carbonylation of furans/ hydrotreat etc.

SIP
(hydrotreat farnesene 4 moles H_2)

fermentation

Alkyl-substituted cyclohexanes can be sourced from aromatics and phenols – but is there value?

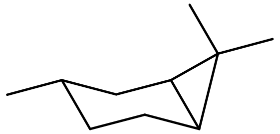


Reducing cost

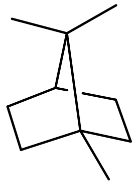
- Lowest cost feedstock
  - Use lignin leaving sugars for products
- Solve another societal problem
  - Convert wet waste to higher value jet fuel rather than biogas
- Use current infrastructure
  - Use infrastructure in place for guayule harvesting & preprocessing
- Other costs
  - Separations
  - Replacing energy value of lignin
  - Hydrogen

Other ring structures (ring sizes and fused rings) are available through fermentation or catalysis

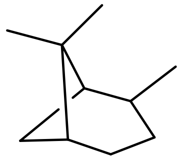
Hydrogenated Terpenes



carane

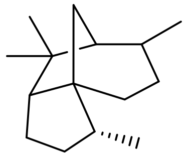


camphane

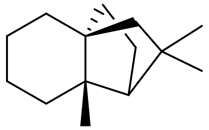


pinane

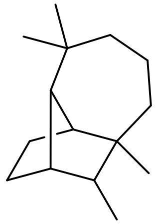
Hydrogenated Sesquiterpenes



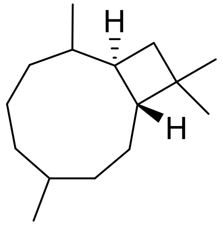
alpha-cedrane



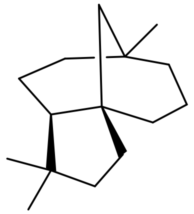
alpha-neoClovane



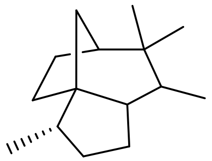
longifolane



beta-carphyllane

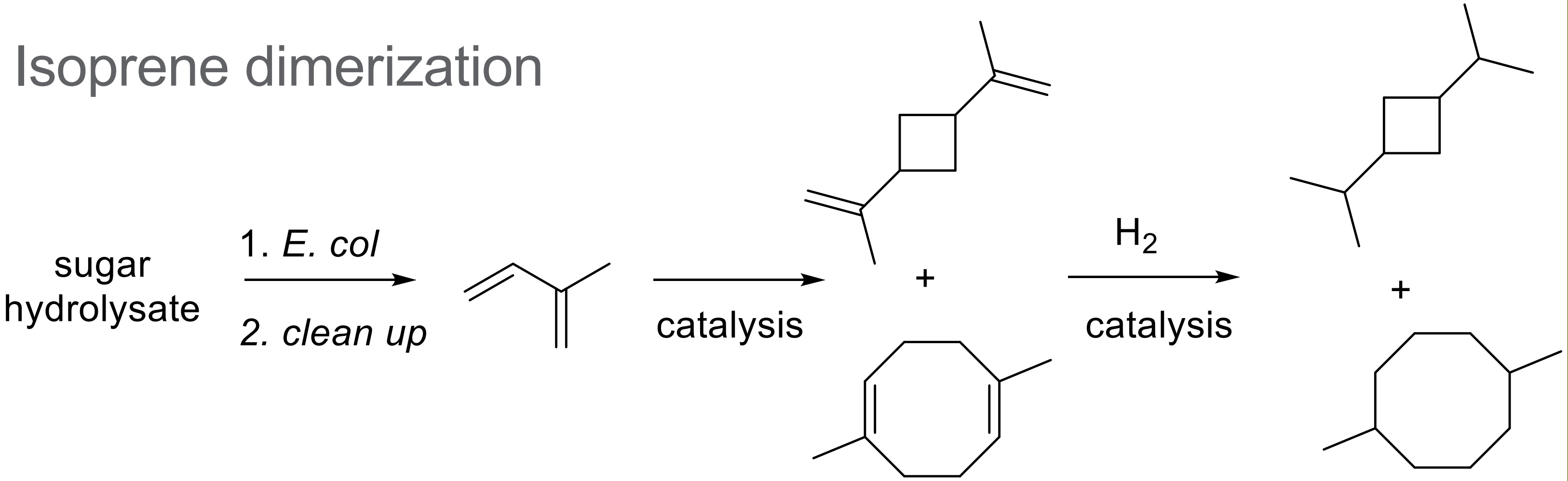


clovane



epi-isoziaene

Isoprene dimerization



Reducing cost

- While there are may routes, not sure if the cost structure works for any
- Isoprene is intriguing

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Three things from this talk

- We must reduce cost
- There are environmental benefits for lowering the aromatic and sulfur content of jet fuel
  - Strategic effort on isoalkanes and cycloalkanes
  - Science gaps on cycloalkanes
- Jet fuel properties “energy content, low temperature fluidity, thermal stability”

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Thank you

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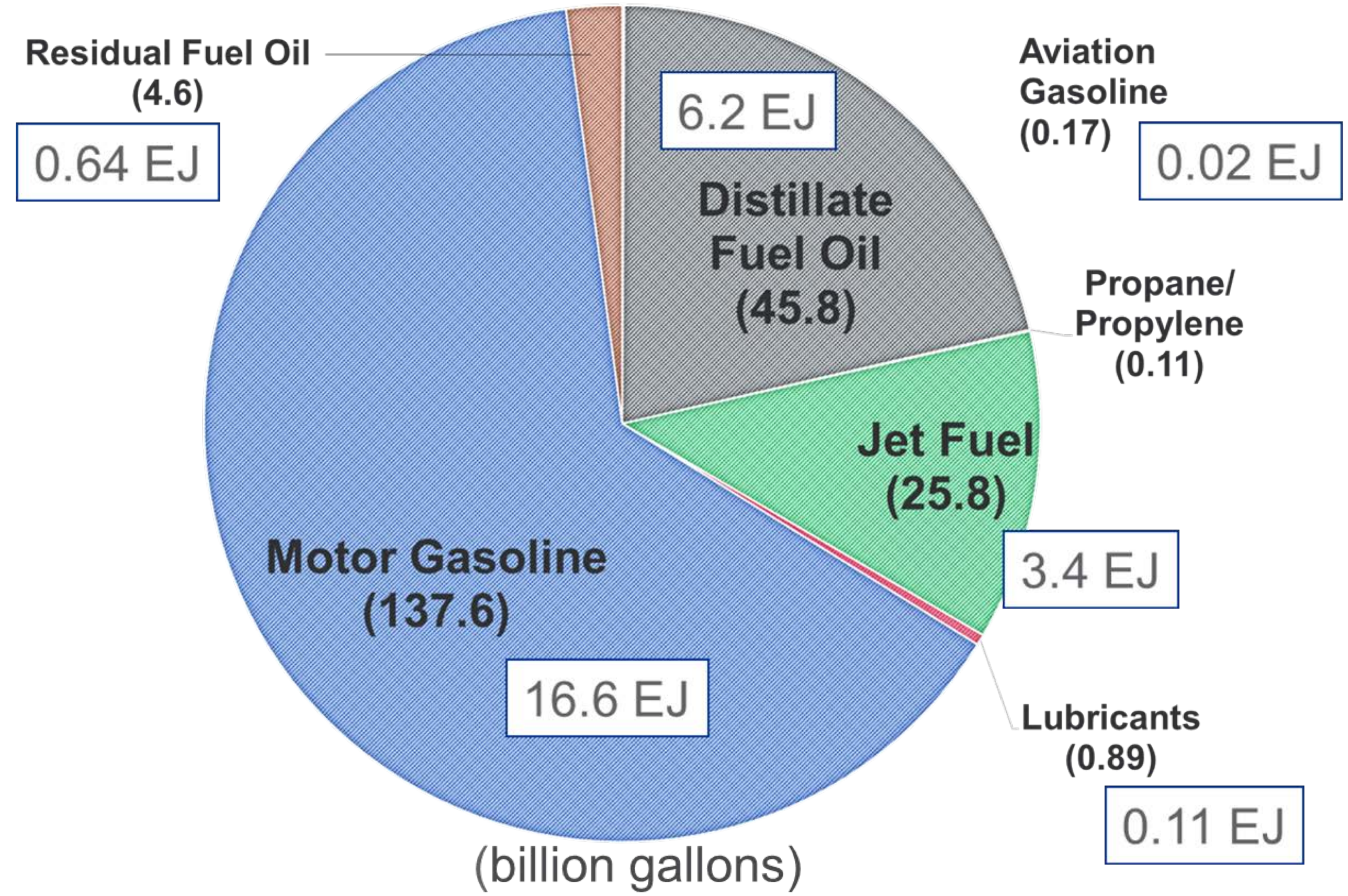
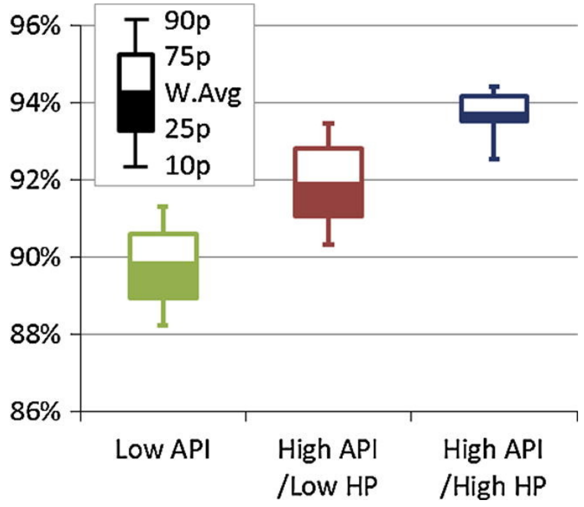
U.S. uses 27 EJ of petroleum products, 3.4 EJ of jet fuel

Petroleum products (215 billion gallons)[1]

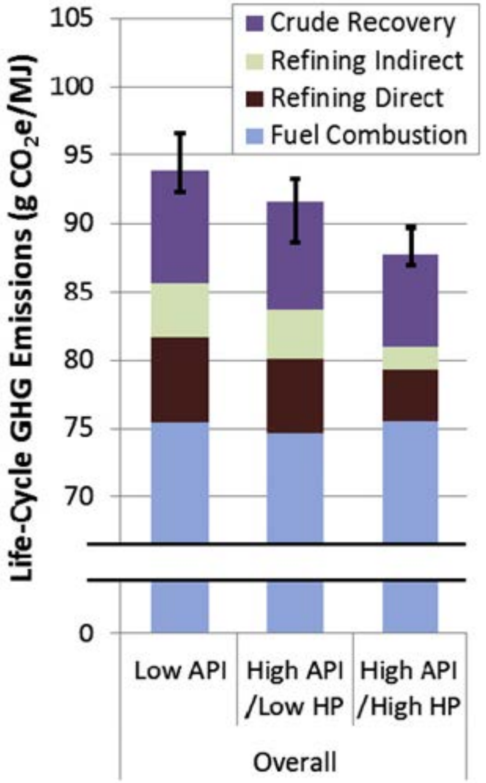


Petroleum refinery[2]

efficiency



CO_2



- 30 EJ of primary energy needed
- Life cycle = 90 g CO_2/MJ

[1]https://www.eia.gov/totalenergy/data/monthly/index.php#petroleum
[2] Han et al. Fuel 157 (2015) 292-298 (https://doi.org/10.1016/j.fuel.2015.03.038)

U.S. and world Jet fuel demand is growing

- Producing jet fuel from renewable carbon makes sense because opportunities to further improve fuel economy or electrify are limited

How will we meet future demand?