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PNNL-SA-106313

Renewable routes to jet fuel

JOHNATHAN HOLLADAY, KARL ALBRECHT, RICH HALLEN

Japan Aviation Environmental Workshop—Innovative concepts for carbon neutral growth
5 November 2014

Outline

- Jet fuel
- Pathways
  - Fuel properties
  - Pathways correlate to product and feedstock
  - Energy carriers: syn gas, fats, sugars, whole biomass
- Conclusions

Fuel characteristics

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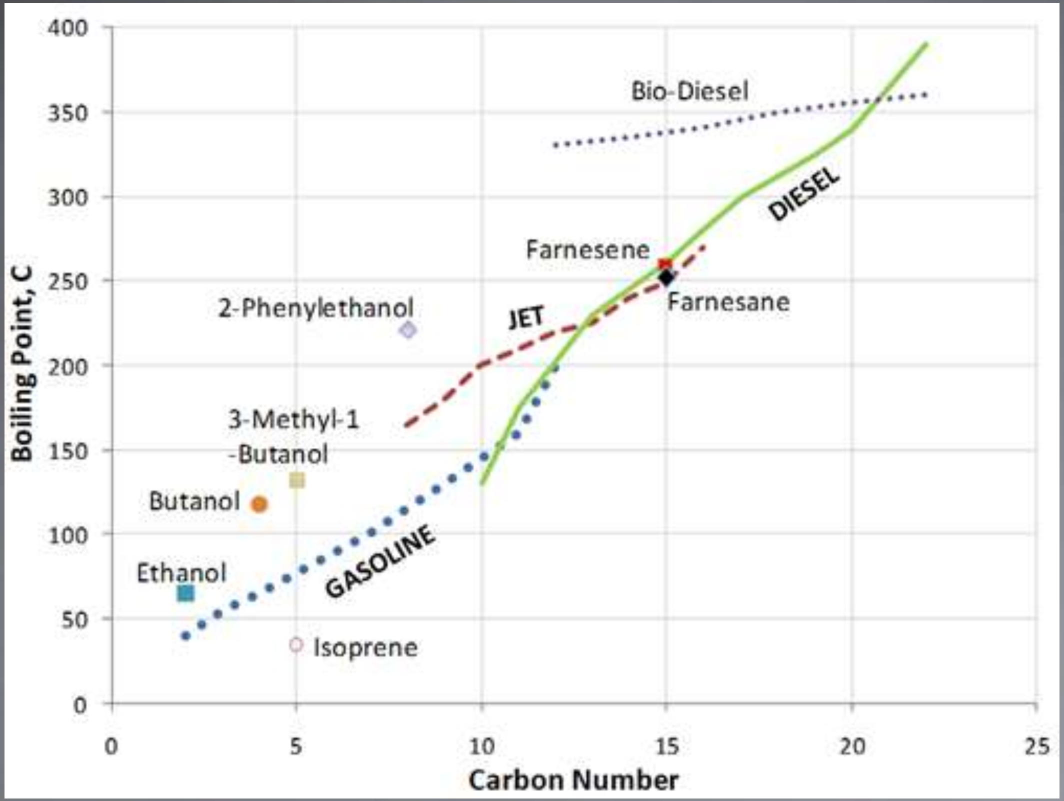
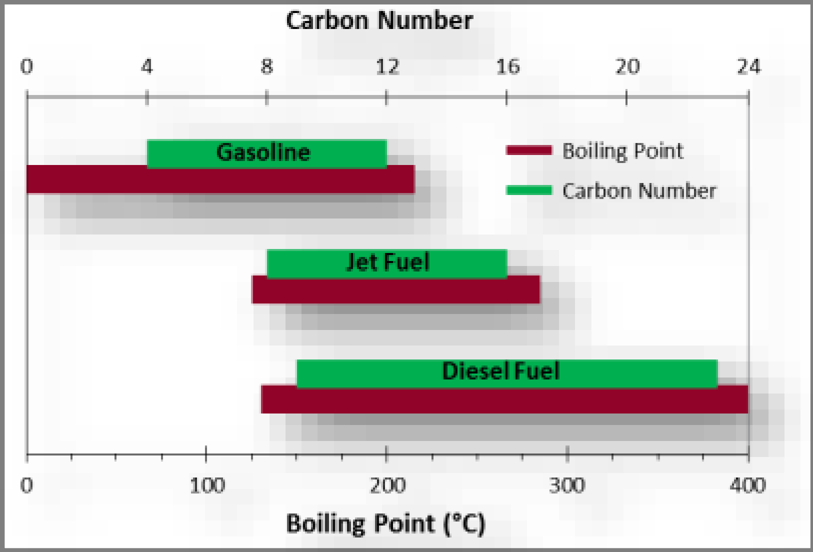
Desired Characteristics

- Miscible with petroleum-based fuels and transportable in current pipelines
- Meet performance & storability criteria designed for jet engines—it must be jet fuel
- Optimize desired hydrocarbon chain/boiling point for aviation (mid-distillates)



Lower cost
- **Reduce H_2 demand and pressure**
- **Improve product quality**



Compound classes in jet fuels

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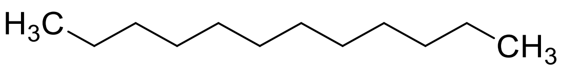
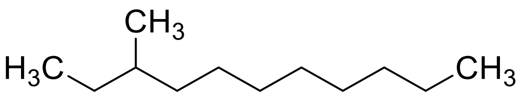
Ideal Carbon Length C8-C16

Paraffins

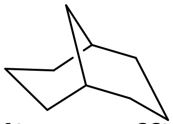
70 - 85%



Normal Paraffins



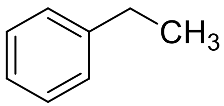
Iso-paraffins

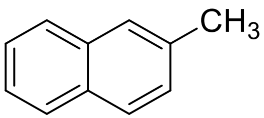


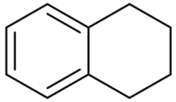
Cyclic Paraffins

Aromatic

< 25%

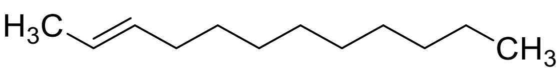


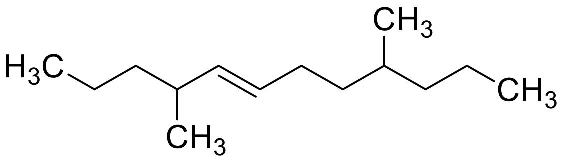




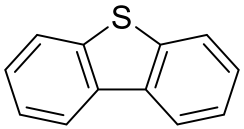
Olefins

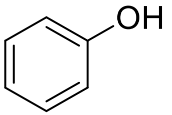
< 5%

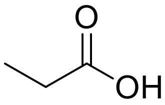




***S, N, O containing Compounds* < 5%**







We desire fuels with composition similar to above

(i.e. a replacement or "drop-in" fuel)

Typical petroleum jet fuel: JetA and JP-8

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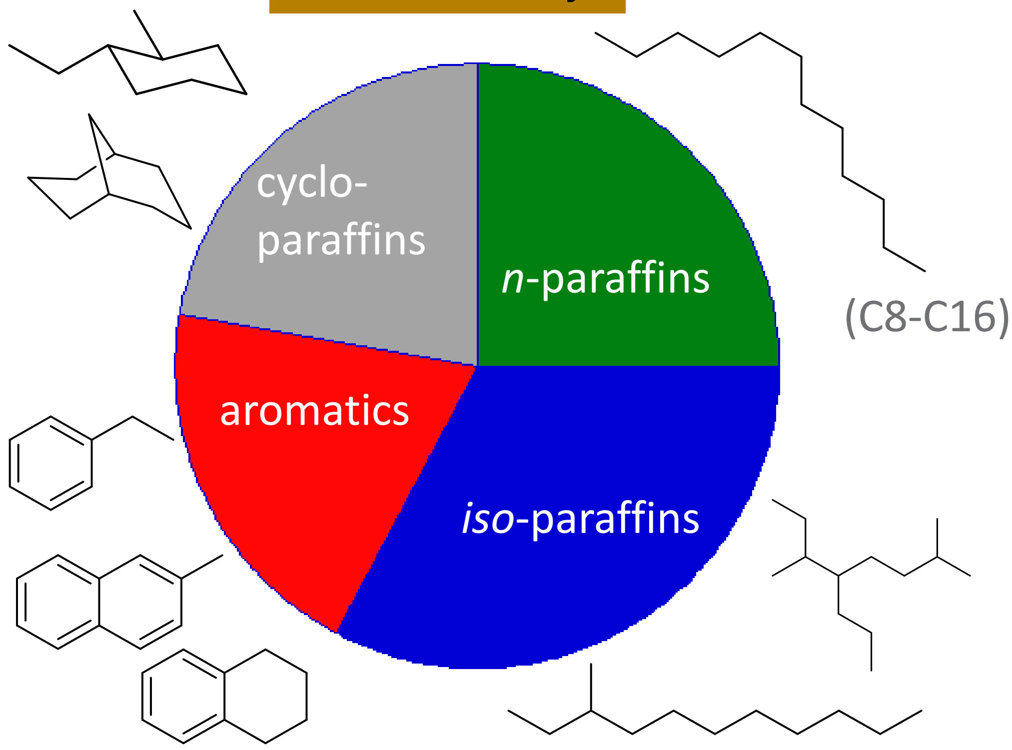
Ideal Carbon Length C8-C16

Fractions vary!



- Iso-paraffins and n-paraffins are good (Btu content)
- Aromatics are bad above certain amount (minimum needed to ensure seal swell)

- Jet is designed around propulsion system
- Hydrocarbon mixture gives properties needed
  - Energy density
  - Freeze point
  - Flash point
  - Lubricity
  - etc

Source: Dr. Timothy Edwards, Air Force Research Laboratory

Routes to fuels (energy carriers)

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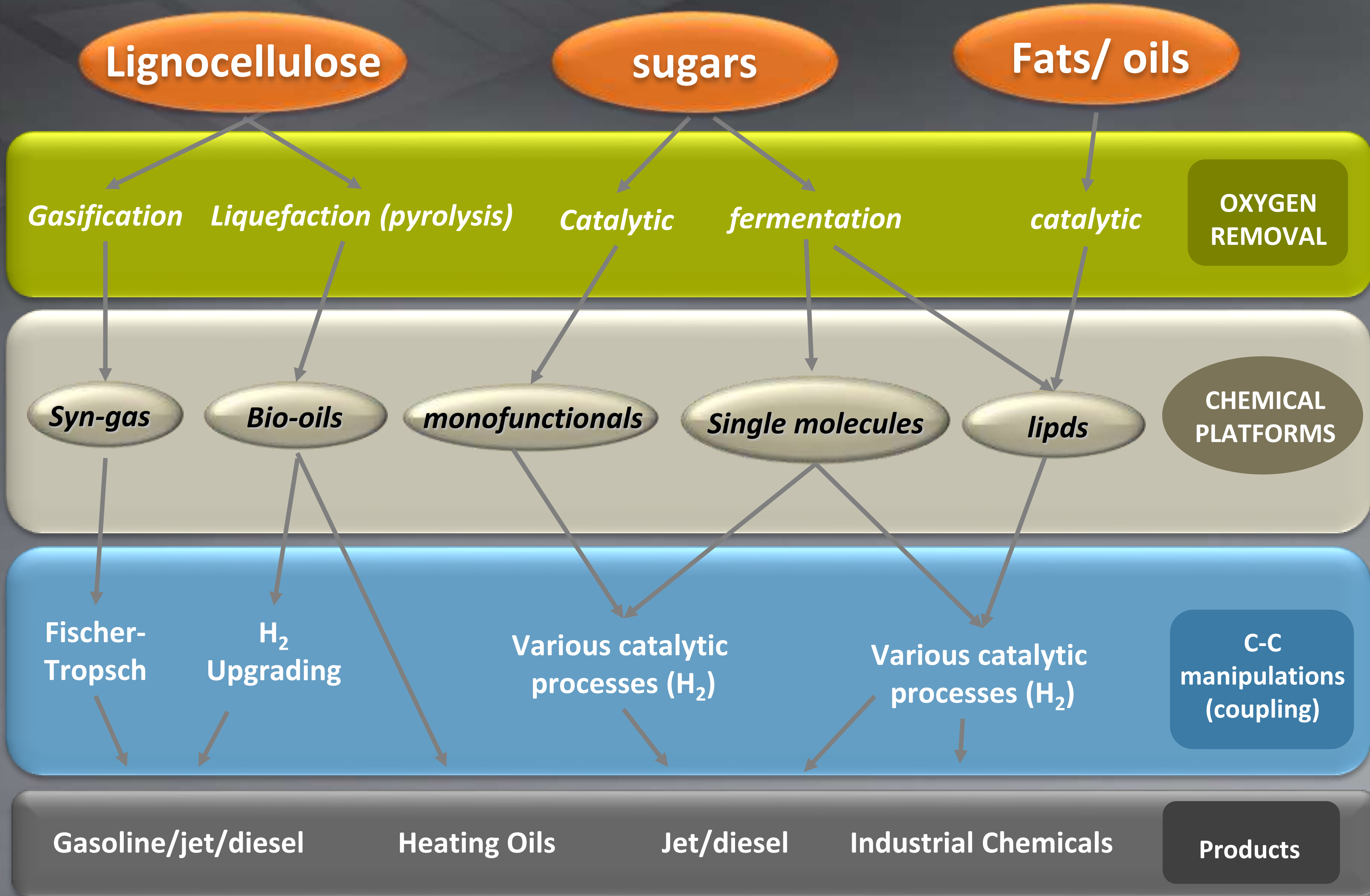

Optimal choices vary by region and are a function of feedstock and product slate

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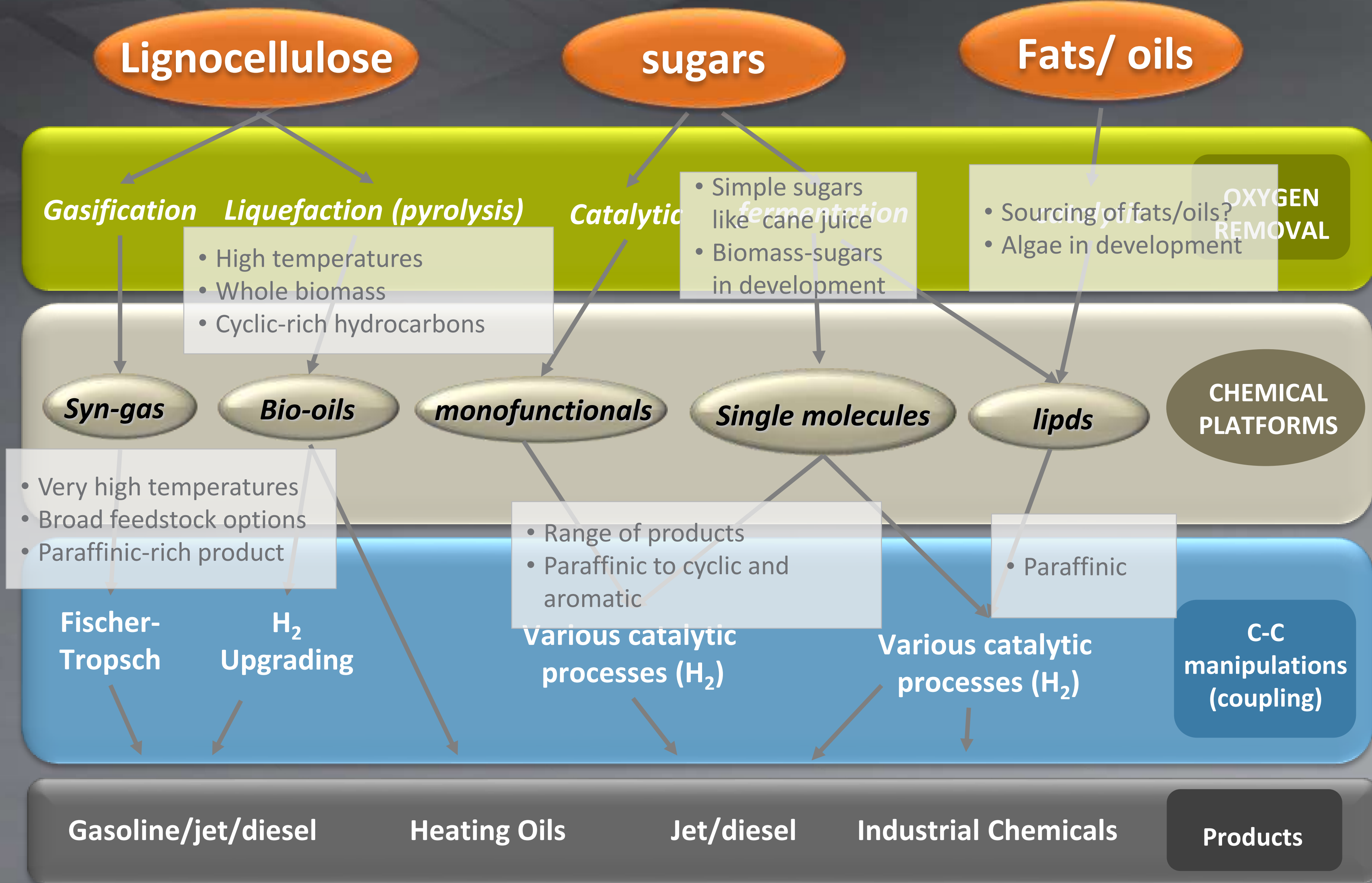

Fischer-Tropsch (FT) jet fuel

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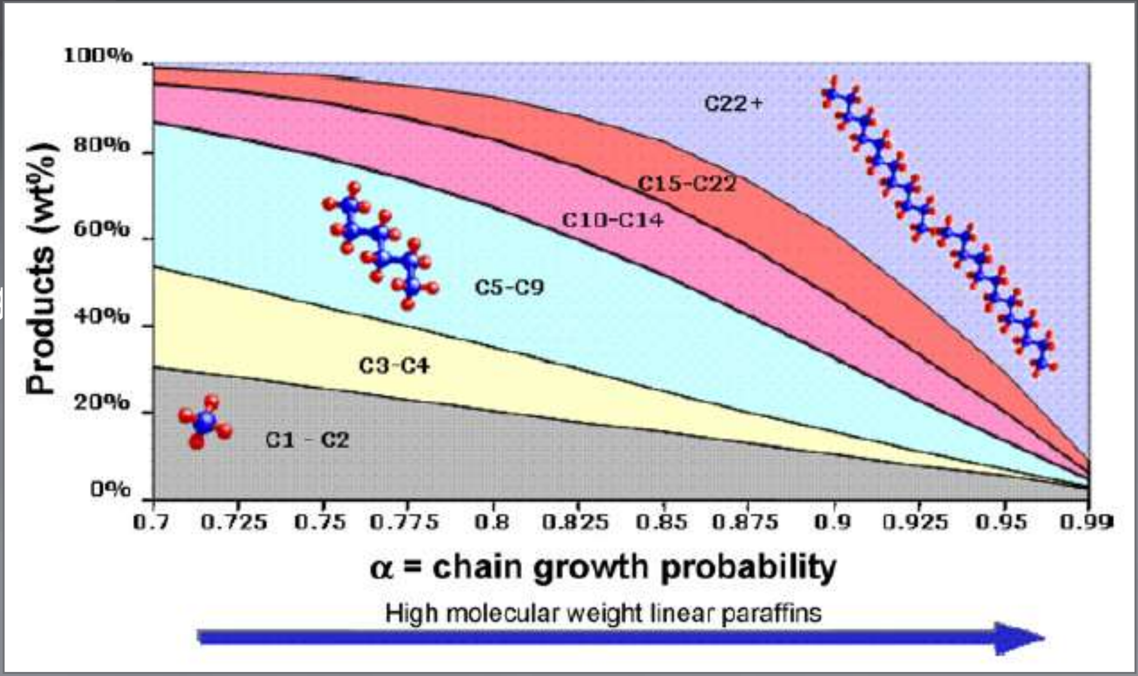
- FT converts syngas to fuel
- Approved for 50% blends
- Process is complex
  - Gasification (O_2 plant)
  - FT synthesis (C-C coupling, crackIng, isom)
  - Heat integration required
- Inefficiencies favor large scale
- Chemistry favors wax or methane

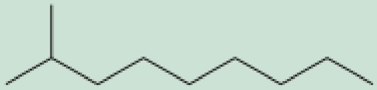


Perego, C.; Bortolo, R.; Zennaro, R., *Catalysis Today* **2009,** 142, (1,2), 9-16

$$nCO + (2n+1)H_2 \xrightarrow{} H—(CH_2)—H + nH_2O$$

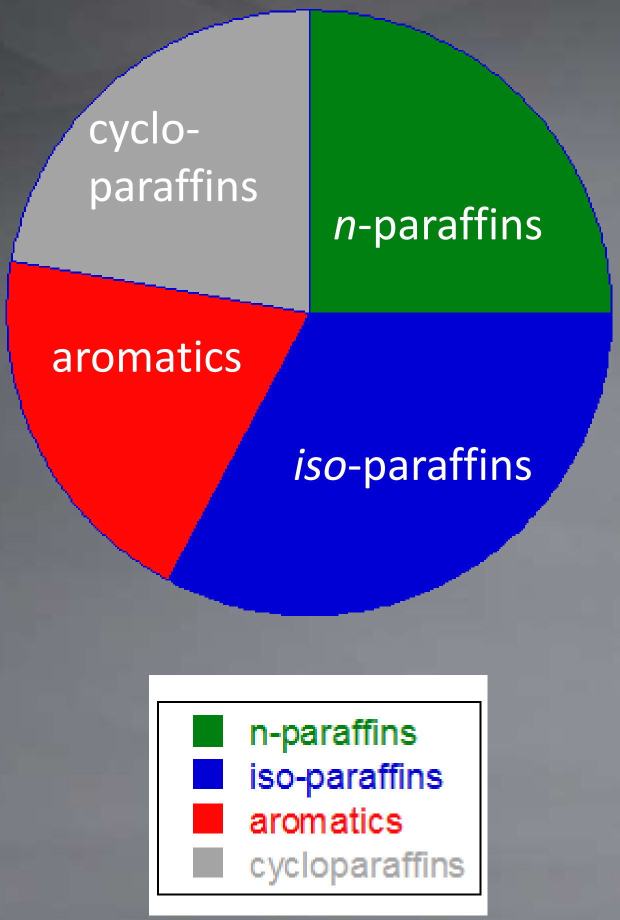
carbon monoxide | hydrogen | heat | paraffin (wax) | water (steam)

Hydrocracking and isomerization improves cold temperature properties

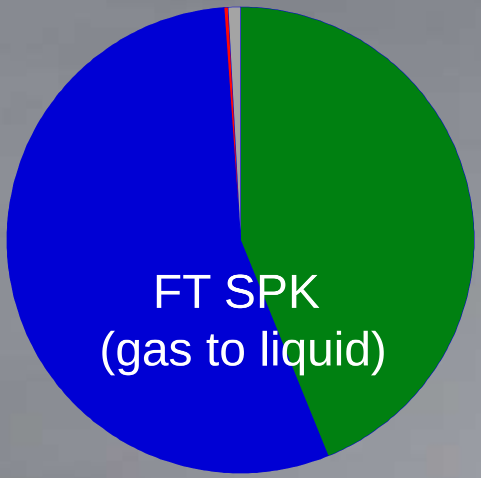
Freeze Point, °C					
$C_{10}H_{22}$	FP	$C_{12}H_{26}$	FP	$C_{14}H_{30}$	FP
	-30		-10		-5.5
	-72		-46		-26
Jet A	-40 (max)	Jet A1	-47 (max)		

FT Synthetic paraffinic kerosene (SPK) jet fuel

Jet A, JP-8



FT jet fuel
Approved for 50% blend



Feedstocks

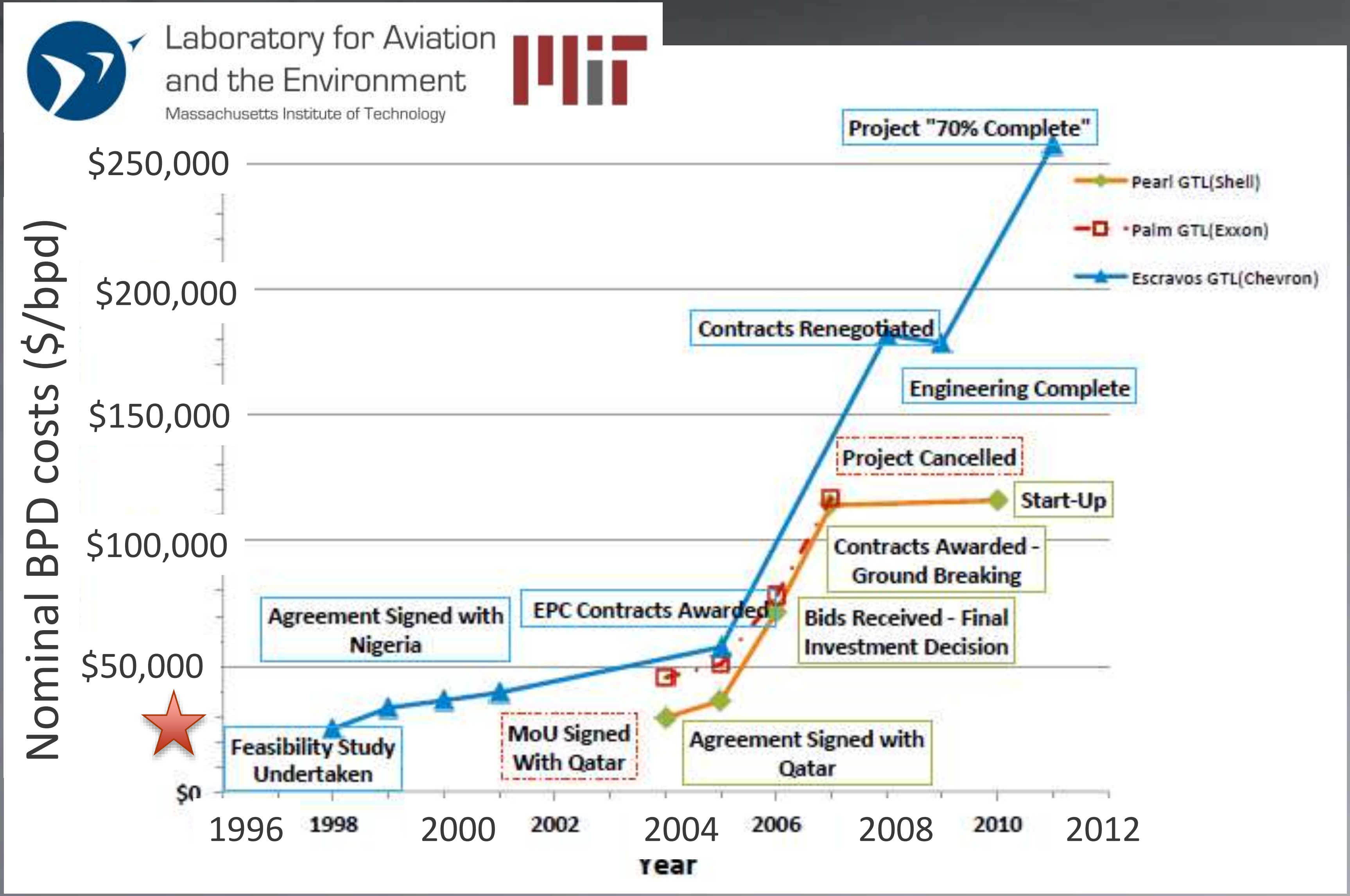
Dry biomass

Municipal solid waste

Source: Dr. Timothy Edwards, Air Force Research Laboratory

FT has a history of escalating capital costs

Robert Malina, Nov. 27, 2012



Capital cost perspective

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Some capital cost estimates in US$ per barrel per day ($/bpd)

- Greenfield refinery: $25,000-40,000/bpd
- FT (Biomass to liquid, 5,000 bpd plant): $68,000 — 408,000/bpd Robert Malina
- Corn ethanol: $16,000 — 34,000/bpd http://www.usda.gov/oce/reports/energy/EthanolSugarFeasibilityReport3.pdf
- Cellulosic ethanol: $77,000 — 285,000 (US Department of energy)

U.S. Department of Defense awards

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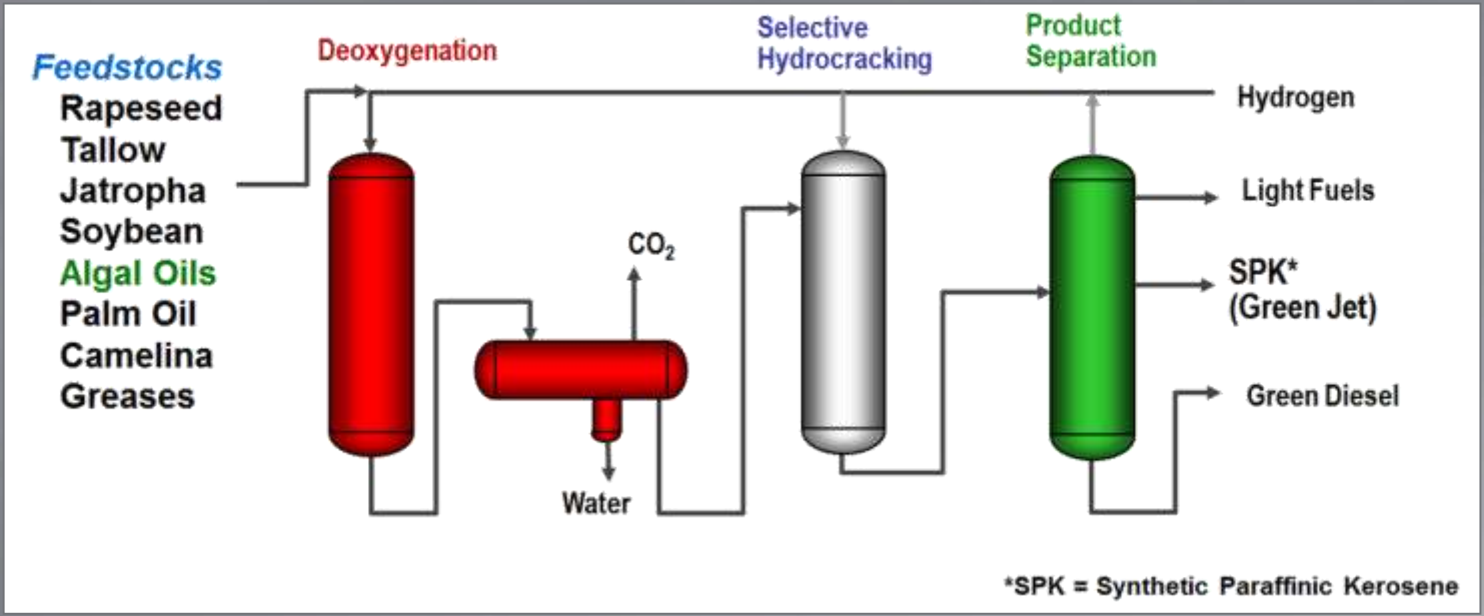
Project	Location	Feedstock	Capacity (million gallons/year)
Fulcrum	McCarran, NV	Municipal solid waste	10
Red Rock	Lakeview, OR	Woody biomass	12
Emerald	Gulf Coast	Fats, oils, and greases	82

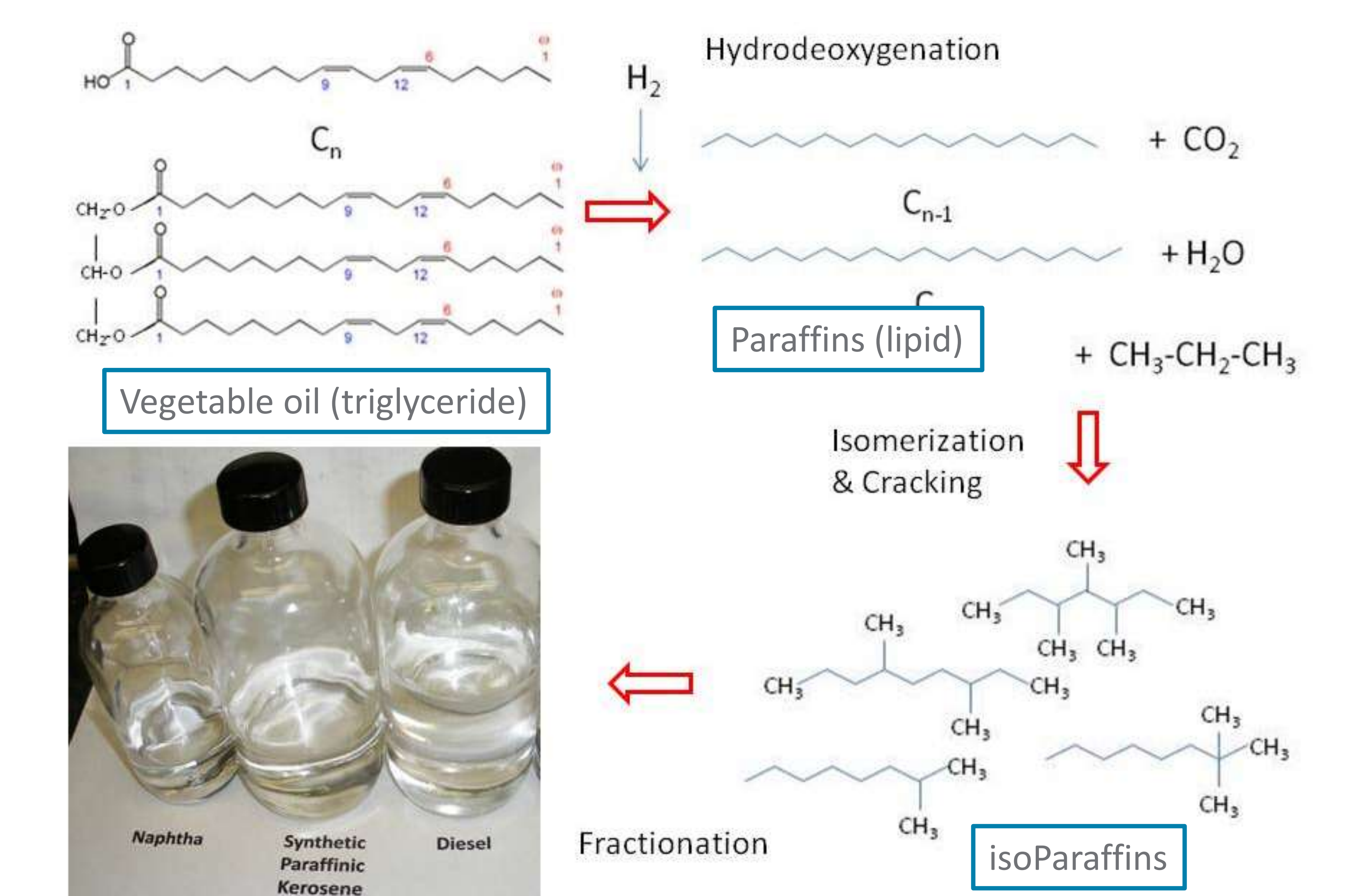
- Production anticipated to begin in 2016/2017
- These fuels have been approved for use as jet fuel by ASTM at up to 50/50 blends
- Fuels successfully demonstrated during Rim of the Pacific (RIMPAC) demonstration in 2012 for ships and planes
- Fuels can be utilized in Navy’s warfighting platforms with no degradation to performance or mission

Hydroprocessed esters and fatty acids (HEFA)

- June 2011—ASTM D7566 approves HEFA 50% blend
  - allows fuels from fats derived from jatropha, camelina and other fats
  - Sometimes called HRJ (hydrotreated renewable jet) or Bio-SPK (synthetic paraffinic kerosene)

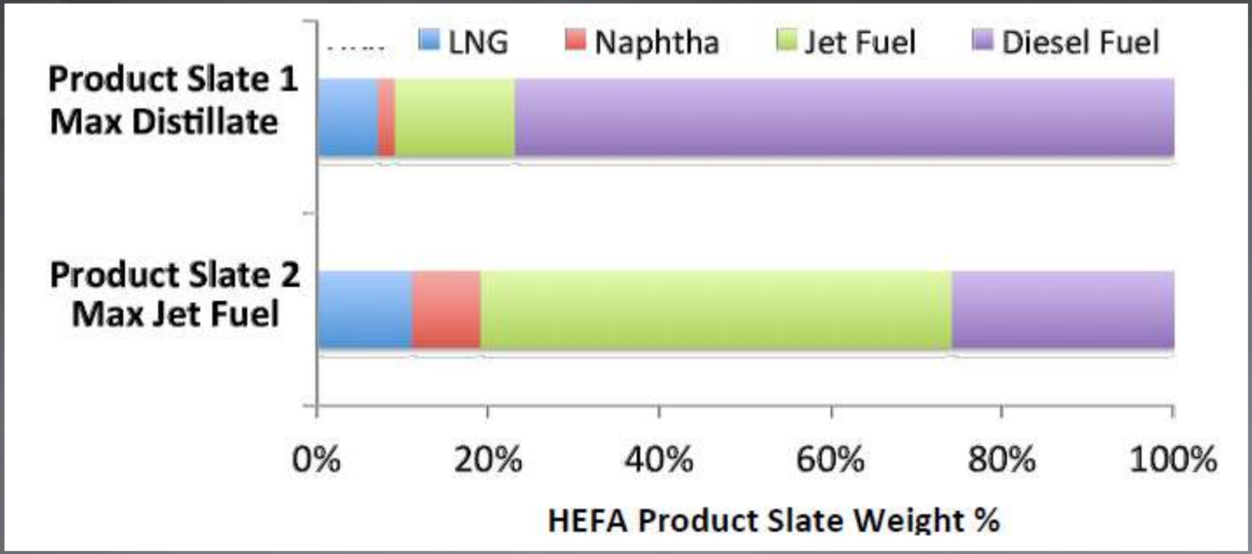


Chemistry to make HEFA jet fuel



Courtesy of NAABB/UOP

HEFA product slate
(LNG, naphtha, jet fuel, diesel fuel)



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 and availability of the feedstock

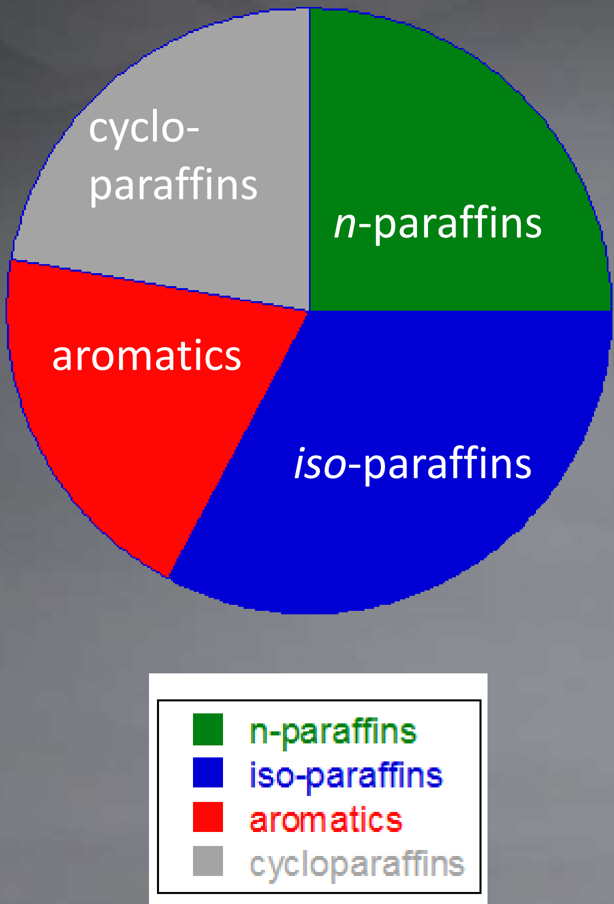
Algae potential source in the future

Regional (niche) opportunities

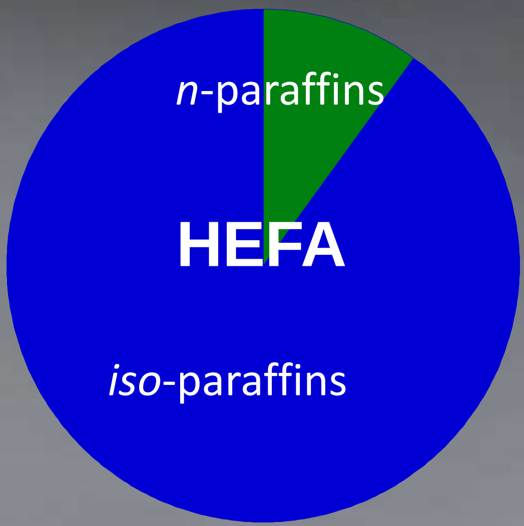
NAABB

HEFA jet fuel summary

Jet A, JP-8



Product



Challenge is feedstock cost/ availability

Feedstock

Source: Dr. Timothy Edwards, Air Force Research Laboratory

Direct sugar to hydrocarbon (DSHC)

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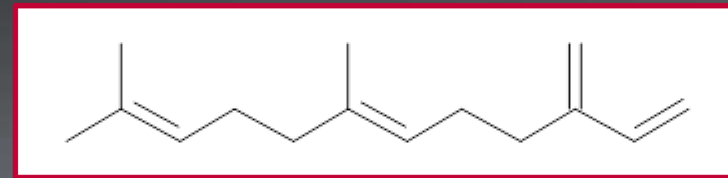
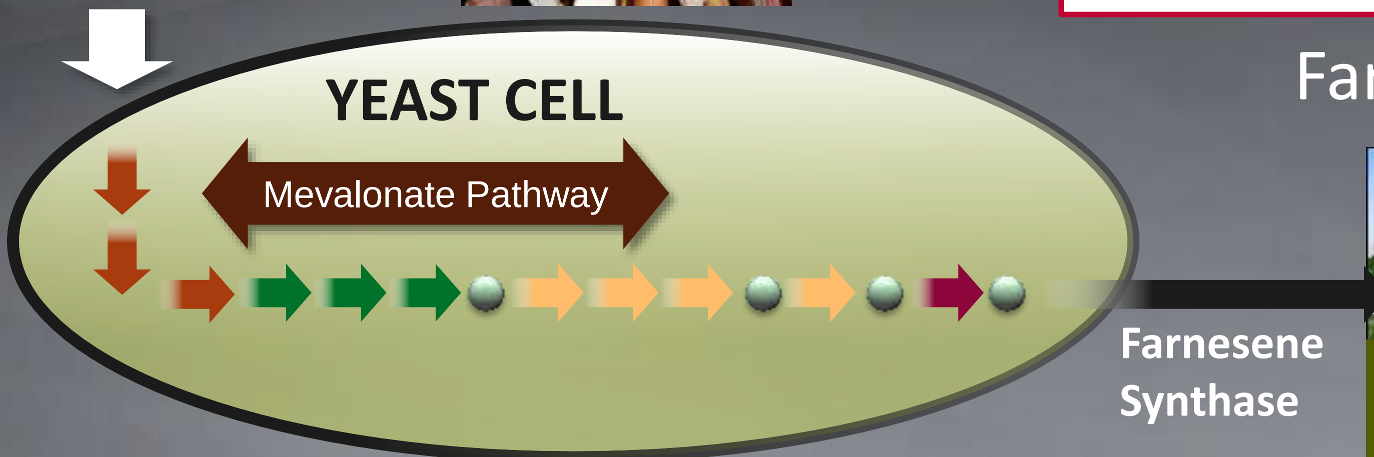
Sugar



Farnesene

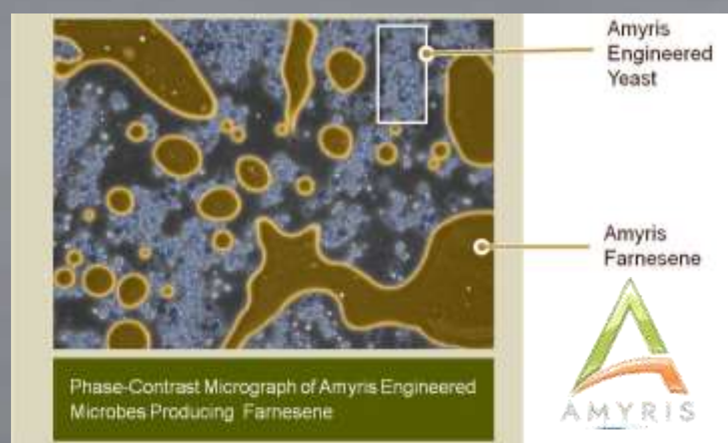


Farnesene Synthase

Diesel, jet & Chemical Precursor

Fermentation of Sugars

- Require pretreatment to release sugars
- Lignin is not converted
- Organism development needed for complex sugars



Phase-Contrast Micrograph of Amyris Engineered Microbes Producing Farnesene

[1] Cane juice
[2] Fermentation broth
[3] Separations
[4] Purification

Amyris-Total and DSHC fuel

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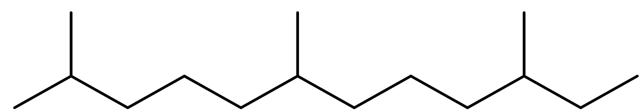
- Total Major oil/chemical company
  - 300 airports in 75 countries
  - 1.5 million refuelings each year
  - Relationship with Amyris since 2010
- June 16, 2014—Revised standard to ASTM D7566 allowing 10% blend
- Next jet fuel approved by ASTM after HEFA
  - 2012—demonstrated in GE-powered Embraer (Azul airlines)
  - 2013—demonstrated in an Airbus A321
  - 2014—demonstrated in a Boeing 777 (Etihad Airlines)
  - 2014—KLM collaboration, intent to fly
- Renewable farnesane can reduce greenhouse gas emissions by 50%
  - 10% blend reduces GHG by 5%
  - 10% blend reduces particulate matter by 3%

Farnesane (a sesquiterpene)



Rather than a fuel with a broad range of hydrocarbons, farnesane is a single molecule approved for blending at 10%

DSHC (direct sugar to hydrocarbon) summary

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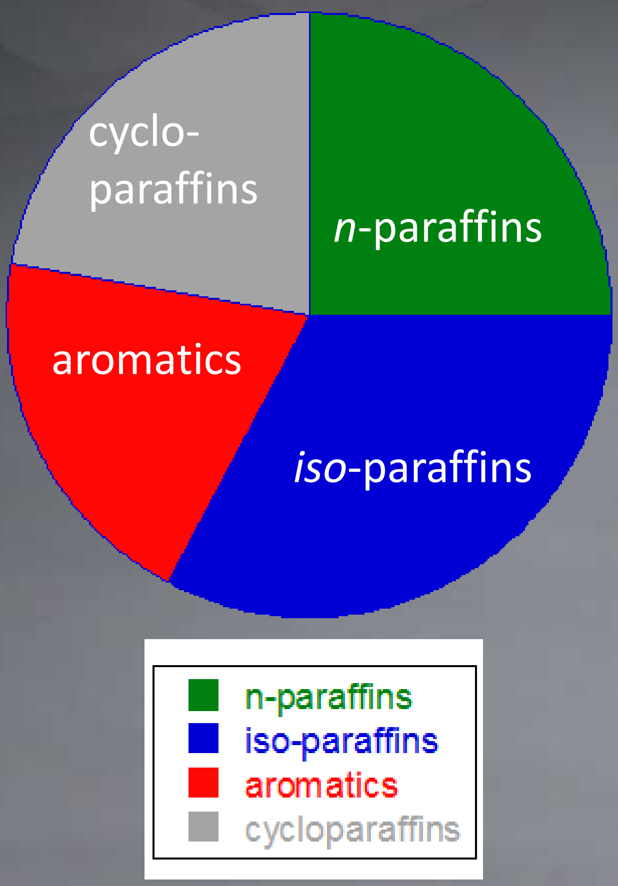
Jet A, JP-8



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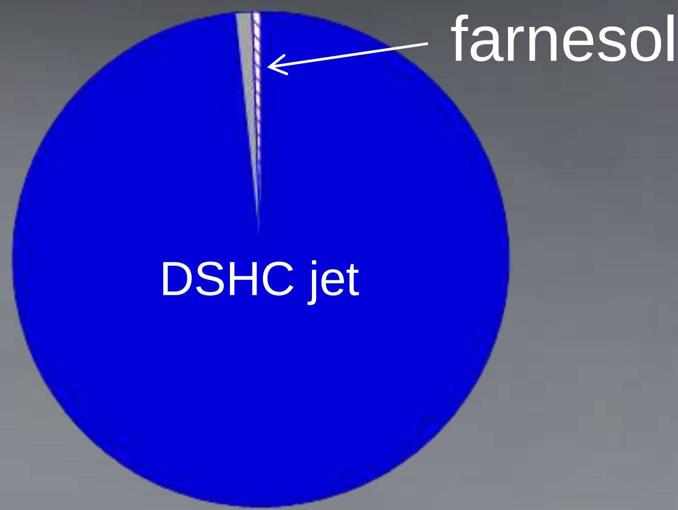

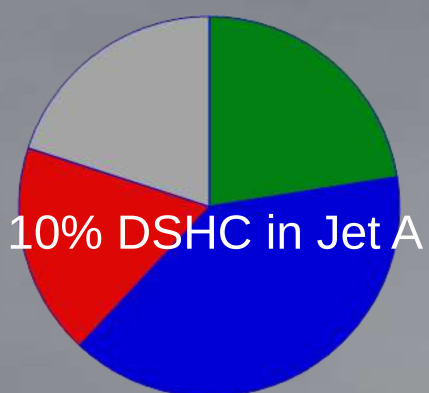

Blending DSHC increases the good components

Feedstock

Cane juice

Agriculture residues? (future)

Source: Dr. Timothy Edwards, Air Force Research Laboratory

Renewable paraffins and naphthenes (RPN)

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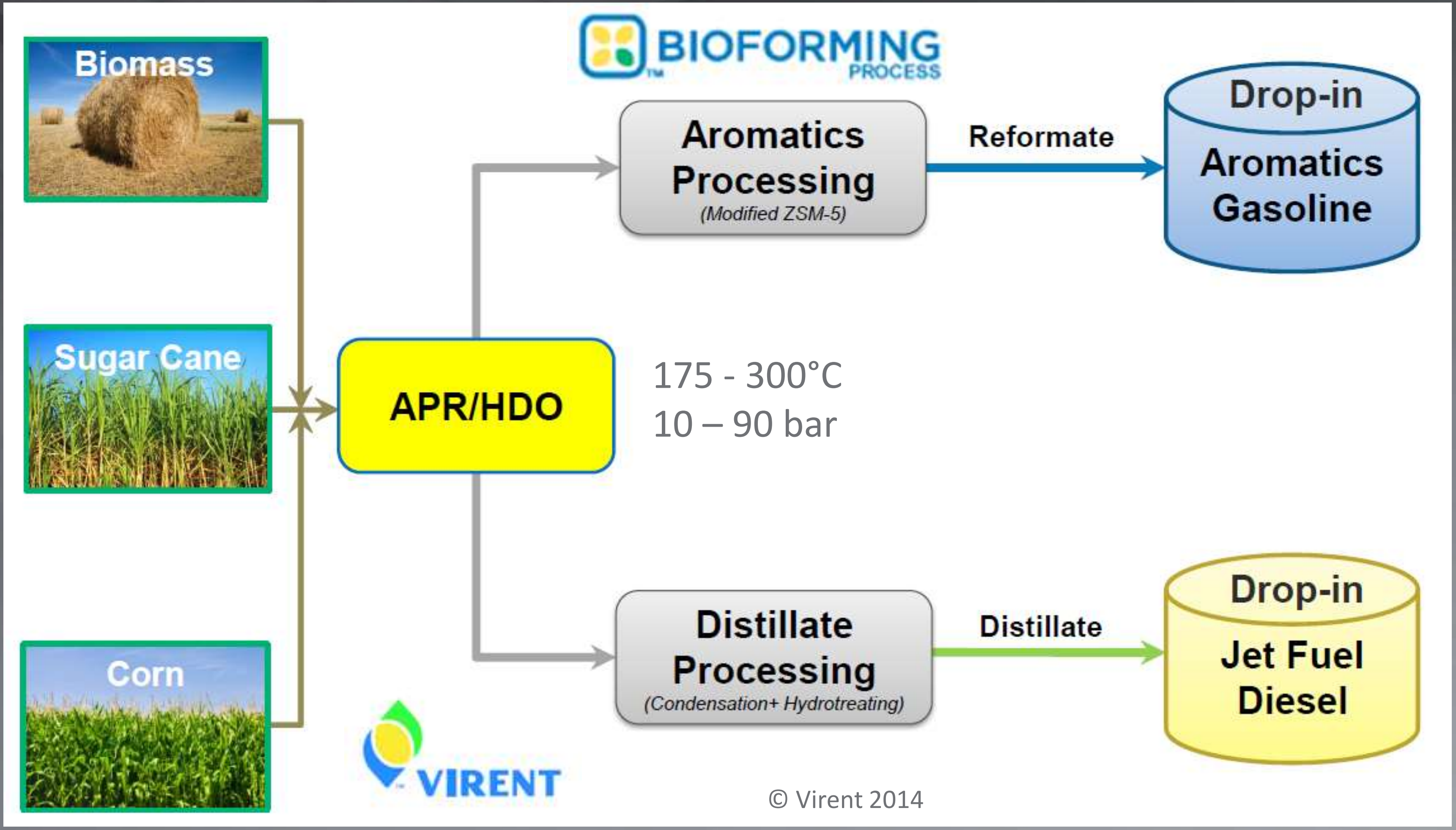

Catalytic Conversion of Sugars (not approved today)

- APR/HDO makes a mixtures of oxygenated compounds
- Further catalytic upgrading gives hydrocarbon fuels

Renewables paraffins and naphthenes (RPN)

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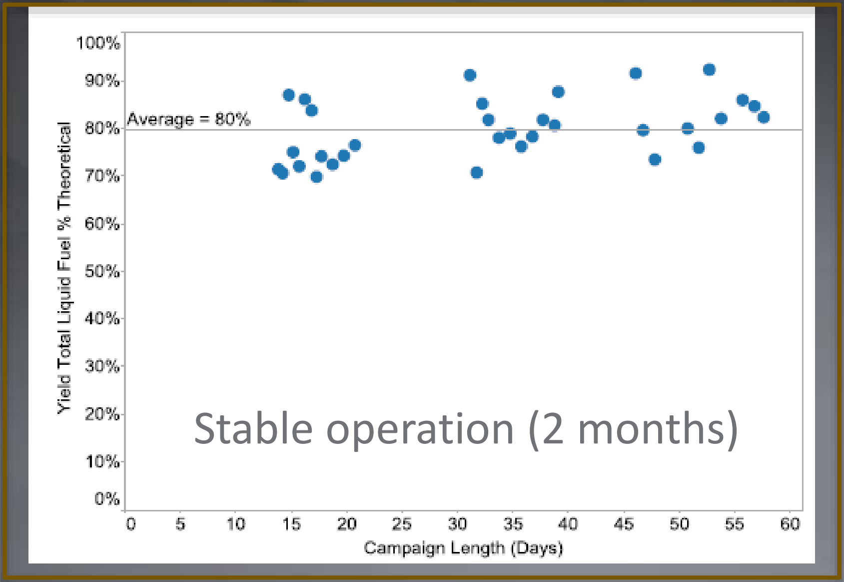

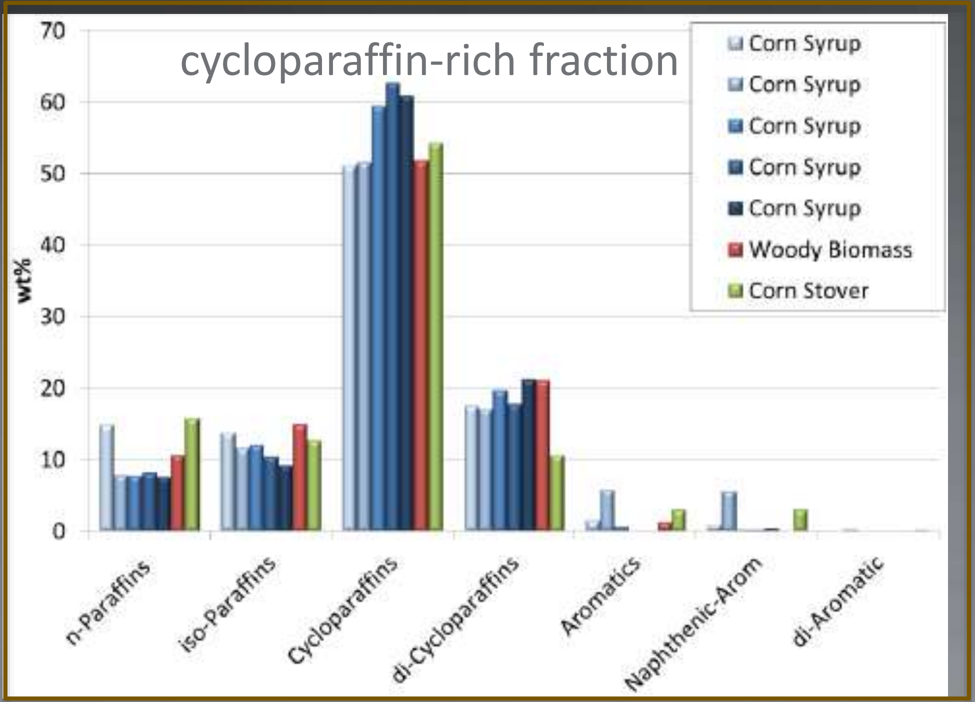

- 15 gal/day liquid fuel (20x lab)
- 100 gal jet fuel produced
- Renewable paraffins and naphthenes (RPN) consisting of C9-C16
- Aromatic renewable jet blendstock (ARJB) consisting of C9 - C11
- Freezing point = −71°C; flash point = 50°C; density = 812 (kg/m^3); thermal stability pass at 325°C; density

RPN (renewable paraffins and naphthalenes) summary

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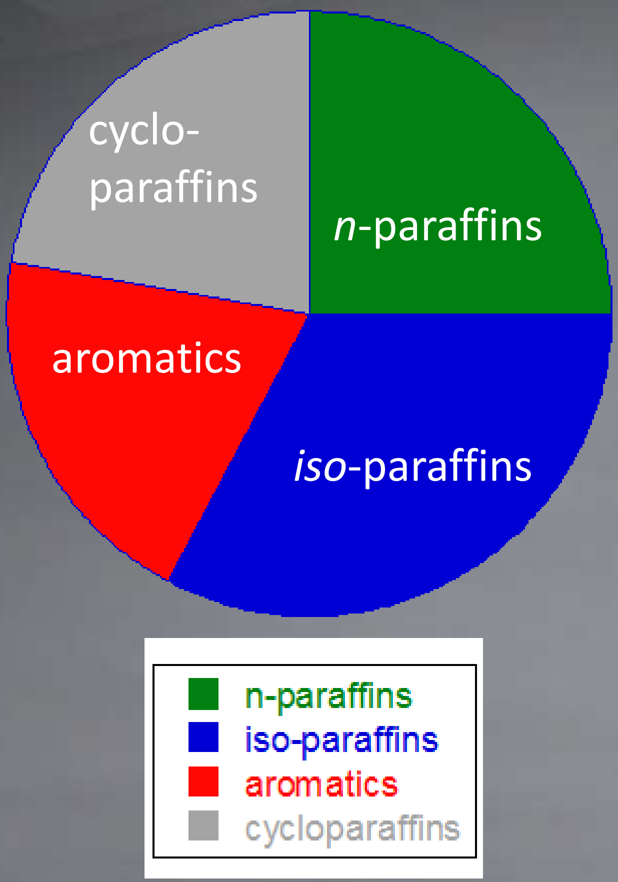
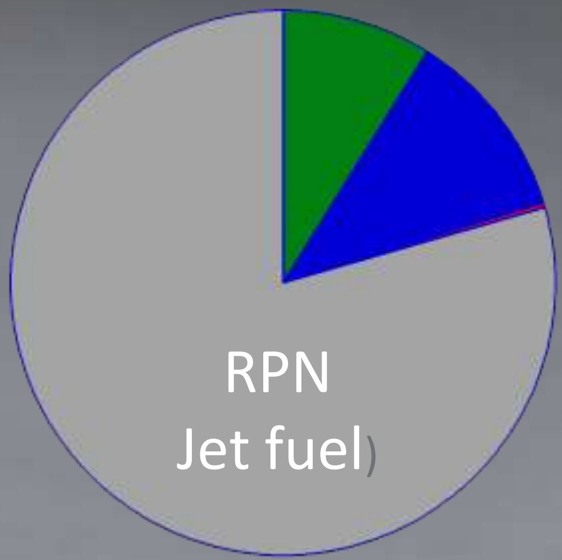
Jet A, JP-8



Product



Unlike previous technologies, this produces a cyclic-rich product

Feedstock

sugars

Agriculture residues (future unless very clean)

Source: Dr. Timothy Edwards, Air Force Research Laboratory

Liquefaction (pyrolysis) technologies

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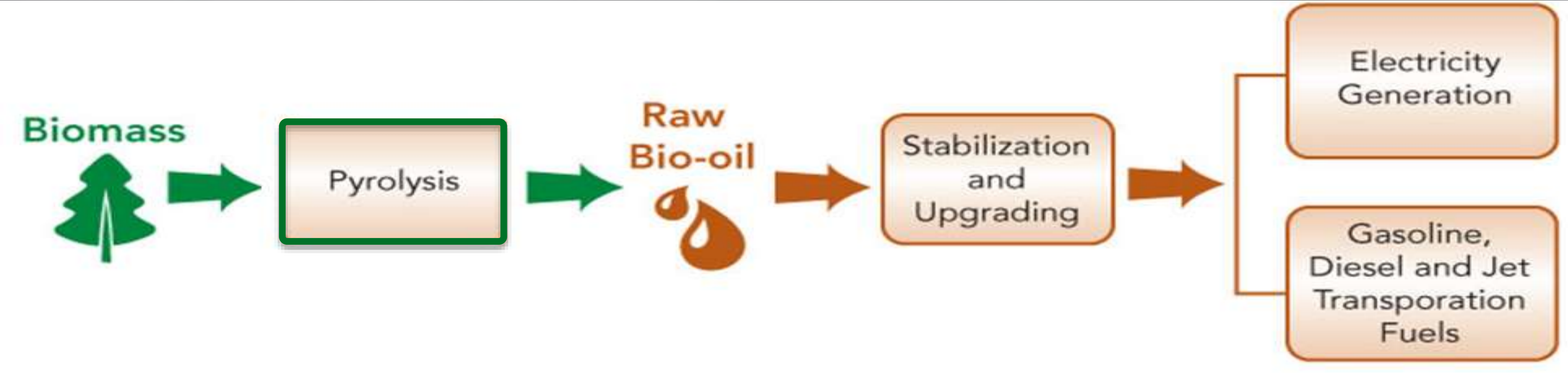
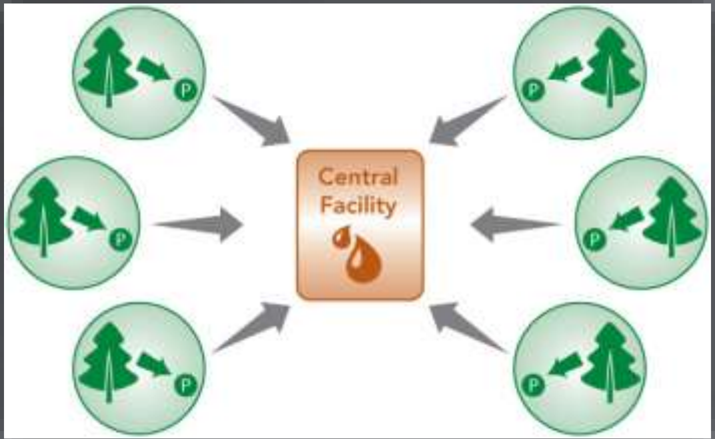




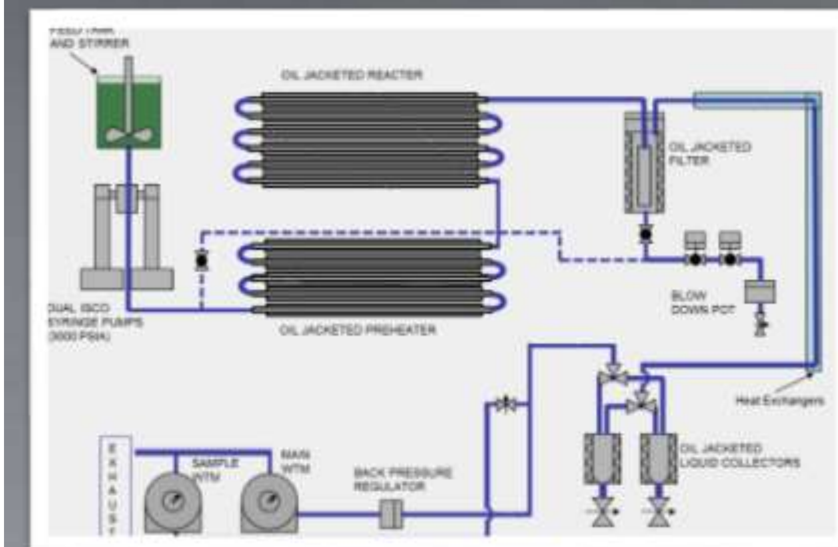
Potential for distributed bio-oil production with processing in central facility

Pyrolysis and Liquefaction
- Multiple variants
- Yield depends on quality of biomass feedstock and variant of technology
- T = typically 500 C, short residence time (1 sec)

Produce hydrocarbon fuels from low quality bio-oil, but…
- Catalyst life is too short
- Catalyst rate is too slow

Liquefaction technologies (pyrolysis)

UOP and Kior have submitted fuels (variants of pyrolysis/upgrading)



All variants produce high amounts of cyclics / aromatics

PNNL and Genifuel are also developing a wet variant

Liquefaction (pyrolysis) summary

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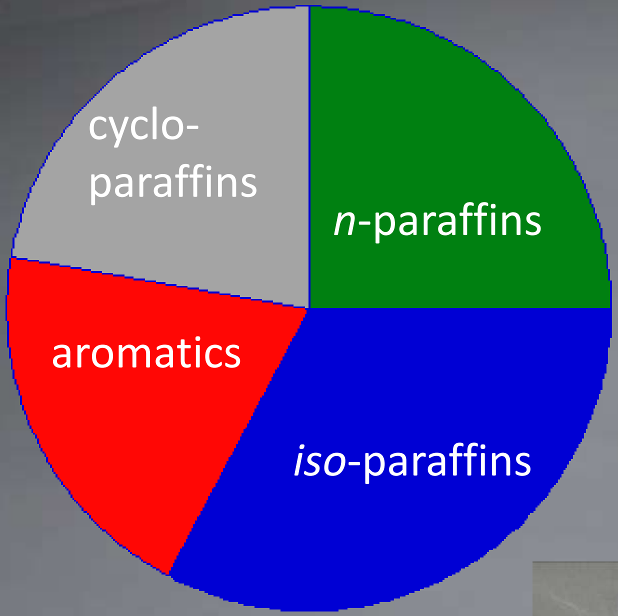
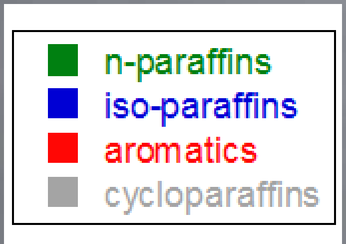
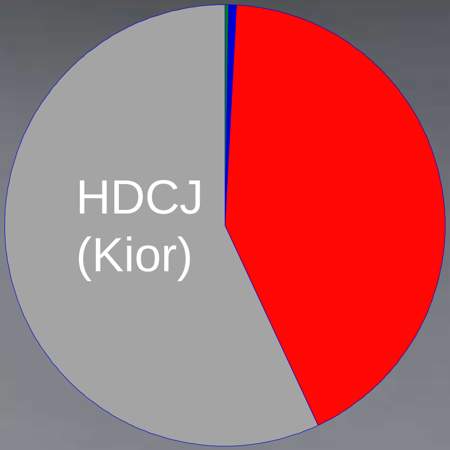
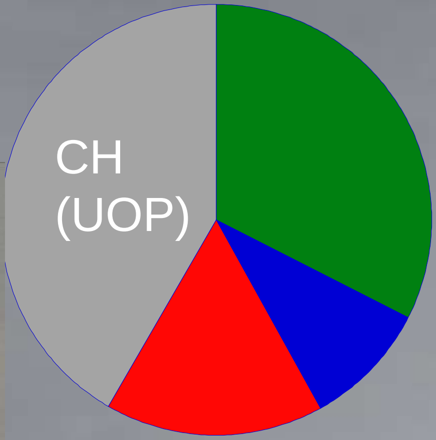
Jet A, JP-8





Products





Feedstock

Forest residues

Agriculture residues

Pyrolytic methods make cyclics and aromatics

Source: Dr. Timothy Edwards, Air Force Research Laboratory

Alcohol to jet

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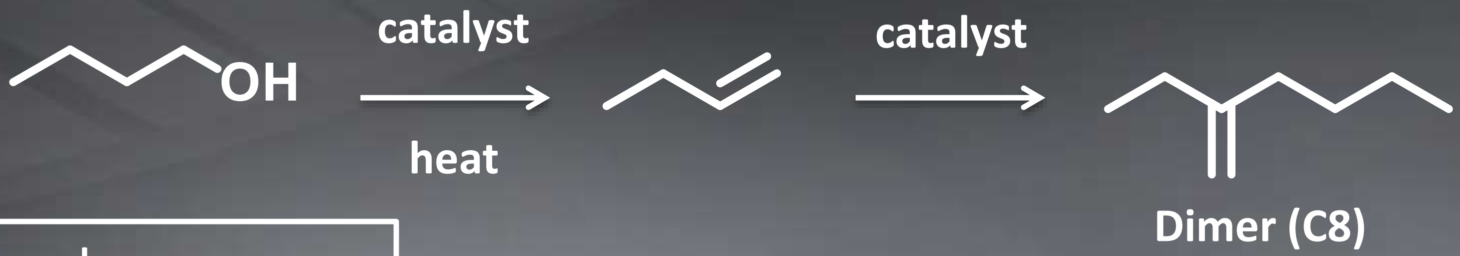
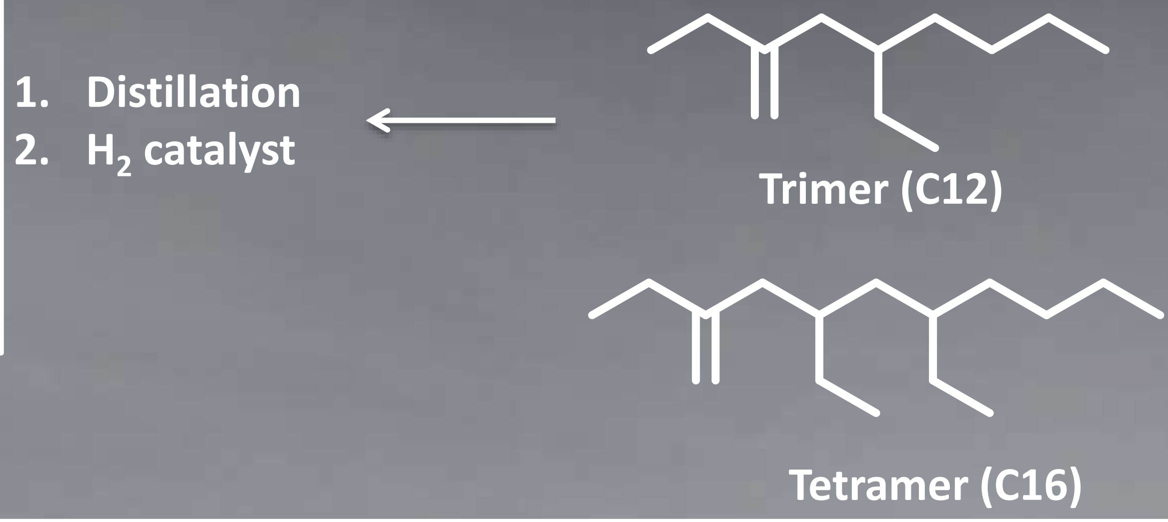


Can make isoparaffins or cyclics dependent on reaction conditions



C4—butanol, i-butanol	C2—ethanol
• Cobalt, Gevo , et al	• Swedish Biofuels (+CO/H_2)
• fuel primarily C12 and C16 (limited mol. chains)	• PNNL/ Imperium (SPK)
	• broad chain length

Many routes to alcohols—LanzaTech highlighted

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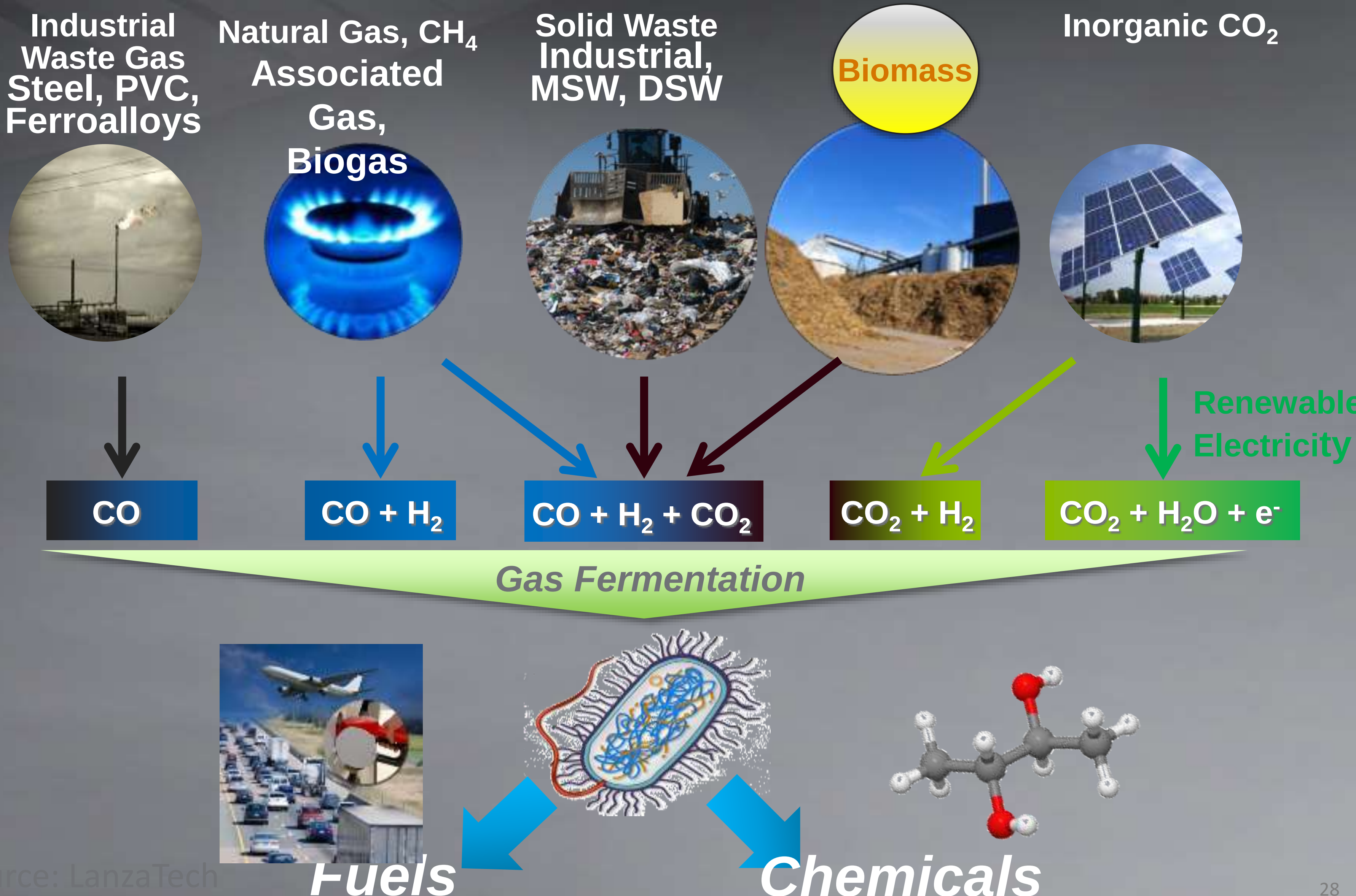


Source: LanzaTech

Jet fuel production from waste gas

Gas fermentation

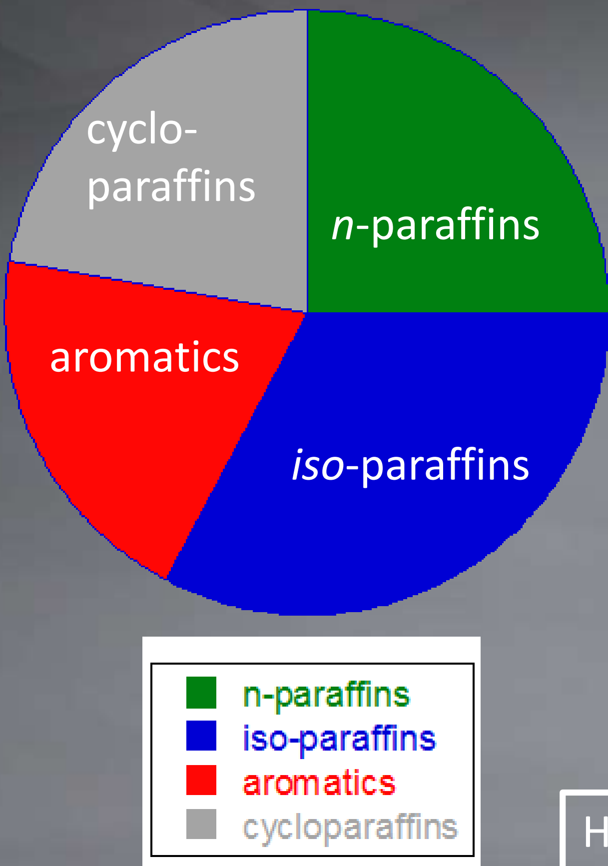
Catalytic upgrading

fractionation

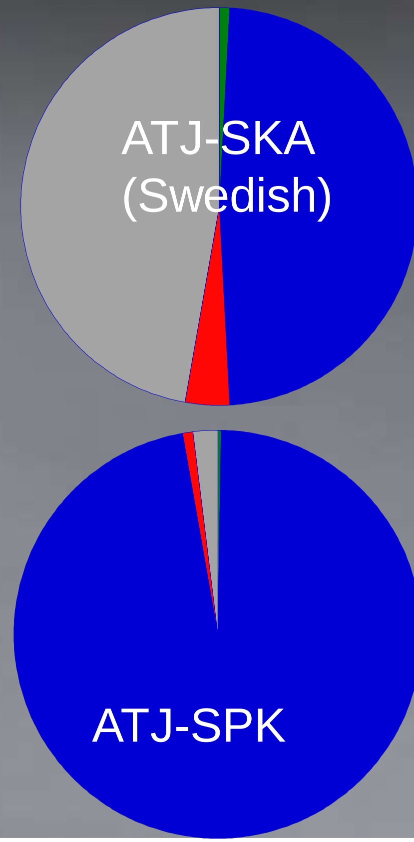
- "Fuel is very stable, wide boiling isoparaffinic kerosene" (C10-C16)
- Exceeds D1655 standards including 325 JFTOT (thermal oxidation), high flashpoint (56°C), low freezing (<-70°C), no gum, "not easy to do"
- 72% GHG reduction (biomass gasification)

ATJ summary

Jet A, JP-8



Product



Hydrocarbon mix
depends on the technology
butanol-produces C8,12 and16
Ethanol give range of hydrocarbons

Feedstock

Butanol /ethanol

cellulosic ethanol

gas fermentation

Source: Dr. Timothy Edwards, Air Force Research Laboratory

Many routes to fuels (energy carriers)

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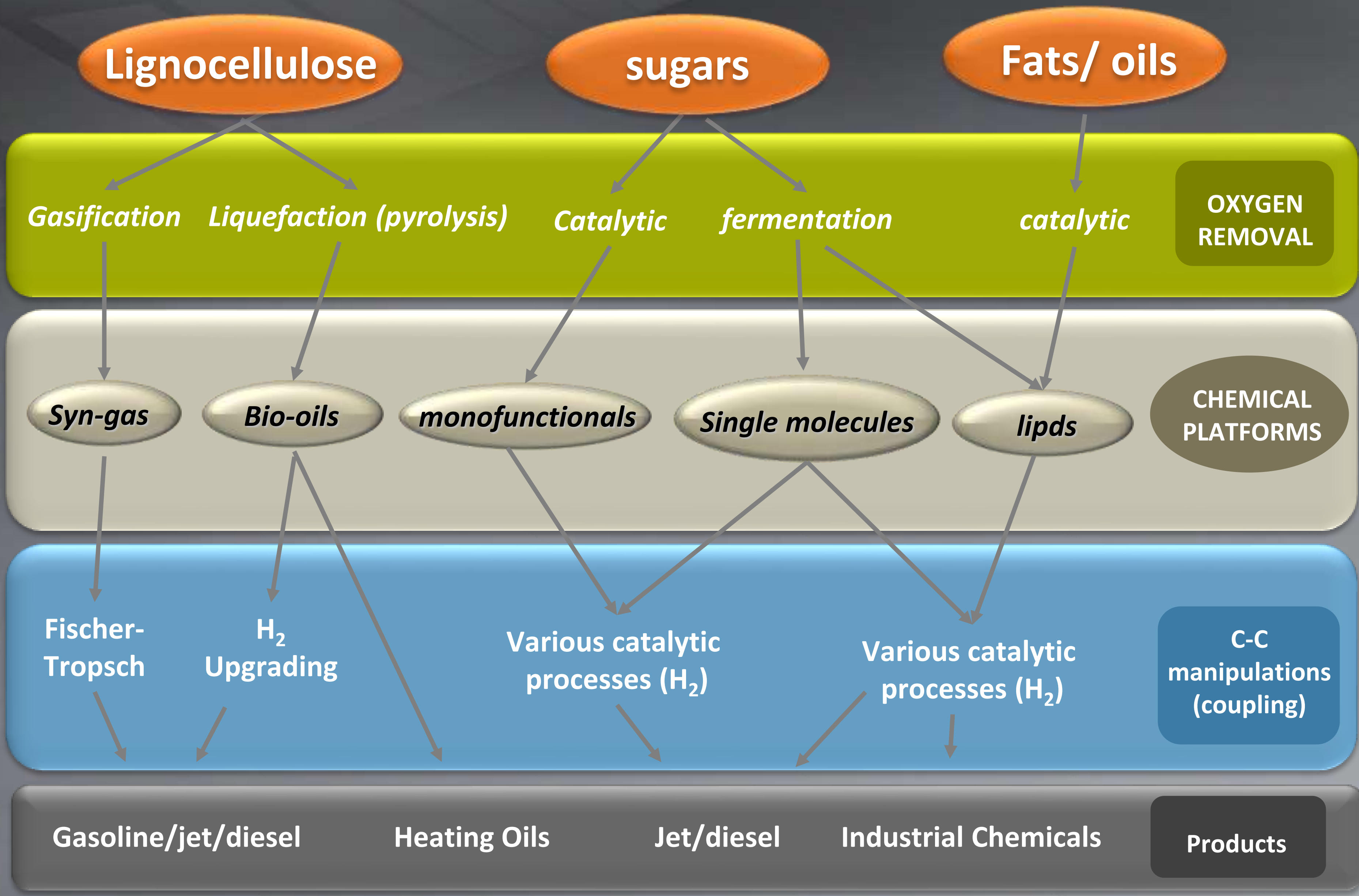
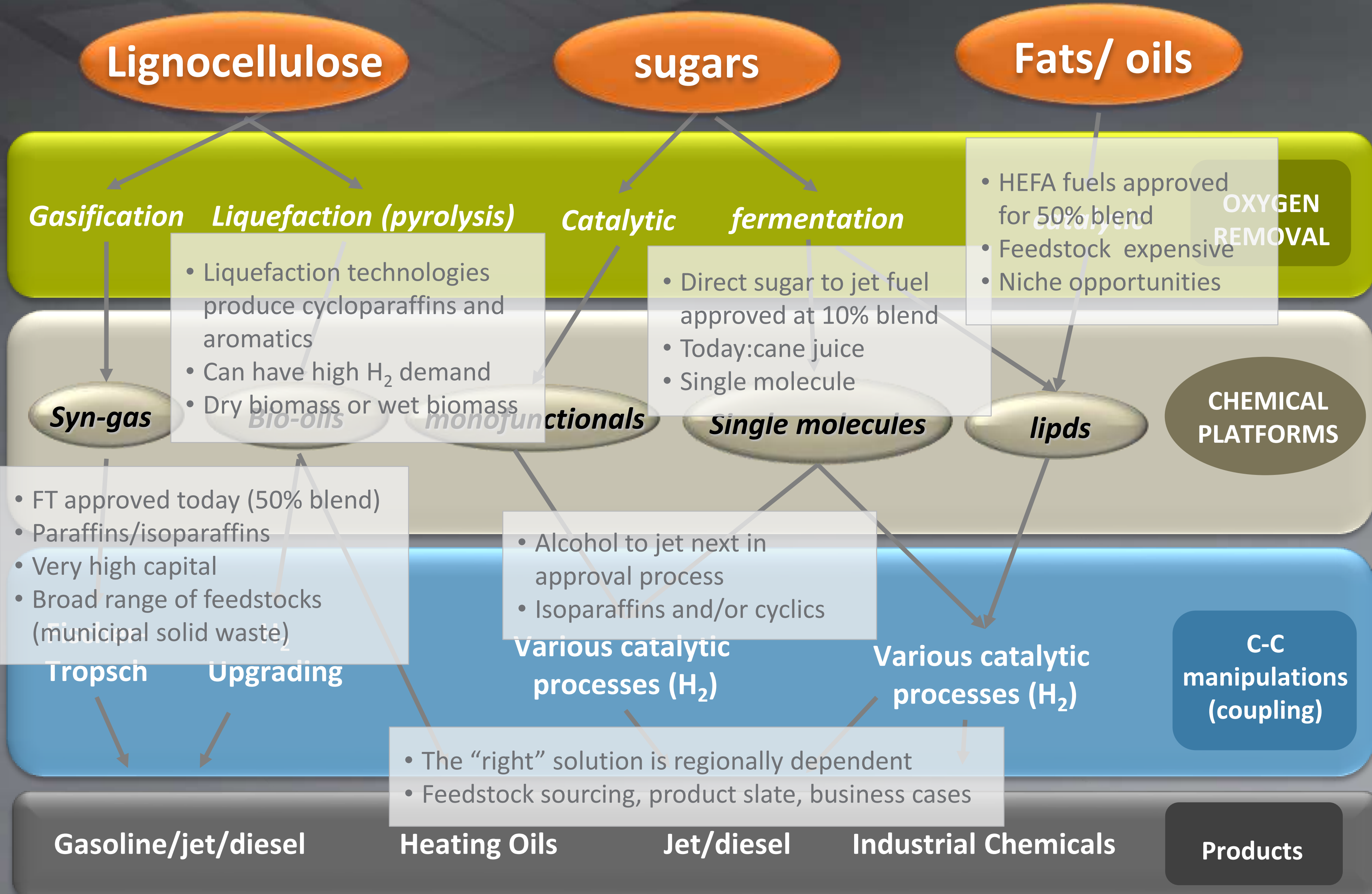


Conclusions



Questions?

- There are a number of viable routes to make renewable jet fuel today
  - Range of feedstocks that are suitable for each technology
  - Product slate differs dramatically
- Three technologies are approved for commercial use
- Two others are in the process for approval
- All still have unique challenges—including high cost
- The right solution depends on the region
  - Feedstock sourcing, tax structure, product slate



Thank you

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ASTM D7566 TASK FORCES

Adapted from Brown, Iowa State 2012 and Tim Edwards, USAF/AFRL

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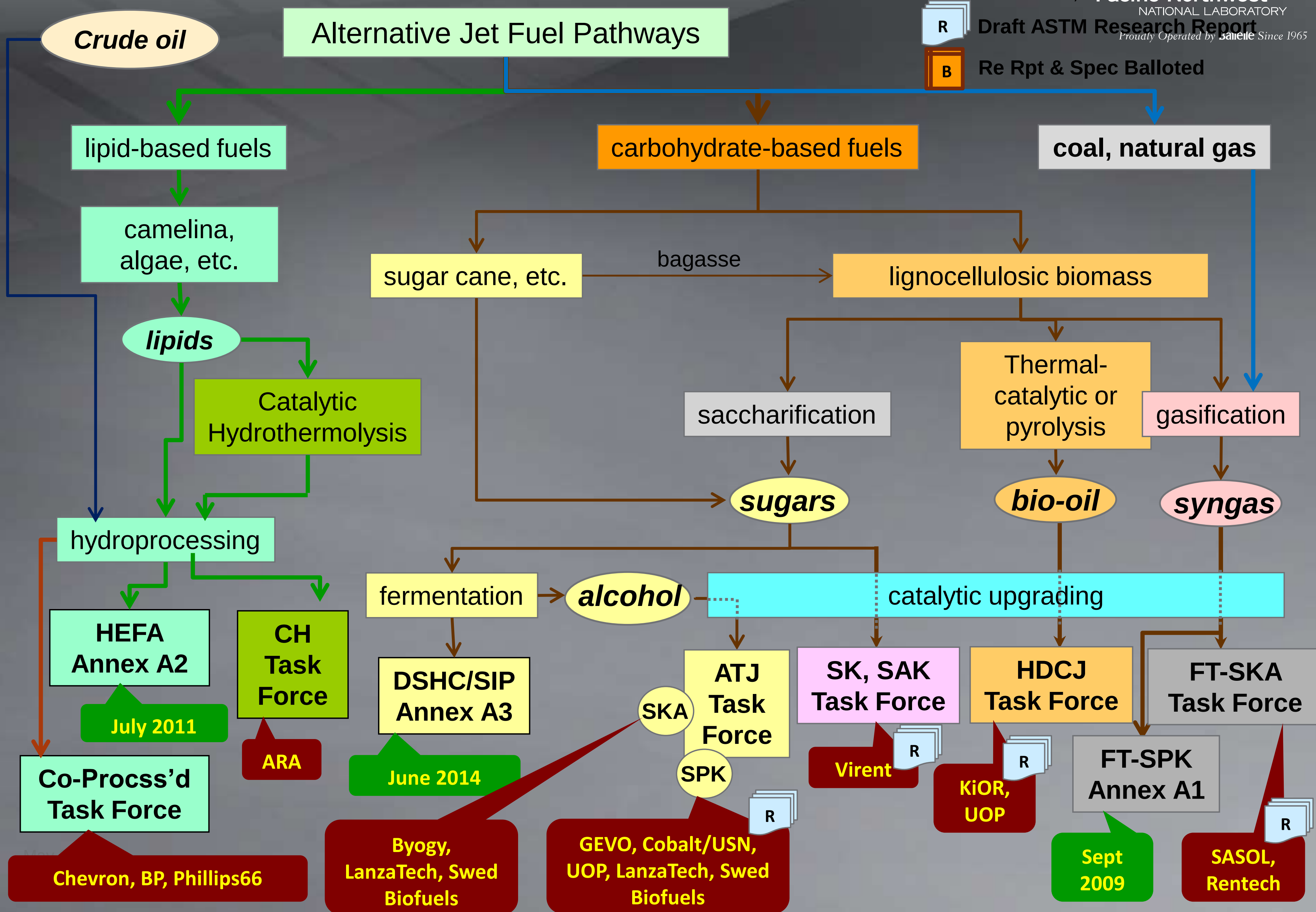

Annual U.S. greenhouse gas emissions ($Tg\ CO_2$ equivalent, 2006)

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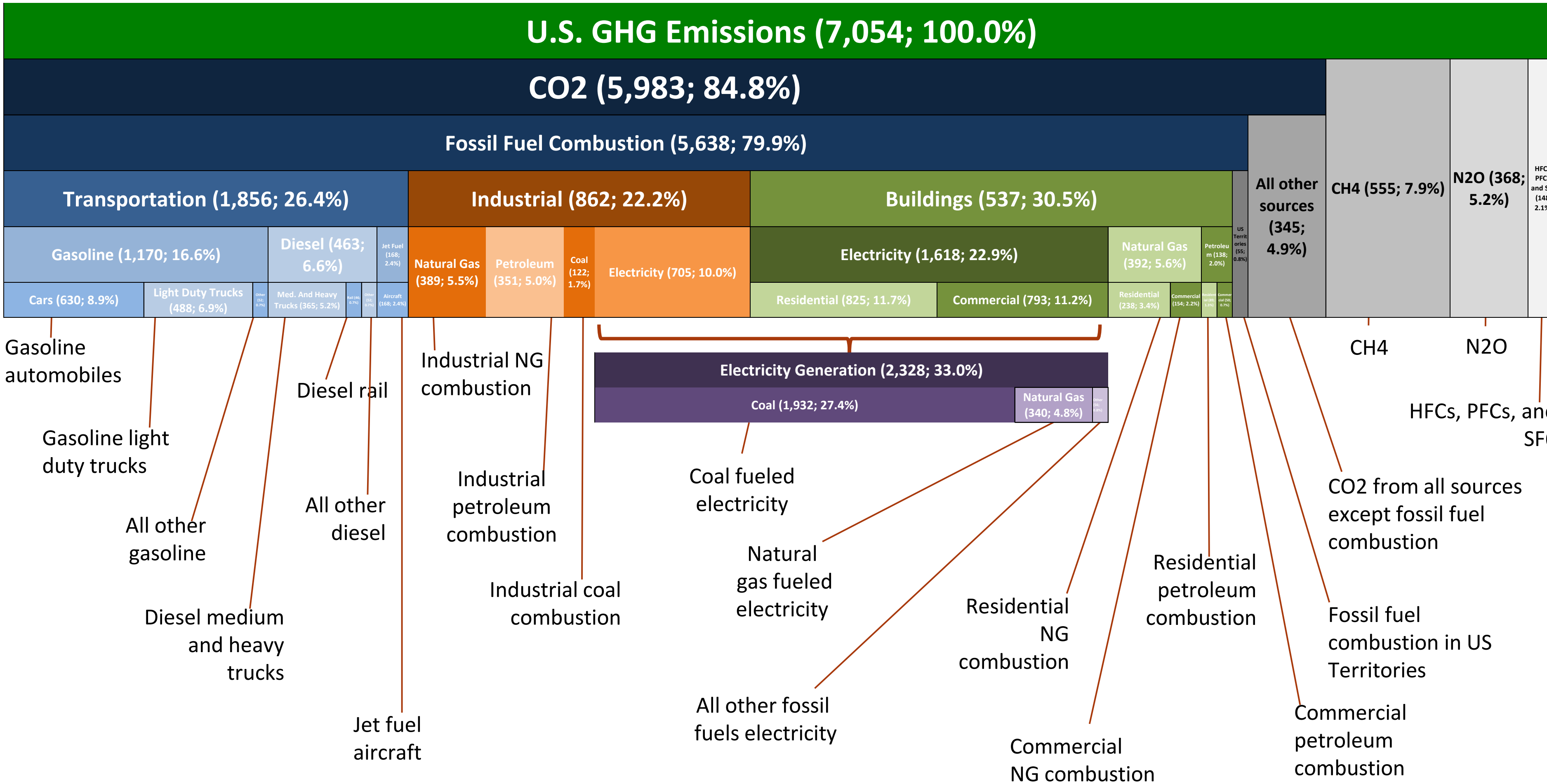

Transportation
(1,856 Tg, 26%)

Electricity Generation
(2,328 Tg, 33%)

Pyrolysis enables 100% renewable jet

UOP
A Honeywell Company

The hydroplane ran on 98% Bio-SPK and 2% renewable aromatics

	Jet A1 Spec	Starting SPK	Woody Pyrolysis Oil Aromatics-SPK
Freeze Point (^{o}C)	-47	-63	-53
Flash Point (^{o}C)	39	42	52
Density (g/mL)	0.775	0.753	0.863

Fuel Properties

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PNNL-SA-105930

- Ethanol to Gasoline (61666-113-D1H)[1]
  - RON = 85
  - MON = 81
  - Final Octane (R+M)/2 = 83 (Regular unleaded is 87; Premium unleaded is 91)
- Ethanol to Jet (61666-107-ETJ-FIN)[2]
  - Density = 0.782 (0.775-0.840 for Jet A/JP-8/Jet A-1)
  - Flash Point = 56°C (ASTM D1655 requires > 38°C)
  - Freeze Point = < -70°C (ASTM D1655 requires < -40°C)
- Ethanol to Diesel (61666-77-H7)[3]
  - Cetane = 53.6 (Diesel fuels are typically in the 40-55 range)
  - Cloud Point = -60.1°C (ASTM D 975 is regional, but an extreme case is < -28°C for MN. European standard EN 590 specifies < -34°C for Class 4 arctic diesel)
  - Pour Point = -66.0°C

[1]RON and MON determined via NIR method for correlated octane number
[2]Ethanol to Jet data generated by the Air Force Research Laboratory
[3]Cetane determined by closed cup derived cetane method

Yields from HEFA

Product Profiles [wt%]	Maximum Distillate	Maximum Jet
Vegetable Oil	100.0	100.0
Hydrogen	2.7	4.0
Total In	102.7	104.0
Water	8.7	8.7
Carbon Dioxide	5.5	5.4
Propane	4.2	4.2
LPG	1.6	6.0
Naphtha	1.8	7.0
Jet	12.8	49.4
Diesel	68.1	23.3
Total Out	102.7	104.0

Transportation energy use by type

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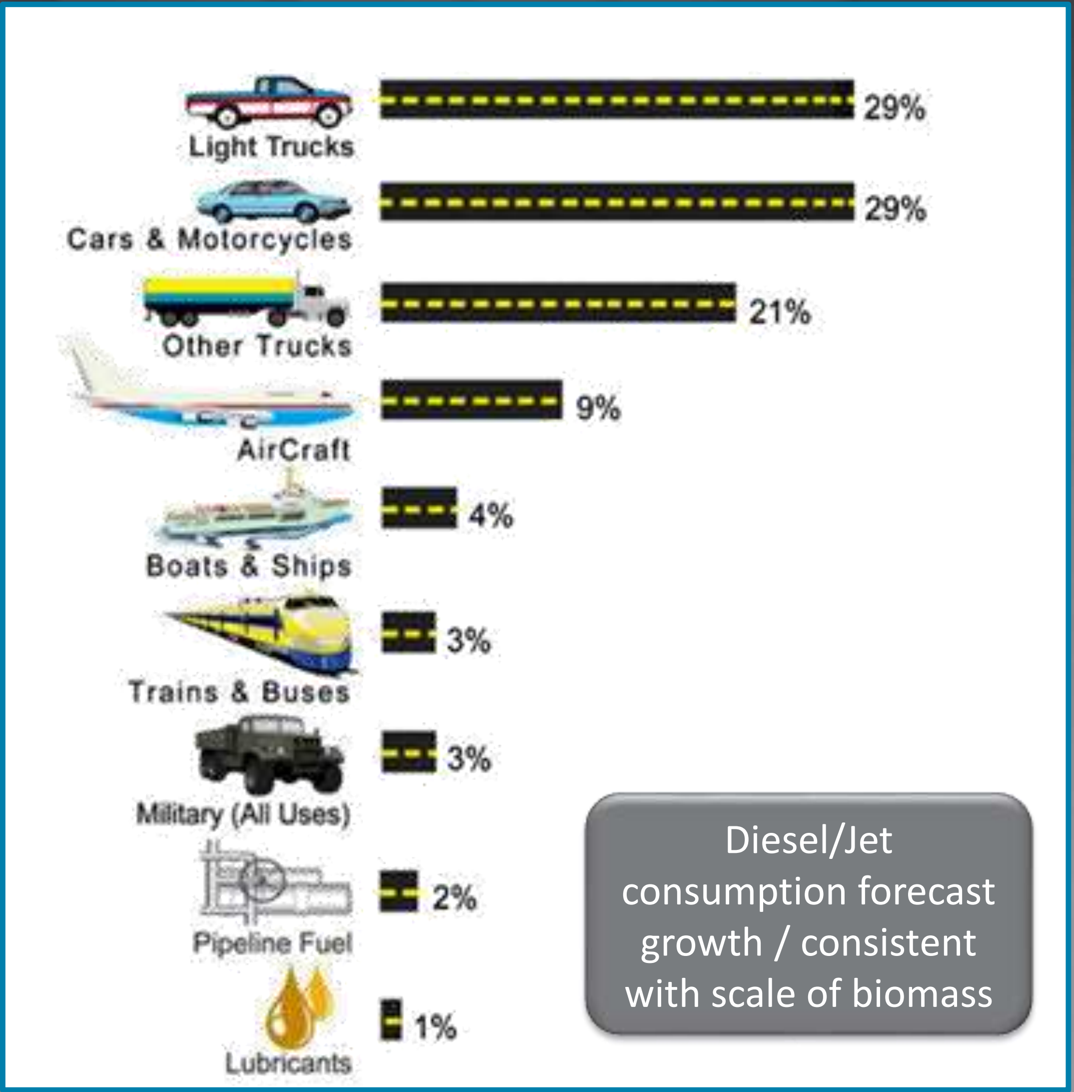
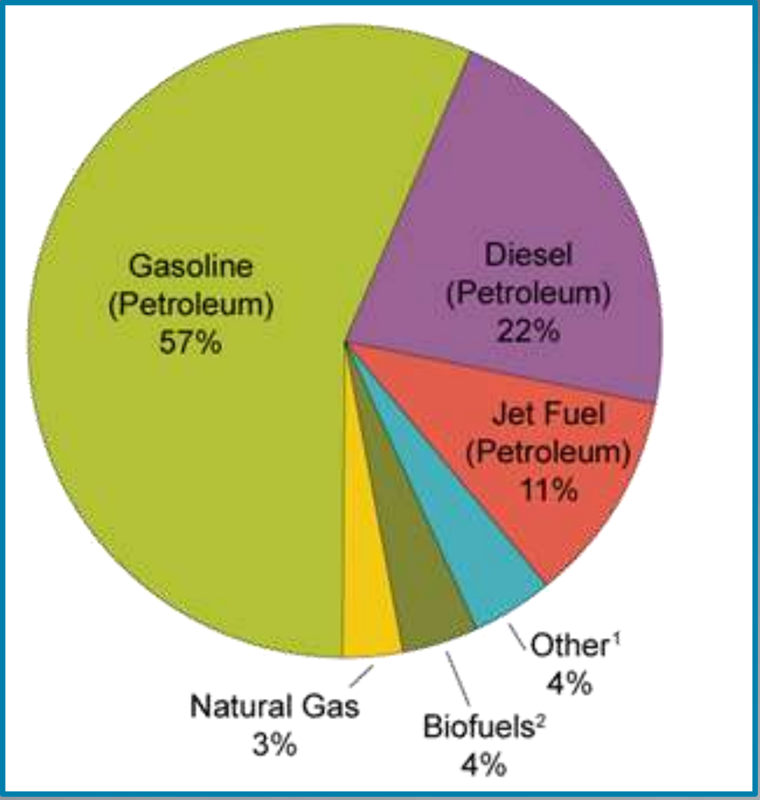


Diesel/Jet consumption forecast growth / consistent with scale of biomass

U.S. Fuel Consumption (2012)

- Gasoline (134 billion gallons)
- Diesel (53 billion gallons)
- Jet (22 billion gallons



Source: U.S. Energy Information Administration
http://www.eia.gov/energyexplained/index.cfm?page=us_energy_transportation

Upgraded HTL oil from algae: 85% diesel (NAABB: Solix, Cellana and TAMU)

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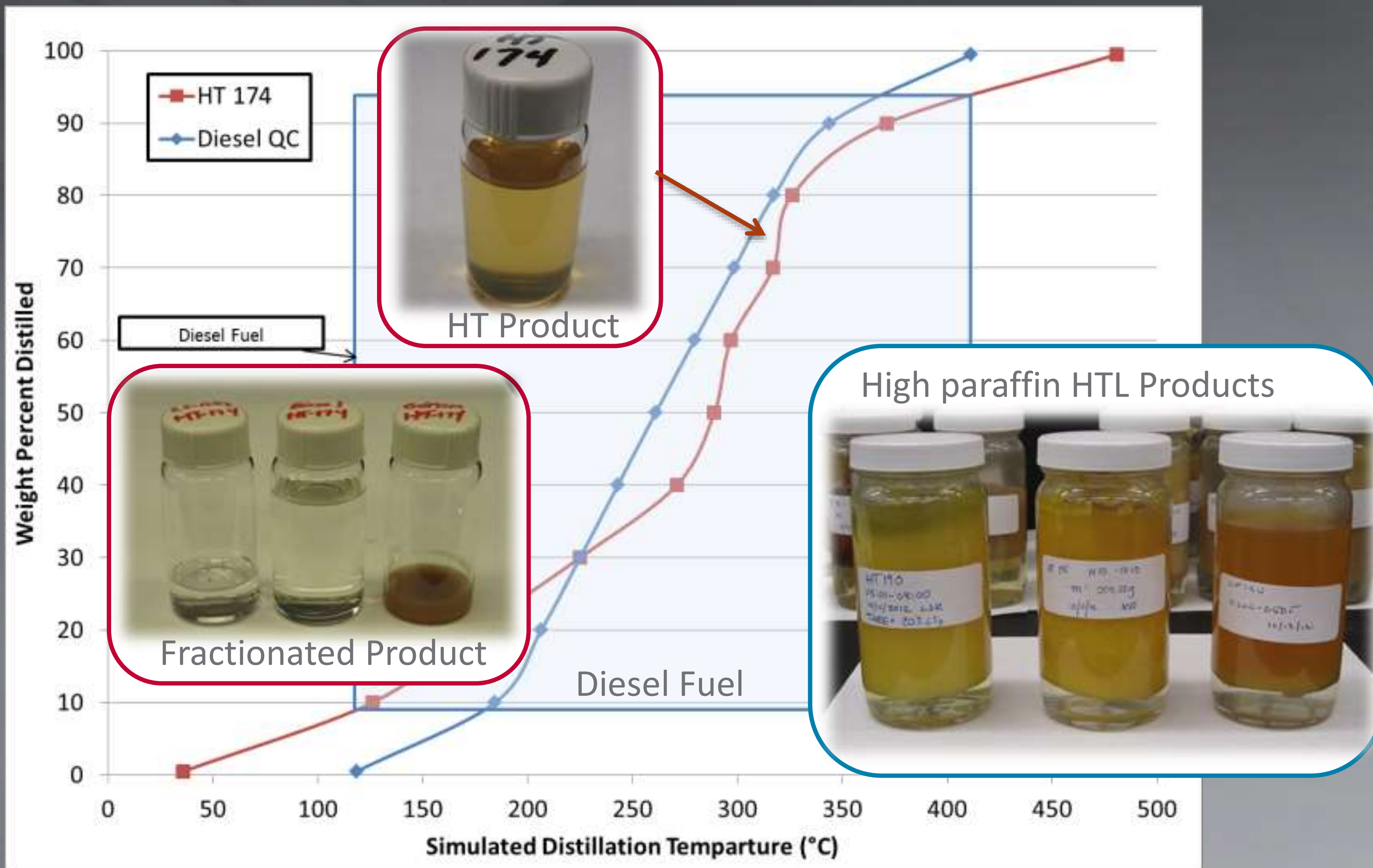

National Alliance For Advanced Biofuels and Bio-products

Catalysis of sugars

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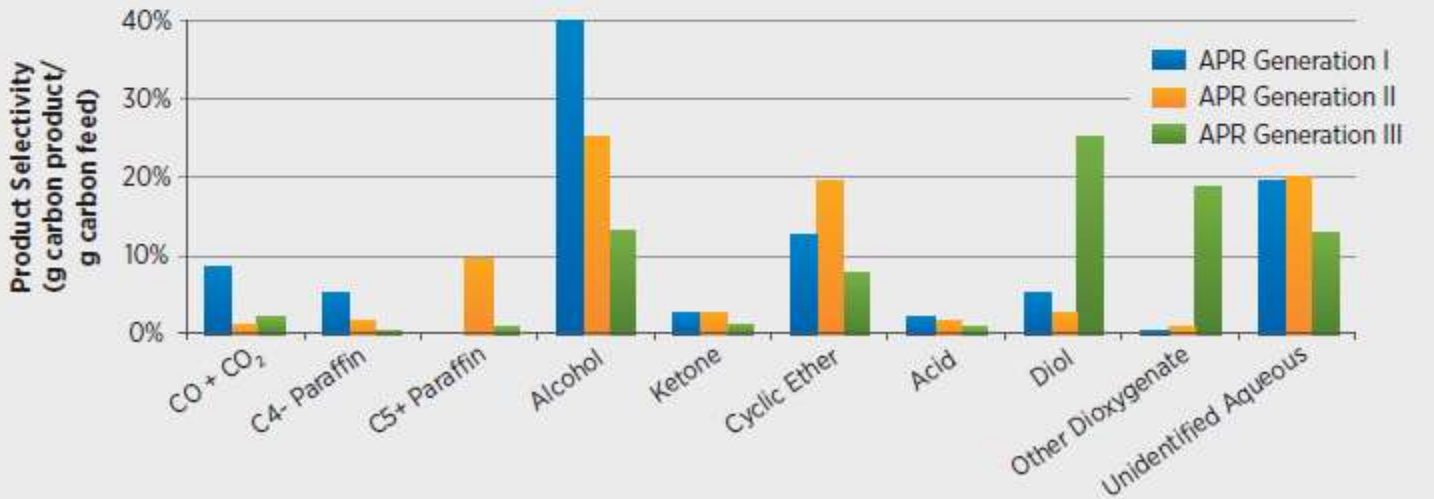
Reducing catalyst costs and improving catalyst performance

Throughout the three-year NABC project, Virent, in collaboration with PNNL and WSU, worked to improve catalyst lifetimes and drive down catalyst costs for the Catalytic Conversion of Sugars (CLS) strategy. The focus on an alternative APR catalyst led to the development of Generation II and III catalysts. Yield improvements were achieved through reducing carbon loss to CO_2 and light paraffins in the APR. Optimization of the Generation II catalyst system was conducted at PNNL where a total of 200 unique formulations were tested using high throughput catalyst testing tools. In addition to catalyst optimization, the team studied deactivation mechanisms and reaction kinetics; a peer reviewed publication is under development. The Generation III catalyst developed by Virent resulted in a 75% reduction in the catalyst cost. Virent evaluated the scale-up of the APR reactor system by investigating a larger reactor system designed to be a 20x scale-up of laboratory units and incorporating an industrial temperature control system, and commercially relevant catalyst particle size and form factor. Evaluation of Virent's Generation III APR catalyst showed good fidelity with laboratory data, validating the commercial reactor design. Further details of the CLS efforts are summarized in section 2.2.



APR/HDO produces a complex mixture of oxygenates

Fermentation of sugars

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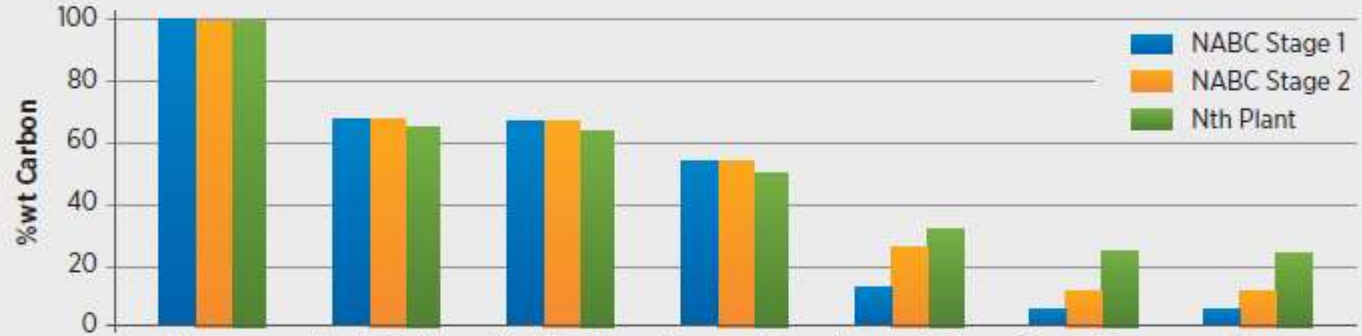
Increasing carbon utilization for hydrocarbon production

Increasing the overall carbon conversion to the hydrocarbon fuels is critical for each of the conversion pathways. During the NABC efforts, the Fermentation of Lignocellulosic Sugars (FLS) Team focused on tracking the biomass carbon losses in the process to improve the overall carbon utilization. The largest percentage of carbon lost within the FLS process is during the removal of lignin solids following biomass deconstruction. Subsequent to lignin removal, the next largest carbon losses are during fermentation, and include fermentable sugars being lost to yeast biomass, CO_2 production during yeast metabolism, and downstream processing. Increasing overall "integrated" farnesene yield from fermentable sugars is therefore the largest cost sensitivity for the FLS process strategy. By focusing on this problem, Amyris and the FLS process strategy team were able to realize a nearly two-fold increase in fermentable carbon going to farnesene from the state of technology at the start of the NABC to the state of technology at the end of Stage II. More details of the FLS accomplishments are summarized in section 2.1.



	Biomass	Lignin Solids	Clarification	Evaporation	Fermentation	Separations	Fene
NABC Stage 1	100%	68%	67%	54%	13%	6%	6%
NABC Stage 2	100%	68%	67%	54%	26%	12%	12%
Nth Plant	100%	65%	64%	50%	32%	25%	24%

Note: *Yield indicated in this figure is not indicative of current production yield using the current hexose sugar stream at commercial production*

Yield today from complex sugars (not indicative of yield from sugar cane)

Fischer-Tropsch (FT) jet fuel

- Syngas based route
- Broad range of feedstocks
- Complex