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Refinery Integration of Renewable Feedstocks

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CAAFI R&D SOAP-Jet webinar series
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Overview

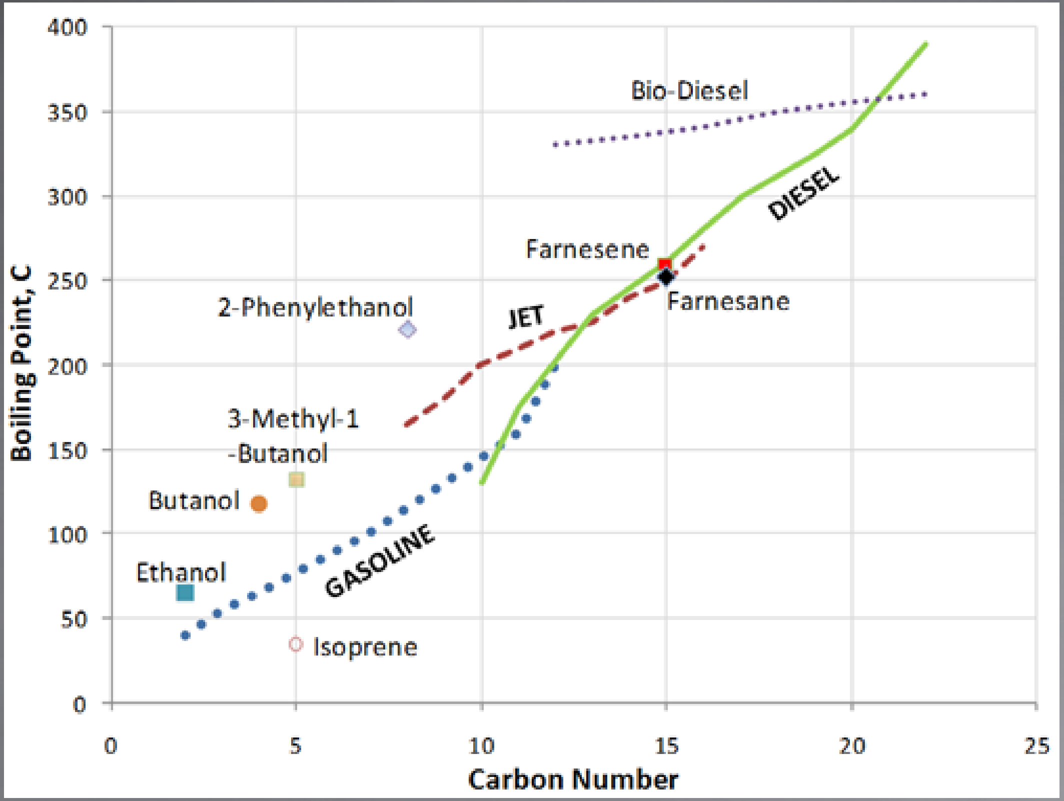
- Fuel characteristics
- Refinery overview
- Modeling assessments
  - National Advanced Biofuels Consortium (NABC)
  - Opportunities
- Technology advancements
  - FCC (co-processing VGO with bio-oil)
  - Hydrotreating (bio-oil and biocrude)
  - Alkylation (alcohol to jet)
- Conclusions and next steps

Fuels and fuel characteristics

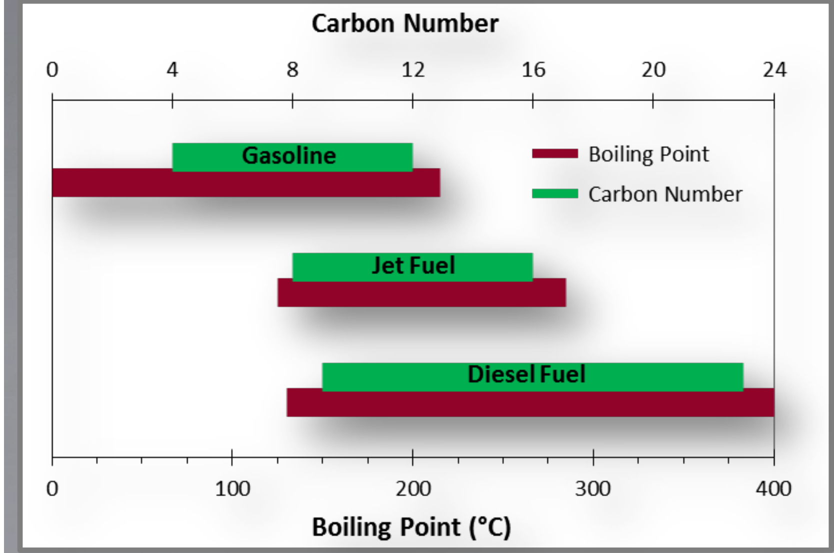
Fuel characteristics

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)



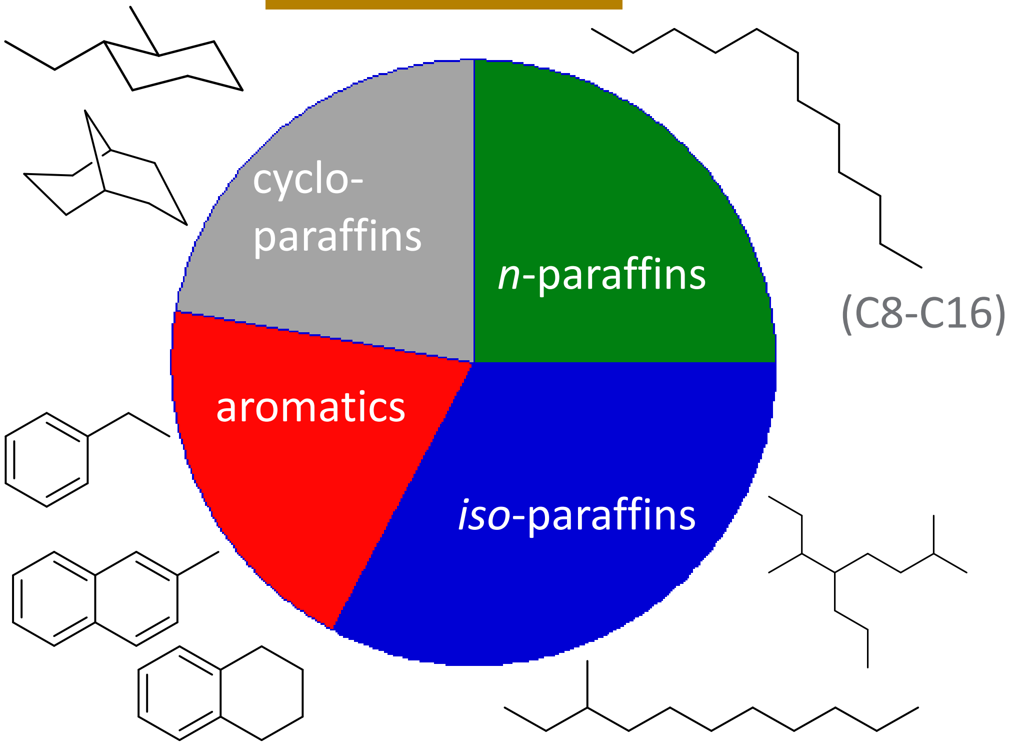
Lower cost
- **Reduce H_2 demand and pressure**
- **Improve product quality**



Typical petroleum jet fuel: JetA and JP-8

Ideal Carbon Length C8-C16

Fractions vary!

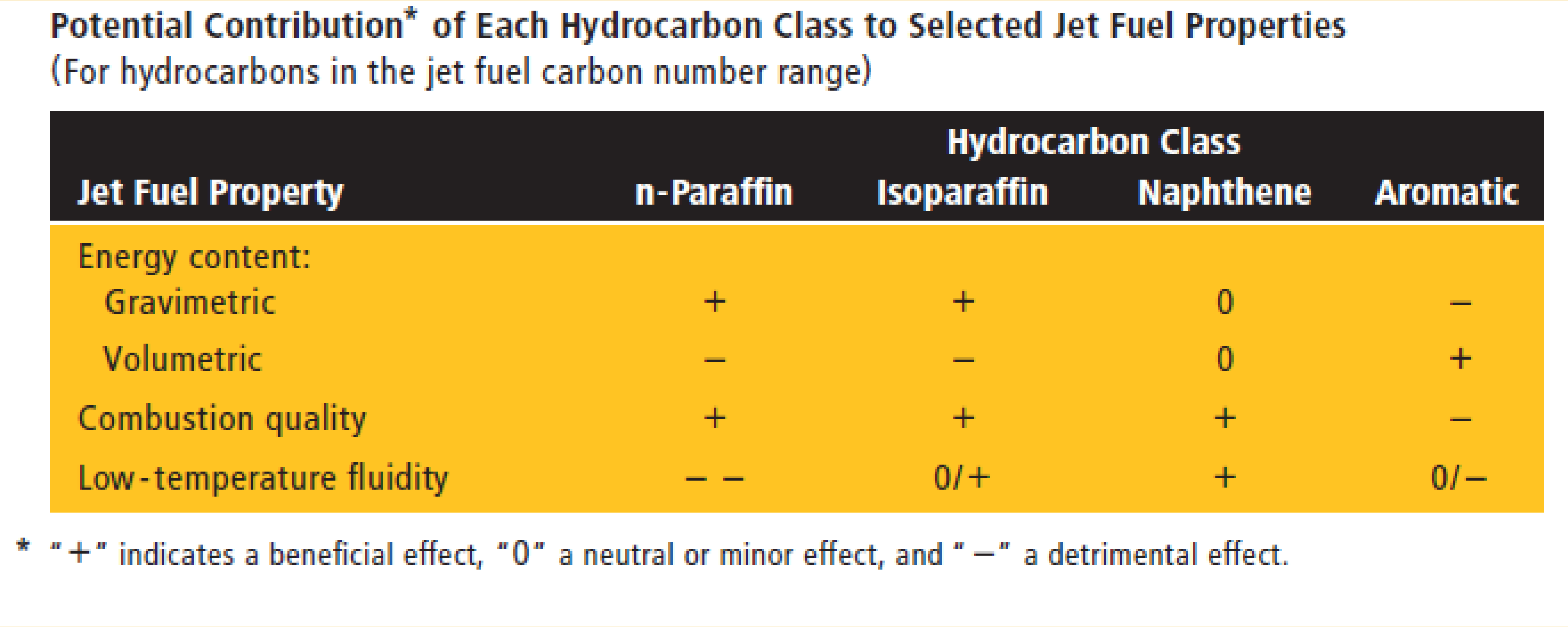


- Iso-paraffins and n-paraffins are good (Btu content)
- Aromatics are bad above certain amount (minimum needed to ensure seal swell)

- 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

Contribution of different hydrocarbon classes



Potential Contribution* of Each Hydrocarbon Class to Selected Jet Fuel Properties
(For hydrocarbons in the jet fuel carbon number range)

Jet Fuel Property	Hydrocarbon Class n-Paraffin	Isoparaffin	Naphthene	Aromatic
Energy content:				
Gravimetric	+	+	0	–
Volumetric	–	–	0	+
Combustion quality	+	+	+	–
Low-temperature fluidity	– –	0/+	+	0/–

* "+" indicates a beneficial effect, "0" a neutral or minor effect, and "–" a detrimental effect.

- Aromatics in jet fuel also helps elastomers in the fuel system to swell and seal properly at low temperature

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

Source: Aviation Fuels Technical Review (FTR-3) prepared by Chevron

Refineries

- Capital cost
- Unit operations within the refinery
- Insertion points

Tesoro Refinery, Anacortes, WA (Scott Butner, PNNL)

Capital costs –
Plant size and economies of scale

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Cellulosic
Biorefinery
<5,000 bpd

Corn Ethanol
5,000 -10,000 bpd

Fischer-Tropsch (CTL)
US – 8,000 bpd
China – 30,000+ bpd
South Africa – 160,000 bpd

US Petroleum Refinery
up to 550,000 bpd

$77,000 — 285,000/bpd (US DOE)

$16,000 — 34,000/bpd (USDA)

http://www.usda.gov/oce/reports/energy/EthanolSugarFeasibilityReport3.pdf

Biomass to liquid, 5,000 bpd (Fischer-Tropsch): $68,000 — 408,000/bpd (Robert Malina)

Refinery conversions: $0 — 140,000/bpd (CERA)

http://www.ihs.com/pdfs/ihs-cera-upgrading-refining-mar-2013.pdf

Bpd = barrels per day liquid fuels

* Sassol proposed GTL facility in Louisiana
96,000 bpd facility est. cost $145,000/bpd)

Bioprocessing and today’s infrastructure

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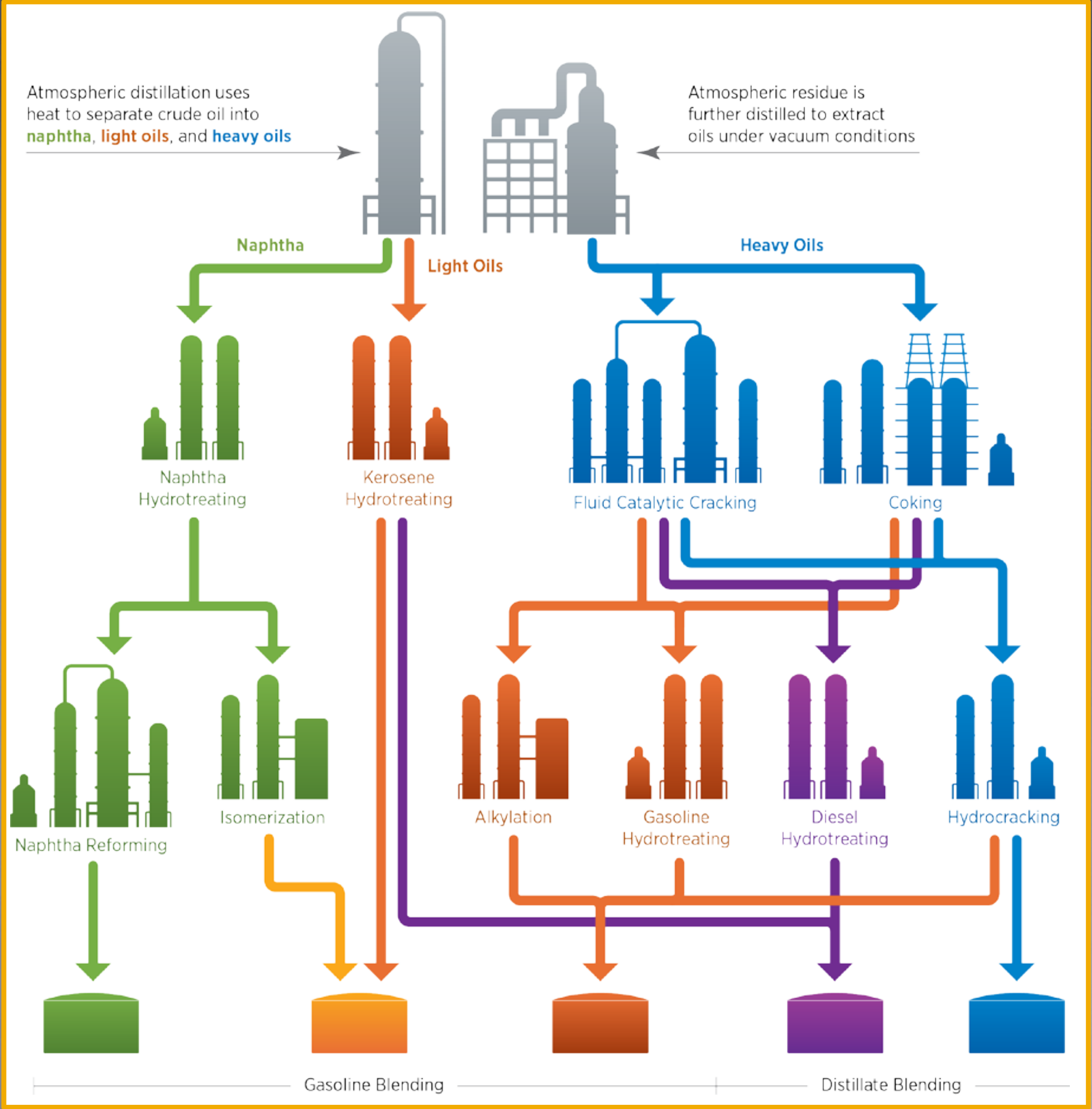
Refining

- Complex but efficient
- ~100 years experience
- ~750 refineries
- ~85M BBL of crude refined daily
- ~50M BBL transport fuels; ~6M BBL of aviation fuel (~250 M gallons/day; 90 B gallons/year)

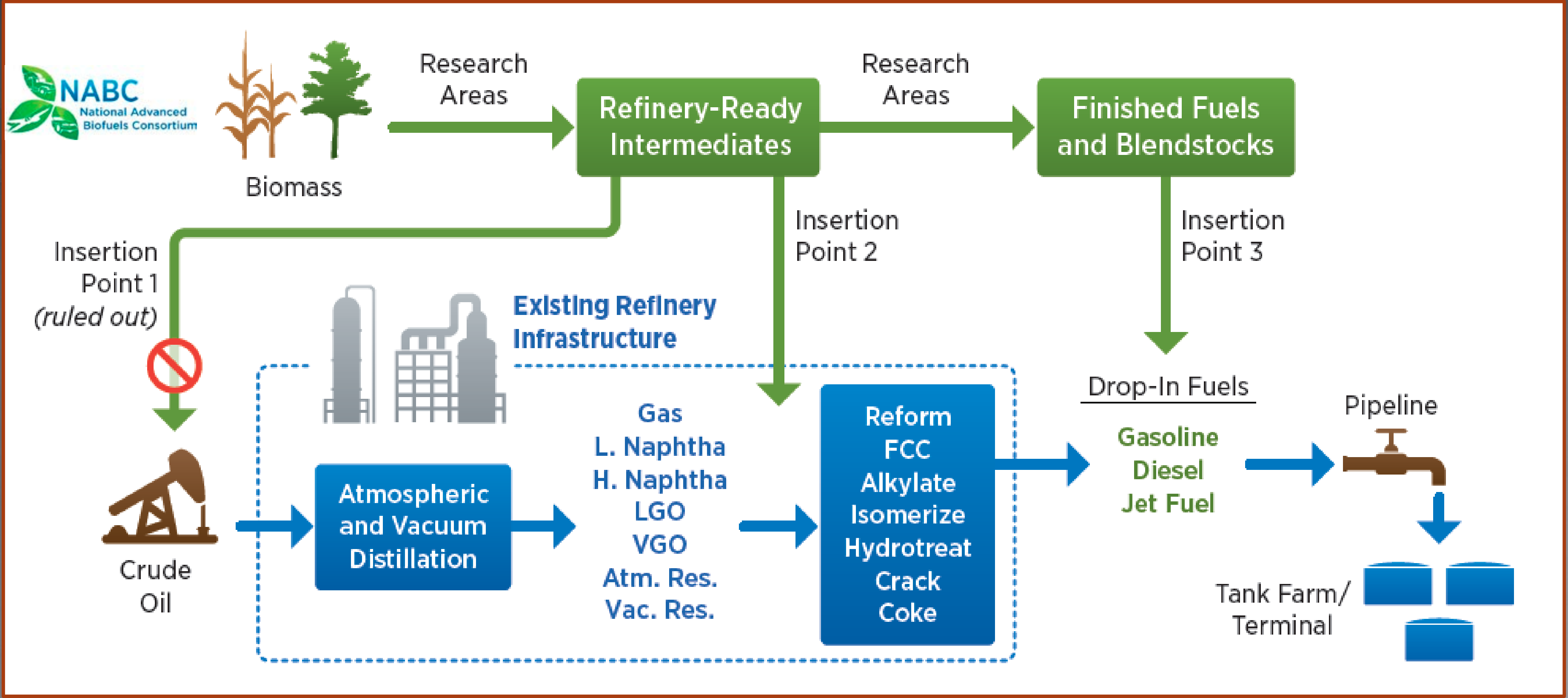
Scientific/technical Challenge

- Catalysts developed for the petrochemical and refining industries are generally not stable to bioprocessing
- Engineering (materials of construction, etc)

Figure Courtesy of NABC

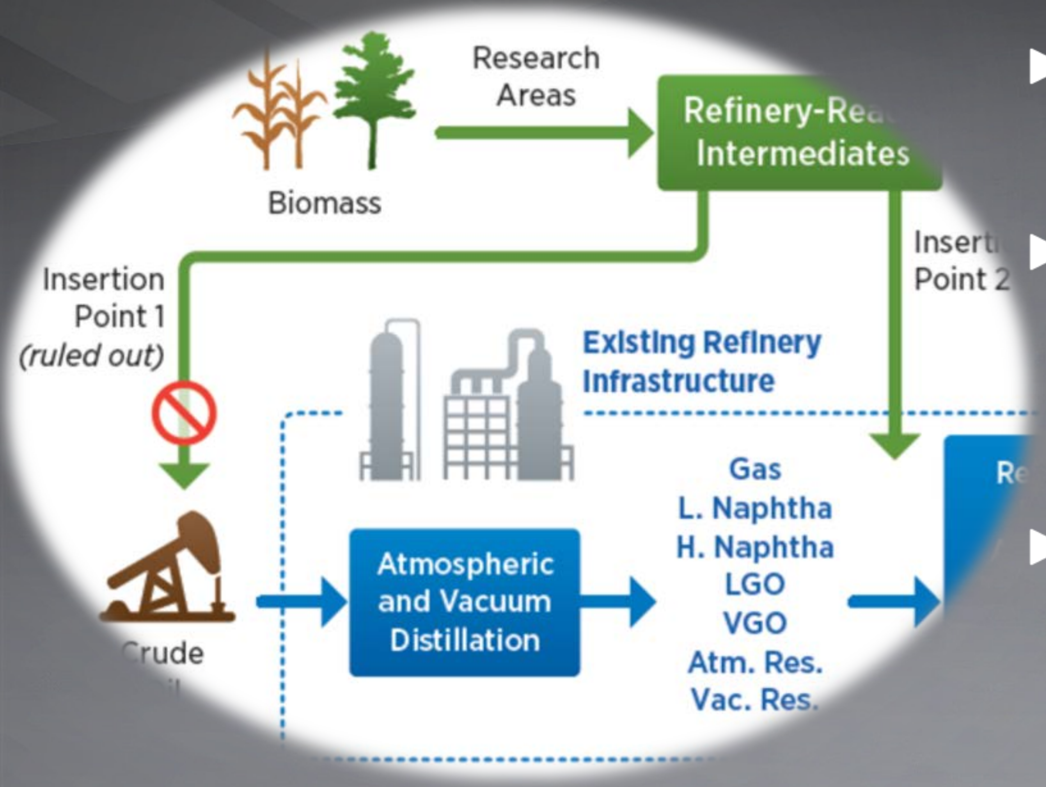


Refinery insertion points



- Renewables may be added to petroleum refineries at different locations.
- The easiest is as a blendstock (insertion point 3),
- Greater capital savings may occur if the renewables use refinery unit operations for processing (Insertion 2)

Insertion point 1

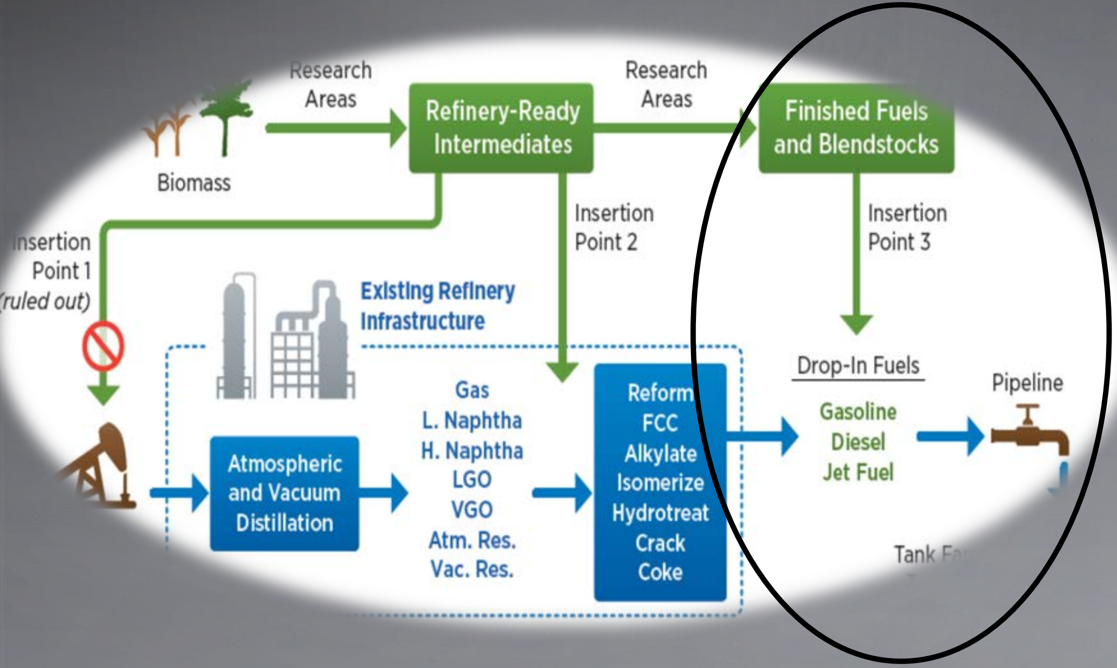


- Crude units separate molecules
  - do not chemically alter the material that they process
- Contaminants would be spread throughout the refinery
  - Rather than be concentrated into facilities that are best able to handle these materials
- Many refineries produce jet fuel directly from the crude unit

Insertion point 1 (blending renewable materials into crude) is not viable *<u>unless</u>* *the material is essentially purely composed of carbon and hydrogen, with minimal levels of olefins*

Insertion point 3

Biomass products blended into near finished fuel

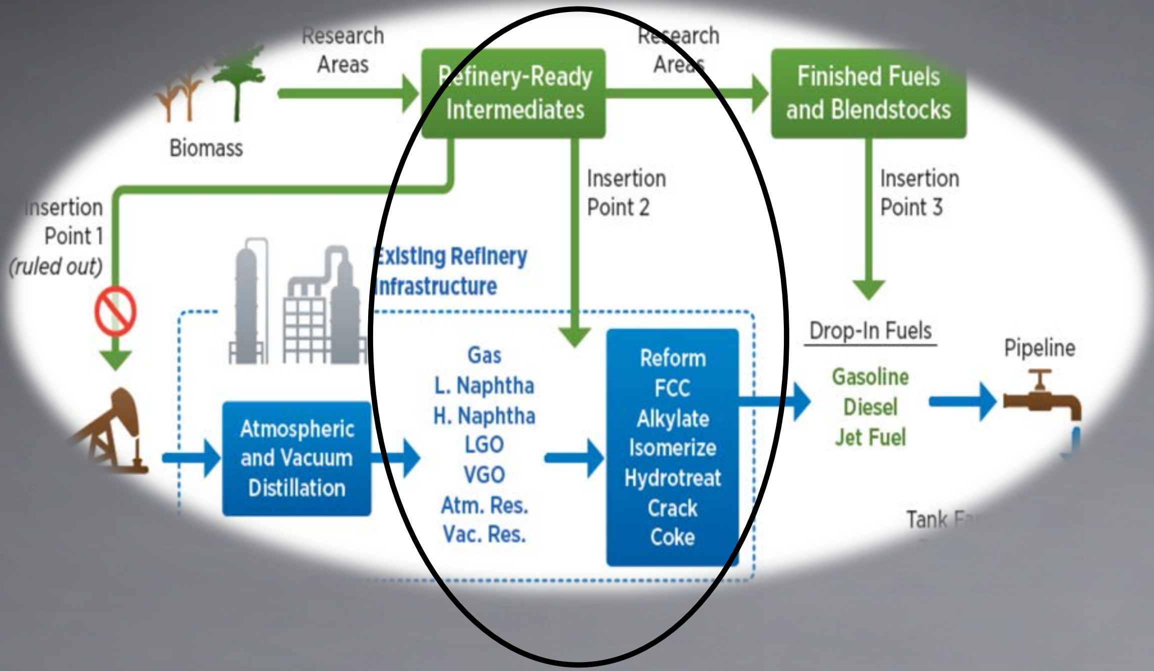


- Biomass is converted to a near-finished fuel or blendstock
- Blended component must meet all applicable standards (ASTM) for finished fuel
- Allows tailoring processes to unique properties of biomass
- Allows blending to be controlled by refiner
  - Strict rules on blending outside of the refinery may require re-testing of controlled properties

- ***Allow use of infrastructure for moving fuels around***
- ***The <u>right</u> renewable can provide value to a refinery*** (bringing low value refinery streams to spec)

Insertion point 2

Biomass Intermediate is fed into facilities within the refinery



- Conversion processes
  - Hydrocrackers
  - Fluid catalytic crackers (FCC)
  - Cokers
- Finishing processes
  - Hydrotreating
    - Naphtha HT
    - Distillate HT
    - etc
  - Specialty units
    - Isomerizing
    - Reforming
    - Alkylating

- ***Must not harm catalyst or reactor (carbon steel)***
- ***Product yield cannot be reduced***
- ***Product quality cannot be compromised***

Conversion Processes

- Decreases molecule sizes to convert heavier materials into distillation ranges of transportation fuels
- Conversion units are also capable of removing some level of contaminants

Unit	C:H increase mode	Cracking mode	Feedstock	Feed boiling Range (°F)
Coker	C rejection as coke	Thermal	Vacuum resid	1050+
FCC	C rejection as coke	Fluid catalyst	Vacuum gas oil	610-1050
Hydro-cracker	H addition using metal cat	Fixed bed catalyst	Vacuum gas oil	450-1050

- Thermal processes affected by free radical generators/traps
- Acid catalysts affected by basic poisons (eg. alkali) & metals

Hydrotreaters

- Remove heteroatoms (such as S, N, O) via catalytic reaction with H_2
  - Allow finished products to meet spec or to protect sensitive units
- Hydrotreating does not materially impact carbon chain length
  - Renewable feedstocks need to be introduced with a compatible chain length to allow on-spec production of fuels

Service	Feed Boiling Range	Temperature	Pressure	LHSV
Naphtha	90-380° F	↓	↓	↑
Kerosene/Diesel	380-610° F			
Vacuum gas oil	610-1050° F			

Red arrows indicate desired direction to move

- Trickle bed reactors contain fixed bed of sulfided NiMo- or CoMo/Al2O3 catalyst particles
  - Sensitive to fouling via solids deposition, coking or polymerization Deactivation via metals, alkali, bio-heteroatoms (eg. P)
  - May have challenges with heat gain across “standard” refinery hydrotreaters may exceed allowable temperature limits

“Specialty” Units

- Isomerizing
  - Converts n-paraffins to isomers (higher octane or alkylation feed)
  - Fixed bed of metal/acid catalyst at lower temp than reforming
- Alkylating
  - Converts isobutane & isobutylene to isooctane
  - HF or H_2S acid catalyst (containment!!), sensitive to feed carbon number
- Reforming
  - Upgrades octane of naphthas by generation of aromatics (+ H_2) from napthenes (+ paraffins)
  - Fixed bed of chlorided Pt/Al_2O_3 catalyst particles at low pressure & high temp, sensitive to S, N in the feed

DOE's Bioenergy Technologies Office sponsored analysis on refinery integration

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- Technical Focus
  - High level assessment of impact of incorporation of bio-derived intermediates in U.S. petroleum refineries
  - Surveys availability of biomass near petroleum refineries in the 2022 timeframe
  - Preliminary considerations of bio-intermediate compatibility with petroleum intermediates
  - Offers a refiner's perspective
  - Public document
- Mission Impacts Supports understanding of infrastructure use
  - Addresses entire barrel
  - Considers advanced biofuels
- Data Sources
  - KDF for biomass resources
  - EIA for refinery resources
  - Publically available bio-intermediate data

http://www.pnl.gov/main/publications/external/technical_reports/PNNL-22432.pdf

High-level impact assessment

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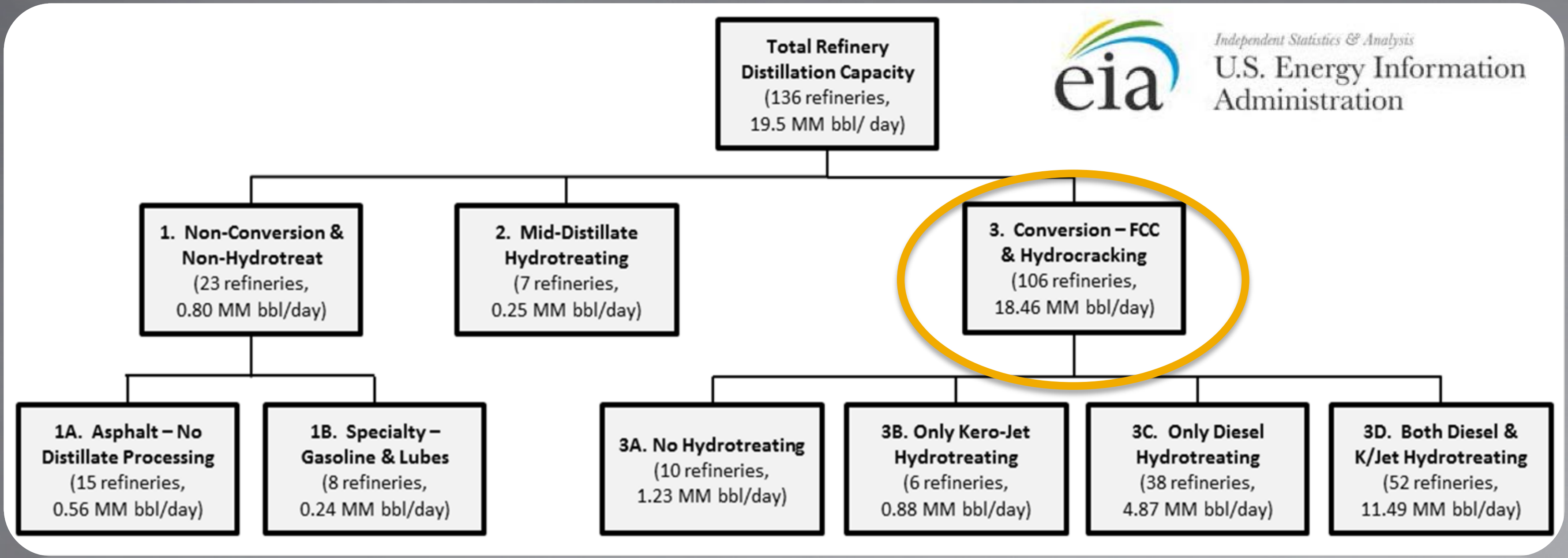
- What refining capacities and capabilities currently exist in the US?
  - Per EIA, 149 refineries total, 136 sufficiently detailed
  - ~20 million barrels/day total capacity (136 refineries)
  - Categorized into three main types:
  - Non-conversion & non-hydrotreating
  - Middle-distillate hydrotreating capability
  - Full conversion – fluidized catalytic cracking and hydrocracking



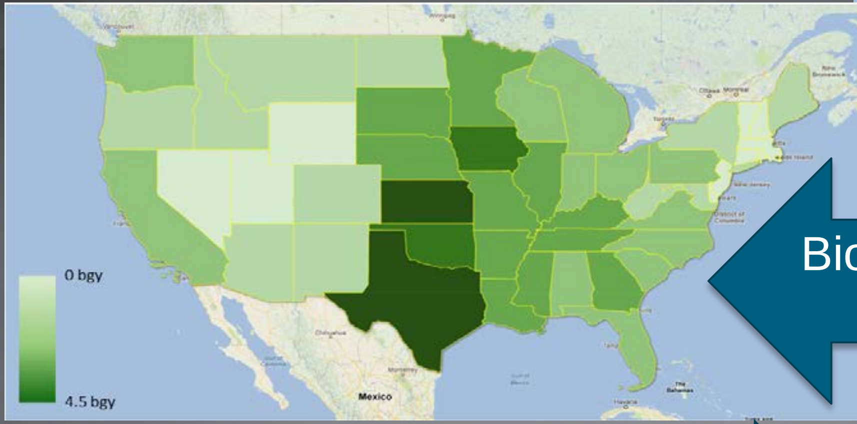
Total Refinery Distillation Capacity (136 refineries, 19.5 MM bbl/ day)

- **1. Non-Conversion & Non-Hydrotreat** (23 refineries, 0.80 MM bbl/day)
  - **1A. Asphalt – No Distillate Processing** (15 refineries, 0.56 MM bbl/day)
  - **1B. Specialty – Gasoline & Lubes** (8 refineries, 0.24 MM bbl/day)
- **2. Mid-Distillate Hydrotreating** (7 refineries, 0.25 MM bbl/day)
- **3. Conversion – FCC & Hydrocracking** (106 refineries, 18.46 MM bbl/day)
  - **3A. No Hydrotreating** (10 refineries, 1.23 MM bbl/day)
  - **3B. Only Kero-Jet Hydrotreating** (6 refineries, 0.88 MM bbl/day)
  - **3C. Only Diesel Hydrotreating** (38 refineries, 4.87 MM bbl/day)
  - **3D. Both Diesel & K/Jet Hydrotreating** (52 refineries, 11.49 MM bbl/day)

Survey of projected 2022 biomass availability near petroleum refineries

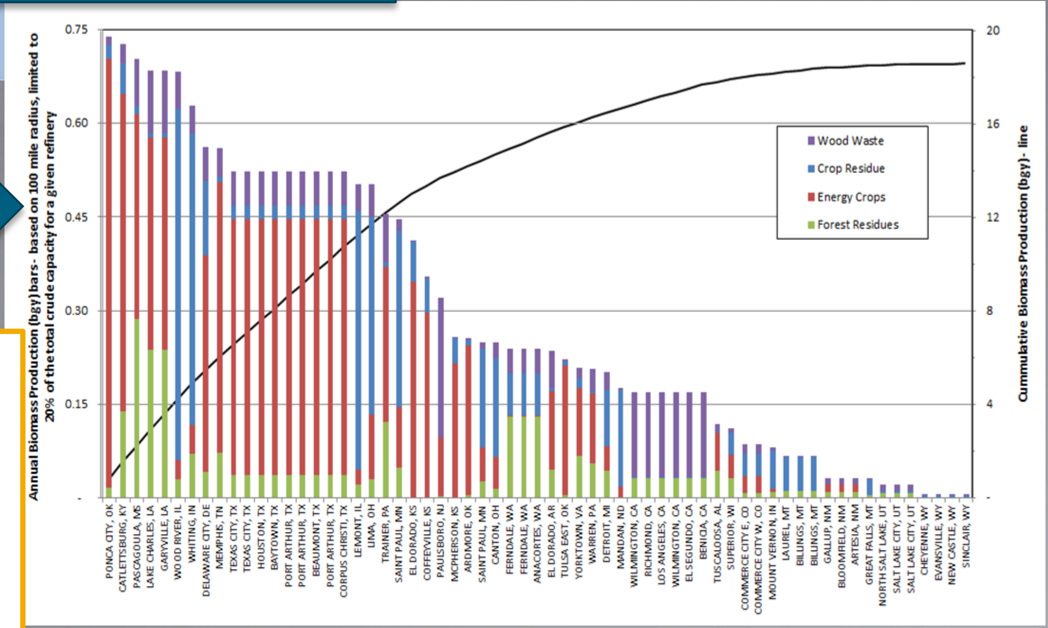
Q: Proximity of biomass suitable for 20% co-processing?

Refinery locations



Bio-oil production in 2022*

Refinery sites with highest likelihood of biofuel production**



* 20% additional yield loss
$60/ton farm gate
85 gal/dry ton conversion

**US refinery sites with highest est. fuel volumes
100 mile radius around each refinery
FCC and HCK refineries only (Cat 3)
Equiv. biofuel intermediate into any refinery limited to 20% of total crude capacity

A: Initial look suggests refineries & biomass may fit

Refiner's perspective

– safety, reliability, predictability, profitability –

Risk	Type of Bio-oil Intermediate	Insertion	Refinery Challenges
Lowest	Well defined, consistent quality, such as single molecules (e.g., ethanol, butanol, farnesene)	Blending units	• Blending, product performance and distribution of products that include the bio-component • Evaluating and managing potential stability, toxicity and environmental issues
Medium	Intermediates requiring only minor treating (e.g. triglycerides, some direct liquefaction oils, some catalytically derived sugar oils)	Hydrotreating followed by blending	Challenges identified above, plus: • Understanding process performance on new feeds and blends with petroleum-based feeds • Enabling larger fractions of bio-oil blending stocks while still meeting product specs. • Providing sufficient hydrogen to meet hydrotreating demands (for reducing oxygen or aromatic contents)
Highest	Intermediates needing boiling range & composition changes for acceptable gasoline, diesel and jet fuel blending stocks (e.g. fast pyrolysis oils, some hydrothermal liquefaction oils, some catalytic pyrolysis oils)	Off-site or dedicated on-site hydrotreating followed by cat- or hydro-cracking	Challenges identified above, plus: • Understanding the impact of bio-oils on all refinery processes • Meeting product quantity and quality needs with feedstocks with less data on conversion behavior

Preliminary Conclusions

- Focus on Gulf Coast
  - Biomass availability, river logistics
  - Primary supply is imported crude (priced off Brent)
  - Limited access to Bakken, Marcellus/Utica, Canadian supplies
- Need to improve bio-intermediate characterization
  - Develop metrics that are meaningful to refineries (pour point, cetane, API, D86, etc)
  - Improve predictions of how the biomaterials will process within the refinery
- Significant risk for co-processing that will need to be reduced

Technology development

- FCC
- Hydrotreating/hydrocracking
- Alkylation

Fluid catalytic cracking

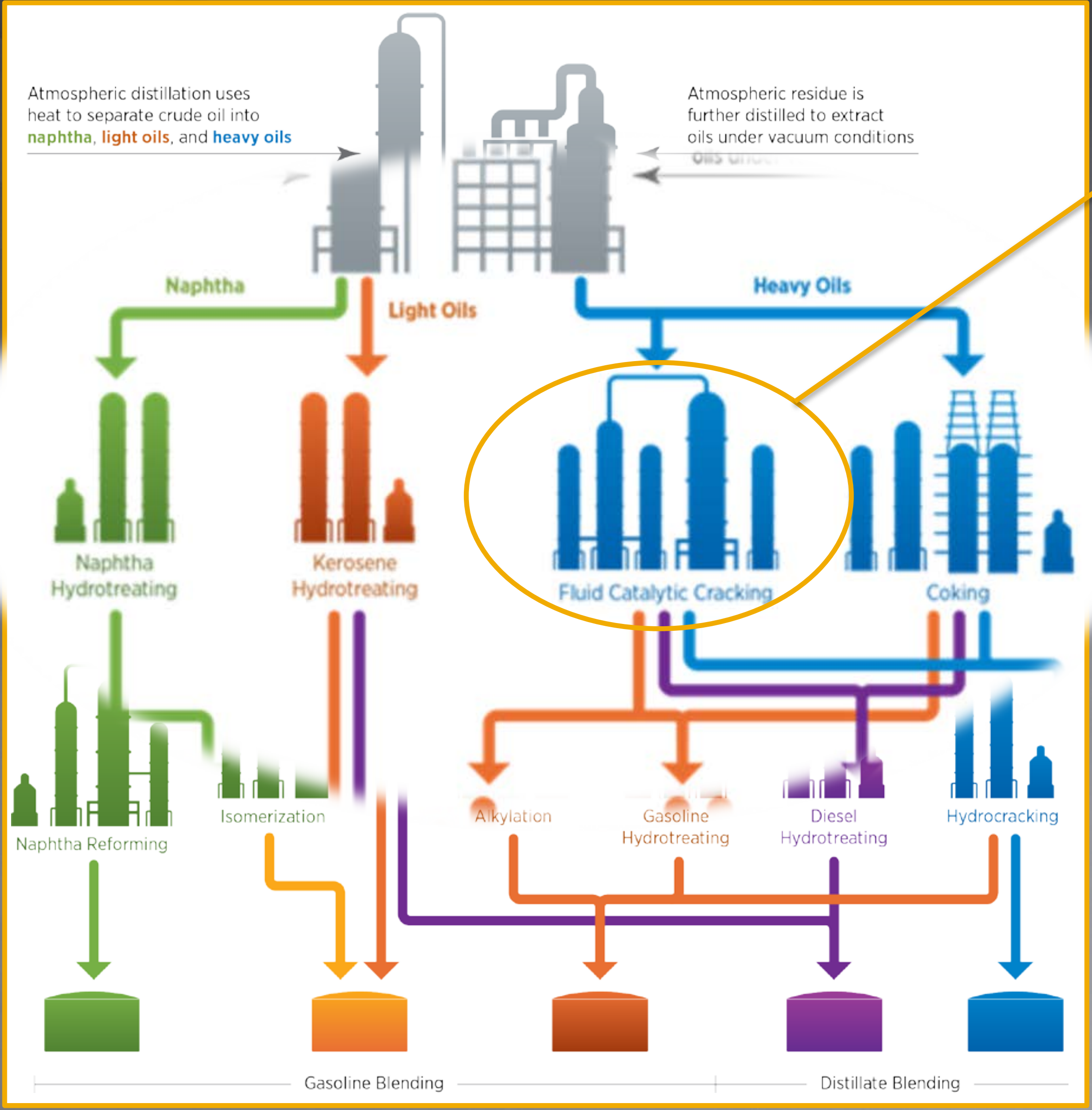


Figure Courtesy of NABC

Fluid catalytic cracking (FCC)

Co-feed to the Fluid Catalytic Cracking (FCC) unit is a favored option

Give data on two bio-oil FCC feed options

Results – Vegetable oil feed
Results – Pyrolysis oil feed

Grace DCR™ pilot plant schematic

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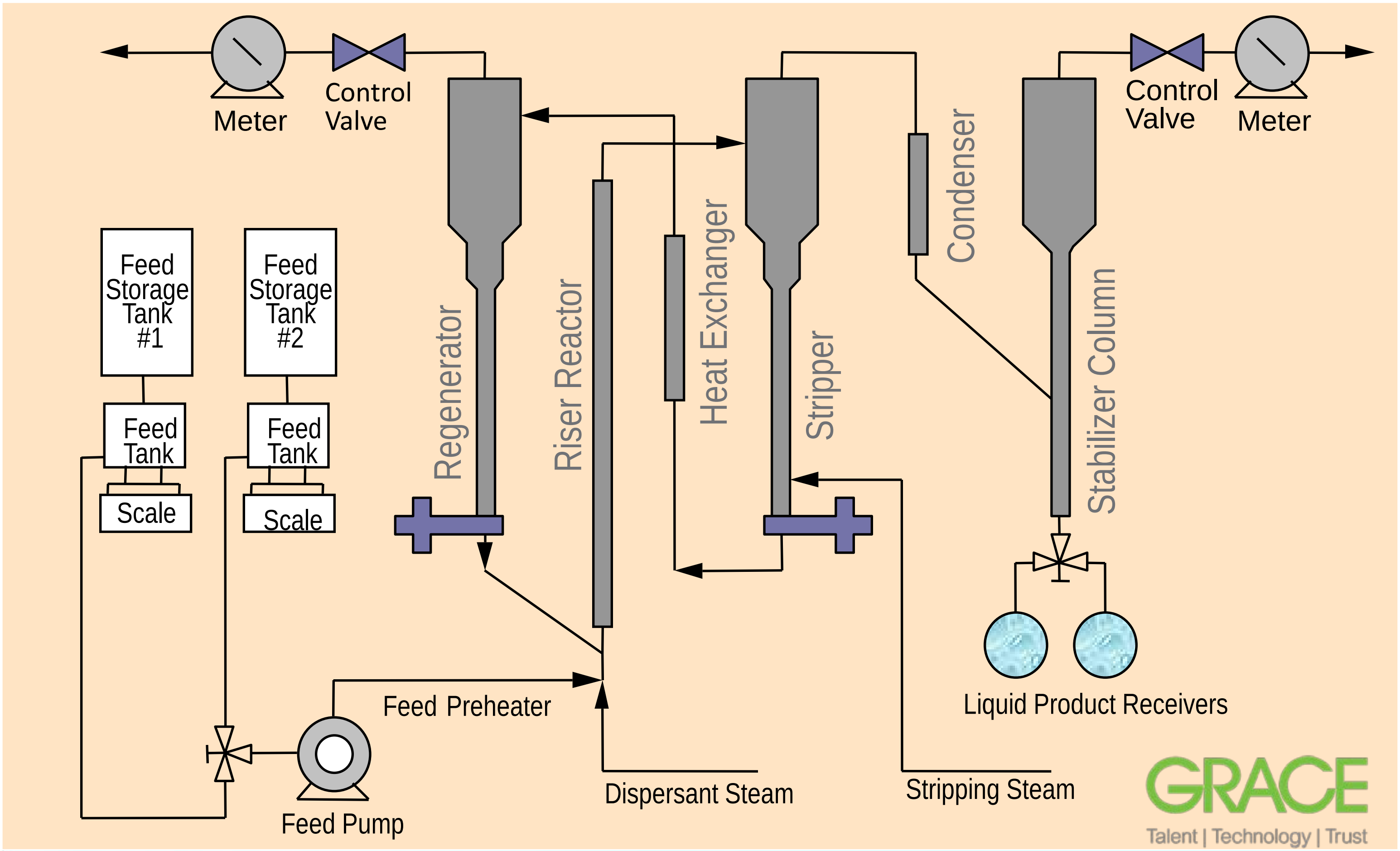


Continuous circulating riser

Work done in WR Grace DCR™ pilot plant

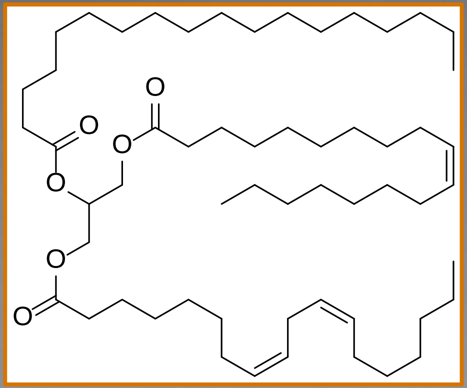
26 licensed DCR pilot units have been constructed throughout the world

FCC yields of soybean oil vs vacuum gas oils

	100% Soybean Oil	100% VGO
C/O Ratio	6.7	9.3
H2 Yield wt%	0.04	0.02
C1 + C2's wt%	1.9	2.1
Total C3 wt%	4.3	6.7
Total C4 wt%	6.2	12.4
Gasoline (C5-430°F) wt%	44.5	53.1
G-Con RON EST	90.9	90.2
G-Con MON EST	79.0	79.5
LCO (430-700°F) wt%	22.0	15.4
Bottoms (700°F+) wt%	3.9	4.9
Coke wt%	4.6	5.2
Fuel Gas CO (wt%)	1.2	0.0
Fuel Gas CO_2 (wt%)	0.9	0.0
Fuel Gas H_2O (wt%) (by difference)	10.3	0.0

Compared to vacuum gas oil, soybean oil produces less gasoline and more light cycle oil (LCO)

Conditions
Rx exit temp = 970°F
Catalyst temp = 1300°F
Feed temp = 250°F
Pressure = 25 psig

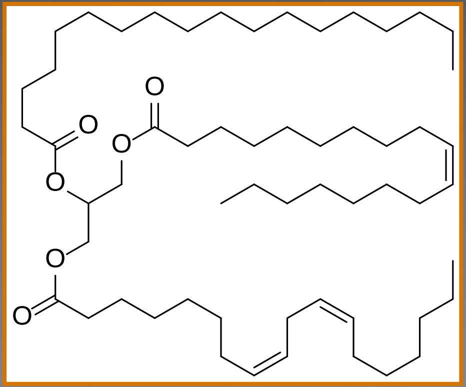


Vegetable oil is chemically as close to petroleum as any biomass feedstock

Not favored technology for jet fuel from veg. oils

Key findings – soybean oil

- Soybean oil cracking changes the riser temperature profile
  - Heat of cracking is only ~15% of conventional VGO
- Most of the oxygen reacts to form water
- Product yield slate is different
  - Sharply lower gasoline
  - Sharply higher Light cycle oil, lower bottoms



Soybean oil could likely be processed in a commercial FCC unit

Processing a blend of pyrolysis oil and VGO

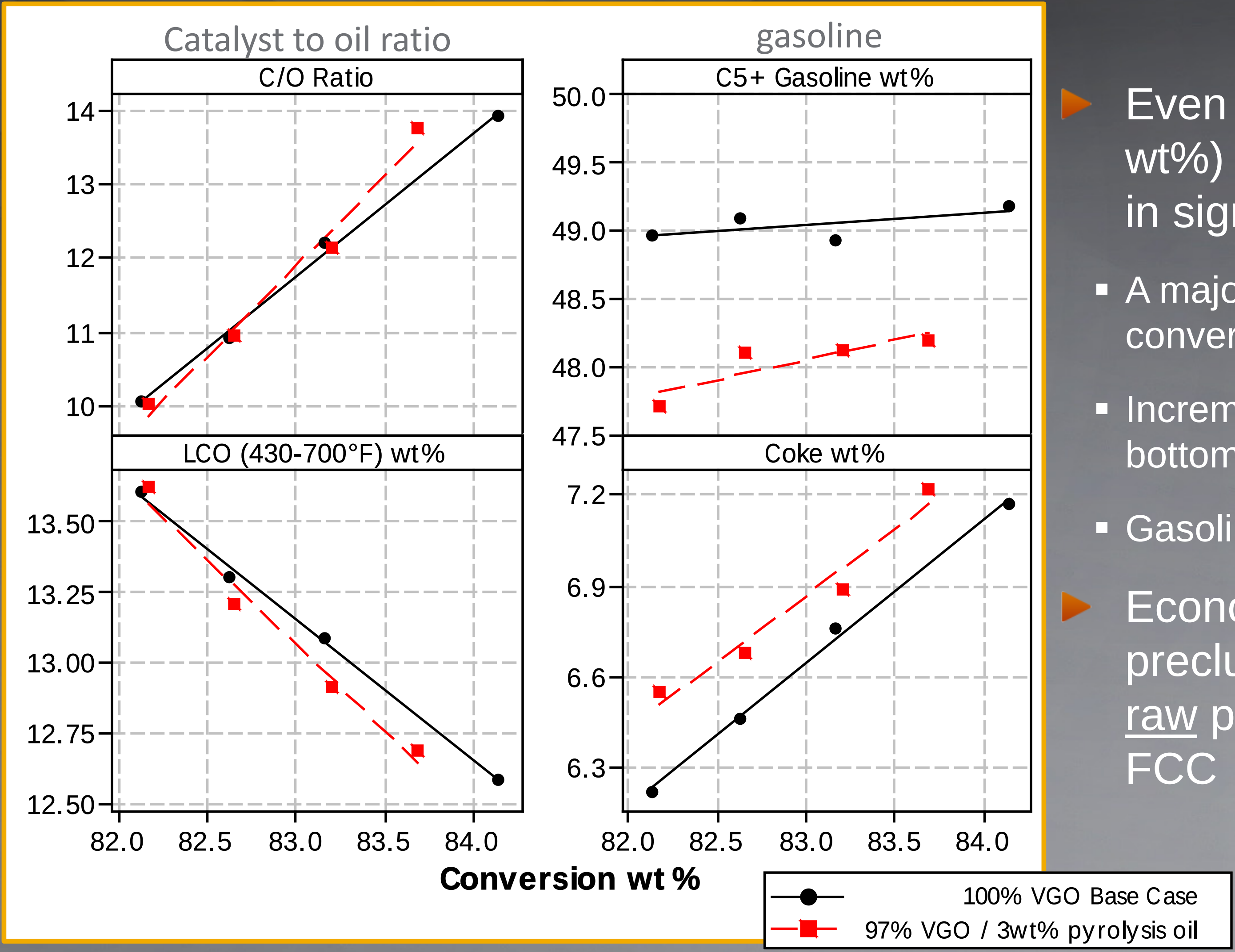
- Co-processing bio-based pyrolysis oil with conventional vacuum gas oil (VGO)
- Processing pyrolysis oil isn't easy and requires changing (co)feed systems; adding surfactants and riser modifications

This is what happened to the drive strap on a gear pump when it seized while pumping 100% pyrolysis oil

Water content (wt%)	23.0
Carbon (as-is) (wt%)	39.5
Hydrogen (as-is) (wt%)	7.5
Oxygen (as-is) (wt%) (by difference)	53.0
Carbon (dry basis) (wt%)	55.5
Hydrogen (dry basis) (wt%)	6.5
Oxygen (dry-basis) (wt%) (by difference)	38.0

Pyrolysis oil is a challenging feed!

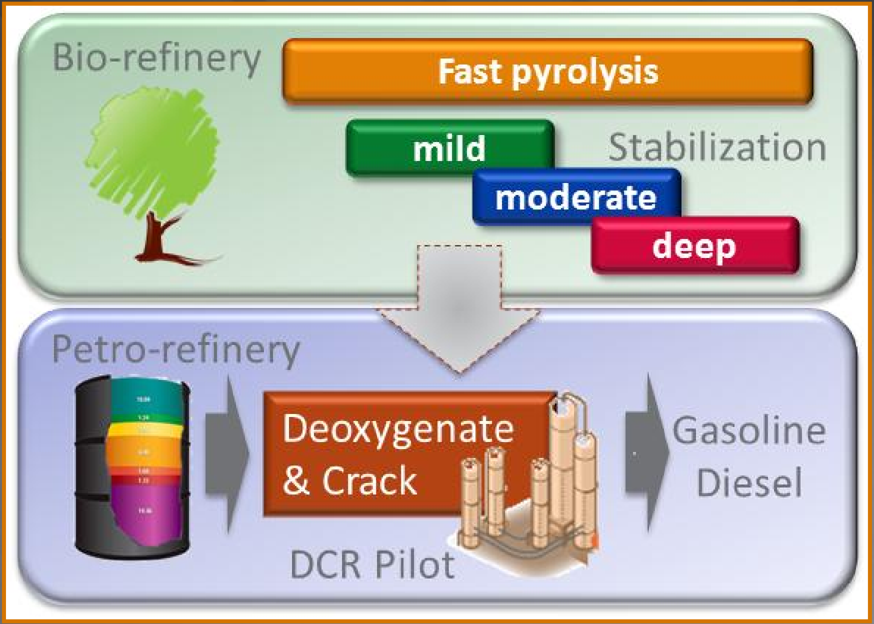
Yield when blending in 3 wt% pyrolysis oil



- Even small amounts (3 wt%) of pyrolysis oil result in significant yield shifts
  - A majority of the pyrolysis oil converts to H_2O, CO and CO_2
  - Incremental yields of coke and bottoms are also very high
  - Gasoline and LCO decrease
- Economics will likely preclude co-processing <u>raw</u> pyrolysis oil in an FCC

Adding raw pyrolysis oil results in more coke, less gasoline and less LCO

Co-processing bio-oil with petroleum FCC oils (vacuum gas-oils)



Bio-refinery

Fast pyrolysis

Stabilization

mild

moderate

deep

Petro-refinery

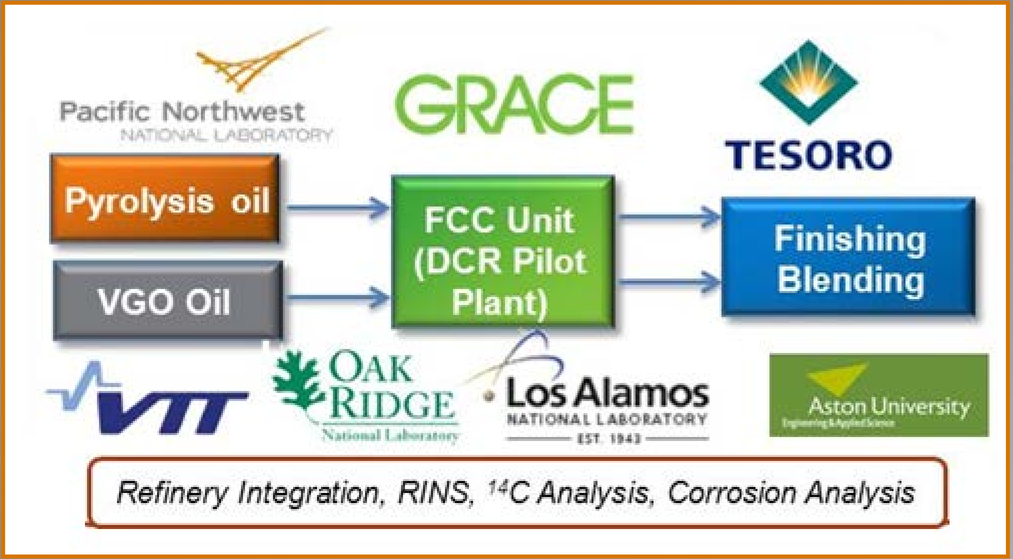
Deoxygenate & Crack

Gasoline
Diesel

DCR Pilot

Tesoro Refinery, Anacortes, WA (Scott Butner, PNNL)

- Understand minimum upgrading of bio-oil for co-processing
- Develop FCC catalysts tuned for bio-oil VGO mixtures
- Understand quality of product
- Determine fate of biogenic carbon in the process



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GRACE

TESORO

Pyrolysis oil

VGO Oil

FCC Unit (DCR Pilot Plant)

Finishing Blending

VTT

OAK RIDGE National Laboratory

Los Alamos NATIONAL LABORATORY EST. 1943

Aston University Engineering & Applied Science

Refinery Integration, RINS, ^{14}C Analysis, Corrosion Analysis

Hydrotreated pine pyrolysis oils from PNNL

Degree of Catalytic Hydrotreating (O content, dry basis)	Maximum VGO feed preheat temperature without nozzle plugging	Percentage pyrolysis oil co-processed	Yield Observations while coprocessing
None (38 wt% O)	~200°F (93°C)	up to 5 wt% with difficulty	Increased coke, reduced gasoline
Mild (22wt% O)	~200°F (93°C)	up to 3 wt% with difficulty	Increased coke, reduced gasoline
Medium (11% O)	Up to 700°F (370°C)	10 wt%	Yields similar to VGO
Severe (2% O)	Up to 700°F (370°C)	10 wt%	Yields similar to VGO

Note: typical FCC feed pre heat temperatures are 300 to 700°F (150-370°C)
Pyrolysis oil levels >10 wt% were not tested since refineries are unlikely to run above these levels

- Mildly hydrotreated material harder to run than raw pyrolysis oil
- Medium and severe hydrotreating led to materials that were easier to run

Other advancements (FCC)

- Ensyn is working on refinery co-processing to produce gasoline and diesel
- Report it to be “in final stages of commercialization”
- 5% blend of RFO™ (pyrolysis oil) with VGO oils for production of spec gasoline and diesel
- Testing done in bench units, pilot units and commercial FCC units
- 2015 extended commercial demonstration
- “Eligible under EPA’s RFS2 program for the generation of D3 [co-processing] and/ or D7 [heating oil] cellulosic RINs.”

Ian Barnett, Issue 36 PyNe Newsletter, IEA Bioenergy Task 34 (Dec 2014)

PNNL’s Ongoing work

- Analysis of corrosion coupons included during co-processing runs
  - Corrosion can be partially addressed through bio-oil stabilization (e.g. light hydrotreating)
- Carbon accounting using isotope analysis
- Oxygen analysis of liquid products
- Full characterization from co-processing of straw based pyrolysis oils

Hydrotreating

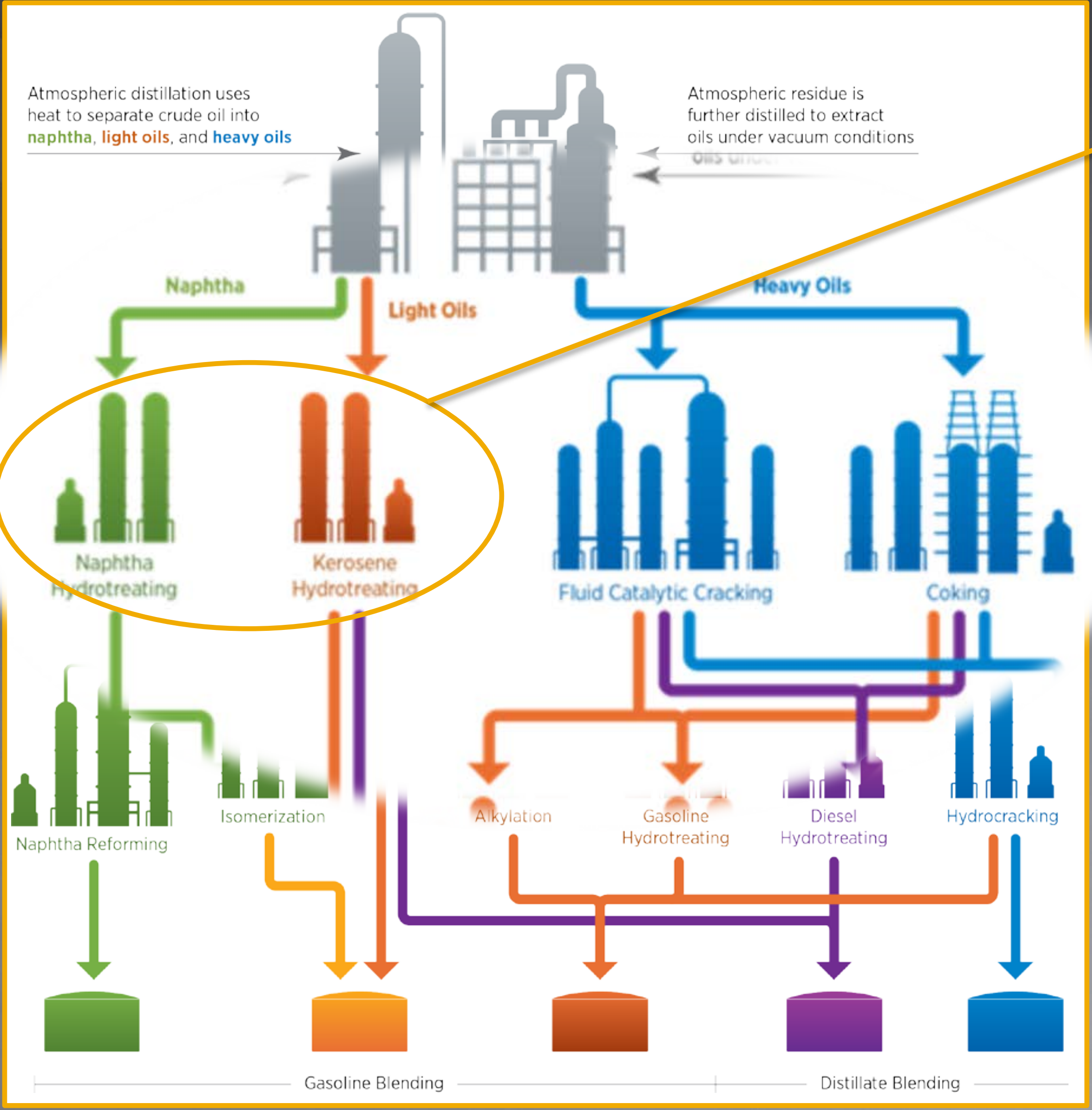


Figure Courtesy of NABC

Hydrotreating

Work done at PNNL

Current studies are on hydrotreating neat bio-oil

Fast pyrolysis bio-oil

- Bio-oil is not miscible with petroleum
- Severe catalyst challenges

Hydrothermal Liquefaction biocrude

- Moves further into mid-distillate/distillate range
- More miscible with petroleum
- Easier to process

Relative H_2 demands in the refinery

- Hydrotreating is designed primarily to remove S and N; removing the large amount of O in biomass may add additional H_2 demand to refineries
- Slides that follow will examine pyrolysis bio-oil hydrodeoxygenation (HDO) and Hydrothermal liquefaction biocrude HDO

H_2 chemical consumption, scf/bbl fd (standard cubic feet/barrel feed)

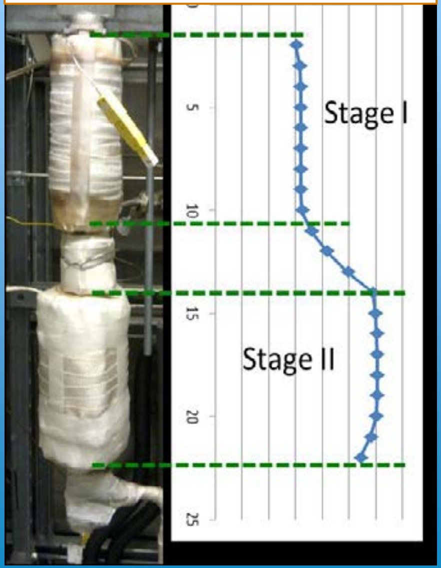
Petroleum hydrodesulfurization				**Petroleum hydrocracking**			**Pyrolysis oil**	**HTL biocrude**
Naptha HDS	Kerosene HDS	ATM resid HDS	Gas oil HDS	Mild HCK	Single STG HCK	Resid HCK	HDO	HDO
45	555	460	422	358	1150	660	~3400	~1800

Hydrotreating reactor configurations and scales

Workhorse equipment

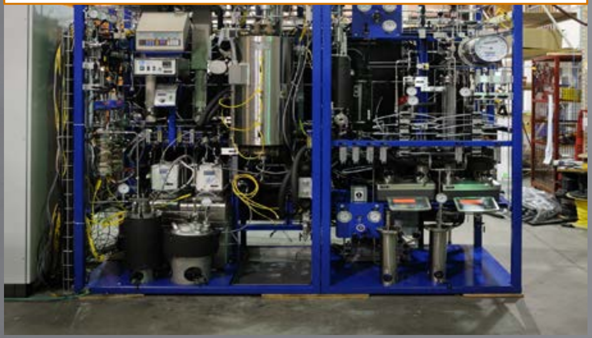
~1.4 cc 8-reactor packed bed system

40 cc dual T zone packed bed reactor



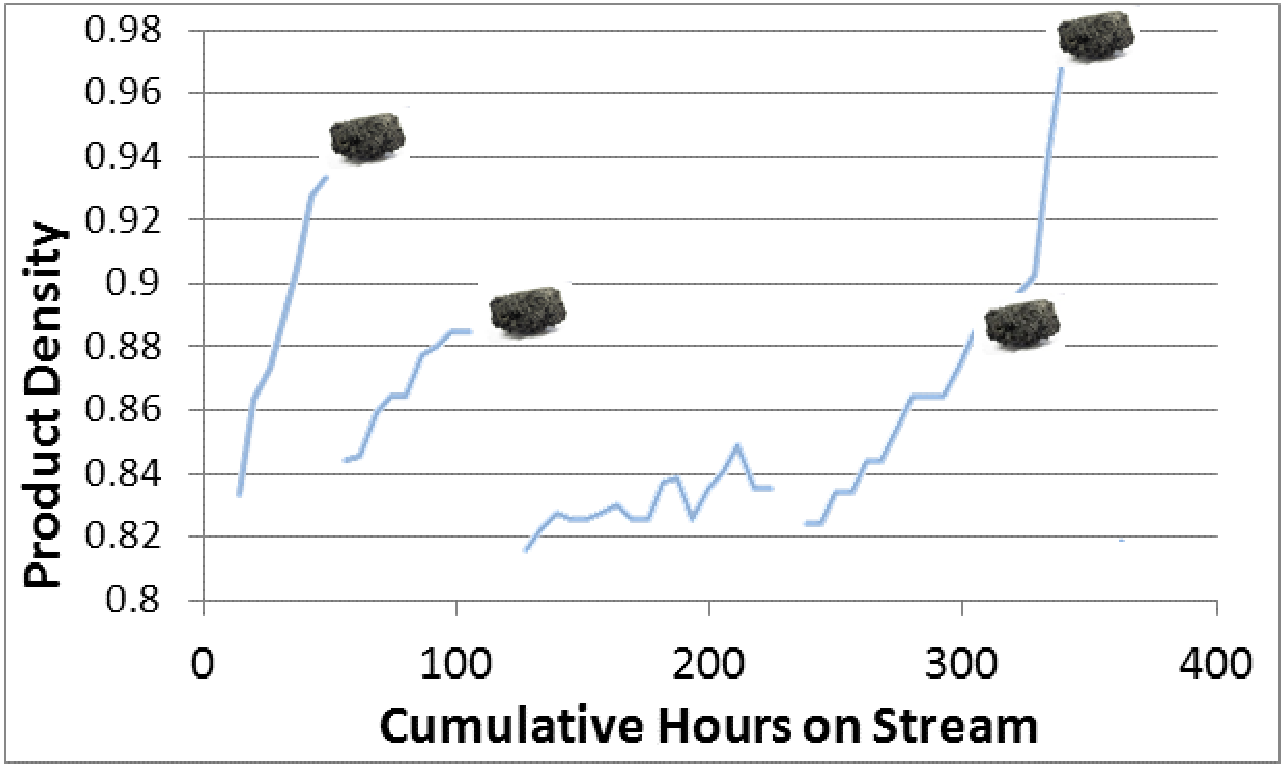
400/800 cc dual T zone packed bed

1 L ebullated bed reactor



19 L 8-zone furnace packed bed

Raw bio-oil leads to plugging (short as 20-50 h on stream)



- Start-up after each plugging event required replacement of about 10% of the catalyst bed

plug

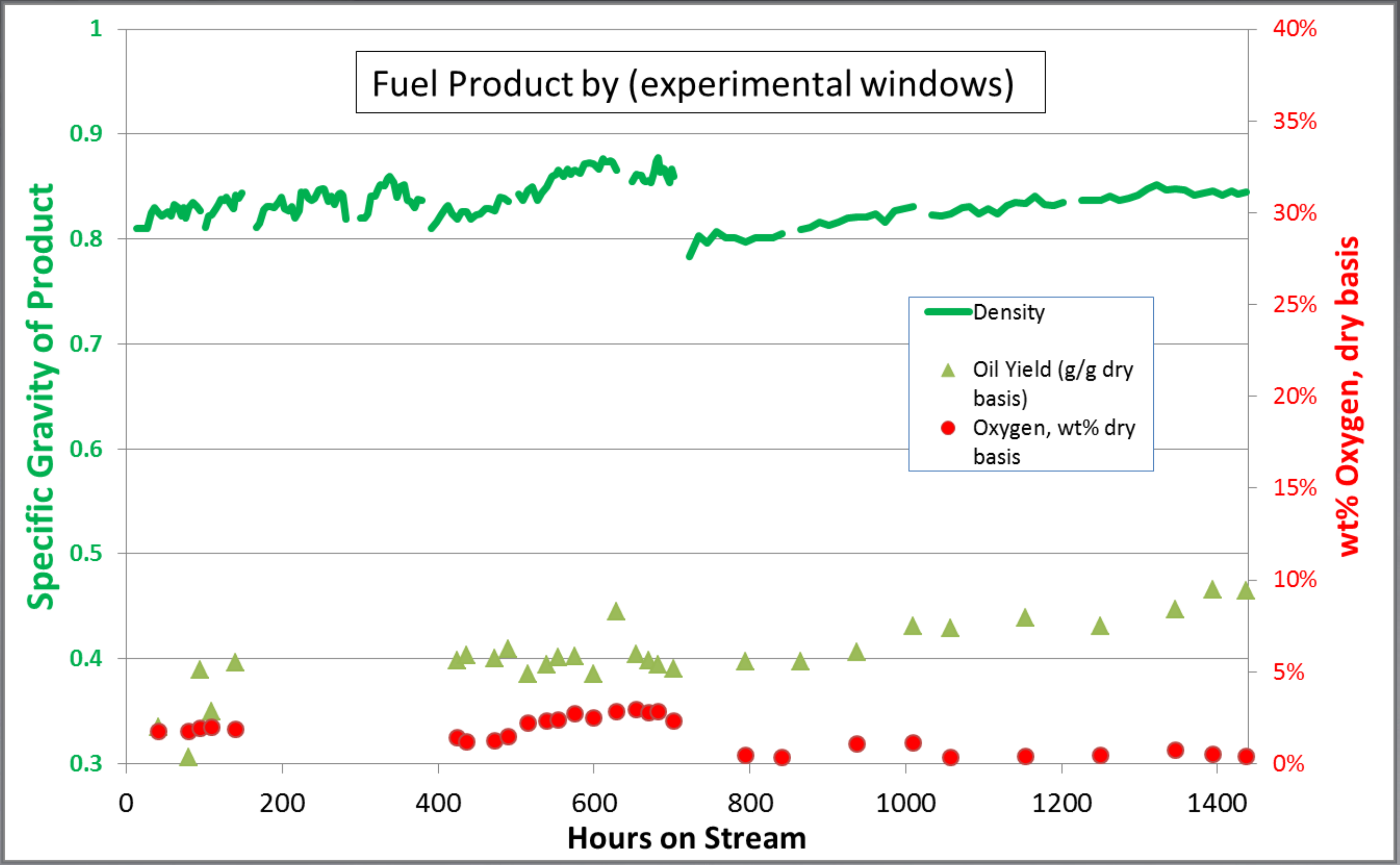
FP oil density: 1.2 g/cc
Catalysts: RuS/C
CoMoS/C
T: 250 - 410°C
P: 15 MPa H_2
Space velocity: 0.1-0.2

H_2 demand = 5 - 8 g H_2/100 g oil (dry basis)

Understanding of plug formation JACS 2014. DOI: 10.1021/ja501592y

Through mild pretreatment we can produce an oil that is processable

A. Zacher



- PNNL demonstrated a **fourfold increase in stable on-stream production** time, and a **threefold increase in weight hourly space velocity** (throughput)
- Reduction in state-of-technology conversion cost of 60% from $12/gge in 2009 to $4.60/gge today (note: gge = gasoline gallon equivalent).

Vacuum distillation curves for hydroprocessed pyrolysis bio-oil (wood)

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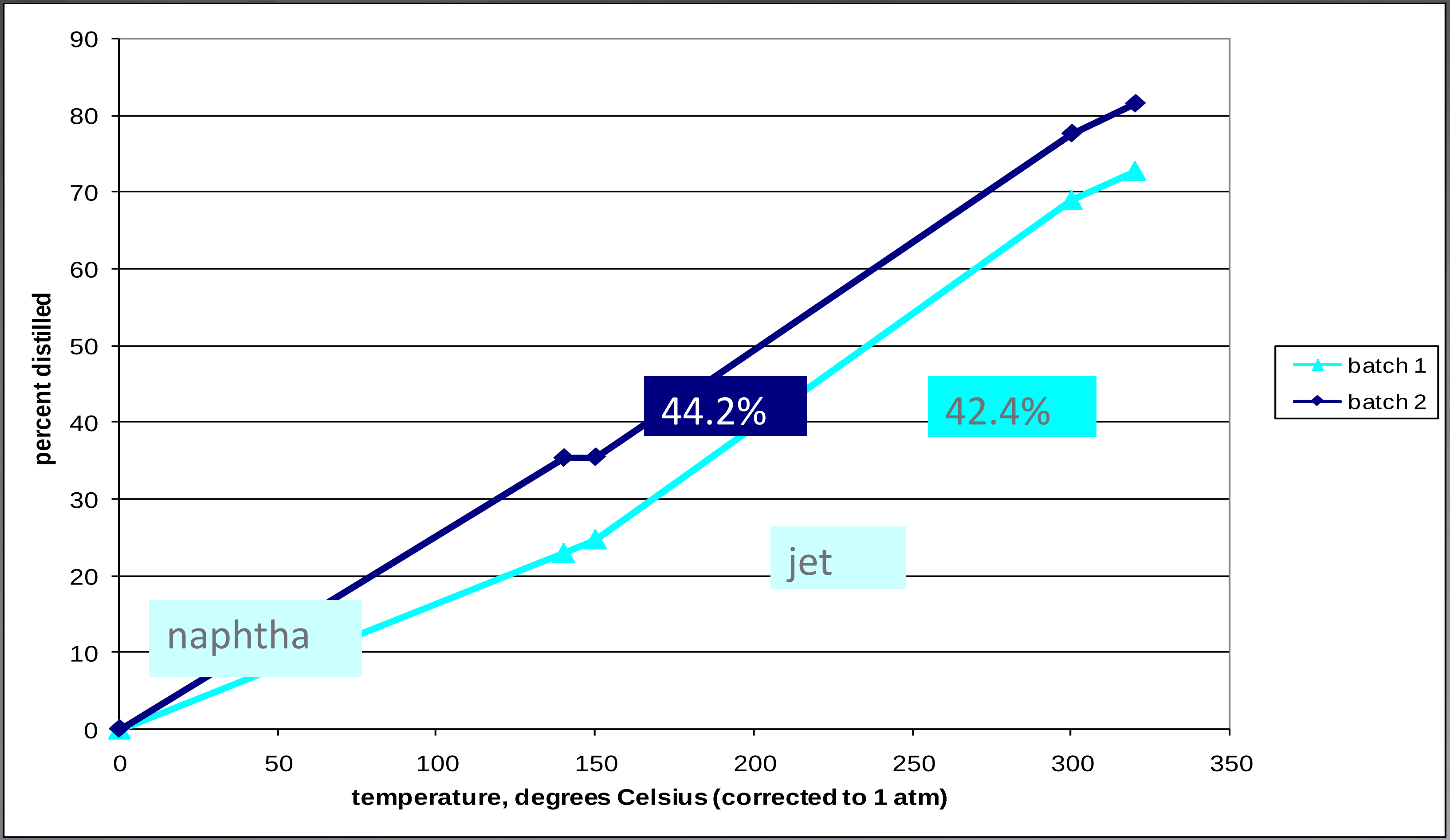


Jet fuel mid-distillate may provide the aromatic/cyclic portion of jet fuel

Future possibility of 100% Renewable Jet

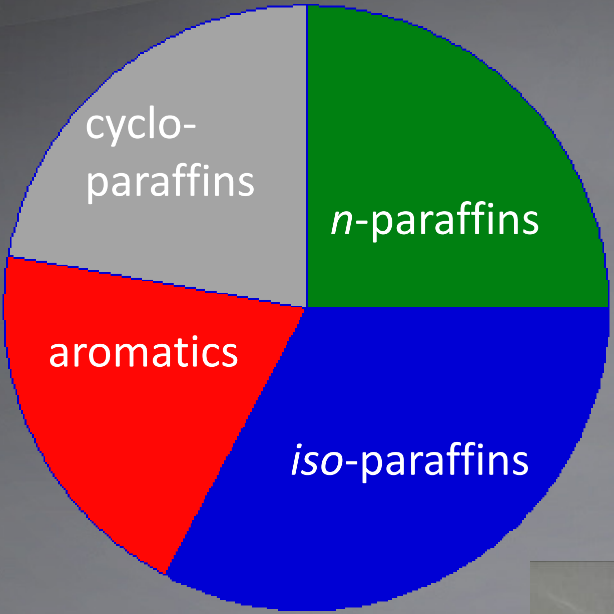
uop
A Honeywell Company

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

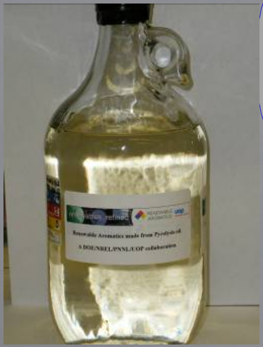
	Jet A1 Spec	***Starting SPK***	***Woody Pyrolysis Oil Aromatics***
Freeze Point (^{o}C)	**-47**	**-63**	**-53**
Flash Point (^{o}C)	**39**	**42**	**52**
Density (g/mL)	**0.775**	**0.753**	**0.863**

Pyrolysis oil summary

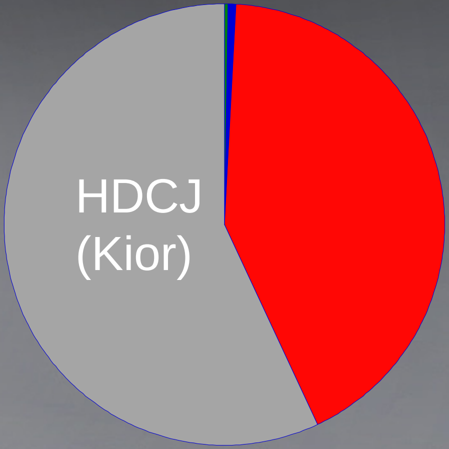
Jet A, JP-8

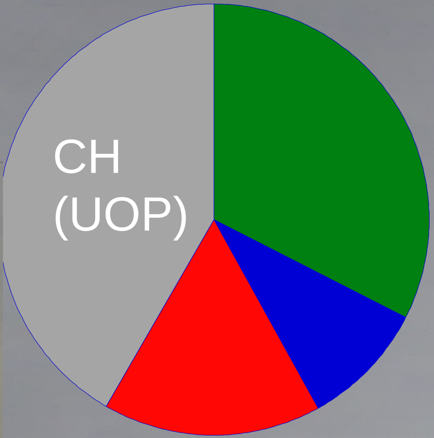


- 🟩 n-paraffins
- 🟦 iso-paraffins
- 🟥 aromatics
- ⬜ cycloparaffins



Products





Feedstock

Forest residues

Agriculture residues

Pyrolytic methods make cyclics and aromatics

Source: Dr. Timothy Edwards, Air Force Research Laboratory

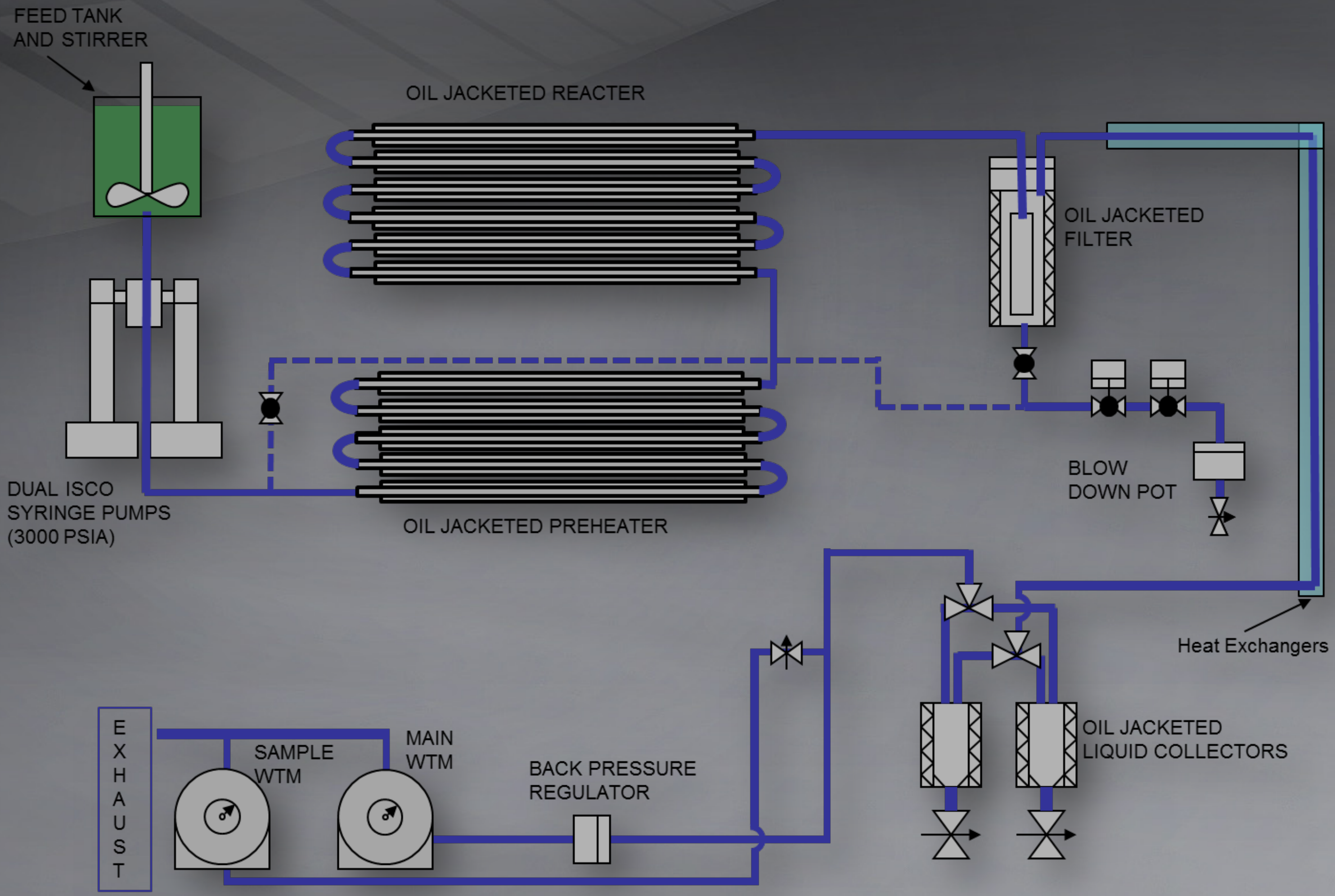
Liquefaction of biomass (FP vs HTL)

Conditions	Fast pyrolysis	Hydrothermal liquefaction
feedstock	Dry Biomass	Wet biomass
operating temperature	450-500°C	350°C
environment	inert gas	aqueous condense phase
catalyst	none	alkali reagent often used
operating pressure	1 atm	200 bar
residence time	< 1 sec	5 to 30 min
carbon yield to bio-oil	70%	50% (typical for lignocellulosics)
oil product quality	**Pyrolysis bio-oil**	**HTL Biocrude**
heating value (HHV)	6,900 Btu/lb	14,200 Btu/lb
oxygen content	40%	15%
water content	25%	5%
viscosity@40°C	low (50 cSt)	high (4,000 cSt)
thermal stability	no	yes

cSt = centistokes

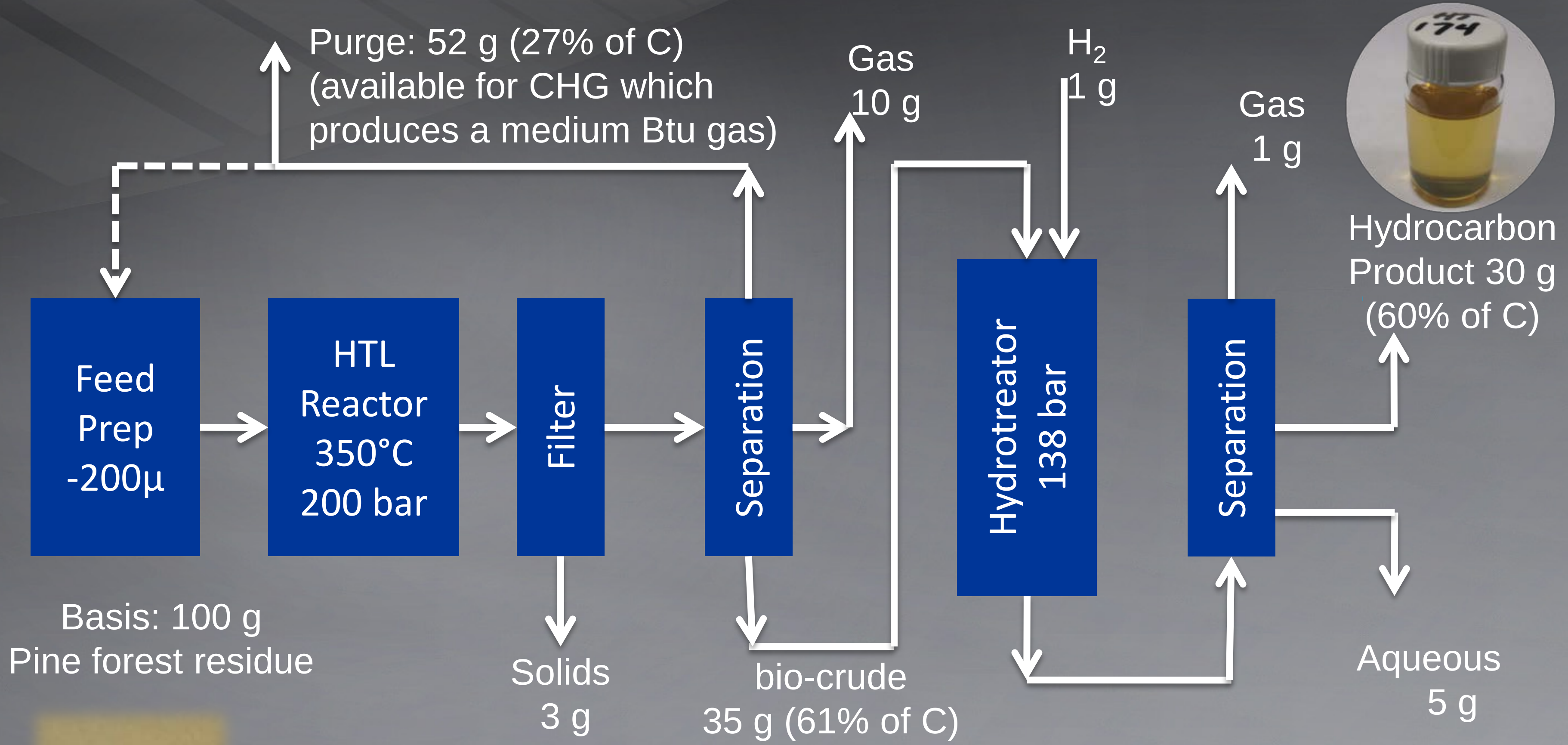
Hydrothermal liquefaction (HTL)

Reactor configuration: plug flow



Typical HTL operation at 350°C, 200 bar; Reactor: 200 to 2,000 mL
(note: at bench scale may use a CSTR as a preheater with wood)

Carbon efficiency achieved for forest residues



Purge: 52 g (27% of C)
(available for CHG which
produces a medium Btu gas)

Gas
10 g

H_2
1 g

Gas
1 g

Hydrocarbon
Product 30 g
(60% of C)

Feed
Prep
-200µ

HTL
Reactor
350°C
200 bar

Filter

Separation

Hydrotreator
138 bar

Separation

Basis: 100 g
Pine forest residue

Solids
3 g

bio-crude
35 g (61% of C)

Aqueous
5 g

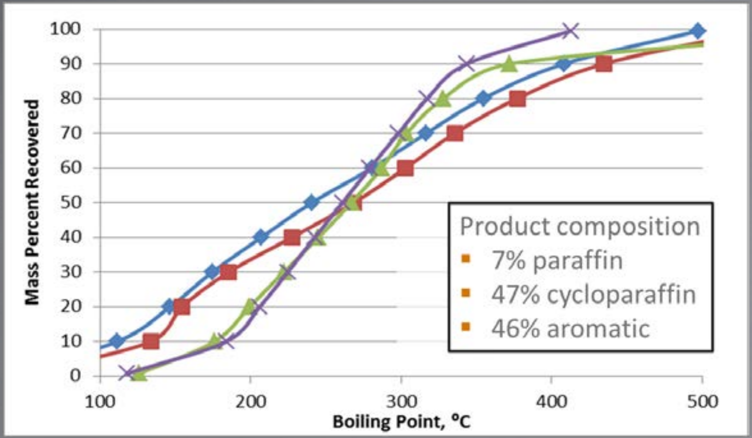
Step	Carbon Efficiency†
HTL biocrude yield	61%
Hydrotreating yield	96%
Combined	59%

Upgrading via hydrotreatment results

HTL bio-crude upgrading

- 70 h test
- One of 4 conditions
- Excellent mass/carbon balances
- Very high de-oxygenation and TAN reduction

Parameter	Unit	Value
Mass Balance	%	101
Carbon Balance	%	99.8
Oil Yield	g dry/g dry feed	0.85
Carbon Yield	g C/g C in feed	0.96
Gas Yield	g gas/g dry feed	0.034
Produced Water Yield	g produced water per g dry feed	0.16
H_2 consumption	g H_2/100g dry feed	3.3



Simulated distillation curve vs diesel

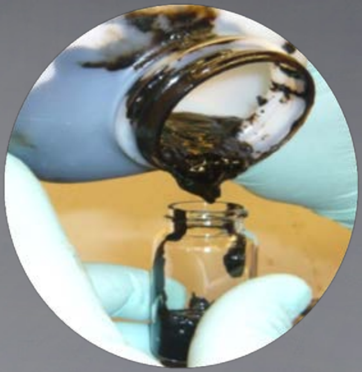
Parameter	Unit	bio-crude	Upgraded
H/C ratio	dry basis	1.14	1.36
Oxygen	Wt% dry	14	0.009
Nitrogen	ppm	3800	520
Sulfur	ppm	650	19
Oil density	g/ml	1.13	0.912
Moisture	Wt%	13	0.35
TAN	mg KOH/g	140*	0.76

* TAN anomaly; HTL biocrude TAN is typically 40

Hydrothermal liquefaction – is suitable for a broad range of wet feedstocks

Algae Paste

Algae HTL Oil



Hydrotreated
Algae HTL Oil

Wood Paste

Wood HTL Oil

Hydrotreated
Wood HTL Oil

Hydroprocessing of HTL algae biocrude

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Hydrotreatment	**Low lipid high lipid**
Catalyst bed temperature, ºC	105-400
Space velocity, L/L/hr	0.20
H_2 Feed: L/h @ 2000 psig	85
H_2 Consumption, g/100g feed	2.6-3.8
Mass balance	91-98%
Oil yield, L/L bio-oil	0.8 – 0.94

Bio-oil Product Composition, dry weight basis	
Carbon, Wt%	84-85%
Hydrogen, Wt%	13.5%
Oxygen, Wt%	1.2-1.8%
Nitrogen, Wt%	0.08-0.25%
Sulfur, Wt%	<0.005%

Process low lipid algae, high lipid algae, cyanobacteria…

Data shown from early work prior to optimizing hydrotreating for HTL biocrude

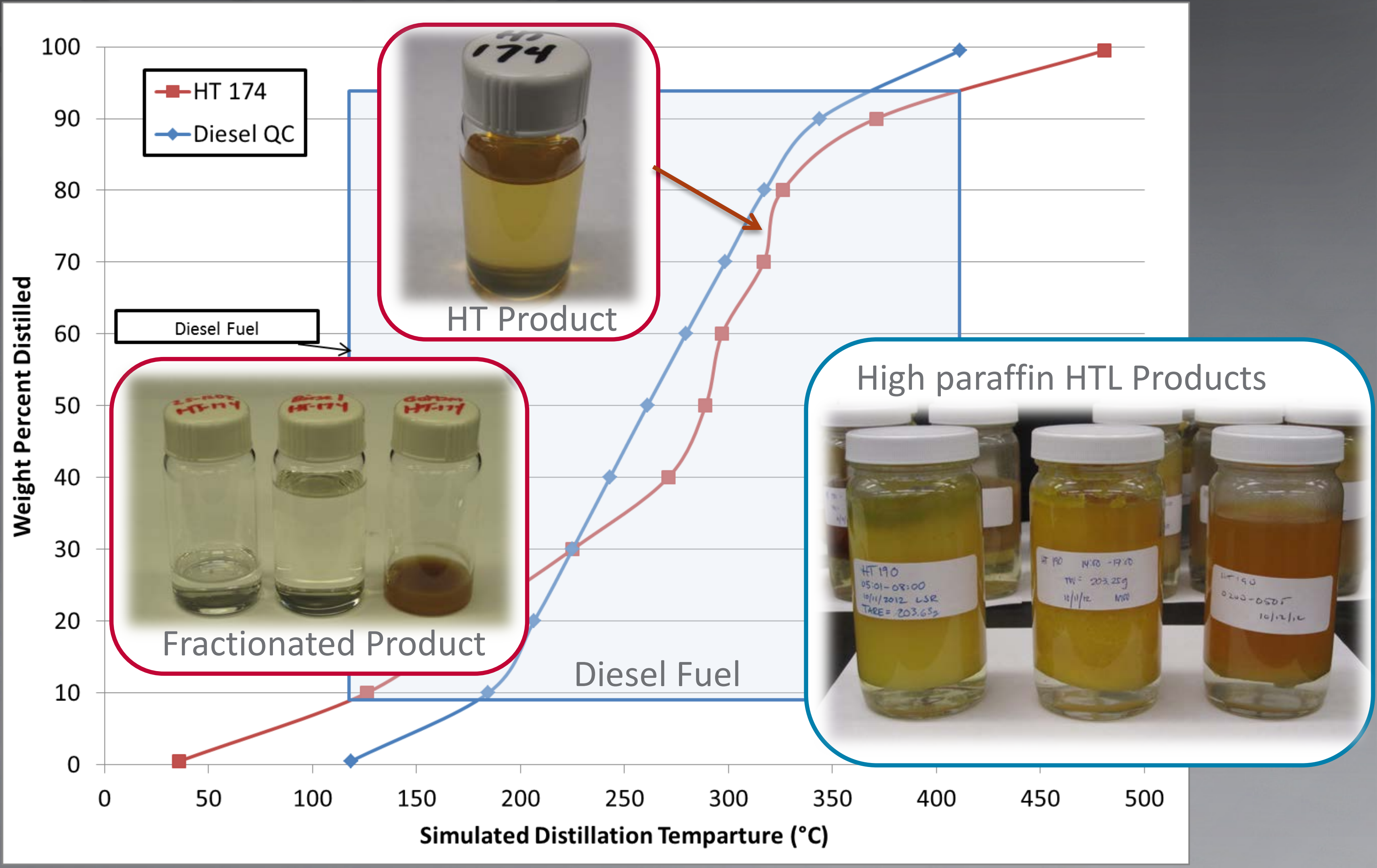
Catalyst: sulfided CoMo on alumina

Observation:
No catalyst performance degradation

TAN <0.1-0.2

Maintain paraffin (without aromatizing)

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



Moving forward

HTL of Algenol spent algae

- Commissioning 1,000 L/day (20wt% BDAF) continuous HTL/CHG system for algal feedstock; NAABB-Reliance-PNNL-Genifuel Hydrothermal System 2014
- Waste sludge R&D starting in FY15 (Genifuel/ Water Environment Research Foundation)

Alkylating

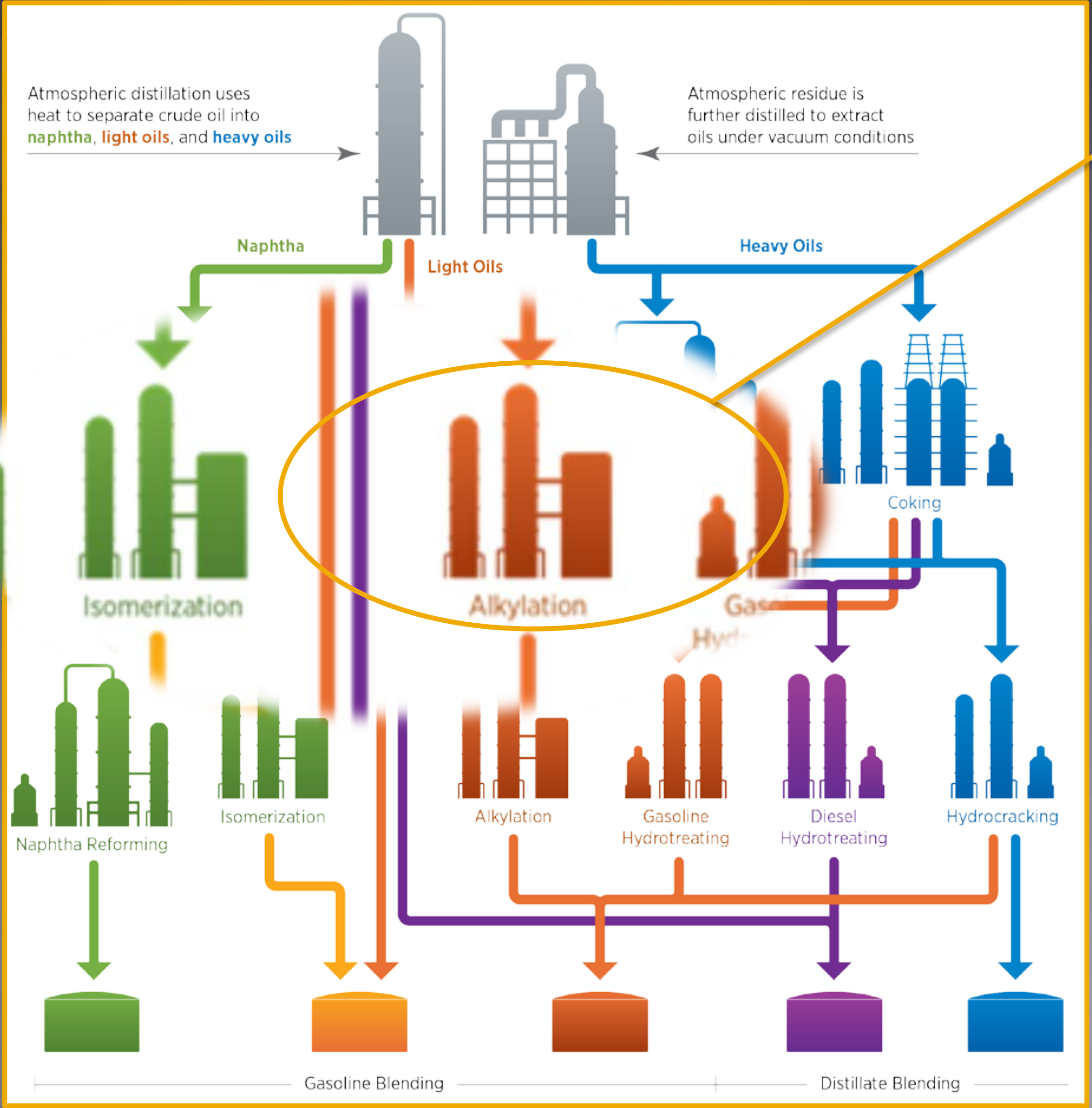


Figure Courtesy of NABC

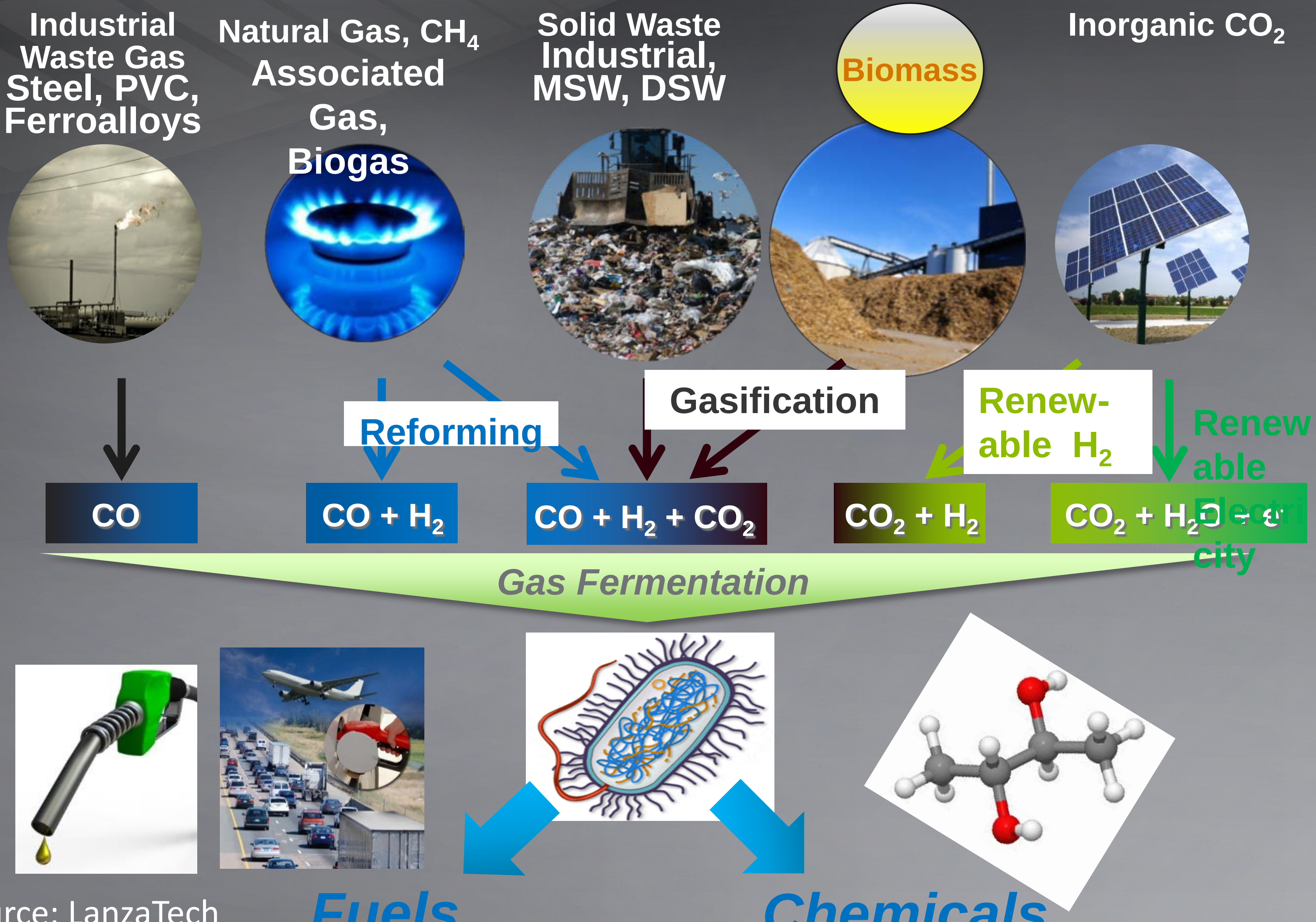
Alkylating

Today will focus on production of jet fuel from ethanol feedstock

Also used as a means to improve quality of fast pyrolysis bio-oils at PNNL

Using alkylating technology from refinery to make high quality fuels

LanzaTech – Recycling carbon for production of alcohol



Industrial Waste Gas Steel, PVC, Ferroalloys

Natural Gas, CH_4 Associated Gas, Biogas

Solid Waste Industrial, MSW, DSW

Biomass

Inorganic CO_2

Reforming

Gasification

Renew- able H_2

Renewable Electricity

CO

$CO + H_2$

$CO + H_2 + CO_2$

$CO_2 + H_2$

$CO_2 + H_2O + e^-$

Gas Fermentation

Fuels

Chemicals

Source: LanzaTech

Alcohol to jet fuel (ATJ)

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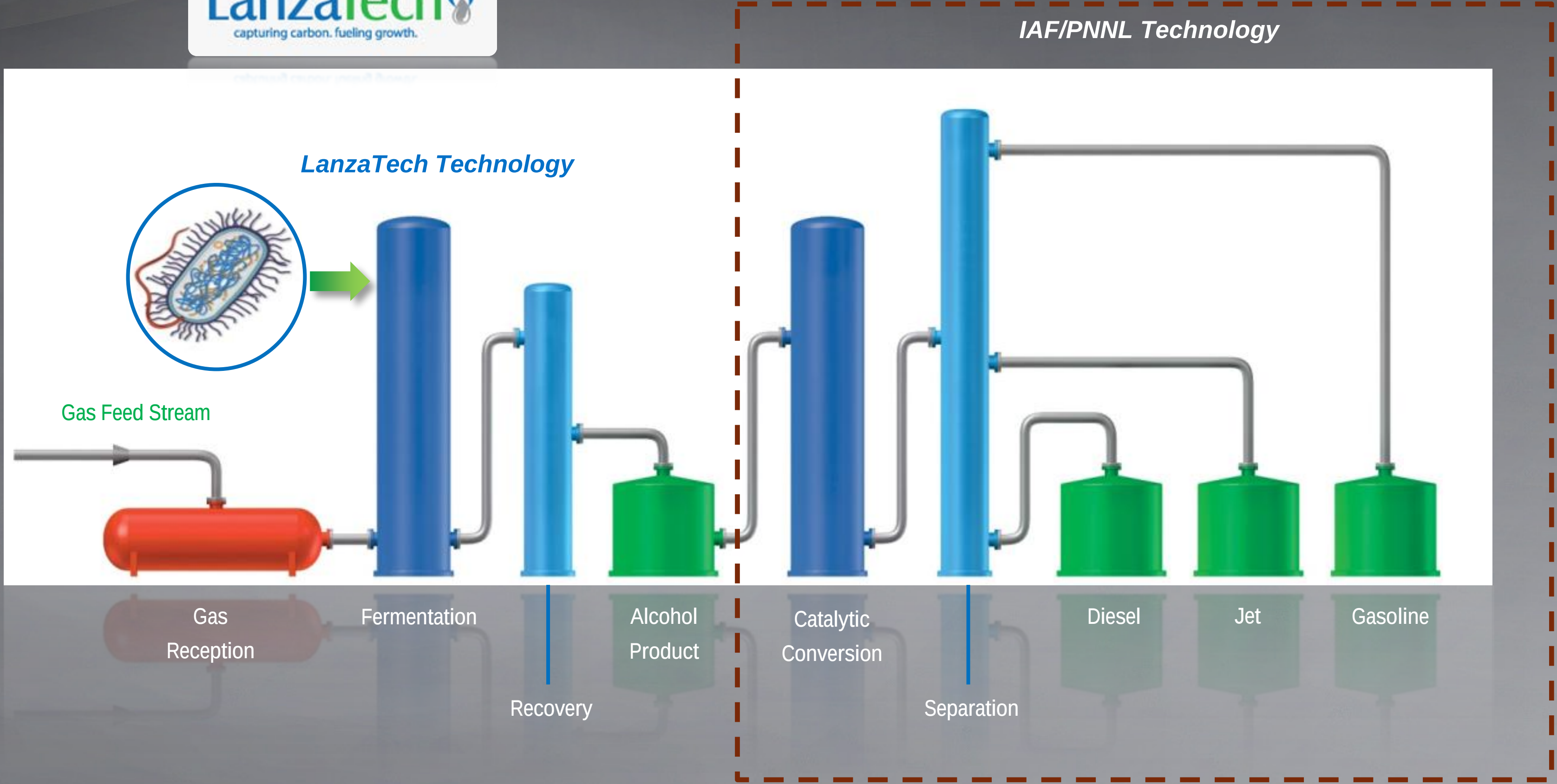
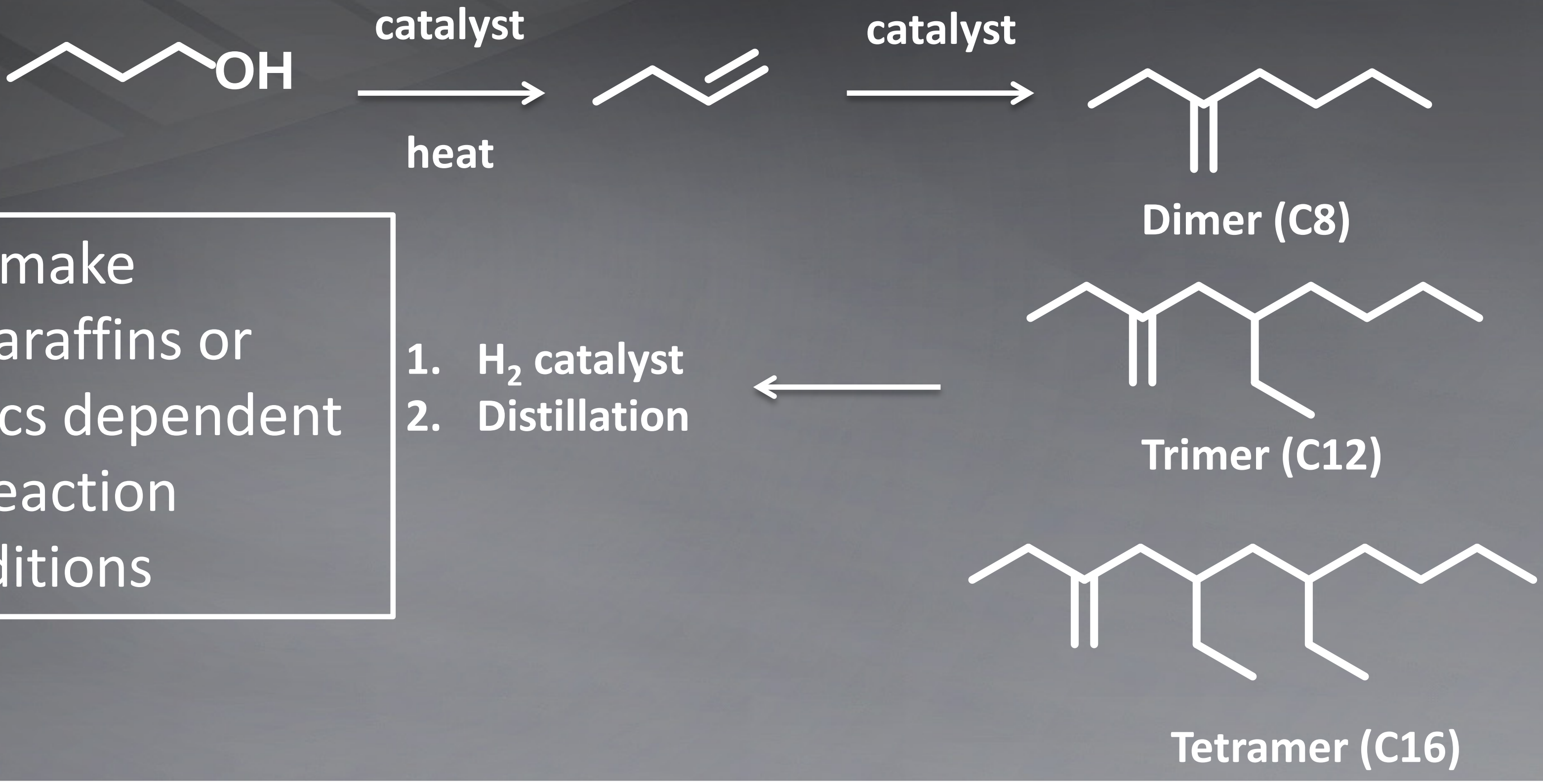
A novel route to drop-in hydrocarbon fuels through recycling waste carbon



Using refinery alkylation chemistry to build carbon chain to jet fuel

Alcohol to jet



Can make isoparaffins or cyclics dependent on reaction conditions

C4—butanol, i-butanol

- Cobalt, Gevo , et al
- fuel primarily C12 and C16 (limited mol. chains)

C2—ethanol

- Swedish Biofuels (+CO/H_2)
- PNNL/ Imperium (SPK)
- broad chain length

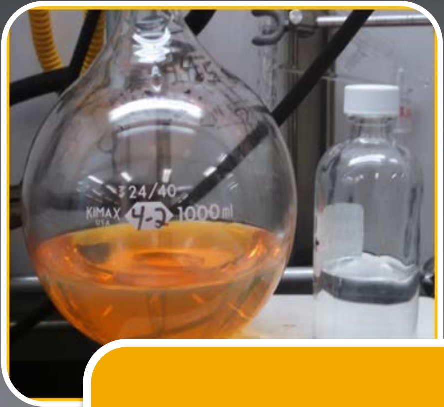
Jet fuel production from waste gas

Gas fermentation

→

Catalytic upgrading

→



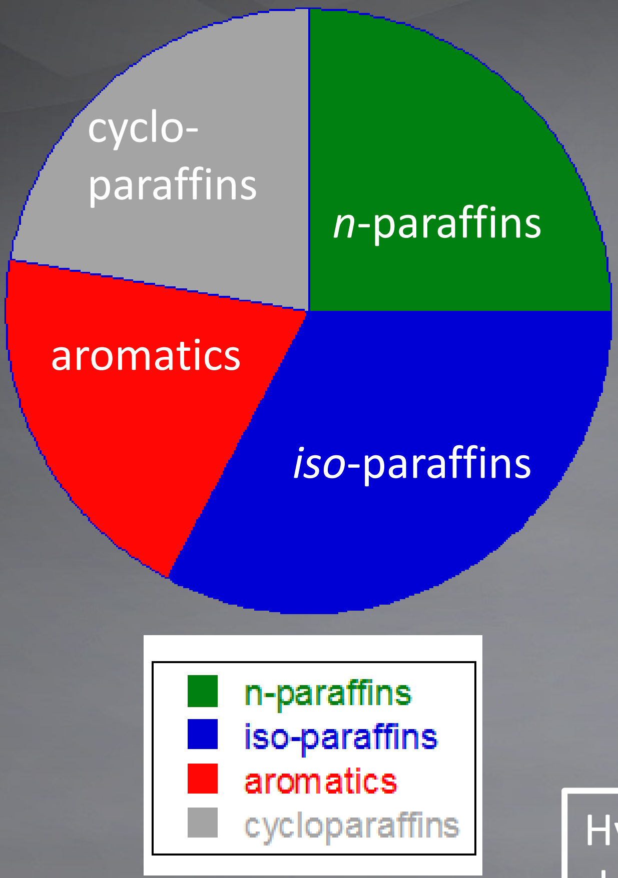
fractionation

- Multi-thousand hours on stream (catalyst life)
- “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”

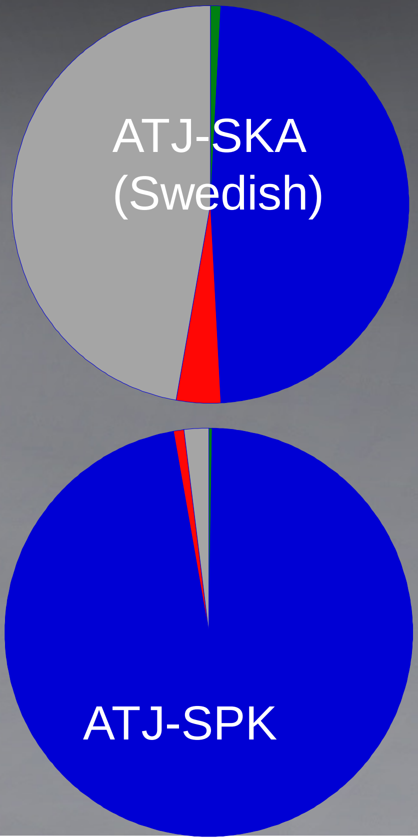
Take home message:
PNNL's unique conversion technology can produce jet fuel from ethanol, which is widely available in large volumes

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

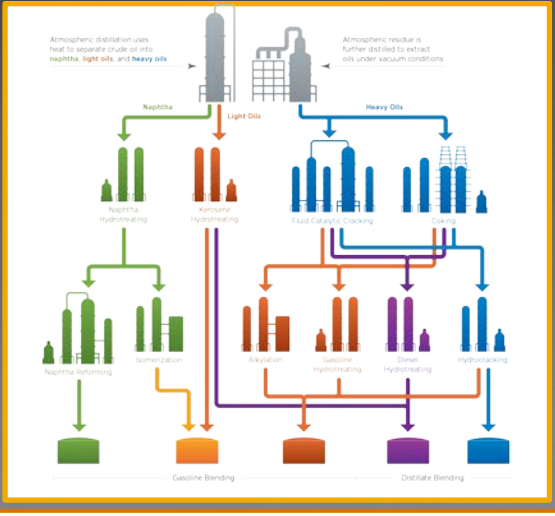
cellulosic ethanol

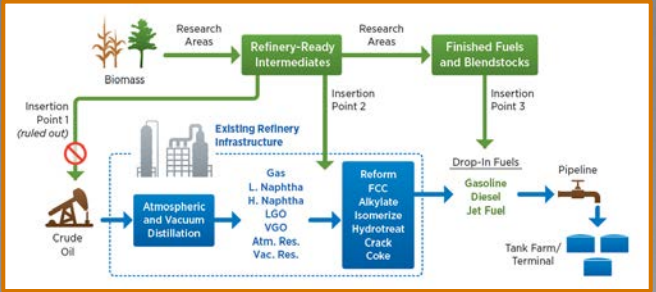
gas fermentation

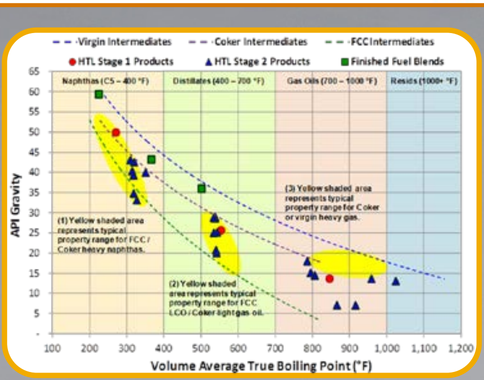
Source: Dr. Timothy Edwards, Air Force Research Laboratory

Conclusions

- In the last 2 years we have made tremendous strides addressing challenges in refinery integration
- FCC operations
  - Are possible with certain bio-oils co-processed with refinery intermediates—produce gasoline-rich streams
- Hydrotreating operations
  - Are required for upgrading bio-oils and also used with biocrudes
  - Pyrolysis/liquefaction lead to cyclic hydrocarbons from wood (unless ring opening is deployed)
  - Hydrogen demand varies by technology, and is significantly reduced with HTL
- Alklyating operations
  - Alcohol to jet moves us out of the classical liquefaction paradigm
- Insertion Point 3 (blendstock) has the lowest risk
- Insertion Point 2 (co-processing) risk remains high
  - Efforts in place to understand value of bio-derived material within the refinery (NREL/PNNL)

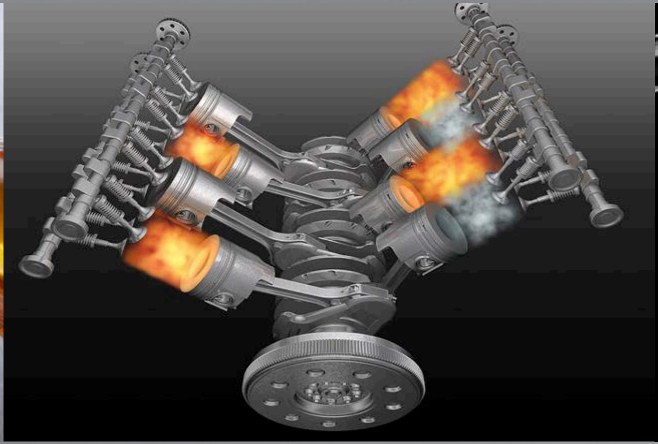






Next steps

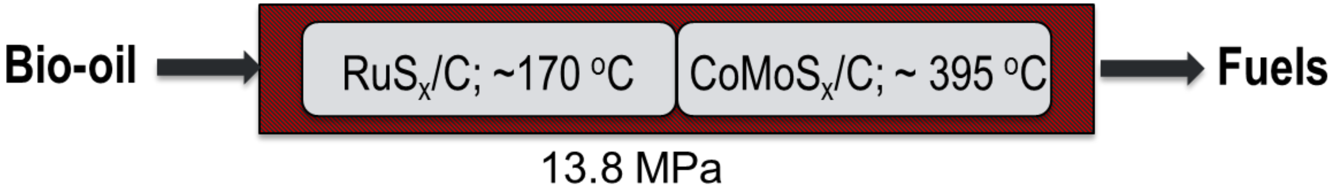
- Moving HTL biocrude to refinery integration (Note: Sapphire presented on this at the Algal Biomass Organization Conference)
- Rather than offering a petroleum substitute, we are looking where can we provide a value added material to refiners and to OEMs
- Focus of efforts unfolding—New Fuels and Vehicle Co-Optima



Back up material

Challenge: catalyst bed stability

PNNL two-stage hydrotreating process



- Loss of catalyst activity

TOS (h)	Oil Yield (g/g dry feed)	H_2 consumption (L/L feed)	Fuel products		
			O (Wt.%)	H/C (dry)	Density (g/ml)
24-50	0.40	444	0.7	1.59	0.86
66-82	0.43	342	2.1	1.47	0.91

- Deactivation of RuS_X/C leads to unstable material, which forms “gunk” resulting in reactor plugging in < 100 h
- $CoMoS_X/C$ also exhibits limitations to its catalyst life and deactivation occurs over <100 h campaign

Elliott *et al Energy Fuels* **2012**, *26*, 3869

HTL carbon yields & oil quality

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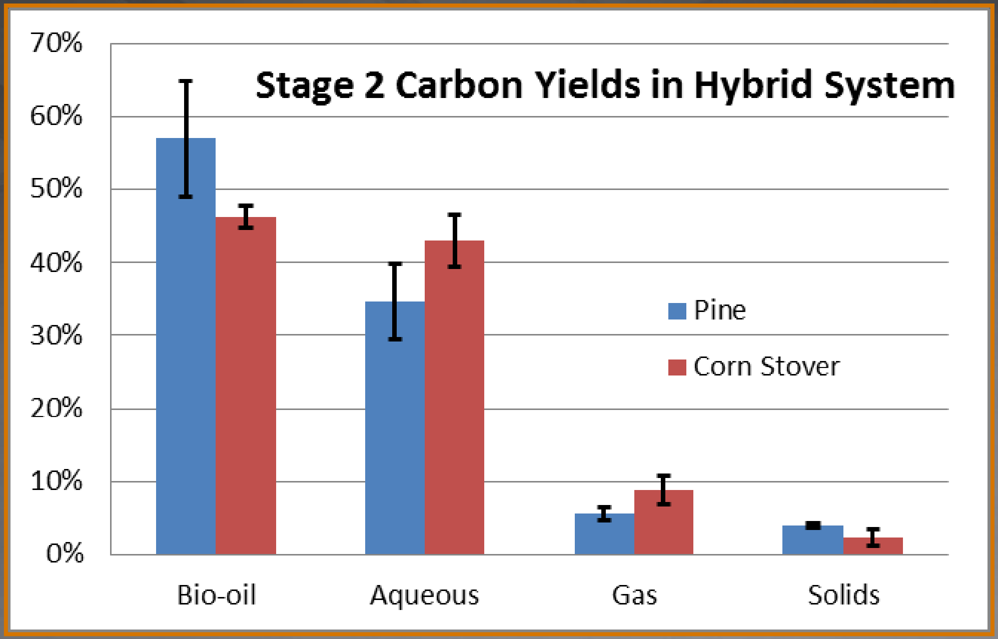

Example of HTL bio-crude Quality

	Pine	Corn Stover
Oxygen (Dry)	12%	17%
Nitrogen	0.29%	1.1%
Sulfur	0.01%	0.04%
Moisture	9%	8%
Density, g/ml	1.11	1.10
Viscosity, cSt, 40°C	3100	3400
Oil TAN mgKOH/g	55	44

- 6 longer duration runs to generate oil for upgrading
- 130 h on-stream, 7 L bio-crude
- Mean balance: Wood 99% (Mass); 88% (carbon)
- Mean balance: Cornstover 96% (Mass); 83% (carbon)

NABC National Advanced Biofuels Consortium

HTL bio-crude from Cellana algae

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Parameter	Low lipid	High lipid
Space Velocity, L/L/h	2.2	2.2
Temperature, °C	350	348
Mass Balance	102%	97%
Total Carbon Balance	91%	96%
Oil Yield, Mass Basis (BD)	65%	64%
Oil Yield, Carbon Basis	81%	82%
Bio-Oil Composition, Dry Weight Basis		
Carbon, Wt%	77.0%	77.6%
Hydrogen, Wt%	10.4%	10.6%
Oxygen, Wt%	8.0%	7.2%
Nitrogen, Wt%	4.2%	4.0%
Sulfur, Wt%	0.3%	0.3%

Density = 0.95 g/ml

Algae from Cellana, *Nanno. salina* low and high lipid