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Liquefaction Technologies for Producing Biocrude for Jet, Diesel and Gasoline

JOHN HOLLADAY

Energy and Environment Directorate

Northwest Wood-Based Biofuels + Co-Products Conference, April 29, 2014

PNNL bioenergy research

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National Impact

Direct Liquefaction of Biomass

Producing catalysts and processes to make fuels directly from whole biomass (wet or dry)

Conversion of sugars and lignin

Producing new processes that make building blocks that are converted to chemicals and fuels

Refinery Integration

Developing solutions for co-processing biomass with fossil resources in existing infrastructure

Deliver Science & Technology to ensure sustainable incorporation of renewables into the fuel and chemical infrastructure

Capabilities

Catalysis

Applying fundamental and applied approaches to produce stable, active and selective catalysts able to operate in high water environments

Fungal Biotechnology

Improving microbes for producing fuel and chemical precursors from complex sugars - integrating processes with catalysis

Advanced Analysis

Addressing site-specific constraints through high resolution geographical info-physical models, processes economic and life cycle analysis

Catalyst R&D at PNNL at different scales

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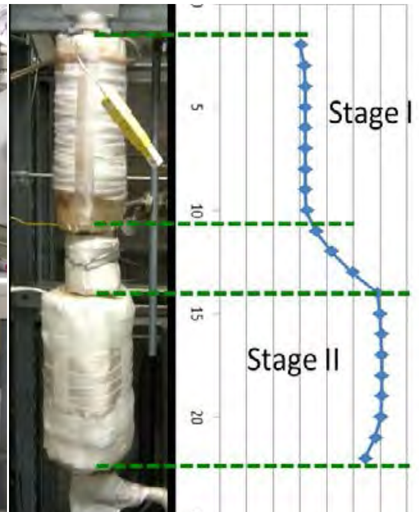
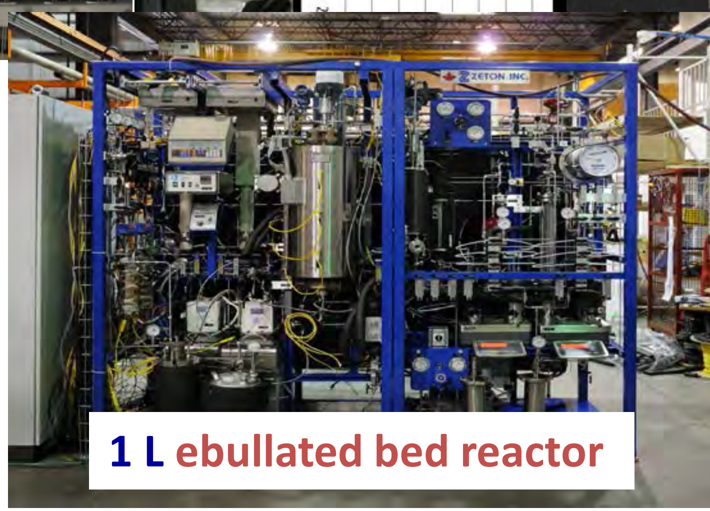
~1.4 ml 8-reactor packed bed system

40 ml dual T zone packed bed reactor



400 ml dual T zone packed bed reactors



1 L ebullated bed reactor

24 L 8-zone furnace packed bed reactor

Pyrolysis central challenge: Catalysis

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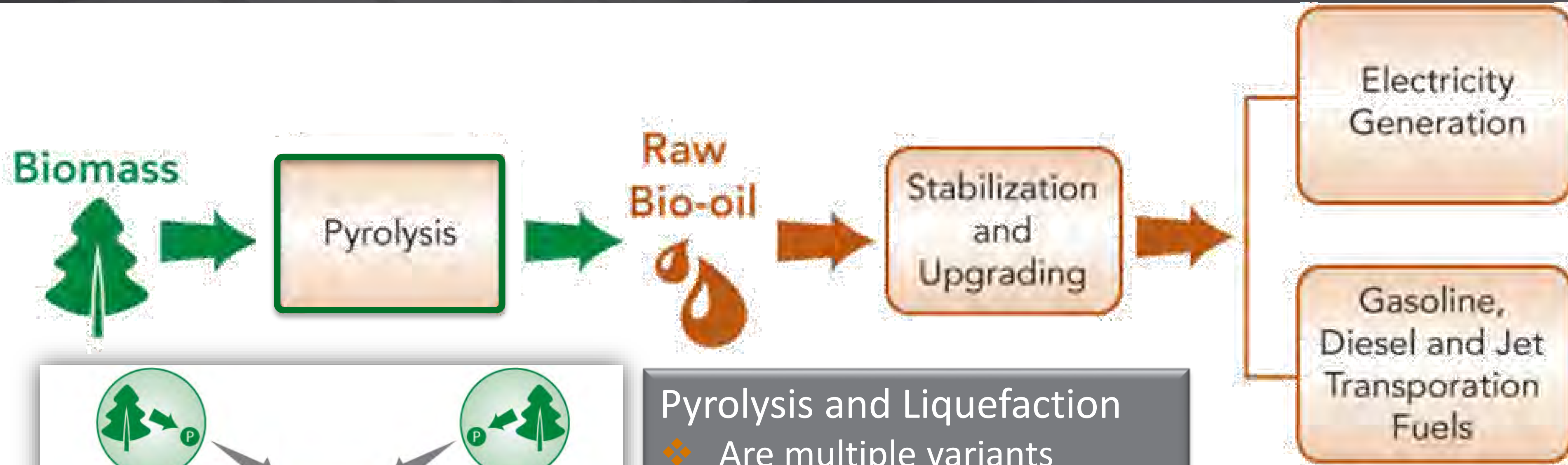

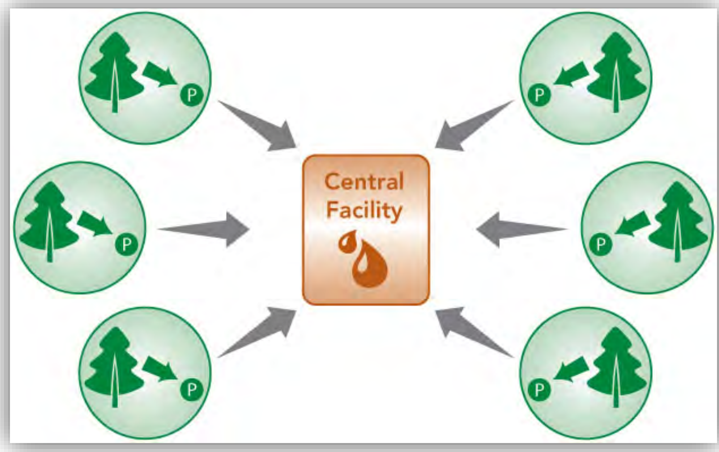

Potential for distributed bio-oil production with processing in central facility

Pyrolysis and Liquefaction

- Are multiple variants
- Yield depends on quality of biomass feedstock and variant of technology
- Primary need for all variants is improved catalysis

Produce hydrocarbon fuels from low quality bio-oil, but…

- Catalyst life is too short
- Catalyst rate is too slow

Fuel characteristics

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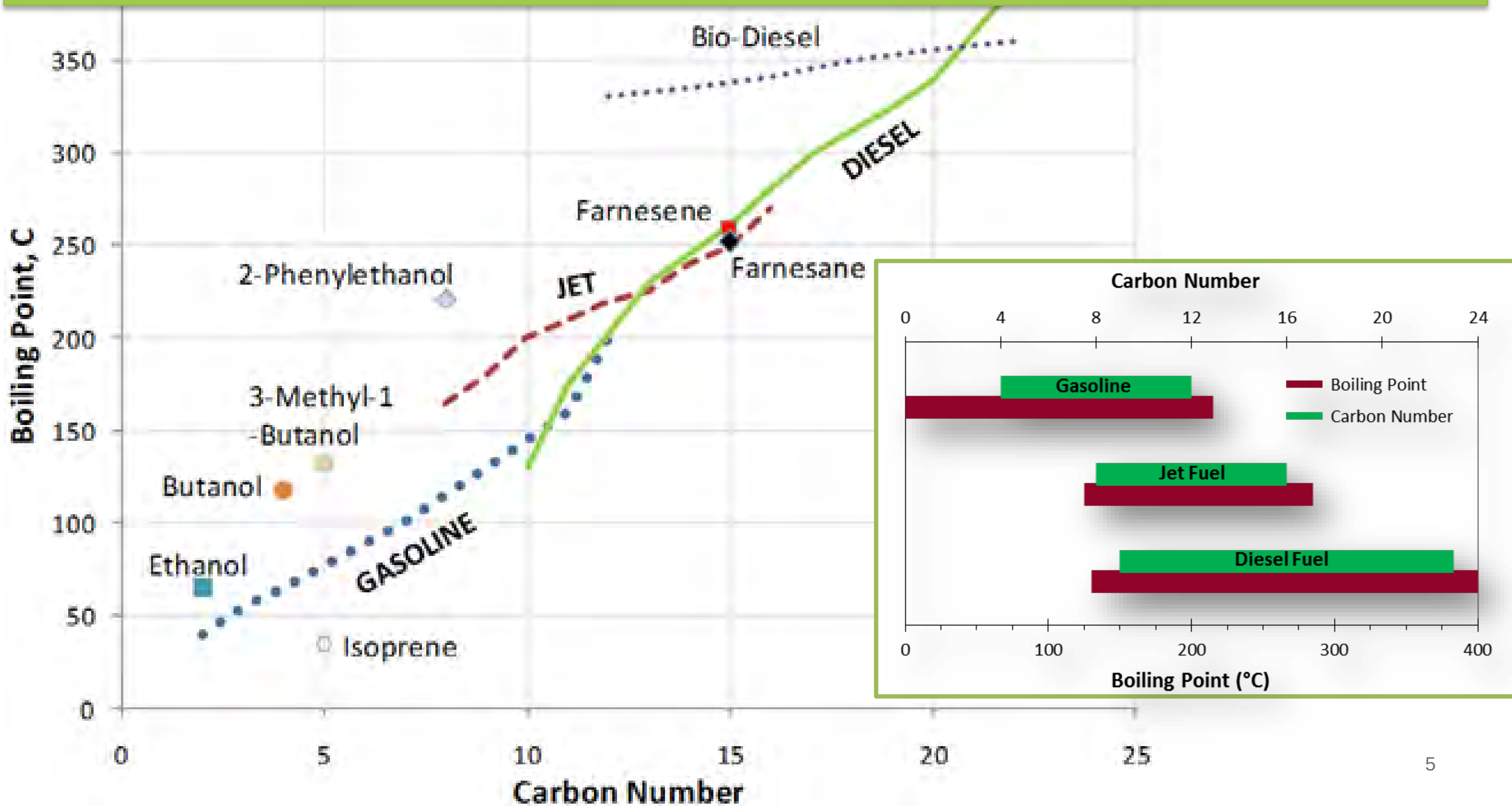
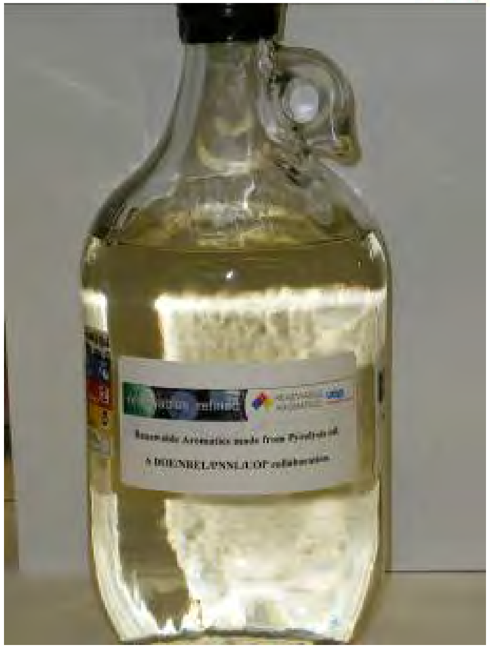
Desired Characteristics

- Miscible with petroleum-based fuels and transportable in current pipelines
- Meet performance & storability criteria designed for jet engines—it must be jet fuel



Pyrolysis enables 100% renewable jet

uop
A Honeywell Company



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

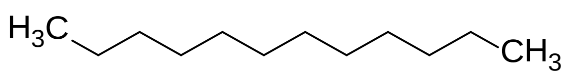
	Jet A1 Spec	*Starting SPK*	*Woody Pyrolysis Oil Aromatics-SPK*
Freeze Point (^{o}C)	**-47**	**-63**	**-53**
Flash Point (^{o}C)	**39**	**42**	**52**
Density (g/mL)	**0.775**	**0.753**	**0.863**

Compound classes in jet fuels

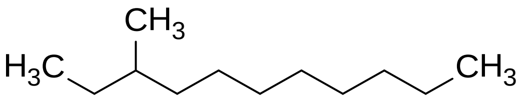
Ideal Carbon Length C8-C16

Paraffins

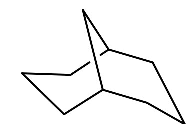
70 - 85%



Normal Paraffins



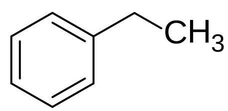
Iso-paraffins

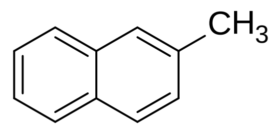


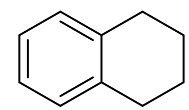
Cyclic Paraffins

Aromatic

< 25%

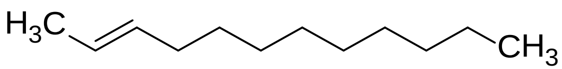


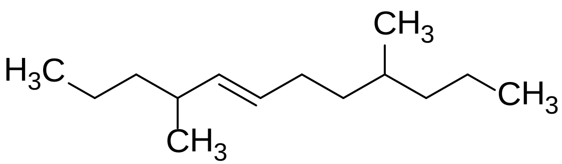




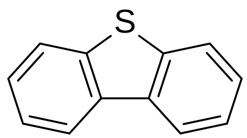
Olefins

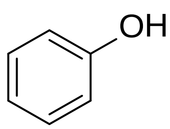
< 5%

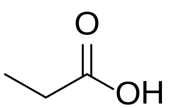




***S, N, O containing Compounds* < 5%**



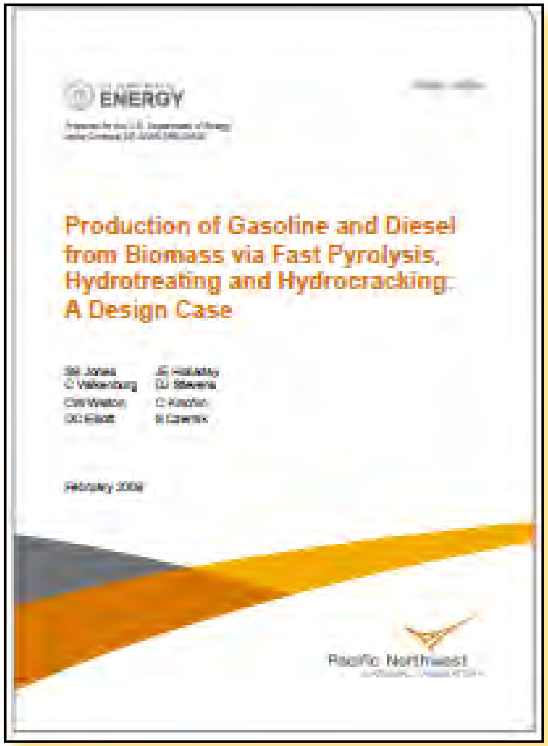




We desire fuels with composition similar to above

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

Fast Pyrolysis and upgrading to fuels economics – 2009 estimate



- Design Case Originally developed in 2009
  - Process appears viable
  - Research needs identified
  - Catalyst maintenance appeared to have biggest impact initially
  - Set research targets for out years

Fast pyrolysis and upgrading to fuels economics – 2009

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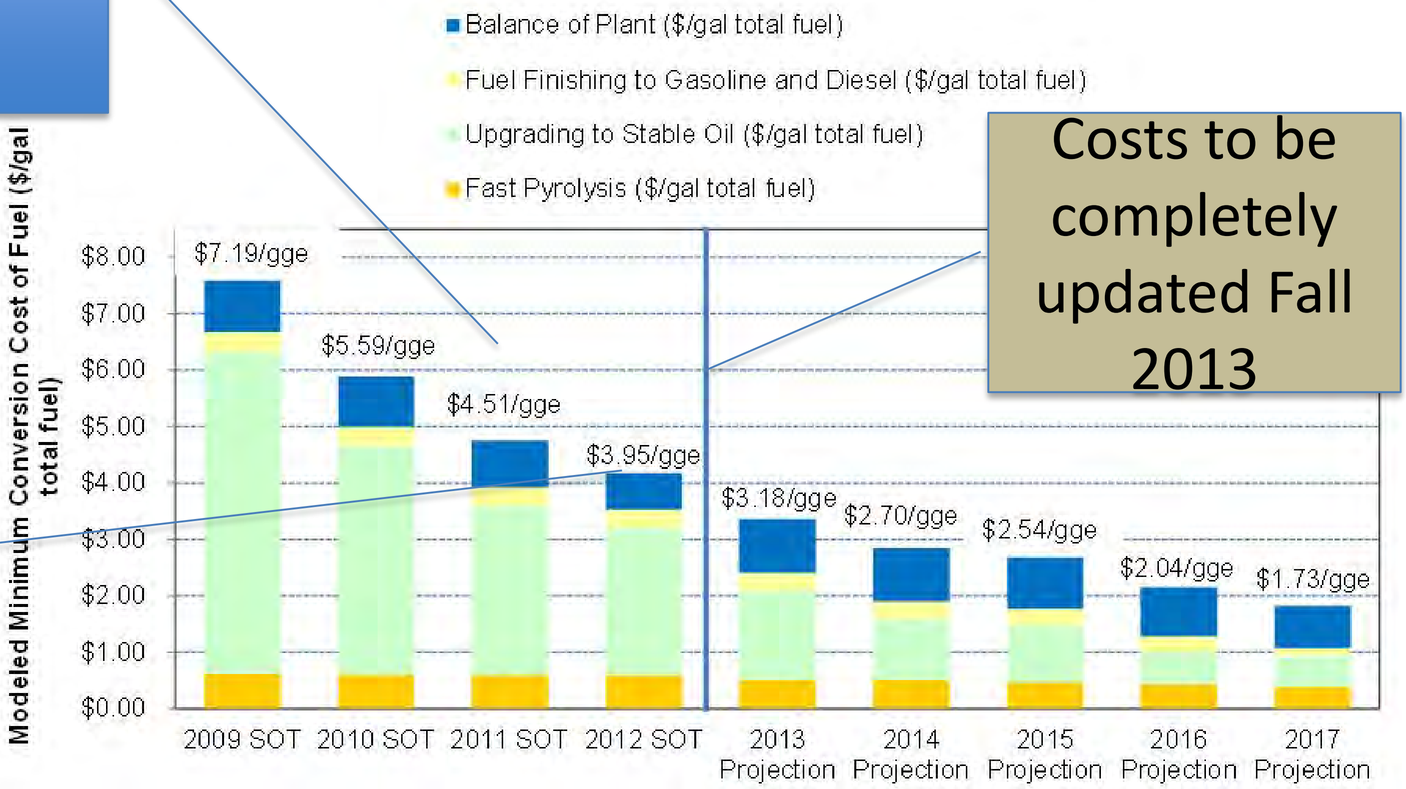
Conversion costs – Integration of experimental results with modeled costs

Reduced the catalyst replacement rate

Modest yield increase

Costs to be completely updated Fall 2013



Fast pyrolysis and upgrading to fuels economics – 2013 Update

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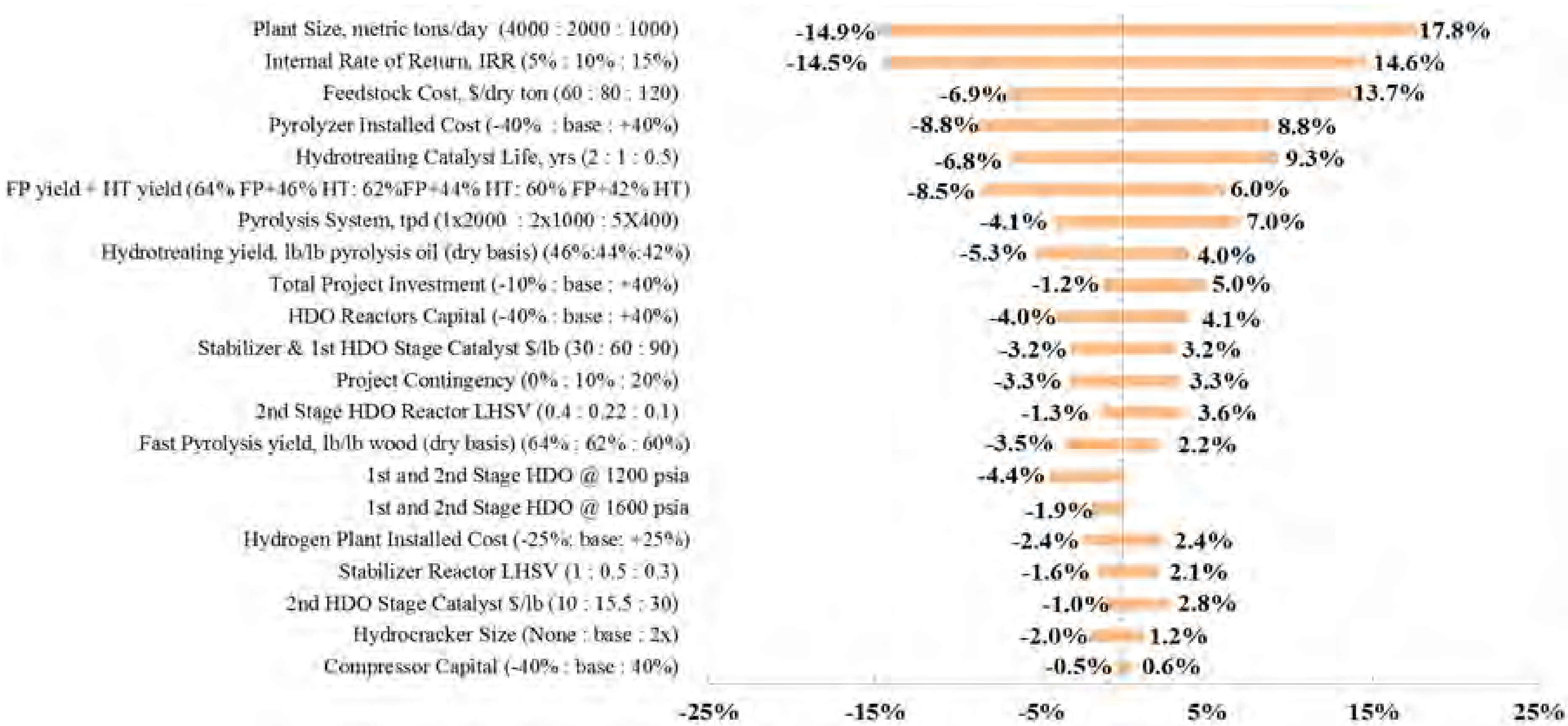
Sensitivity Analysis - $/gallon change from base case



Challenges for upgrading: reactor stability

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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 "char" 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

Previous long-term catalytic experiments (ca. 2011) reached only ~ 100 hour without plugging.

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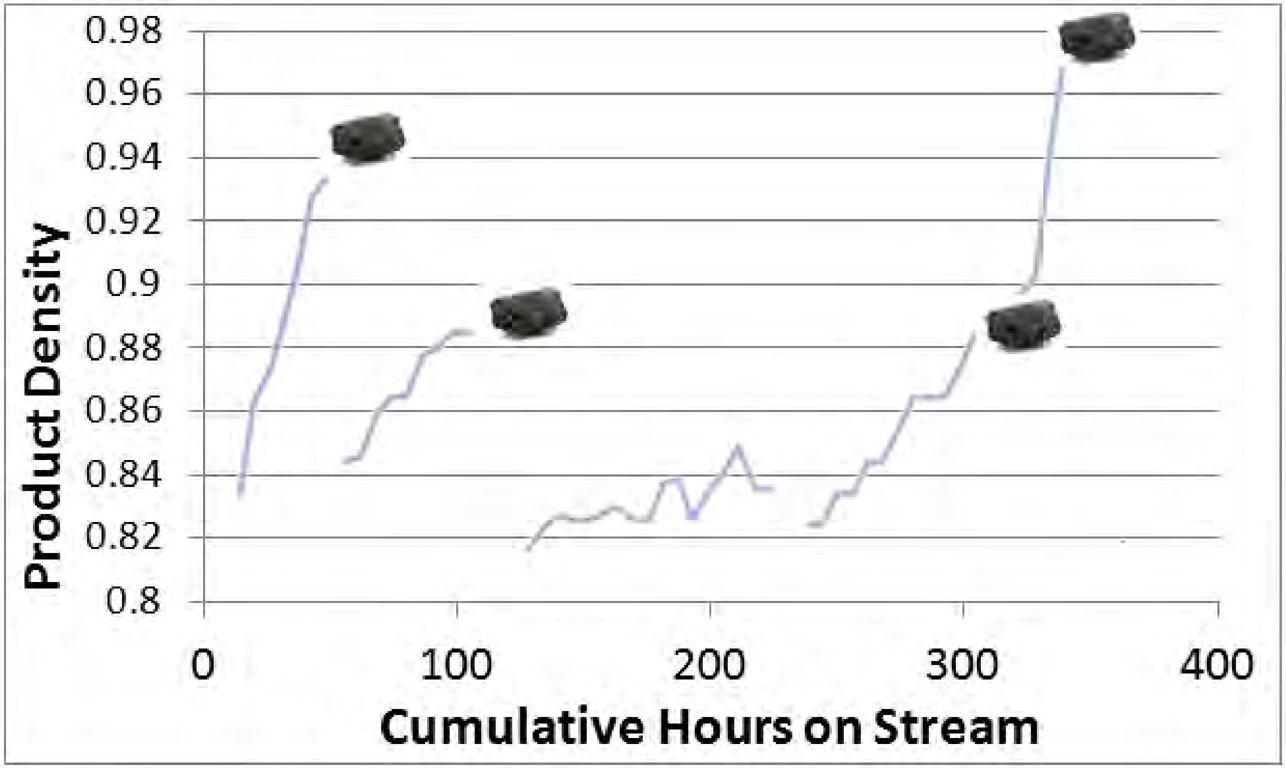


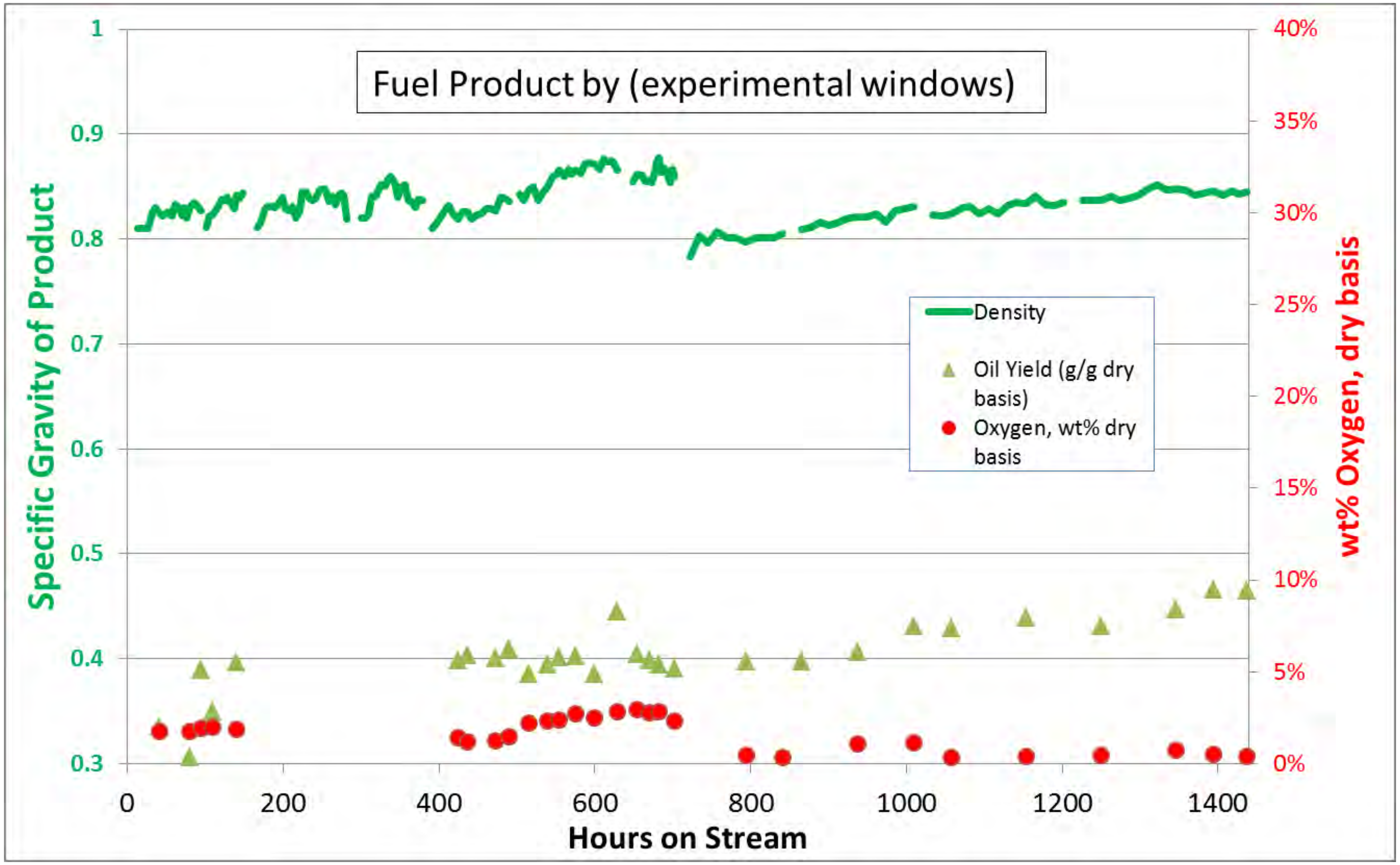
plug

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

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

Plugging: Challenge to Successful Continuous Operation (2011)

State of the art: No plugging after 60 days on stream



- 2013 milestone on extended lifetime testing was completed successfully
- Higher yield and lower oxygen content at higher temperatures were achieved
- Long-term catalyst deactivation still present as indicated by increased density

Slide courtesy of A. Zacher

Successful Completion of 60-day Time-on-Stream Target (2013)

Sustainability pyrolysis oil with upgrading

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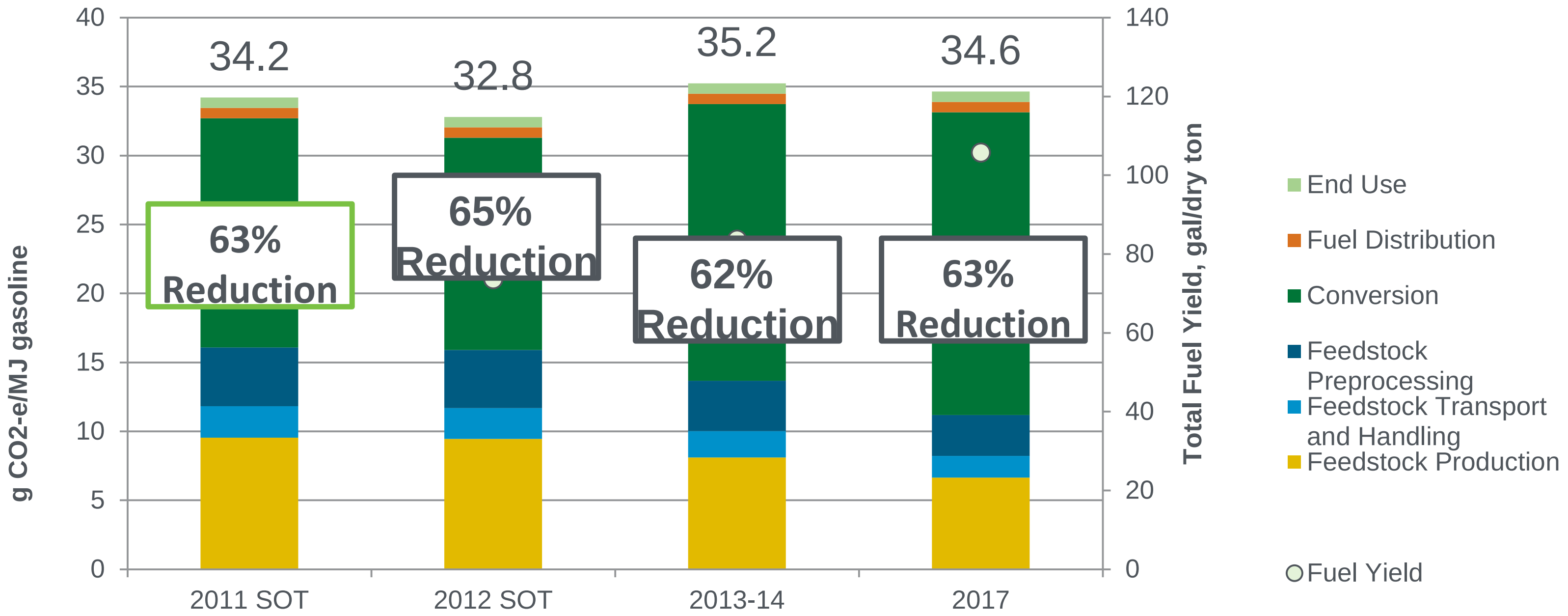
Life cycle GHGs for gasoline from fast pyrolysis and upgrading



- 2017 goal case assumes better yields and economics, but has slightly higher GHGs
- Higher yields lower feedstock contribution but increase conversion contribution
- Preliminary indications are that fuel derived from fast pyrolysis of wood and bio-oil upgrading appears to be >60% GHG reduction (cellulosic biofuel), however, qualification under the RFS is determined by the EPA

What is next: *Ex situ* catalytic fast pyrolysis (vapor upgrading)

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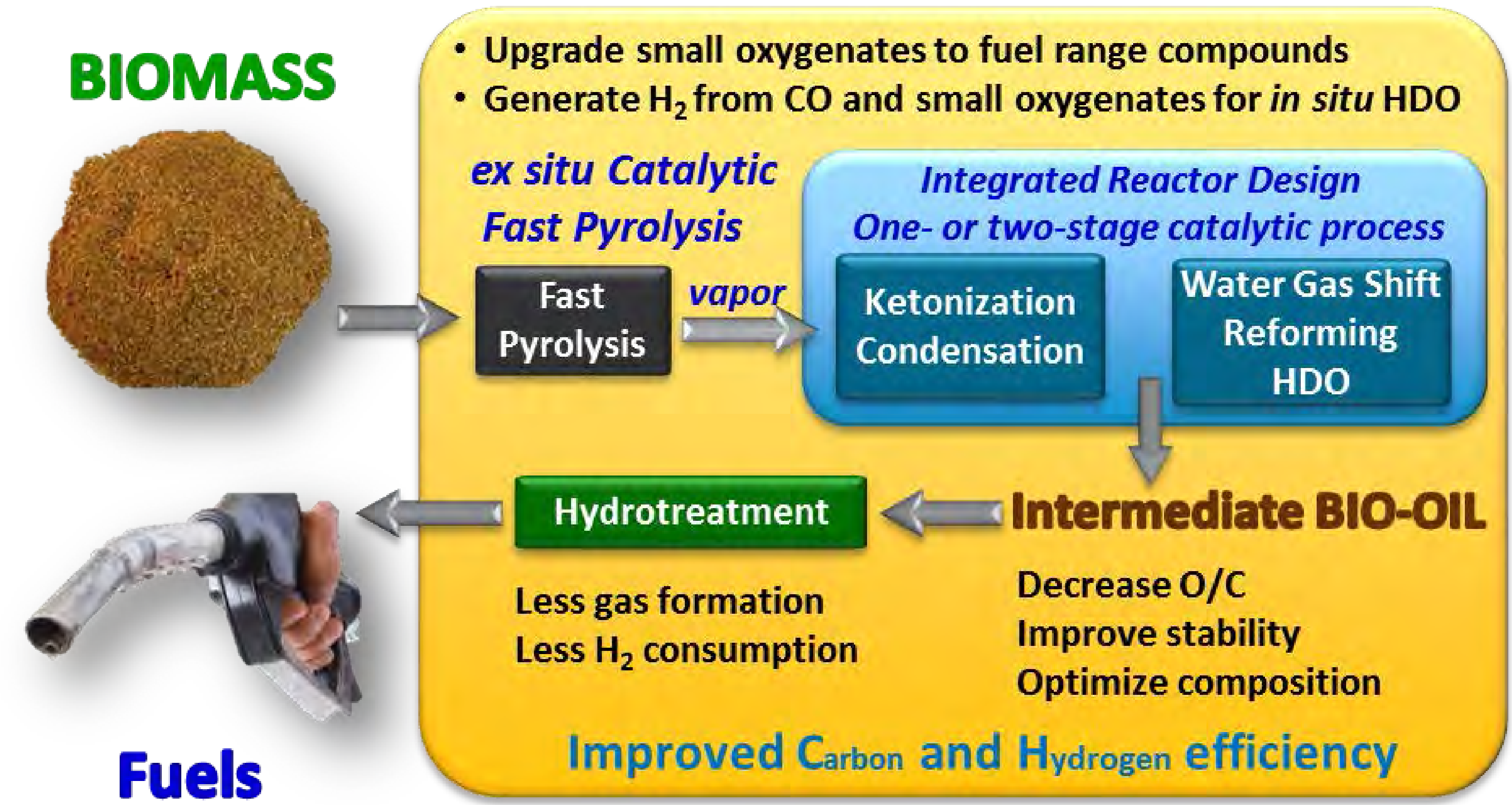
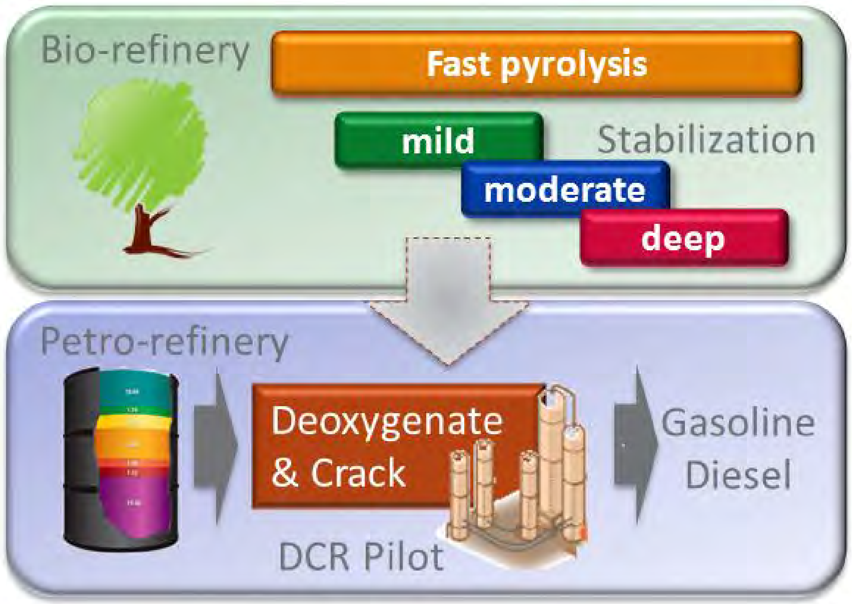


Catalyst Summary

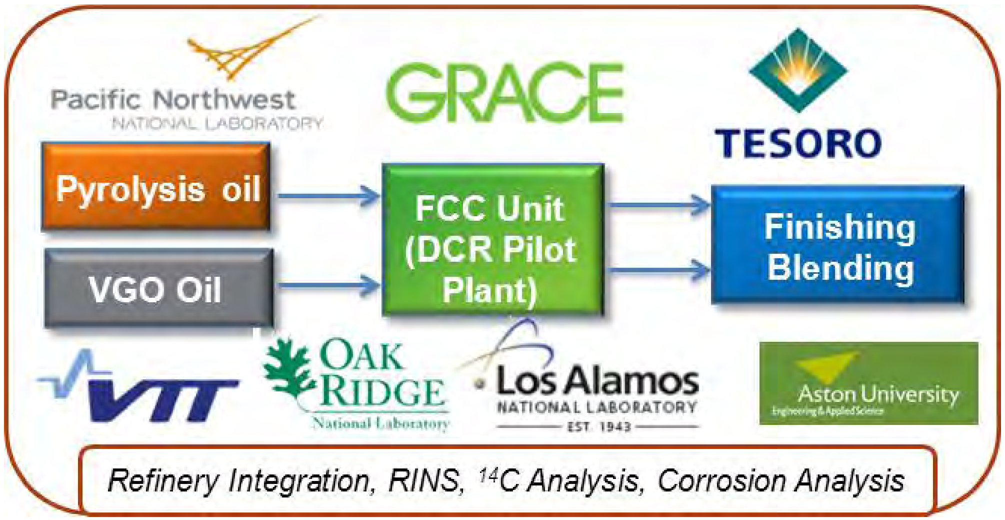
- ✓ Generation 1: PNNL modified zeolite, spent FCC catalysts blend (low-cost)
- ✓ Generation 2: Stable, strong, multifunctional, catalysts designed for bio-oil

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



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



Hydrothermal liquefaction for improved oil

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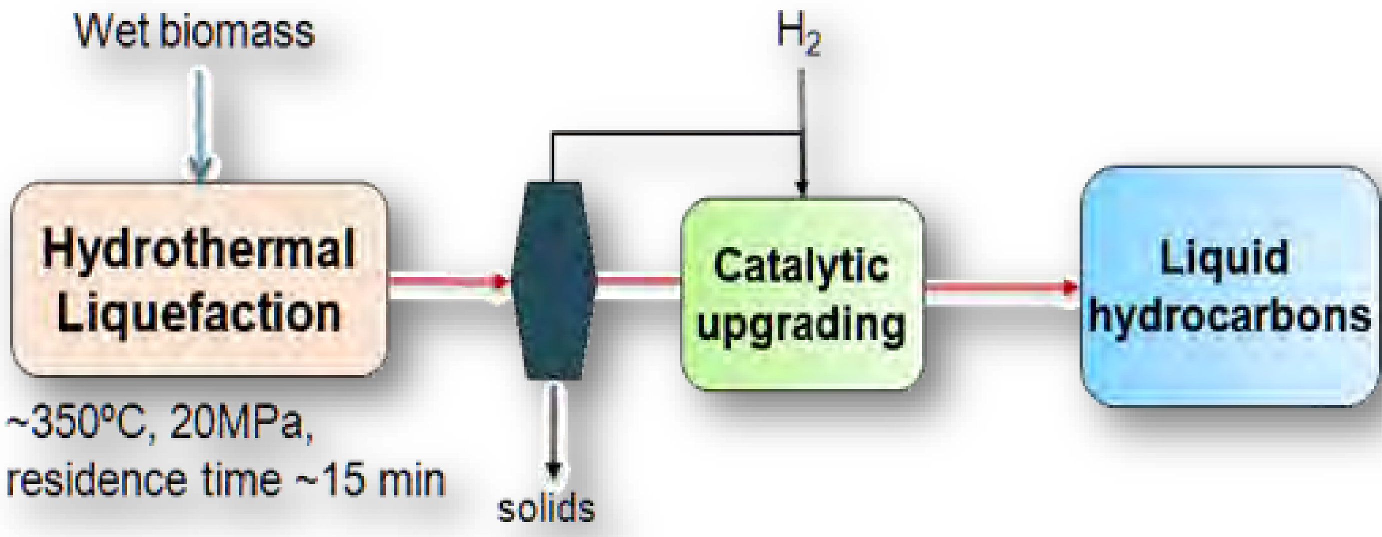

Hydrothermal Liquefaction

- Feed: whole biomass + buffer
  (10 to 20 wt% solids)
- Operation: condensed phase
- Bio-oil: gravity separable;
  (oxygen: 10 to 20 wt%)
- Product yield: ~50%-carbon; 32%-mass

Bio-oil Upgrading

- Operation: feed is thermally stable, low H_2 required
- Yield: 94%-carbon; 84%-mass; 95%-volume
- Product: high yield to distillate range

Liquefaction of Biomass to Bio-Oils

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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 atm
residence time	< 1 sec	5 to 30 min
carbon yield to bio-oil	70% (~40% to HC)	50% (typical for lignocellulosics)
oil product quality		
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

PNNL HTL hybrid reactor (plug flow)

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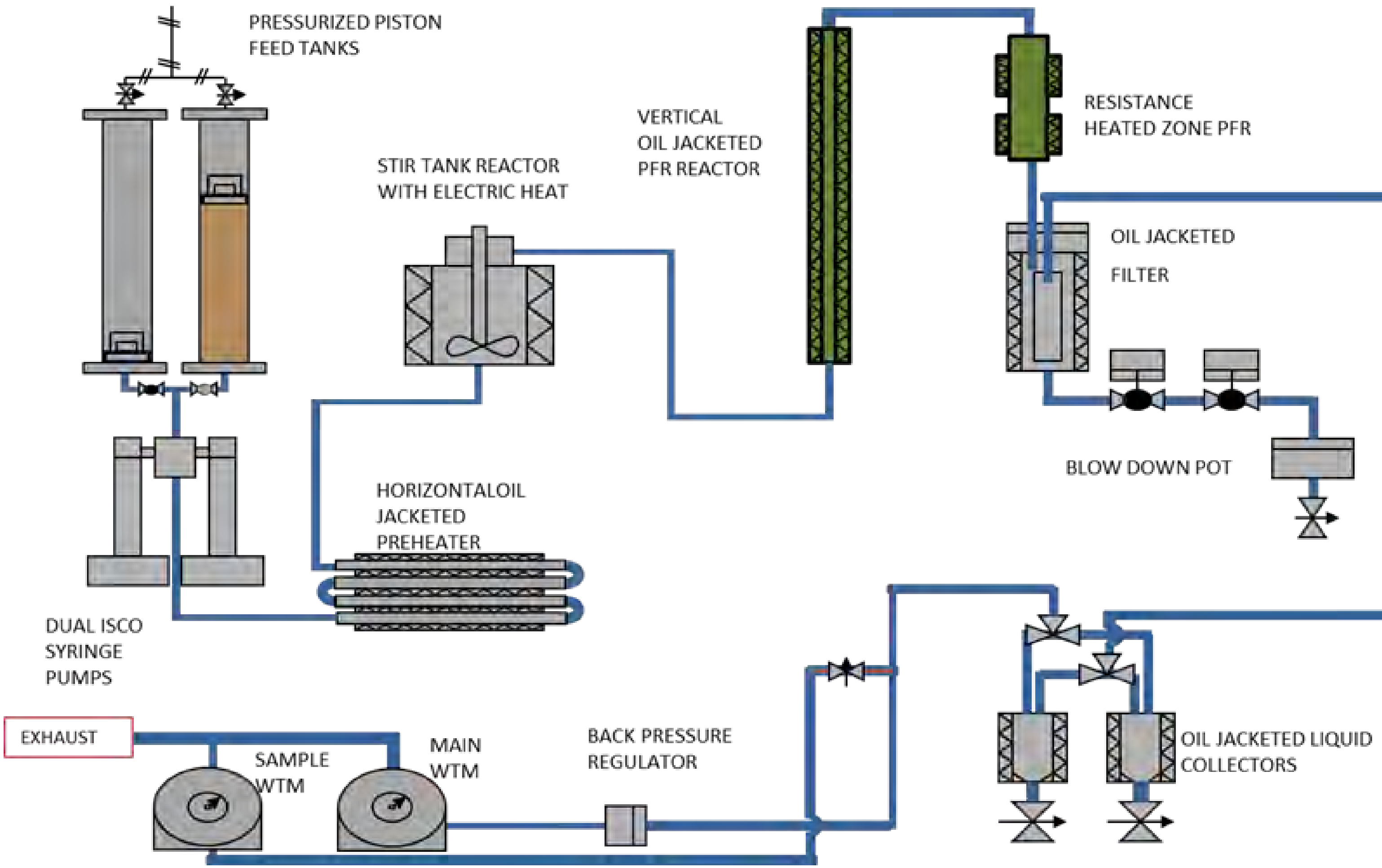
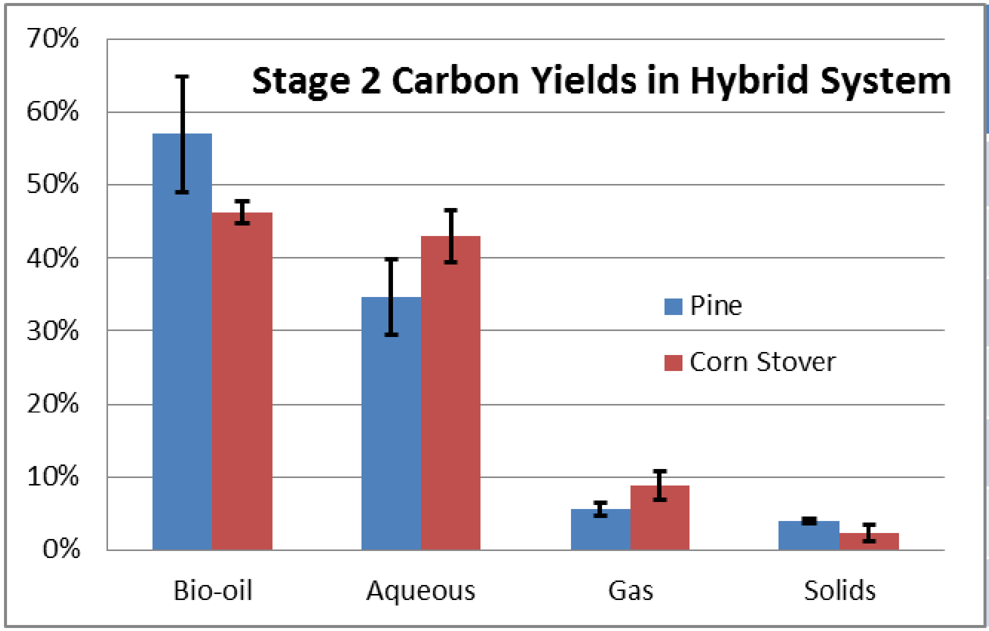


Small CSTR at critical temperature transition

NABC National Advanced Biofuels Consortium

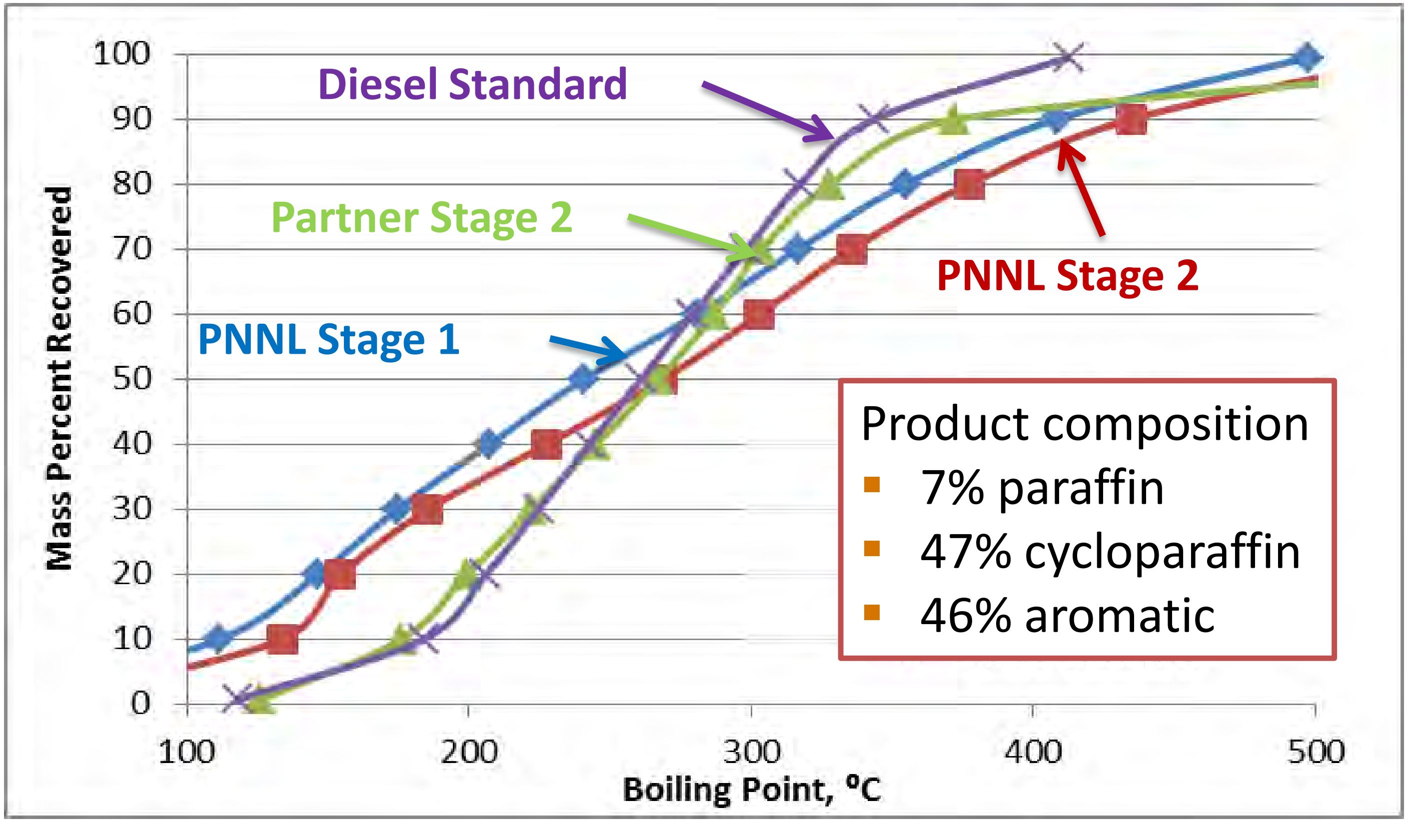
HTL bio-oil quality



	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

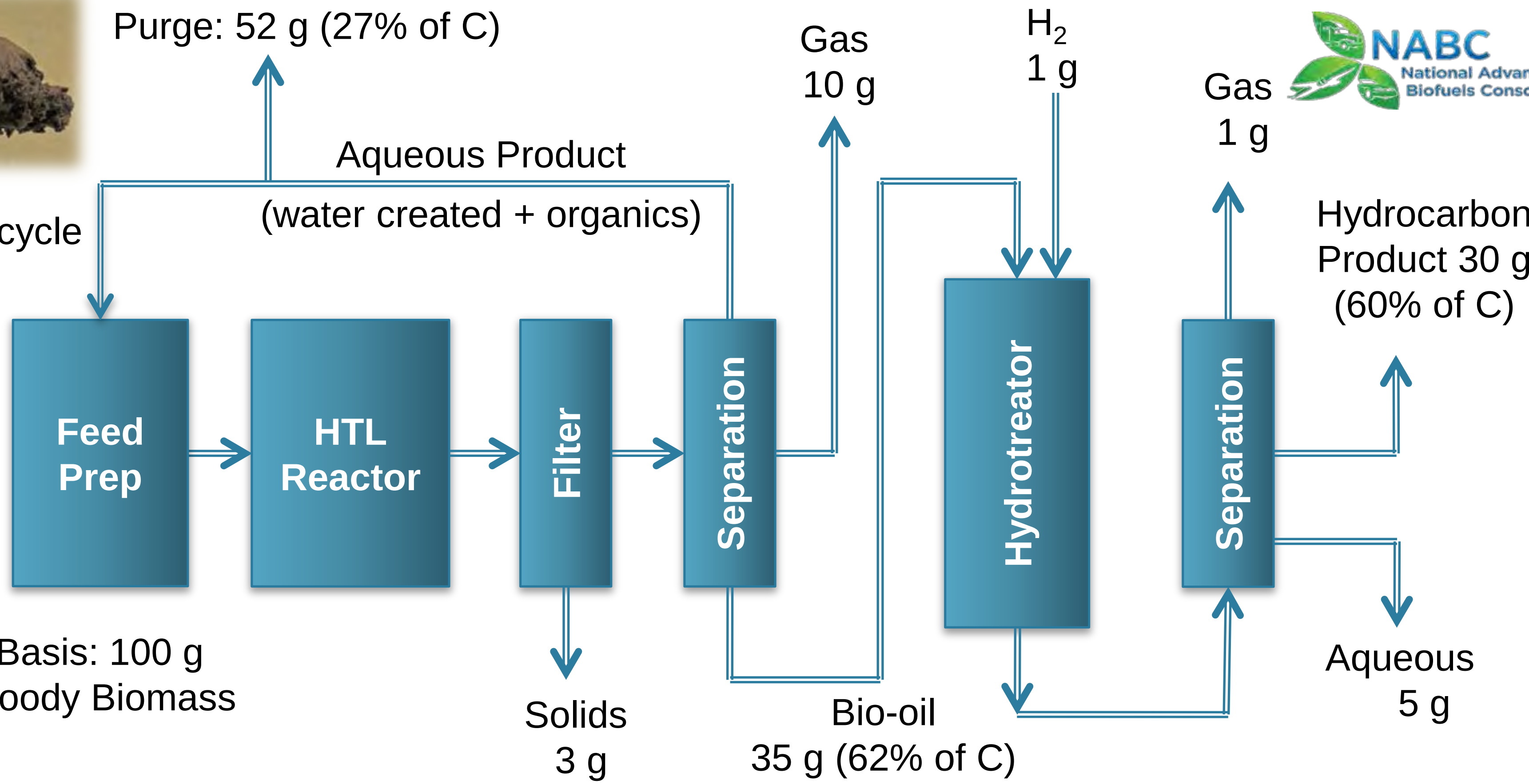
- 130 h on-stream, 7 L bio-oil
- Mean balance: Wood 99% (Mass) and 88% (carbon)
- Mean balance: Cornstover 96% (Mass) and 83% (carbon)
- Lower yield to bio-oil from corn stover observed

Simulated distillation data (fuel quality)



Shift the product to the distillate range

Carbon efficiency achieved



Step	Carbon Efficiency
HTL	62%
Hydrotreat	96%
Combined	60%

Technoeconomic considerations

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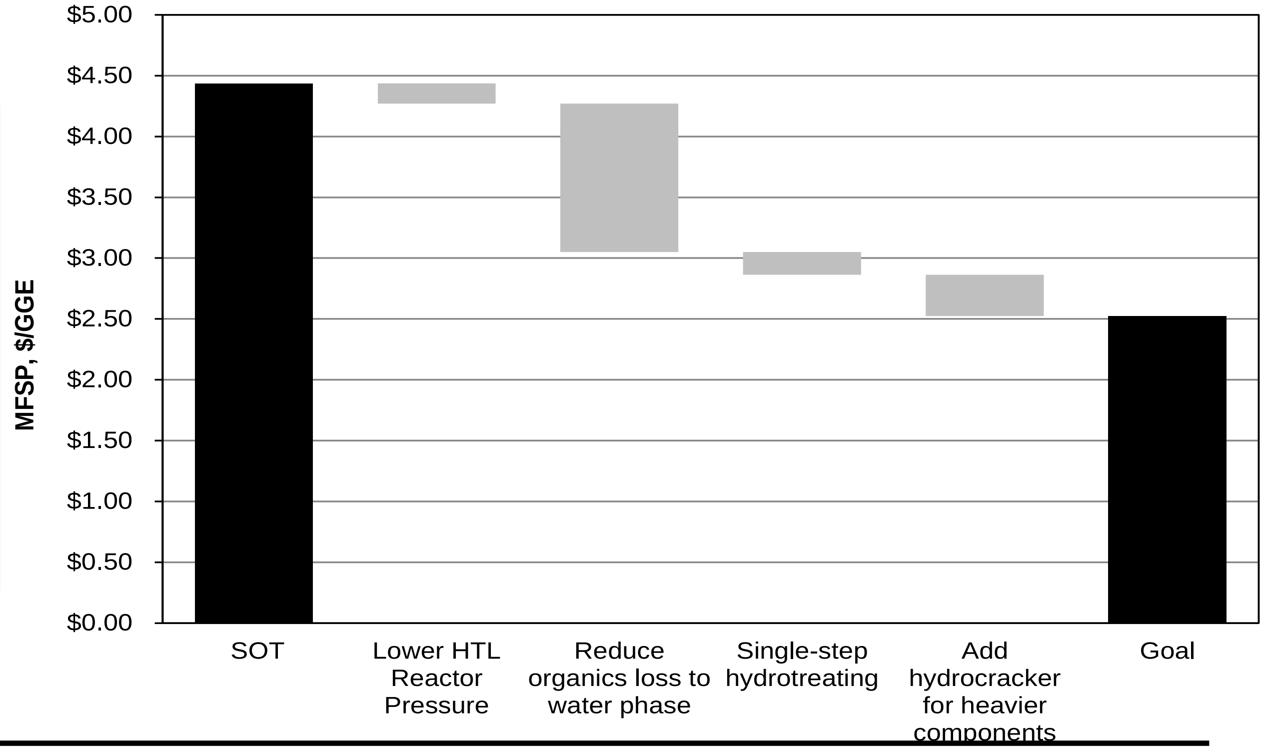
Applied Energy (2014) Yunhua Zhu[1,*], Mary J. Biddy[2], Susanne B. Jones[1], Douglas C. Elliott[1], Andrew J. Schmidt[1]

Feed
- 2000 MT/day

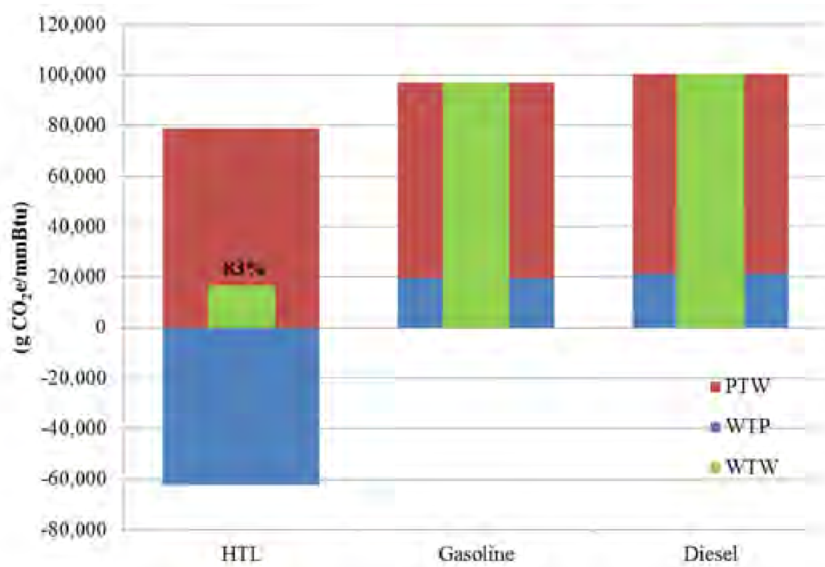
Yield
- (SOT) 44 M GGE/y
- (goal) 70 M GGE/y)

Energy Efficiency
- (SOT) 52%
- (goal) 66%

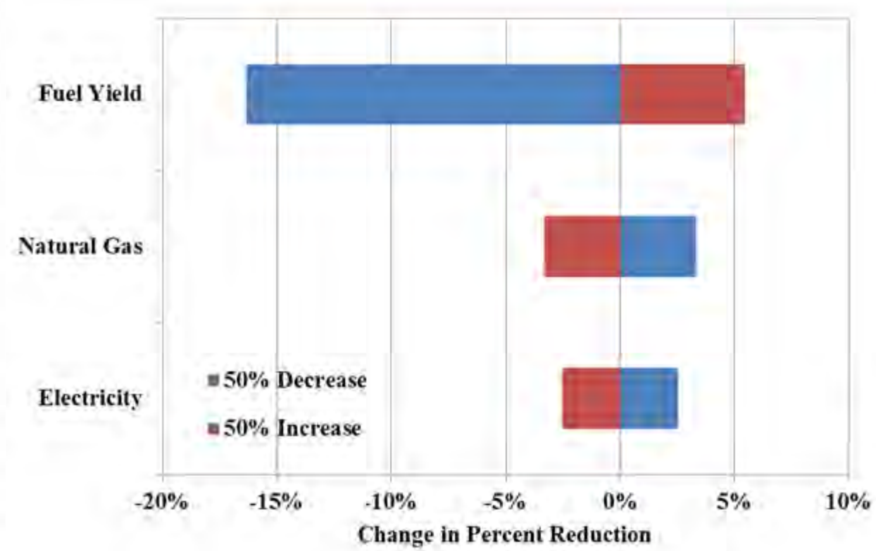


	SOT	Goal
Average return on investment	45.4	40.2
MFSP, $/L product	1.29	0.74
MFSP, $/GGE product	4.44	2.52

HTL life cycle analysis



WTW GHG emissions comparison



Sensitivity analysis results

- No co-products; allocation and displacement results are the same
- HTL emits 83% less GHG vs. diesel or gasoline
- Sensitivity: 50% increase in yield increases GHG reduction by ~5%

NABC
National Advanced Biofuels Consortium

Argonne
NATIONAL LABORATORY

Hydrothermal Liquefaction - Feedstocks

Algae Paste

Algae HTL Oil

Hydrotreated Algae HTL Oil

Wood Paste

Wood HTL Oil

Hydrotreated Wood HTL Oil

Upgraded HTL oil from algae: 85% diesel (paraffinic)

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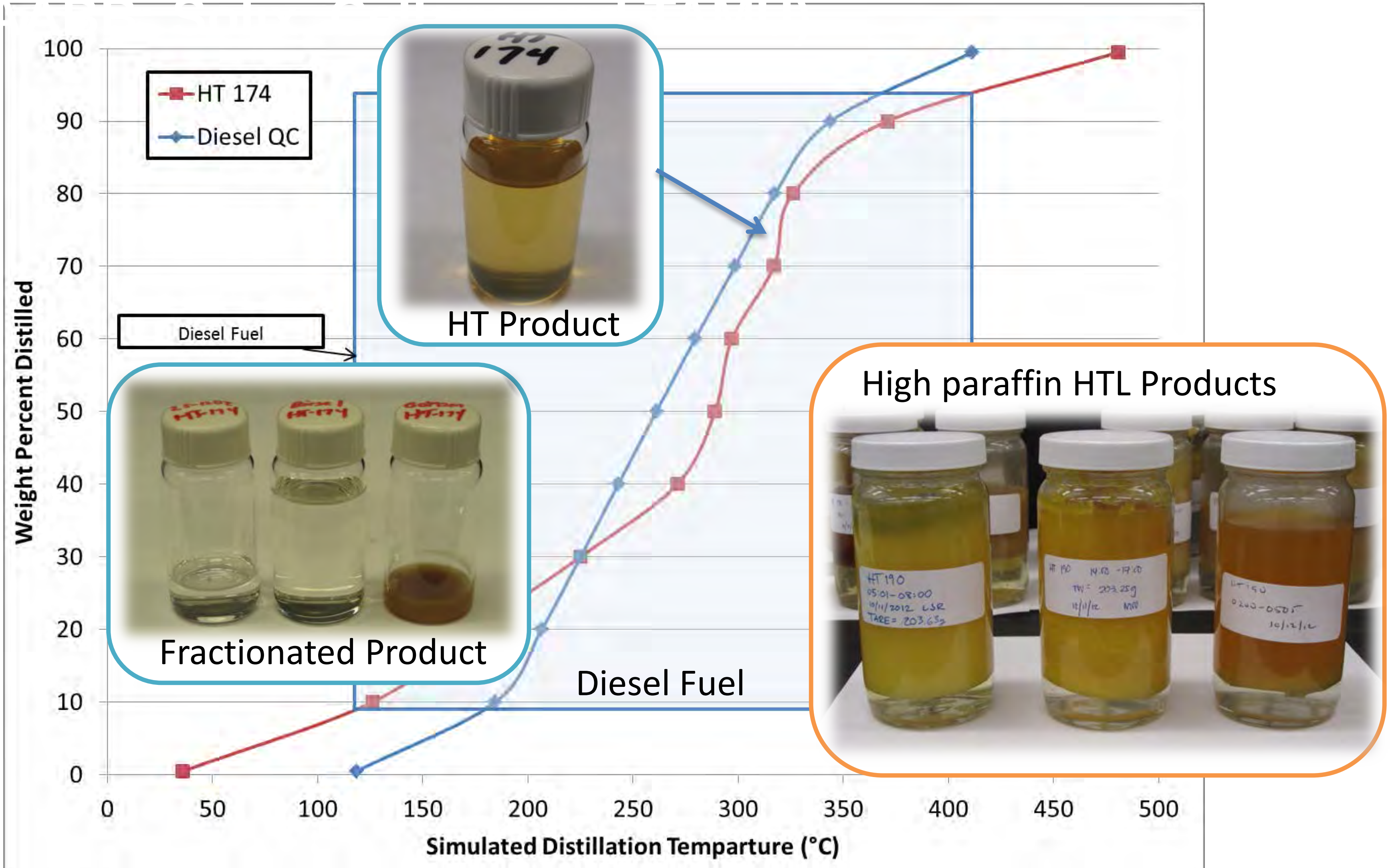

National Alliance For Advanced Biofuels and Bio-products
Pacific Northwest NATIONAL LABORATORY

Alcohol to Jet Fuel (ATJ) Collaborative

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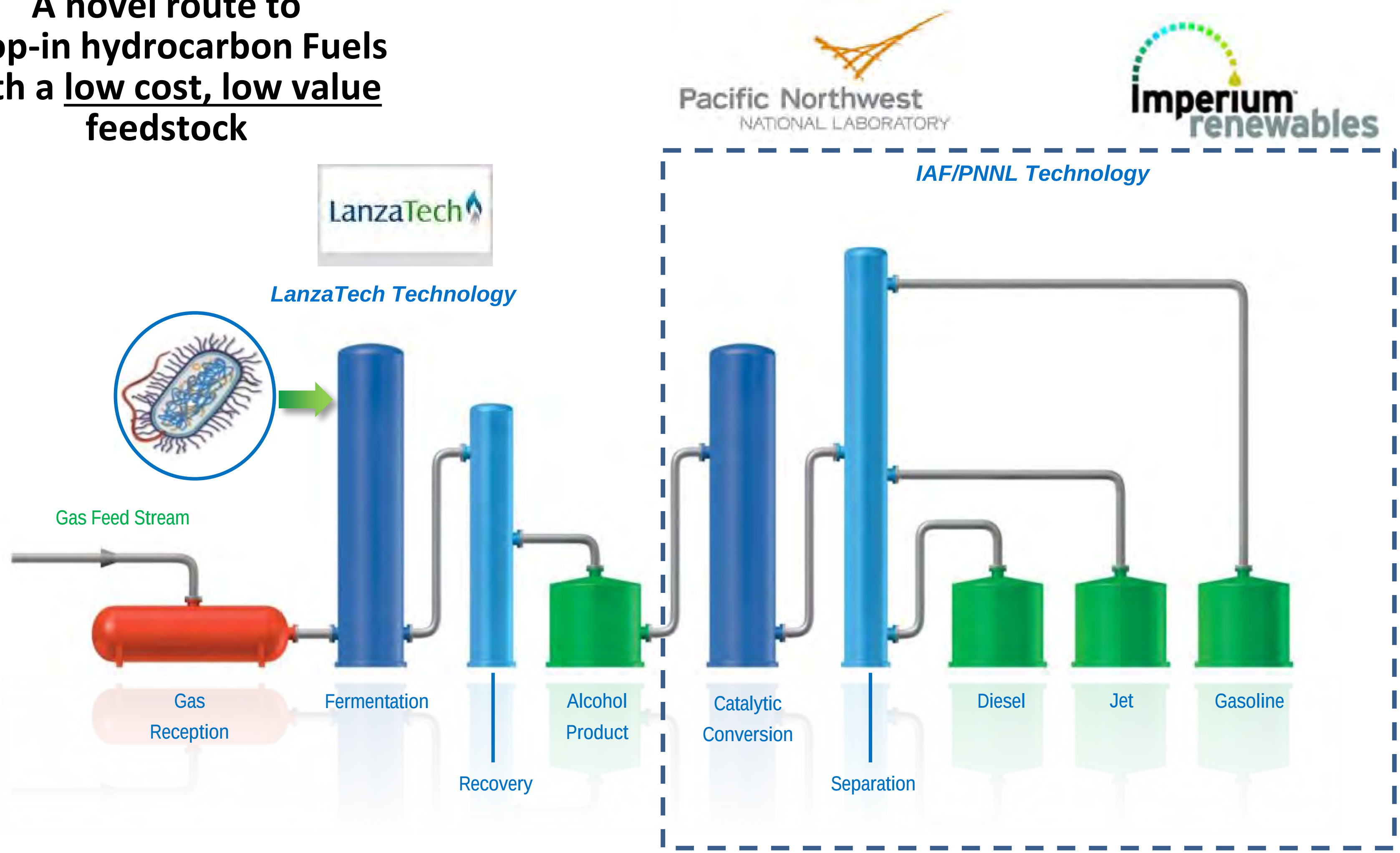
A novel route to Drop-in hydrocarbon Fuels with a <u>low cost, low value</u> feedstock

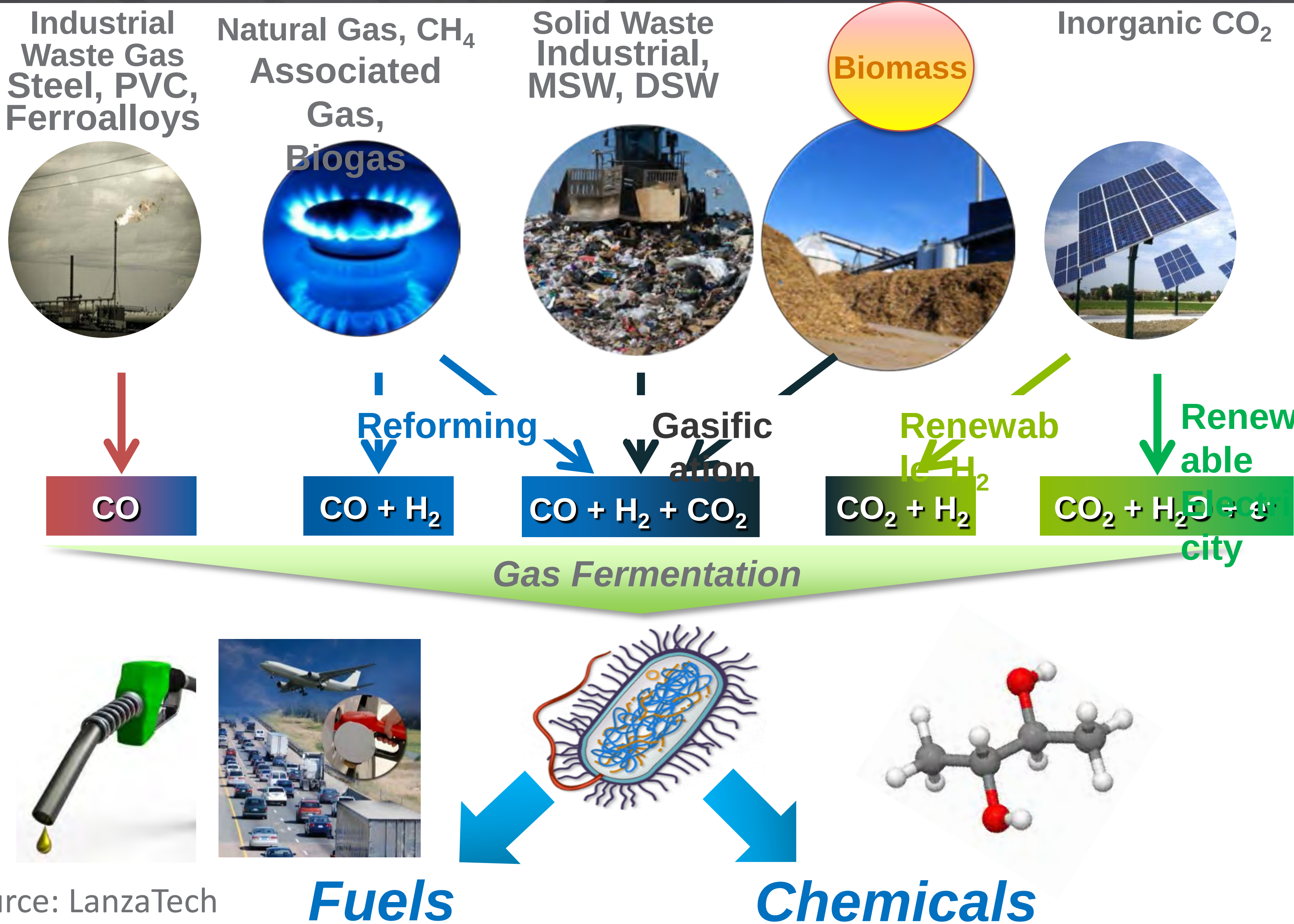


Fuel test results from 2012

- PNNL prepared samples for fuel property evaluation
- Off-site specification testing conducted by AFRL
- Positive results with continued focus on improving yields and limiting aromatics

Specification Test	MIL-DTL-83133H Spec Requirement	PNNL-1	PNNL-2	FT-SPK	JP-8
Aromatics, vol %	≤25	1.9	2.2	0.0	18.8
Olefins, vol %		1.2	1.1	0.0	0.8
Heat of Combustion (measured), MJ/Kg	≥42.8	43.1	43.1	44.3	43.3
Distillation:					
IBP, °C		161	165	144	159
10% recovered, °C	≤205	165	171	167	182
20% recovered, °C		166	173	177	189
50% recovered, °C		171	183	206	208
90% recovered, °C		190	220	256	244
EP, °C	≤300	214	243	275	265
T90-T10, °C	*22*	25	49	89	62
Residue, % vol	≤1.5	1.1	1.1	1.5	1.3
Loss, % vol	≤1.5	1	0.8	0.9	0.8
Flash point, °C	≥38	44	48	45	51
Freeze Point, °C	≤-47	<-60	<-60	-51	-50
Density @ 15°C, kg/L	0.775 - 0.840 *(0.751 - 0.770)*	0.803	0.814	0.756	0.804

LanzaTech is key partner - Recycling carbon for production of alcohol



Source: LanzaTech

Next steps

- **Securing tolling facility for production of renewable jet fuel currently for larger volume demands in 2014**
- **Ethanol will be supplied from Lanzatech's facilities in China or India**
- **Technology used for tolling will be supplied by PNNL/IAF**
- **Fuel production would occur in 2014 with test flights to follow**
  - **Will include enough production to facilitate ASTM certification process**
- **Anticipating additional scale up in 2016**

Producing fuels from whole biomass: Liquefaction technology

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PNNL applying it's core capability in catalysis to solve the unique challenges of producing hydrocarbons from direct liquefaction

PNNL is developing new, robust catalyst to make higher quality, stable, bio-oils and refining technologies to convert bio-oils to fuels

PNNL provides unique suite of continuous reactor capacity and is partners with industry and others in deploying new technologies

Impact:

Research is advancing biofuels to serve refinery industry needs

- ✓ Demonstrated fuel quality (UOP)
- ✓ Developed Process models and design case
- ✓ Solved initial catalyst life issue
- ✓ Developed improved process
- ✓ Partnering with industry to co-process bio-oil with petroleum

Core Capabilities

Catalysis	Computational modeling	Continuous reactor capability	Process and Life-cycle Analysis

Funding source: DOE Office of Energy Efficiency and Renewable Energy

Success Story: Aviation Biofuels

PNNL is working to improve and expand the use of cost-effective, bio-based aviation fuels

PNNL is applying catalysis in a number of hybrid processes that convert complex biomass into distillate range hydrocarbons

PNNL partnerships with industry and universities are delivering cost-effective, infrastructure-compatible aviation biofuels

Impact:

Research is advancing biofuels to serve aviation industry needs

- ✓ PNNL delivers aviation biofuels in 2012 to Air Force for testing
- ✓ PNNL and partners produce first 100% biomass-derived jet fuel, used in hydroplane
- ✓ PNNL co-leads key DOE biofuels research consortiums

Core Capabilities

Catalysis	Biotechnology	Fuel Chemistry	Process and Life-cycle Analysis

Funding source: DOE Office of Energy Efficiency and Renewable Energy

Conclusions

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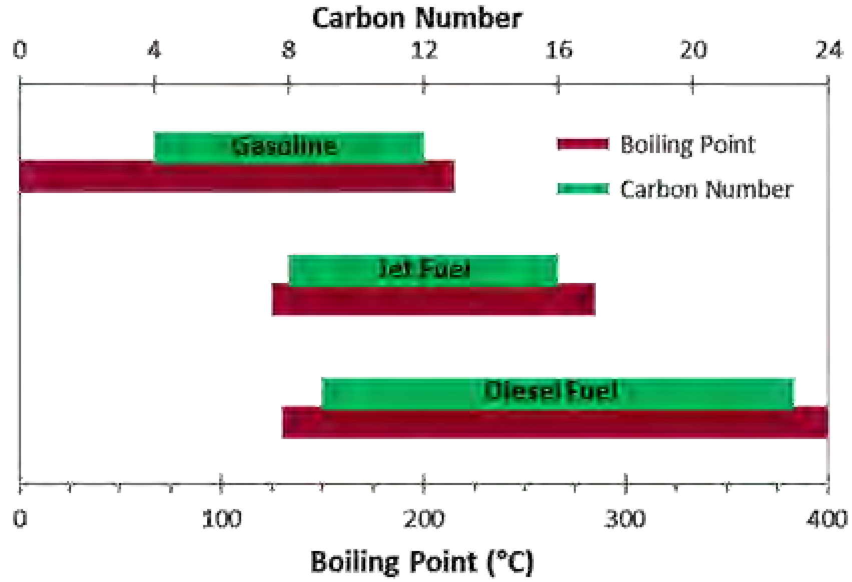
- The last 2 years has resulted in tremendous strides that address critical issues in liquefaction
- Liquefaction technologies will lead to cyclic hydrocarbons (unless ring opening catalysts are employed)
- Hydrogen demand varies by technology
- Alcohol to jet moves us out of the classical liquefaction paradigm

Fraction	Upgraded Pyrolysis Oil		
	Cat-PO 0.28% O	Non-cat 0.4% O	Non-cat 1.4% O
Gasoline	40%	42%	36%
Diesel	60%	49%	48%
Heavies	<1%	9%	16%
Jet A	56%	38%	30%

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



Thank you for your time

Pacific Northwest NATIONAL LABORATORY

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Other Feedstock Resources – Better Utilize Wastes

- Roosevelt Landfill
  - 81 percent of permitted disposal in WA
  - 3 unit trains arrive daily (100 unit cars each)
- Columbia Ridge Landfill
  - 85% of permitted waste in OR
  - 2009 waste from CA and HI
- 14 million tons of material waste produced
  - Recycling diverts 6 million (some of this is composted)
- 7-8 million tons of organic available (all at less than $50 per ton)

Waste could be a primary feedstock

- Municipal solid waste, wet wastes, gas wastes
- How to improve RINs