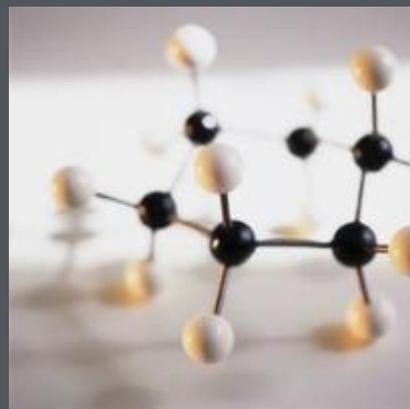


# Thermochemical Conversion Processes to Aviation Fuels

U.S. DEPARTMENT OF  
**ENERGY**

Energy Efficiency &  
Renewable Energy

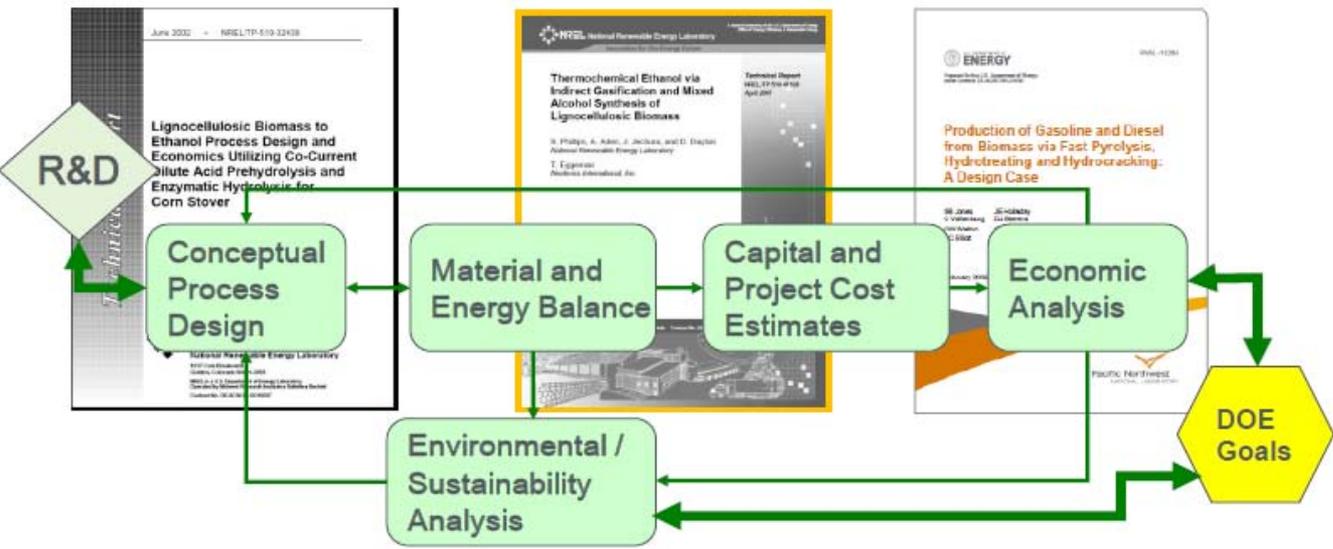


Advanced Bio-based Jet Fuel  
Cost of Production Workshop

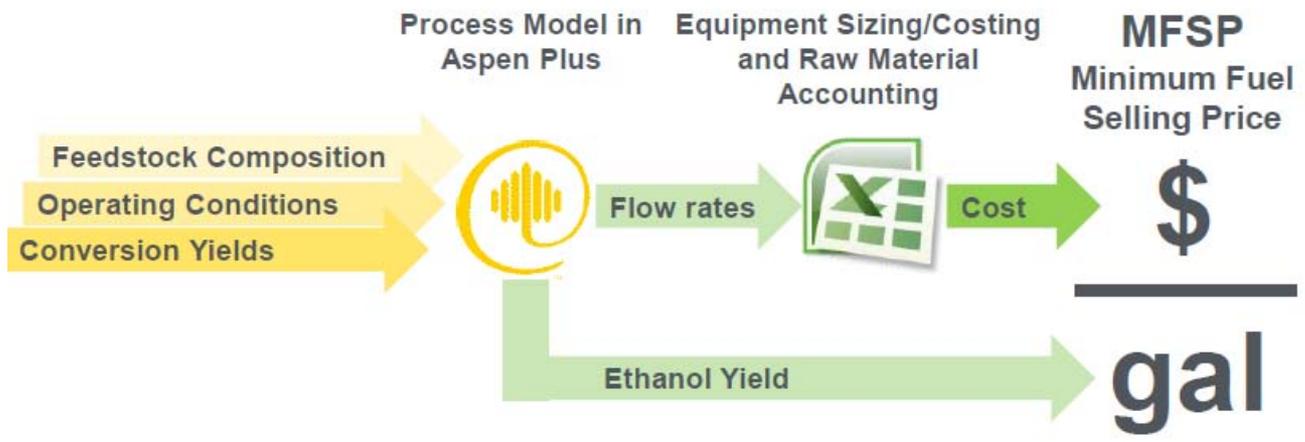
John Holladay (PNNL)  
November 27, 2012

- Building on the Approach previously described by Mary
- Syngas routes from alcohols (sans Fischer-Tropsch)
- Pyrolysis approaches (Lignocellulosics)
  - Fast Pyrolysis
  - Catalytic Fast Pyrolysis (in situ and ex situ)
- Pyrolysis approaches (Algae)
  - Hydrothermal Liquefaction

# Approach



- Transparent, peer reviewed
- Iteration with R&D teams
- Collaboration with E&C firms

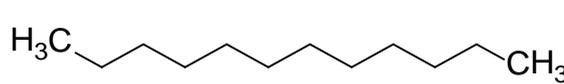


- Transparent, assumptions
- $n^{\text{th}}$ -plant costs
- Costs include IRR, equity payback and taxes
- MSP for zero NPV

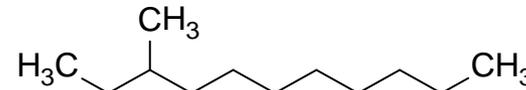
Provides a common basis to evaluate a range of technologies

## Ideal Carbon Length C8-C16

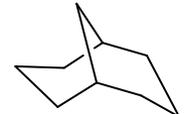
**Paraffins**  
70 - 85%



*Normal Paraffins*

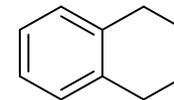
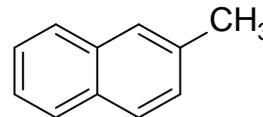
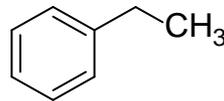


*Iso-paraffins*

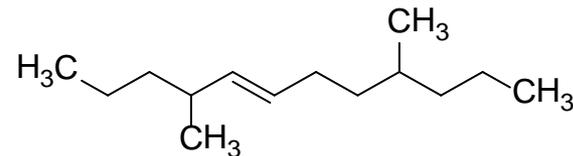
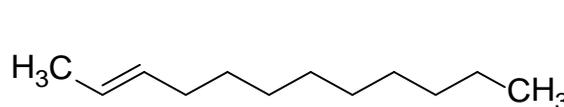


*Cyclic Paraffins*

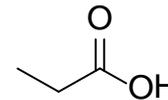
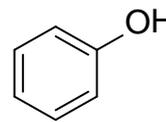
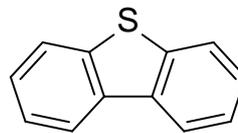
**Aromatic**  
< 25%



**Olefins**  
< 5%



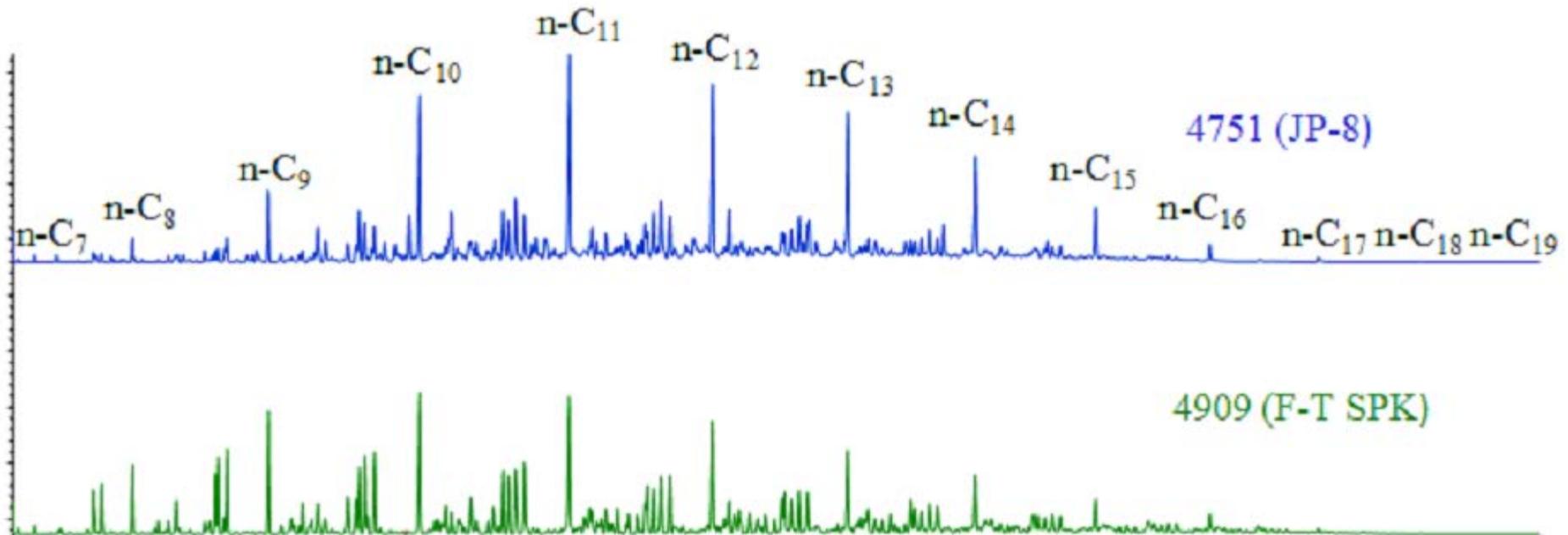
**S, N, O containing  
Compounds < 5%**



We desire fuels with composition similar to above  
(i.e. a replacement or “drop-in” fuel)



## *Fuel Molecules in JP-8 and Fischer Tropsch Synthetic Paraffinic Kerosene (SPK)*



# Contribution of Different Hydrocarbons to Jet Fuel

**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.

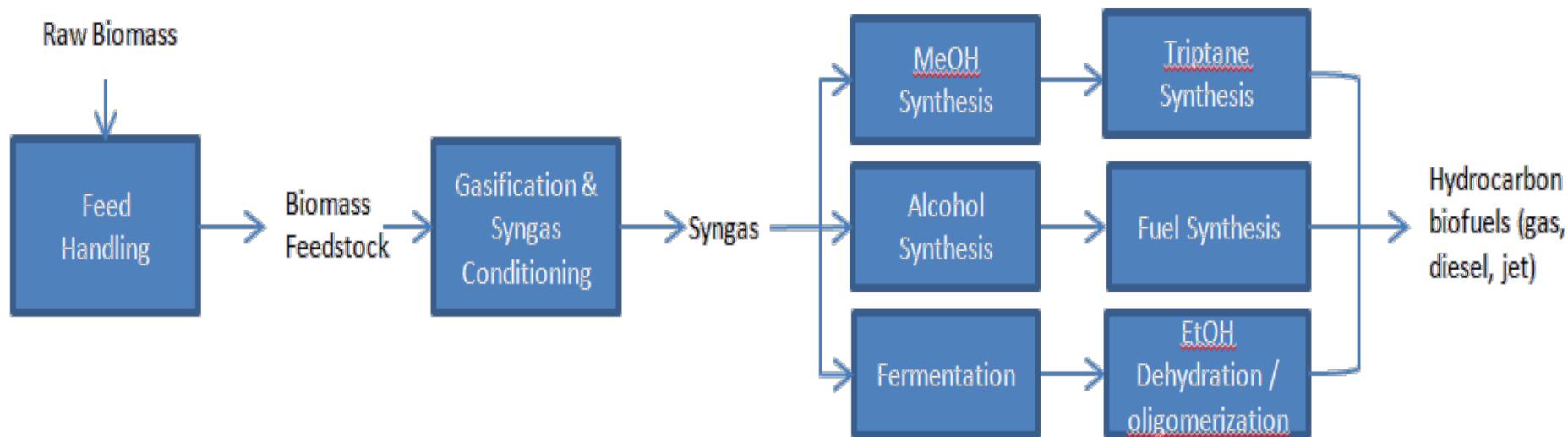
Hydrodeoxygenation of natural oils  
or 2-step oxygenate to fuels

Pyrolysis or 1-step  
Oxygenates to Fuels

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

# Syngas to Fuels

## Critical Needs and Uncertainties

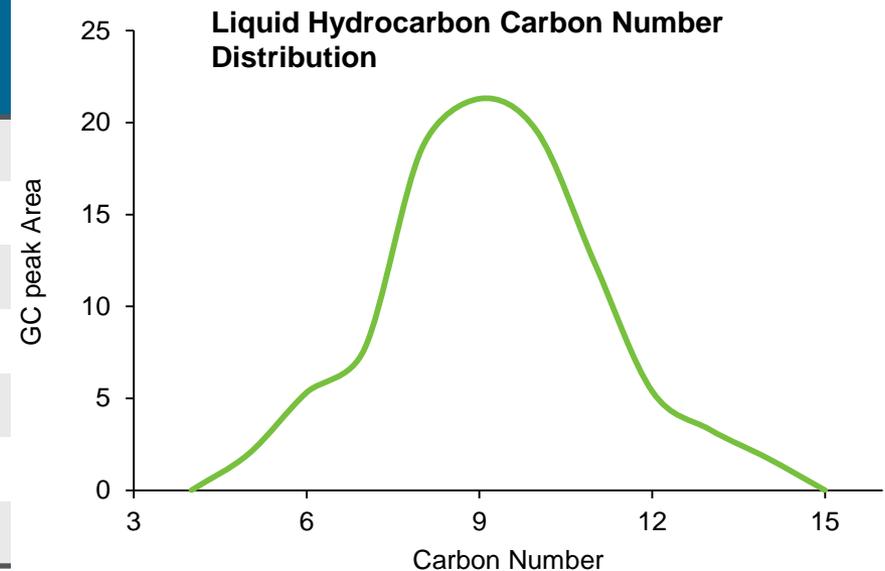


- ▶ EERE is modeling three syngas based routes to hydrocarbon fuels
  - Methanol to triptane-type molecules
    - fuel quality, capital cost, catalyst life, overall economics
  - Mixed alcohols to jet fuels
    - Oxygenate production efficiency vs methanol, fuel quality; catalyst stability, overall economics
  - Syngas fermentation to alcohols followed by dehydration/oligomerization
    - Minimum syngas cleanup
    - Cost of alcohol with minimal processing (non-fuel grade intermediate)
    - Catalyst poisons in broths

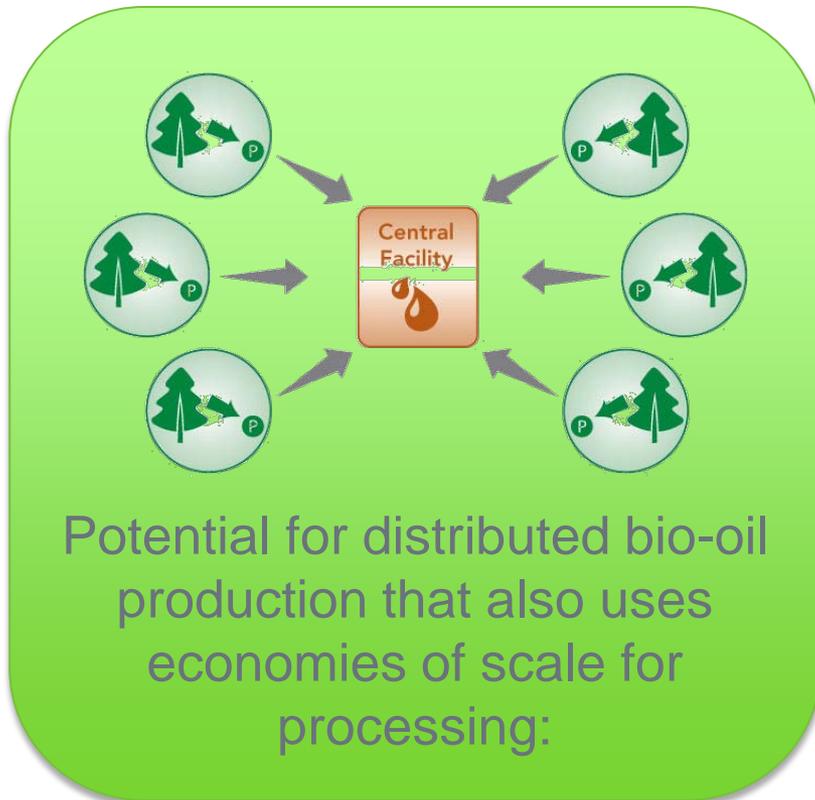
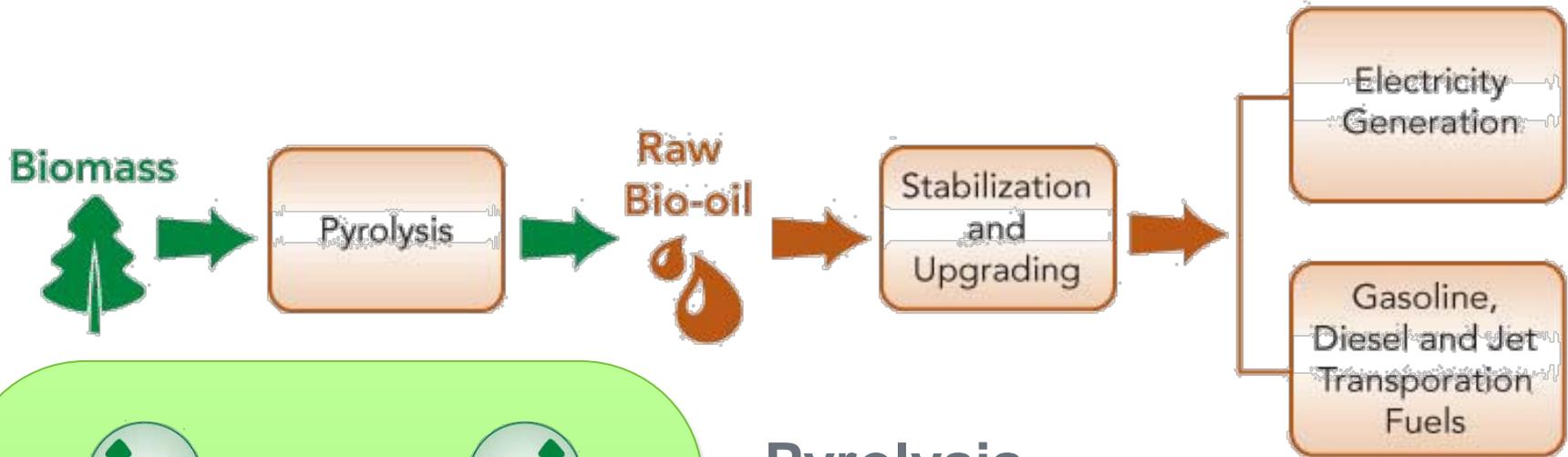
# Mixed Alcohol Product (Example)

- ▶ Mixed alcohol product from PNNL Syngas to Alcohols Project
- ▶ Demonstrated feasibility of upgrading mixed oxygenate streams to hydrocarbon fuels
- ▶ In this demonstration the product contains primarily aromatic components in the gasoline range with ~50% overlap with jet

Feed Compounds	Feed Concentration (wt%)
Methanol	0 to 2.5
Ethanol	8 to 28
C3+ Alcohols	1 to 3
Acetic Acid	4 to 14
C2+ Aldehydes	6 to 17
Ethyl Acetate	1 to 18
Water	41 to 60



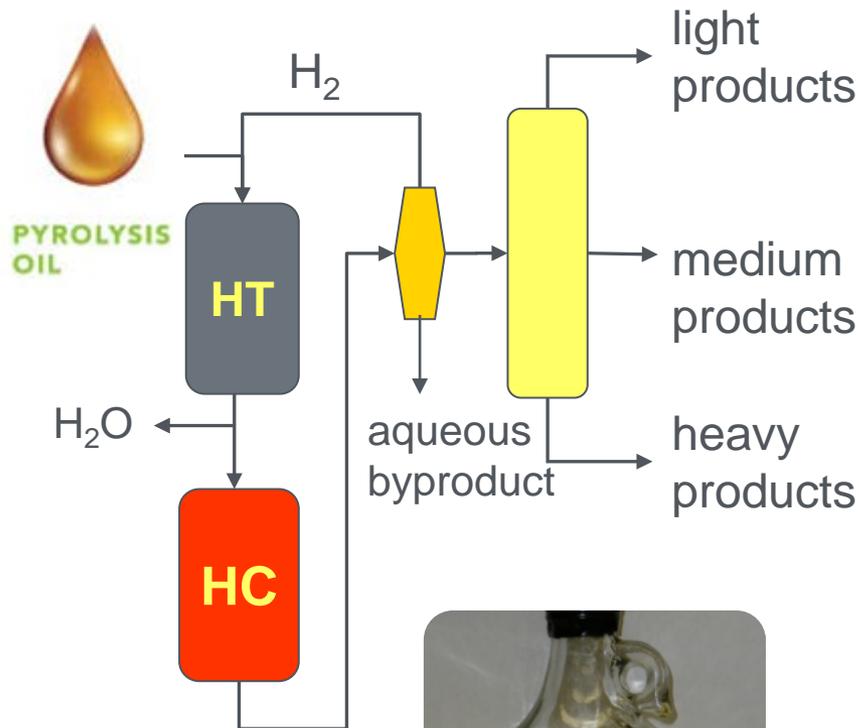
# Pyrolysis Oil Stabilization and Upgrading



## Pyrolysis

- Biomass 10% moisture, 2 – 6 mm
- Rapid heating (500°C, <1 s)
- Condense and trap vapor
  - Good carbon yields (70%)
  - High water: 35 – 40%
  - Highly acidic ( $Tan > 100$ ,  $pH = 2.5$ )
  - Thermally low stability
  - Low HHV: 16 – 19 MJ/kg
  - Distillation residue up to 50%
- Variants with catalyst produce oils of higher quality (lower yield)

# Fast pyrolysis oil is converted to fuels in a 2-step process

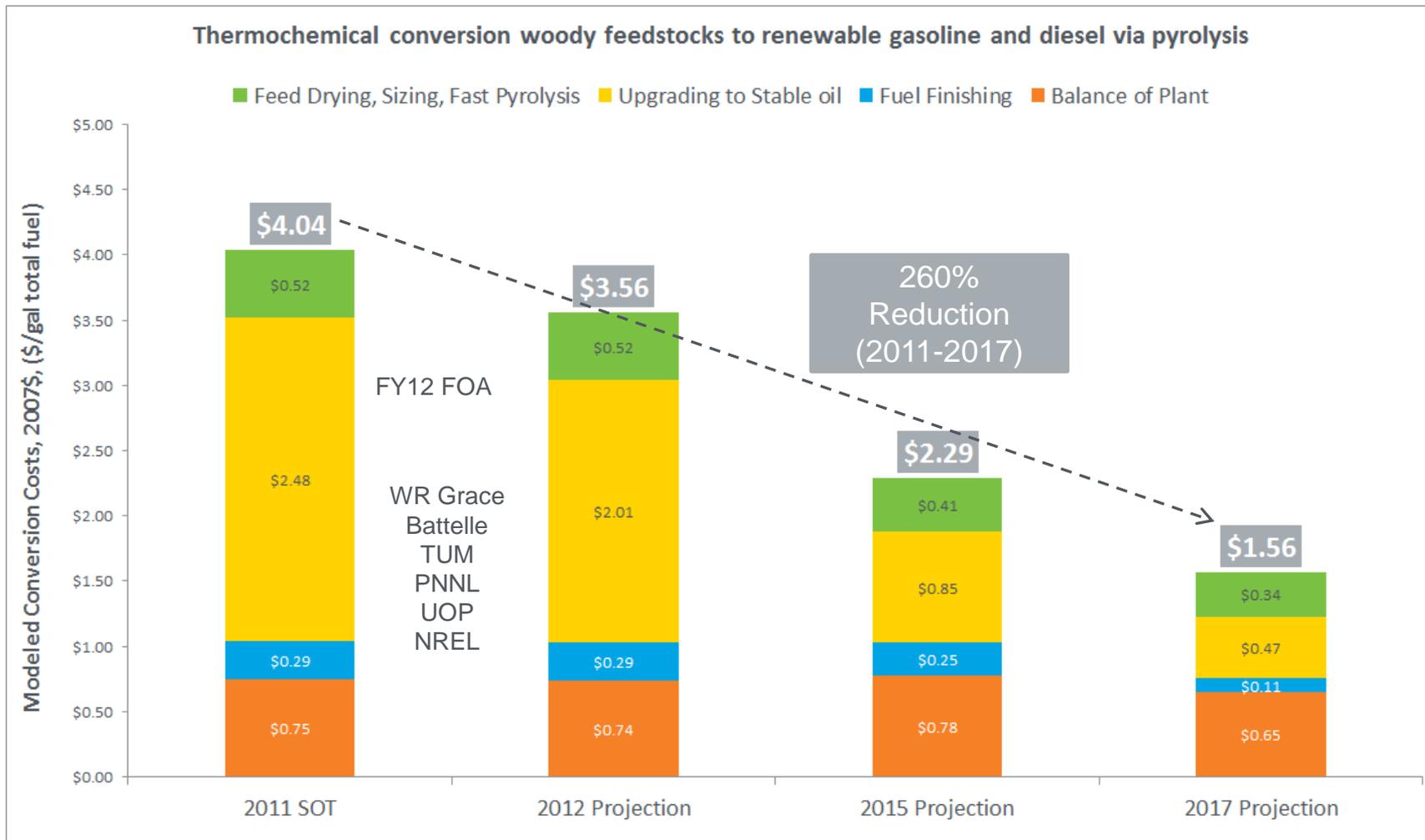


Continuous processing done in fixed and non-fixed bed reactors

- 150 – 450 °C, 75 – 150 bars
- 0.1 – 1.5 LHSV
- 1 – 10 m<sup>3</sup> H<sub>2</sub>/L bio-oil
- Wide range of catalysts

	Hydroprocessed Bio-oil (from Mixed Wood)		Petroleum Gasoline
	Min	Max	Typical
Paraffin, wt%	5.2	9.5	44.2
Iso-Paraffin, wt%	16.7	24.9	
Olefin, wt%	0.6	0.9	4.1
Naphthene, wt%	39.6	55.0	6.9
Aromatic, wt%	9.9	34.6	37.7
Oxygenate, wt%		0.8	

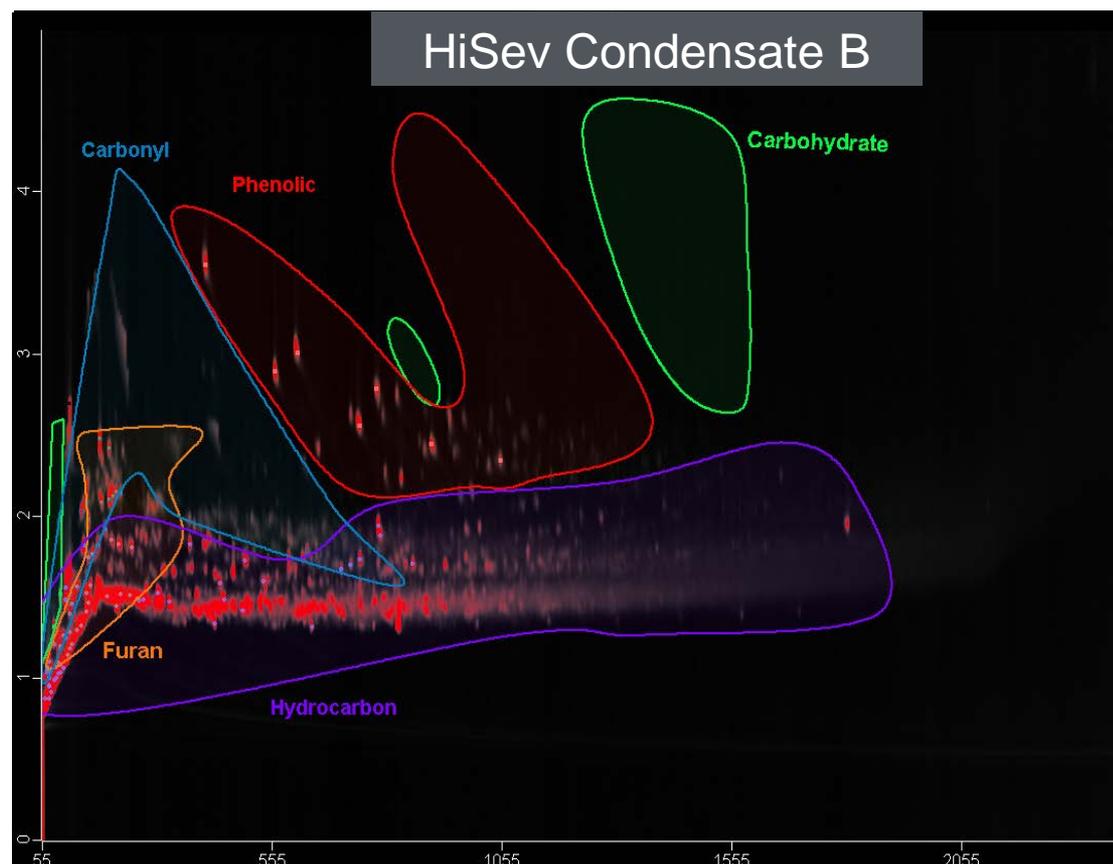
## 2007 Constant Dollar Conversion Costs - Excludes Feedstock Cost



**Goal:** produce drop-in hydrocarbon fuels in the gasoline, diesel, and jet range

## Accomplishments:

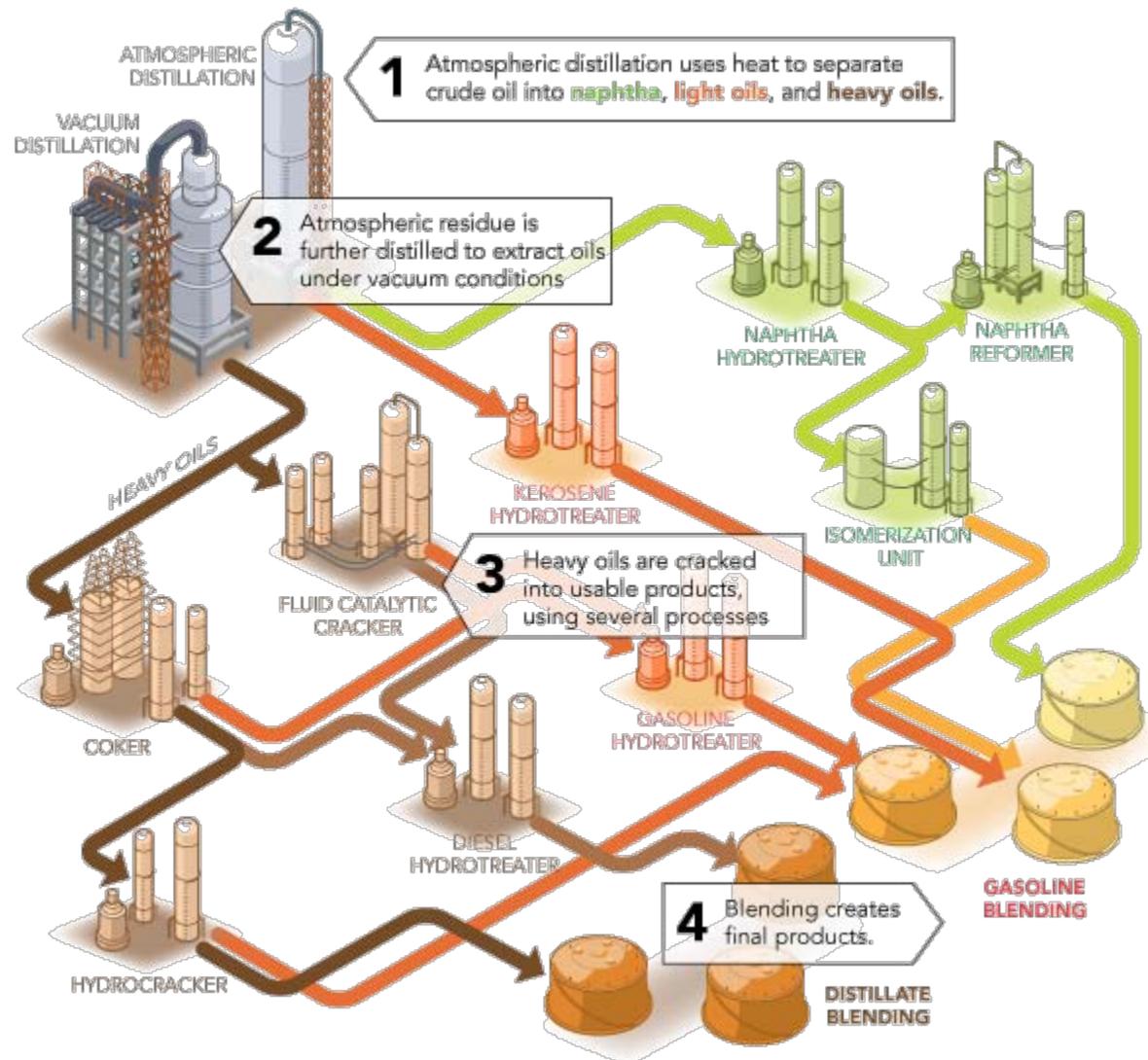
- Currently gasoline-range fraction is suitable for blending, however, diesel-range fraction has low cetane
- Utilized 2D GC-GC/MS analysis capabilities to better characterize upgraded products
  - Utilizes sequential gas chromatography (molecular weight and polarity)
  - Product identification by mass spectrometry to provide improved characterization



**Next:** Leverage existing industry interactions to ensure fuel quality

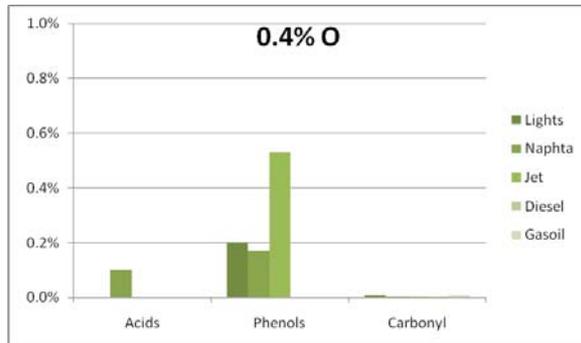
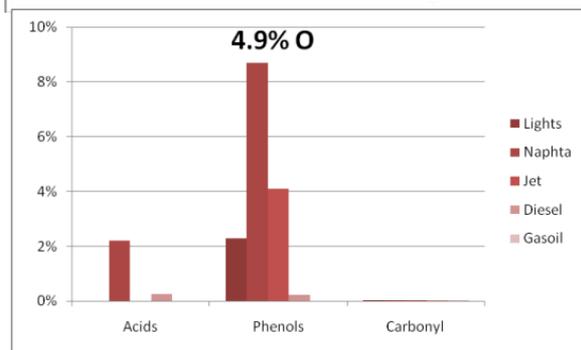
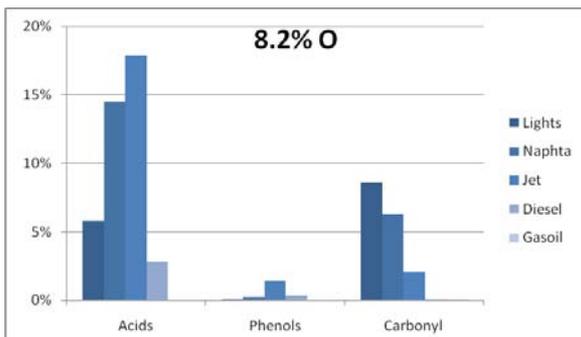
# NABC—Use Existing Infrastructure Also Subject of 2012 FOA

- Complex but efficient conversion processes
- ~100 years experience
- Refinery partners in National Advanced Biofuels Consortium (NABC) are helping identify how biomass may fit into this construct
- Analysis of materials and experimentation on how the materials may interact in the refinery



# Bio-oil Stabilization for Refinery Integration

**Goal:** produce materials with lower oxygen content, TAN, and minerals



## Accomplishments:

- Stabilize via Hydrotreating
  - Low-severity hydrotreating--bio-oil oxygen content to 5-8%
  - Extending catalyst lifetime by using mild hydrotreating as an initial step in the upgrading
  - Demonstrated 21 days of catalyst lifetime within dual bed
- Produced significant quantities of stabilized bio-oil to provide analyses of earlier point-of-entry into the refinery (Valero/NREL/PNNL)
  - Produced liter-quantities of stabilized bio-oil with oxygen contents of 0.4%, 4.9%, and 8.2%
  - Jet and heavier fractions of 5% oxygen oil have low acids and carbonyls and may be suitable for refineries

## Next:

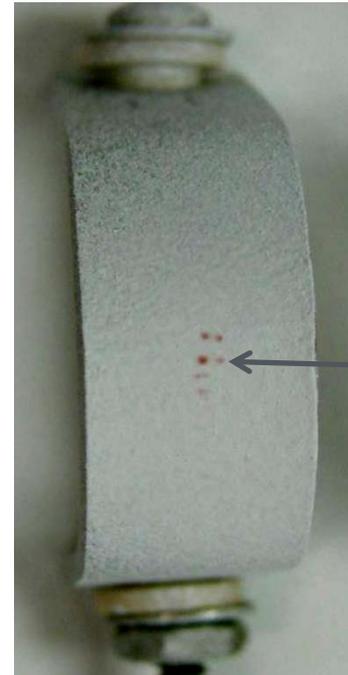
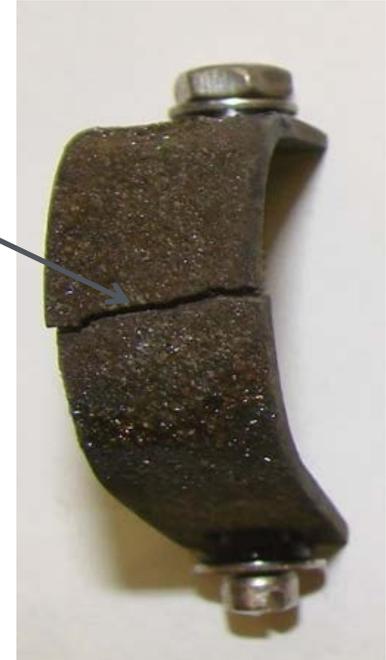
1. Continue stabilization and upgrading projects
2. Continue to leverage industry experience
3. NABC refinery integration efforts
4. New project with PNNL/W.R. Grace

# Materials of Construction

## Corrosion of Samples In Bio-Oil

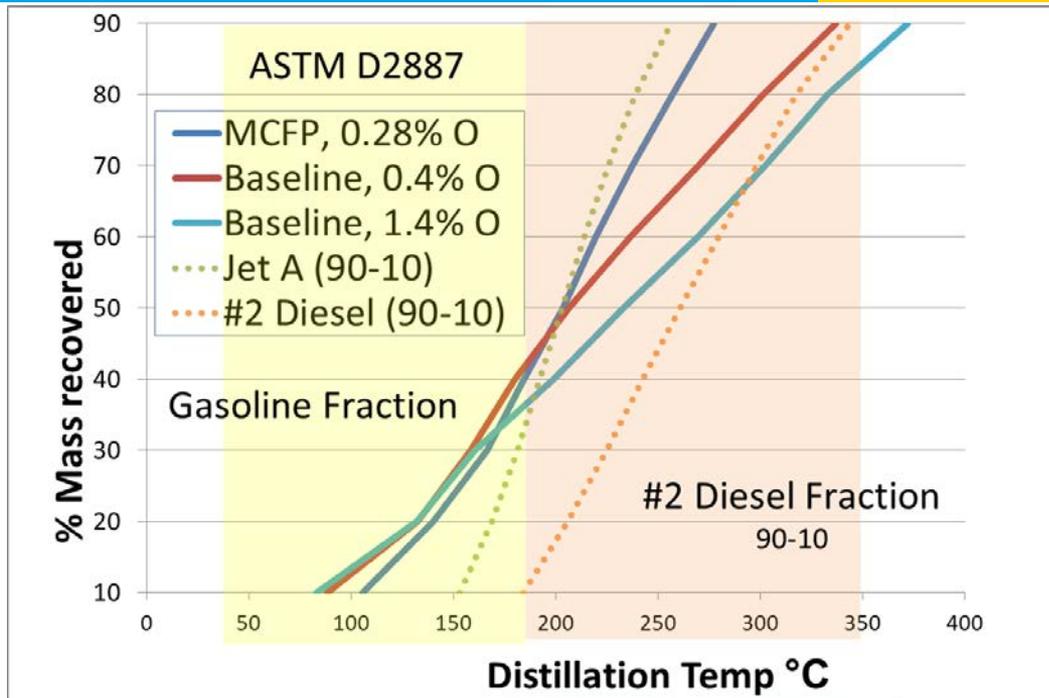
- Through wall cracks have been found in carbon steel and 2¼ Cr-1 Mo samples after exposure at 50°C
- Samples of 304L and 18 Cr – 2 Mo stainless steels developed crack indications after 750 hr at 50°C
- Exposure of these samples is being continued to determine if more extensive cracking will develop

Through wall crack in carbon steel



Crack indications in stainless steel

# Understand Fuel Opportunities



Fraction (BP range)	Upgraded Pyrolysis Oil		
	Cat-PO 0.28% O	Non-cat 0.4% O	Non-cat 1.4% O
Gasoline IBP-184°C	40%	42%	36%
Diesel 184-344°C	60%	49%	48%
Heavies > 344°C	<1%	9%	16%
Jet A (overlap) 153-256°C	56%	38%	30%

From Zacher A, *et al* "Mild Catalytic Fast Pyrolysis of Biomass and Catalytic Hydrotreating to Liquid Transportation Fuels" PNNL-SA-82908



- ▶ 100% renewable turbine fuel demonstrated through collaboration with UOP (SPK), Boeing, NREL (Py-oil) and PNNL (upgrading)

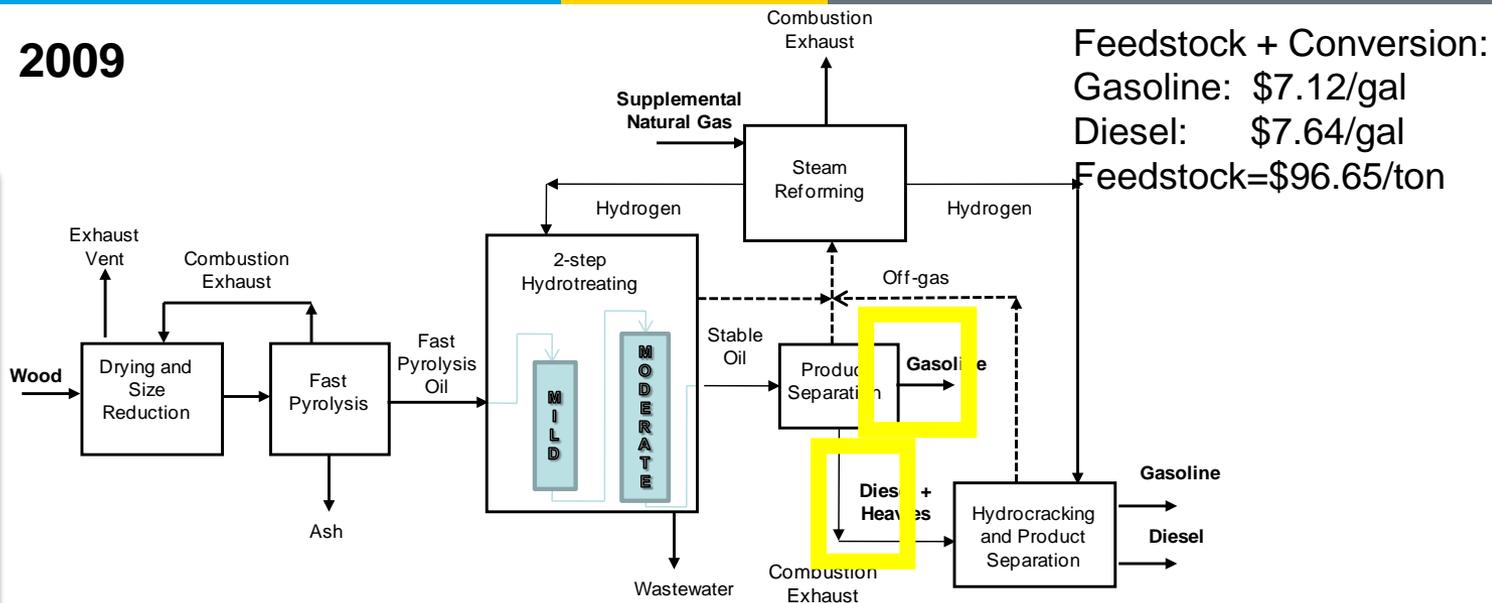
***The hydroplane ran on 98% Bio-SPK and 2% renewable aromatics***

# Valuation of Fuel Mixtures Gasoline and Diesel

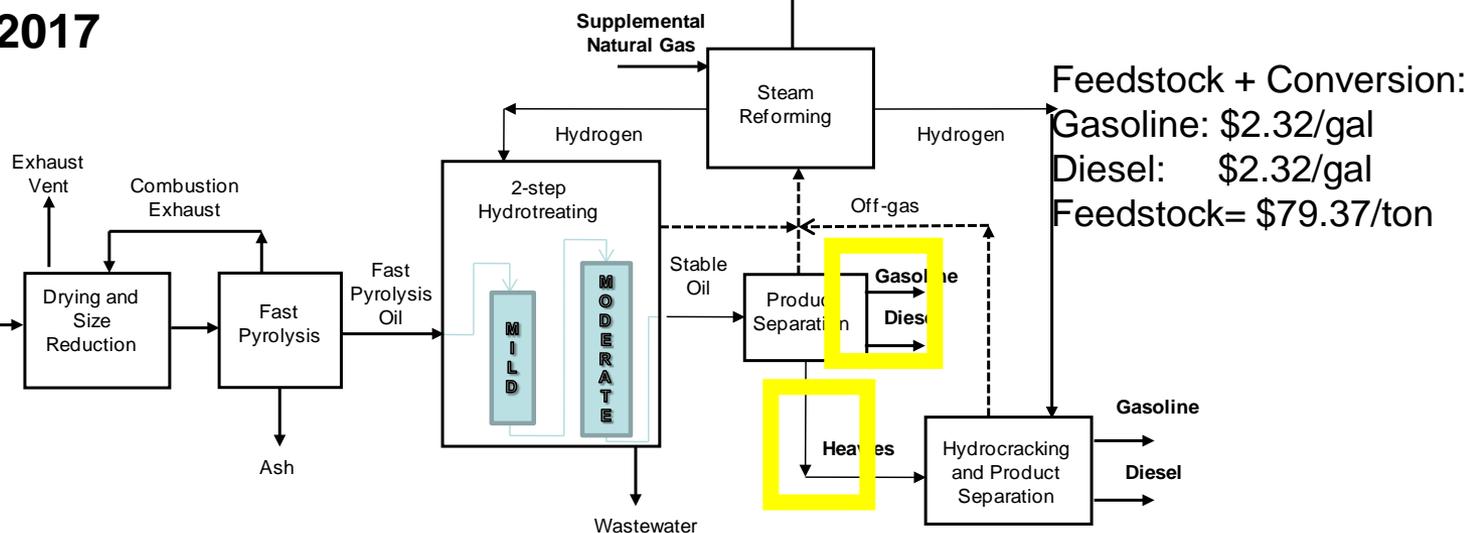
Developed a methodology for valuation of the gasoline and diesel products from pyrolysis

Costs in 2007 constant dollars (April 2012 MYPP)

**2009**

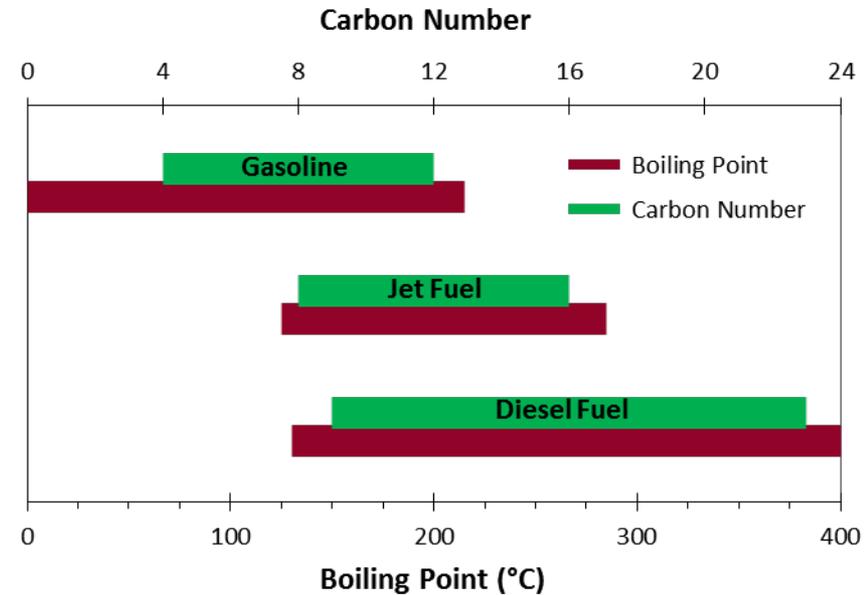


**2017**



# Jet Fuel Valuation and Impact on other Fuel Products

Area%	Upgraded Bio-oil	
	Non-cat	Catalytic PO
Paraffinic	28.4%	14.6%
Olefinic	2.2%	2.4%
Cyclic HC	50.6%	50.6%
Hydroaromatic	2.7%	7.4%
Aromatic	15.8%	25.0%
PAH	0%	0%



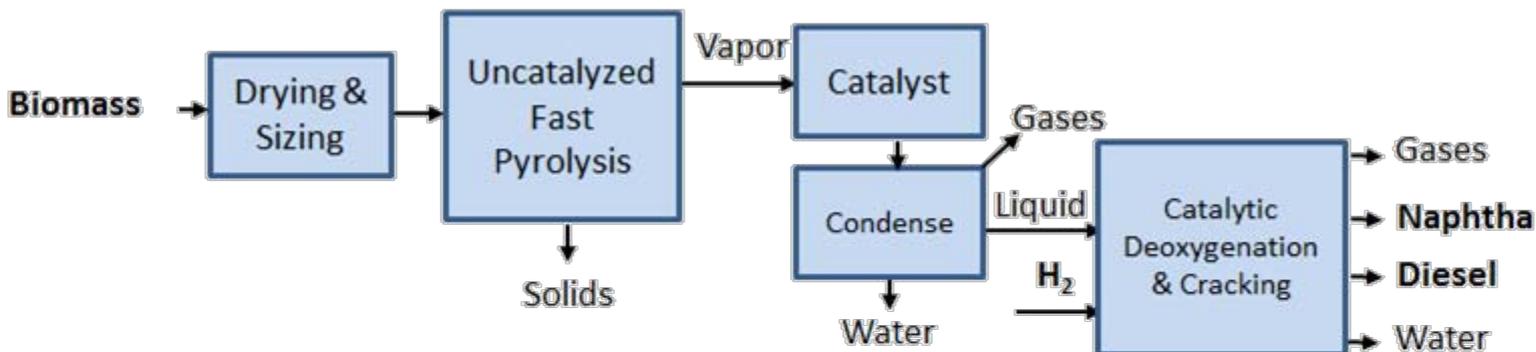
## Improve hydrocarbon quality for aviation use

- If cyclic-rich portion will be used as fuel, need to initiate fuel qualification activities
- Residual oxygen-containing molecules are rich in phenolics that boil in the jet range
- Add catalyst step for ring opening (rather than just hydrocracking)
- All while reducing hydrogen use, overall pressure and catalyst costs

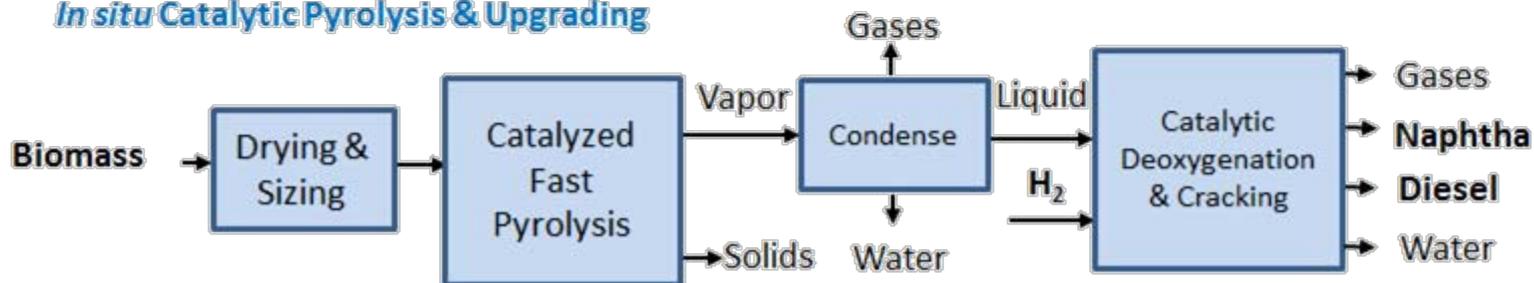
Jet fuel is a mid cut. Removing it may devalue both the gasoline and diesel fractions

# Catalytic Variants to Liquefaction Routes

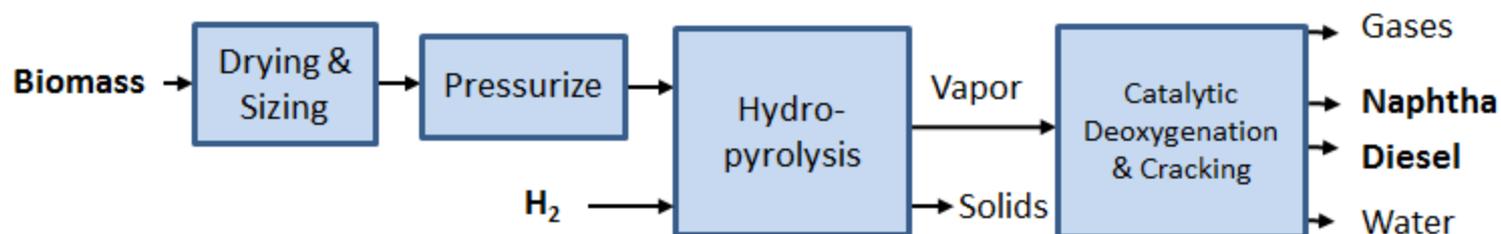
## Ex situ Catalytic Pyrolysis & Upgrading



## In situ Catalytic Pyrolysis & Upgrading



## Hydropyrolysis and Upgrading



Catalyst

- Metals
- Amount
- Attrition

Fuel

- Yield
- Quality (benzene)

System

- Complexity
- pressure

# Direct Liquefaction Routes

	Uncatalyzed Fast Pyrolysis and liquid phase upgrading	In-situ vapor phase catalytic pyrolysis	Ex-situ vapor phase catalytic pyrolysis	Hydropyrolysis with vapor phase upgrading	Hydrothermal liquefaction and upgrading
<b>Feedstock requirements</b>	2 - 6 mm	?	2 - 6 mm	?	?
<b>Bio-oil Production</b>	Single reactor - atmospheric  High CW usage required by rapid quench system & no heat recovery	Single reactor - atmospheric  Possible heat recovery and reduced CW demand	Two reactors - atmospheric  Possible heat recovery and reduced CW demand	Two reactors - ~300 psi Good heat recovery possible and reduced CW demand. <b>Catalyst maintenance not known, nor is method of lighting off first reactor</b>	Single reactor ~3000 psi.  <b>Issues with feeding a high pressure slurry.</b>
<b>Intermediate Bio-oil quality</b>	~50% oxygen plus associated water.  <b>More difficult to upgrade, little control over oxygen content</b>	Lower oxygen content in product, likely easier to upgrade	Lower oxygen content, likely easier to upgrade. Two reactors allow more control over gas/liquid/solid, possible lower catalyst inventory than in-situ	Hydrocarbon product	Lower oxygen content in product, likely easier to upgrade. Some ability to affect oxygen content.
<b>Upgrading to hydrocarbon Capital</b>	<b>At least two upgrading reactors in series. Reactors see 100% of the produced water, plus feedstock moisture Feed preheat to first reactor may be difficult</b>	Potentially a single, smaller upgrading reactor Reactors see small fraction of produced water	Potentially a single, smaller upgrading reactor Reactors see small fraction of produced water	not needed	Potentially a single, smaller upgrading reactor Reactors see small fraction of produced water
<b>Upgrading catalyst life</b>	<b>Still short</b>	Potentially longer, depends upon degree of vapor upgrading	Potentially longer, depends upon degree of vapor upgrading	not an issue	Potentially longer, depends upon degree of vapor upgrading
<b>Hydrogen Production</b>	<b>offgas conditioning needed prior to use at H2 plant?</b>	<b>offgas conditioning needed prior to use at H2 plant?</b>	<b>offgas conditioning needed prior to use at H2 plant?</b>	<b>offgas conditioning needed prior to use at H2 plant?</b>	<b>offgas conditioning needed prior to use at H2 plant?</b>
<b>Maximum Hydrocarbon Yield &amp; quality</b>	TBD: Highest from analysis so far, potential to make equal amounts of gasoline and diesel range material, <b>high distillate aromatic content</b>	<b>TBD: Lower than conventional pyrolysis and upgrading so far, high distillate aromatic content</b>	<b>TBD: Lower than conventional pyrolysis and upgrading so far, high distillate aromatic content</b>	TBD: Similar to conventional pyrolysis so far. High distillate aromatic content <b>IH2 makes 2-3.5 times as much gasoline material as diesel</b>	TBD: Similar to conventional pyrolysis so far. <b>High distillate aromatic content</b>
<b>Waste water treatment</b>	No wastewater from fast pyrolysis. Wastewater from upgrading to hydrocarbons very low in organics	<b>WW could have high concentration of dissolved organics</b>	<b>WW could have high concentration of dissolved organics</b>	WW very low in organics (assuming <1% oxygen remains in bio-oil)	<b>WW have high concentration of dissolved organics</b>
<b>Capital cost uncertainties</b>	<b>Upgrading reactors</b>	<b>CPY &amp; upgrading reactors, WWT</b>	<b>VPU &amp; upgrading reactors, WWT</b>	<b>HYP &amp; VPU reactors</b>	<b>HTL reactor, WWT</b>
<b>Distributed processing flexibility</b>	Yes, can uncouple raw oil production from upgrading and hydrogen generation, no front end WWT needed	Yes, can uncouple raw oil production from upgrading and hydrogen generation, <b>but front end includes WWT</b>	Yes, can uncouple raw oil production from upgrading and hydrogen generation, <b>but front end includes WWT</b>	<b>Limited, cannot uncouple oil production and hydrogen production; can possibly uncouple VPU</b>	Yes, can uncouple raw oil production from upgrading and hydrogen generation, <b>but front end is expensive &amp; includes WWT</b>

**A techno-economic model for fast pyrolysis of biomass to gasoline and diesel has been developed**

**The predicted, n<sup>th</sup>-plant Minimum Fuel Selling Price for 2017 has increased from \$2.04/gal from work in 2009 to \$2.32/gal (2007\$)**

**Contributors to the increase in MFSP:**

- Increased grower payment contribution to feedstock cost to stimulate volumes

**Enhancements made to the model**

- Increased integration of feedstock handling and pyrolysis
- Establishment of 2017 feedstock cost (formerly only went to 2012)

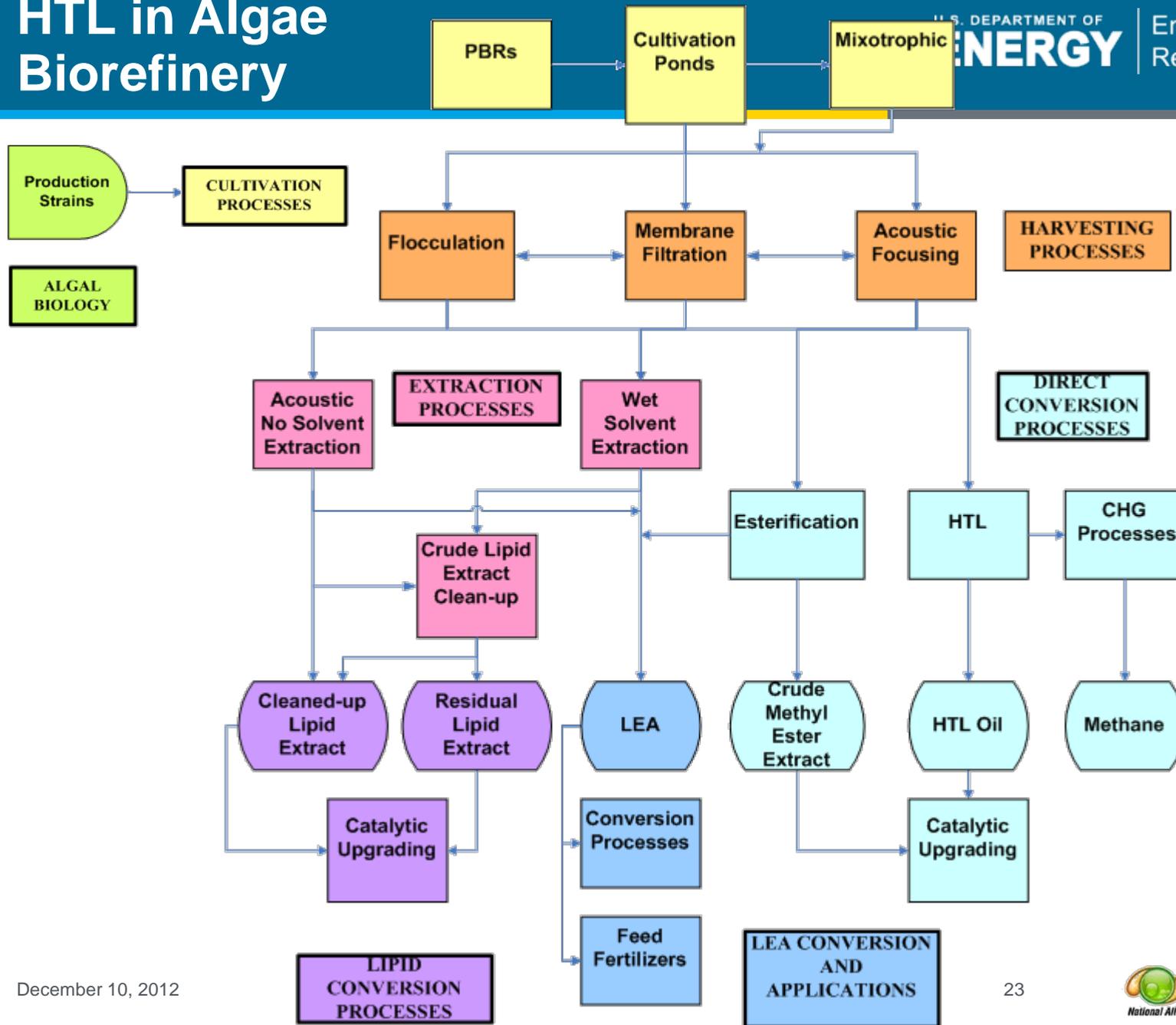
**Model drives targeted research to focus on the technical barriers to enable meeting the 2017 economic targets**

- Increased lifetimes of catalysts (conditioning and fuel synthesis)
- Biocrude quality (oxygen content, fundamental understanding and corrosion)
- Improved fuel yields

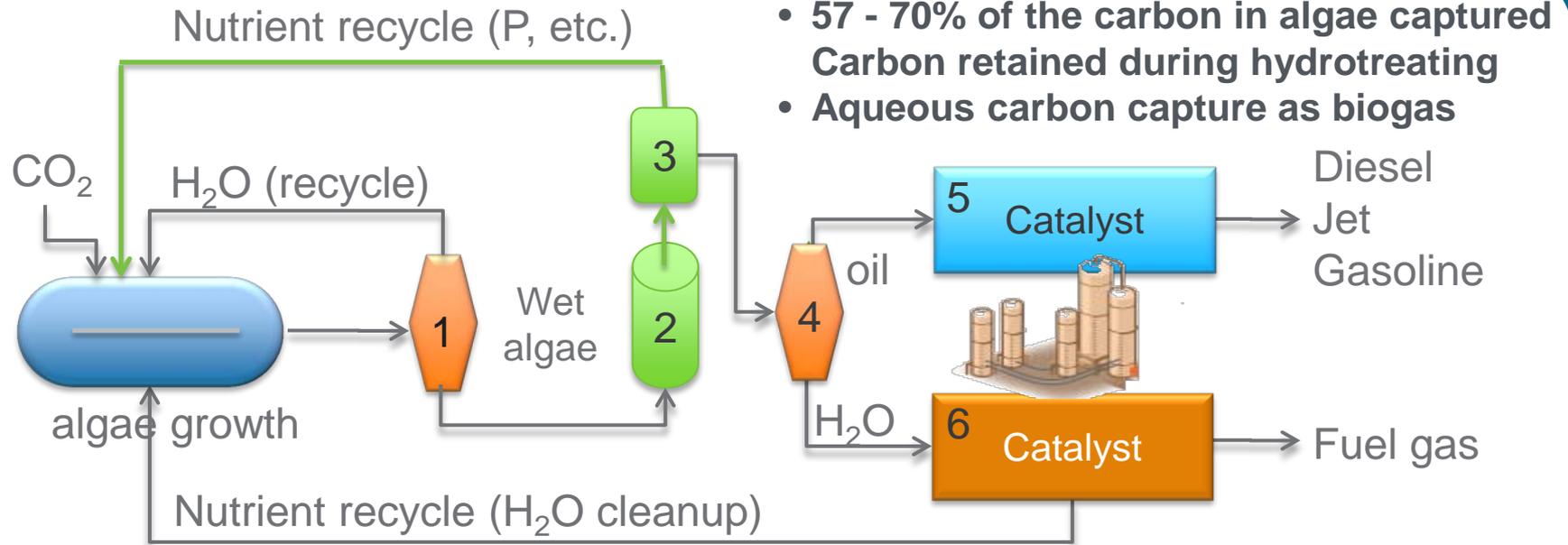
**Scheduled in depth revisit of techno-economics of biomass direct liquefaction routes as new knowledge is obtained in FY2012 leading to new detailed techno-economic analyses in FY2013**

# Questions

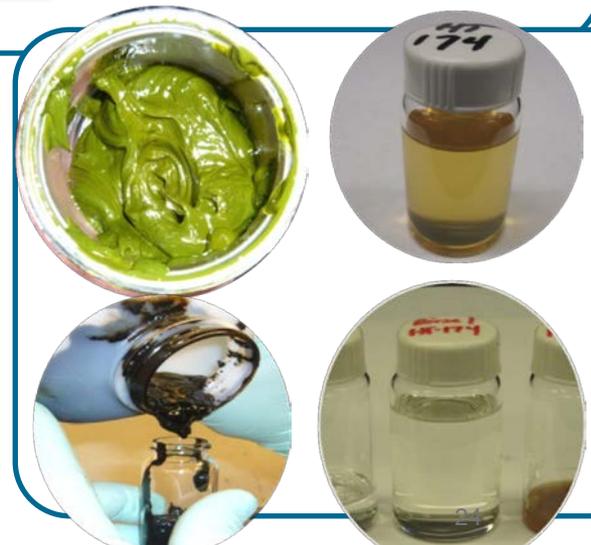
# HTL in Algae Biorefinery



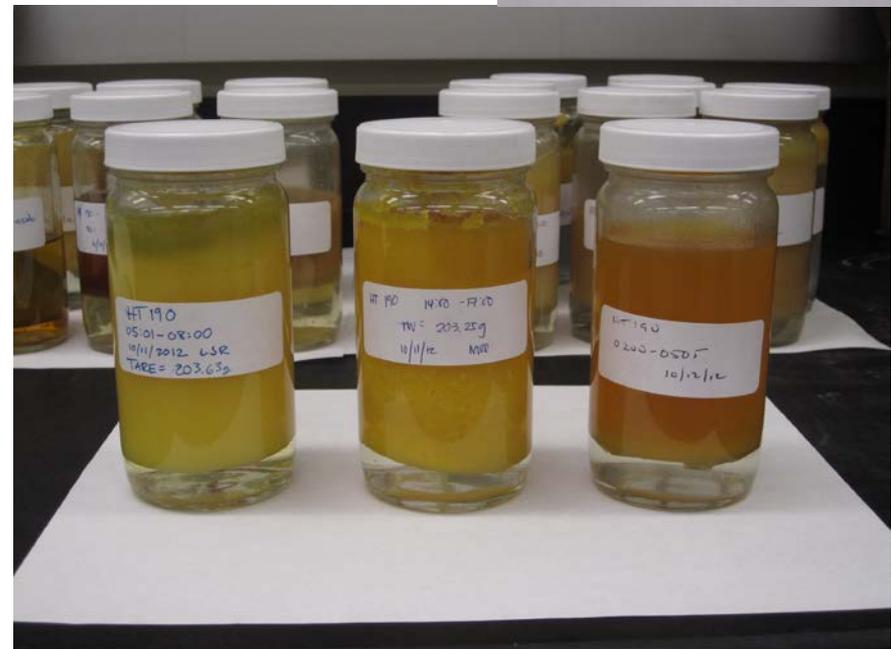
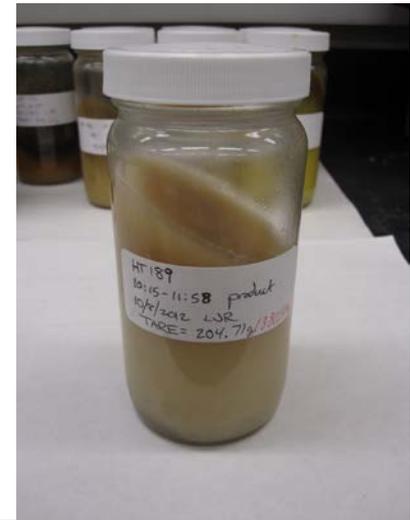
# Hydrothermal Liquefaction of Algae



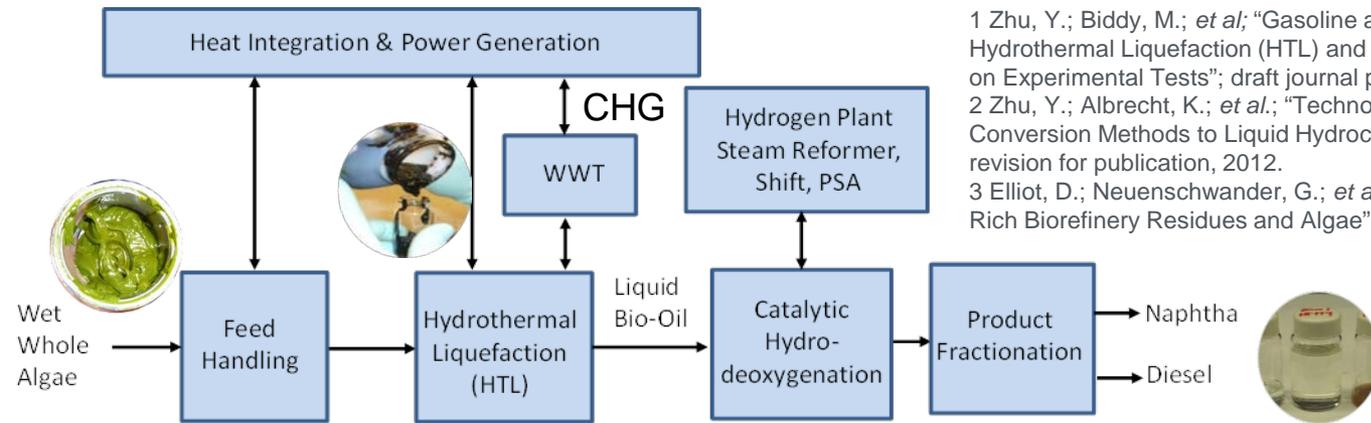
1. algae de-watered from 0.6 g/l to 100 g/L
2. hydrothermal liquefaction
3. solid precipitate separation (phosphate capture)
4. oil/water phase separate
5. oil hydrotreater to produce hydrocarbons—diesel/gasoline)
6. aqueous phase carbon is catalytically converted to fuel gas and nutrients recycled (N, K, some CO<sub>2</sub>, etc)



- ▶ Deoxygenated to long chain normal paraffin (waxes)
  - Additional “Refinery” processing
    - Isomerization
    - Cracking
- ▶ Commercial technology available for “purified” plant oils but development is continuing for algae
  
- ▶ HTL direct conversion route for algae examined
- ▶ Crude bio-oil upgraded to normal paraffins



# Whole Algae Hydrothermal Liquefaction and Upgrading



1 Zhu, Y.; Biddy, M.; *et al.*; "Gasoline and Diesel Production from Woody Biomass via Hydrothermal Liquefaction (HTL) and Upgrading – A Techno-Economic Analysis based on Experimental Tests"; draft journal publication currently in NABC review, 2012.

2 Zhu, Y.; Albrecht, K.; *et al.*; "Techno-economic Analysis of Two Different Microalgae Conversion Methods to Liquid Hydrocarbon Fuels"; NAABB internal report, currently in revision for publication, 2012.

3 Elliot, D.; Neuenschwander, G.; *et al.*; "Catalytic Hydrothermal Gasification of Lignin-Rich Biorefinery Residues and Algae"; Report No. PNNL-18944., October 2009

**Feed handling:** Wet whole algal biomass (~ 20% solids) is pumped to the HTL reactor pressure of ~3000 psia.<sup>1</sup>

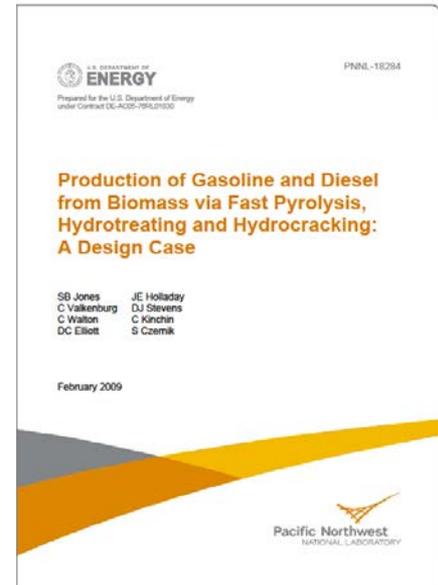
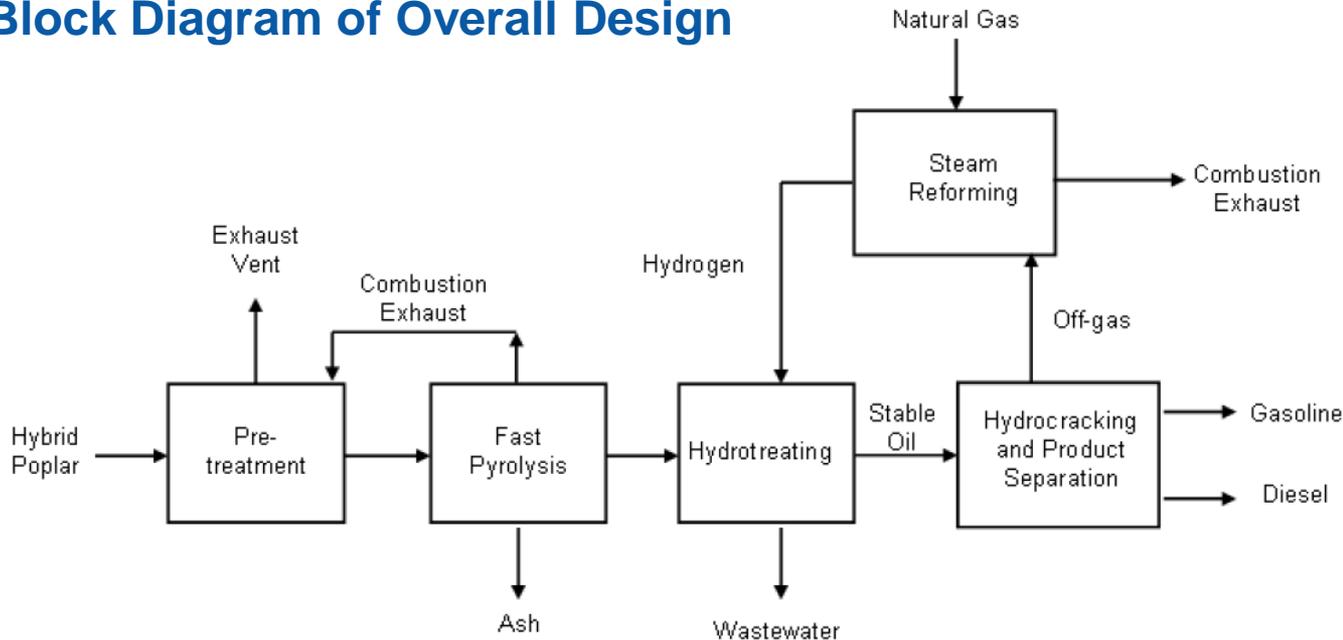
**Hydrothermal Liquefaction (HTL):** Whole wet algae at a 20 wt% solids content is hydrothermally treated in subcritical water (2000-3000 psi and 300-350 °C) and 4 v/v/h liquid hourly space velocity (LHSV).<sup>2</sup>

**Waste Water Treatment:** Waste water from the HTL process (and upgrading if it is co-located) is sent to a catalytic hydrogasification (CHG) process to convert all organics to CO<sub>2</sub> and CH<sub>4</sub>. For CHG, the wastewater stream is pumped to ~3000 psia, and preheated to 370 °C, then fed to a fixed bed catalytic reactor.<sup>3</sup>

**Catalytic Hydrodeoxygenation (HDO):** The organic phase from HTL processing is catalytically hydrotreated to remove oxygen and most of the nitrogen. Bench scale experiments using HTL oil is were run at 407 °C and ~2000 psia to convert the oil to hydrocarbon, water and gas over a two-stage fixed bed reactor system. The overall LHSV is 0.16 v/v/h.<sup>2</sup>

- 2000 dry metric tons/day of hybrid poplar wood chips input
- Hybrid poplar arrives at 50 wt% moisture and is dried to 7 wt% moisture
- Feedstock particle size 2-6 mm
- Pyrolysis at approximately 500 °C
- Dual stage hydrotreating (approximately 240 and 370 °C)
- Hydrogen production via steam reforming of off-gas and supplemental natural gas
- Hydrotreating of fast pyrolysis oil to a hydrocarbon blend stock with < 2% oxygen
- Hydrocracking of the heavy portion of the hydrocarbon blend stock is required
- Plant is assumed to be established (n<sup>th</sup>) plant design, rather than first of its kind
- 10% Internal Rate of Return
- 20 year plant life
- 2007 constant dollars
- 15% equipment contingency added to hydrotreating sections
- 35% equipment contingency added to the pyrolysis units
- Stream factor 90%
- Start up time 6 months
  
- A stand alone plant model and a plant co-locating with an existing refinery model were developed
- Process model built in CHEMCAD<sup>©</sup>
- Capital costs from literature and/or Aspen Economic Analyzer<sup>©</sup>

## Block Diagram of Overall Design



- Published 2009
- Reviewers: Biomass Program, NREL, Conoco-Phillips, Ensyn, UOP, VTT, Iowa State University
- Proposed diesel and gasoline fuel production price: \$2.04/gallon (n<sup>th</sup> plant, 2007\$, stand alone plant, feedstock cost of \$50.70/dry ton)
- Consistent with assumptions in the 2007 technical report *Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass* NREL/TP-510-41168