Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Catalytic Upgrading of Intermediate Products to Hydrocarbon Fuels

Karl Albrecht, Andy Schmidt, Yunhua Zhu, Richard Hallen
With Special Recognition to Doug Elliott for initiating bio-oil upgrading in the 80's

Presented by Richard Hallen

Chemical and Biological Process Development Group
Bioproducts, Sciences, and Engineering Laboratory
Pacific Northwest National Laboratory, Richland, WA
richard.hallen@pnnl.gov

Renewable Fuel Terminology

Drop-In Fuel => Infrastructure Compatible Fuel => Hydrocarbon Fuel

Ethanol is an approved fuel but not infrastructure compatible

Biodiesel is an approved fuel but not infrastructure compatible

HRJ/HEFA is an approved fuel and infrastructure compatible

Drop-In Fuel => An alternative fuel that meets all the requirements of current fossil fuel specifications and does not require any modification to equipment or infrastructure. (http://renewablejetfuels.org)

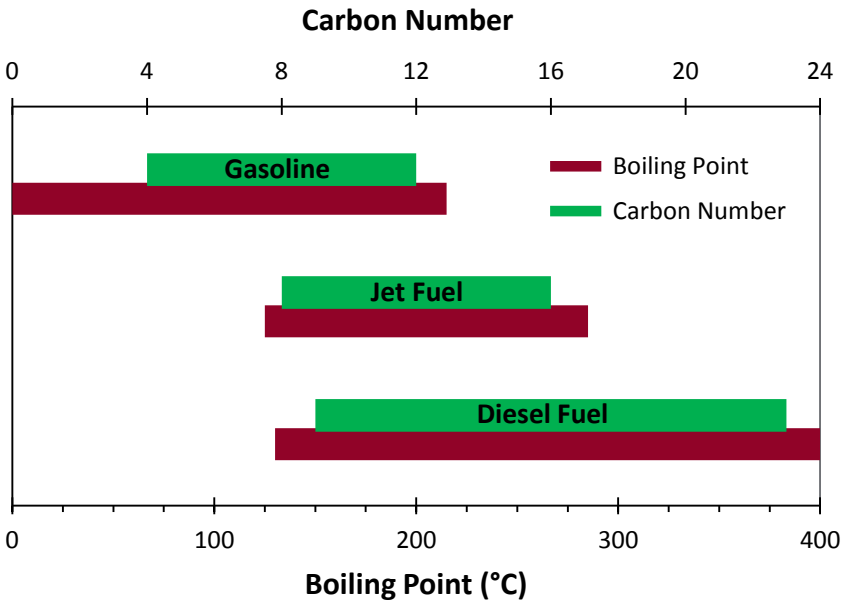
Background on Intermediate Products

- Direct Conversion Processes
  - Pyrolysis
  - Hydrothermal liquefaction
- Indirect Conversion Processes
  - Gasification
    - Syngas to alcohols
      - Thermochemical
      - Biological
    - Syngas to FT liquids
  - Pretreatment for deconstruction
    - Thermochemical
    - Biological
- Plant Derived Lipids
  - Terrestrial
  - Marine/Aquatic

Characteristics of Bio-Products

- High oxygen content
- Heteroatom contamination
  - N, P, S
- Ash
- Wrong carbon chain length
- Wrong chemical properties
- Wrong physical properties
- Regulatory limits/specifications

Fuel Composition and Properties



- Gasoline = Octane Number
- Diesel = Cetane Number
- Jet = Energy Density

- Vapor Pressure
- Flash Point
- Freeze Point
- Distillation Range
- Many Others

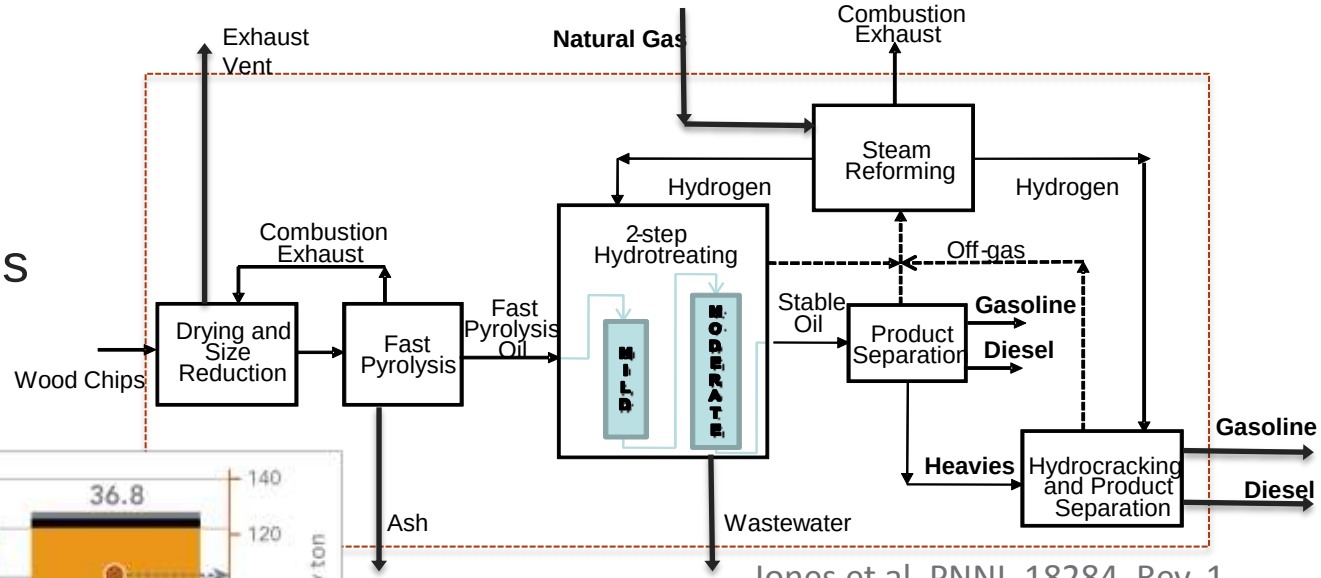
Composition of "average" jet fuel and a world average

Class	JP-8POSF-3773	World Survey Average
Paraffins (*n*- and *i*-)	57.2	58.8
Cycloparaffins	17.4	10.9
Dicycloparaffins	6.1	9.3
Tricycloparaffins	0.6	1.1
Alkylbenzenes	13.5	13.4
Indans/tetralins	3.4	4.9
Indenes	<0.2	<0.2
Naphthalene	<0.2	0.13
Naphthalenes	1.7	1.55
Acenaphthenes	<0.2	<0.2
Acenaphthylenes	<0.2	<0.2
Tricyclo aromatics	<0.2	<0.2

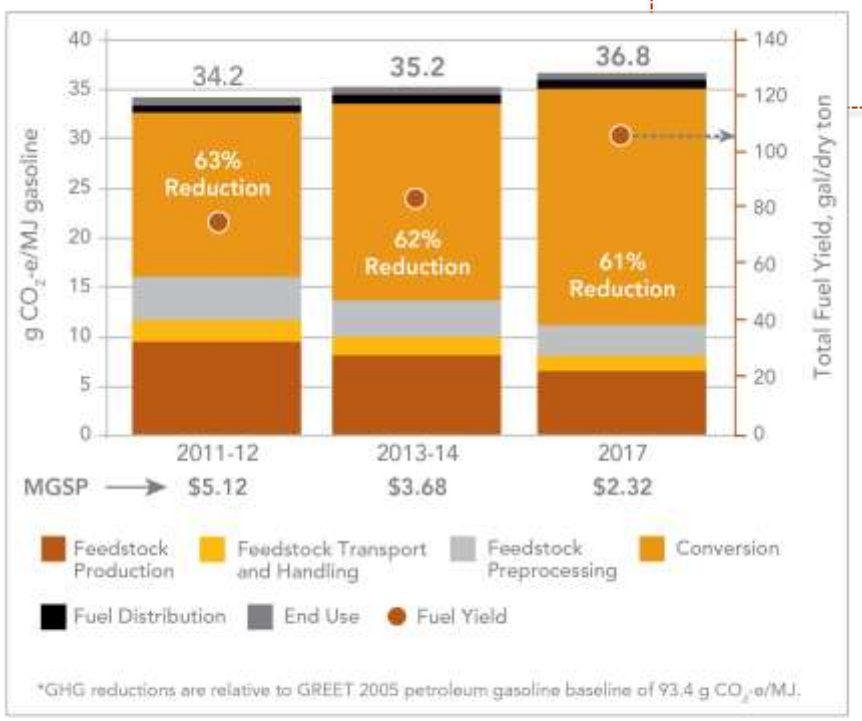
Source: Natelson et al., "Experimental investigation of surrogates for jet and diesel fuels" Fuel 87 (2008) 2339–2342; A supplement to Chevron's *Aviation Fuels Technical Review*

Detailed Pathway Analyses for Pyrolysis

- Assessment recently reported for the upgrading of pyrolysis bio-oils to drop-in fuels



Jones et al, PNNL-18284, Rev. 1



Snowden-Swan et al, PNNL-SA-89122

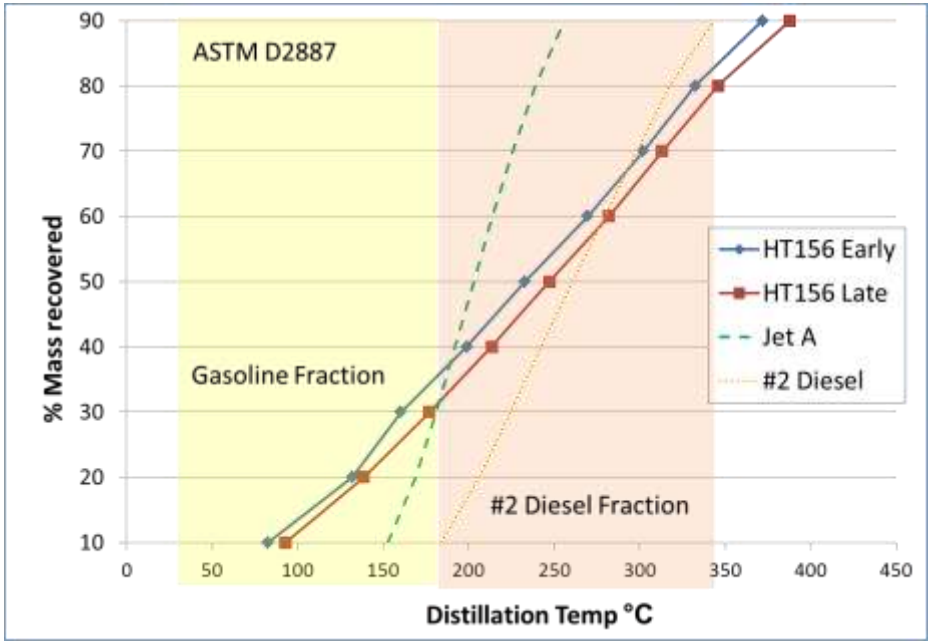
- Detailed assessment needed for many of the other routes

Hydrotreater Key for Upgrading

- Doug Elliott initiated bio-oil upgrading in the 80's
- Current bench-scale hydrotreater based on 20 years of research and development
- Adapted for the challenges of upgrading bio-oils
- Operational flexibility
- ~110 hydrotreater runs from 2003 to 2012
- Pilot scale system under construction and will be installed and operational at PNNL in 2013

Upgraded Pyrolysis Product

- Pyrolysis bio-oil upgraded at PNNL via 2-stage hydrotreater
- Product distribution by distillation range
  - ~32% Gasoline
  - ~42% Diesel
  - ~30% Jet (overlap)



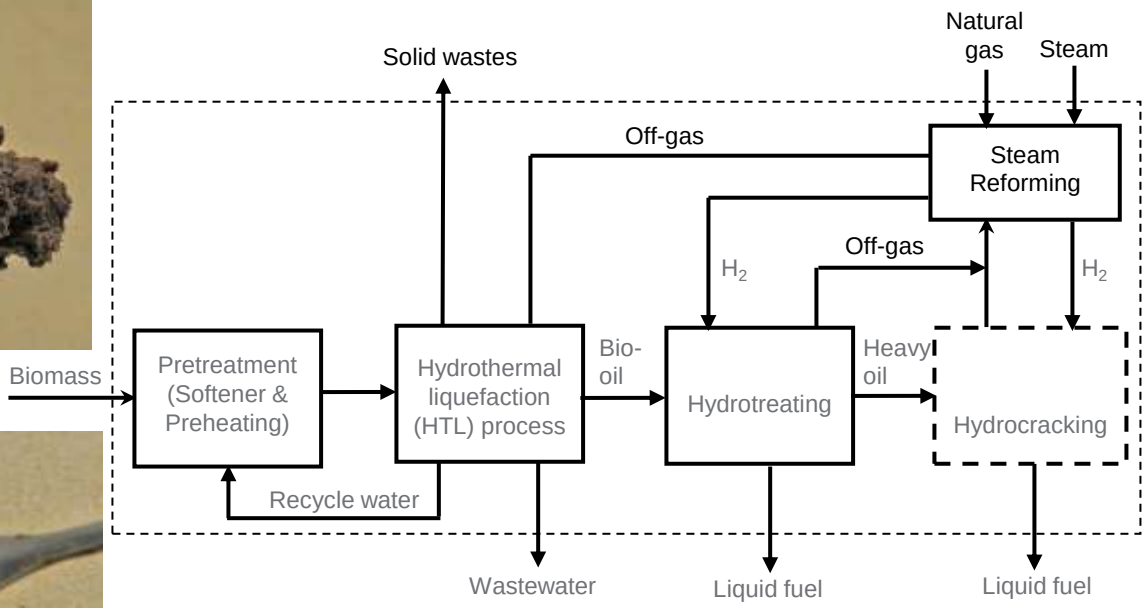
- 100% renewable turbine fuel demonstrated through collaboration with UOP, Boeing, and PNNL

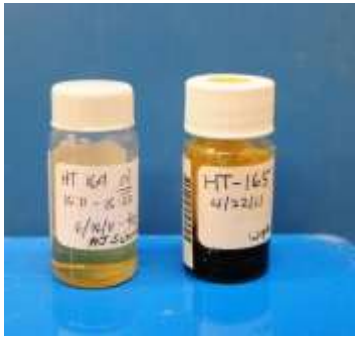
The hydroplane ran on 98% Bio-SPK and 2% renewable aromatics

Hydrothermal Liquefaction Route

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- Direct liquefaction route for lignocellulosic feedstocks
- NABC pathway to infrastructure compatible renewable fuels





- Assessment for refinery integration underway

NABC National Advanced Biofuels Consortium

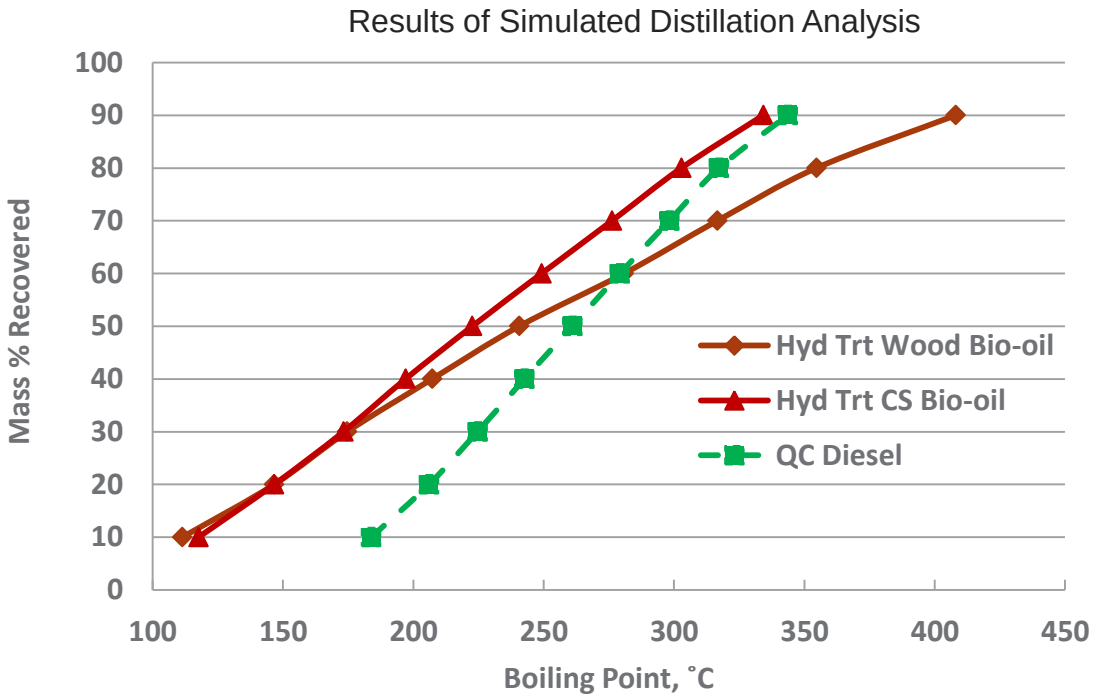
This work was supported by the National Advanced Biofuels Consortium, which is funded by the U.S. Department of Energy's Office of Biomass Program with funds from the American Recovery and Reinvestment Act.

Upgraded HTL Product

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

- HTL bio-oils upgraded with hydrotreater similarly to pyrolysis bio-oils
- HTL bio-oils are more stable, lower in oxygen, but can be high viscosity

- Wood (FPR pine) and corn stover HTL bio-oils upgraded
- Hydrocarbon distillate range
  - ~30% Gasoline
  - ~50% Diesel
  - ~30% Jet (overlap)

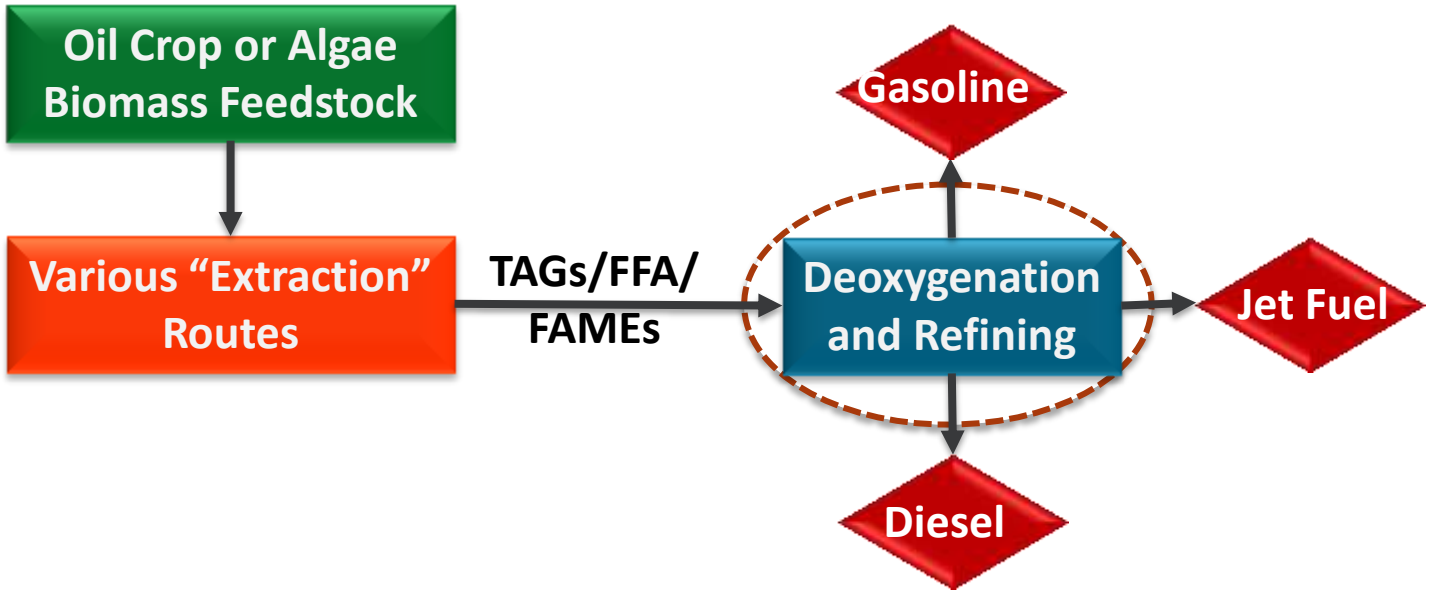


NABC National Advanced Biofuels Consortium

This work was supported by the National Advanced Biofuels Consortium, which is funded by the U.S. Department of Energy's Office of Biomass Program with funds from the American Recovery and Reinvestment Act.

Plant Derived Lipids

- Plant and Algae derived lipid products “close” to fuels
- Carboxylate oxygen needs to be removed
  - Hydrodeoxygenation
  - Decarbonylation
  - Decarboxylation
  - Other routes, thermal cracking
- High yield of long chain normal paraffin (high cetane number)



Algae-Derived Lipids

- 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

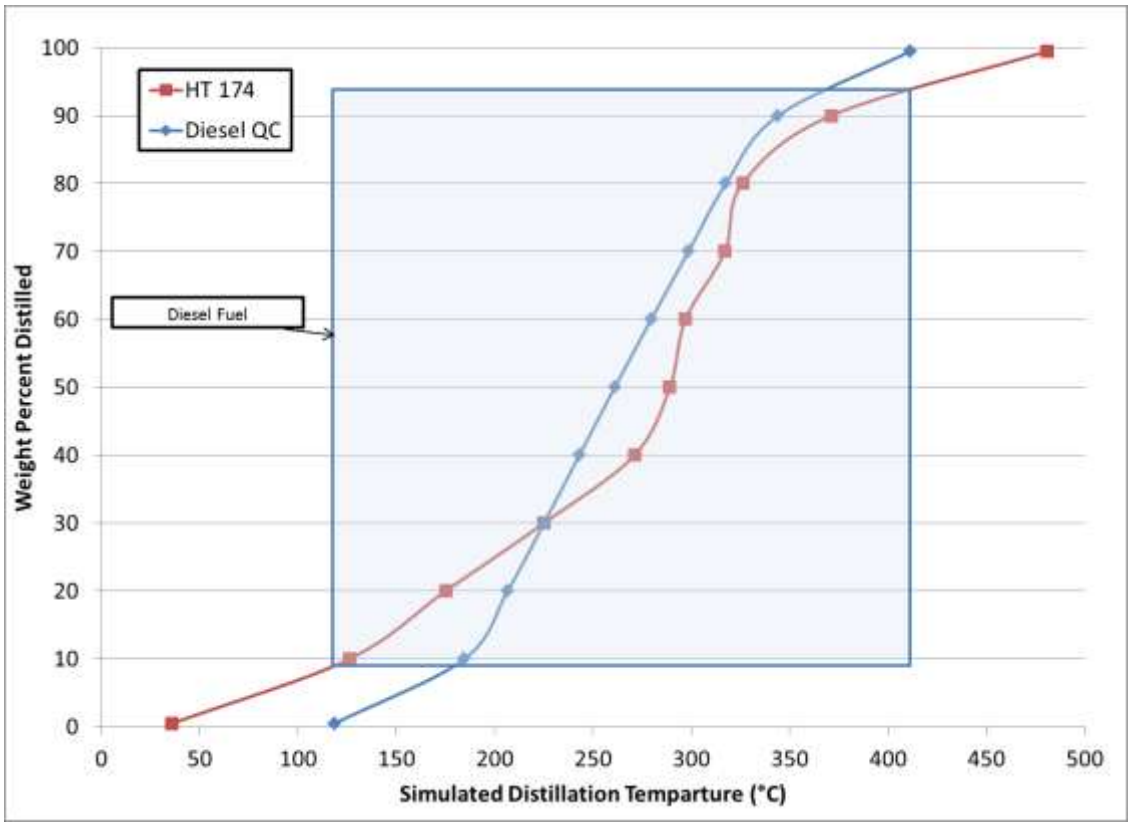
- HTL direct conversion route for algae examined
- Crude bio-oil upgraded to normal paraffins

NAABB
National Alliance For Advanced Biofuels and Bio-products

Algae Derived Lipids

- HTL “extracts” all lipids and converts non-lipid biomass to bio-oil
- HTL algae bio-oils relatively low in oxygen (~5%) but high in nitrogen (~5%)
- With hydrotreating and mild hydrocracking, fuel grade hydrocarbons are produced

- Fractionate, or
- Integrate in refinery



Acknowledgment

- Upgrading HTL bio-oils from lignocellulosic biomass work was supported by the National Advanced Biofuels Consortium, funded by the U.S. Department of Energy's Office of Biomass Program with funds from the American Recovery and Reinvestment Act.

- Upgrading of algae derived bio-oils was supported by the National Alliance for Advanced Biofuels and Bio-Products, funded by the US Department of Energy under Contract DE-EE0003046.

NABC National Advanced Biofuels Consortium

NAABB National Alliance For Advanced Biofuels and Bio-products

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy