Introduction to ORNL Bioenergy Technologies Program

Tim Theiss

Program Manager

ORNL Bioenergy Technologies Program

Presented by Brian West

Work supported by

DOE Bioenergy Technologies Office

ORNL Facilities and Expertise Supporting BETO

- Feedstock, Supply & Logistics
- Materials compatibility
- Bioderived materials for 3-D printing
- Conversion
- End Use (Engine and Vehicle R&D)

A BILLION DRY TONS OF SUSTAINABLE BIOMASS

HAS THE POTENTIAL TO PRODUCE

1.1 MILLION Direct Jobs
and keeps about
$250 BILLION
in the U.S.
(direct contribution and inflation adjusted)

85 BILLION* kWh of electricity to power **6 MILLION** households. Plus **1050 TRILLION BTUs** of thermal energy.

50 BILLION gallons of biofuels displacing almost **25%** of all transportation fuels.

50 BILLION POUNDS of biobased chemicals and bio-products, replacing a significant portion of the chemical market.

400 MILLION TONS of CO_2e reductions every year.

STEPS TO BUILDING THE BIOECONOMY

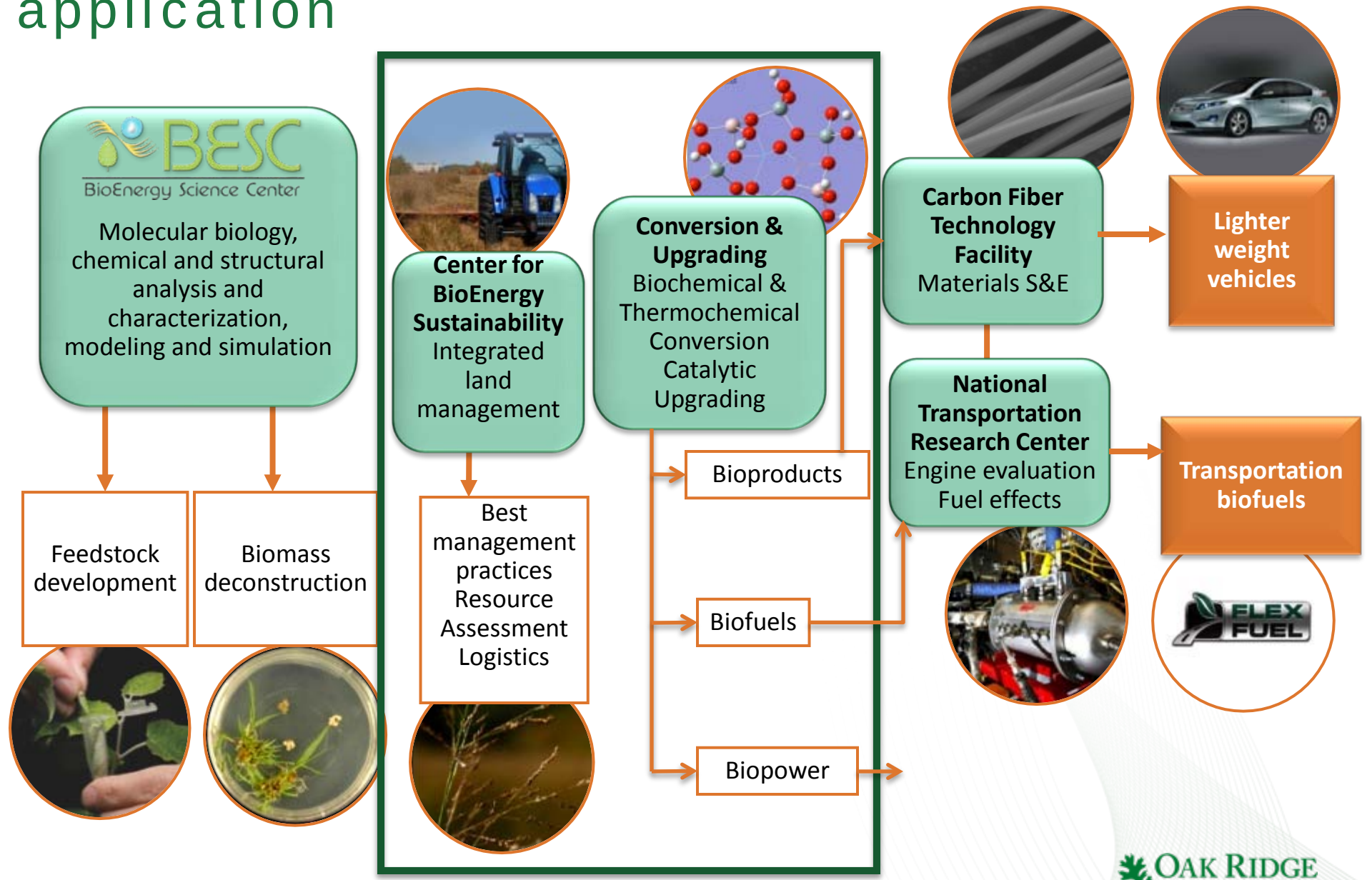
1. Accelerate research & technology development
2. Develop production, conversion and distribution infrastructure
3. Deploy technology
4. Create markets and delivery systems

Projections based on:

- 2016 Billion Ton Study Report (Forthcoming)
- EIA 2015 AEO
- 2015 USDA Long-Term Forecast
- Various data sources

* Includes 27 billion kWh and 90 TBtu from livestock anaerobic digestion

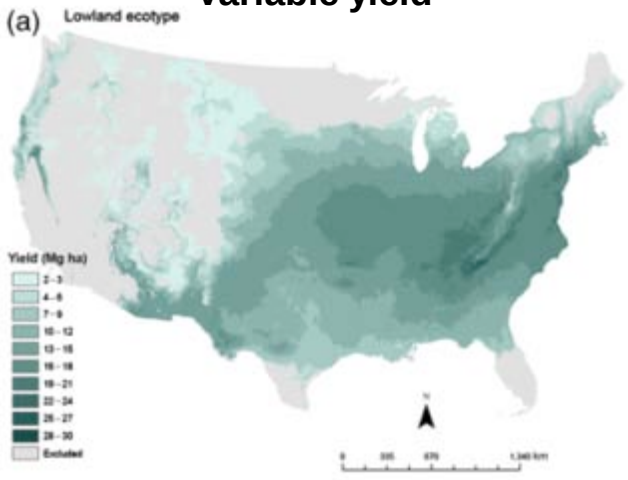
Bioenergy spans from basic sciences to application



Biomass is a challenging feedstock for industrial processes

Variable quality

Variable yield



Jager et al. (2010)

Flammable

Photo from: http://nevadaiowajournal.com)

Equipment availability and performance

Spoilage

Seasonal availability

Photo from University of Tennessee

Feedstock type and bale shape significantly impact fire growth

Stover rectangular bales

Stover round bales

Switchgrass rectangular bales

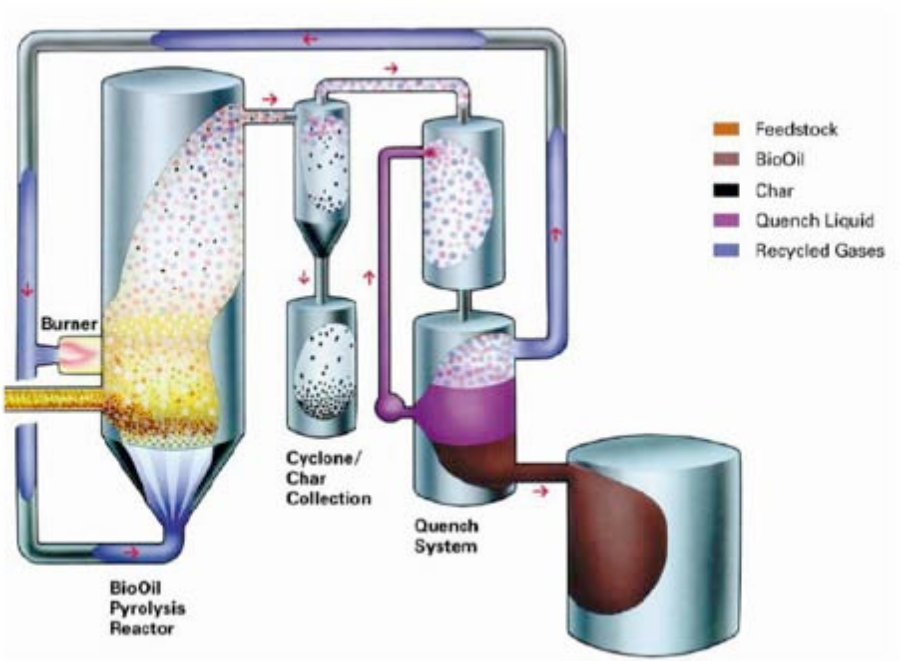
Observations

- Switchgrass burns much better than stover
- Lower density of round bales enabled fire more access to O_2
- After netwrap was burned away, outer layers of round bales fell away exposing fresh material to fire

courtesy of Dan Steppan, UL; Photos courtesy of Bob Davidson, Davidson Code Concepts

Fast pyrolysis is an efficient pathway to lignocellulosic liquid fuels

A Fast Pyrolysis Process (Dynamotive)



- Whole biomass
- Temperature: 450 C
- Pressure: 1 atm
- Residence time: 1-2 s
- Atmosphere: inert
- High yield in liquids (bio-oils)
- Inexpensive
- Viable as small scale operation
- Bio-oils are highly acidic

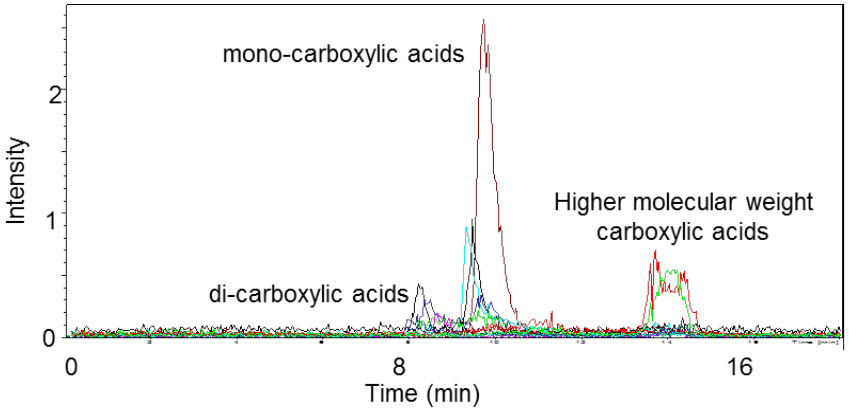
Bio-oil composition	
C (wt%)	40.1
H (wt%)	7.6
O (wt%)	52.1
Moisture (wt%)	23.9

Materials Degradation In Biomass-Derived Oils

- Investigate and determine cause of degradation of materials in biomass liquefaction systems by

- chemically characterizing the corrosive components in the oils
- conducting laboratory corrosion tests with bio-oils
- providing corrosion samples and pipe spool pieces for exposure in operating liquefaction systems
- examining degraded components provided by system operators
- determining the degradation mechanism of samples and components

- Objective is to identify suitable materials so that corrosion does not prevent development of any biomass liquefaction technology



Acid analysis of typical bio-oil

Corrosion samples provided to NREL

Pipe spool piece provided to Iowa State Univ.

ChemCatBio overcoming challenges for catalysis for bioenergy conversion processes

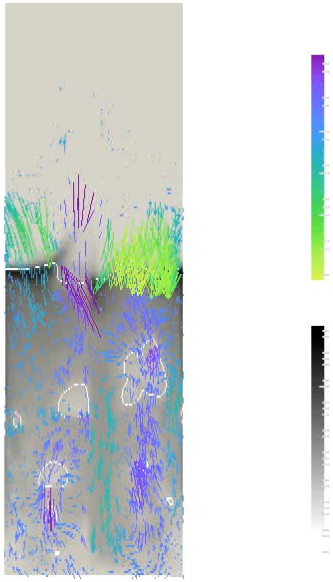
ORNL roles in ChemCatBio include developing innovative catalysts and accelerating progress via modeling and characterization

ChemCatBio
Chemical Catalysis for Bioenergy

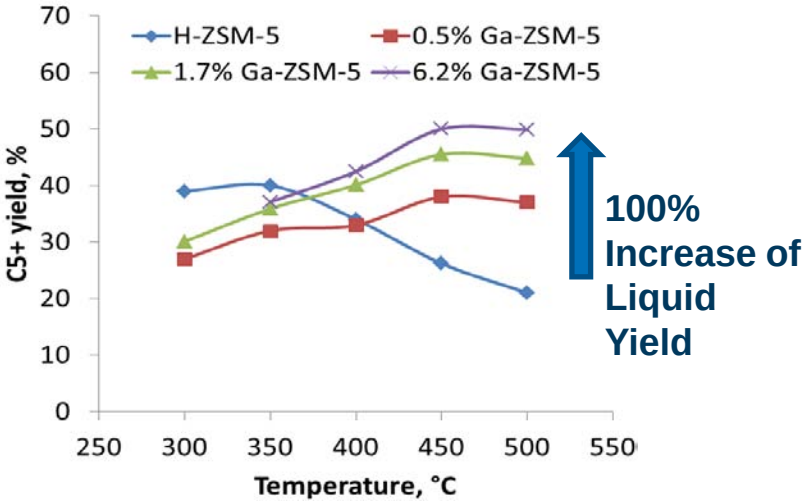
The 5-NL Consortium for Computational Physics and Chemistry (CCPC) is modeling atomic, meso, and process scale conversion

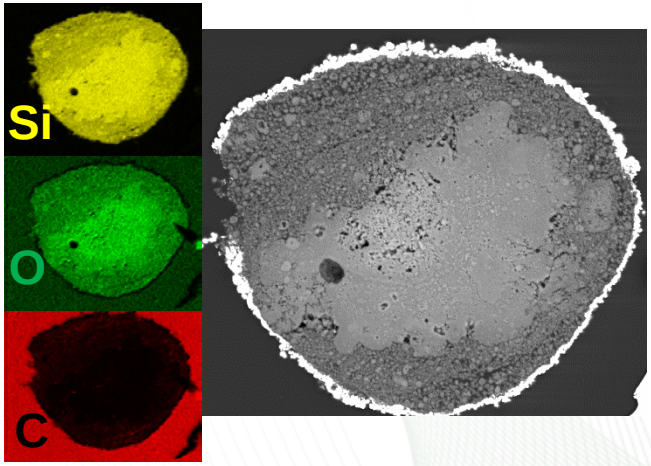
CCPC

www.cpcbiomass.org



Innovative catalysts increasing yield and selectivity for catalytic upgrading





ORNL's advanced material characterization techniques defining catalyst morphology and degradation mechanisms

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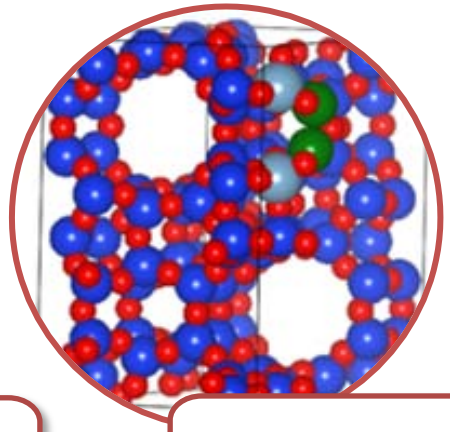
Biofuels development: From basic science to evaluation and commercialization



Enable development of biofuels (ethanol) to enhance conversion of biomass

Zeolite catalyst converts ethanol to hydrocarbon fuel for blending with gasoline

Studies on NTRC engine platform show promising combustion properties

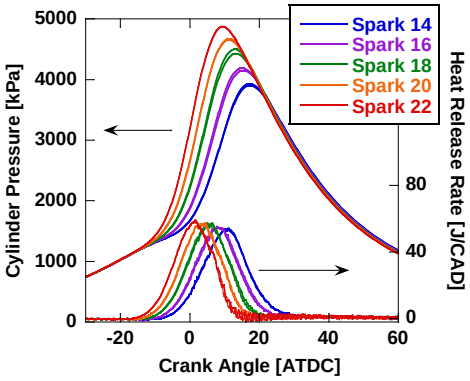
Licensed to Vertimass; Scale up process ongoing with Vertimass and Technip

BER

LDRD/EERE-BETO

Tech Transfer

- ETSD evaluation demonstrated the fuel has a “high efficiency potential” due to its high octane rating
- Vertimass has validated DOE BETO program cost analysis



SCIENTIFIC REPORTS

nature

Narula, Li, Casbeer, Geiger, Debusk, Keller, Buchanan, Davison *Scientific Reports* **5** *Nature,* **350**, (2015)

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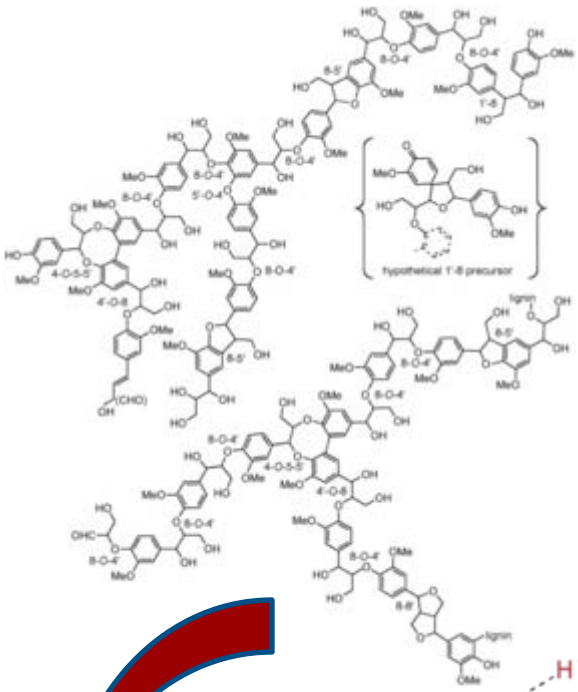
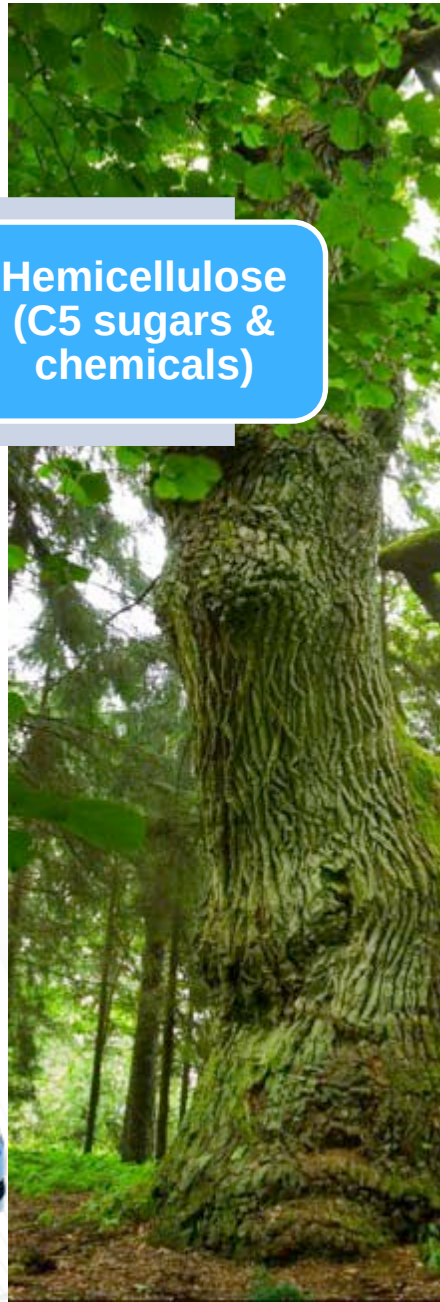
Lignin-Derived High Performance Thermoplastics: Renewable Composites Applications

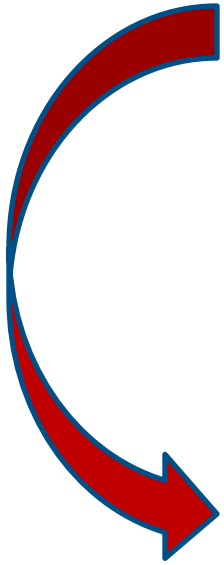


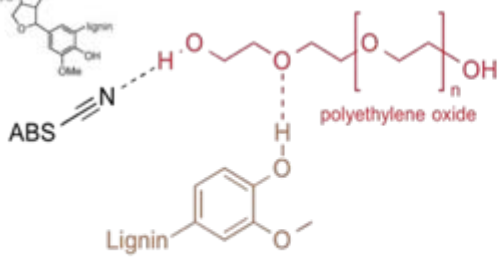
Lignin (residue)

Cellulose (sugar and biofuel)

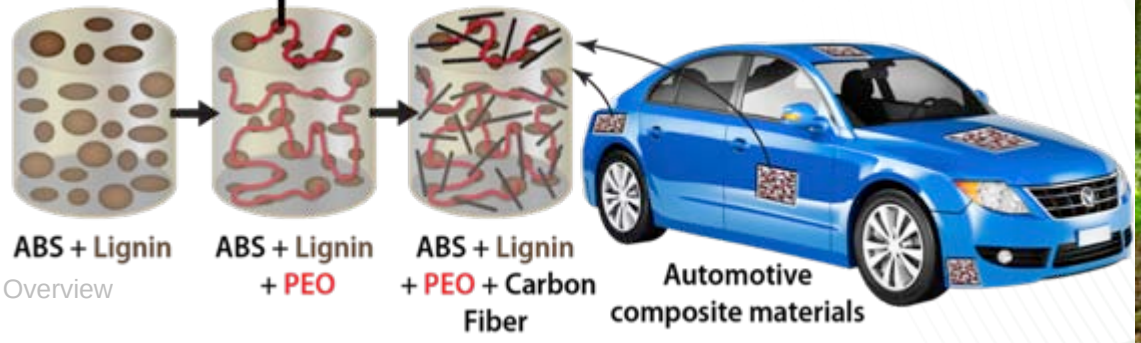
Hemicellulose (C5 sugars & chemicals)







High performance thermoplastics are being made as substitute for ABS, a automotive composite resin



Bio-Derived Materials for Additive Manufacturing *Harvesting, storing, processing, and transporting bio-derived materials for 3D printing*

By integrating basic and early-stage applied energy capabilities, ORNL is leading the way to developing new bio-derived materials for a variety of applications using large-scale additive manufacturing. Have now printed with at least 10 feedstocks, including *Populus* an energy crop.

Advantages

- ✓ Lower cost and environmental impact than petroleum-derived products
- ✓ Rural economic development using local feedstocks
- ✓ Increased pathways for recycling
- ✓ Sustainable manufacturing practices
- ✓ Lightweight and renewable feedstocks
- ✓ Improves economics of biofuel production

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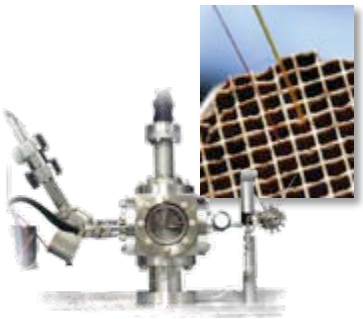
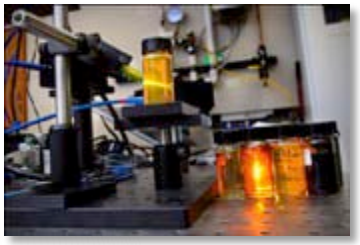
Fuels, Engines, and Emissions Research Center: Extensive laboratories and diverse expertise coupled with BIG SCIENCE resources

- **Propulsion systems and fuel technologies**
  - Seven engine dynamometer cells
  - Vehicle Research Laboratory (VRL)
  - Vehicle Systems Integration (VSI) laboratory
- **Aftertreatment and materials characterization**
  - Wet chemistry and catalyst reactor laboratory
  - Analytical chemistry laboratory
  - Catalyst fundamentals laboratory
- **Biomass-to-fuel catalyst technology development**
  - Pyrolysis upgrading, corrosion compatibility laboratory
- **Diagnostics development laboratory**
- **Simulation and thermodynamics on all scales**





Department of Energy Supported Wide Range of Mid-Level Blends Studies 2007-2012.

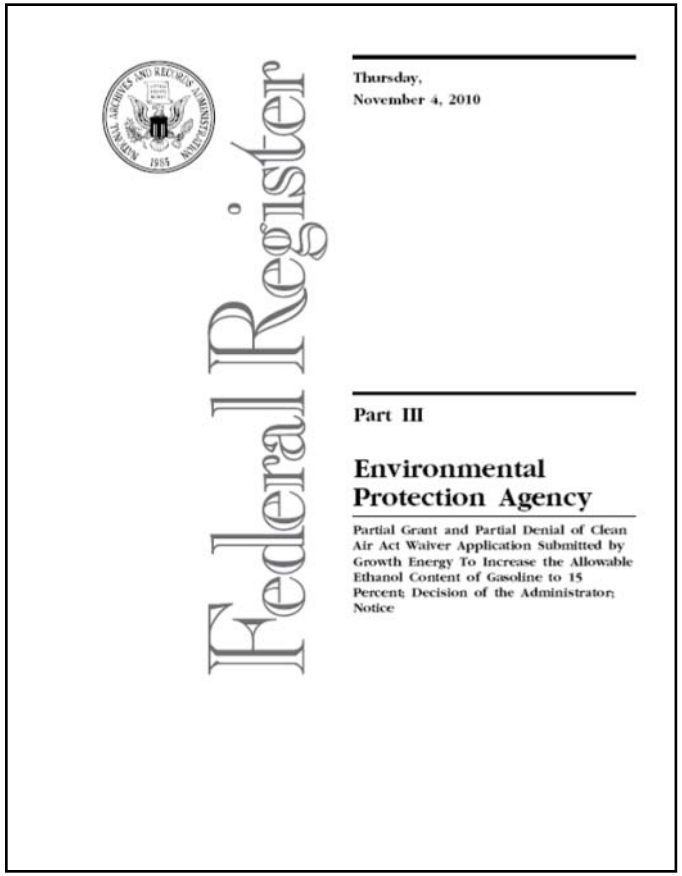
ORNL and NREL led several efforts, worked closely with stakeholders to study:

- **Vehicles, small nonroad engines (SNRE) and other non-automotive engines**
- **Emission control durability**
- **Regulated and unregulated tailpipe emissions**
- **Fuel economy**
- **Materials compatibility**
- **Driveability (or operability in case of non-road engines)**
- **Evaporative emissions**

- **Numerous reports, papers, presentations….**
  - *Full bibliography available*

EPA cited DOE Studies in Partial Waiver Rulings in 2010 & 2011

"…E15 will not cause or contribute to [2001 and newer] motor vehicles exceeding their applicable exhaust emission standards"



Federal Register

Thursday,
November 4, 2010

Part III

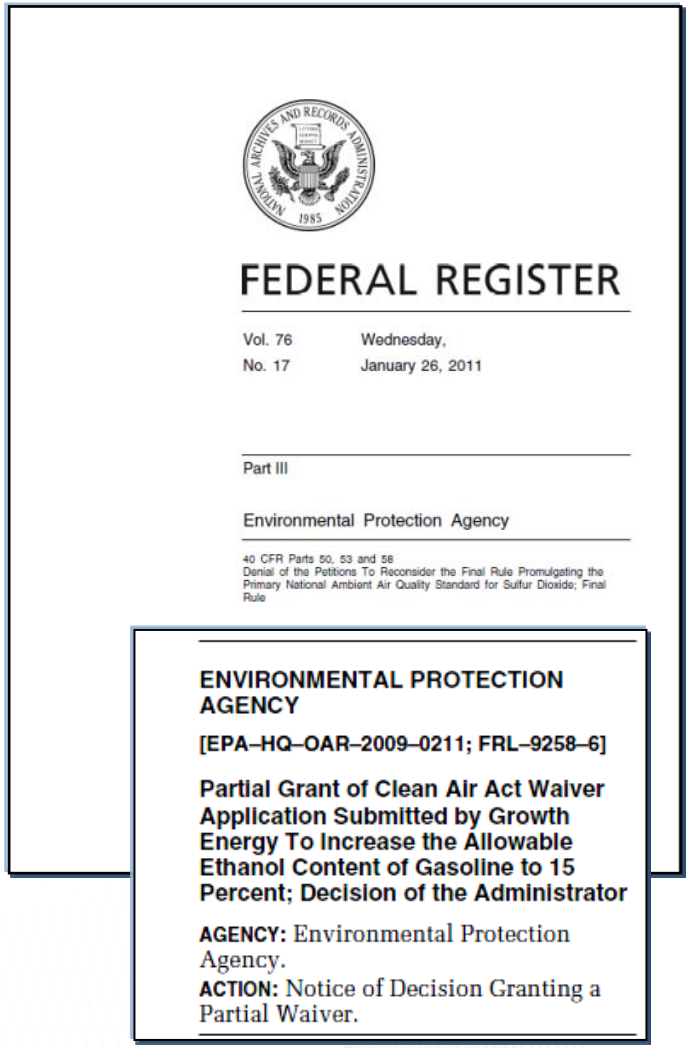
Environmental Protection Agency

Partial Grant and Partial Denial of Clean Air Act Waiver Application Submitted by Growth Energy To Increase the Allowable Ethanol Content of Gasoline to 15 Percent; Decision of the Administrator; Notice

ORNL work also cited in Tier 3 Emissions Rule

ORNL developed a method for calculating NMOG from NMHC during iBlends to more rapidly provide emissions results to EPA staff monitoring the program.

EPA adopted the ORNL method in the Tier 3 rule, allowing manufacturers to compute NMOG rather than requiring speciation of tailpipe emissions measurements (substantial time and cost savings).



FEDERAL REGISTER

Vol. 76 No. 17

Wednesday, January 26, 2011

Part III

Environmental Protection Agency

40 CFR Parts 50, 53 and 58
Denial of the Petitions To Reconsider the Final Rule Promulgating the Primary National Ambient Air Quality Standard for Sulfur Dioxide; Final Rule

ENVIRONMENTAL PROTECTION AGENCY

[EPA–HQ–OAR–2009–0211; FRL–9258–6]

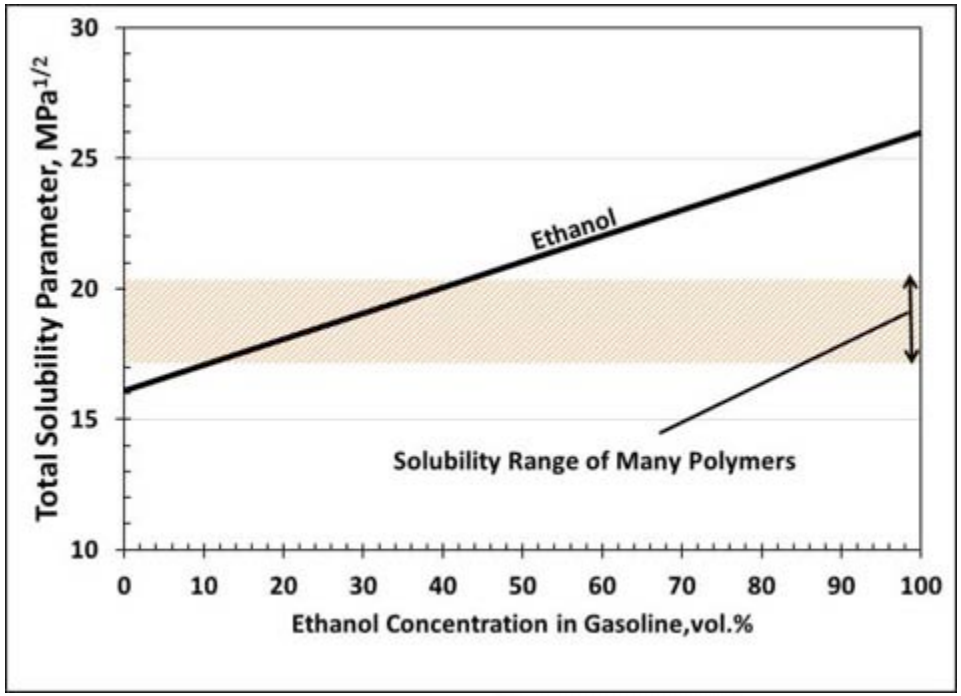
Partial Grant of Clean Air Act Waiver Application Submitted by Growth Energy To Increase the Allowable Ethanol Content of Gasoline to 15 Percent; Decision of the Administrator

AGENCY: Environmental Protection Agency.

ACTION: Notice of Decision Granting a Partial Waiver.

Detailed fuel chemistry is very important to assessing materials compatibility

- **Compounds in typical fuel blends are all good solvents for some materials**
  - Solubility is determined by thermodynamic similarity: “like dissolves like”
  - Fuel contains a breadth of chemical compounds, so “like” is dependent upon how much of each compound is present
- **Chemical and biological processes can occur that produce acids and gums in fuel**
  - Often involve common contaminants

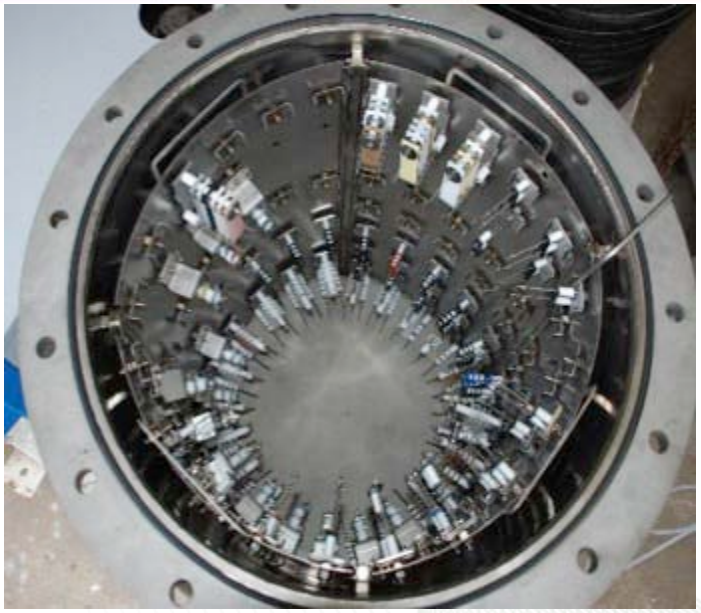


ORNL has conducted empirical studies and Hansen solubility analyses for understanding polymer compatibility with alternative fuels

- **Empirical studies with 11 different fuel chemistries and over 4000 fuel-material interactions**

Material Type	Test Fuels										
	Fuel C	CE10a	CE17a	CE25a	CE50a	CE85a	CiBu16a	CiBu24a	No. 2 Diesel	Bio20	Bio oil
Metals	X	X	X	X	X	X	X	X			X
Elastomers	X	X	X	X	X	X	X	X	X	X	X
Plastics	X	X		X	X	X	X	X	X	X	X

- Successfully used Hansen solubility analyses to assess compatibility of over 40 additional bio-blendstock fuel chemistries as part of the DOE Co-Optima effort.
- We have close working relationships and collaborations with PEI, API, UL, CRC, Steel Tank Institute, EPA.



Impact

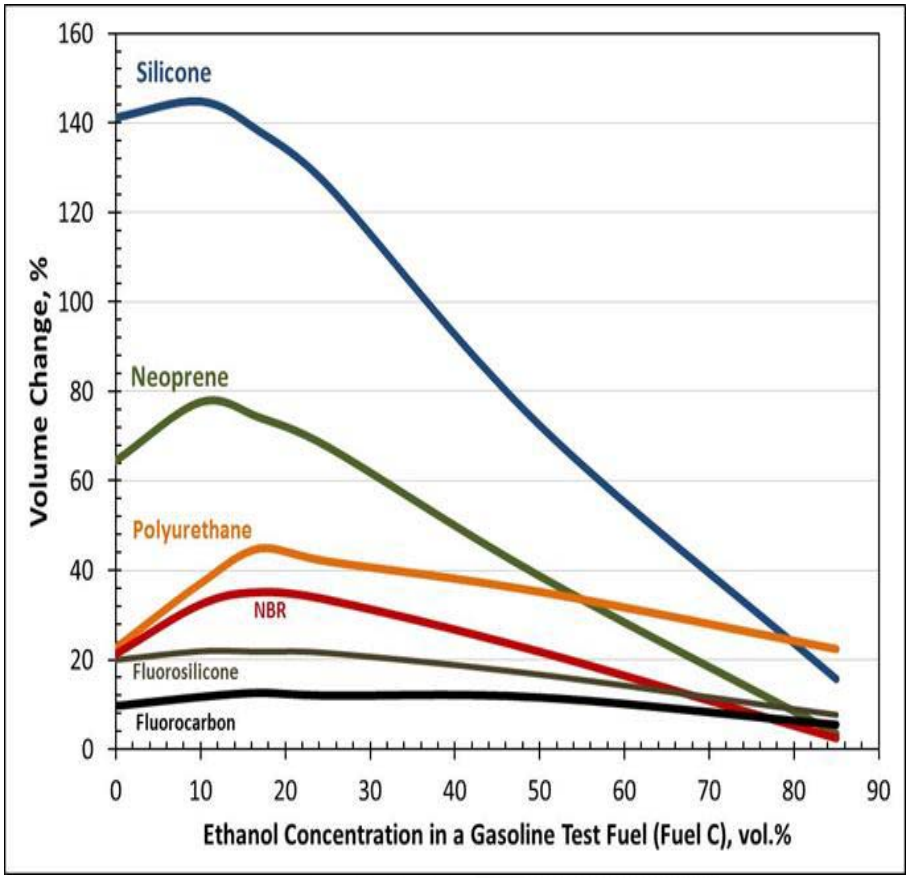
- ORNL compatibility studies cited by EPA as part of their E15 ruling. ORNL also conducted risk assessment study for EPA.
- ORNL efforts led to modifications of gasoline fuel dispensers.
- ORNL fuel compatibility expertise recognized by many industries (BP, Butamax, Steel Tank Institute, API, Fuel Freedom Foundation, etc.)
- ORNL expertise was recently solicited by Sasol: Based on ORNL guidance, Sasol is considering replacing all of their polyethylene piping in South Africa.
- ORNL study revealed the cause of automotive fuel seal failures when Brazil switched from E100 to E22.

120 ISOBUTANOL COMPATIBILITY: WHAT THE RESEARCH SHOWS

Three years ago, the *PEI Journal* first explored the benefits of renewable isobutanol and the possible contribution it could make to the transportation fuel future envisioned by the Renewable Fuel Standard (RFS). The article also described a large-scale materials compatibility evaluation being conducted at Oak Ridge National Laboratory. Three years later, the results of that research are in. *By Wolf H. Koch and James J. Baustian*

Key Findings:

- Metal corrosion requires the presence of an acid or aqueous phase.
- Solubility (volume swell) depends on component and its concentration as shown in the chart for elastomers and ethanol-gasoline fuel blends. Fuel blends are often worse that the neat components.
- Low levels of ethanol are less compatible to common elastomers than higher concentrations.
- In general, plastic materials show good compatibility to bio-oils and bio-intermediates. However, ketones are a problem, especially with many high performance materials.
- Current infrastructure is designed for nonpolar fuels. The heighted polarity of many bio-fuels matches that of polymers causing pronounced swelling.



- Solubility analysis is a useful means of predicting compatibility. However, empirical validation is important prior to implementation.

Thank you!

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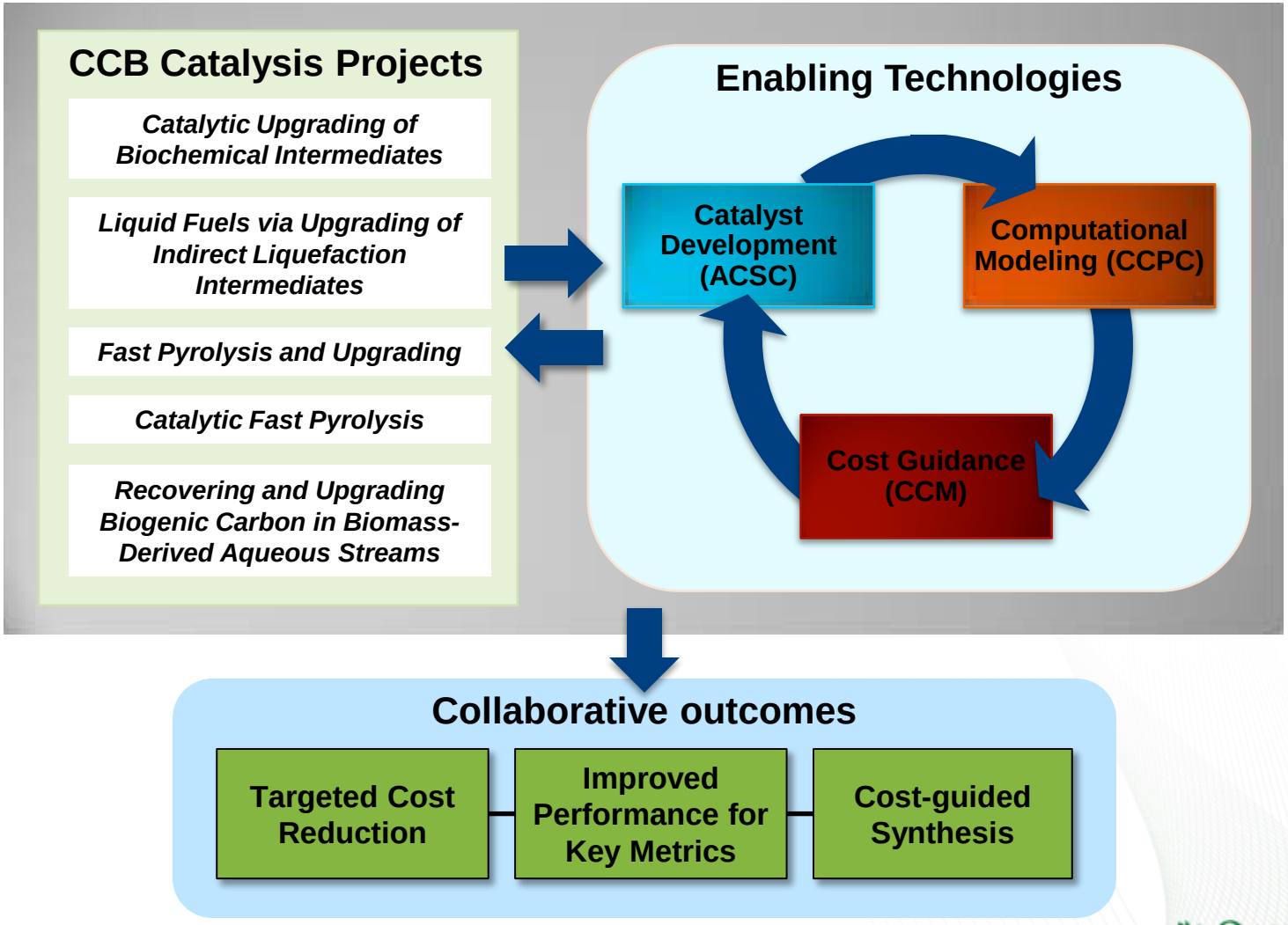
BETO ChemCatBio structure

ChemCatBio
Chemical Catalysis for Bioenergy

Establish an integrated and collaborative portfolio of catalytic and enabling technologies



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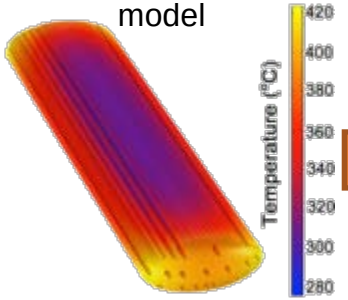
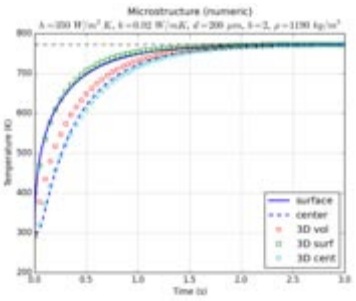
Technical Approach: Complex realism to effective simplicity

Complex effects of biomass particles captured in low-order particle models for use in reactor scale models

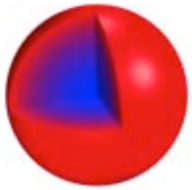
Complex, 3D particle model



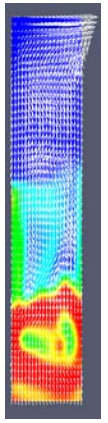
Results fit to low-order model



Low order particle model that capture complex behavior

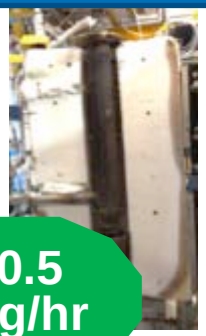


Reactor-scale model



Resulting reactor models enable scalable prediction of pyrolysis yield

2" Fluidized Bed Reactor

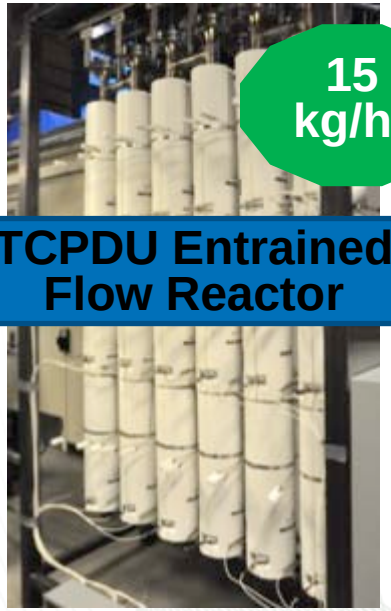


0.5 kg/hr

DCR Fluidized Bed Reactor

2 kg/hr

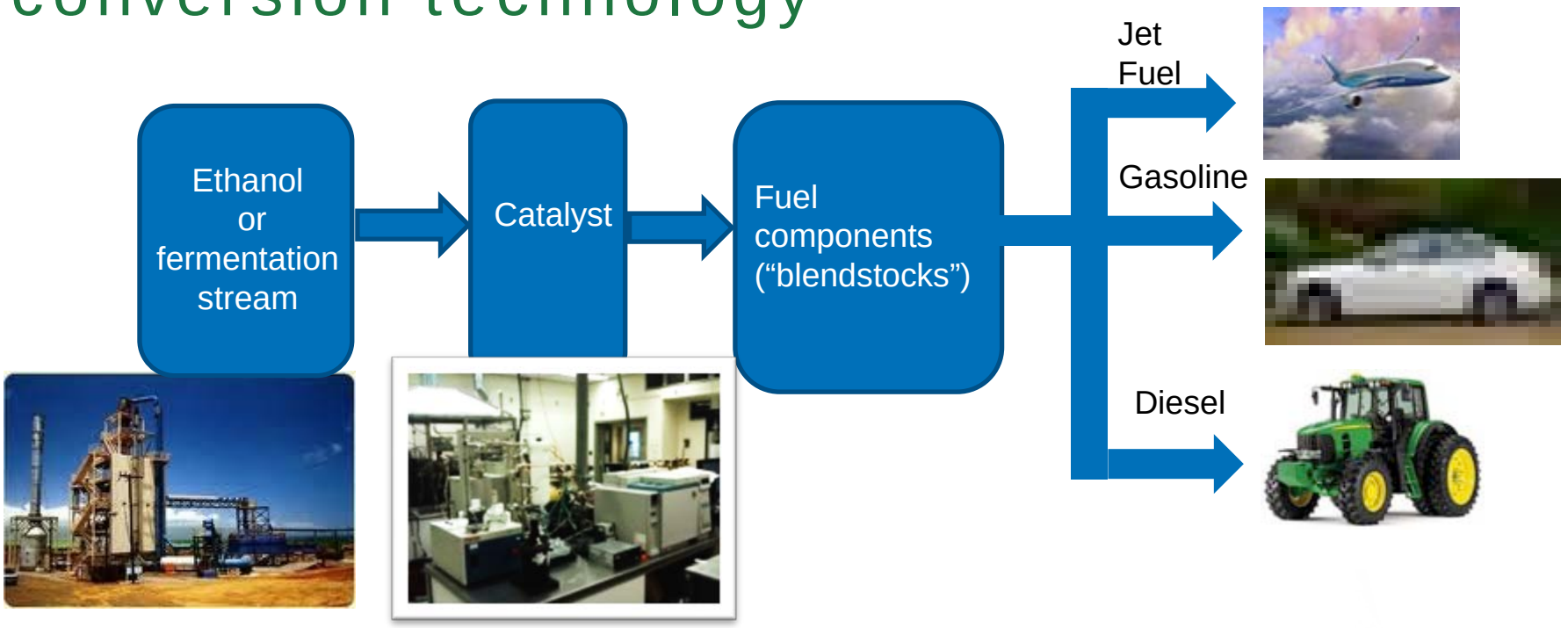
TCPDU Entrained Flow Reactor



15 kg/hr

All Three Reactors at NREL

ORNL has developed and licensed a new conversion technology



- Ethanol in fuel is limited by regulation and infrastructure
- Direct catalytic conversion of ethanol to hydrocarbon fuel blendstock demonstrated
- Technology appears robust & economically attractive
- Licensed to Vertimass, LLC in March 2014
- Directed toward gasoline but can be "tuned" for diesel or jet fuel
- Technology is being optimized and scaled-up for production

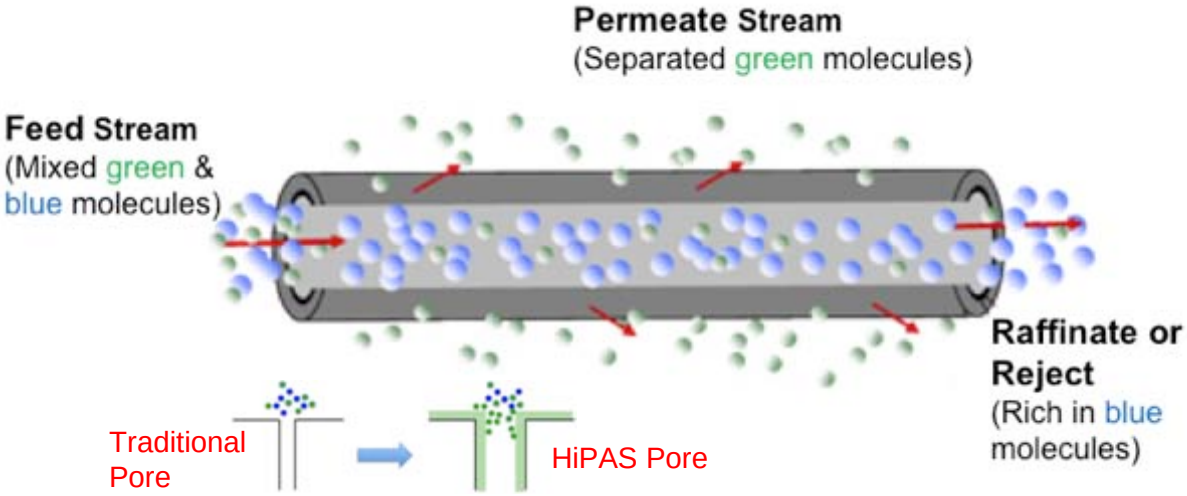
Vertimass

OAK RIDGE National Laboratory

Award-winning membranes demonstrated in bio-oil processing

- ORNL developed a new class of tunable, selectively permeable membranes with high flow rates.
- Integrating these membranes into the biomass conversion process could reduce costs and accelerate the production of high-quality (low-water content) products.
- NREL is evaluating the membranes with real bio-oil processing capabilities.
- Using the membranes in a real pine pyrolysis vapor-water mixture, researchers demonstrated the efficient separation of ≥ 90% of water from hydrocarbons.

Revolutionary Separation Mechanisms:



Enhanced surface selectivity makes it possible to employ larger pores to achieve >100X higher permeation flux

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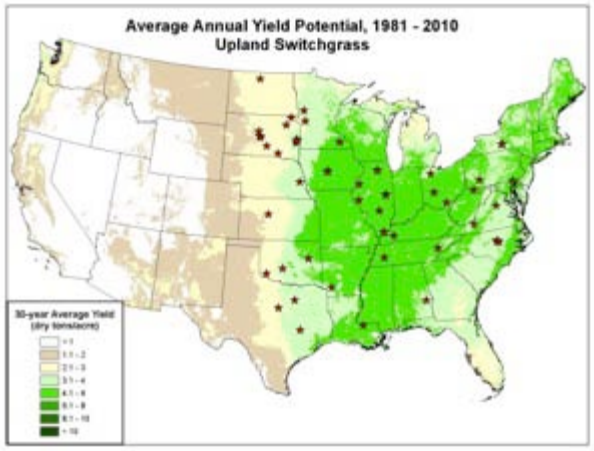
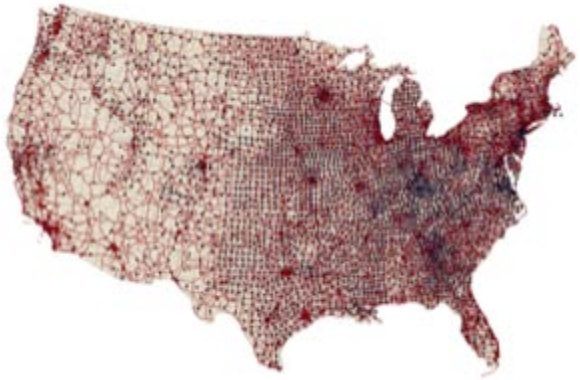
Enhancements of the BT16

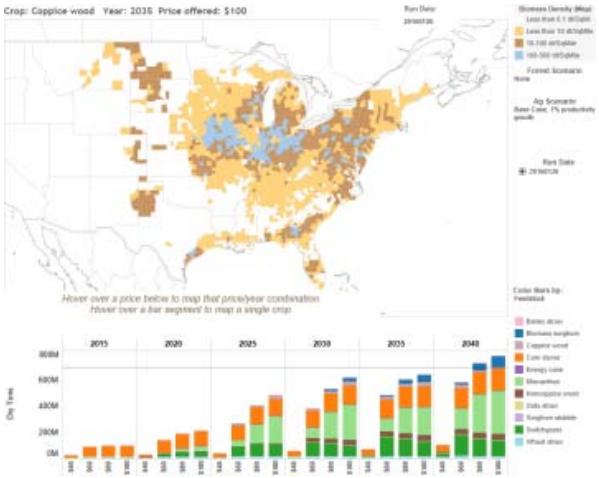
Modeled crop yields



Scenario study of delivered supplies



Interactive visualization



Adding algae and other energy crops


Photo source: BioFlora.com


Photo source: S. Long Lab, University of Illinois


Photo source: energy-daily.com