Process and Product Development with PNNL

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PNNL bioenergy technologies
Core competencies

Dedicated facilities
- 55+ scientists and engineers
- 325+ patents
- $15M of DOE funded equipment
- 2,500 ft² high-bay

Expertise
- Catalysis
- Fungal biotechnology
- Process development
- Strategic analysis

High Throughput Center (HTC)
- Automated material handling
- Material screening
- Analytics & data visualization
High-throughput catalyst discovery

New catalysts for enhanced biogenic carbon management

General rules for catalysts are known – but you must test new materials to discover new catalysts

- More than a shot-gun approach: We use established catalyst rules-of-thumb to initiate a wide search space of plausible candidates – and branch out from there
- Access to a large library of 100’s of catalysts
- Batch (0.5-5 cm³) and flow processing (0.05-1.0 cm³)
- Automated materials handling for preparation of numerous custom catalysts simultaneously
- Advanced analytics to employ combinatorial methods to elucidate ternary and tertiary material interactions

Significance and impact

- Three commercial licenses granted from catalysts discovered and developed using these instruments
- Numerous patents granted -- at least 4 with minimal or no office actions demonstrating the novelty of these new materials
- New bio-derived feedstocks need new catalysts with stability in water-rich environments and activity near impurities
Unique capability – continuous flow reactors

- Capabilities and know-how developed at multiple scales
- Continuous flow reactors
- Continuous improvement operation strategies and systems
  - Production of samples at all scales to support related research

Nominal temperature: Up to 450°C
Nominal pressure: Up to 2000 psi
Success story

Renewable propylene glycol

Breakthrough produces a clean alternative to petroleum; leads to new processing facility

Impact:

Propylene glycol, a chemical used in many products, now derived from green sources

- Cost-competitive
- ADM facility can annually produce up to 100,000 metric tons of PG
- Chemical meets industrial and USP standards
- ADM is exclusive licensee

PNNL discovers catalyst that efficiently converts sugar alcohols and glycerol to propylene glycol (PG)

Archer Daniels Midland advances PNNL discovery, builds Illinois production facility
An example:

Exceptionally high quality fuel with environmental benefits

✓ 98% isoparaffin

Product Quality Ethanol to Jet & Diesel

▸ Meets all ASTM specifications for jet

▸ Cetane = 53.6 (Diesel fuels are typically in the 40-55 range)

▸ Cloud Point = -60.1°C *(ASTM D 975 is regional, but an extreme case is < -28°C for MN. European standard EN 590 specifies < -34°C for Class 4 arctic diesel)*

▸ Pour Point = -66.0°C

Handler et al. Industrial and Engineering Chemistry
Taking it to the next level with our partner, LanzaTech!

**Scientific approach**

- Ethanol → dehydration → **oligomerization** → hydrogenation → fractionation → synthetic paraffinic kerosene (ATJ-SPK)
- **Targeted fuel components** – isoparaffins

**Significance and impact**

- Produced 4,000 gal of jet fuel (synthetic paraffinic kerosene) and 600 gal of diesel fuel (1,500 gallons starting from steel mill waste gas)
- Demonstrated catalyst/process multi-thousand hours with regeneration
- Validated feasibility and reproducibility at pilot scale

**Particulate Matter Reduction**
A powerful driver: Turning liabilities into revenues
Recycling carbon: produce biofuels while solving another problem

CO-rich waste gas → Ethanol → Synthetic paraffinic kerosene (ATJ-SPK)

Waste sludges → biocrude → diesel fuel

biotechnology → catalysis

thermal chemistry → catalysis
**Success story**

**Continuous process for algae to fuels**

Breakthroughs enable scale-up of hydrothermal liquefaction technology in less than four years from idea conception.

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**Impact:**

Near-term technology for deployment with favorable economics:

- Scalable and ideal for wet feedstocks
- Blendstocks suitable for refinery integration
- High-quality jet and diesel fractions
- One of several algal HTL piloting efforts

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*Generation 2 HTL*

PNNL discovers technique for converting whole algae to biocrude; leverages catalysis to turn biocrude into jet and diesel.

Genifuel, Reliance, PNNL build continuous 1 metric ton/day HTL/CHG pilot system for algal feedstocks.
Modular hydrothermal liquefaction system (MHTLS) *Generation 3 HTL

**The capability**
- 12-16 liters/hour
- Solid-liquid separations at operating conditions
- Liquid-liquid separations for biocrudes that are heavier, or lighter, than water
- Product-feed heat recovery

**Accomplishments**
- 2 ½ year effort of multi-faceted team from DOE, PNNL, and industry
- Multiple commissioning runs met all operational objectives, confirming the value of this new capability
- kg – scale biocrude from algae
- Aqueous phase sent to ASU for recycling/algae cultivation studies
Transforming the energy landscape can only be successful through collaboration…
Additional Slides
Multi-liter wiped-film distillation

**Generate liter quantities of compounds and mixtures for fuel testing**

- Typical feed rate: 0.1-3 kg/h
- Continuous wiped-film reboiler allows for efficient distillation
  - Vacuum operation – lowers overall temperature
  - Short feed residence time – minimizes degradation of temperature-sensitive compound
- Hybrid configuration includes 2” diameter packed bed column
- Controllable reflux ratio for increased precision of mixtures

**Significance and impact**

- Sample generation for high volume fuel tests (e.g., RON & MON for gasoline)
- Packed column and reflux allow for precise temperature cuts when distilling gasoline, jet and diesel blendstocks
- Biologically derived fuel blends and co-products may be separated from broths via low temperature operation with short residence times
Biotechnology: EMSL user facility, platform chemical discovery through initial process development
Challenge: poor tolerance of microbial production hosts toward high concentrations of excreted product
• Concentrations > 100 g/L for viable economics

Biosystem design success story
Resequencing of over 200 strains and subsequent reconstruction of sets of mutations has provided unparalleled insight on the genomic basis of tolerance.

https://www.emsl.pnl.gov/emslweb/

Microbial communities success story
Integrated omics revealed the structure and function of a complex cellulose-degrading microbial community, which could lead to greater use of plant biomass for biofuel production.
Fungal genomics – Aspergillus & L. starkeyi

Lignocellulosic sugars, and by-products

Acetyl-CoA

Polyketides

Hydrocarbon fuels, products

Cycloalkanes (JP-10 like), branched alkane fuels

Fatty Acids (lipids)

Terpenes

Biochem

Alkane/alkene fuels, lubricants

CO₂

Cell Mass

Energy for Growth

TCA Cycle

Organic Acids

CO₂

Maximize ‘TRY’

- High titer for downstream processing efficiency
- High rate to minimize CapEx/OpEx
- High yield to maximize use of high-cost biomass

Robust organisms that convert complex hydrolysates containing inhibitors and mixed sugars

Genetic Engineering
- Advanced genetic tools
- Rational design, reverse genetics
- Strains for Bioprocess Development

Systems Biology/Genomics
- Forward genetics
- Transcriptomics
- Gene candidates for Genetic Engineering

Bioprocess Development
- Bioreactors
- TRY Assessment
- Samples for Systems Biology

Tech Transfer:
Bioenergy/Industry
- Biocatalyst
- Bioprocess Description
- Development Tools
- TEA
Bioreactor operation and optimization using chemometric data and machine learning

- **Raman Spectra**
- **Near-infrared Spectra**
- **Dielectric Spectra**
- **Sample Offline Assays** (sugars, dry cell mass, lipids, etc.)
- **Process Variables** (temp, pH, DO, airflow, % CO2, etc.)
- **Events** (inoculation, substrate feeding, control changes, antifoam, etc.)
- **Batch Recipe** (biomass type, pretreatment, microbial strain, nutrients, etc.)

**Bioreactor**

**Control System**

**Operator**

**Integrated Data**

**Time-stamp**

**Chemometric Software**

**LabKey**