



# Process and Product Development with PNNL

CORINNE DRENNAN

[corinne.drennan@pnnl.gov](mailto:corinne.drennan@pnnl.gov)

Advanced Development & Optimization Workshop

12 December 2017

# PNNL bioenergy technologies

## Core competencies



### Dedicated facilities

- ▶ 55+ scientists and engineers
- ▶ 325+ patents
- ▶ \$15M of DOE funded equipment
- ▶ 2,500 ft<sup>2</sup> high-bay

### Expertise

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



### High Throughput Center (HTC)

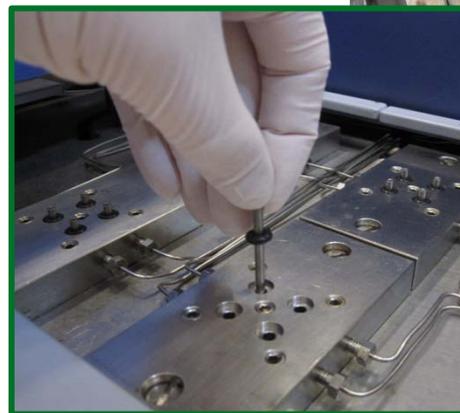
- Automated material handling
- Material screening
- Analytics & data visualization

# New catalysts for enhanced biogenic carbon management



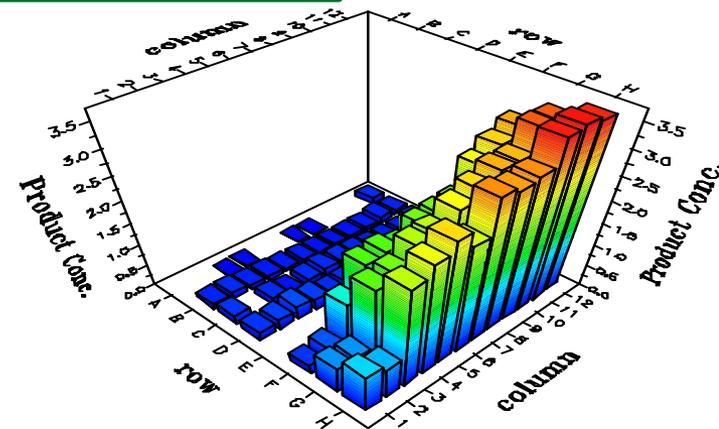
## ***General rules for catalysts are known – but you must test new materials to discover new catalysts***

- ▶ 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 cm<sup>3</sup>) and flow processing (0.05-1.0 cm<sup>3</sup>)
- ▶ 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



8 x 1.4mL beds

Catalyst  
Screening



3-40mL beds

Catalyst  
Evaluation



400/800ml bed

Process  
Development



1 liter fixed and moving  
bed

Nominal temperature: Up to 450C  
Nominal pressure: Up to 2000psi



20 liter bed + distillation

# Renewable propylene glycol

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



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

Archer Daniels Midland advances PNNL discovery, builds Illinois production facility

## Impact:

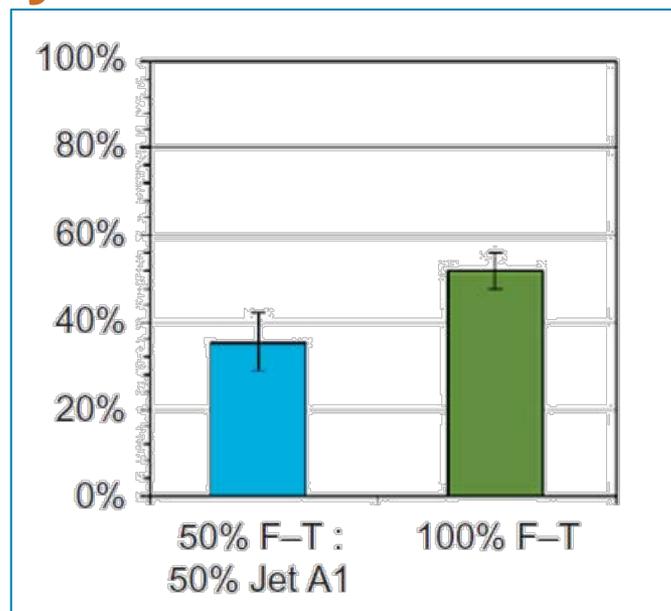
Propylene glycol, a chemical used in many products, now derived from green sources

- ✓ 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

An example:

# Exceptionally high quality fuel with environmental benefits

✓ 98% isoparaffin



particulate matter  
reduction

## ***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 =  $-60.1^{\circ}\text{C}$  (*ASTM D 975 is regional, but an extreme case is  $< -28^{\circ}\text{C}$  for MN. European standard EN 590 specifies  $< -34^{\circ}\text{C}$  for Class 4 arctic diesel*)
- ▶ Pour Point =  $-66.0^{\circ}\text{C}$

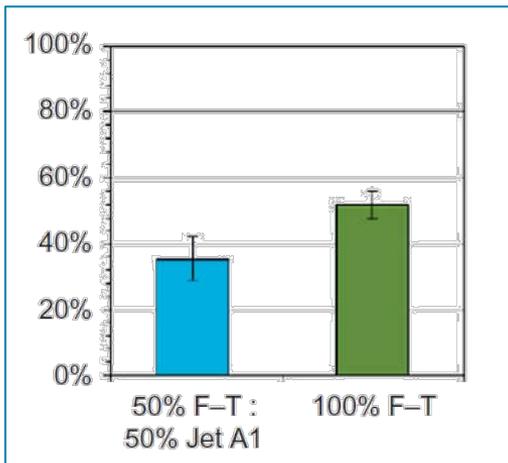
Handler et al. Industrial and Engineering Chemistry

Lobo et al. Environ. Sci. Technol. 45 (2011) 10744-10749

# Taking it to the next level with our partner, LanzaTech!

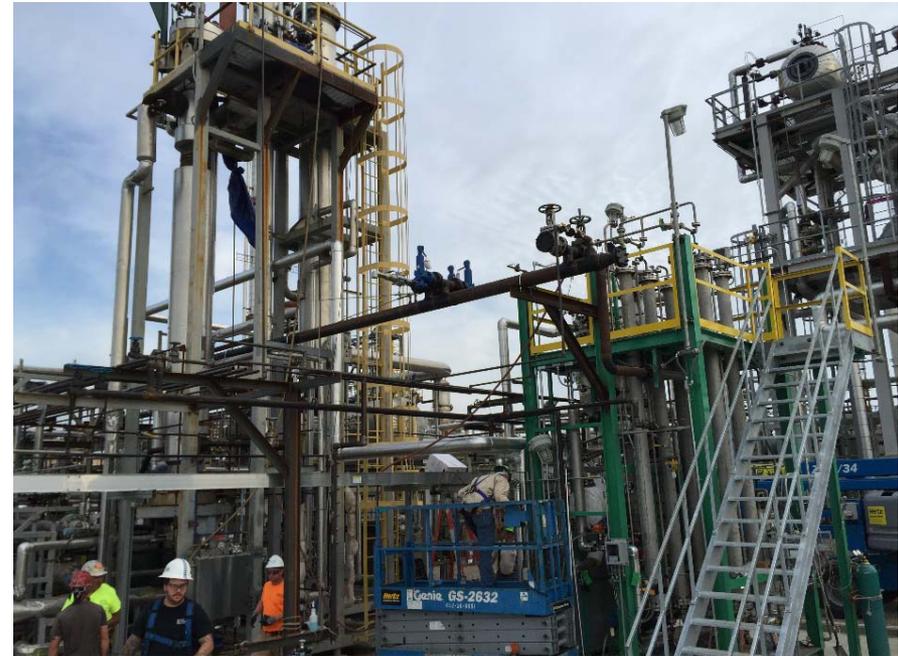
## Scientific approach

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



### Particulate Matter Reduction

Lobo et al. Environ. Sci. Technol. 45 (2011) 10744-10749



## 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



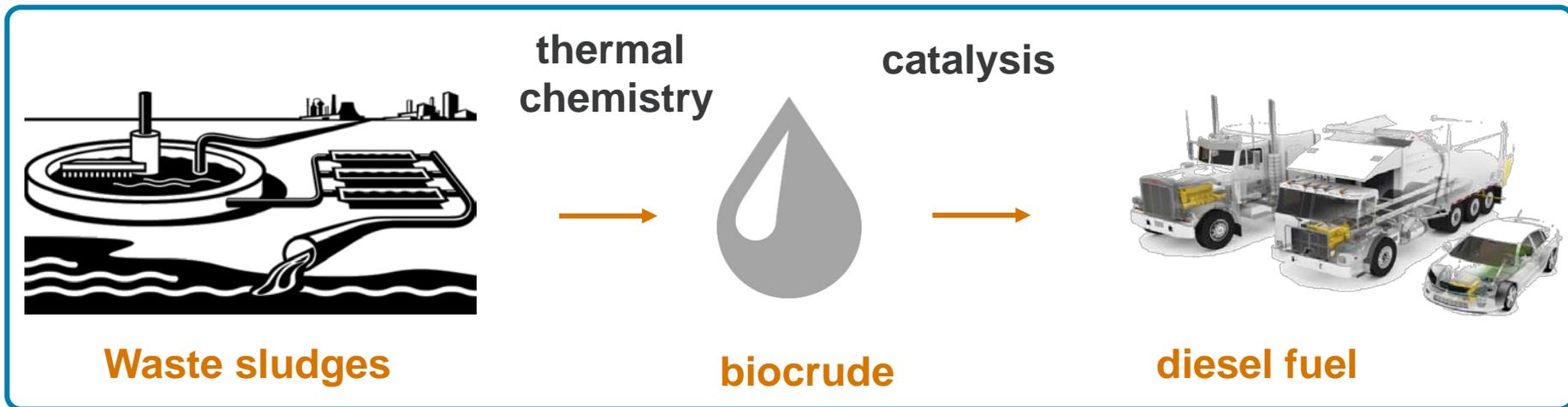
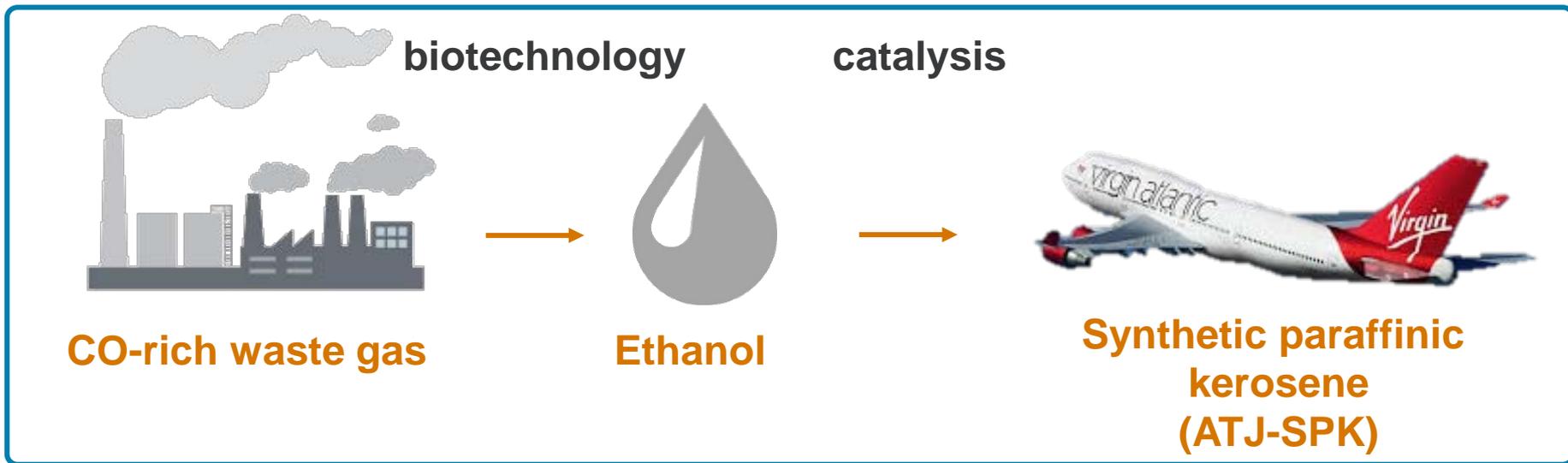


**Pacific Northwest**  
NATIONAL LABORATORY

*Proudly Operated by **Battelle** Since 1965*

# A powerful driver: Turning liabilities into revenues

# Recycling carbon: produce biofuels while solving another problem



# Continuous process for algae to fuels

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



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

## 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

# 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...





**Pacific Northwest**  
NATIONAL LABORATORY

*Proudly Operated by **Battelle** Since 1965*

# Additional Slides



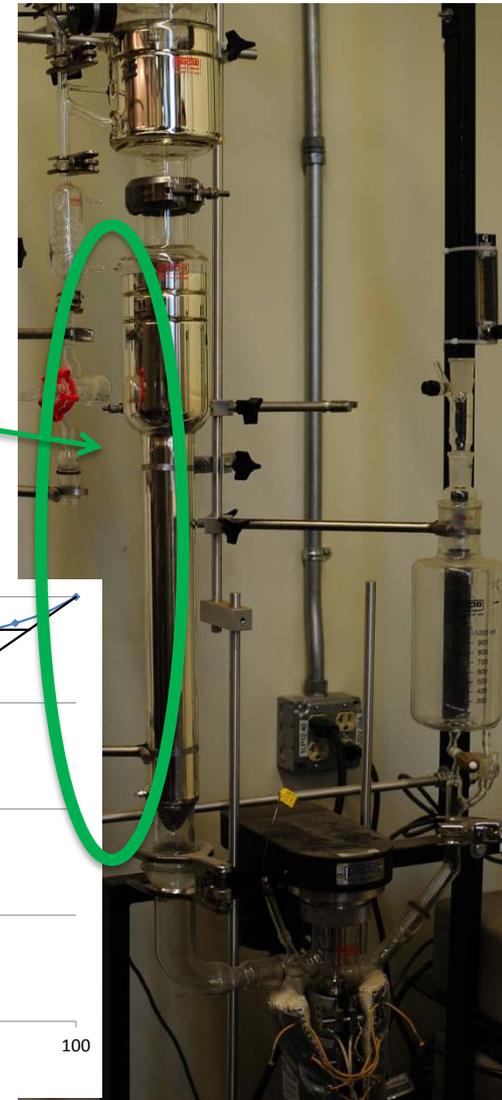
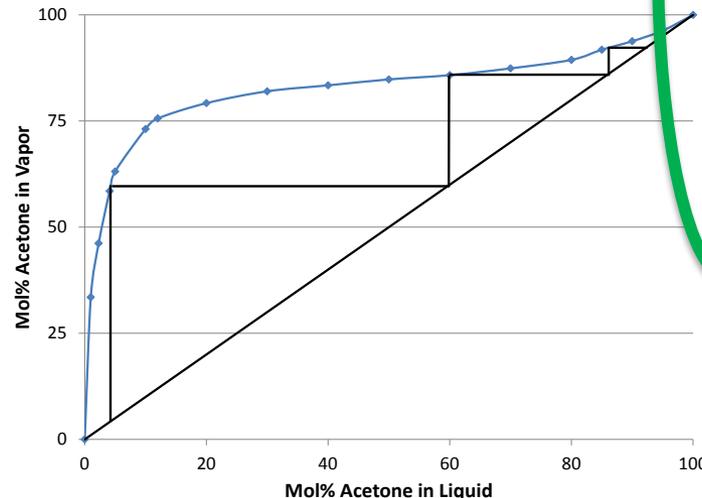
# Multi-liter wiped-film distillation

## 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



# Applied multi-omics, cell isolation and systems analysis, microscopy

## Challenge: poor tolerance of microbial production hosts toward high concentrations of excreted product

- Concentrations > 100 g/L for viable economics

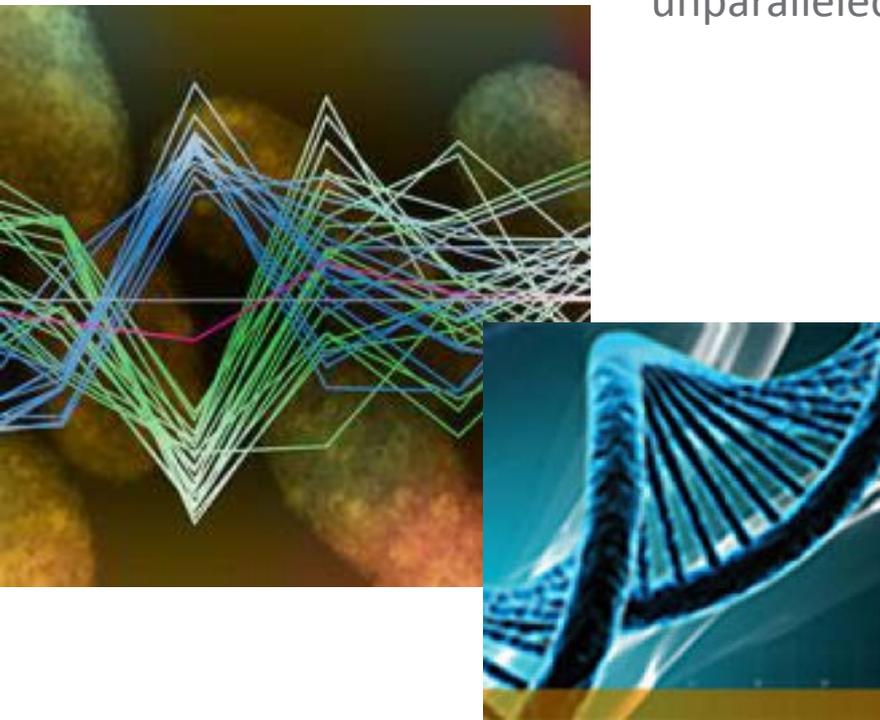
### Biosystem design success story

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.

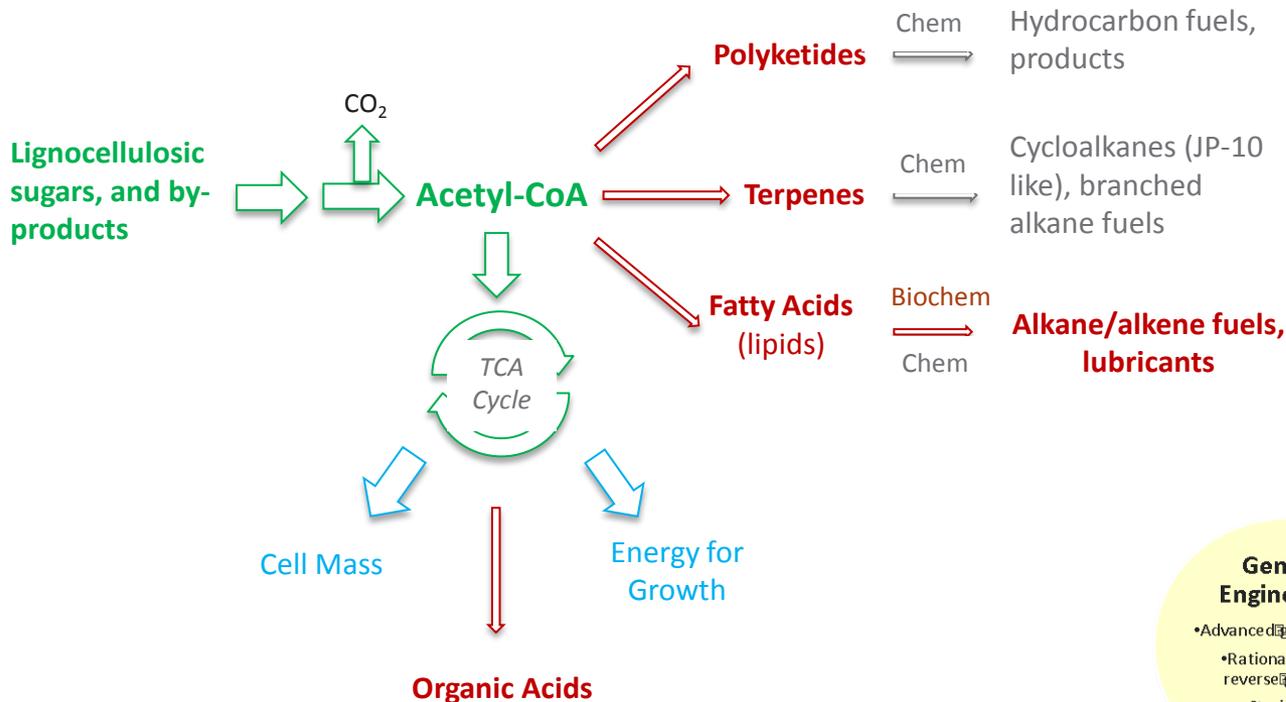


# Fungal genomics – *Aspergillus* & *L. starkeyi*



Pacific Northwest  
NATIONAL LABORATORY

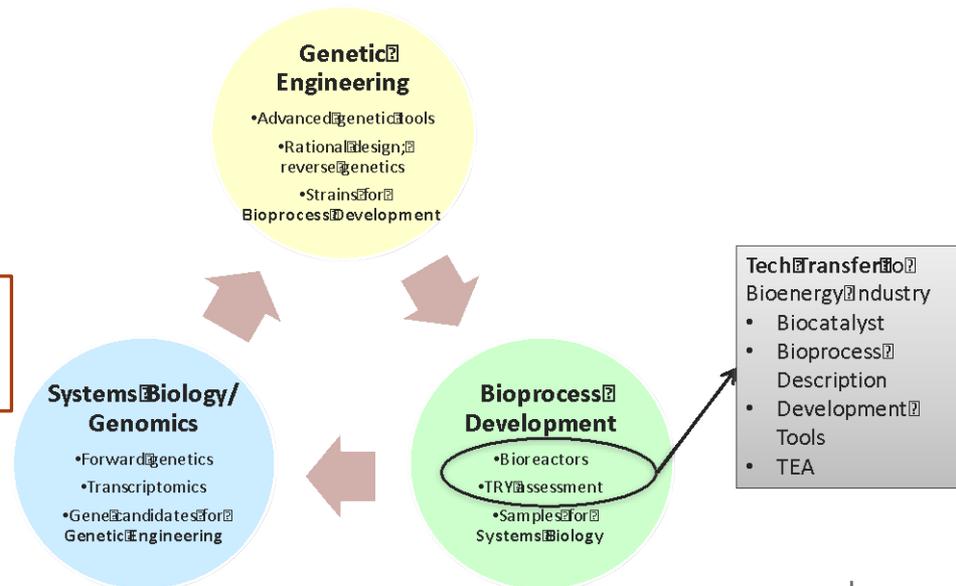
Proudly Operated by **Battelle** Since 1965



### 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



# Bioreactor operation and optimization using chemometric data and machine learning

