

# 2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

U.S. DEPARTMENT OF  
**ENERGY**

Energy Efficiency &  
Renewable Energy



## 11.2.2.2 Opportunities for Biomass-Base Fuels and Products to Address the Entire Barrel of Oil in a Refinery

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May 20, 2013 Charlie Freeman

## Technology Area Review: Analysis and Sustainability

Organization: Pacific Northwest  
National Laboratory

PNNL-SA-95231

This presentation does not contain any proprietary, confidential, or otherwise restricted information

- The goal of the analysis to address the entire barrel of oil is to support meeting the strategic DOE program performance goals by “**developing analytical tools, models, methods, and datasets** to advance the understanding of bioenergy and its related impacts”\*
- The goal of the pathways analysis portion of this project directly supports the DOE strategic analysis activities to “**by 2013, select, complete techno-economic modeling, and set goals and targets** for at least two hydrocarbon pathways”\*

\* BETO Multi-Year Program Plan

## Timeline

- Start: October 1, 2011
- Continuing through FY14
- Completion: work is ongoing

## Budget

- Funding for FY11 \$0
- Funding for FY12 \$160k
- Funding for FY13 \$160k
- 2 years funding at an average of 160k/year

## Barriers

- At-A: Lack of comparable, transparent and reproducible data
- Im-F: Cost of production
- It-E: Engineering modeling tools

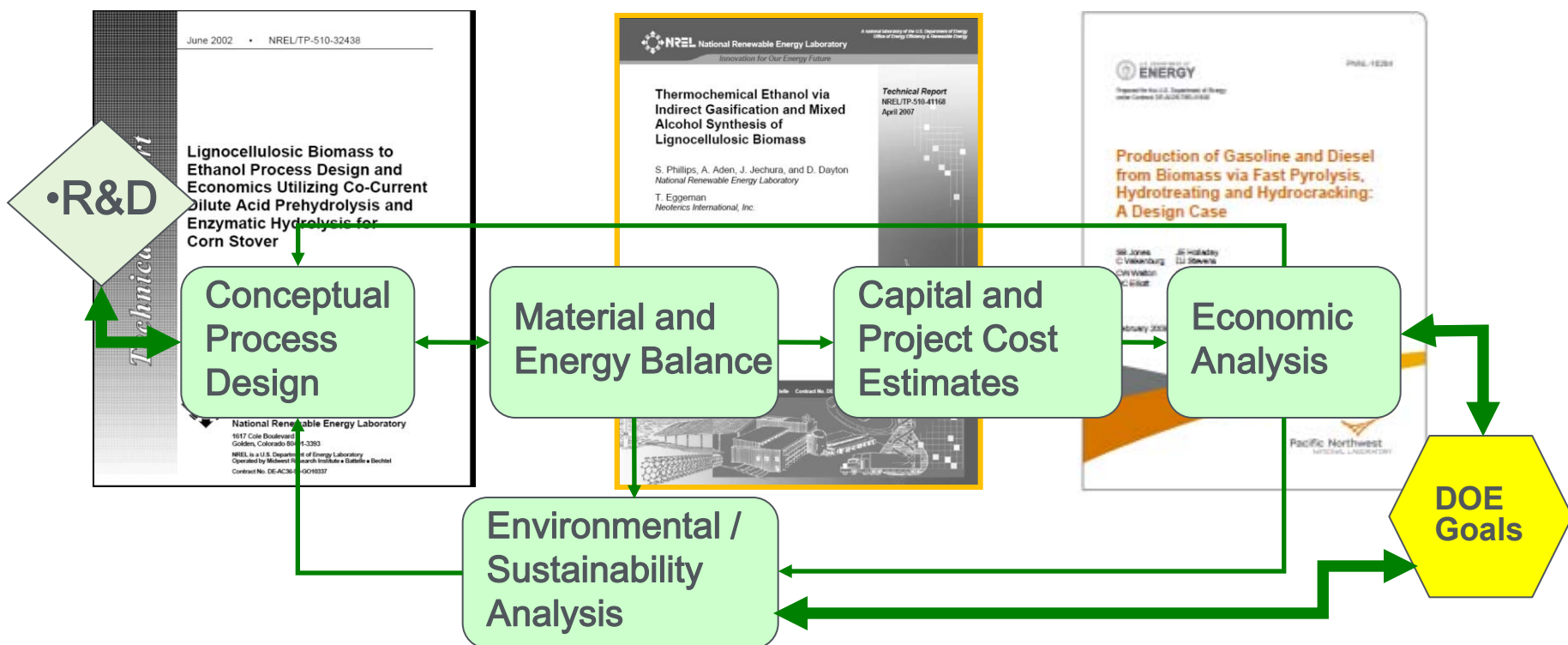
## Partners

- John Shinn (refinery expert, retired from Chevron)
- NREL (pathways analysis) – joint project management

- **History:** new start for FY12
- **Context:** BETO's portfolio expands to hydrocarbon fuels
  - 12/11 CTAB\* Roadmapping Workshop identified critical technology areas
  - BETO Pathway Selection Working Group prioritized pathways
  - DOE laboratories enlisted to leverage existing TEAs and rapidly develop new analysis for the pathways of interest
- **Objective:** Support the BETO pathways analysis to enable the production of hydrocarbon fuels
  - Develop preliminary economics in support of the FY12 pathway prioritization
  - Develop detailed economics and technical targets for FY13 &14 of select pathways
  - Analysis to support understanding of use of existing infrastructure

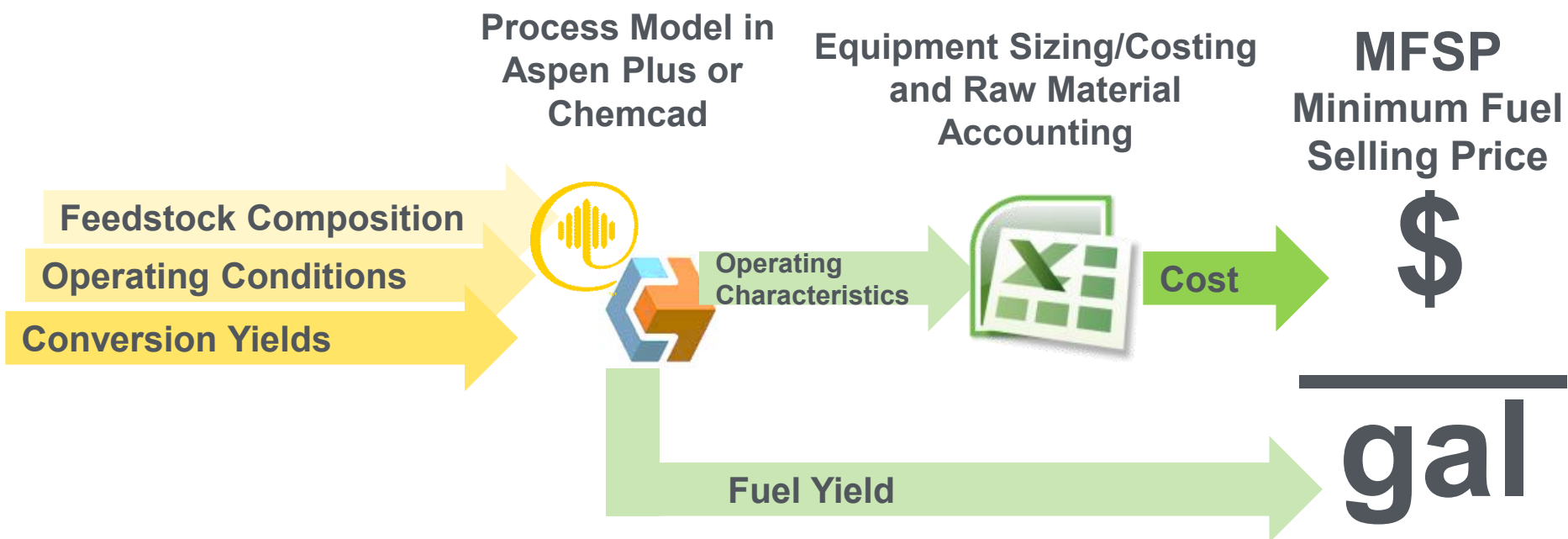
\*CTAB: Conversion Technologies for Advanced Biofuels

# Techno-Economic Analysis: Approach



- Collaborate with engineering & design firm to enhance credibility, quality
- Conceptual design reports are transparent, highly peer reviewed
- Iteration with researchers and experimentalists is crucial

# Techno-Economic Analysis: Approach



- Modeling is rigorous and detailed with transparent assumptions
- Assumes  $n^{\text{th}}$ -plant equipment costs
- Discounted cash-flow IRR calculation includes return on investment, equity payback, and taxes
- Determines the minimum selling price required for zero NPV

This project has two separate tasks:

## **Task 1: Technology Pathways Technical Memos**

- Techno-economics to support Pathway Analysis (NREL & PNNL)
- Preliminary analyses for multiple pathways
- Assist BETO in assessing future R&D needs

## **Task 2: Biomass-Base Fuels and Products to Address the Entire Barrel of Oil**

- Co-processing biomass derived intermediates
- Petroleum refinery capacity and capability assessment

## Technology Pathways Technical Memos

- FY12 NREL and PNNL collaboration to perform analysis for hydrocarbon biofuels pathways
- Integrated efforts with INL for feedstock interface and costs
- 18 pathways identified with 13 TEAs performed
- Consistent economic assumptions utilized to estimate preliminary MFSP
- DOE BETO selected 7 pathways for further development
- Vetted assumptions and basis with researchers and scientists
- Reviewed by key stakeholders in DOE BETO

# Technical Accomplishments Task 1

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## Technology Pathways Technical Memos



- FY13 collaborative TEA efforts between NREL and PNNL to document and publish 7 technology pathways
- Provides process design highlights and identifies data gaps, uncertainties and future research needs
- Starting point for developing joint NREL and PNNL design reports for hydrocarbon biofuels pathways in FY13 and FY14 for core platform tasks

## Biomass-Base Fuels and Products to Address the Entire Barrel of Oil

- Assesses at a high level, the impact of introducing bio-derived intermediates into U.S. petroleum refineries
- Surveys availability of biomass near petroleum refineries in the 2022 timeframe
- Considers bio-intermediate compatibility with petroleum intermediates
- Offers a refiner's perspective

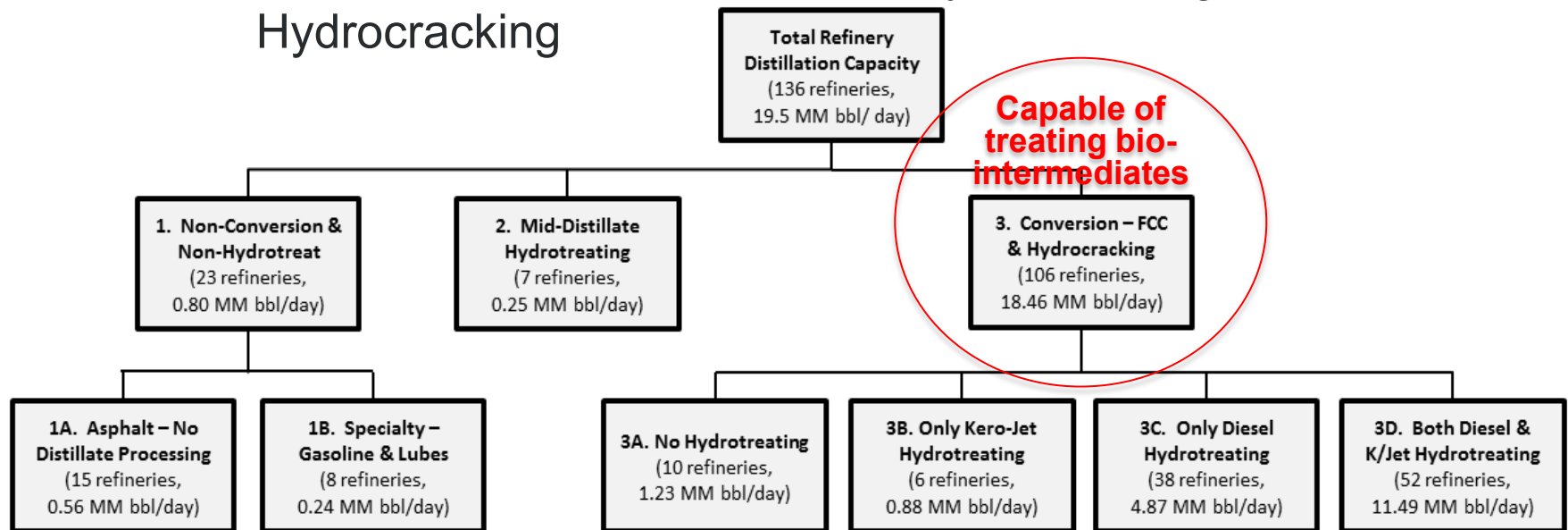
## DOE Mission Impacts

- Supports understanding of infrastructure use and potential to reduce costs
- Addresses entire barrel
- Considers advanced biofuels



## What is the total US refining capacity and capabilities?

- Per EIA, 149 refineries total, 136 sufficiently detailed
- ~20 million barrels/day total capacity (136 refineries)
- Categorized into three main types:
  1. Non-conversion & non-hydrotreating
  2. Middle-distillate hydrotreating capability
  3. Full conversion – Fluidized Catalytic Cracking and Hydrocracking

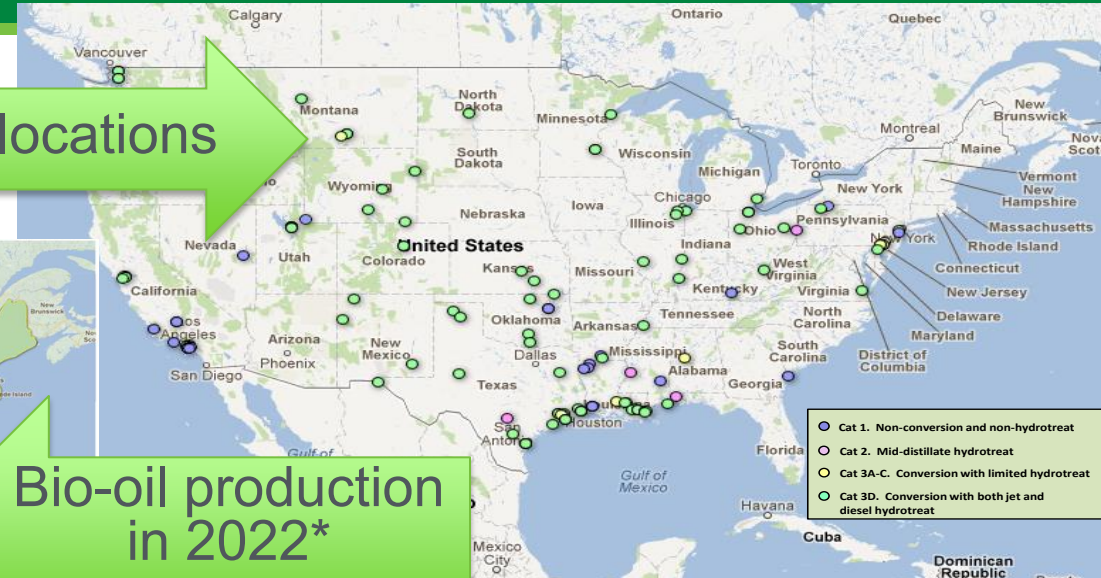


# Technical Results

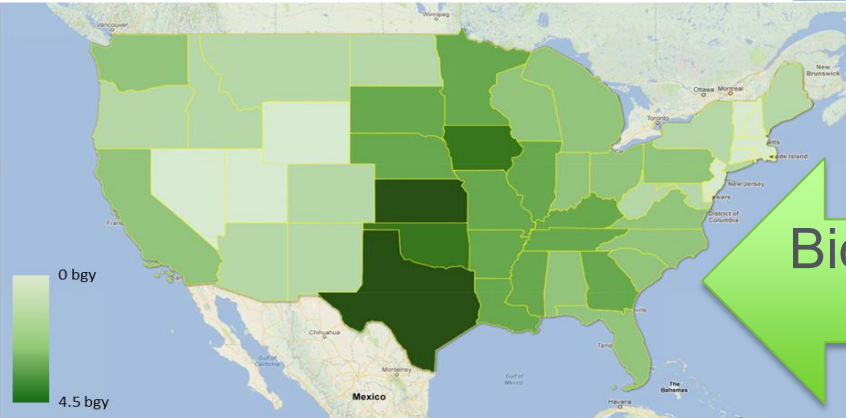
## Task 2

Q: Sufficient refining capacity in future for 20% co-processing?

Refinery locations



Bio-oil production in 2022\*

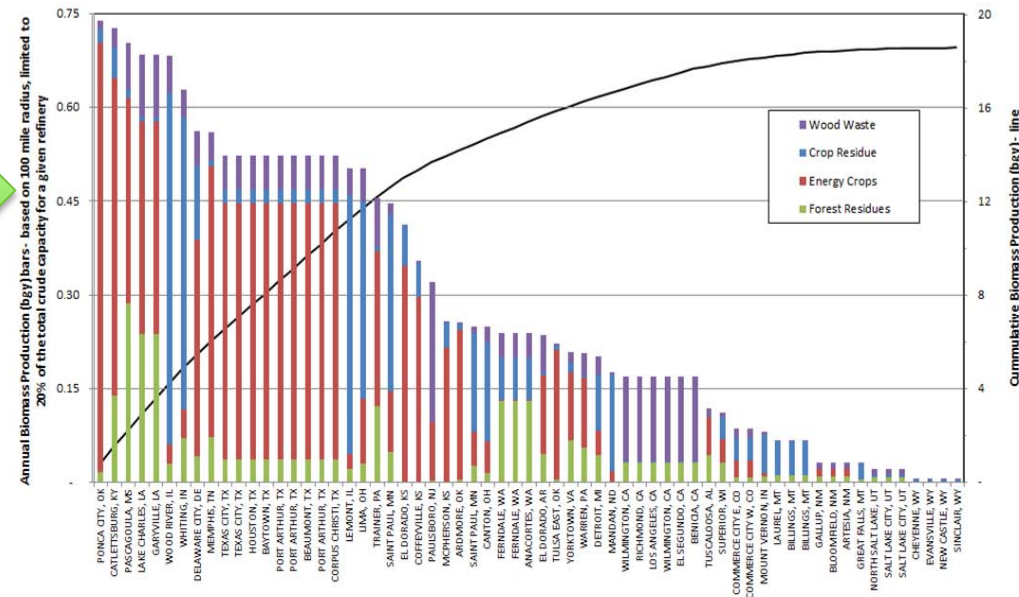


Refinery sites with highest biofuel production potential\*\*

A: Initial look suggests capacity is available

\* 20% additional yield loss  
\$60/ton farm gate  
85 gal/dry ton conversion

\*\*US refinery sites with highest est. fuel volumes  
100 mile radius around each refinery  
FCC and HCK refineries only (Cat 3)  
Equiv. biofuel intermediate into any refinery limited to 20% of total crude capacity



# Technical Results

## Task 2

## How do bio-intermediate properties compare with conventional?

Partially hydrotreated  
pyrolysis more cyclic  
than crude derived  
cuts

Very little  
published  
data

No data  
for diesel  
or  
heavier  
cuts  
available

|                   | Light Naphtha Cut |                                         |            | Heavy Naphtha Cut |                                         |            | Kerosene Cut      |                                         |           | Diesel Cut        |                                         |        |
|-------------------|-------------------|-----------------------------------------|------------|-------------------|-----------------------------------------|------------|-------------------|-----------------------------------------|-----------|-------------------|-----------------------------------------|--------|
|                   | 15 - 75 °C        | C5 - 71 °C                              |            | 75 - 165 °C       | 71 - 182 °C                             |            | 165 - 250 °C      | 182 - 260 °C                            |           | 250 - 345 °C      | 260 - 338 °C                            |        |
|                   | North Slope Crude | Hydrotreated Pyrolysis Oil from Biomass |            | North Slope Crude | Hydrotreated Pyrolysis Oil from Biomass |            | North Slope Crude | Hydrotreated Pyrolysis Oil from Biomass |           | North Slope Crude | Hydrotreated Pyrolysis Oil from Biomass |        |
|                   |                   | 8.2% O                                  | 0.4% O     |                   | 8.2% O                                  | 0.4% O     |                   | 8.2% O                                  | 0.4% O    |                   | 8.2% O                                  | 0.4% O |
| Wt% Yield         | 5                 | 5                                       | 14         | 13                | 20                                      | 30         | 12                | 19                                      | 22        | 17                | 17                                      | 21     |
| Aliphatics (vol%) |                   |                                         |            |                   |                                         |            |                   |                                         |           |                   |                                         |        |
| Paraffins         | 86                | 7.9                                     | 28.3       | 46                | 15.4                                    | 5.9        | 37                | 10                                      | 33        | 30                |                                         |        |
| Isoparaffins      |                   | 32.8                                    | 14.9       |                   | 26.8                                    | 38.8       |                   |                                         |           |                   |                                         |        |
| Naphthenes        | 13                | 31.8                                    | 51.3       | 39                | 46                                      | 20.3       | 44                |                                         |           | 38                |                                         |        |
| Aromatics (vol%)  |                   | 10.9                                    | 5.6        | 14                | 11.8                                    | 27         | 15                | 52                                      | 38        | 31                |                                         |        |
| Olefins (vol%)    |                   | 16.7                                    | 0.07       |                   | 0.01                                    | 8.3        |                   |                                         |           |                   |                                         |        |
| Benzene (vol%)    |                   | 0.3                                     | 0.5        |                   | 0.4                                     | 0.8        |                   |                                         |           |                   |                                         |        |
| Unidentified      |                   |                                         |            |                   |                                         |            |                   | 30                                      | 25        |                   |                                         |        |
| <b>TOTAL</b>      | <b>99</b>         | <b>100</b>                              | <b>101</b> | <b>99</b>         | <b>100</b>                              | <b>101</b> | <b>96</b>         | <b>92</b>                               | <b>96</b> | <b>99</b>         |                                         |        |
| H/C molar ratio   | 2.23              | 1.96                                    | 2.04       | 1.96              | 1.88                                    | 1.85       | 1.89              | 1.69                                    | 1.7       | 1.75              | 1.56                                    | 1.55   |
| Acidity*          | 0.001             | 102                                     | ND         | 0.009             | 123                                     | ND         | 0.03              | 67                                      | ND        | 0.098             | 20                                      | 0.1    |
| RON               | 71                | 79                                      | 64         | 64                | 71                                      | 88         |                   |                                         |           |                   |                                         |        |

\*Table Sources: Christiansen, Earl, et al. "Biomass Fast Pyrolysis Oil Distillate Fractions" Energy & Fuels 2011, 25, 5462-5471

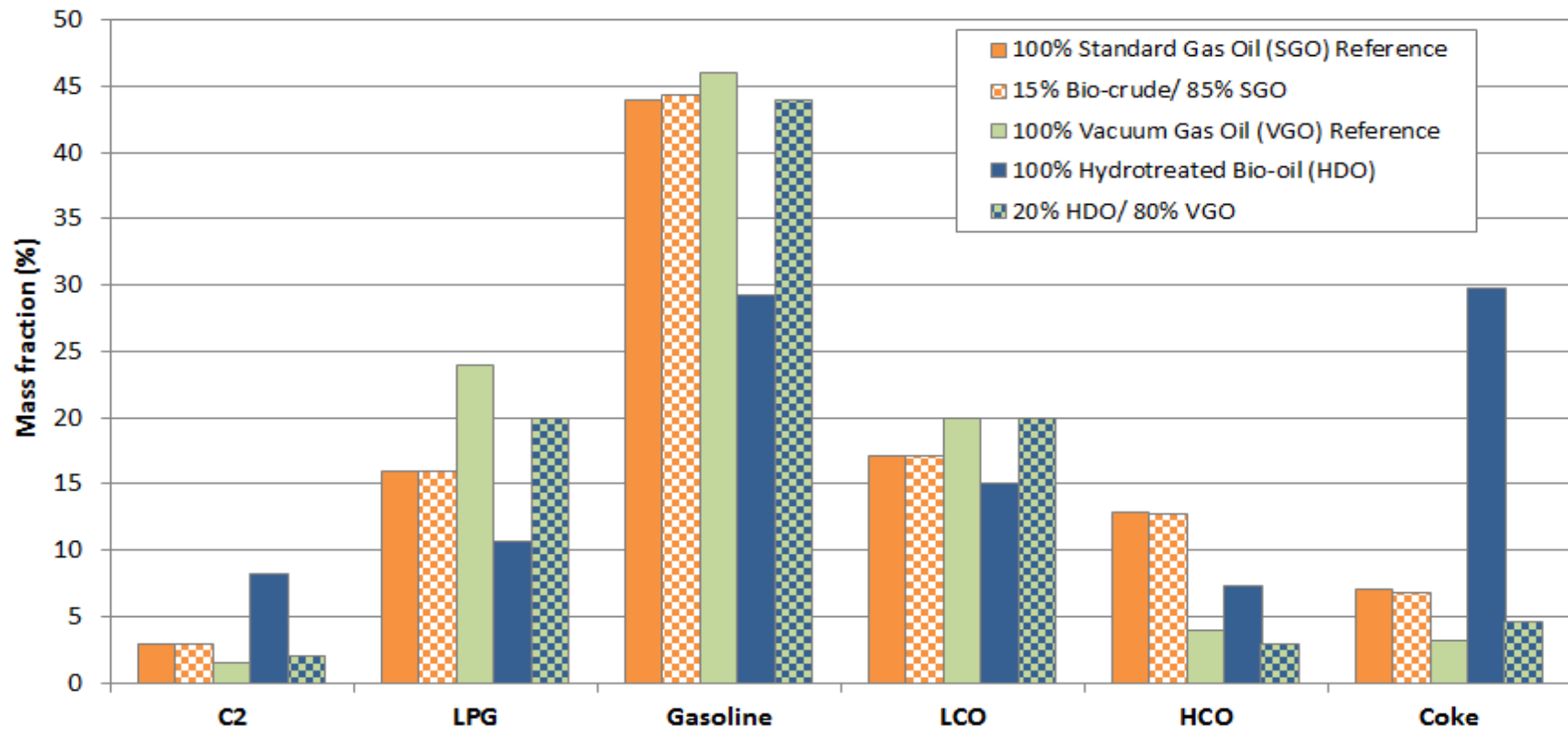
BP Crude Marketing, Alaska North Slope Crude Assay <http://www.bp.com/extendedsectiongenericarticle.do?categoryId=16002777&contentId=7020196>

# Technical Results

## Task 2

### Co-processing bio-derived oils up to 20% of FCC feed appears feasible

- Raw pyrolysis oil needs pre-treatment to be miscible with petroleum feeds
- Little published data, mostly small scale FCC type applications



Graph Sources: Agblevor, F.A., et al., Co-processing of standard gas oil and biocrude oil to hydrocarbon fuels. Biomass and Bioenergy, 2012. 45: p. 130-137  
Fogassy, G., et al., Biomass derived feedstock co-processing with vacuum gas oil for second-generation fuel production in FCC units. Applied Catalysis B: Environmental, 2010. 96(3-4): p. 476-485

# Technical Results

## Task 2

### Refiner's Perspective: Safety, Reliability, Predictability, Profitability

| Risk           | Type of Bio-oil Intermediate                                                                                                                                                                                           | Insertion                                                                      | Refinery Challenges                                                                                                                                                                                                                                                                                                                                                                          |
|----------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>Lowest</b>  | Well defined, consistent quality, such as single molecules (e.g., ethanol, butanol, farnesene)                                                                                                                         | Blending units                                                                 | <ul style="list-style-type: none"> <li>Blending, product performance and distribution of products that include the bio-component.</li> <li>Evaluating and managing potential stability, toxicity and environmental issues</li> </ul>                                                                                                                                                         |
| <b>Medium</b>  | Intermediates requiring only minor treating (e.g. triglycerides, some direct liquefaction oils, some catalytically derived sugar oils)                                                                                 | Hydrotreating followed by blending                                             | Challenges identified above, plus: <ul style="list-style-type: none"> <li>Understanding process performance on new feeds and blends with petroleum-based feeds.</li> <li>Enabling larger fractions of bio-oil blending stocks while still meeting product specs.</li> <li>Providing sufficient hydrogen to meet hydrotreating demands (for reducing oxygen or aromatic contents).</li> </ul> |
| <b>Highest</b> | Intermediates needing boiling range & composition changes for acceptable gasoline, diesel and jet fuel blending stocks (e.g. fast pyrolysis oils, some hydrothermal liquefaction oils, some catalytic pyrolysis oils). | Off-site or dedicated on-site hydrotreating followed by cat- or hydro-cracking | Challenges identified above, plus: <ul style="list-style-type: none"> <li>Understanding the impact of bio-oils on all refinery processes.</li> <li>Meeting product quantity and quality needs with feedstocks with less data on conversion behavior.</li> </ul>                                                                                                                              |

- **Conclusions:**
  - Most U.S. refineries have capabilities and capacities (at least at this level of analysis) to process bio-intermediates
  - Gulf Coast refining important – bulk of capacity & proximity to projected biomass volumes
  - Partnerships with refiners is key
- **Gaps identified:**
  - More experimental co-processing data needed (in addition to that expected from the 2012 Bio-oil Commoditization solicitation)
  - Methods and standards needed to characterize and predict impact
- **Summary report completed: PNNL 22432**
- **FY13 task to begin development of process models to assess biomass intermediate co-processing**

# Milestones/Metrics and Progress

| Title/Description                                                      | Due Date | Completed |
|------------------------------------------------------------------------|----------|-----------|
| Categorize refinery types and capacities                               | Mar -12  | ✓         |
| Review of assumptions and refineries                                   | Jun -12  | ✓         |
| Complete initial mapping of biomass blendstocks to refinery processes  | Sep -12  | ✓         |
| Identify gaps and opportunities for meeting MYPP reference case target | Dec-12   | ✓         |
| Complete characterization of HCK and FCCU                              | Dec-12   | ✓         |
| Develop process models for HCK and FCCU                                | Mar-13   | ✓         |

- **Task 1 supports** the Bioenergy Technologies Office **strategic goal** “*to develop technologies for converting feedstocks into cost-competitive liquid transportation fuels*” through **pathways analysis** leading to **technical targets** for cost reduction
- **Task 2** helps DOE and industry **understand critical issues and risks** related to hydrocarbon production particularly through the **use of existing infrastructure**

- **Provide robust analysis of costs and benefits, sustainability metrics and environmental impacts**
  - Ensure consistent and appropriate assumptions across all Biomass design cases
  - Frequent meetings with platform leads and laboratories
  - Monthly Analysis & Sustainability telecons
  - Quarterly formal reporting to HQ
- **Availability of up-to-date information** on the technical status, barriers and markets in order to assess costs and risks and direct research towards areas of greatest impact
  - Early identification of barriers, gaps and research needs
  - Collaboration with and review from labs and industry
  - Draw on existing relationships with refining experts to provide input and review for refinery co-processing analysis; forge new partnerships as needed

| ML, DL or Go/No Go | Description                                                                                                                      | FY13 Q3 | FY13 Q4 | FY14 Q1 | FY14 Q2 | FY14 Q3 | FY14 Q4 |
|--------------------|----------------------------------------------------------------------------------------------------------------------------------|---------|---------|---------|---------|---------|---------|
| B.1.ML.3           | Develop cost models for HCK and FCCU with potential for bio-intermediates to achieve \$3/gal target                              |         |         |         |         |         |         |
| B.1.ML.4           | Complete summary report of completed costs per refining functional area and impact of bio-intermediates towards the \$3/gal goal |         |         |         |         |         |         |
| C.1.ML.1           | Refinery operation characterization for two processes                                                                            |         |         |         |         |         |         |
| C.1.ML.2           | Refinery process model                                                                                                           |         |         |         |         |         |         |
| C.1.ML.3           | Refinery process cost model                                                                                                      |         |         |         |         |         |         |
| C.1.ML.4           | Summary report                                                                                                                   |         |         |         |         |         |         |

## TASK 1: Pathways Analysis (with NREL)

- 2-3 additional gasification based tech memos (FY13)
- Updated design case for Fast Pyrolysis and Upgrading and technical targets (FY13)
- Algae HTL Design Case and targets (FY13)
- Catalytic Pyrolysis Design Cases (In-Situ and Ex-Situ) and technical targets (FY14)
- FY15 reduce number of pathways

## TASK 2: Leveraging Conventional Refinery Infrastructure (with NREL)

- Complete preliminary models for FCCU and HCK
- Expand model (partner with NREL), engage industry
- FY15 determine if sufficient data available for continuation

## **1) Approach**

- Tech Memos: multi-lab analysis with iterative review between researchers, modelers, and headquarters; Refinery project reviewed with refining expert

## **2) Technical accomplishments**

- 7 published Tech Memos (with NREL), after assessment of 18 pathways and development of 13 TEAs
- Preliminary refinery insertions analysis report completed: PNNL-22432

## **3) Relevance**

- Provides new pathways input for the MYPP

## **4) Critical Success factors and challenges**

- Robust analysis through consistent basis and vetted assumptions
- Collaboration with labs and industry

## **5) Future Work**

- Task 1: New design cases to further detail pathways and set research targets
- Task 2: Enhance refinery modeling to better understand co-processing costs

## **6) Technology transfer**

- Published documentation

Bioenergy Technologies Office – Zia Haq, Alicia Lindauer, Kristen Johnson

PNNL Team – Aye Meyer, Asanga Padmaperuma, Miki Santosa, John Shinn (Retired Chevron consultant to PNNL project)

NREL – Mary Biddy

# Additional Slides

# Responses to Previous Reviewers' Comments

- This project was a new start in FY12 and hence has not been previously reviewed

## Publications

### **Whole Algae Hydrothermal Liquefaction Technology Pathway**

<http://www.nrel.gov/docs/fy13osti/58051.pdf>

[http://www.pnnl.gov/main/publications/external/technical\\_reports/PNNL-22314.pdf](http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-22314.pdf)

### **Algal Lipid Extraction and Upgrading to Hydrocarbons Technology Pathway**

<http://www.nrel.gov/docs/fy13osti/58049.pdf>

[http://www.pnnl.gov/main/publications/external/technical\\_reports/PNNL-22315.pdf](http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-22315.pdf)

### **Ex-Situ Catalytic Fast Pyrolysis Technology Pathway**

<http://www.nrel.gov/docs/fy13osti/58050.pdf>

[http://www.pnnl.gov/main/publications/external/technical\\_reports/PNNL-22317.pdf](http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-22317.pdf)

### **Biological Conversion of Sugars to Hydrocarbons Technology Pathway**

<http://www.nrel.gov/docs/fy13osti/58054.pdf>

[http://www.pnnl.gov/main/publications/external/technical\\_reports/PNNL-22318.pdf](http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-22318.pdf)

### **Catalytic Upgrading of Sugars to Hydrocarbons Technology Pathway**

<http://www.nrel.gov/docs/fy13osti/58055.pdf>

[http://www.pnnl.gov/main/publications/external/technical\\_reports/PNNL-22319.pdf](http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-22319.pdf)

### **In-Situ Catalytic Fast Pyrolysis Technology Pathway**

<http://www.nrel.gov/docs/fy13osti/58056.pdf>

[http://www.pnnl.gov/main/publications/external/technical\\_reports/PNNL-22320.pdf](http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-22320.pdf)

### **Syngas Upgrading to Hydrocarbon Fuels Technology Pathway**

<http://www.nrel.gov/docs/fy13osti/58052.pdf>

[http://www.pnnl.gov/main/publications/external/technical\\_reports/PNNL-22323.pdf](http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-22323.pdf)

### **PNNL-22432 Initial Assessment of U.S. Refineries for the Purposes of Potential Bio-Based Oil Insertions**