DOE Bioenergy Technologies Office (BETO)  
2017 Project Peer Review

Refinery Integration
4.1.1.31 NREL
4.1.1.51 PNNL

March 7, 2017
Analysis and Sustainability

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PNNL

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

**GOAL:** develop detailed process models of three key petroleum refining conversion systems converting mixtures of conventional and biomass derived intermediates

**OUTCOME:** identify costs, opportunities, technical risks, information gaps, research needs associated with co-processing

**RELEVANCE:** reduce biofuel production costs through use of existing infrastructure

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Biomass → Bio-refinery Bio-intermediates

- Lipids
- Partially Hydrotreated Bio-oil
- HTL Biocrude
Quad Chart Overview

Timeline

» Start: October 1, 2014
» End: September 30, 2016
» Completion: 100%

Budget

<table>
<thead>
<tr>
<th></th>
<th>FY12-14 Costs</th>
<th>FY 14 Costs</th>
<th>FY 15 Costs</th>
<th>FY16 Costs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DOE Funded</strong></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>NREL</td>
<td>$0k</td>
<td>$128K</td>
<td>$200k</td>
<td>$199k</td>
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<tr>
<td>PNNL</td>
<td>$260k</td>
<td>$228k</td>
<td>$224k</td>
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</table>

Barriers Addressed

» **At-A** lack of transparent and reproducible analysis
  ☐ Publish models and results for use by stakeholders

» **Ct-K** Petroleum Refinery integration of Intermediates
  ☐ Assess economic and sustainability impacts
  ☐ Identify gaps and future research needed

Partners

» Partners:
  ☐ NREL (44%), PNNL (56%)

» External Reviewers:
  ☐ Refining catalyst vendor (2)
  ☐ Refinery #1 modeling contact (2)
  ☐ Refinery #2 modeling contact
  ☐ Refining industry independent contractor

» Assistance from Aspen Tech
Challenge: Lack of understanding of the economic viability, value proposition to the petroleum refiner, and technical risk for upgrading bio-derived intermediates through use of existing infrastructure

Question: How to assess the trade-offs for co-processing conventional petroleum feeds with biomass derived intermediates in a petroleum refinery?

Overall Objective: Develop suite of models to understand impacts, opportunities and gaps associated with co-processing

Technical Objectives (since FY15 peer review):

- Develop first-of-a-kind process models:
  - Updated hydrocracker (HCK) and fluidized catalytic cracker (FCC) models based on external reviewer comments
  - Expanded refinery units considered by adding hydrotreating (HT) models

- Assess biomass intermediates:
  - Expanded conversion pathways explored by including lipids and hydrothermal liquefaction biocrudes

- Conduct economic analysis: improved methodology based on reviewer input

- Publish results and findings (in process)
Approach (Management)

**Approach structure**
- Joint NREL and PNNL effort to **leverage capabilities** at both labs
- **Project Management Plan** and **Annual Operating Plans** in place
  - Quarterly **milestones** and **deliverables** (see additional slides)
  - Quarterly progress check-ins with BETO (teleconference)
  - BETO **Merit Reviewed**
  - **Go/No-Go** May 2015 allowing BETO to assess project value and direction

**Alignment with BETO Portfolio**

NREL & PNNL BETO Research
- Thermochemical Conversion
- Biochemical Conversion
- Algal Conversion

NREL & PNNL BETO Analysis
- Past analysis
  - NABC
  - PNNL Refinery Integration
- Current analysis
  - Thermochemical Analysis
  - NREL Refinery Blend Model

NREL/PNNL Refinery Integration Project

MODELS

COST DATA

Compositions
Conditions

NREL/PNNL BETO Research
Refinery Integration
(Future Experimental)
Approach (Technical)

Potential Challenges and Risk Mitigation

- **Researcher proximity**: 2 separate laboratories involved
  - Use same software platforms and revision levels
  - Regularly scheduled calls
  - Data exchanges

- **Oxygenated molecules compatibility** with petroleum feeds: work with ASPEN TECH to devise strategies within ASPEN HYSYS framework

- **Consistent and appropriate assumptions**:
  - Reviewed technical basis and economic assumptions at start of project with BETO
  - Reviewed assumptions with industry experts early on into project

Critical Success Factors

- **Engage stakeholders**
- **Make results public**
- **Deliver product on-time, on-budget**
Approach (Technical)

Detailed Process Models

Feedstock Composition (VGO/intermediate mix)
Operating Conditions
Conversion Yields

Aspen HYSYS®

Flow Rates

Excel for Raw Material Accounting

Cost

Estimated Value of Intermediate to a Refiner

Product Yield (LPG/Naphtha/Distillate/Heavy Oil)

BBL
Critical success factors: Stakeholder Review

- Feedback from refining experts necessary to ensure that models, methods and future plans were headed in the right direction
- Engaged 4 separate refining related entities
  - FCC catalyst vendor (2 contacts from same company: 1 with refining technologies and renewables expertise; 1 with expertise in FCC evaluations focusing on catalysts and feedstocks)
  - Refiner #1 (2 contacts from same company – one with FCC expertise and one with HCK expertise)
  - Refiner #2 (17 years in refining processes modeling research)
  - Retired refiners now working as independent consultants
- FY15-16:
  - Sent the FY14 year-end report document to all and Aspen models to those interested
  - Revised models and methods (details in upcoming slides) based on feedback
  - Also worked with Aspen Tech to improve modeling techniques
Technical Accomplishments

Key Milestone

Publishing Comprehensive Report: compilation of all work performed under this project.

Contents:

- Introduction
- Candidate Biomass Intermediates for Co-Processing
- Refinery Co-Processing Literature Review
- Potential Impacts with Co-processing in Petroleum Refineries
- Process Model Development
- Techno-Economic Modeling
- Sustainability Metrics
- Resource Assessment
- Conclusions and Recommendations
- References
- Appendices
Survey of Candidate Biomass Derived Intermediates

<table>
<thead>
<tr>
<th>Bio-intermediates</th>
<th># Properties Found</th>
<th>CHNOS</th>
<th>Density</th>
<th>Viscosity</th>
<th>TAN</th>
<th>Composition</th>
<th>Co-processing data</th>
<th># Independent Sources</th>
<th>HDO Data</th>
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<tr>
<td>Algae HTL</td>
<td>5</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>GC/MS</td>
<td>FCCU, HCK</td>
<td>3</td>
<td>✓</td>
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<tr>
<td>Algal LE</td>
<td>2</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
<td>% acids, triglycerides</td>
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<td>1</td>
<td>✓</td>
</tr>
<tr>
<td>Wood HTL</td>
<td>5</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>SimDis</td>
<td></td>
<td>3</td>
<td>✓</td>
</tr>
<tr>
<td>Stover HTL</td>
<td>4</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td>1</td>
<td>✓</td>
</tr>
<tr>
<td>HYP</td>
<td>4</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>GC/MS, SimDis</td>
<td></td>
<td>3</td>
<td>✓</td>
</tr>
<tr>
<td>CPO</td>
<td>5</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>GC/MS</td>
<td>✓</td>
<td>14</td>
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<tr>
<td>HDO (partial)</td>
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<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>GC/MS, SimDis</td>
<td>✓</td>
<td>4</td>
<td>✓</td>
</tr>
<tr>
<td>Biological Conv</td>
<td>4</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>SimDis</td>
<td></td>
<td>1</td>
<td>✓</td>
</tr>
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</table>

HTL=hydrothermal liquefaction; LE= lipid extracted; HYP=hydropyrolysis; CPO=catalytic pyrolysis; HDO=hydrodeoxygenation

Biomass Derived Intermediates Chosen for Study:

- Partially hydrotreated pyrolysis oil
- Triglycerides (new since FY15 review)
- HTL Biocrude (new since FY15 review)

Petroleum Derived Feed Chosen for Study:

Vacuum Gas Oil (VGO)
Review of Co-Processing Literature

► FCC – 12 publications
  - Blends of VGO with raw, catalytic and hydrotreated pyrolysis oil
  - Variety of conditions, catalysts, scales
  - Informed modeling, but trends difficult to discern

► Hydrocracking/Hydrotreating – 15 publications
  - Mostly related to co-processing of petroleum gas oils with vegetable-derived oils (lipid containing)
  - Variety of conditions and catalysts
  - Informed HYSYS modeling (described later)
  - Brief summary of commercial entities exploring lipid co-processing

► Fossil Lessons: Summarized methods and learnings from coal liquefaction oil co-processing work from late 1970 to early 1990’s

► Example lessons learned
  - Pre-fractionating wide-boiling intermediates allows more refinery entry points
  - Reinforced need to completely characterize biomass derived intermediates
  - Catalyst characterization beyond brief “proof of concept” needed
Technical Results
Refinery Impacts

Sampling of topics discussed in detail in the report

Potential benefits to Refiner

- Capacity relief to crude distillation capacity, FCC regenerator and wet gas compressor
- Reduced sulfur and nitrogen loads
- Reduced acid gas treatment load
- Economics and regulatory compliance

Potential risks to Refiner

- Catalysts impacts
- Thermal stability
- Miscibility
- Acidity and corrosion potential
- Presence of organic oxygenates
- Changes in maintenance and operations
**Technical Results**

**Model Development**

- **FCC** AspenPlus model: pure compounds, stoichiometric reactor
- 0%, 10%, 20% partially hydrotreated bio-oil blend with VGO

**Since FY15 Peer Review**

- Incorporated external reviewer input
- Added constraint scenarios to fixed feed rate cases
  - Char production constraint
  - Wet gas compressor constraint
- Collected sustainability metrics
- Transfer developed models in other BETO projects
**Technical Results**

**Model Development**

- **HCK** AspenPlus model using pure compounds and stoichiometric reactor
- 0%, 10%, 20% partially hydrotreated bio-oil blend with VGO

**Since FY15 Peer Review**

- Incorporated external reviewer input
- Added constraint scenario to fixed feed rate cases
  - Fixed H2 availability
  - Fixed reactor outlet temperature
- Collected sustainability metrics
- Transfer developed models for use in other projects
Technical Results
Model Development

- New since FY15 Review: HYSYS hydrotreating model using pseudo-components for VGO, pure compounds for triglycerides

- Feed: 0%, 10% and 20% blends
  - Kinetic model for triglycerides
  - HYSYS built in correlations for VGO
  - Triglyceride shift product distribution
New since FY15 Review: HYSYS hydrotreating model using pseudo-components for VGO and HTL biocrude derived from distillation curves, densities and heteroatom content

Feed: 0%, 10% and 20% blends

Reactions:
- Stoichiometric for biocrude oxygenate conversion
- HYSYS built in correlations for S and N reduction
**Technical Results Economics**

- **Improved analysis** per external reviewer feedback
  - Pricing basis a function of crude oil benchmark price (WTI)
  - **Answers:** At what crude price does co-processing become economically attractive to refiners (without policy incentives)

**FCC Co-Processing Example: Bio-Oil Breakeven Analysis**

### Value: Refinery Integration models + TEA enable valuations of bio-oils as refinery feedstocks vs. WTI

### Price: TEA from biomass to bio-oil intermediate defines price / cost to refiners
Also assessed as “effective MSP” (minimum selling price for intermediate) defined as:

\[
\text{Effective MSP (\$/Gal)} = \frac{\text{Bio-Oil Feedstock Cost (\$/Day)} - \Delta \text{FCC Gross Margin (\$/Day)}}{\text{Total FCC Liquid Products (Gal/Day)} \times \text{Biomass-Derived Products (%)}}
\]

**FCC example: “MSP” pricing**

- **@ WTI=$40/bbl**: 
  MSP values = $3.40-$4.00/gge

- **@ WTI=100/bbl**: 
  MSP < $3/gge

GGE = gasoline gallon equivalent
**Technical Results**

**Resource Assessment**

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**GOAL:** Improve FY13 study of potential co-processing fuel volumes

<table>
<thead>
<tr>
<th>Basis</th>
<th>FY13 Study</th>
<th>Improved FY16 Study</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Model Platform</strong></td>
<td>Spreadsheet</td>
<td>Integrated into existing Biomass Assessment Tool</td>
</tr>
<tr>
<td><strong>Biomass Resource</strong></td>
<td>• Billion Ton 2011</td>
<td>• Billion Ton 2016</td>
</tr>
<tr>
<td></td>
<td>• Scale: State level from aggregated county level data</td>
<td>• Scale: Farm level disaggregated from county level data</td>
</tr>
<tr>
<td></td>
<td>• 2022 projection</td>
<td>• Easy to do cost and year scenarios</td>
</tr>
<tr>
<td></td>
<td>• $60/ton</td>
<td></td>
</tr>
<tr>
<td><strong>Transport</strong></td>
<td>Not included</td>
<td>Road, barge and rail</td>
</tr>
<tr>
<td><strong>Intermediate</strong></td>
<td>Hydrotreated bio-oil (fixed yield; no costs)</td>
<td>HTL biocrude ($/gge vs scale; yields by biomass type)</td>
</tr>
</tbody>
</table>

**Example Result:**
- 2017 & 2022 and $60 & $80/ton scenarios
- Feasible bio-oil production: 8-14 BGY for least cost route

**Relevance:** New tool available for use with other BETO projects; can input other biomass intermediates

**Publication:** Manuscript in preparation to *Biofpr*
Technical Results
Gaps and Barriers

Sampling of Identified Gaps and Barriers:

► Technical Gaps and R&D needs:
  - No published experimental data for hydrocracking mixtures of VGO and bio-oil are available
  - Hydrocracker and hydrotreater yields and hydrogen consumption effects are limited for wide boiling type feeds
  - Limited experimental data for co-processing mixtures in FCC units are available; literature data show conflicting results
  - Physical property data are limited
  - Limited kinetic data for co-processing

► Modeling, Economic and Sustainability Analysis Gaps
  - Consideration of other, lower cost intermediates should be assessed in the future as data become available,
  - Investigate the level of upgrading to the bio-derived intermediate to meet the requirements for introduction into the refinery and the impact on sustainability metrics,
  - Investigate the cost and sustainability implications of transportation of the bio-derived intermediate to the refinery processing unit.
Project Goal: develop detailed process models of three key petroleum refining conversion systems converting mixtures of conventional and biomass derived intermediates

Project Importance:

- Use of existing infrastructure to reduce biofuel cost of production
- Prior to project, no available tools or publically available information to assess co-processing impacts (cost, risk, opportunities)
- This project developed needed tools:
  - First-of-a-kind models and methods for co-processing
  - Economic methods reflecting a range of crude oil scenarios/prices
  - Resource assessment tool to estimate potential fuel volumes
  - Vetted assumptions with industry and adopted feedback to consider additional real-world constrained scenarios

Models developed in this project helped to support inclusion of refinery integration state of technology case in 2017 MYPP
Supports BETO Strategic Plan (December 2016): “demonstrating, validating, and creating partnerships for petroleum refinery integration could be a critical cost-reduction strategy. This would minimize near- and mid-term capital expenditures risk by leveraging existing conversion and upgrading infrastructure”

Supports BETO Multi-Year Program Plan (March 2016) critical conversion research area to “Work with petroleum refiners to address integration of biofuels into refinery processes” and to reduce the cost of conversion to $3/gge by 2022.

**Ex situ catalytic pyrolysis conversion to fuel blendstocks example**

The capital cost associated with hydrotreating and hydrogen generation amounts to ~$0.50/gge in the standalone plant costs shown at left. These costs could be eliminated / greatly reduced through co-processing.
Project Relevance

Relevance to Bioenergy Industry

- Engaged key stakeholders in the industry for their review and feedback on underlying assumptions, and share their insight based on experience on the issues of risk and technical information needs for risk assessment
- Identified technical hurdles and integration barriers for potential private industry and BETO sponsored research and development
- Publication of methods and tools fills previously existing data gap

Technology transfer:

- Transferred models and methods to appropriate BETO projects for continued use/improvement towards understanding opportunities for renewable fuel cost reduction
- Publishing report and HYSYS models for use by stakeholders
Future Work

- Sun setting project, no further work under this project

- Models and methods will be used in other projects:
  - Existing conversion analysis projects at NREL and PNNL (thermochemical, biochemical, algae)
  - Planned new NREL/PNNL research project related to addressing data gaps identified from this project
**Summary**

**Overview:** Addressing the need to understand co-processing issues

**Approach:** Develop tools, share inputs between labs & review results with external experts, publish results

**Technical Accomplishments/Progress/Results - FY14-16**

- 3 refinery models (HCK, FCC, HT) developed
- 3 types of biomass intermediates (pyrolysis bio-oil, HTL biocrude, lipid feed) assessed
- Economic assessment method developed
- Resource assessment tool completed
- Publishing results
- Publishing example models

**Relevance:** by assessing use of existing infrastructure, this project aligns with BETO’s mission to reduce biofuel production costs. *Learnings and models will be transferred to other BETO projects*

**Future work:** project completed
Acknowledgements

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Resource Assessment
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Kyle Larson
Additional Slides

Response to reviewers comments
Publications and presentations
Project milestones
Modelling detail example
Abbreviations and acronyms
2015 Peer Review:

- “Not quite sure why FCC and hydrocracking were chosen”
- “Does the first round…suggest that there is an economically viable path to bio-oil integration in the refinery?”

Response:

- FCC and hydrocracking were chosen initially because biomass derived intermediates with a broad boiling range require molecular size reduction. Also, the use of FCC’s is expected to decrease with decreased gasoline demand (per EIA) and should have available capacity to handle biomass derived intermediates.

- Initial economics were based on heating value differences because of low confidence in Aspen-derived densities, as opposed to volume swell used by industry. Rather than publish results that would likely later change, it was decided to address this by developing a method that would overcome density issues and enable a more traditional approach to economics.
NREL/PNNL FY14-16 work

- Presented at AIChE Spring meeting (April 2015)
- Presented at AIChE Fall meeting (November 2016)
- Published comprehensive report (March 2017)
- Published HYSYS hydrotreating model (March 2017)
- Resource assessment article for peer reviewed journal underway (FY17)
## Milestones and Metrics

<table>
<thead>
<tr>
<th>Title/Description</th>
<th>Due</th>
<th>Completed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Define conventional feedstocks and up to 5 bio-intermediate streams to feed hydrocracker and FCCU processes (joint PNNL/NREL)</td>
<td>Dec-13</td>
<td>On-time</td>
</tr>
<tr>
<td>Complete base Aspen models for the 2 refinery processes (joint PNNL/NREL) to include a stoichiometric based reactor, heat integration and product separation and summarize in a brief (joint PNNL/NREL)</td>
<td>Mar-14</td>
<td>On-time</td>
</tr>
<tr>
<td>Complete co-processing cost estimates for at least two intermediates (oils with different oxygen contents)</td>
<td>Jun-14</td>
<td>On-time</td>
</tr>
<tr>
<td>Complete reviewed hydrocracker models with 2-3 process configurations (PNNL), FCC models with 2-3 process configurations (NREL) and report (PNNL/NREL) summarizing model assumptions, and outcomes identifying gaps, potential issues and opportunities for co-processing. - ML/DL).</td>
<td>Sep-14</td>
<td>On-time</td>
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<tr>
<td>Revise models (HCK PNNL and FCC NREL primary focus) to incorporate industrial/stakeholder reviewer feedback from FY14 and new literature/experimental data leading towards the Q2 deliverable and summarize in a brief to BETO</td>
<td>Dec-14</td>
<td>On-time</td>
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<tr>
<td>Define and use models (HCK PNNL primary focus; FCC NREL primary focus) to collect sustainability metrics (e.g. GHG emissions, net fossil energy consumption) that are relevant to BETO's economic and sustainability goals, and summarize in a brief to BETO</td>
<td>Mar-15</td>
<td>On-time</td>
</tr>
<tr>
<td>Go/No-Go decision: Model Utility</td>
<td>May-15</td>
<td>On-time</td>
</tr>
<tr>
<td>Joint NREL-PNNL publication including a literature review of refinery integration data, and key economic results with a focus on data gaps, roadblocks and opportunities for bio-fuel cost reduction</td>
<td>Sep-15</td>
<td>On-time</td>
</tr>
<tr>
<td>Consider alternative biomass derived feedstocks for co-processing, potentially produced from hydrothermal liquefaction or via fermentation, and develop hydrotreating model. Develop list of sustainability metrics to be collected and summarize in a brief to BETO</td>
<td>Dec-15</td>
<td>On-time</td>
</tr>
<tr>
<td>Complete base and co-feed hydrotreater models from Q1 FY16 and summarize in a brief to BETO</td>
<td>Mar-16</td>
<td>On-time</td>
</tr>
<tr>
<td>Complete biomass availability on a county level and proximity analysis to existing petroleum refineries for current and future scenarios; leverage HCK, FCC and hydrotreater model outputs. Summarize in a brief</td>
<td>Sep-16</td>
<td>On-time</td>
</tr>
<tr>
<td>Final deliverable: NREL, PNNL ANL white paper draft for publication</td>
<td>Sep-16</td>
<td>On-time</td>
</tr>
</tbody>
</table>
General comments:
- Reduce flowrates (or add capital) for blended feeds to account for process constraints such as
  - FCC coke make
  - HCK hydrogen availability
- Heating value vs. volume swell
- Re-evaluate co-product basis (gasoline & diesel fraction, vs offgas, LPG) and consider a range of values
- Consider fixed costs: labor, maintenance, depreciation in addition to variable costs

Unit specific comments
- FCC: heat balance methods; consider higher catalyst loss
- HCK: losses to light material; catalyst deactivation (increase cost or reduce throughput; consider heavy oil hydrocracker

Feedback on sensitivities
- Vary crude prices
- Capital expenses to accommodate 20 wt% bio-oil
- Re-consider 100% conversion of oxygenates and discount products accordingly
- Coke production in both units
- Other variable costs such as waste water treatment, gas clean-up, additional wastes

Feedback on data gaps
- Bio-oil and petroleum miscibility
- Metallurgy impacts
- Effect of oxygenates on pump seals

Feedback on data sources: parallels with other work
- Oil shale and tight oil pilot work
- Vegetable oil/triglyceride cc-processing work
- Coal liquid co-processing work
Abbreviations and Acronyms

- ANL: Argonne National Laboratory
- AOP: Annual operating plan
- BETO: Bioenergy Technologies Office
- BBL: Barrel
- FCC: Fluidized catalytic cracker
- GGE: Gasoline gallon equivalent
- HCK: Hydrocracker
- HT: Hydrotreating
- LCA: Life-cycle analysis
- MFSP: Minimum fuel selling price
- MSP: minimum selling price
- MYPP: Multi-year program plan
- NABC: National Advanced Biofuels Consortium
- NREL: National Renewable Energy Laboratory
- PMP: Project management plan
- PNNL: Pacific Northwest National Laboratory
- VGO: Vacuum gas oil