NREL
NATIONAL RENEWABLE ENERGY LABORATORY

NREL Thermochemical Platform Analysis





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on behalf of Abhijit Dutta, Jack Ferrell, and Eric Tan

U.S. Department of Energy
Bioenergy Technologies Office
2017 Project Peer Review
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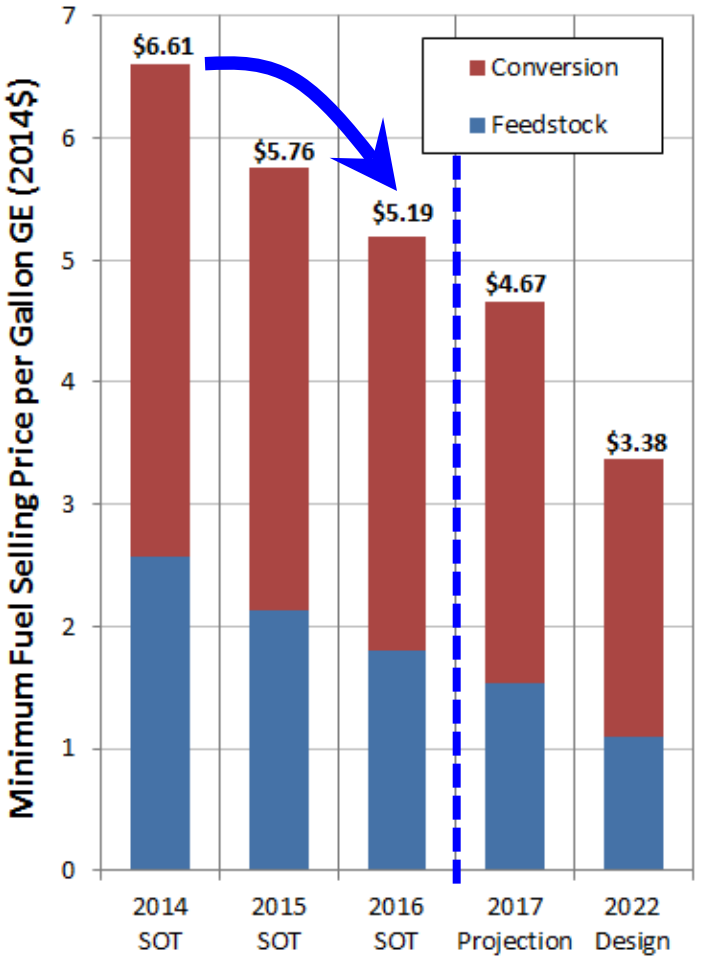
Goal Statement

- Provide process design and technoeconomic analysis (TEA) for the thermochemical conversion platform to **inform and guide NREL/BETO R&D priorities**
  - **Outcome: Enable consistent business metric** for comparing diverse biomass conversion options ($)
- Develop benchmark process models and economic-analysis tools to:
  - **Assess cost-competitiveness** and establish technical / cost targets for biofuels pathways
  - **Track progress towards targets** through annual state of technology (SOT) assessments
  - **Quantify sustainability metrics** associated with modeled biorefinery conversion operations
  - **Disseminate results and learnings** from rigorous, objective modeling and analysis in a transparent manner (design report and SOT process)



Example: *Ex situ* catalytic fast pyrolysis "waterfall plot" shows how TEA is used to quantify and track R&D impact

Quad Chart Overview

Timeline for TC Platform Analysis

Start Date	October 1, 2016
End Date	September 30, 2019
% Complete	10% (4 months of 3 years)

Budget (WBS 2.1.0.302)

	FY2012 –FY2014 Costs	FY2015 Costs	FY2016 Costs	Planned FY2017 End Date
DOE Funded	$3,030k	$2,000k	$1,900k	*$5,850k (Request)*
Cost Share	No cost share (100% DOE-BETO funding)			

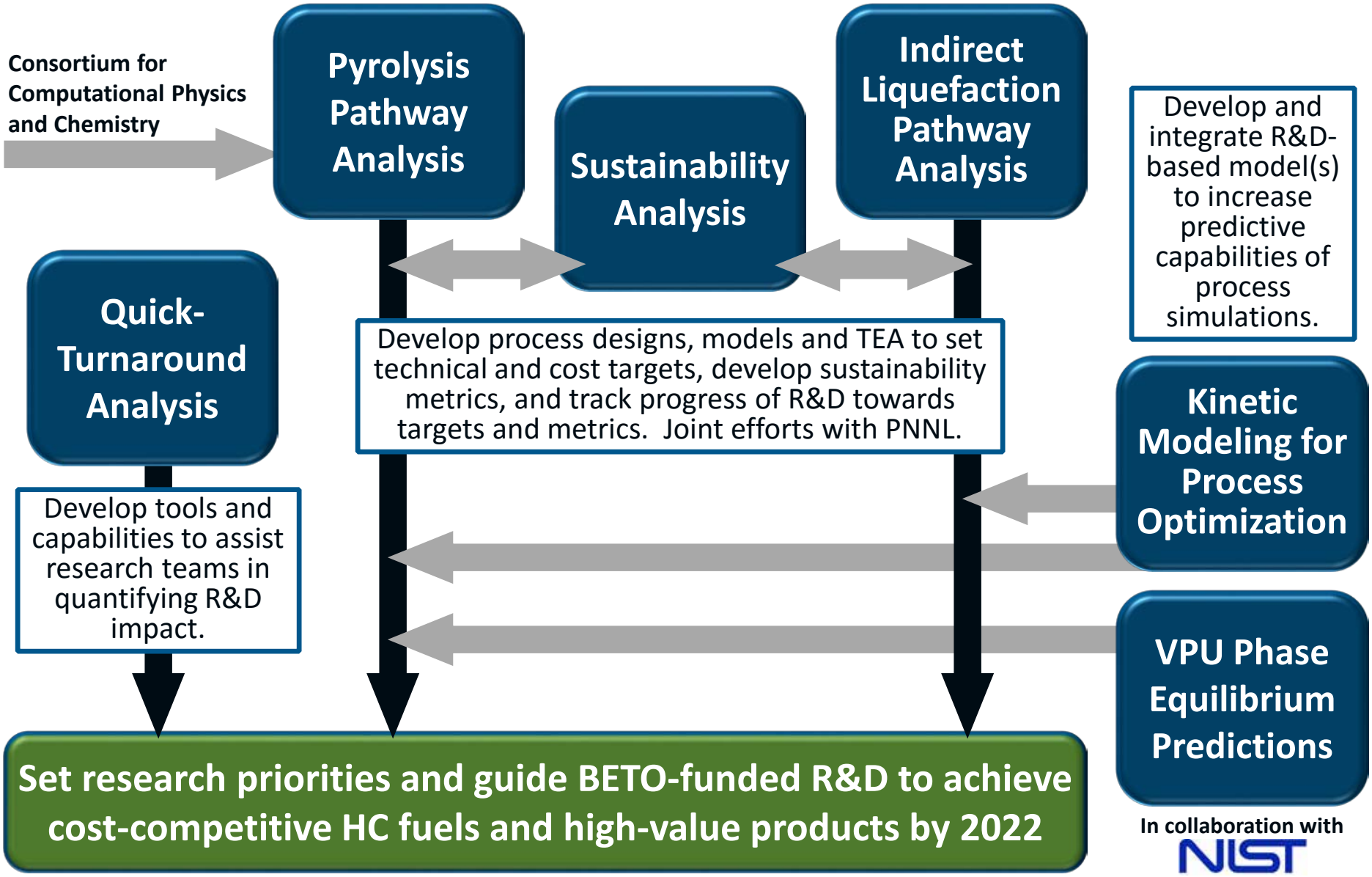
Barriers Addressed by Quantifying, Informing, and Guiding R&D:

Tt-R. Process Integration, Tt-F. Deconstruction to Bio-Oils, Tt-J. Catalytic Upgrading of Bio-Oils, Tt-H. Bio-Oil Stabilization and Vapor Cleanup, Tt-I. Catalytic Upgrading of Syngas

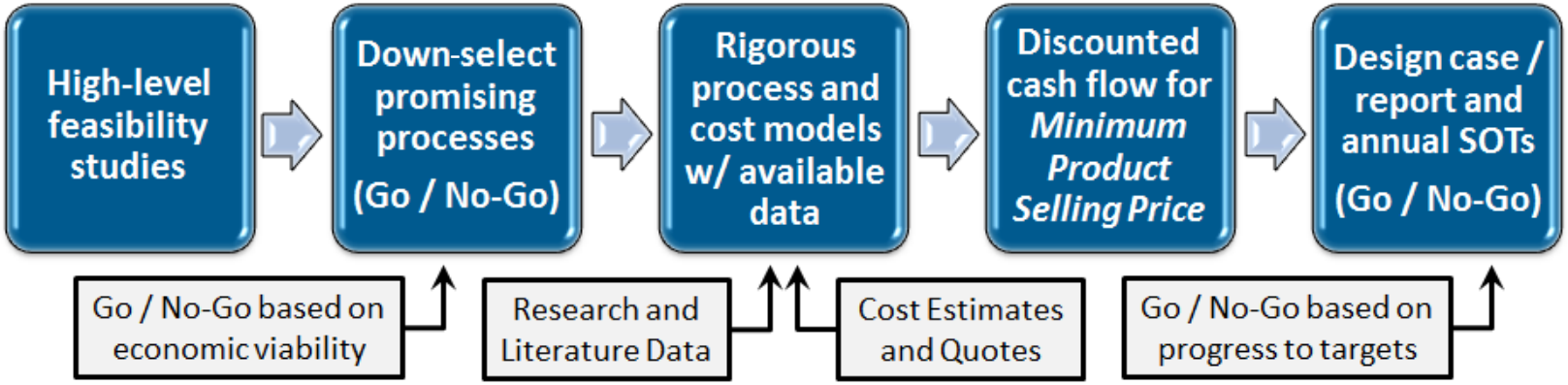
Partners

- NREL (experiments and research)
- PNNL (TEA / sustainability analysis)
- Idaho National Lab (feedstock)
- Harris Group Inc. (capital cost estimates)
- DWH Consulting (capital costs / engineering)
- NIST (phase equilibrium modeling)
- Colorado School of Mines (reactor modeling)
- Consortium for Computational Physics and Chemistry (reactor modeling)
- Johnson Matthey (catalyst technologies)
- Petrobras (petroleum refiner) via CRADA

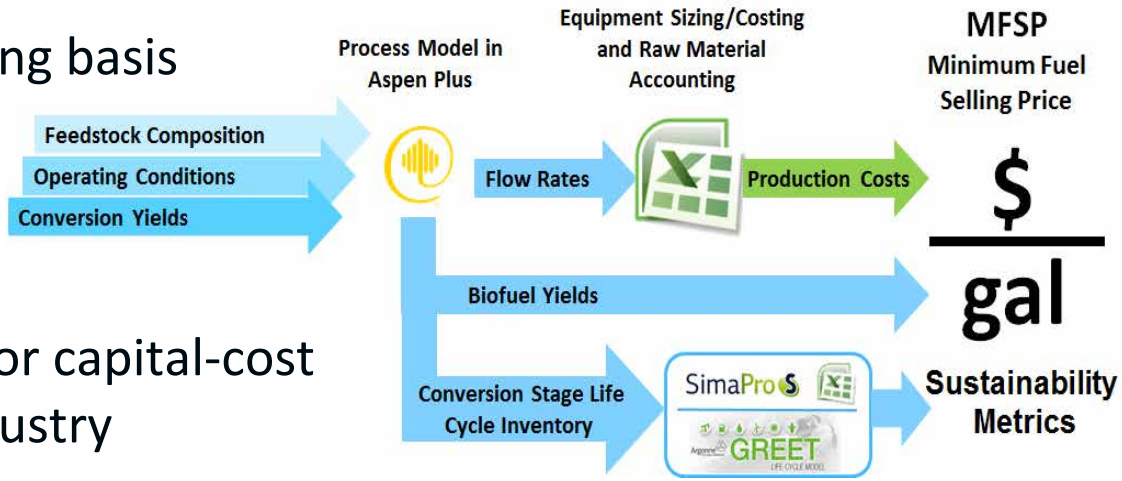
Project Overview



Technical Approach

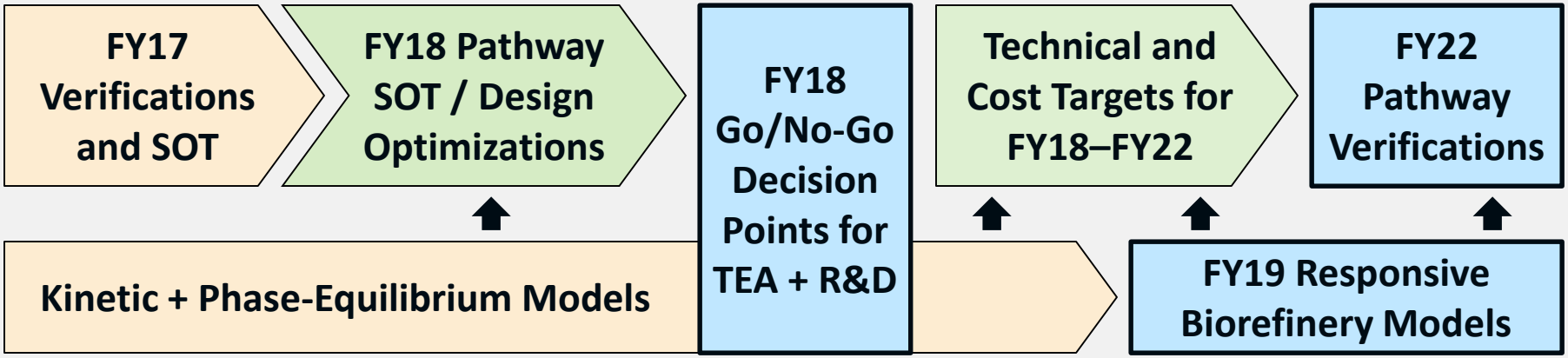


- **R&D Priorities ➔ R&D Advances ➔ Improved Yields ➔ Optimized Processes ➔ Reduced MFSP**
- Process model in Aspen Plus based on BETO-funded research data, published literature, and industry input
- n^{th}-plant operating and financing basis to represent mature industry
- Discounted cash-flow analysis to calculate MFSP
- Credibility of analysis via vendor capital-cost estimates and vetting with industry



Management Approach

Annual Operating Plan (AOP) defines Milestones, Schedule, and Go/No-Go points



Critical Success Factors

- **Set research priorities and technical targets that results in reduced MFSPs**
- Publish **conceptual biorefinery designs** for cost-competitive and sustainable biofuels and bio-products
- Provide feedback to research team(s) on **alternative R&D strategies and priorities**
- Assess **infrastructure integration** concepts
- **Timely responses** to clients and partners

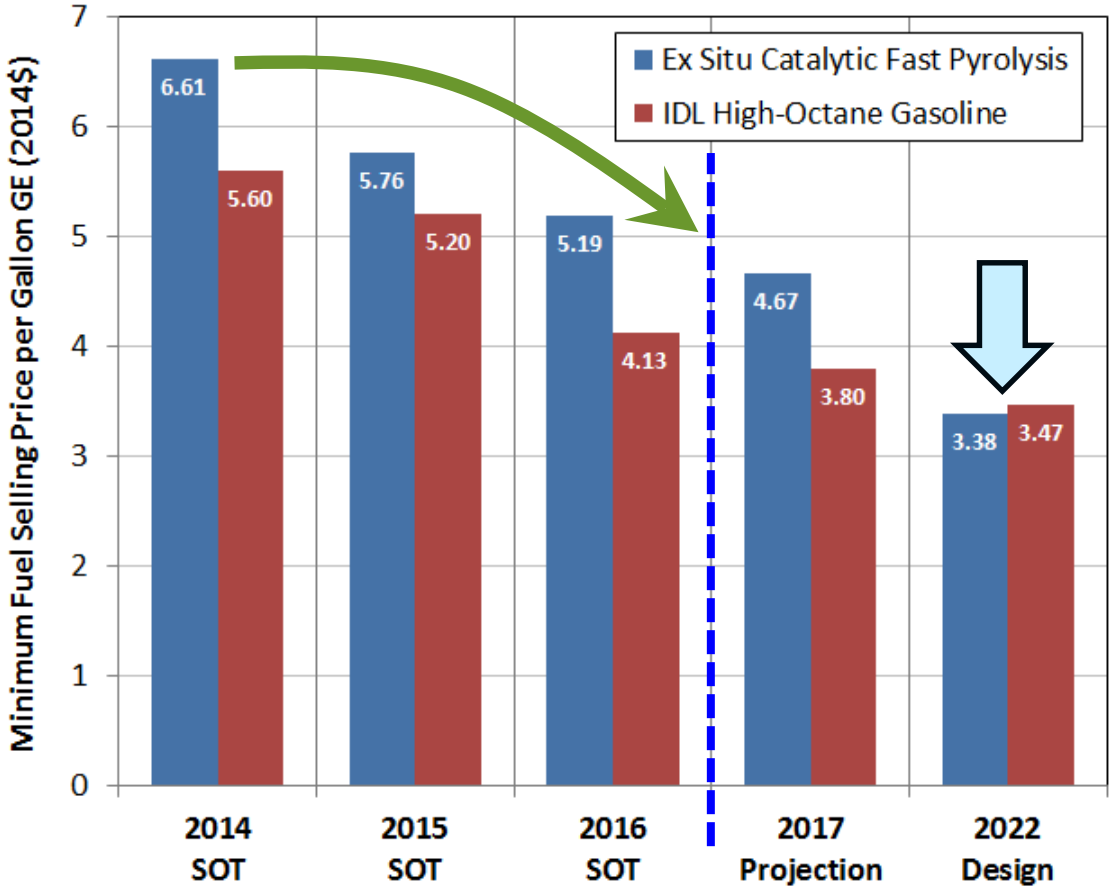
Technical Challenges [Mitigation]

- Work with **limited data** during early stages **[sensitivity analysis]**
- Design process models with capabilities for assessing **alternate R&D approaches [versatile models with adaptability]**
- Balance **rigor** with **time and budget [impact-specific efforts]**
- Data for **process optimization [R&D-based models + strategic partnerships]**

Technical Accomplishments: Progressing to Targets

Analysis is used to track impact and guide direction of R&D

- Compare different technologies on consistent business basis ($)
- Set targets with R&D teams
- Quantify impact of R&D advances
- Feedback to R&D based on sensitivities and alternative process designs



Target cases published in joint design reports (PNNL, INL)

Incorporate R&D advances into models to quantify impact

Enable sensitivity analysis and design alternatives through model flexibility

Technical Accomplishments: Integrating BETO R&D

Leveraging **prior R&D** for gasification and syngas clean-up

R&D on upgrading intermediates

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Assessing options for **distillate fuels**

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Alternative process designs and **infrastructure integration** strategies and models

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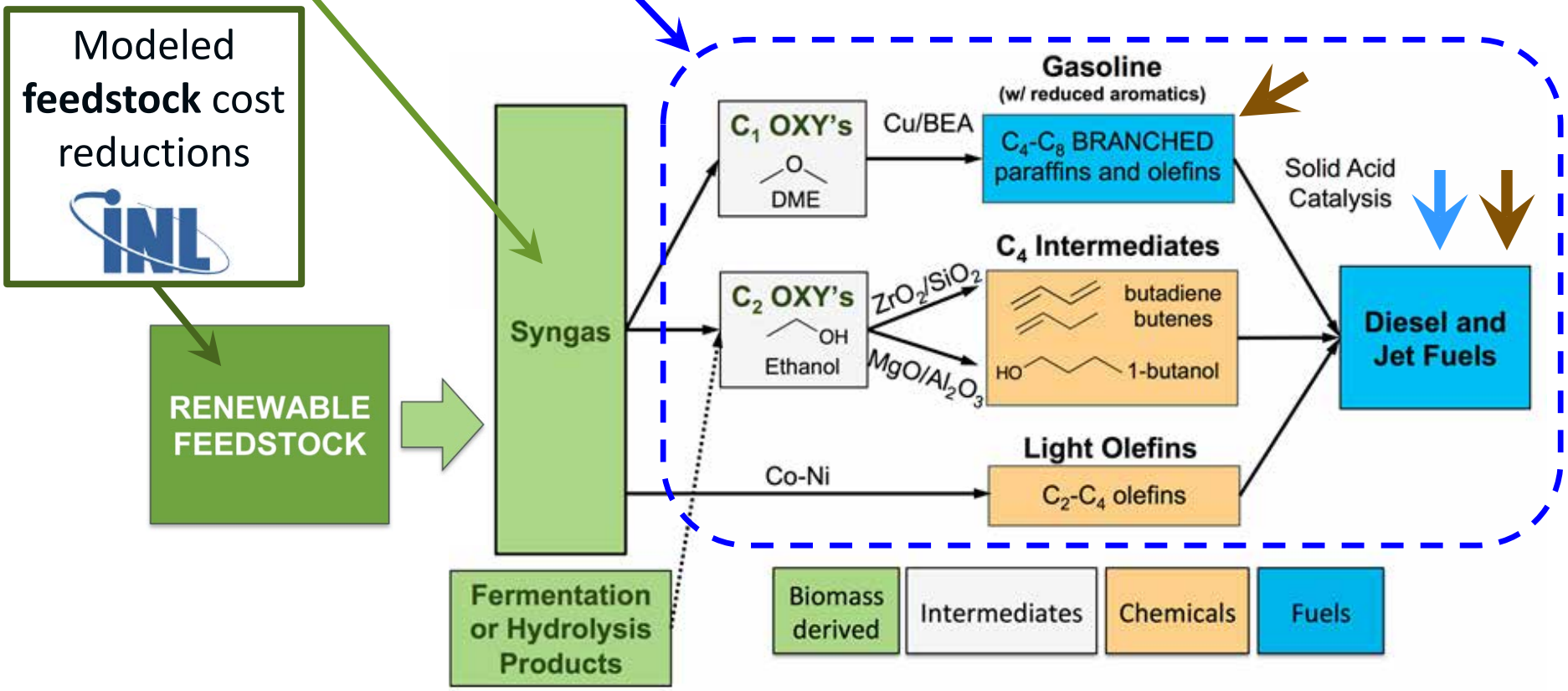
PETROBRAS

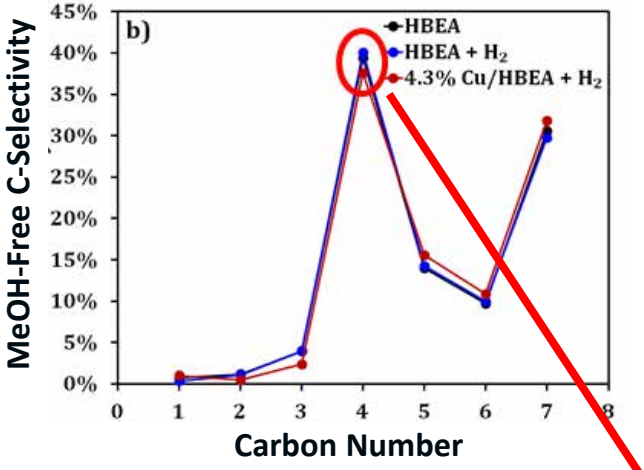
Modeled **feedstock** cost reductions

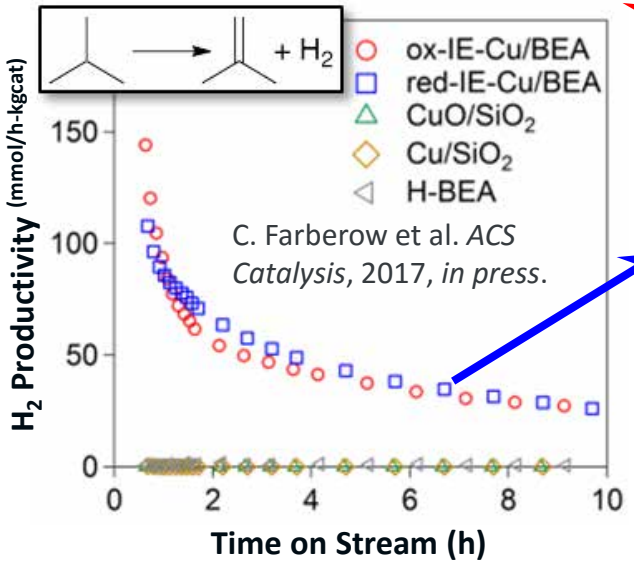
INL

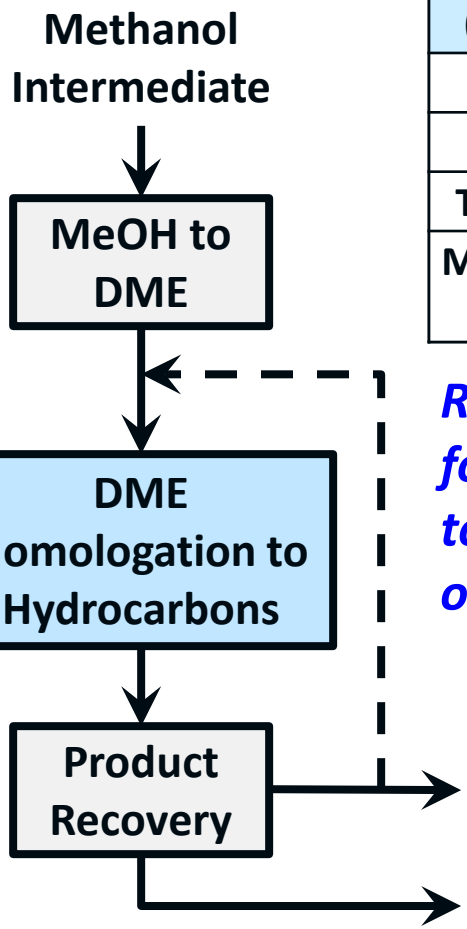


Technical Accomplishments: IDL HOG C_4 Recycle

TEA informed R&D to target recycle, reactivation, and reincorporation of C_4 compounds to maximize C_5+ yield.







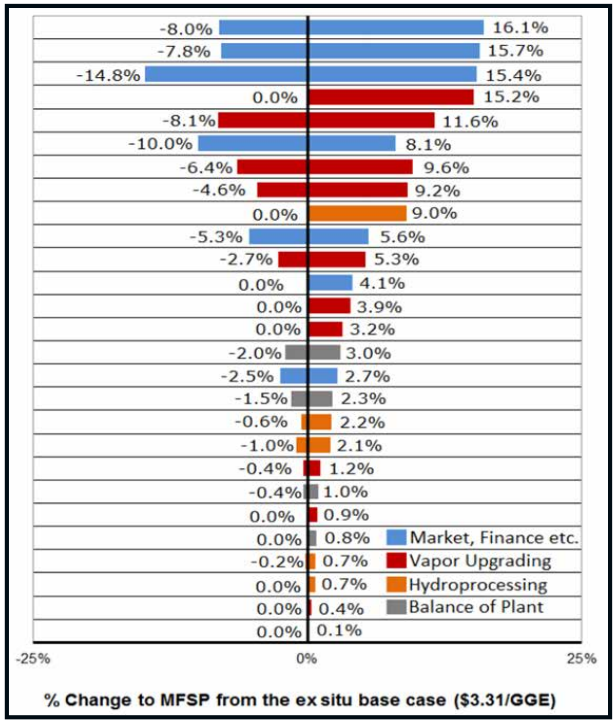
Yields (Gal / Ton)	2015 SOT No Recycle	2016 SOT C_4 Recycle
Mixed–C_4	18	0
Gasoline	40	61
Total Liquid	58	61
$MFSP_{Conversion}$ ($/GGE)	$3.30	$2.55

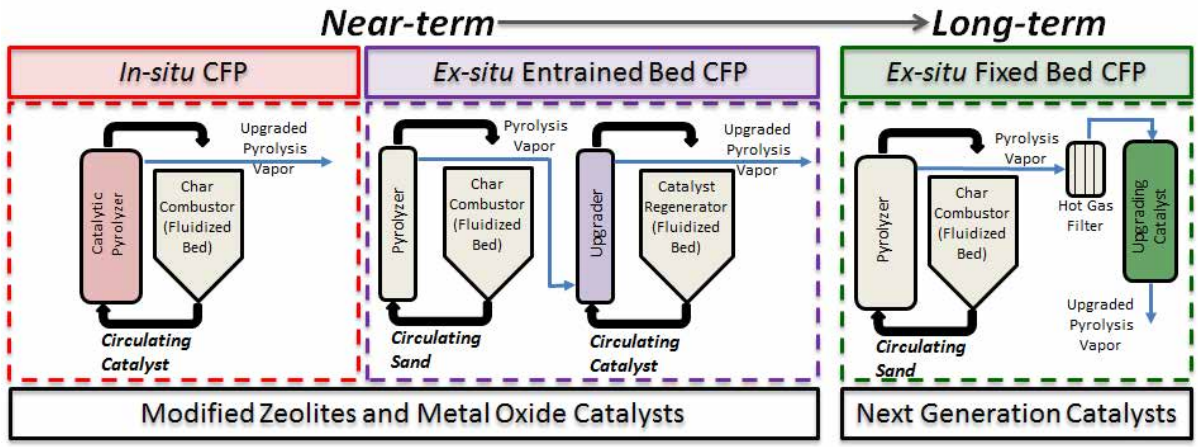
R&D advanced catalyst activity for isobutane dehydrogenation to enable recycle and maximize overall yield of target product.

Technical Accomplishments: Sensitivities & Alternatives

Analysis to prioritize R&D and assess alternative process configurations

- "Tornado plots" from sensitivity analysis quantify impacts of major technical parameters
- Develop alternative process options to address major technical targets
  - Olefin coupling for IDL jet/diesel products
  - Fixed-Bed Ex Situ CFP design





Abhijit Dutta, Joshua A. Schaidle, David Humbird, Frederick G. Baddour, Asad Sahir. ***Conceptual Process Design and Techno-Economic Assessment of Ex Situ Catalytic Fast Pyrolysis of Biomass: A Fixed Bed Reactor Implementation Scenario for Future Feasibility*** http://link.springer.com/article/10.1007/s11244-015-0500-z

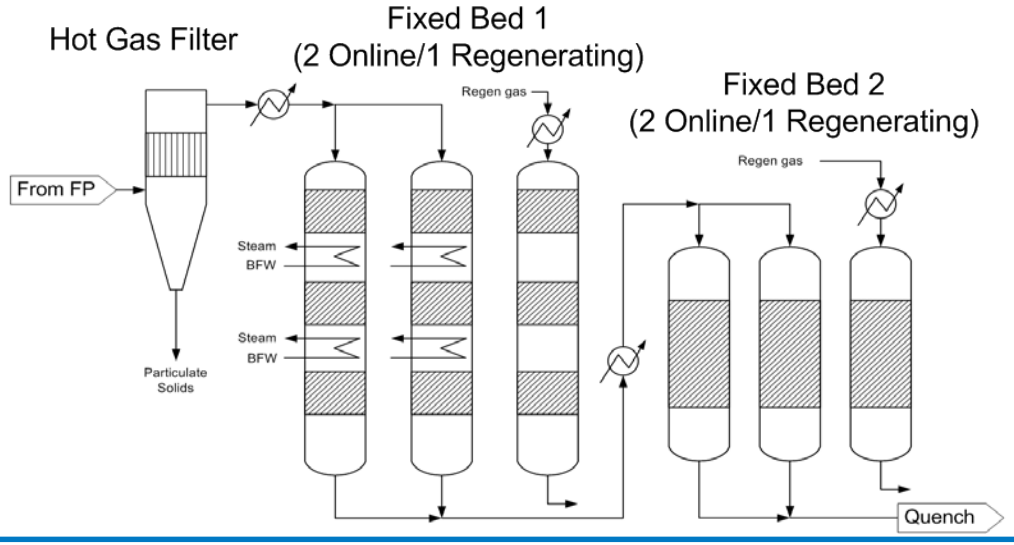
Technical Accomplishments: Fixed Bed Ex Situ CFP

Potential Fixed Bed Design Advantages

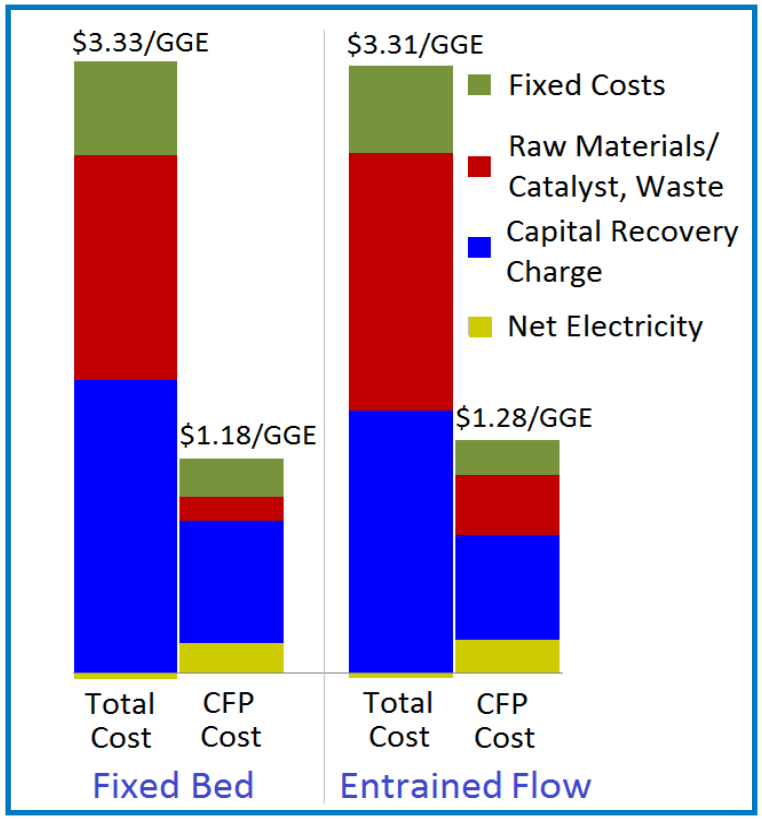
- Catalyst flexibility
  - o Precious metals
- Targeted chemistry
  - o Staged reactors / catalyst beds
  - o Grading for activity and poisons
  - o Tuned selectivity

Key Research Needs Identified by TEA

- Prove targeted chemistry on pyrolysis vapors
- Minimize coking
- Minimize cracking
- Develop efficient regeneration
- Reclaim spent catalyst precious metals effectively



Modeled cost comparison of fixed bed and entrained flow *ex situ* designs with *similar target yields*



Fixed Bed CFP is viable and will be further pursued in project

References: Fixed Bed System, *Topics in Catalysis* (2016), 59:2–18; Entrained Bed System, 2015 Design Report http://www.nrel.gov/docs/fy15osti/62455.pdf

Relevance: Providing Business Perspective to R&D

- **Directly informs, supports, and guides BETO-funded R&D** for cost-competitive fuels and products via TC pathways
  - Defines targets and track R&D progress with consistent metrics
  - Sensitivity analysis and alternate process designs to reduce risk
  - Guide research teams to redirect R&D strategies
  - Publish industry-vetted analysis to inform industry stakeholders
- **Increasing predictive capabilities** of process models
- Incorporating **BETO-wide R&D** and **cross-cutting analysis** to achieve **responsive biorefinery designs**
  - Multiple feedstocks
  - Multiple pathways and products
  - Optimizable models
  - Responsive to varying market conditions
- **Models & analysis tools available to industry stakeholders**

Future Work: Near-Term

Platform Analysis to Guide R&D Towards Cost Targets

- CFP and IDL SOTs (TEA and Sustainability)
- Evaluate Alternative R&D Strategies
  - Aqueous Carbon Valorization
  - Biorefinery Scaling Analysis
  - Recycling Light Ends and NG Co-Feeding
  - Membrane Separations
  - Refinery Co-Processing
- Increase modeling capabilities for optimization and infrastructure integration
  - Kinetic Models for DME Homologation and Olefin Coupling
  - Improved Pyrolysis LLE and VLE Models
  - FCC, Hydrocracking and Hydrotreating Models

    (Petrobras and NREL/PNNL Strategic Analysis Refinery Integration)

Future Work: Long-Term

Integrate BETO-wide R&D and analysis to achieve industry-relevant, market-responsive biorefinery designs

TC Feedstock Interface: Feedstock yields versus type and quality

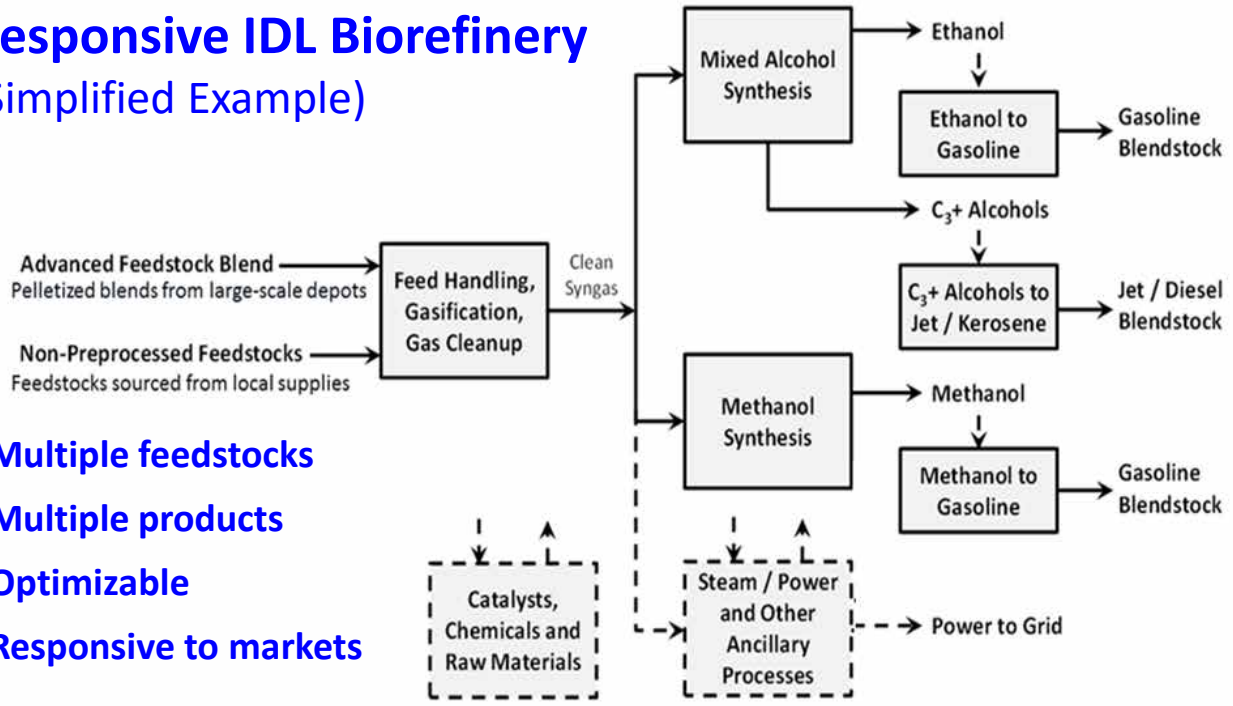
Conversion R&D: Improve and demonstrate yields for products via multiple pathways

Integration: Blending and co-processing in refinery units

TC Platform Analysis Model Development: Enable optimization with kinetic and VLE/LLE models

Cross-Cutting Analysis and Sustainability: Co-optimization of TEA and supply-chain sustainability

Responsive IDL Biorefinery
(Simplified Example)



- **Multiple feedstocks**
- **Multiple products**
- **Optimizable**
- **Responsive to markets**

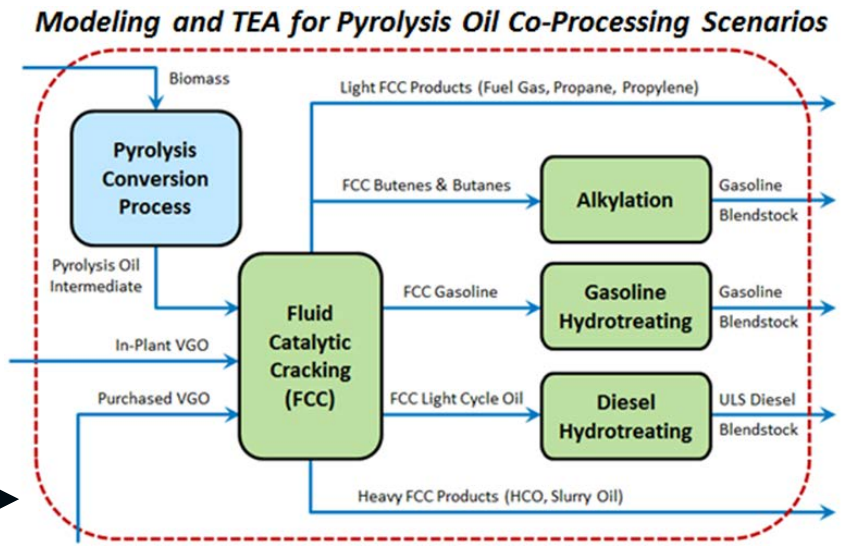
Future Work: Supporting Activities

Integrate R&D and Analysis to Achieve BETO Targets

- Quantify technical, cost, and sustainability metrics
- Alternative scenarios to increase probability of achievement
- Deliver timely and highly informative responses to BETO / partners
- Continue to integrate sustainability metrics into analyses
- Publish results in NREL / PNNL reports, BETO MYPP, and journals
- Continue to develop and maintain partnerships with industry

Develop New Capabilities

- Quick-turnaround analysis (QTA)
- Product quality analysis and tools
- Infrastructure integration analyses →



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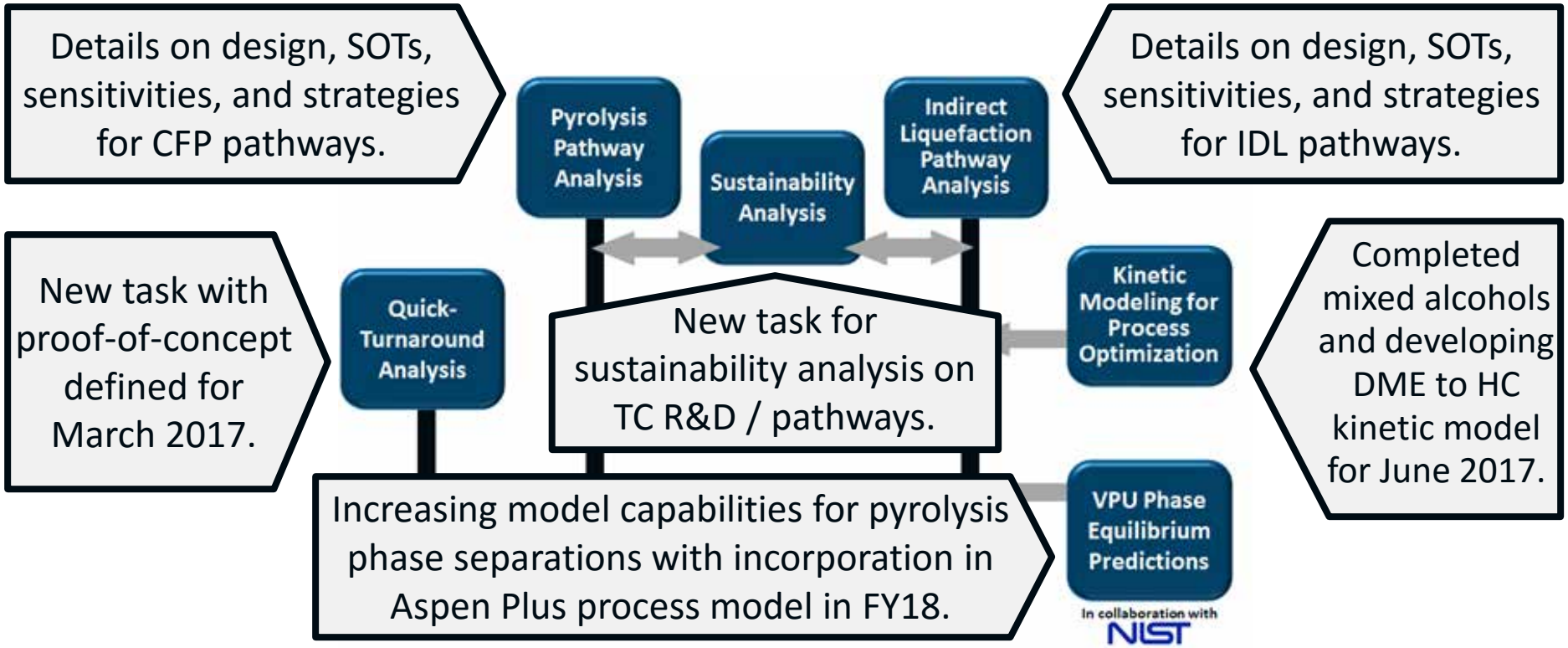
Additional Content for Reviewers

- Overview of Additional Accomplishments
- Project Abstract and Principal Investigator Biography
- Completed and Future Project Milestones
- Responses to 2015 Peer Review Comments
- Publications and Presentations Since 2015 Peer Review
- Contacts for NREL TC Platform Analysis Projects
- Related Projects
- Industrial Partners
- Additional Slides on Tasks and Other Analysis

Overview of Additional Accomplishments

Note: For more information on NREL TC Platform Analysis and related R&D, please review **additional project content following the presentation.**

Publications and Presentations | **Completed and Planned Milestones** | **Related Projects & Industrial Partners** | **Additional Content for Tasks in Project**



Project Abstract and PI Biography

NREL Thermochemical Platform Analysis (WBS 2.1.0.302)

NREL Thermochemical Platform Analysis (WBS 2.1.0.302) provides process design and techno-economic analysis (TEA) for the Thermochemical Conversion Platform to inform and guide NREL/BETO research and development (R&D) priorities. TEA provides a consistent, business-relevant basis for comparing diverse conversion options through use of process and economic models which translate key technical parameters into overall economics (dollars and cents). TEA results are used for setting future R&D targets and evaluating experimental progress and any deficiencies against those targets. Outcomes of integrated TEA modeling are utilized by BETO to guide program plans, and by other NREL/partner projects to quantify the impact of research on key technology barriers.

This work is highly relevant to BETO goals as TEA directly informs, supports and guides R&D for cost-competitive fuels and products. By providing a framework to translate technical performance into cost reductions within conceptual biorefinery designs, our TEA models are leveraged to direct R&D towards the most economically impactful outcomes.

This project has made major achievements since 2015 Peer Review, including completion of State of Technology assessments to quantify R&D cost reductions on catalytic fast pyrolysis and indirect liquefaction pathways, sensitivity analysis for process alternatives, development of new analysis capabilities, and future scope for developing complex, industry-relevant, market-responsive biorefinery designs.

Michael Talmadge, Principal Investigator

Michael (Mike) Talmadge is a Senior Process Engineer in the National Bioenergy Center (NBC) at NREL. Mike earned a BS in Chemical Engineering from the Pennsylvania State University in 1999 and an MBA from Villanova University in 2010. Mike has 16 years of experience in fuel production technologies with the first decade of his career spent in petroleum refining process technology development and operations with ExxonMobil Research and Engineering Company and Valero Energy Corporation. Since joining NREL in 2010, Mike has supported the development of biomass–derived fuel technologies through process modeling and techno– economic analysis of pathways from biomass to fuels and products. He has also contributed to the development of strategies to incorporate biomass–derived intermediates and finished fuel blendstocks into existing petroleum refining infrastructure through the NABC and collaborative work with Petrobras. Mike has led the NREL Thermochemical Platform Analysis project as Principal Investigator since early 2015.

NREL Employee Webpage: http://www.nrel.gov/bioenergy/bios/michael-talmadge.html

Completed Milestones (FY2015)

Milestone Type	Milestone Name and Description	Due Date and Status
Quarterly Progress Measure	(Task 1: Pyrolysis) Inclusion of the impact of alkali on the pyrolysis of cellulose into fast pyrolysis reactor model. This work will modify the currently implemented literature-based kinetic model to capture yield trends observed in experiments with potassium-impregnated cellulose.	12/31/2014 Completed
Quarterly Progress Measure	(Task 1: Pyrolysis) State of Technology (SOT) assessment based on the FY14 in situ/ex situ fast pyrolysis vapor upgrading design case. Include current research information into the process model and document scale-up assumptions for calculating current product cost for the process. The analysis team will provide preliminary SOT analysis results to BETO prior to the March 2015 peer review. The final milestone report will include sustainability metrics for the conversion process.	3/31/2015 Completed
Quarterly Progress Measure and Go / No-Go	(Task 2: Gasification) State of Technology (SOT) assessment based on the FY14 biomass to high-octane gasoline design report. Include current research information into the process model and document scale-up assumptions for calculating current product cost for the process. The analysis team will provide preliminary SOT analysis results to BETO prior to the March 2015 peer review. The final milestone report will include sustainability metrics for the conversion process.	3/31/2015 Completed
Quarterly Progress Measure	(Task 4: Syngas Modeling) Develop a kinetic model for mixed alcohol synthesis on a K-CoMoSx catalyst along with parameter estimation using bench-scale data sets collected for the 2012 mixed alcohols demonstration. At least two (2) data sets that were not run as replicates of any of the data sets used for parameter estimation will be used to compare model predictions with experimental results to show model effectiveness.	4/30/2015 Completed
Annual Milestone	(Task 1: Pyrolysis) Analysis of research scenarios for in situ/ex situ fast pyrolysis vapor upgrading. This study will include analysis to show the impacts of alternate process operations compared to the base case outlined in the FY14 design report; alternates will include the use of (1) hot gas filters, (2) fixed bed upgrading reactors in addition to other identified options based on research results. The purpose of this milestone is to provide analysis for research alternatives that were not captured in the FY14 design report base case. The results will be compared with the FY14 design report and FY14 State of Technology along with identification of research targets for cost-competitiveness with at least one of the alternate process configurations.	6/30/2015 Completed
Quarterly Progress Measure	(Task 2: Gasification) Prepare a draft report for peer reviews documenting one (1) biomass conversion pathway via gasification of biomass and using the produced syngas for the production of oxygenated intermediates with further conversion to hydrocarbons for use in liquid fuel blends. The report will document in detail one (1) base target case showing key process metrics that need to be met for the base case scenario in order to enable the production of cost-competitive transportation fuels from biomass. Joint milestone with PNNL.	7/15/2015 Completed

Completed Milestones (FY2015 *continued*)

Milestone Type	Milestone Name and Description	Due Date and Status
Quarterly Progress Measure	(Task 3: TEA Assessments) Develop milestone report, building on data mined in FY14. This milestone report will be focused on process models and economic analysis for current SOT basis, target basis, identified data gaps to address as well as provide recommendations for path forward for at least two (2) direct liquefaction pathways.	9/30/2015 Completed
Quarterly Progress Measure	(Task 5: Pyrolysis Upgrading Phase Equilibrium) Report on relevant compounds identification by NREL, recommendations by NIST-TRC for liquid-liquid equilibrium experiments, and the status of experimental work by third-party subcontractor.	9/30/2015 Completed
Annual Milestone	(Task 2: Gasification) Submit to BETO for publication approval after addressing comments from external peer reviews a report documenting one (1) biomass conversion pathway via gasification of biomass and using the produced syngas for the production of oxygenated intermediates with further conversion to hydrocarbons for use in liquid fuel blends. The report will document in detail one (1) base target case showing key process metrics that need to be met for the base case scenario in order to enable the production of cost-competitive transportation fuels from biomass. Joint milestone with PNNL.	9/30/2015 Completed
Quarterly Progress Measure	(Task 2: Gasification) State of Technology assessment for the biomass to high-octane gasoline pathway based on FY15 experimental results. Include current research information into the process model and document scale-up assumptions for calculating current product cost for the process. Sustainability metrics for the conversion process will be included.	10/26/2015 Completed
Quarterly Progress Measure	(Task 1: Pyrolysis) State of Technology assessment for the in situ/ex situ fast pyrolysis vapor upgrading pathways based on FY15 experimental results. Include current research information into the process model and document scale-up assumptions for calculating current product cost for the process. Sustainability metrics for the conversion process will be included.	11/13/2015 Completed
Quarterly Progress Measure	(Task 5: Pyrolysis Upgrading Phase Equilibrium) Provide proof of concept of LLE predictions using data for a set of surrogate compounds with functional groups relevant to fast pyrolysis oils/upgraded oils, and at least one physical property method. The data used may be from existing literature sources or experiments. Predictive capabilities will be tested by generating predictions for similar, but not identical compound/data sets used for model parameters development; these model predictions will be compared with relevant experimental data that is available.	12/31/2015 Completed

Completed Milestones (FY2016)

Milestone Type	Milestone Name and Description	Due Date and Status
Quarterly Progress Measure (Regular)	Task 1: Pyrolysis – State of Technology determination for the ex situ catalytic fast pyrolysis pathways based on FY15 experimental results. Include current research information into the process model and document scale-up assumptions for calculating current product cost for the process. Include sustainability metrics for the conversion process as well. QPM will be communicated to BETO through written, internal technical report.	11/13/2015 Completed
Quarterly Progress Measure (Regular)	Task 2: Indirect Liquefaction – State of Technology determination for the Thermochemical Pathway to High-Octane Gasoline Blendstock Through Methanol / Dimethyl Ether Intermediates based on FY15 experimental results. Include current research information into the process model and document scale-up assumptions for calculating current modeled product cost for the process. Include sustainability metrics for the conversion process as well. QPM will be communicated to BETO through written, internal technical report.	12/4/2015 Completed
Quarterly Progress Measure (Regular)	Task 4: Pyrolysis Upgrading Phase Equilibrium – Provide proof of concept of LLE predictions using data for a set of surrogate compounds with functional groups relevant to fast pyrolysis oils/upgraded oils, and at least one physical property method. The data used may be from existing literature sources or experiments. Predictive capabilities will be tested by generating predictions for similar, but not identical compound/data sets used for model parameters development; these model predictions will be compared with relevant experimental data that is available.	12/31/2015 Completed
Annual Milestone (Regular)	Task 1: Pyrolysis, Task 3: Syngas Conversion Modeling, Task 4: Pyrolysis Upgrading Phase Equilibrium – Evaluations of Go / No-Go for listed Tasks / projects. Refer to “Go / No-Go Decisions” section for details and criteria. Go/No-Go for Task 2 (IDL) was successfully completed in March 2015.	3/31/2016 Completed
Quarterly Progress Measure (Regular)	Task 1: Pyrolysis – Provide techno-economic analysis for at least two (2) research approaches, outside the current scope of research pathways outlined in the FY14 design report (NREL/TP-5100-62455). These analyses will require modifications to process equipment, heat balance and development of cost reduction strategies. Demonstrate how required modifications to the design in NREL/TP-5100-62455 will impact the process and conversion costs. Alternative options may include valorization of aqueous waste stream and fractional condensation.	6/30/2016 Completed

Completed Milestones (FY2016 *continued*)

Milestone Type	Milestone Name and Description	Due Date and Status
Quarterly Progress Measure (Regular)	Task 3: Syngas Conversion Modeling – Determine kinetic parameters needed as input for a kinetic model of high-octane gasoline synthesis. Compile all readily available parameters. Develop a plan for obtaining values of all other kinetic parameters from density functional theory calculations, correlations in the literature and/or experimental data fitting.	6/30/2016 Completed
Annual Milestone (Regular)	Task 1: Pyrolysis – Beginning with the surrogate compounds in the FY14 design report (NREL/TP-5100-62455) and available experimental information, outline at least two (2) potentially viable options for integration of intermediate products and/or finished blendstock from ex situ catalytic fast pyrolysis into the existing refinery infrastructure while meeting relevant product specifications (ASTM). This milestone will help set product specifications for anticipated FY17 updates to the FY14 design report. It is anticipated that sufficient data may not be available for a complete specification; educated assumptions will be made to cover uncertainties.	8/30/2016 Completed
Quarterly Progress Measure (Regular)	Task 4: Pyrolysis Upgrading Phase Equilibrium – Development of NIST-modified predictive model(s) for liquid-liquid equilibrium (LLE) predictions involving water-hydrocarbon-oxygenate systems. In addition to water and hydrocarbons, model development will consider key oxygenated functional groups; emphasis will be on a subset of predominant functional groups present in vapor-upgraded pyrolysis oils. Description of the benefits of LLE experiments conducted thus far on the improvement of predictive capabilities will be included, with the example(s) of one or more specific system of compounds.	9/30/2016 Completed
Quarterly Progress Measure (Regular)	Task 1: Pyrolysis – Prepare a report that summarizes new and novel technologies being developed outside of core-BETO funded efforts. This report will summarize these technologies and highlight their potential to improve the economics and/or sustainability of the liquefaction process designs, as well as discuss their potential for implementation at commercially relevant scales.	9/30/2016 Completed

TC Analysis FY2016 Go / No-Go Summary

"Go" recommendations per achievement of Go / No-Go Criteria

- Pyrolysis Pathway Analysis (Task 1)
- Syngas Conversion Modeling (Task 3)
- Pyrolysis Upgrading Phase Equilibrium (Task 4)

Note: IDL Pathway Analysis had FY15 Go / No-Go

Pyrolysis Pathway Analysis:
Design Report and targets published. Continue developing process alternatives.


NREL

Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels
Thermochemical Research Pathways with *In Situ* and *Ex Situ* Upgrading of Fast Pyrolysis Vapors

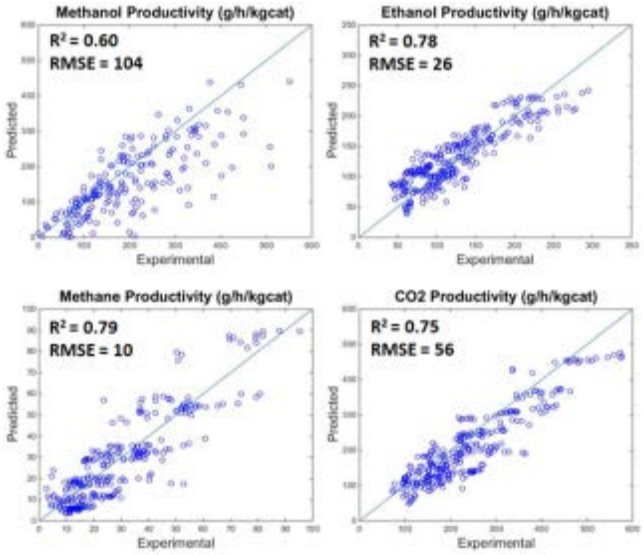
Abhijit Dutta, Asad Sahir, and Eric Tan
National Renewable Energy Laboratory

David Humbird
DWH Process Consulting

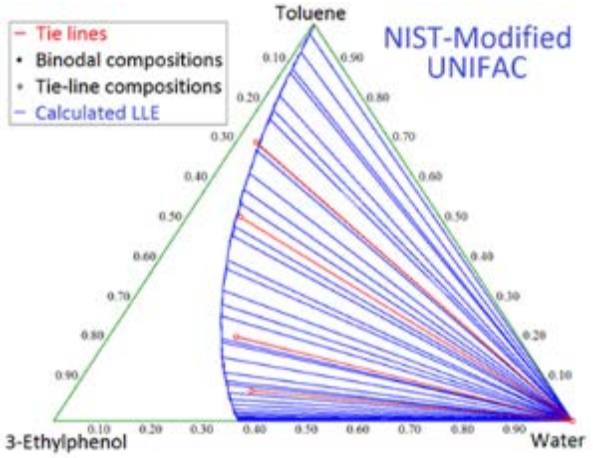
Lesley J. Snowden-Swan and Pimphan Meyer
Pacific Northwest National Laboratory

Jeff Ross, Danielle Sexton, Raymond Yap, and John Lukas
Harris Group Inc.

Syngas Conversion Modeling:
Developed kinetic model for mixed alcohols and fully integrated into process TEA model.



Pyrolysis VPU Phase Equilibrium:
Proved concept that phase equilibrium predictions can be improved for pyrolysis products through experiments and revised model development



Planned Milestones (FY2017)

Level	Performance Measure	Planned Date
Quarterly Progress Measure	FY16 State of Technology (SOT) Assessments: SOT assessments for the (i) ex situ catalytic fast pyrolysis and (ii) IDL high octane gasoline (HOG) pathways with respect to the FY2016 cost targets of (i) $5.34/GGE and (ii) $4.13/GGE, respectively (2014 dollars). (Task 1 and Task 2)	11/11/16 Q1-FY17
Quarterly Progress Measure	QTA Proof-of-Concept: Demonstrate proof-of-concept with initial QTA model, propose options for next steps, and confirm future scope with BETO (Task 5)	03/31/17 Q2-FY17
Quarterly Progress Measure	Kinetic Model for DME Homologation: Develop a kinetic model for DME homologation on a Cu-modified BEA catalyst with parameters estimated by fitting the model to bench-scale kinetic data. The model will describe DME conversion and the rate of production of (1) the C2-C3 fraction, (2) the C4 fraction and (3) gasoline range hydrocarbons (C5+) over the range of conditions (i.e., temperatures and pressures) studied experimentally. (Task 3)	06/30/17 Q3-FY17
Annual SMART Milestone	FY17 State of Technology (SOT) Assessments: SOT assessments for the (i) ex situ catalytic fast pyrolysis and (ii) IDL high octane gasoline (HOG) pathways with respect to the FY2017 cost targets of (i) $4.67/GGE and (ii) $3.63/GGE, respectively (2014 dollars). The major outcome of the SOT assessments is identification of major technical targets at risk of non-achievement and quantifying how non-achievement impacts product costs. The feedback loop from the analysis to the research effort may result in opportunities to redirect research direction, or recommend continued focus on the current approach, with minimal impact to cost and schedule. (Task 1 and Task 2)	09/30/17 Q4-FY17

Planned Milestones (FY2018)

Level	Performance Measure	Planned Date
Quarterly Progress Measure	TEA for Alternative Pathway Configurations and/or Integration Strategies: Develop techno-economic analysis for at least two (2) research approaches that are outside the current base pathway configuration outlined in the FY14 *Ex Situ / In Situ* Catalytic Fast Pyrolysis design report (NREL/TP-5100-62455) and demonstrate how required modifications to the base design configuration will impact the process and conversion costs. In addition, develop an assessment for a syngas-based (IDL) pathway for the deployment of the high-octane gasoline technology at smaller scales, reporting on scale-dependent costs and overall sustainability impacts, including those from feedstock variations. (Task 1 and Task 2)	12/15/17 Q1-FY18
Quarterly Progress Measure	Incorporate and Demonstrate LLE Model: Incorporate and demonstrate use of the most promising NIST-developed LLE model in Aspen Plus, showing predictions for a surrogate model compound system, along with relevant experimental data used for validation. (Task 4)	01/30/18 Q2-FY18
Go / No-Go	Go / No-Go FY18 for Catalytic Fast Pyrolysis Analysis: Perform TEA based on performances of fixed-bed and fluidized-bed ex situ CFP systems to date. This Go/No-Go will be used for decision-making regarding ex situ CFP capital equipment purchase for fixed-bed systems and HGF / enhancements in current fluidized-bed systems to meet FY22 targets. (Task 1 and Task 4 jointly with the Catalytic Fast Pyrolysis, Integration and Scale-Up -WBS# 2.4.1.301, and TC Capital - WBS# 2.4.1.302 projects)	02/28/18
Go / No-Go	Go / No-Go FY18 for Indirect Liquefaction Analysis: Perform TEA on integrated IDL pathway from biomass to high-octane gasoline and jet-range blendstocks (via DME homologation and olefin coupling, respectively) with incorporated kinetic model for the DME homologation. This is a joint effort with the Liquid Fuels via Upgrading of Syngas Intermediates research team. This Go/No-Go will serve as the opportunity to adjust research direction based on the enhanced process model and sensitivity analysis on gasoline to jet ratios, identify needed design modifications for the IDL process and inform the technical and cost target development for FY18 and beyond. (Task 2 and Task 3 in joint effort with Liquid Fuels via Upgrading of Syngas Intermediates project)	02/28/18

Planned Milestones (FY2018 *continued*)

Level	Performance Measure	Planned Date
Quarterly Progress Measure	Expand Capabilities of DME Homologation Kinetic Model: (1) Expand the DME homologation kinetic model to describe paraffin/olefin ratio, production rate of C7s, and catalyst deactivation. Collect experimental kinetic data for DME homologation with a C4 recycle stream and demonstrate the ability of the model to describe this data, including refitting parameters as necessary. (2) Integrate kinetic model into the Aspen Plus process model applied in techno-economic analyses. (Task 3 Joint milestone with Liquid Fuels via Upgrading of Syngas Intermediates project)	06/30/18 Q3-FY18
Annual SMART Milestone	Define TC Pathway Targets for FY18–FY21: In consultation with research teams, and using current experimental information, update technical and cost targets for the pathway development research efforts from FY18 to FY21 (those out-year targets are currently interpolated between FY17 and the FY22 design report case). With the new targets and actual experimental performance from FY18, the analysis team will complete the State of Technology (SOT) assessments for the (i) ex situ catalytic fast pyrolysis and (ii) IDL high octane gasoline (HOG) pathways with respect to the FY2018 technical and cost targets. The outcome of this effort is R&D technical targets and production cost targets for the CFP and IDL pathways from FY18- FY19. (Task 1 and Task 2)	09/30/18 Q4-FY18

Planned Milestones (FY2019)

Level	Performance Measure	Planned Date
Quarterly Progress Measure	Quick-Turnaround Analysis (Task 5): Provide beta-version of QTA tool with at least two (2) intermediate-to-product pathways for BETO review and testing. (Task 5)	12/14/18 Q1-FY19
Quarterly Progress Measure	Initial VLE Model: Demonstrate initial VLE predictions using NIST-developed model(s) with comparisons to the Wiltec experimental information used for the model development and validation. (Task 4)	03/31/19 Q2-FY19
Quarterly Progress Measure	Kinetic Model for Olefin Coupling: Develop a kinetic model for olefin coupling (C_4-C_8) on Amberlyst-35, or a similar acidic resin catalyst. Estimate kinetic parameters by fitting the model to bench-scale kinetic data. (Task 3)	06/30/19 Q3-FY19
Annual SMART Milestone	FY19 State of Technology (SOT) Assessments: State of Technology (SOT) assessments for the (i) ex situ catalytic fast pyrolysis and (ii) IDL high octane gasoline (HOG) pathways with respect to the updated technical and cost targets established in FY2018. The major outcome of the SOT assessments is identification of major technical targets at risk of not achievement and quantifying how non-achievement impacts product costs. The feedback loop from the analysis to the research effort may result in opportunities to redirect research direction, or recommend continued focus on the current approach with minimal impact to cost and schedule. (Task 1 and Task 2)	09/30/19 Q4-FY19
"Stretch" Milestone	FY19 TC Analysis "Stretch" Milestone: Develop and demonstrate process design model and/or biorefinery complex linear programming (LP) model for a responsive biorefinery concept based on (1) Catalytic Fast Pyrolysis and (2) Indirect Liquefaction that can be customized for potential licensing to industrial partners. The biorefinery model will have the capability to process multiple biomass feedstocks, produce both fuels and co-products, have an optimized separations strategy based on developed VLE/LLE models, and respond to changes in feedstock slate, raw material and product pricing and unit operation capacity constraints (design, turndown and maintenance-driven shutdowns).	09/30/19 Q4-FY19

Responses to 2015 Peer Review Comments

Overall Impressions from Reviewers:

- Excellent, high quality work. Why doesn't industry know about it or use it? Need more outreach, presentations, etc.
- This project is making good progress and provides useful insights to researchers about where opportunities exist to reduce costs. There is good coordination with related analyses at other laboratories.
- Like other DOE Design Cases dealing with Nth plants, this one does not provide economics relevant to early adopters for the first several plants where costs will be much higher. First plants will require much greater capital and contingency expenditures, for example, and the present analyses do not adequately address these. DOE should consider other types of analyses to assist with early commercial adoption of emerging technologies.
- TEA is an important area, and this project implies the work across the national laboratories is tightly joined up. This strong collaboration sometimes does not come across from the presentations given by individual projects. ISBL is easier to get from Aspen modeling—assume that the costs presented are U.S. Gulf Coast. OSBL is very difficult as it is often very site specific. The group should work closely with an EPC contractor to stay calibrated, given that cost estimating with the Aspen approach is only good within 25% at best. It is easy at this high level to "over model." Results should be used to provide directional guidance, as they often are. But, they are far less exact than often presented.

PI Response to Reviewer Comments:

- Thank you for your helpful feedback and guidance. We recognize the uncertainties associated with estimating capital costs for emerging technologies. We will continue to work with engineering firms to develop high-quality capital cost estimates within the limits of our available funding and budgets. We will also continue to leverage published and quoted cost data for commercially available processes and equipment.
- We understand that first-generation, pioneer plants will be much higher cost relative to those for a mature industry as projected by our analysis. We maintain the capability for assessing pioneer plant costs and will continue to offer the capability to BETO as requested.
- As mentioned in other responses, we make efforts to present our work and make many of our tools available in the public domain. We also welcome and seek collaborative projects with industry partners.

Publications and Presentations since 2015 Peer Review

Slide 1 of 3

- Humbird, D.; Trendewicz, A.; Braun, R.; Dutta, A. One-Dimensional Biomass Fast Pyrolysis Model with Reaction Kinetics Integrated in an Aspen Plus Biorefinery Process Model. ACS Sustainable Chem. Eng. 2017. DOI: 10.1021/acssuschemeng.6b02809.
- Tan, E. C. D., Snowden-Swan, L. J., Talmadge, M., Dutta, A., Jones, S., Ramasamy, K. K., Gray, M., Dagle, R., Padmaperuma, A., Gerber, M., Sahir, A. H., Tao, L. and Zhang, Y. (2016), Comparative techno-economic analysis and process design for indirect liquefaction pathways to distillate-range fuels via biomass-derived oxygenated intermediates upgrading. Biofuels, Bioprod. Bioref.. doi:10.1002/bbb.1710
- Jasperson, L.V.; McDougal, R.J.; Diky, V.; Paulechka, E.; Chirico, R.D.; Kroenlein, K.; Iisa, K.; Dutta, A. Liquid−Liquid Equilibrium Measurements for Model Systems Related to Catalytic Fast Pyrolysis of Biomass, Journal of Chemical Engineering Data (2016). http://dx.doi.org/10.1021/acs.jced.6b00625
- Pinho, Andrea; Almeida, Marlon B; Mendes, Fabio L; Casavechia, Luiz Carlos; Talmadge, Michael S; Kinchin, Christopher, Helena L. Chum (2017). "Fast pyrolysis oil co-processing from pinewood chips with vacuum gas oil in an FCC unit for second generation fuel production." Fuel, 188, 462-473. http://dx.doi.org/10.1016/j.fuel.2016.10.032
- Michael Talmadge, Helena Chum, Christopher Kinchin, Yimin Zhang, Mary Biddy, Andrea de Rezende Pinho, Marlon B.B. de Almeida, Fabio Leal Mendes, Luiz Carlos Casavechia, Barry Freel. "Analysis for co-processing fast pyrolysis oil with VGO in FCC units for second generation fuel production", Oral Presentation at TCS 2016, Chapel Hill, NC, November 1-4, 2016.
- Asad H. Sahir, Michael Talmadge and Mary Biddy. "Finished fuel blending models for assessing integration of biomass-derived products with petroleum refinery products", Oral Presentation at TCS 2016, Chapel Hill, NC, November 1-4, 2016.
- Eric C.D. Tan, Lesley Snowden-Swan, Michael Talmadge, Abhijit Dutta, Susanne Jones, Karthikeyan Ramasamy, Michel Gray, Robert Dagle, Asanga Padmaperuma, Mark Gerber, Asad Sahir, Ling Tao, Yanan Zhang. "Indirect Liquefaction of Biomass to Transportation Fuels Via Mixed Oxygenated Intermediates", Oral Presentation at 2016 AIChE Annual Fall Meeting, San Francisco, CA, November 13–18, 2016.

Publications and Presentations since 2015 Peer Review

Slide 2 of 3

- Asad H. Sahir, Michael Talmadge, Mary Biddy. "Finished Fuel Blending Models for Assessing Integration of Biomass-Derived Products with Petroleum Refinery Products", Oral Presentation at 2016 AIChE Annual Fall Meeting, San Francisco, CA, November 13–18, 2016.
- Asad H. Sahir, Michael Talmadge, Mary Biddy, Mark Bearden, Steven Phillips, Susanne Jones. "Process Models to Assess the Co-Processing of Gasoil and Bio-Based Feedstocks in Hydroprocessing Unit Operations", Oral Presentation at 2016 AIChE Annual Fall Meeting, San Francisco, CA, November 13–18, 2016.
- Louis Jasperson, Rubin McDougal, Vladimir Diky, Eugene Paulechka, Robert Chirico, Kenneth Kroenlein, Kristiina Iisa, Abhijit Dutta. "Liquid-Liquid Equilibrium (LLE) Measurements and Modeling for Biomass Catalytic Fast Pyrolysis Products", Poster Presentation at TCS 2016, Chapel Hill, NC, November 1-4, 2016.
- Eric Tan, Lesley Snowden-Swan, Michael Talmadge, Abhijit Dutta, Susanne Jones, Karthikeyan Ramasamy, Michel Gray, Robert Dagle, Asanga Padmaperuma, Mark Gerber, Asad Sahir, Ling Tao, Yanan Zhang. "Comparative TEA for Indirect Liquefaction Pathways to Distillate-Range Fuels via Oxygenated Intermediates", Poster Presentation at TCS 2016, Chapel Hill, NC, November 1-4, 2016.
- Michael Talmadge, Liaw Batan, Patrick Lamers, Damon Hartley, Mary Biddy, Ling Tao, Eric Tan. "Optimizing Biorefinery Design and Operations via Linear Programming Models", Poster Presentation at TCS 2016, Chapel Hill, NC, November 1-4, 2016.
- Dutta, Abhijit, Joshua A. Schaidle, David Humbird, Frederick G. Baddour, and Asad Sahir. "Conceptual Process Design and Techno-Economic Assessment of Ex Situ Catalytic Fast Pyrolysis of Biomass: A Fixed Bed Reactor Implementation Scenario for Future Feasibility." Topics in Catalysis, Volume 59, Issue 1, pp 2-18. Print and Web. http://link.springer.com/article/10.1007/s11244-015-0500-z
- Tan, E.C.D., Talmadge, M., Dutta, A., Humbird, D., Snowden-Swan, L., Hensley, J., Schaidle, J., and Biddy, M.J. "Conceptual Process Design and Economics for the Production of High-Octane Gasoline Blendstock via Indirect Liquefaction of Biomass through Methanol/Dimethyl Ether Intermediates," Biofuels, Bioproducts and Biorefining, (2015). [DOI: 10.1002/bbb.1611]

Publications and Presentations since 2015 Peer Review

Slide 3 of 3

- Dutta, A. "Process Design and Economics Targeting Cost-Competitive Production of Hydrocarbon Fuel Blendstocks from Biomass via In Situ and Ex Situ Upgrading of Fast Pyrolysis Vapors", TCBiomass2015, Chicago, IL, Nov 2-5, 2015.
- Tan, E.C.D., Talmadge, M., Dutta, A., Hensley, J., Schaidle, J., Biddy, M., and Snowden-Swan, L., "A Target Design and Techno-Economic Analysis for Indirect Liquefaction of Biomass to High-Octane Gasoline Blendstock via Methanol and Dimethyl Ether Intermediates", TCBiomass2015, Chicago, IL, November 2-5, 2015.
- Tan, E.C.D., Talmadge, M., Dutta, A. "Combined Sustainability Assessment and Techno-Economic Analysis for the Production of Biomass-Derived High-Octane Gasoline Blendstock", 2015 AIChE Annual Fall Meeting, , Salt Lake City, UT, November 8 – 13, 2015.
- Tan, E.C.D. "Improved Estimates of Air Pollutant Emissions from Biorefinery", 2015 AIChE Annual Fall Meeting, Salt Lake City, UT, November 8 – 13, 2015.
- Sahir, A.; Dutta, A. "Exploring the Synergies in Process Engineering Between Catalytic Fast Pyrolysis and Processes Based on Conventional Energy Feedstocks." 2015 AIChE Annual Fall Meeting, Salt Lake City, UT, Nov 8 – 13, 2015.
- Tan, E. C. D.; Talmadge, M.; Dutta, A.; Hensley, J.; Schaidle, J.; Biddy, M.; Humbird, D.; Snowden-Swan, L. J.; Ross, J.; Sexton, D.; Yap, R.; Lukas, J. (2015). Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbons via Indirect Liquefaction: Thermochemical Research Pathway to High-Octane Gasoline Blendstock Through Methanol/Dimethyl Ether Intermediates. 189 pp.; NREL Report No. TP-5100-62402; PNNL-23822. http://www.nrel.gov/docs/fy15osti/62402.pdf
- Trendewicz, A.; Evans, R.; Dutta, A.; Sykes, R.; Carpenter, D.; Braun, R. (2015). Evaluating the Effect of Potassium on Cellulose Pyrolysis Reaction Kinetics. Biomass and Bioenergy. Vol. 74, March 2015; pp. 15-25; NREL Report No. JA-5100-63820. http://dx.doi.org/10.1016/j.biombioe.2015.01.001
- Dutta, A.; Sahir, A.; Tan, E.; Humbird, D.; Snowden-Swan, L. J.; Meyer, P.; Ross, J.; Sexton, D.; Yap, R.; Lukas, J. (2015). Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels: Thermochemical Research Pathways with In Situ and Ex Situ Upgrading of Fast Pyrolysis Vapors. 275 pp.; NREL Report No. TP-5100-62455; PNNL-23823. http://www.nrel.gov/docs/fy15osti/62455.pdf

Contacts for NREL TC Platform Analysis Projects

Pyrolysis, Gasification/IDL, Sustainability and Quick-Turnaround Analysis

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Related Projects

Related NREL tasks and associated WBS numbers are as follows:

- Thermochemical Feedstock Interface (WBS: 2.2.1.304)
- Consortium for Computational Physics and Chemistry (WBS: 2.5.1.302)
- Development and Standardization of Techniques for Bio-oil Characterization (WBS:2.5.2.301)
- Integration and Scale Up (WBS: 2.4.1.301)
- Thermochemical Capital Equipment (WBS: 2.4.1.302)
- Liquid Fuels via Upgrading of Syngas Intermediates (WBS: 2.3.1.305)
- Reforming Pyrolysis Aqueous Waste Streams to Process Hydrogen and Hydrocarbons (WBS: 2.3.1.311)
- Catalytic Pyrolysis Science (WBS: 2.3.1.313)
- Catalytic Upgrading of Pyrolysis Products (WBS: 2.3.1.314)
- Catalyst Development and Testing (WBS: 2.3.1.315)
- Sustainability Analysis (WBS: 4.2.1.30)
- NREL-Petrobras CRADA (WBS: 2.4.2.303)
- NREL/PNNL Strategic Analysis Refinery Integration (WBS: 4.1.1.31)

Related tasks at other national laboratories and associated WBS numbers are as follows:

- Analysis and Sustainability Interface – PNNL (WBS: 2.1.0.301)
- Life-Cycle and Sustainability Analysis – ANL (WBS: 4.1.1.10)

Industrial Partners and Commercialization

Close collaboration with industrial partners and expected continued efforts by partners towards future commercialization:

- **National Institute of Standards and Testing (NIST):** Collaboration to advance phase-equilibrium predictions for pyrolysis pathways and integrate with process models to increase predictive capabilities.
- **Johnson Matthey:** CRADA for developing Catalytic Fast Pyrolysis catalysts
- **Enerkem:** NREL partner on a Technology Commercialization Fund will produce 85% triptane for product quality and fuel testing analyses.
- **Johnson Matthey:** NREL pilot runs with fixed-bed met technical targets for reforming biomass-syngas.
- **Dow Chemical:** Alcohol synthesis catalyst improvements for the 2012 mixed alcohols demonstration.
- **Petrobras:** Tools and analysis approaches developed through CRADA
- **ASTM D02 Membership:** Members of the NREL TC Platform team participate the ASTM D02 (Liquid Fuels) technical committees.

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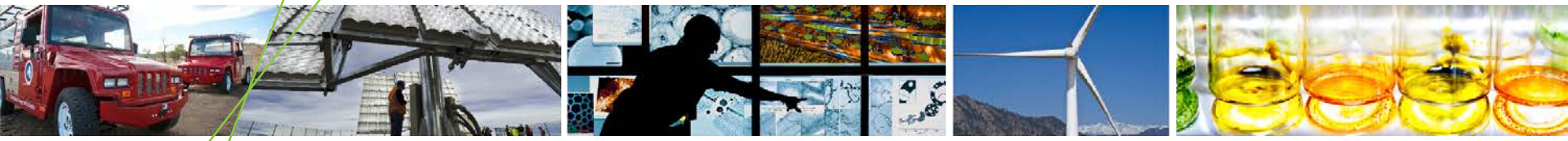
Additional Content for Reviewers

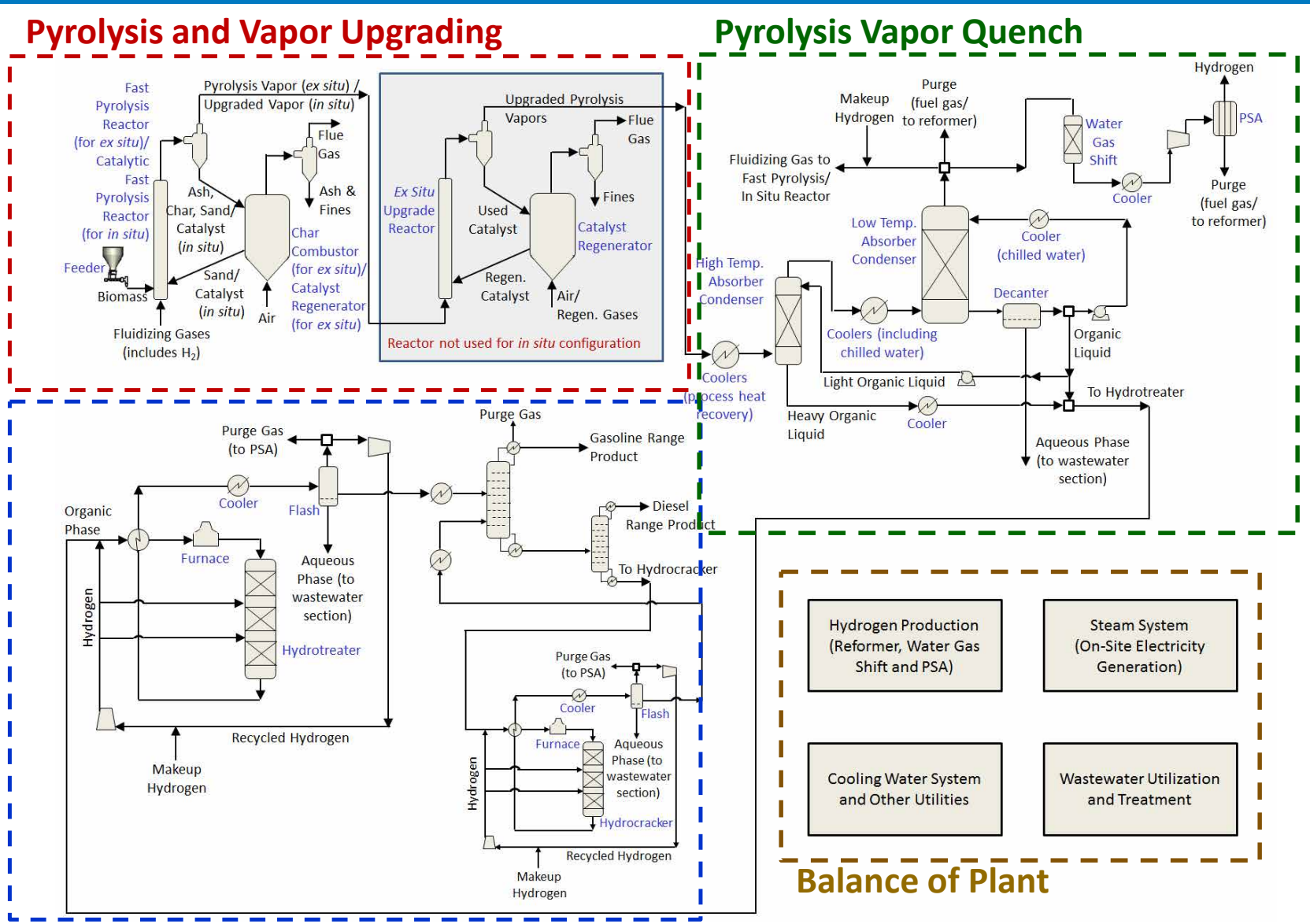


Task: Pyrolysis Pathway Analysis

Principal Investigator: Abhijit Dutta

Collaborative Partners: Pacific Northwest National Lab
Idaho National Lab
Harris Group Inc.
DWH Process Consulting LLC

Ex-Situ Entrained Flow CFP Conceptual Process Overview



[Source: http://www.nrel.gov/docs/fy15osti/62455.pdf](http://www.nrel.gov/docs/fy15osti/62455.pdf)

Ex-Situ CFP FY2022 Process Design Highlights

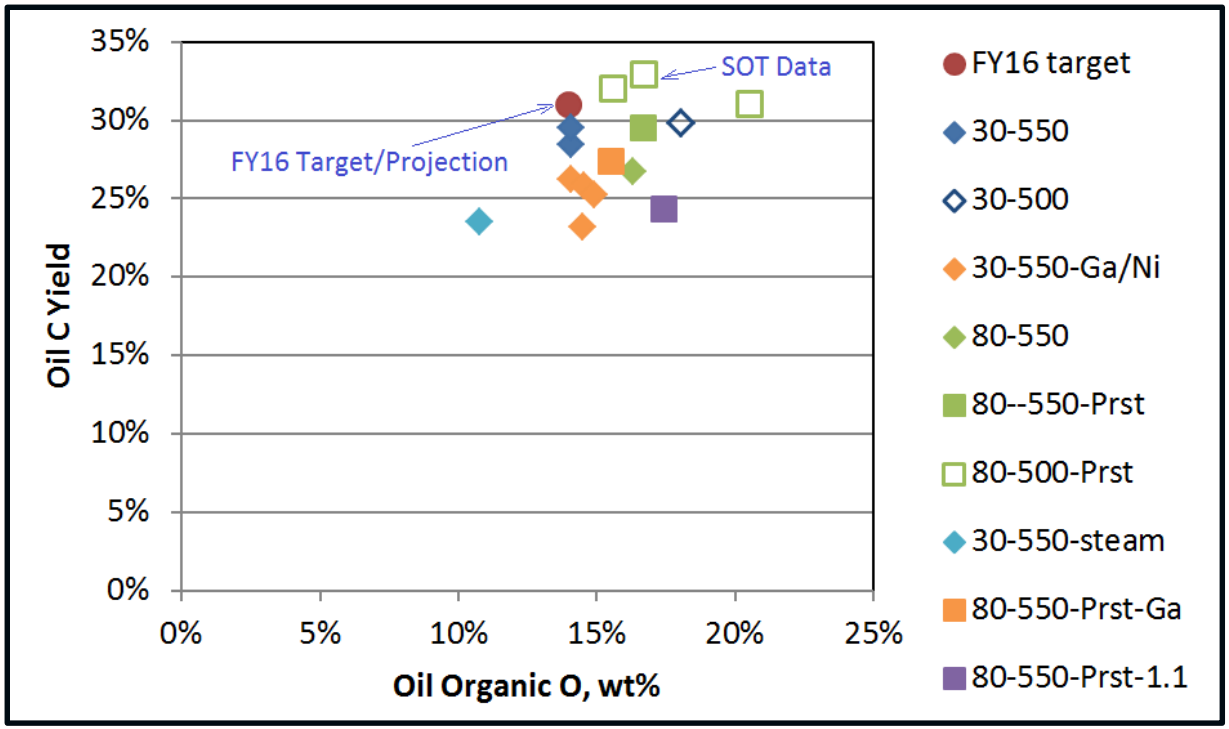
- **Off-gases satisfy hydrogen demand**
  - No supplemental natural gas necessary
- **Electricity produced from char, coke, and excess off gases**
  - Excess electricity to grid
- **Wastewater sent to thermal oxidizer after concentration**
  - Valorization of carbon in aqueous stream not considered at this stage
- **Base process has ~5 bars (75 psia) of hydrogen partial pressure with ~8 bars (120 psia) total pressure**
  - Pressure below hydrogen embrittlement
  - Lower capital because of vessel volumes
  - Lower cost for possible hot gas filter use
  - Benefits to chemistry to be experimentally evaluated

Catalytic Fast Pyrolysis (CFP) Overview

- **Upstream deoxygenation and hydrogenation**
  - Reduced downstream cost (capital and operating)
- **Potential reduction in organic liquid hydroprocessing requirements**
  - Volume reduction, aqueous phase previously separated
  - Lower oxygen content in feed
  - Reduced number of reactors
  - Potential for lower severity
- **Ability to affect the chemistry and molecular composition in reactive vapor phase**
  - Impact product slate, distillate product
  - Reduce gas phase losses

Ex-Situ CFP FY2016 SOT Highlights

- SOT MFSP of $5.19/GGE in 2014$ (projection was $5.34)
- Different catalysts tested – further optimization possible
- Higher carbon yield during CFP, and overall process
- Higher organic O-content and higher aqueous C loss
- Higher gas yield
- Lower coke yield



Legend shows SAR-Temperature-Catalyst
Prst: Pre-steamed, SAR: Silica-to-alumina ratio

Ex-Situ CFP Pathway SOT and Projection Summaries

Process Parameter	2014 SOT	2015 SOT	2016 Projection	2016 SOT	2017 Projection	2022 Design
Hydrogen Addition to Vapor Upgrading	Initial focus on use of hydrogen to reduce coke and non-condensable gases; after 2017 incorporate hydrogen to improve product quality by increasing H/C ratio					
Molecular Combination (Coupling)	Initial work using model compounds; after 2017 demonstrate using pyrolysis vapors					
Additional Process Options	Base cases assume fluidized catalysts (modified zeolites); consider the option to use catalysts that are feasible in fixed bed reactors (preceded by a hot gas filter)					
Vapor Products	Wt% of dry biomass unless noted. Values rounded off except for smaller improvements.					
Non-Condensable Gases	35	36	32	**34**	30	23
Aqueous Phase (% C Loss)	25 (2.9)	25 (2.9)	25 (2.4)	**24 (3.4)**	26 (2.3)	30 (1.3)
Solids (Char + Coke)	12 + 11	11 + 9.5	12 + 10.5	**12 + 8.3**	12 + 10.2	12 + 8.0
Organic Phase	17.5	18.6	20.2	**21.8**	22.0	27.2
H/C Molar Ratio	1.1	1.1	1.2	**1.1**	1.3	1.6
Carbon Efficiency (%)	27	29	31	**33**	34	44
Oxygen Content (% of organic)	15.0	13.3	14.0	**16.8**	12.5	6.4
Hydroprocessing C Eff. (% of org.liq.)	88	90	89	**87**	90	94
Carbon Eff. to Fuel Blendstocks (%)	23.5	26.0	27.6	**28.3**	30.6	41.5
Energy Efficiency to Fuels (% LHV)	30.4	33.4	36.0	**37.0**	40.2	56.6
Diesel-Range Product (% GGE basis)	15	15	14	**15**	14	55
Minimum Fuel Selling Price ($ / GGE)	$6.61	$5.76	$5.34	**$5.19**	$4.67	$3.38

Note: All costs are presented in 2014$.

Sustainability Metrics for *Ex-Situ* CFP Pathway

SOT vs. Projection: SOT sustainability metrics closely match projections based on technical targets

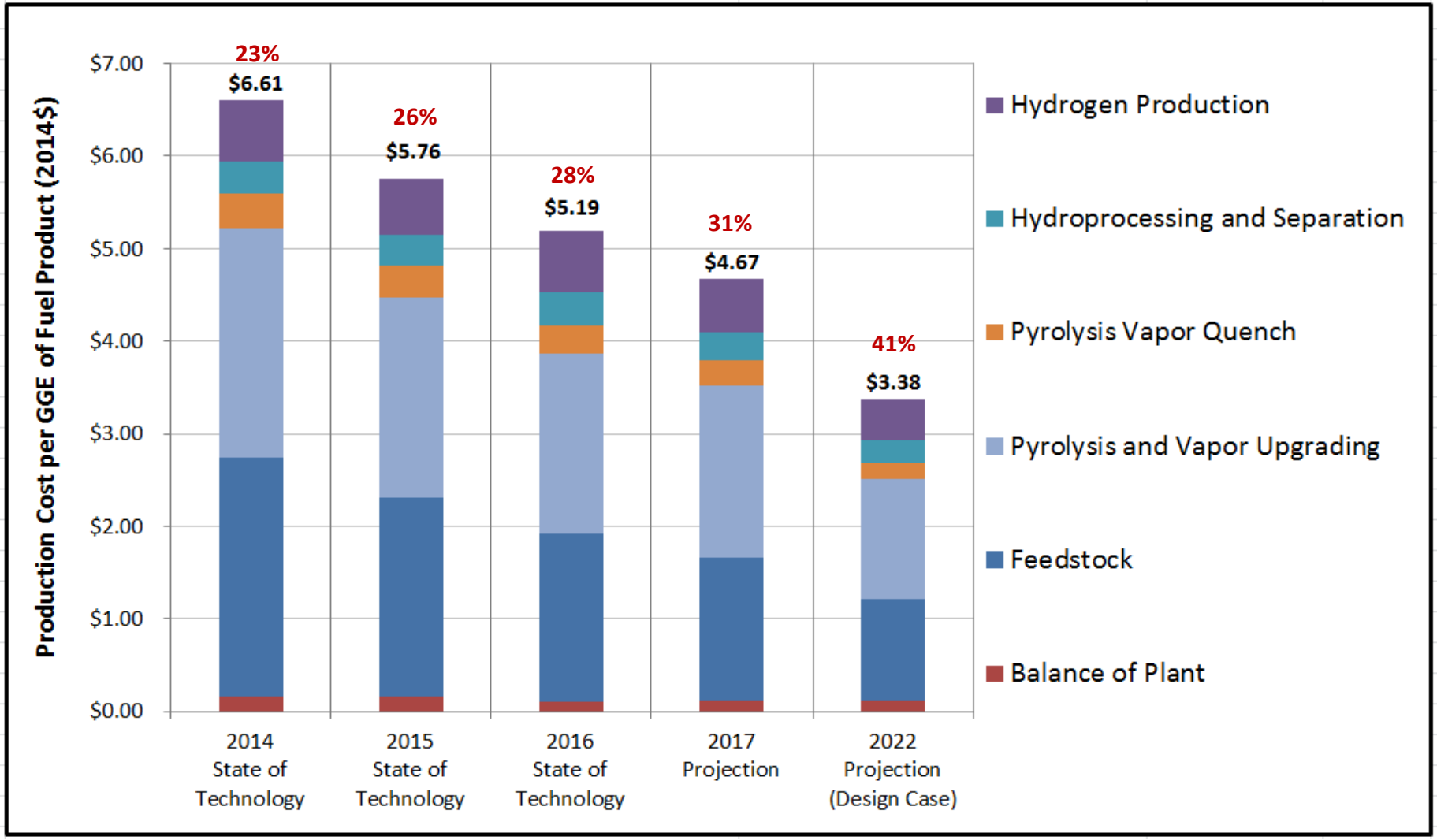
Trends in Modeled Sustainability Metrics*	2014 SOT	2015 SOT	2016 Projection	2016 SOT	2017 Projection	2022 Projection
Fossil GHG Emissions† (g CO2-e / MJ Fuel)	-41.5	-35.5	-27.9	**-25.1**	-19.3	-1.2
Fossil Energy Consumption† (MJ FE / MJ Fuel)	-0.47	-0.40	-0.31	**-0.28**	-0.22	-0.01
Total Fuel Yield (GGE / Ton)	42	46	50	**51**	56	78
Carbon Efficiency to Fuel Blendstock (%C in Feedstock)	23.5	25.9	27.6	**28.3**	30.6	41.5
Water Consumption (gal H2O / GGE Fuel Blend)	1.4	1.4	1.2	**1.3**	1.1	0.7
Electricity Production (kWh/GGE)	21.0	18.0	16.0	**14.7**	13.1	6.2
Electricity Consumption (for entire process, kWh/GGE)	12.7	11.0	10.4	**9.6**	9.1	5.7

*** For conversion process only**

† Includes electricity credit

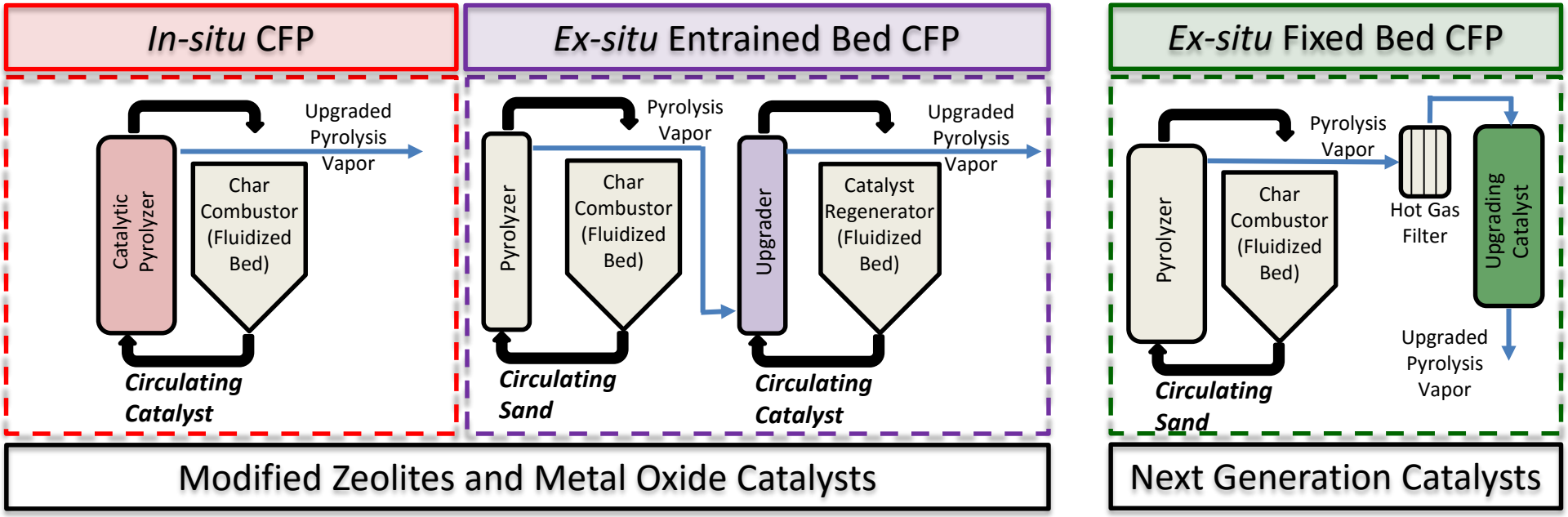
Waterfall Chart for *Ex-Situ* CFP Pathway

Modelled Minimum Fuel Selling Price (MFSP) and C-Efficiency



CFP Process Design Options

Near-term → ***Long-term***



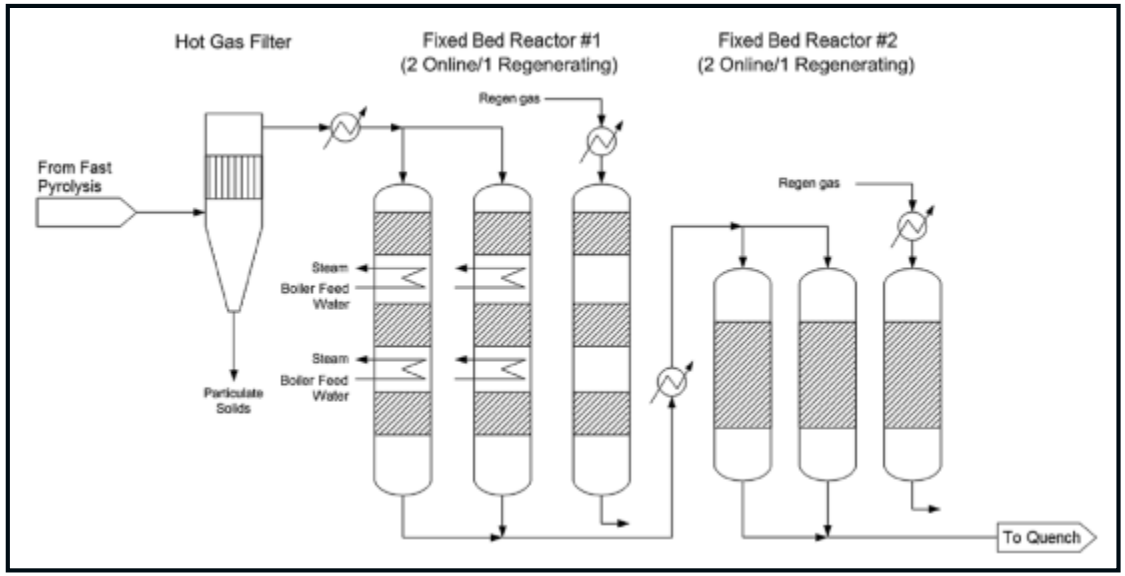
- Operating conditions tied to fast pyrolysis
- Catalyst mixed with biomass, char, and ash
- Lower capital investment
- Higher catalyst replacement rates

- Operating conditions can differ from fast pyrolysis
- Biomass, ash, and char are reduced or removed; more benign environment for catalyst
- Higher capital investment
- Lower catalyst replacement rates

- More diverse catalysts are feasible
- Access to greater catalytic chemistry
- Long catalyst lifetimes required
- Hot gas filter required

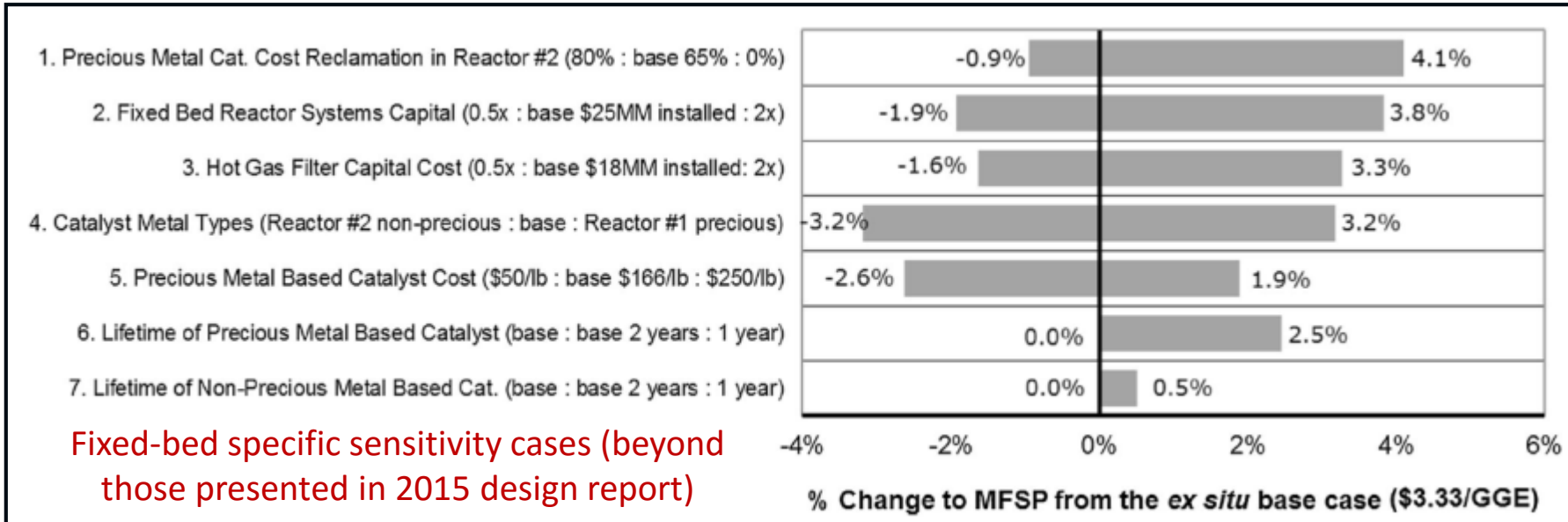
Hybrids of all or some of these systems are also possible

Ex Situ CFP with Fixed Bed System



Key findings for research:

- Modeled costs similar for same yield as fluidized bed systems
  - Added capital for hot gas filter
- Does not require continuous catalyst replacement
  - Precious metals can be used
  - Allows added functionality
- Operational feasibility decided by coking and regeneration



Fixed-bed specific sensitivity cases (beyond those presented in 2015 design report)

Dutta et al., Topics in Catalysis (2016) 59:2–18

Other Pyrolysis Pathway Analyses

- Analysis for **Aqueous Carbon Upgrading** for *in situ* (literature data)
  - High volume commodity chemicals (e.g. BTX, olefins) not economical
  - Oxygenated chemicals (e.g. cyclopentenone & phenols) more attractive and recommended
  - Assessing **Biological Conversion of TC Aqueous Streams** (Beckham)
  - Need to develop concentration methods without boiling
    - Will allow reduced energy and operating costs
    - Will help reduce reactor volume and capital costs
- **Membranes** for separation of aqueous carbon can be effective
  - HiPAS Membrane flux needs to improve to 1 LMH (liter/m2/h)
- **Hydrotreating of Catalytic Fast Pyrolysis oils**
  - Initial indications that carbon efficiency may not vary linearly with oxygen content of the organic phase
- **Integration of Kinetic Model** with 1-dimensional fluid dynamics
  - Demonstrated the feasibility of integration of more detailed fast pyrolysis models with biorefinery models used in TE
- Leveraging **refinery integration** and **hydrocarbon blending models** from NREL/PNNL Strategic Analysis and Petrobras-NREL CRADA projects for **CFP oils.**

Future Challenges and Strategies for CFP Pathways

Key Challenges for CFP

- Co-optimization of reactor configuration and catalyst
- Design and development of scalable, cost-effective catalysts capable of achieving:
  - Higher yield to organic phase products
  - Increased lifetime
- Shift product selectivity towards distillates
- Determine relationship between CFP severity, hydrotreating severity, finished fuel properties, and MFSP
- Pilot-scale process integration

Strategies

- Evaluate process at multiple scales with different reactor configurations with both model compound and whole pyrolysis vapor feeds
- Multi-lab collaborative catalyst design effort
- Hydroprocess CFP oils, vary degree of severity

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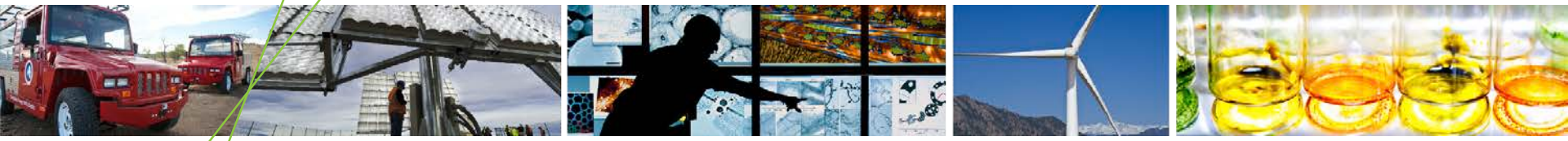


Task: Pyrolysis Product Phase-Equilibrium Modeling

Principal Investigator: Abhijit Dutta

Phase Equilibrium for Catalytic Fast Pyrolysis Products

Purpose: Model phase behavior of CFP products
Value: Develop predictive phase modeling capability. Improve process modeling & TEA for cost reduction.
Approach: Joint work by NIST/TRC*, Wiltec and NREL

- Extensive literature search by NIST
- Fast pyrolysis analytical results from NREL
- Identification of key compounds by NREL & NIST
- Liquid-Liquid Equilibrium (LLE) experiments by Wiltec Research
- Predictive modeling for LLE by NIST/TRC
  - NIST-Modified-UNIFAC (uses functional groups)
  - NIST COSMO-SAC (fully predictive: uses charge distribution of molecules)

Future Work:

- Model validation for multicomponent systems
- Integration and use with biorefinery models
- Vapor-Liquid Equilibrium (VLE) of CFP products

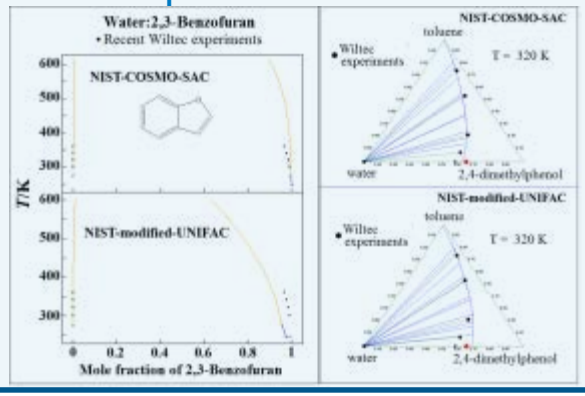
*NIST/TRC: NIST Thermodynamics Research Center

LLE Experiments by Wiltec Research

Binary systems: (1) 2-ethylphenol + water, (2) 3-ethylphenol + water, (3) 4-ethylphenol + water, (4) 2-methoxyphenol + water, (5) 3-methoxyphenol + water, (6) 4-methoxyphenol + water, (7) indene + water, (8) 2,3-benzofuran + water.

Ternary systems: (1) 3-ethylphenol + water + toluene, (2) 3-methoxyohenol + water + toluene, (3) phenol + water + toluene, (4) 2,4-dimethylphenol + water + toluene.

Model predictions in good agreement with binary and ternary experiments at temperatures of interest



Journal of chemical & engineering data

Liquid–Liquid Equilibrium Measurements for Model Systems Related to Catalytic Fast Pyrolysis of Biomass

Louis V. Jasperson, Rubin J. McDougal, Vladimir Diky, Eugene Paulechka, Robert D. Chirico, Kenneth Kroenlein, Kristiina Iisa, and Abhijit Dutta

NIST National Institute of Standards and Technology U.S. Department of Commerce Thermodynamics Research Center

Wiltec Research Company, Inc.

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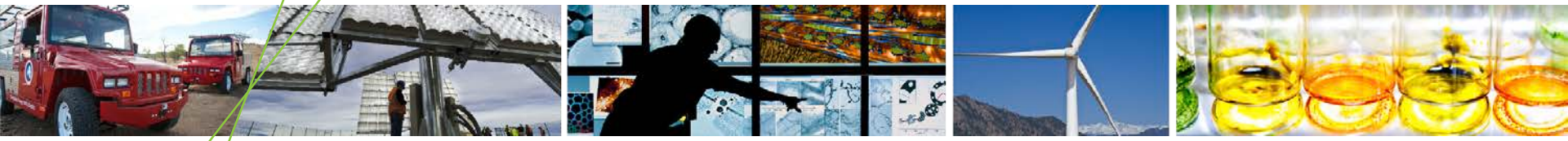
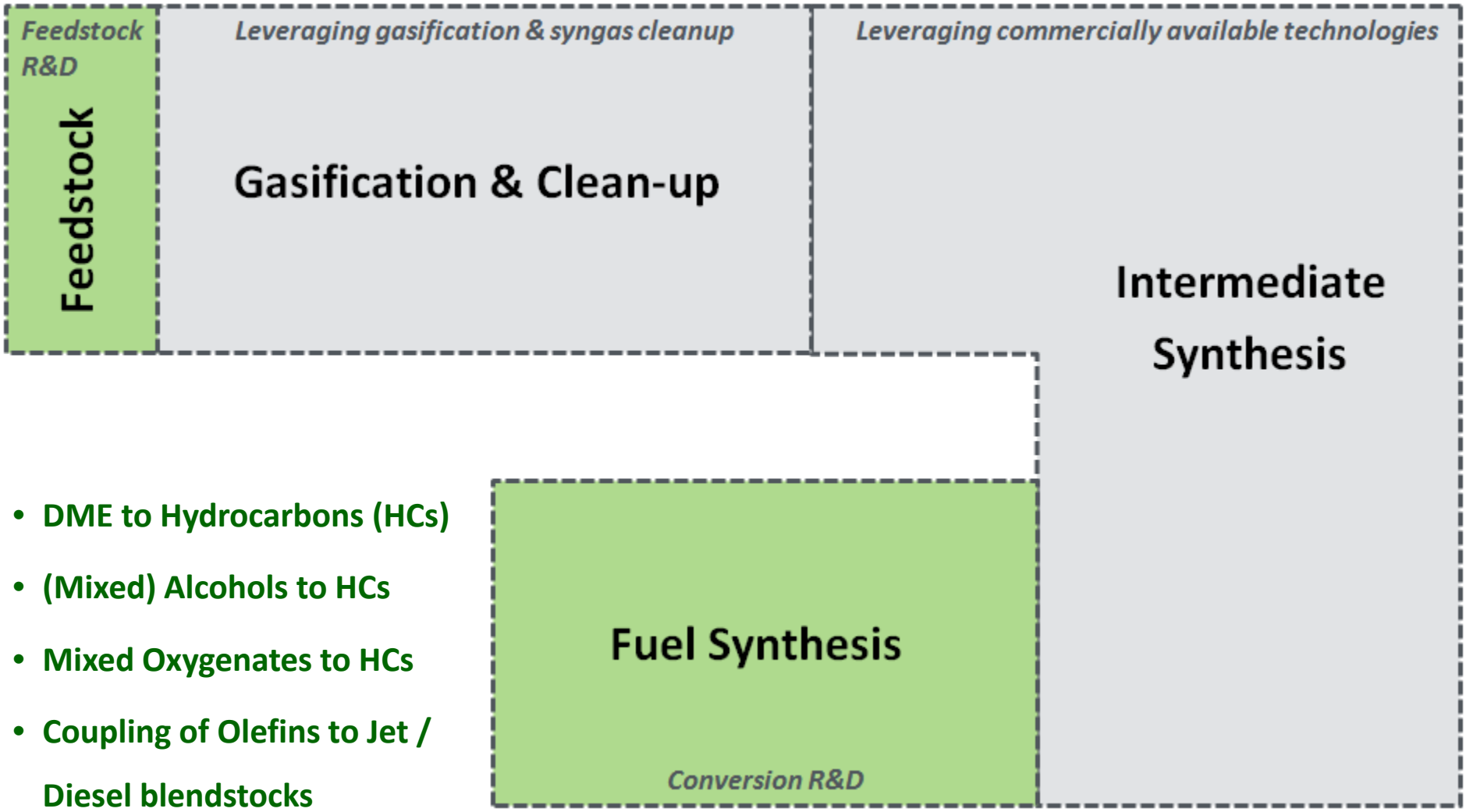


Task: Gasification Pathway Analysis

Principal Investigators: Michael Talmadge and Eric Tan

Collaborative Partners: Pacific Northwest National Lab
Idaho National Lab
Harris Group Inc.
DWH Process Consulting LLC

IDL Pathway Overview



- DME to Hydrocarbons (HCs)
- (Mixed) Alcohols to HCs
- Mixed Oxygenates to HCs
- Coupling of Olefins to Jet / Diesel blendstocks

Comparative TEA for IDL Distillate Pathways

Joint NREL/PNNL analysis of pathways via oxygenated IDL intermediates

Pathway	1A	1B	2A	2B
Oxygenate Intermediate	Ethanol and C3+ Alcohols via Mixed-Alcohol Synthesis	Ethanol via Syngas Fermentation	Rhodium (Rh)-Catalyzed Mixed Oxygenates	Ethanol via Syngas Fermentation
Process Downstream of Intermediate	Alcohol condensation (Guerbet), dehydration, oligomerization, and hydrogenation	Alcohol condensation (Guerbet), dehydration, oligomerization, and hydrogenation	Carbon coupling / deoxygenation to isobutene, oligomerization, and hydrogenation	Carbon coupling / deoxygenation to isobutene, oligomerization, and hydrogenation

Modeling and Analysis

Biofpr Biofuels Bioproducts & Biorefining

Comparative techno-economic analysis and process design for indirect liquefaction pathways to distillate-range fuels via biomass-derived oxygenated intermediates upgrading

Eric C. D. Tan, National Renewable Energy Laboratory, Golden, CO, USA
Lesley J. Snowden-Swan, Pacific Northwest National Laboratory, Richland, WA, USA
Michael Talmadge, Abhijit Dutta, National Renewable Energy Laboratory, Golden, CO, USA
Susanne Jones, Karthikeyan K. Ramasamy, Michel Gray, Robert Dagle, Asanga Padmaperuma, Mark Gerber, Pacific Northwest National Laboratory, Richland, WA, USA
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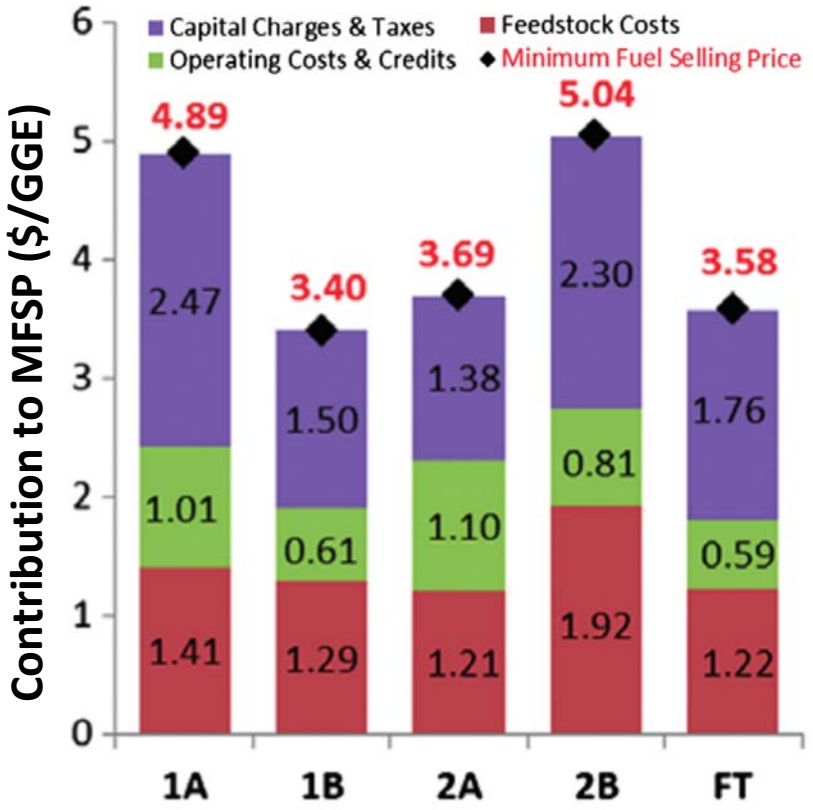
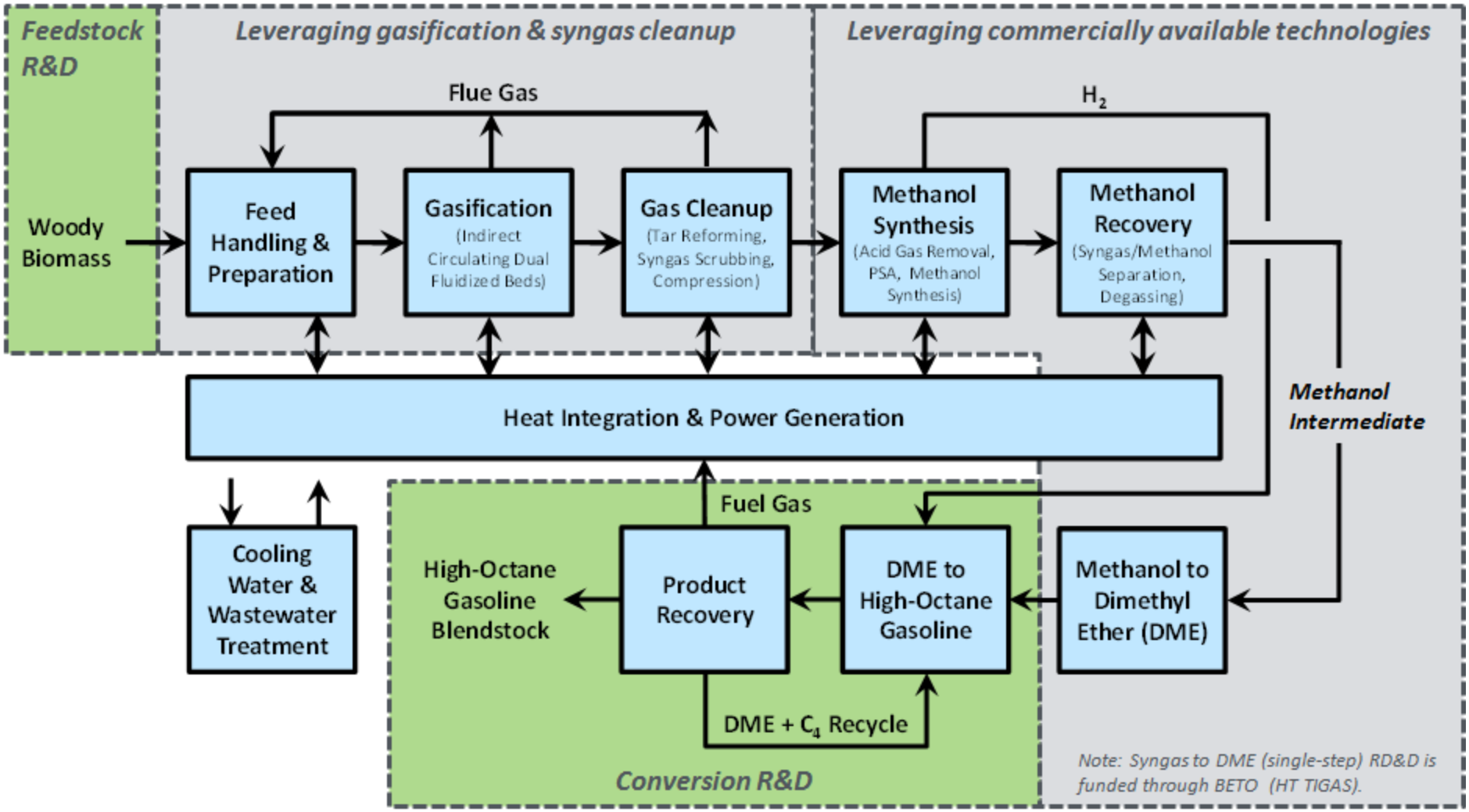
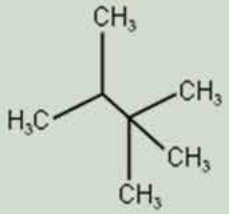
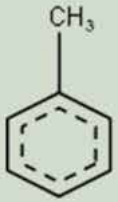
Received June 28, 2016; revised August 3, 2016; accepted August 4, 2016
View online at Wiley Online Library (wileyonlinelibrary.com)
DOI: 10.1002/bbb.1710; *Biofuel, Bioprod. Bioref.* (2016)



IDL High-Octane Gasoline (HOG) Design PFD



High-Octane Gasoline vs. Traditional MTG

Process Attribute	High-Octane Gasoline Pathway Target	Methanol to Gasoline (MTG) Pathway	Impact on Techno-Economic Analysis
Molecular structures favored in synthesis reactions	Branched paraffins 	Aromatics 	High octane product rich in branched paraffins, similar to a refinery alkylate. H-saturation decreases density, increasing product volume.
Example Compound Specific Gravity	Triptane 0.70	Toluene 0.87	
Hydrocarbon synthesis catalyst	Beta-Zeolite (12-membered rings)	ZSM-5 (10-membered rings)	Different pore sizes and structures result in different compound selectivities.
Octane number of gasoline-range product	RON: 95+ MON: 90+	RON: 92 MON: 83	Octane number increases value of product as a finished fuel blendstock.
Selectivity of C_5+product	C_5+ product only (~65 Gal / Ton)	~ 85% C_5+ (~55 Gal / Ton)	High selectivity to primary (premium quality) product maximizes overall product value.
Severity of synthesis operating conditions	180 – 230 Deg. C (350 – 450 Deg. F) 130 PSIA	345 – 510 Deg. C (650 – 950 Deg. F) 315 PSIA	The lower severity operating conditions result in lower capital and operating costs relative to MTG.
Coke formation	Coke formation is minimized by hydrogen addition and selectivity to branched paraffins rather than aromatics.	High propensity for coke formation due to aromatic coke pre-cursors.	Minimizing coke formation helps to maximize product yield / carbon efficiency and maximizes catalyst regeneration and replacement cycles.

IDL HOG FY2022 Process Design Highlights

- Methanol intermediate converted to high-octane, branched C_7-rich gasoline blendstock via beta-zeolite catalyst in a fixed-bed.
  - C_3– compounds from the reactor products are utilized as fuel gas.
  - C_4 compounds are recycled to the reactor to maximize gasoline yield.
  - C_5+ compounds are recovered as gasoline blendstock.
- No fossil energy imports in base design case.
- Current operating and financing assumptions (2014$, 90% reliability, etc).
- Competitive carbon efficiency and MFSP relative to mixed alcohols due to lower severity conditions (alcohol synthesis pressure).
  - MFSP = **$ 3.47 / GGE** (2014$)
  - Yield = **65 Gal / Ton** High-Octane Gasoline Blendstock
  - Carbon Efficiency = **31.2 %**

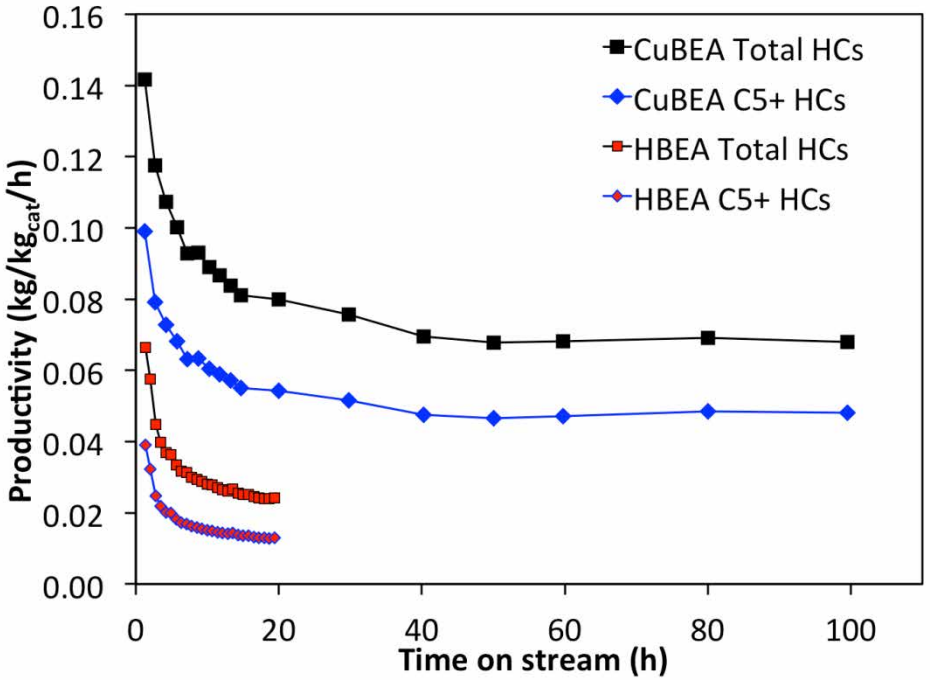
IDL HOG FY2016 SOT Highlights

- Major research challenge to maximize C_5+ product and meet the FY16 SOT targets required reactivation of C_4 alkanes and reincorporation into C_5+ products.
  - NREL-developed, metal-modified zeolite catalyst (Cu/BEA) was found to reactivate isobutane via dehydrogenation.
- Performed simulated recycle experiments with isobutane co-fed with DME and H_2 over Cu/BEA.
- Demonstrated C_4 reincorporation and performance of NREL Cu/BEA catalyst met FY2016 MFSP target.
- Demonstrated jet / diesel production by olefin coupling and developed sensitivity scenarios.

IDL Pathway FY2016 SOT Experimental Data

Catalyst lifetime – without co-fed C4

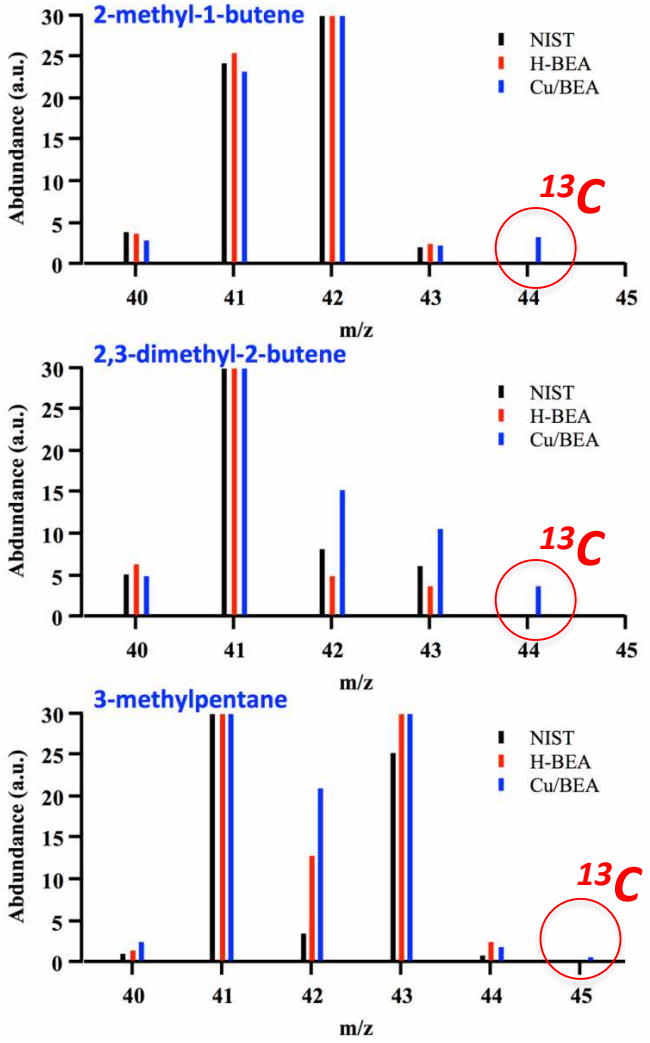
100 h time on stream performance by Cu/BEA exhibits stable 2–3X productivity vs HBEA



-100 h catalyst stability is unique in this reaction
-Pressure rise with HBEA prevents testing to longer times on stream
-Active site for C_4 reactivation determined to be ionic Cu(I)-zeolite sites

C_4 reincorporation – DME + H_2 + C_4H_{10}

Observe ^{13}C from ^{13}C-labeled isobutane in C_5 and C_6 products



IDL Pathway SOT and Projection Summaries

Process Parameter	2014 SOT	2015 SOT	2016 Projection	2016 SOT	2017 Projection	2022 Design
Hydrocarbon Synthesis Catalyst	Commercially available beta-zeolite		**NREL beta-zeolite modified with promoter metal(s)** →			
H_2 Addition to HC Synthesis	No	Yes →				
Utilization of C_4 Reactor Products	Co-Product		**Recycle to Synthesis Reactor** →			
Single-Pass DME conversion	15%	15%	20%	**19%**	30%	40%
Productivity of Hydrocarbon Synthesis Catalyst (kg/kg-cat/h)	0.02	0.03	0.04	**0.04**	0.05	0.10
Carbon Selectivity to C_5+ Product	46.2%	48.3	86.1%	**91.1%**	89.9%	93.1%
Carbon Selectivity to Aromatics (HMB represents coke / pre-cursers)	25% Aromatics (10% HMB)	20% Aromatics (9% HMB)	8% Aromatics (4% HMB)	**8% Aromatics (4% HMB)**	4% Aromatics (2% HMB)	0.5% as HMB
Coupling of C_4-C_8 Olefins to Jet	No	→ Sensitivity Scenarios →				
C_5+ Product Yield (Gallons / Ton)	39.7	39.9	61.8	**60.5**	64.2	64.9
Carbon Efficiency to C_5+ Product	20.7%	20.8%	29.9%	**29.3%**	31.0%	31.2%
C_4 Product Yield (Gallons / Ton)	17.9	17.7	0.0	**0.0**	0.0	0.0
Carbon Efficiency to C_4 Product	7.5%	7.4%	0.0%	**0.0%**	0.0%	0.0%
Minimum Fuel Selling Price ($ / GGE)	$5.60	$5.20	$4.13	**$4.13**	$3.80	$3.47
Conversion Impact to MFSP ($ / GGE)	$3.49	$3.31	$2.57	**$2.55**	$2.41	$2.09

Note: All cost values are presented in 2014$.

IDL Pathway Technical Parameters (FY2016 SOT)

IDL High Octane Gasoline FY2016 SOT Summary Compared to Original Projections

Process / Economic Metrics	Units	FY2016 SOT	FY2016 Projection
Minimum Fuel Selling Price (MFSP)	**$ / GGE**	**4.13**	**4.13**
	$ / Gallon	4.01	3.95
Conversion Contribution to MFSP	**$ / GGE**	**2.55**	**2.57**
	$ / Gallon	2.48	2.46
Gasoline (C5+) Product Yield	GGEs / Dry Ton	58.7	59.1
	Gallons / Dry Ton	60.5	61.8

DME-to-HC Experimental Metrics		Units	FY2016 SOT	FY2016 Projection
Reactor Temperature		°C	200	200
DME Conversion	Single-Pass	%	19.2%	20.0%
	Overall Process	%	85.1%	83.9%
Total Hydrocarbon Catalyst Productivity		kg / kg-cat / hr	0.044	0.040
Carbon Selectivity to C5+ Product		%	91.1%	86.1%

Sustainability Metrics	Units	FY2016 SOT	FY2016 Projection
Carbon Efficiency to Hydrocarbon Products	% C in Feedstock	29.3%	29.9%
Energy Efficiency to Hydrocarbon Products	% LHV of Feedstock	42.7%	43.1%
Water Consumption	Gal H2O / Gal C5+	5.5	5.8
Fossil GHG Emissions	g CO2-e / MJ Fuel	1.1	0.8
Fossil Enegy Consumption	MJ Fossil Energy / MJ Fuel	0.015	0.011

Sustainability Metrics for IDL Pathway

SOT vs. Projection: SOT sustainability metrics closely match projections based on technical targets

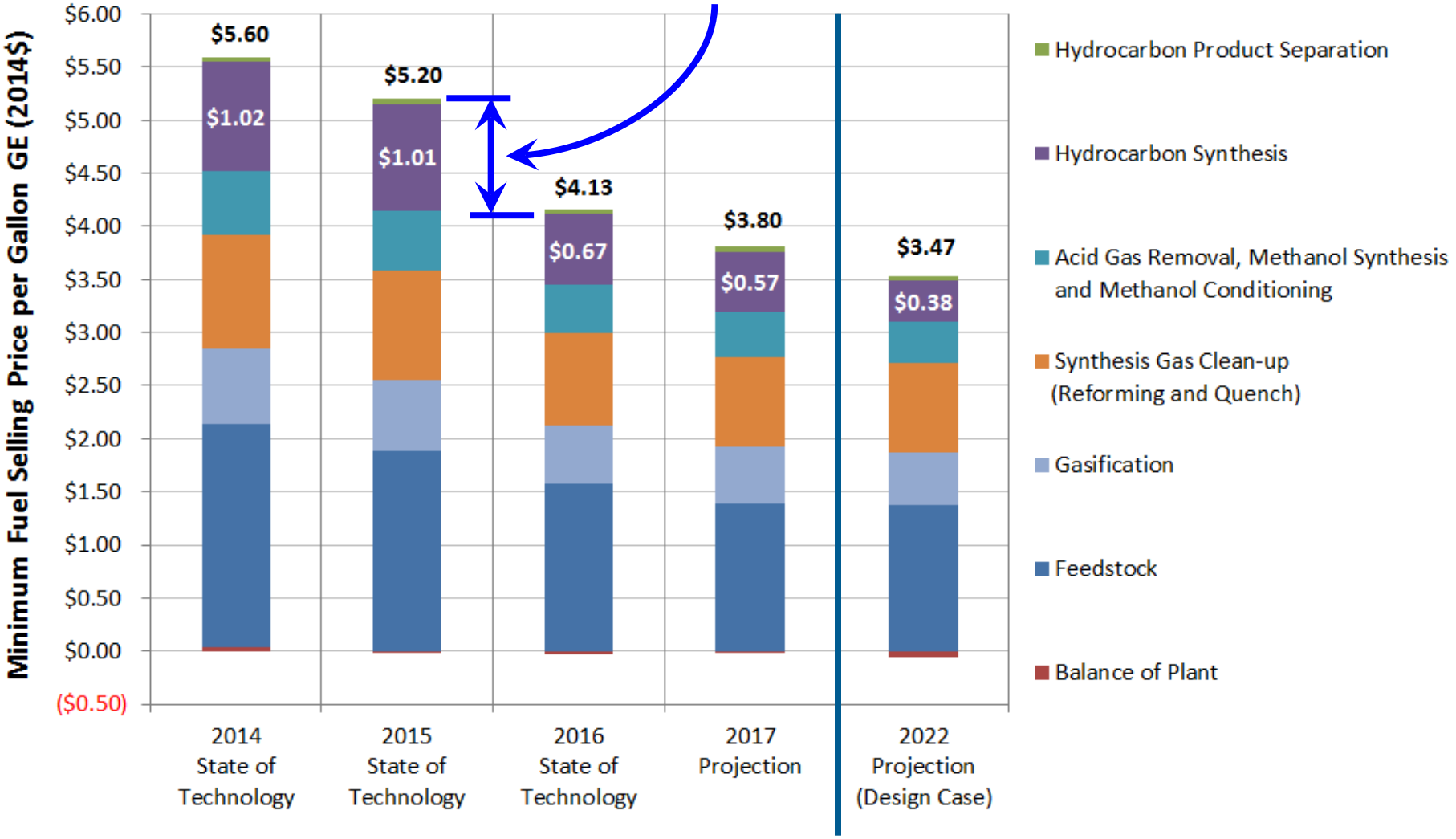
Trends in Modeled Sustainability Metrics	2014 SOT	2015 SOT	2016 Projection	2016 SOT	2017 Projection	2022 Projection
Fossil GHG Emissions (g CO2-e / MJ Fuel)	1.64	1.65	0.81	**1.12**	0.96	0.60
Fossil Energy Consumption (MJ FE / MJ Fuel)	0.023	0.022	0.011	**0.011**	0.013	0.006
Total Fuel Yield (Gal / Ton)	57.5	57.7	61.8	**60.5**	64.2	64.9
Total Fuel Yield (GGE / Ton)	51.3	52.2	59.1	**58.7**	61.4	61.9
Carbon Efficiency to C5+ (%C in Feedstock)	20.7	20.8	29.9	**29.3**	31.0	31.2
Carbon Efficiency to HCs (%C in Feedstock)	28.2	28.3	29.9	**29.3**	31.0	31.2
Water Consumption (Gal H2O / Gal C5+ HCs)	12.4	7.4	5.8	**5.5**	5.2	1.7

Note: Metrics apply to conversion of biomass to products only

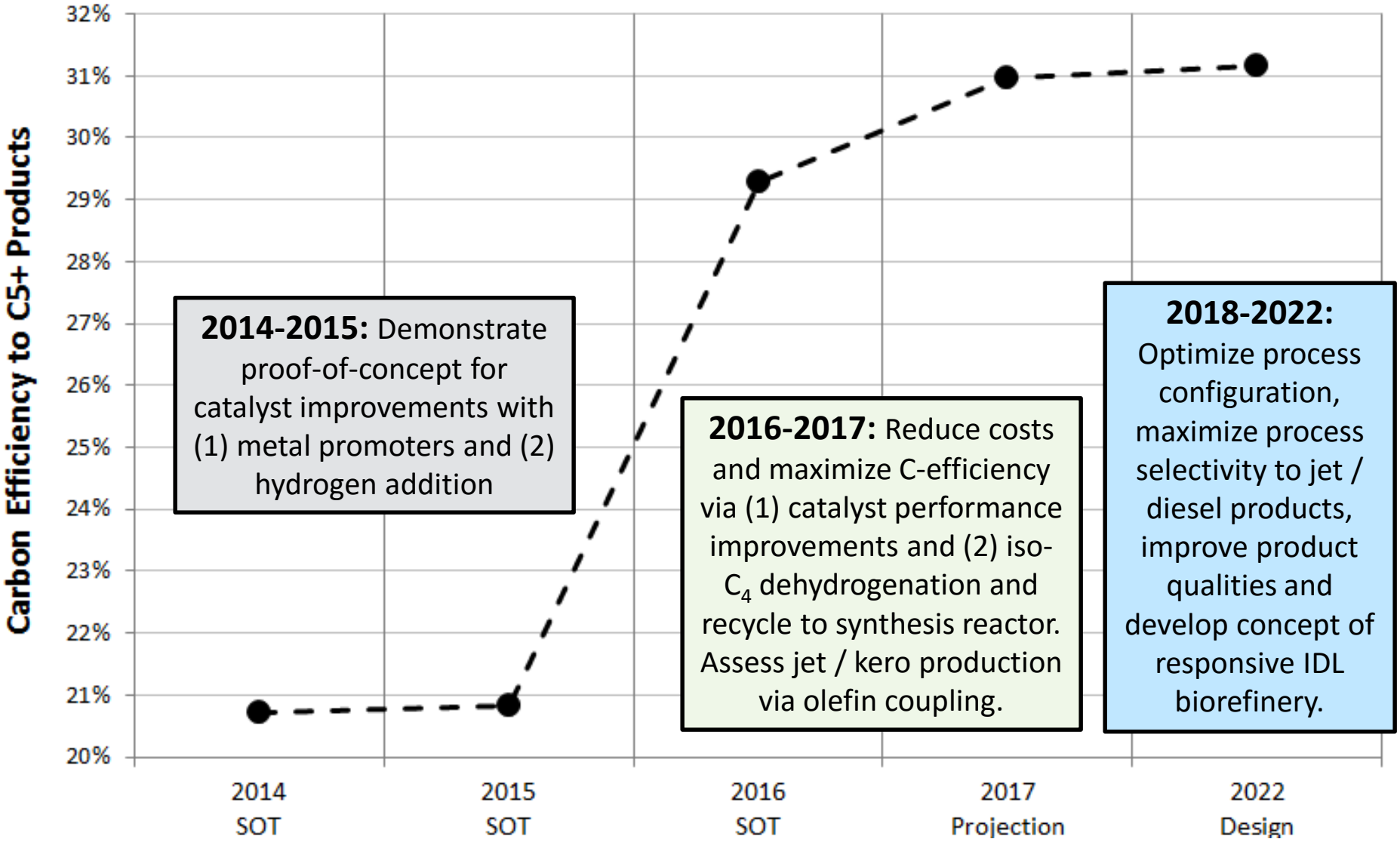
Waterfall Chart for IDL Pathway

FY2016 achievements result in MFSP reduction of $1.07 per GGE

(1) Feedstock cost reduction, (2) improved catalyst productivity + selectivity, (3) isobutane reactivation and recycle

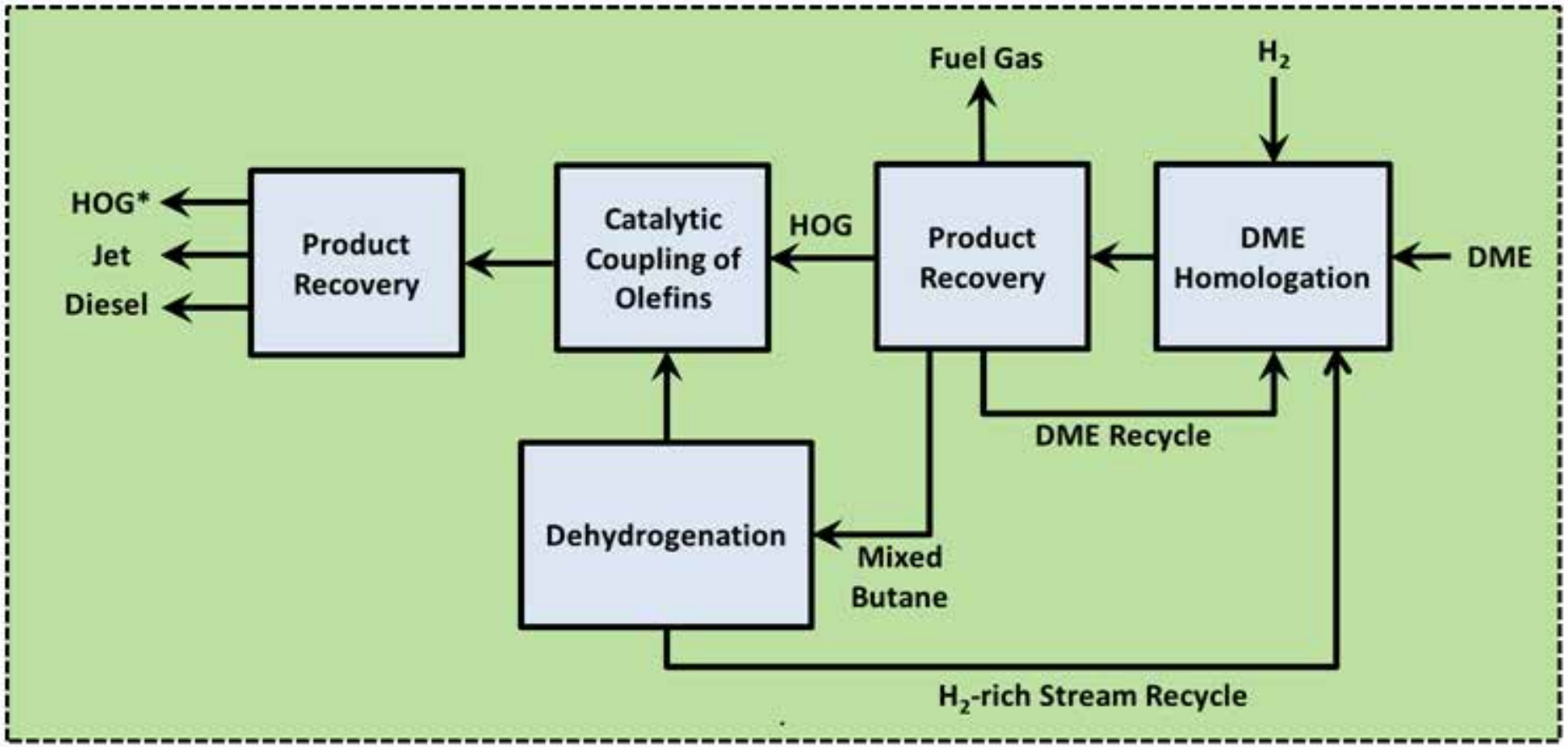


Phases of IDL Pathway Development



Sensitivity for Olefin Coupling to Jet Fuel

IDL Pathway with Jet / Diesel-Range Products



Sensitivity for Olefin Coupling to Jet Fuel

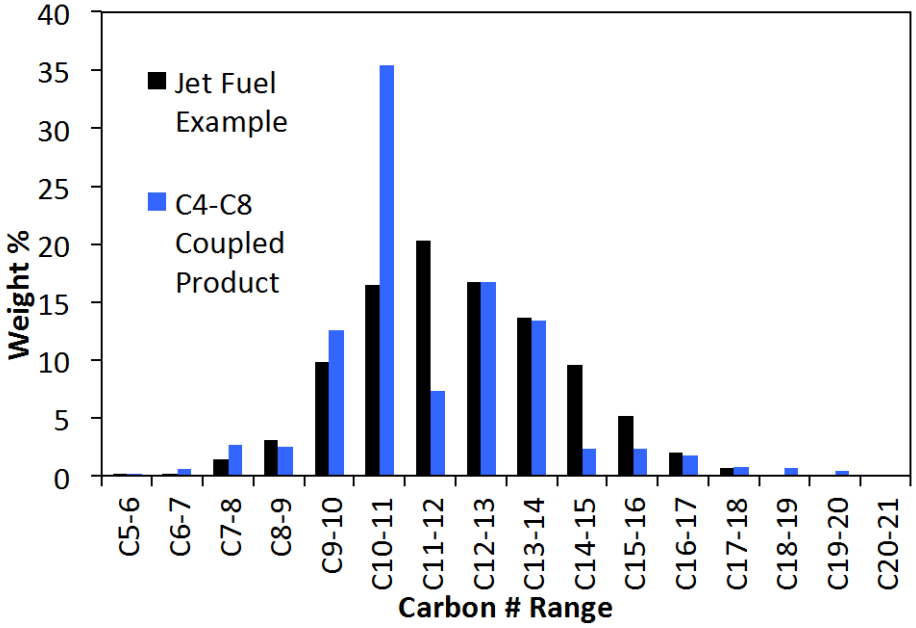
IDL Pathway Base Scenario + Olefin-Coupling Sensitivity

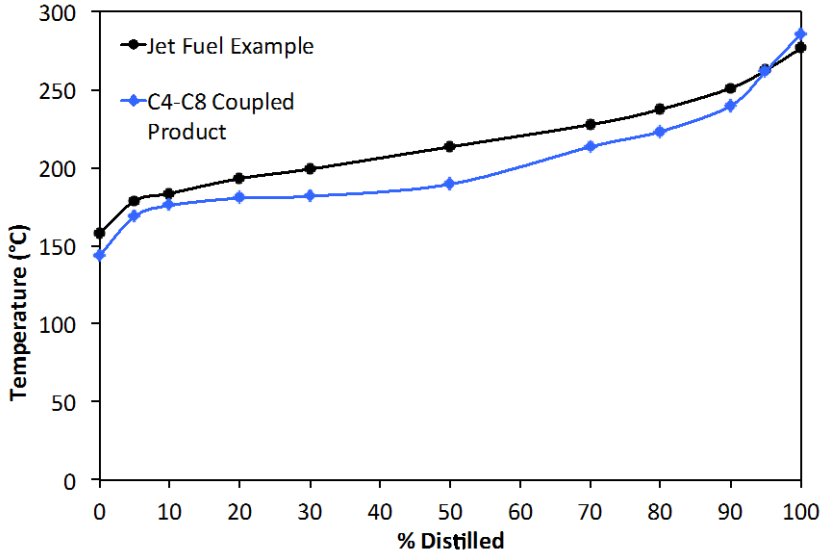
	2016 Projection	2016 State of Technology (SOT) Scenarios	
Case Description	**Base:** No olefin coupling	**Base:** No olefin coupling	**Sensitivity:** With olefin coupling
MFSP (2014$ / GGE)	**4.13**	**4.13**	**4.59**
High-Octane Gasoline Yield (GGE / Ton)	59.1	58.7	41.7
Mixed Butane Product Yield (GGE / Ton)	---	---	---
Jet Yield (GGE / Ton)	---	---	9.5
Diesel Yield (GGE / Ton)	---	---	0.8
Total Fuel Yield (GGE / Ton)	**59.1**	**58.7**	**52.0**

GGE yield drops in current olefin-coupling scenario due to large recycle streams. Analysis focus in FY2017 will be optimizing the process configuration to minimize recycle flows and boost jet / diesel yields.

Product Analysis for HOG Pathway: Jet/Diesel

C_4-C_8 olefin coupling produces a C_8-C_{20} distribution of HCs, with >90% being suitable as a jet fuel blendstock





Fuel Properties	Jet Fuel ASTM D1655 Limits	Synthetic Fuel from Olefin Coupling
Viscosity (mm^2/s)	8.0 max	7.6
Freeze Point (°C)	–40 max	–81
Density (kg/m^3)	775 – 840	783
LHV (MJ/kg)	42.8 min	43.8

M. Behl, et al., *Energy & Fuels* 29 **2015** 6078, NREL Milestone Report Dec 2015.

Future Challenges / Approaches for IDL Pathway

Key Challenges for DME-to-HCs and Olefin Coupling

- **Productivity / Yield**
  - Optimize light paraffin (C_{4-}) recycle to increase yield of C_{5+} molecules using next-generation DME-to-HC catalyst to control paraffin:olefin product ratios.
  - Continue to shift selectivity away from aromatics to paraffins
  - Maximize yields of jet / diesel-range products.
- **Catalyst Regeneration and Process Integration**
  - Develop industrially-relevant mitigation and regeneration protocols
  - Demonstrate continuous process for C_4+ olefin coupling

Strategies

- Understand structure-function relationships – metallic and ionic Cu species
- Catalyst design and modification – explore the role of Lewis acid sites
- Develop and optimize responsive biorefinery models
- Product quality analysis (w/ LDRD + TCF projects)
- Reaction and process engineering – validate DME-to-HCs at large bench scale

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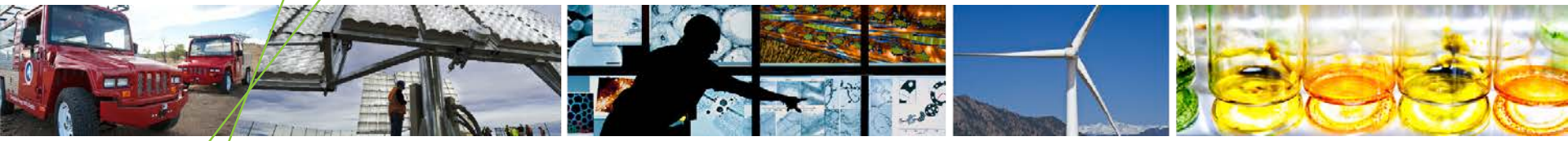
Additional Content for Reviewers



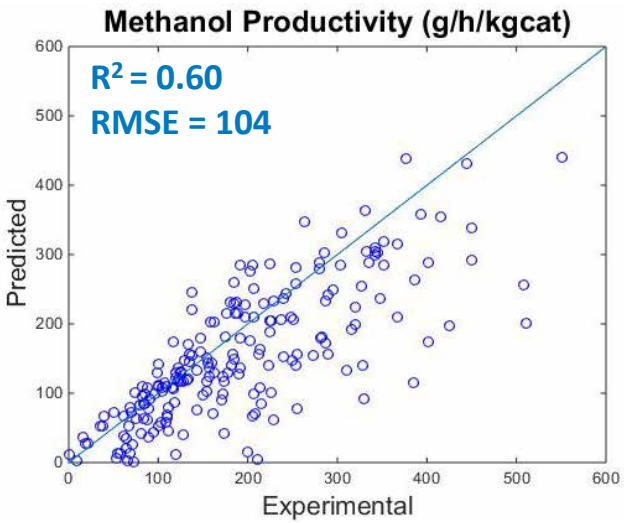
Task: Kinetic Modeling for Process Optimization

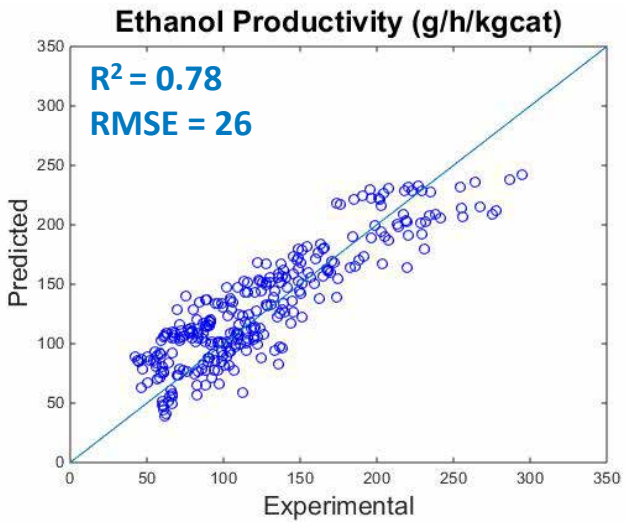
Principal Investigators: Jack Ferrell, Carrie Farberow and Erick White

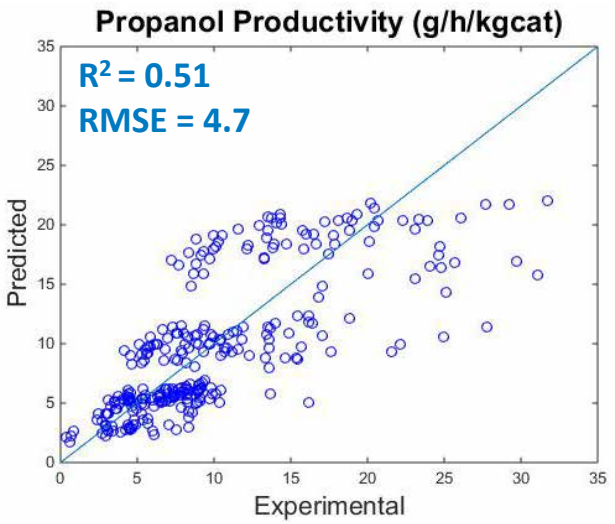
Kinetic Modeling for Process Optimization

- **Develop a new tools for process modeling:**
  - **Projections** for catalyst behavior **in scaled-up industrial reactors** will be modeled by coupling bench-scale kinetic models with mass and heat transfer effects, along with the impacts of various operating conditions (including **recycles**)
  - **Inform research about optimal operating conditions**
- **Conversion of syngas to mixed alcohols over a K-CoMoS$_x$ catalyst will be used for initial evaluation and validation**
  - Significant quantities of **experimental data** are currently available
  - **Microkinetic models for other systems** being developed in **collaboration with computational group** for energetics of elementary steps
- **Finished reaction modeling tool applicable to multiple systems, both biological & thermochemical, with sufficient expt. data**
- **Reaction models are compatible with Aspen Plus, which will:**
  - **Improve** quality of **techno-economic projections**, and allow for process optimization
  - Enhance confidence in model projections for new technologies upon potential scale-up and commercialization

Kinetic Modeling for Process Optimization

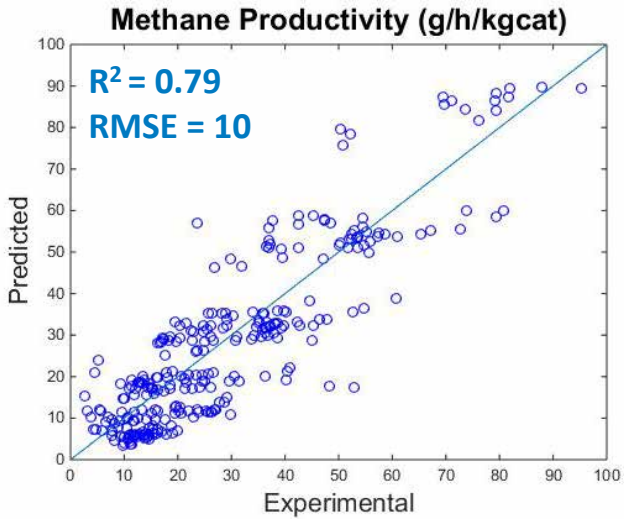


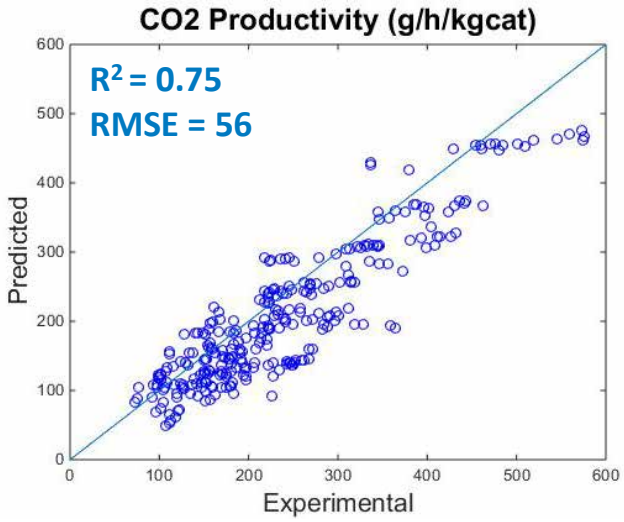




Accomplishment:

Kinetic model predicts experimentally observed productivities for all major reaction products.

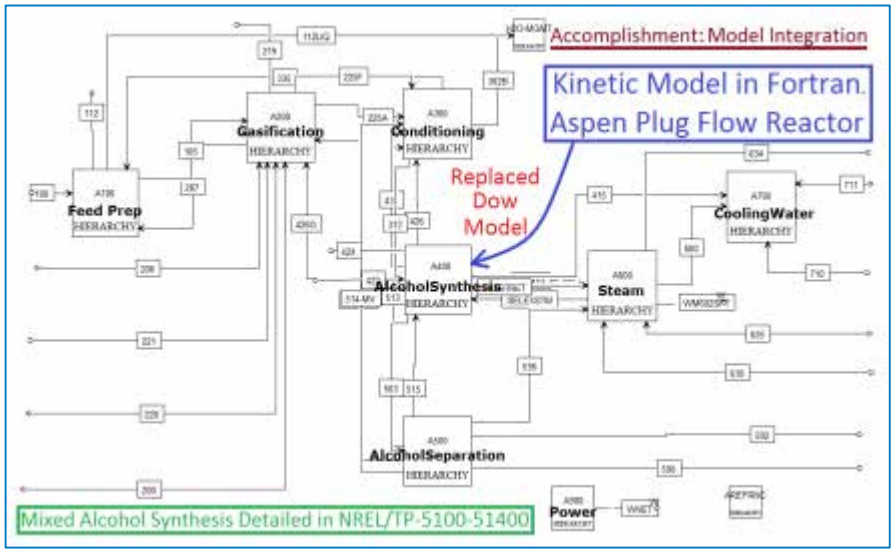




Kinetic Modeling for Process Optimization

Completion of mixed alcohol modeling efforts in FY16 enabled a shift of focus toward modeling reactions in support of the IDL task

- Q2 Go/No-Go: Demonstrated full integration of mixed alcohols kinetic model into an Aspen Plus plant simulation TEA model
- Q3 QPM: Developed a plan for parameterizing a DME homologation kinetic model based on a literature review and consideration of the intended applications of the model.



FY17 – 19 OUTCOME:

Develop kinetic models for DME homologation and olefin coupling, which will ultimately be incorporated into process-scale reactor models, allowing for more predictive and tunable process modeling and analysis capabilities.

Ongoing and Planned Research Activities:

- Defined plan for collecting kinetic data set for DME homologation on Cu/BEA, including ranges of experimental conditions. Initial data collection to be completed 12/31/16.
- Develop kinetic model with parameters estimated by fitting the model to kinetic data set. The FY17 model will describe:
  - DME conversion
  - Rate of production of:
    - C2-C3 fraction
    - C4 fraction
    - gasoline range hydrocarbons (C5+)