Techno-economic analysis for co-processing fast pyrolysis liquid in fossil refineries

NREL: Michael Talmadge, Christopher Kinchin, Helena Li Chum, Avantika Singh, Nick Carlson, Abhijit Dutta

Petrobras: Andrea de Rezende Pinho, Marlon BB de Almeida, Luiz Carlos Casavechia

Presented at BIOFIT Policy Conference
January 18, 2022

Agenda

- Intro to NREL
- Overview of refinery analysis
- Results of NREL-Petrobras analysis
- New refinery analysis capabilities and applications
- Questions and discussion

NREL Mission and Programs

*Visit **NREL.gov** for more information*

The National Renewable Energy Laboratory (NREL) advances the science and engineering of energy efficiency, sustainable transportation, and renewable power technologies and provides the knowledge to integrate and optimize energy systems.

Renewable Power	Sustainable Transportation	Energy Efficiency	Energy Systems Integration
Geothermal	**Bioenergy**	Advanced Manufacturing	Energy Security and Resilience
Solar	Hydrogen and Fuel Cells	Buildings	Grid Modernization
Water	Transportation and Mobility	State, Local, and Tribal Governments	Integrated Energy Solutions
Wind			

- Chemistry and Nanoscience
- Computational Science
- Energy Analysis
- Energy Storage
- Materials Science

NREL National Bioenergy Center

Visit ***nrel.gov/bioenergy***

The National Bioenergy Center (NBC) works to advance and develop innovative and cost-effective solutions that move the production of biofuels, bioproducts, biochemicals, and bioenergy to market.

Techno-Economic, Sustainability, Market Analysis

NBC Research Areas

- Biomass Feedstocks
- Biochemical Process Development and Integration
- Biomass Deconstruction and Pretreatment
- Biogas Upgrading and Waste-to-Energy
- Biological and Catalytic Conversion of Sugars and Lignin
- Algal Biofuels
- Thermochemical Process Integration, Scale-Up, and Piloting
- Heterogeneous Catalysis for Thermochemical Conversion

Purpose of Refinery Analysis

- Leverage **global refining capacity** (220 billion-gal/year FCC) **to reduce cost of biofuels**.
- Apply an analysis approach to estimate the **value of bio-blendstocks and bio-oils**.
- Identify valuable properties and chemical co-products to **generate market pull** from refiners.
- Quantify **cost and environmental impacts** on refinery operations.

Techno-economic Analysis

Quantifies production cost for bio-blendstocks

Refinery Impact Analysis

Quantifies potential bio-product value to refiners

Break-Even Value (BEV) = f (Prices, Demands, Configurations, Properties, etc.)

Difference between BEV (including policy incentives) and minimum selling price (MSP) represents the potential benefits/value for refinery and supply chain.

History of NREL Refinery Analysis

2010 – 2014: National Advanced Biofuels Consortium

- Property comparisons of bio- and fossil- intermediates
- Initial biofuels blending model in Aspen PIMS

NABC National Advanced Biofuels Consortium

BR PETROBRAS

2014 – 2017: NREL-Petrobras Co-Processing Analysis

- Fluid Catalytic Cracking (FCC) and product finishing yield models coupled with economics for initial optimization capabilities.

2016 – 2021: Co-Optima Refinery Analysis (collaboration with PNNL and ANL)

- Complete refinery models with various configurations quantify values of bio-blendstocks and bio-intermediates.
- Tools integrated with Aspen Plus quantify environmental benefits.
- Refinery models are now capable of direct blending bio-blendstocks and co-processing bio-intermediates via hydroprocessing and FCC.

Co-Optimization of Fuels & Engines

PNNL = Pacific Northwest National Lab and ANL = Argonne National Lab.

NREL-Petrobras FCC Co-Processing Analysis

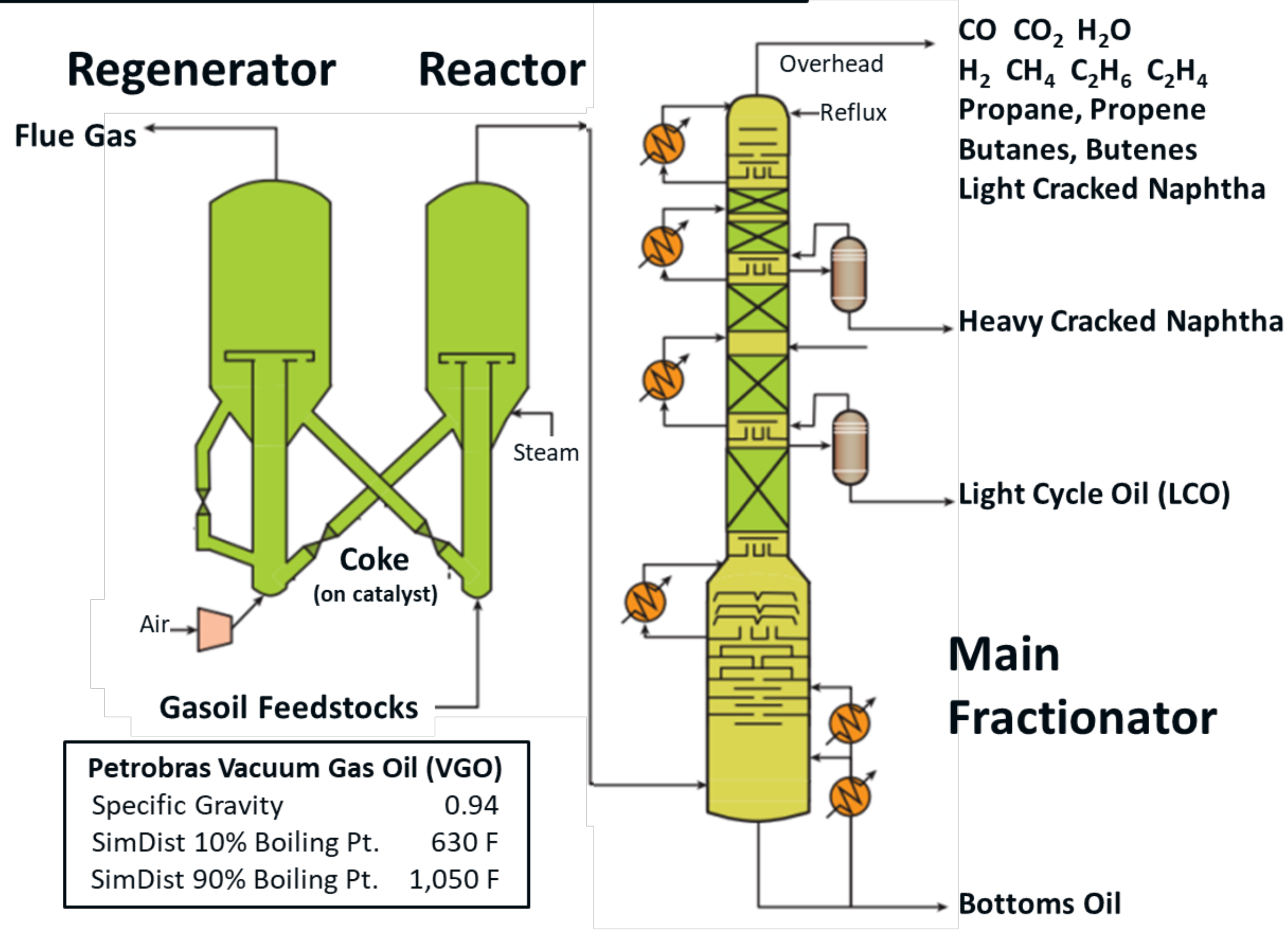
Assess the technical and economic feasibility of co-processing raw, biomass-derived pyrolysis oil with fossil feedstocks in FCC to produce renewable hydrocarbon fuels and chemicals.

Leverage existing FCC capacity to reduce economic risk of biofuels production.

- 90-billion gallons/year in US
- 220-billion gallons/year globally

FCC Conversion = 100 – LCO – Bottoms

PFD Source: CEP, May 2014



Petrobras Vacuum Gas Oil (VGO)	
Specific Gravity	0.94
SimDist 10% Boiling Pt.	630 F
SimDist 90% Boiling Pt.	1,050 F

Petrobras FCC Co-Processing Experiments

Petrobras "SIX" demo unit has same hardware as a commercial FCC

- Feed nozzles
- Riser cyclone
- Packed stripper
- Heat balanced
- Mass flowrate: 200 kg/h
- Riser: L=18 m

Co-Processing Experiments

- Two pine-derived pyrolysis oils with consistent physical properties
- Mass balance range of 96 – 100%
- 3-hour test runs
- Cumulative time w/ py-oil > 400 hours
- Up to 20 wt% pyrolysis oil in FCC feed
- 54 experimental data points

Fuel Processing Technology 131 (2015) 159-166

Co-processing raw bio-oil and gasoil in an FCC Unit

Andrea de Rezende Pinho [a,*], Marlon B.B. de Almeida [a], Fabio Leal Mendes [a], Vitor Loureiro Ximenes [a], Luiz Carlos Casavechia [b]

[a] PETROBRAS, Centro de Pesquisas e Desenvolvimento Leopoldo A. Miguez de Mello (CENPES), Ilha do Fundão, Av. Horácio Macedo, 950, Rio de Janeiro, RJ, Brazil
[b] PETROBRAS-SIX, Rodovia do Xisto BR 476, km 143, São Mateus do Sul, PR, Brazil

Fuel 188 (2017) 462-473

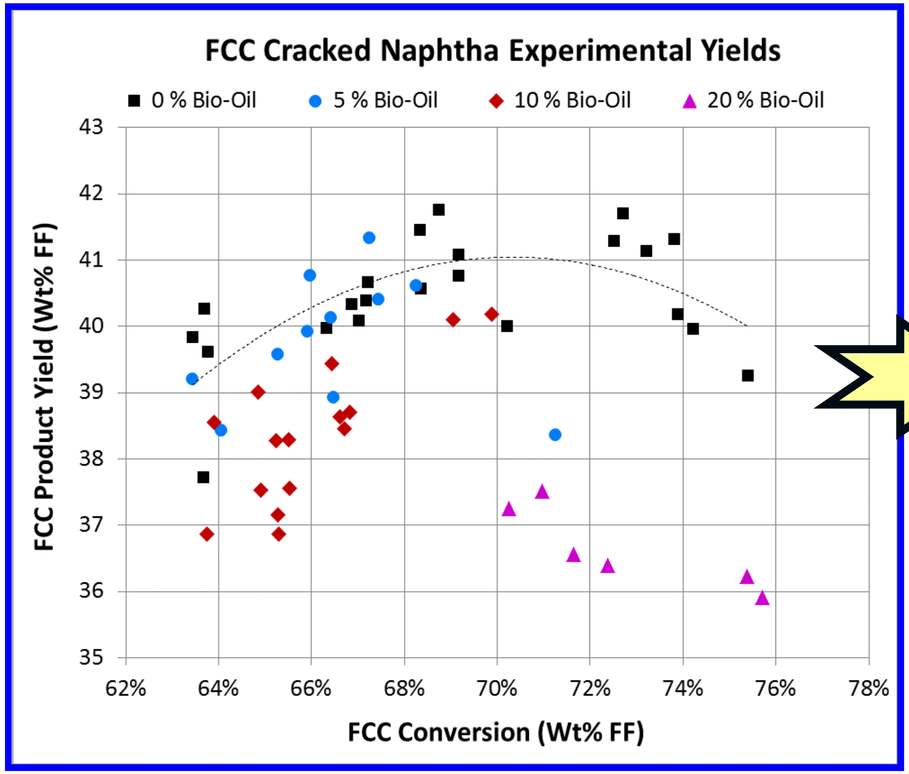
Fast pyrolysis oil from pinewood chips co-processing with vacuum gas oil in an FCC unit for second generation fuel production

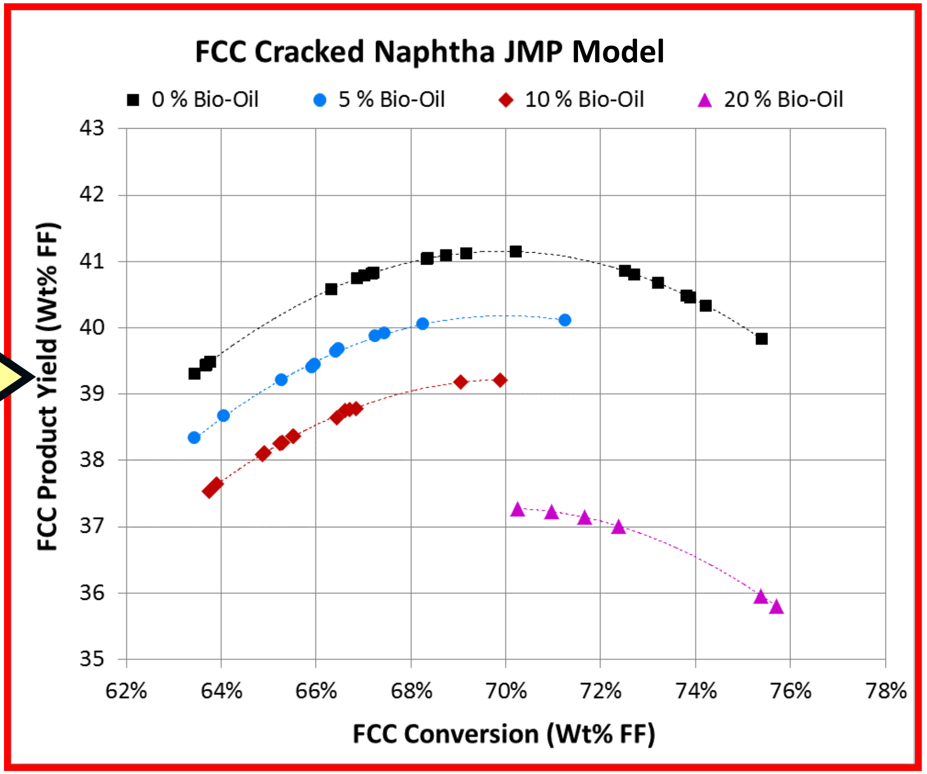
Andrea de Rezende Pinho [a,*], Marlon B.B. de Almeida [a], Fabio Leal Mendes [a], Luiz Carlos Casavechia [b], Michael S. Talmadge [c], Christopher M. Kinchin [c], Helena L. Chum [c]

[a] PETROBRAS, Centro de Pesquisas e Desenvolvimento Leopoldo A. Miguez de Mello (CENPES), Ilha do Fundão, Av. Horácio Macedo, 950, Rio de Janeiro, RJ, Brazil
[b] PETROBRAS-SIX, Rodovia do Xisto BR 476, km 143, São Mateus do Sul, PR, Brazil
[c] NREL – National Renewable Energy Laboratory, 15013 Denver West Parkway Golden, CO 80401-3305, USA

NREL-Petrobras Yield Model from Experimental Data

- Utilized statistical software package to derive yield models from experimental data.
- Yield models, combined with economics, enable optimizations to identify most profitable operating points.

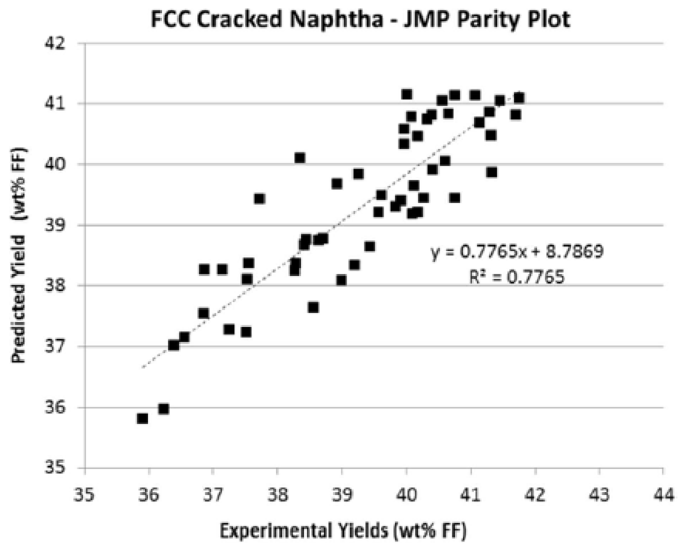


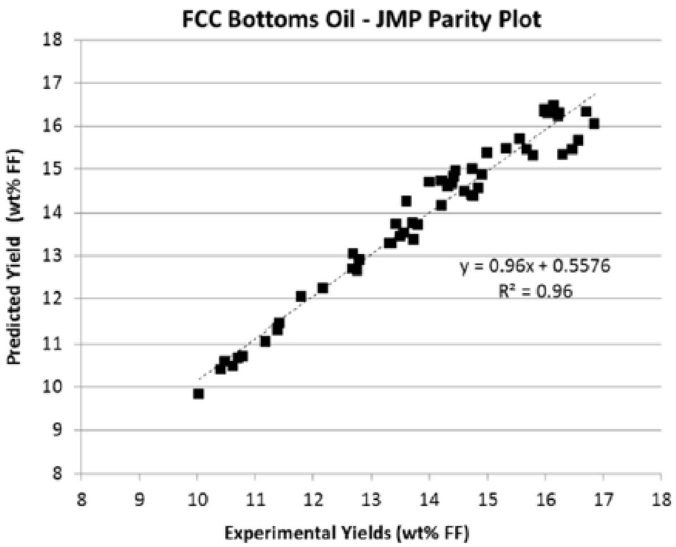


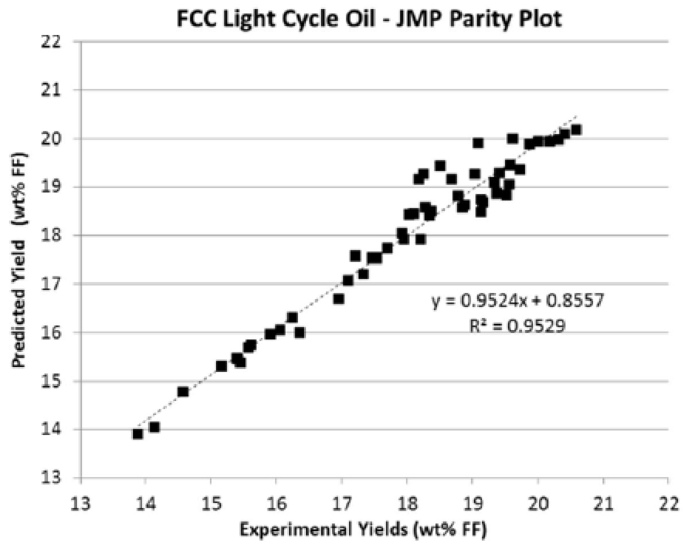
Complete FCC Yield Model	Oxygen Species	Refinery Fuels	LPG Products	Liquid Products
	CO CO_2 Water	Dry Gas (C_2-)	Propane Propylene	Cracked Naphtha
		Coke	i-Butane n-Butane	Light Cycle Oil (LCO)
			Butenes	Bottoms Fuel Oil

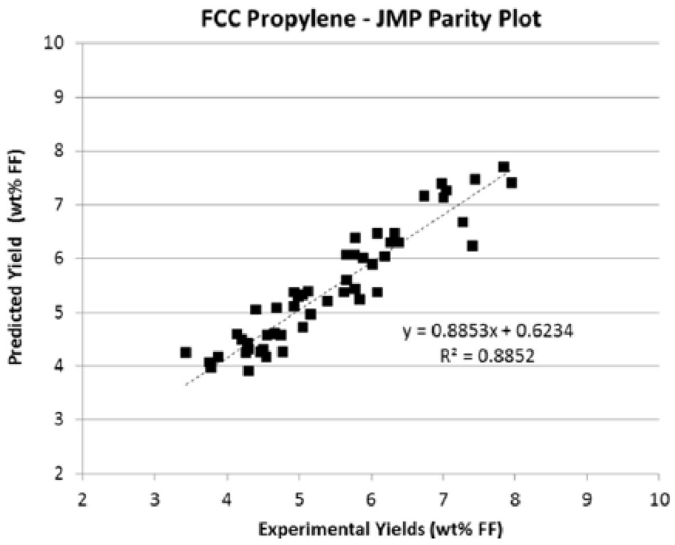
Yield Model Validations with Experimental Data

- Validated yield model predictions for all raw products from FCC unit.
- Utilized Aspen HYSYS model to further validate model predictions as a function of FCC reactor severity.



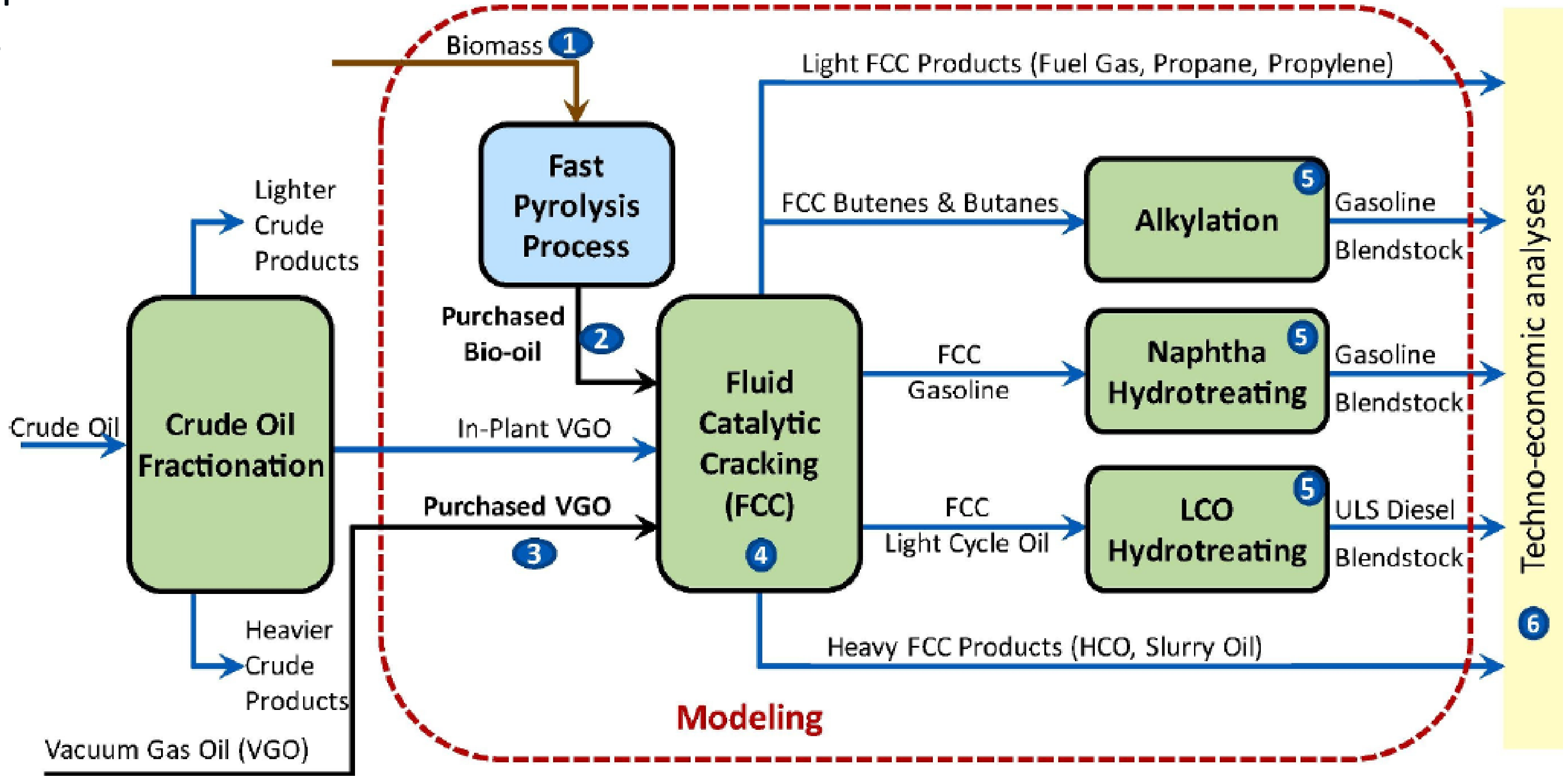






Scope of NREL-Petrobras Analysis

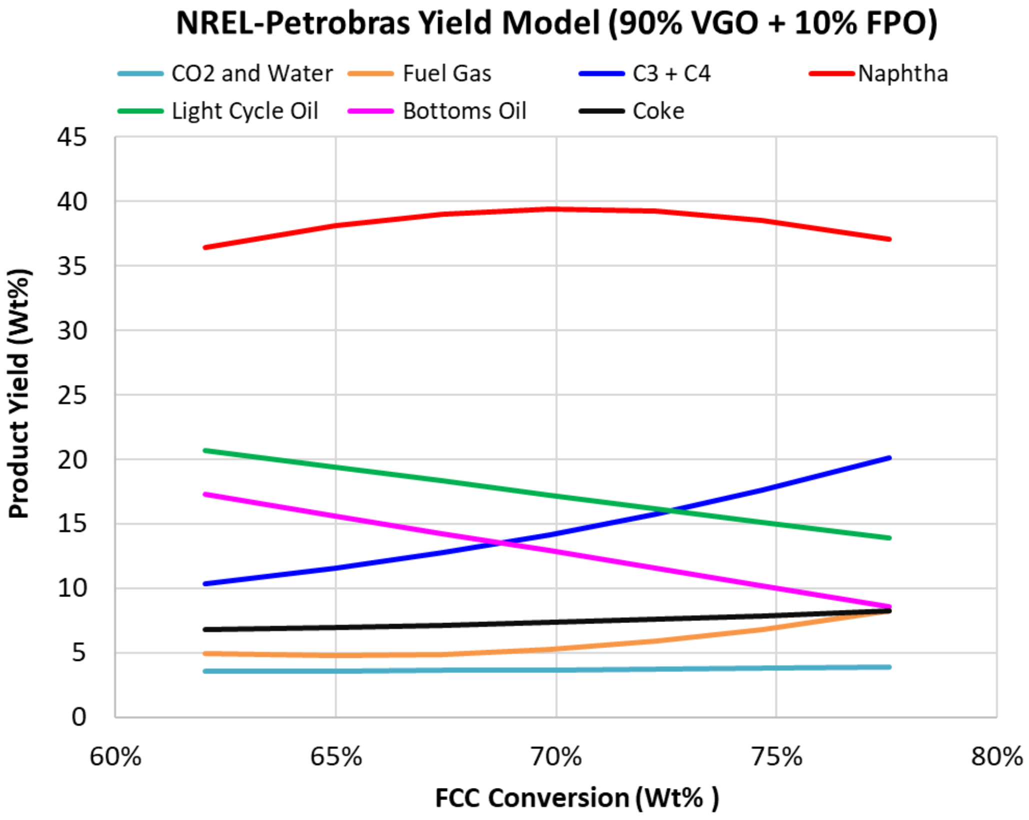
- Scope includes downstream product upgrading units for finished blendstocks:
  - i-C_4 and C_4-olefins converted to high-octane gasoline blendstock via **alkylation**.
  - **Cracked naphtha hydrotreating** to gasoline blendstock.
  - **LCO hydrotreating** to ULSD blendstock.



Enabling Optimization with Yield and Pricing Models

- Add product pricing model to convert complex FCC yields to single value ($/unit FCC feed)
- Profit = value of products minus
  - Cost of feeds
  - Costs of catalysts, utilities, H_2, royalties
  - Amortized capex

Refinery Process Yield Model + Variable Pricing Model

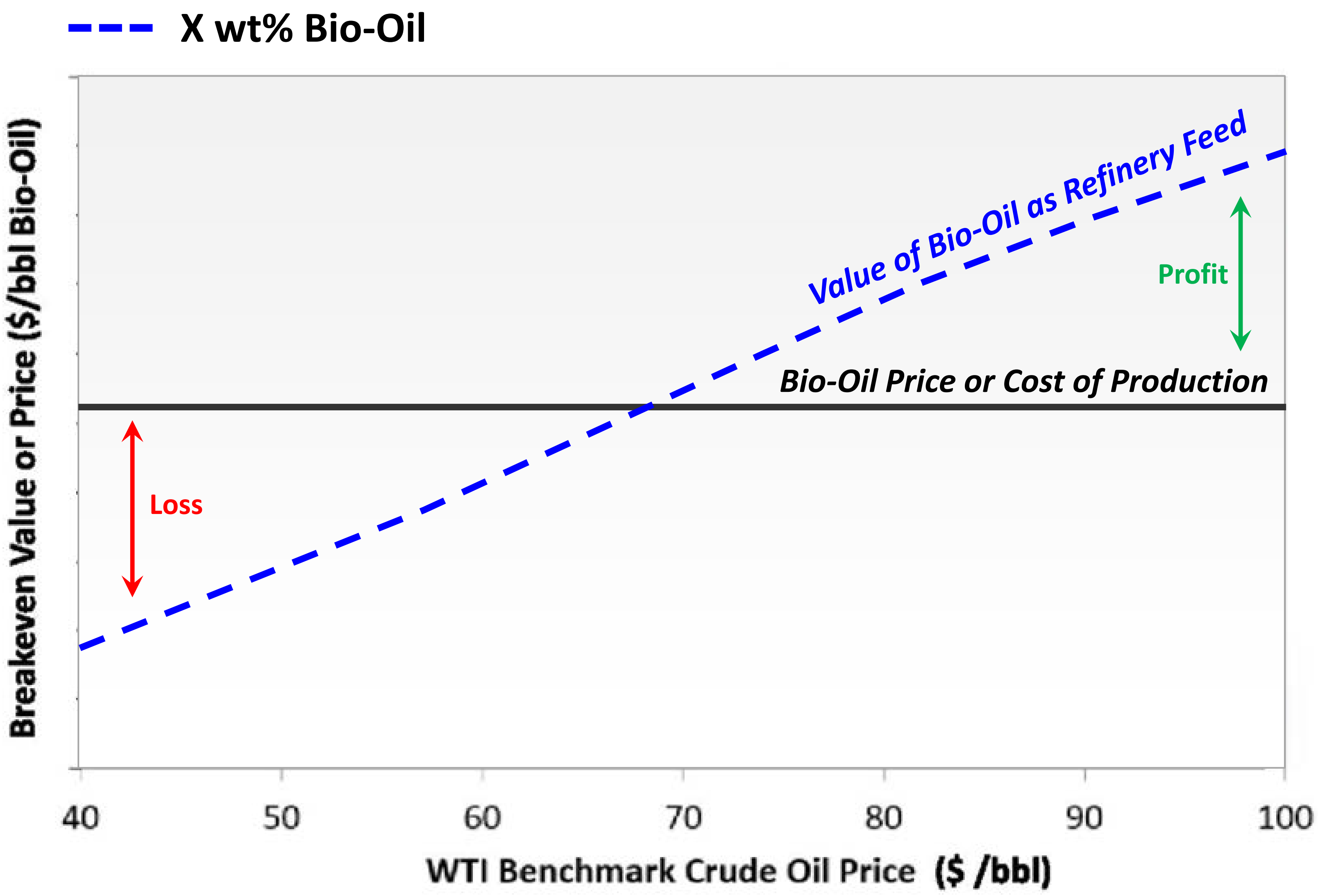


West Texas Intermediate (WTI) 80 ($/BBL)

Products	**Price**	**Unit**
Natural Gas	0.1195	$/LB
Propane	0.9979	$/GAL
Propylene	2.2232	$/GAL
n-Butane	1.2233	$/GAL
i-Butane	1.2998	$/GAL
Conventional Regular Gasoline	2.2661	$/GAL
Conventional Midgrade Gasoline	2.3501	$/GAL
Conventional Premium Gasoline	2.5619	
Reformulated Regular Gasoline	2.3669	$/GAL
Reformulated Midgrade Gasoline	2.5061	$/GAL
Reformulated Premium Gasoline	4.0000	$/GAL
Alkylate Intermediate	2.5617	$/GAL
Jet Fuel	2.4149	$/GAL
Ultra Low Diesel Fuel (ULSD)	2.4193	$/GAL
California Diesel Fuel (CDF)	2.0000	$/GAL
Heating (No 2) Oil	2.3891	$/GAL
Light Cycle Oil (LCO)	2.3916	$/GAL
Vacuum Gas Oil (VGO)	2.2587	$/GAL
Residual (No 6) Oil - 0.3% Sulfur	1.3910	$/GAL
Residual (No 6) Oil - 1% Sulfur	1.0540	$/GAL
Residual (No 6) Oil - 3% Sulfur	0.7574	$/GAL

Illustrative Example for Presentation of Results

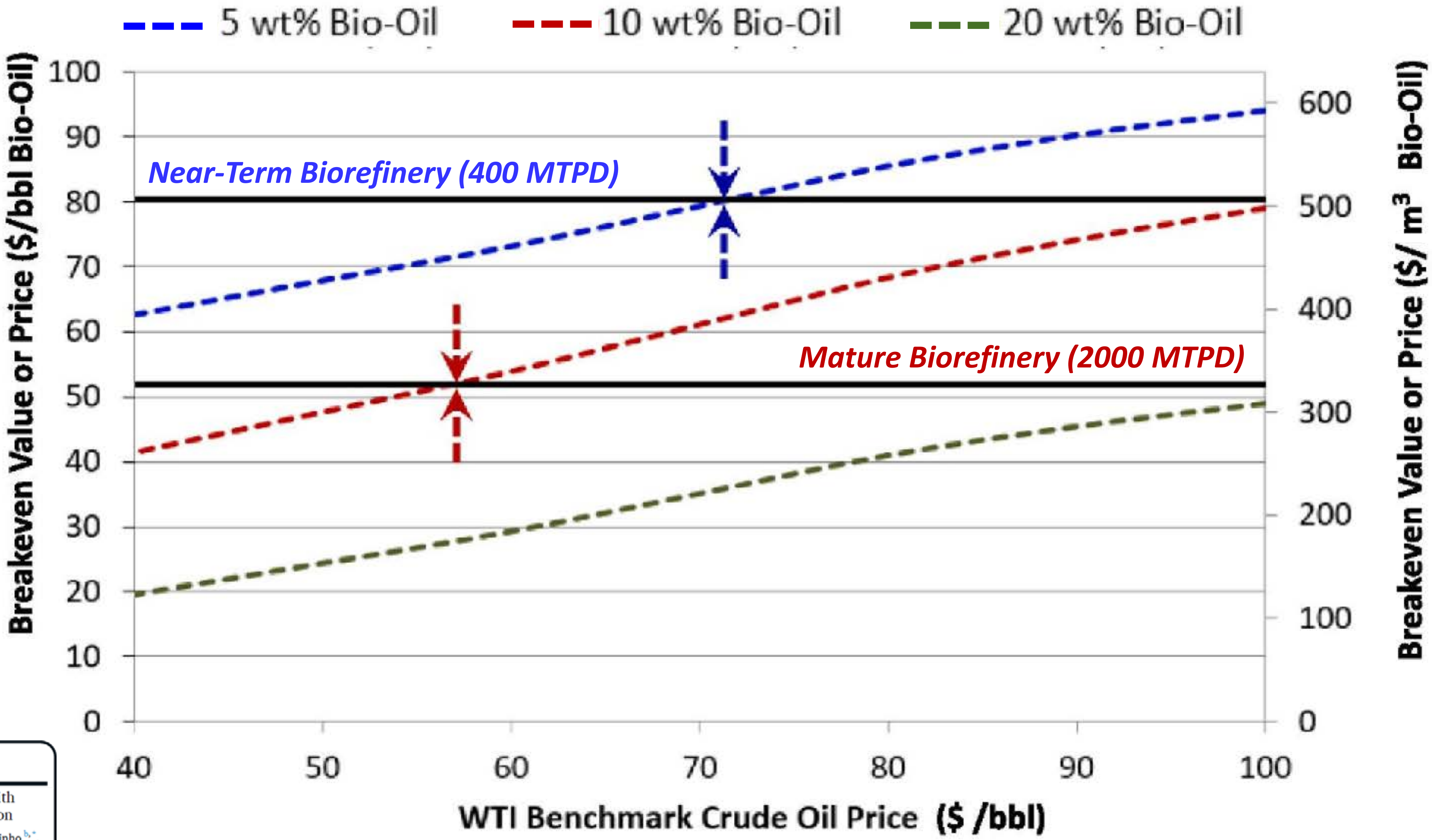
- Dark, solid lines represent costs of bio-oil production at different biorefinery scales.
- Colorful, dotted lines represent the values of bio-oil as refinery (FCC) feedstock.



Breakeven Value for Fast Pyrolysis Oil Co-Processing

Breakeven Analysis

- Revenue equals cost at “Breakeven Point”
- “Pyrolysis Oil Breakeven Value” = f(value of products)
- Profit realized when cost < “Breakeven Value”



Fuel 293 (2021) 119960

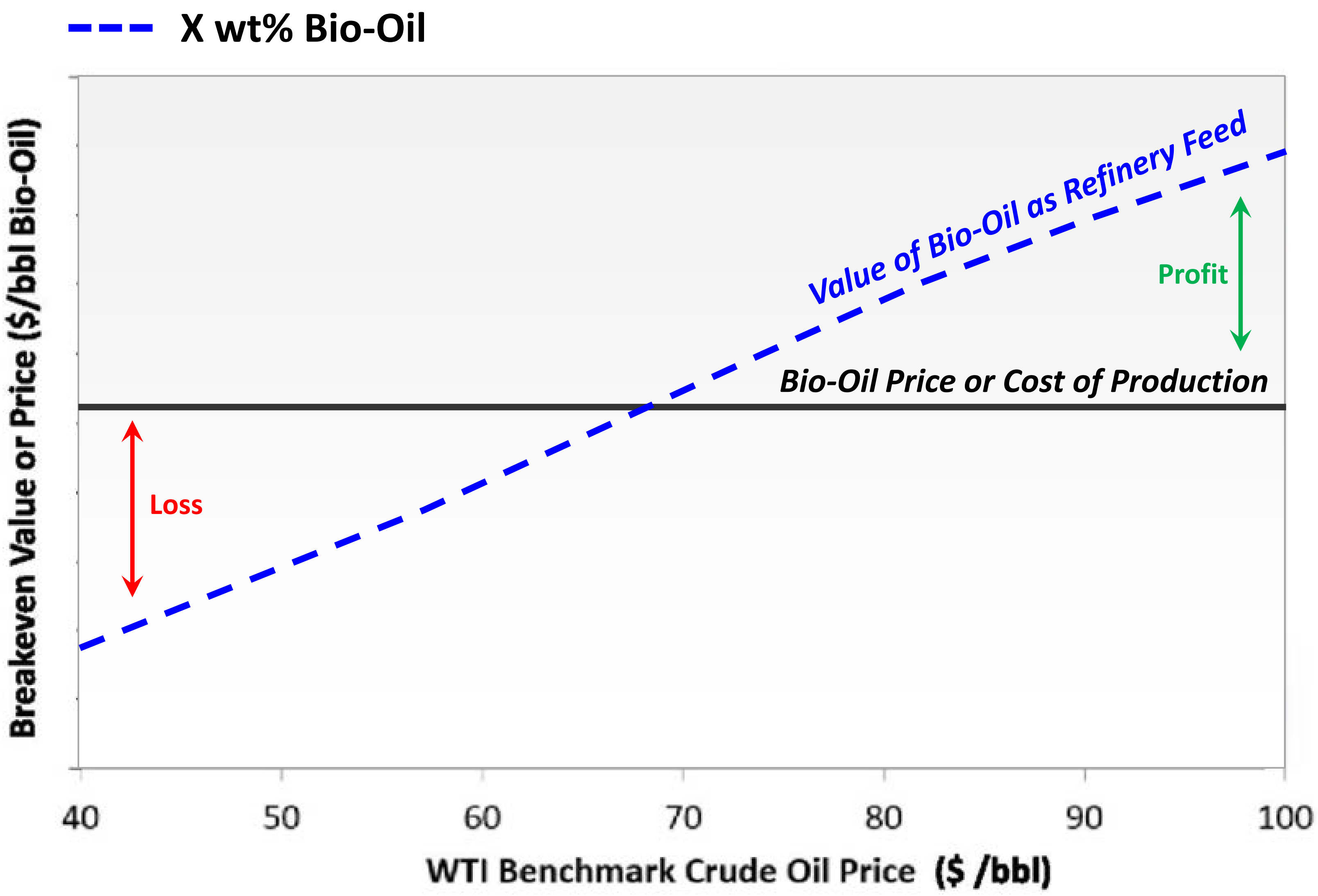
Techno-economic analysis for co-processing fast pyrolysis liquid with vacuum gasoil in FCC units for second-generation biofuel production

Michael Talmadge [a,*], Christopher Kinchin [a], Helena Li Chum [a], Andrea de Rezende Pinho [b,*], Mary Biddy [a], Marlon B.B. de Almeida [b], Luiz Carlos Casavechia [c]

[a] NREL - National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, CO 80401, USA
[b] PETROBRAS, Centro de Pesquisas e Desenvolvimento Leopoldo A. Miguez de Mello (CENPES), Ilha do Fundão, Av. Horácio Macedo, 950, Rio de Janeiro, RJ, Brasil
[c] PETROBRAS-SIX, Rodovia do Xisto BR 476, km 143, São Mateus do Sul, PR, Brasil

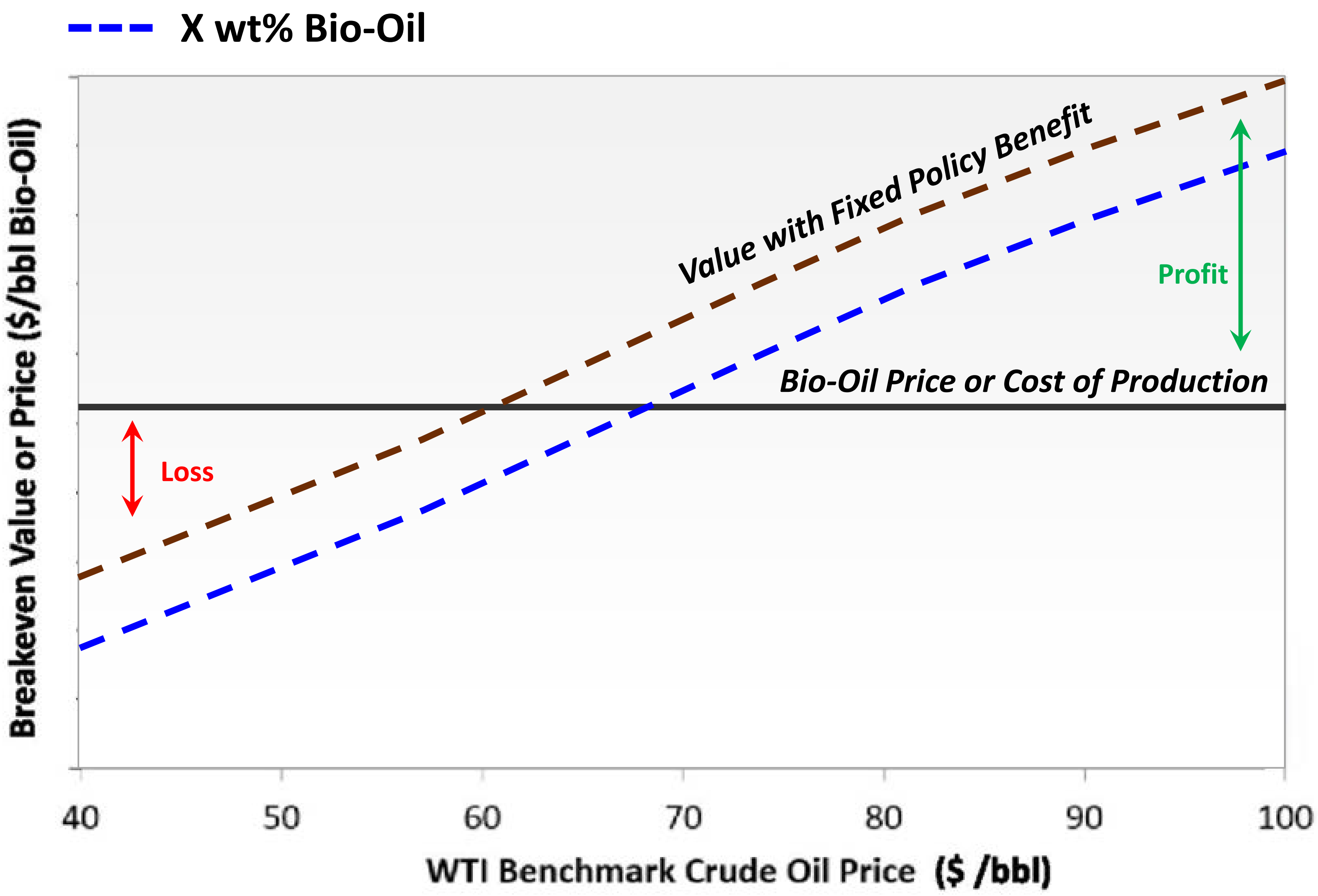
Policy Insights with Illustrative Example

- Biomass and derivative prices are NOT tied to crude prices.
- Refineries have high level of risk due to uncertainty in product market prices.
- Future tech development will increase value and decrease cost.
- Refiners need policy help in near-term when market values are low.



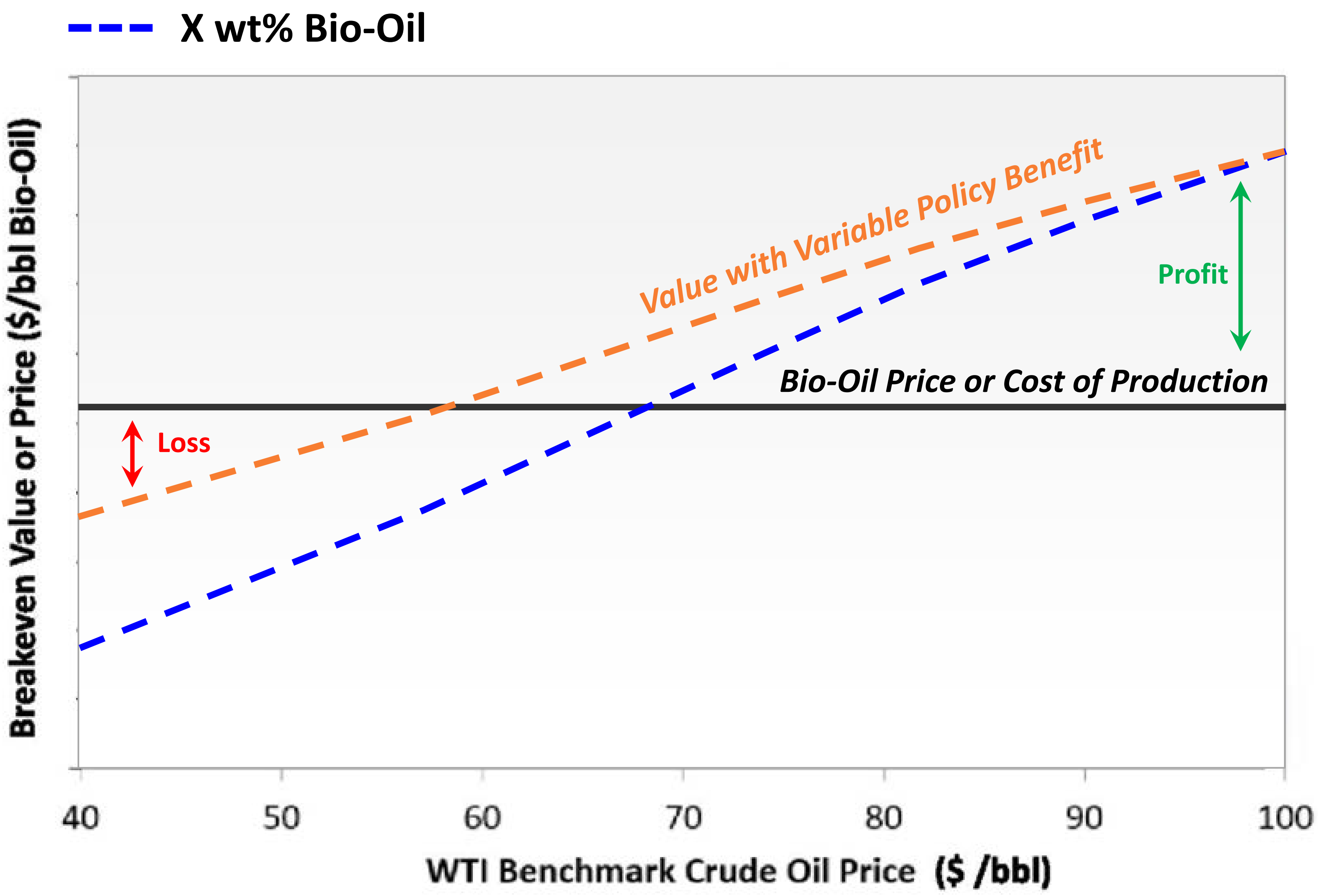
Policy Insights with Illustrative Example

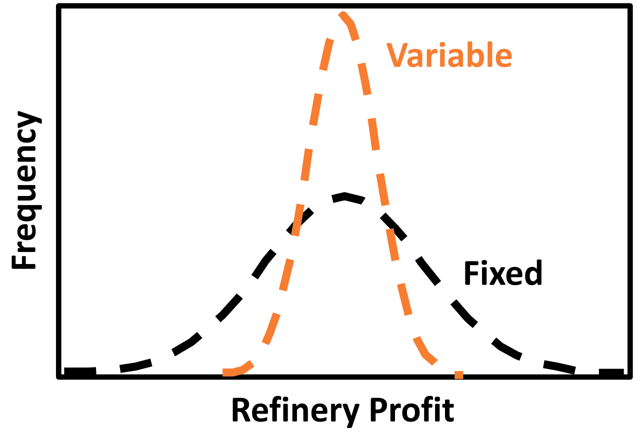
- Fixed-value policy may be relatively costly for tax-payer/consumer.
- Risk of economic loss may remain substantial.



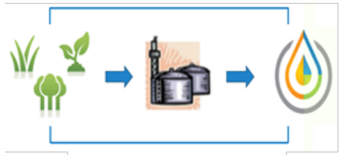
Policy Insights with Illustrative Example

- Variable policy may reduce risk of economic loss while minimizing excessive profit.
- Modeled results show impact on risk probability.





Overview of Refinery Analysis with Aspen PIMS



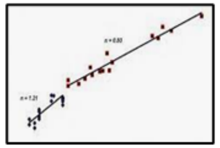
Refinery configuration and unit capacity basis from EIA.

Bio-blendstock/-intermediate cost, props, yields from TEA.

ASTM fuel specifications consistent with industry.

Crude and product pricing data from OPIS and PRISM.

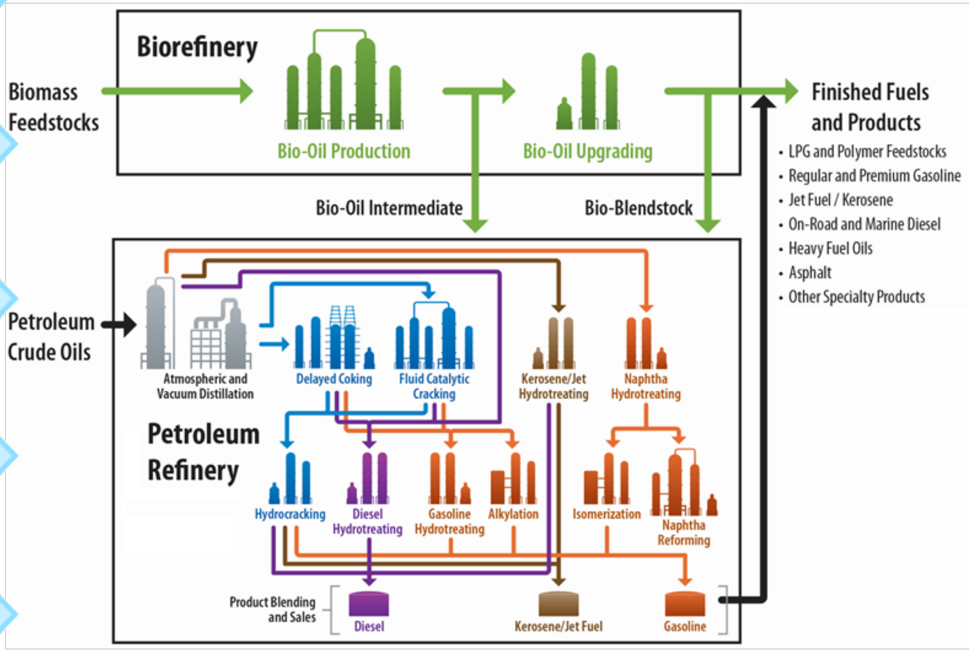
Market projections from EIA, OPIS, ADOPT.



Refinery capital investment basis from published sources.

Direct industry input through several on-going projects.

Biorefinery Models



Refinery Models in Aspen PIMS By AspenTech

Integrated with LCA calculations.

Bioeconomy Optimizations.

R&D needs via data gaps.

Outputs:

- Complete operational and economic profiles for optimized refinery solutions.
- Valuations of bio-feedstocks.
- Effective policy designs to de-risk biofuels production in refineries.
- Basis for US refinery network of “meta-models” for bioeconomy modeling.

Davison Circulating Riser (DCR) for Co-Processing

Evaluate FCC co-processing strategies by feeding CFP oils or other biogenic materials (FOGs, waxes) with VGO into the riser to produce BC-containing fuels

Key System Specifications – DCR for Co-processing

Feed Type: Liquids

Feed Rate: 1.2 kg/hr

Catalyst Type and Form Factor/Size: Refinery-type, zeolite-based, fluidizable (FCC), 80-100 micron.

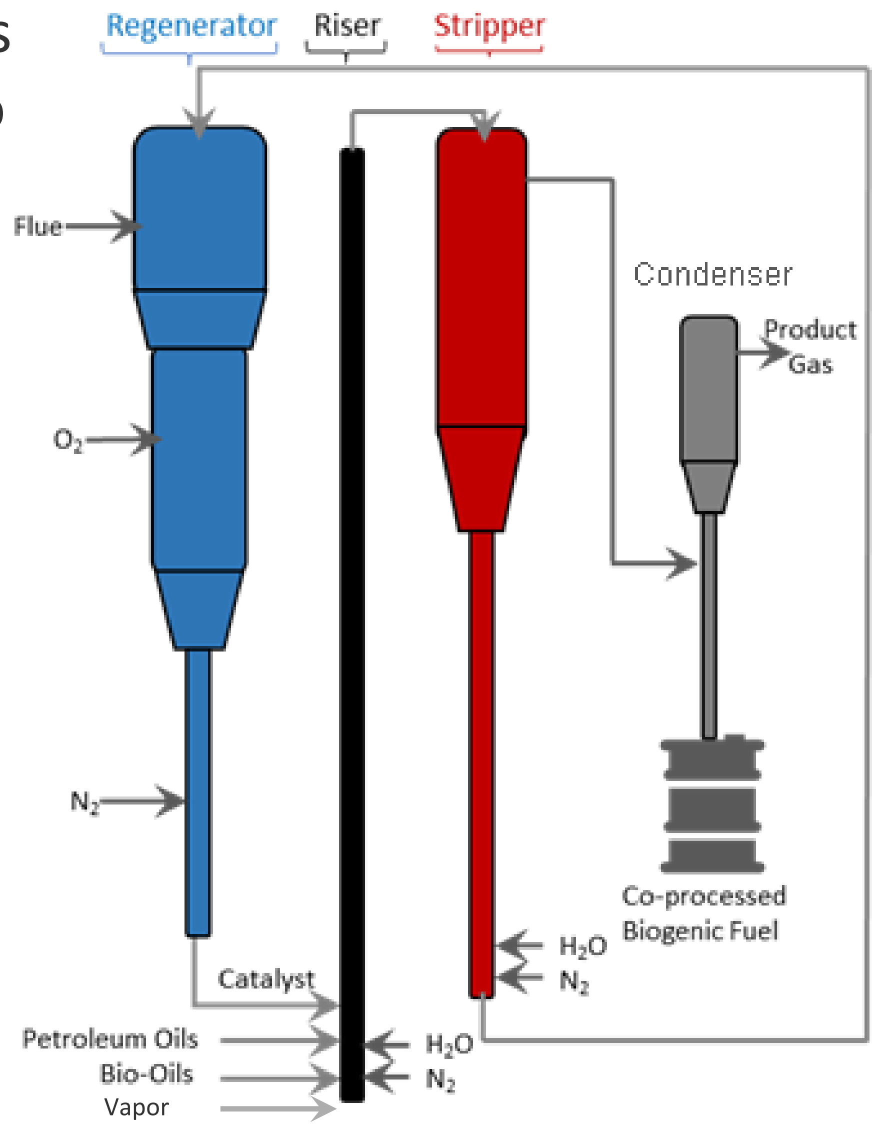
Catalyst Charge/Feed Rate: 1.8 kg, circulation rate 7-10 kg/hr

Operating Temperature Range: 475-550°C

Operating Pressure Range: 2-2.6 bar

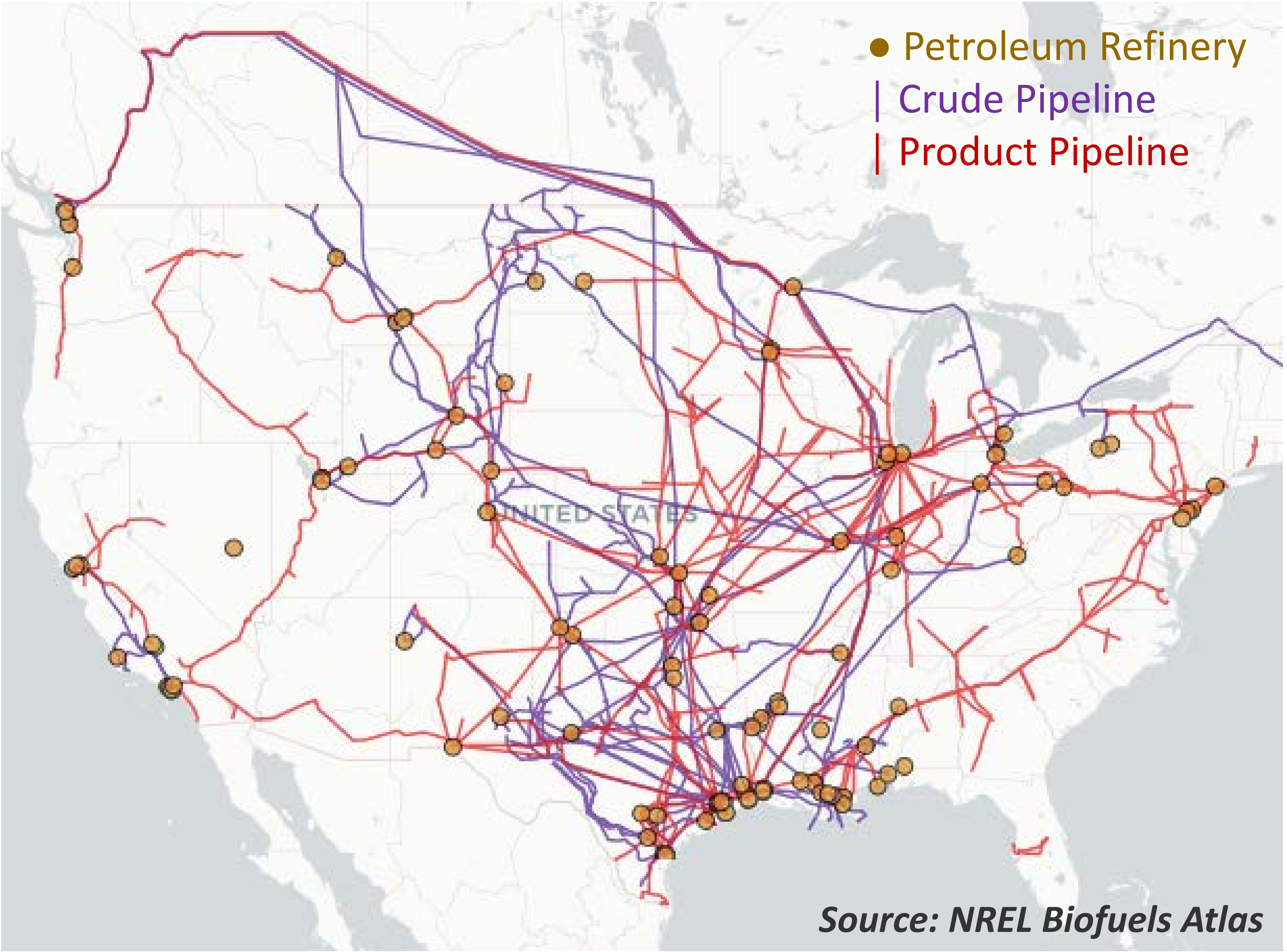
Reactor Configuration(s): Riser reactor + stripper + regenerator

Additional Specifications: Catalyst recirculated for stripping (HC removal) and regeneration (coke removal). DCR mimics FCC refinery operations by cracking large molecules to fuel-range molecules.



Future Goals for Refinery Analysis

- Identify low-carbon and low-cost strategies for renewable fuels and chemicals that leverage existing refineries.
- Continue to collaborate with industry partners on commercializing attractive business cases.
- Inform effective policy designs with modeled results.



Source: NREL Biofuels Atlas

Developing New Modeling Capabilities

- Integrate **emerging technologies** (and feedstocks) for bio-oil production
  - Catalytic fast pyrolysis
  - Hydropyrolysis
  - Hydrothermal liquefaction
- Develop analysis for **renewable olefins and aromatics** from refineries
- Integrate **environmental calculations** for multi-objective optimizations (ANL)
- Explore **alternative integration points**
  - Hydroprocessing (PNNL/NREL)
  - Residuum Fluid Cat Cracking (RFCC)
  - Delayed Coker
  - Fluid/Flexi-Coker
  - Marine Fuels
- Utilize refinery models in **bioeconomy resource optimizations**

PNNL = Pacific Northwest National Lab and ANL = Argonne National Lab.

Source Publications

- Pinho, Andrea de Rezende, Marlon B.B. de Almeida, Fabio Leal Mendes, Luiz Carlos Casavechia, Michael S. Talmadge, Christopher M. Kinchin, and Helena L. Chum. 2017. "Fast Pyrolysis Oil from Pinewood Chips Co-Processing with Vacuum Gas Oil in an FCC Unit for Second Generation Fuel Production." Fuel 188 (January): 462–73. https://doi.org/10.1016/j.fuel.2016.10.032.
- Talmadge, Michael, Christopher Kinchin, Helena Li Chum, Andrea de Rezende Pinho, Mary Biddy, Marlon B.B. de Almeida, and Luiz Carlos Casavechia. 2021. "Techno-Economic Analysis for Co-Processing Fast Pyrolysis Liquid with Vacuum Gasoil in FCC Units for Second-Generation Biofuel Production." Fuel 293 (June): 119960. https://doi.org/10.1016/j.fuel.2020.119960.
- Talmadge, Michael S., Robert M. Baldwin, Mary J. Biddy, Robert L. McCormick, Gregg T. Beckham, Glen A. Ferguson, Stefan Czernik, et al. 2014. "A Perspective on Oxygenated Species in the Refinery Integration of Pyrolysis Oil." Green Chemistry 16 (2): 407–53. https://doi.org/10.1039/C3GC41951G.
- Dutta, Abhijit, Mukarakate, Calvin, Iisa, Kristiina, Wang, Huamin, Talmadge, Michael, Santosa, Daniel, Harris, Kylee, Baddour, Frederick, Hartley, Damon, Cai, Hao, Ou, Longwen, Schaidle, Joshua, and Griffin, Michael. 2021. "Ex Situ Catalytic Fast Pyrolysis of Lignocellulosic Biomass to Hydrocarbon Fuels: 2020 State of Technology". United States. https://doi.org/10.2172/1805204. https://www.osti.gov/servlets/purl/1805204.
- Talmadge, M.; Jiang, Y. J.; Askander, J.; Singh, A. 2020. "Strategies for Co-processing in Refineries: Techno-economic & Refinery Impact Analysis". NREL: Golden, CO, 2020; https://www.nrel.gov/docs/fy20osti/76131.pdf.
- Talmadge, M., H. Chum, C. Kinchin, Y. Zhang, M. Biddy, A. de Rezende Pinho, M. B. B. de Almeida, F. L. Mendes, L. C. Casavechia, and B. Freel. "Analysis for co-processing fast pyrolysis oil with VGO in FCC units for second generation fuel production." TCS—Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products, Chapel Hill, NC. 2016.

Acknowledgements for NREL-Petrobras Project

The research reported was a result of the Memorandum of Understanding to Advance Biofuels Cooperation between the governments of Brazil and the United States started in 2007 and continued through the Strategic Energy Dialogue since 2011. The Brazilian Ministry of Mines and Energy (Dr. Ricardo Dornelles) provided significant encouragement to these activities. The U.S. Department of Energy (Rhia Davis), through the staff of the Office of Energy Efficiency and Renewable Energy International Programs (Dr. Robert Sandoli) and the Bioenergy Technologies Office (Dr. Valerie Reed and Dr. Jonathan Male), led the bilateral work and enabled and encouraged the collaboration. The Cooperative Research and Development Agreement Number 12-500, Biomass Pyrolysis to Hydrocarbons, in the Refinery Context, between Petroleo Brasileiro SA and the Alliance for Sustainable Energy, was conducted by researchers at Petrobras/CENPES/SIX and the National Renewable Energy Laboratory. We thank a very large number of involved managers and staff of these organizations for facilitating this productive bilateral collaboration.

The information presented includes contributions of funding, materials for experimentation, experimental research, and model / analysis development from the following:

U.S. Department of Energy	Dr. Jonathan Male, Dr. Valerie Reed, Liz Moore, Alicia Lindauer, Rhia Davis, Dr. Robert Sandoli
Brazil Ministry of Mines	Dr. Ricardo Dornelles
National Renewable Energy Laboratory (NREL)	Earl Christensen, Ed Wolfrum, Abhijit Dutta, Eric Tan, Esther Wilcox, Josh Schaidle, Adam Bratis, Tom Foust
Petrobras	CENPES/PDEDS/QM group, Henrique Wilmers de Moraes, Marco Antonio Gomes Teixeira, Luiz Alexandre Sacorague, Cleber Goncalves Ferreira
Ensyn	Barry Freel, Robert Graham
Fibria	Matheus Guimarães

In addition to the funding and analysis contributions for assessing co-processing in FCC operations, the SOT analysis includes raw pyrolysis oil TEA estimates, which were developed with critical inputs from Idaho National Laboratory (INL) and Pacific Northwest National Laboratory (PNNL). We sincerely thank the following participants from INL and PNNL:

Idaho National Laboratory (INL)	Patrick Lamers, Damon Hartley, David Thompson, Jacob Jacobson, Kara Cafferty
Pacific Northwest National Laboratory (PNNL)	Susanne Jones, Pimphan Meyer, Lesley Snowden-Swan, Asanga Padmaperuma

Acknowledgements for NREL Thermochemical Analysis

DOE BETO for funding and support

NREL

Nick Carlson
Daniel Carpenter
Earl Christensen
Abhijit Dutta
Kylee Harris
David Humbird
Kristina Iisa
Kim Magrini
Calvin Mukarakate
Connor Nash
Mark Nimlos
Dan Ruddy
Josh Schaidle
Avantika Singh
Michael Talmadge
Eric Tan
Suphat Watanasiri
Matt Wiatrowski
Nolan Wilson

PNNL

Corinne Drennan
Yuan Jiang
Susanne B. Jones
Aye Meyer
Steve Phillips
Lesley Snowden-Swan
Huamin Wang

INL

Damon Hartley
David Thompson

ANL

Hao Cai
Longwen Ou

Thank you!
Questions?

www.nrel.gov

www.nrel.gov/bioenergy

NREL/PR-5100-81884

This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE). Funding provided by U.S. Department of Energy Office of Energy Efficiency and Renewable Energy, Bioenergy Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

NREL Transforming ENERGY