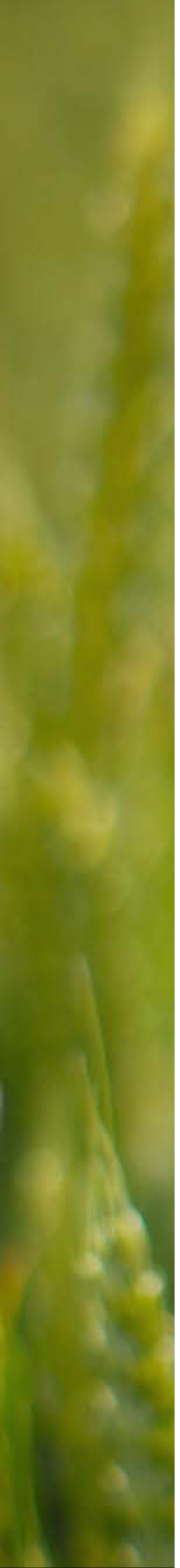

NATIONAL RENEWABLE ENERGY LABORATORY

Pacific Northwest
NATIONAL LABORATORY

Strategies for Co-processing in Refineries

Techno-economic & Refinery Impact Analysis

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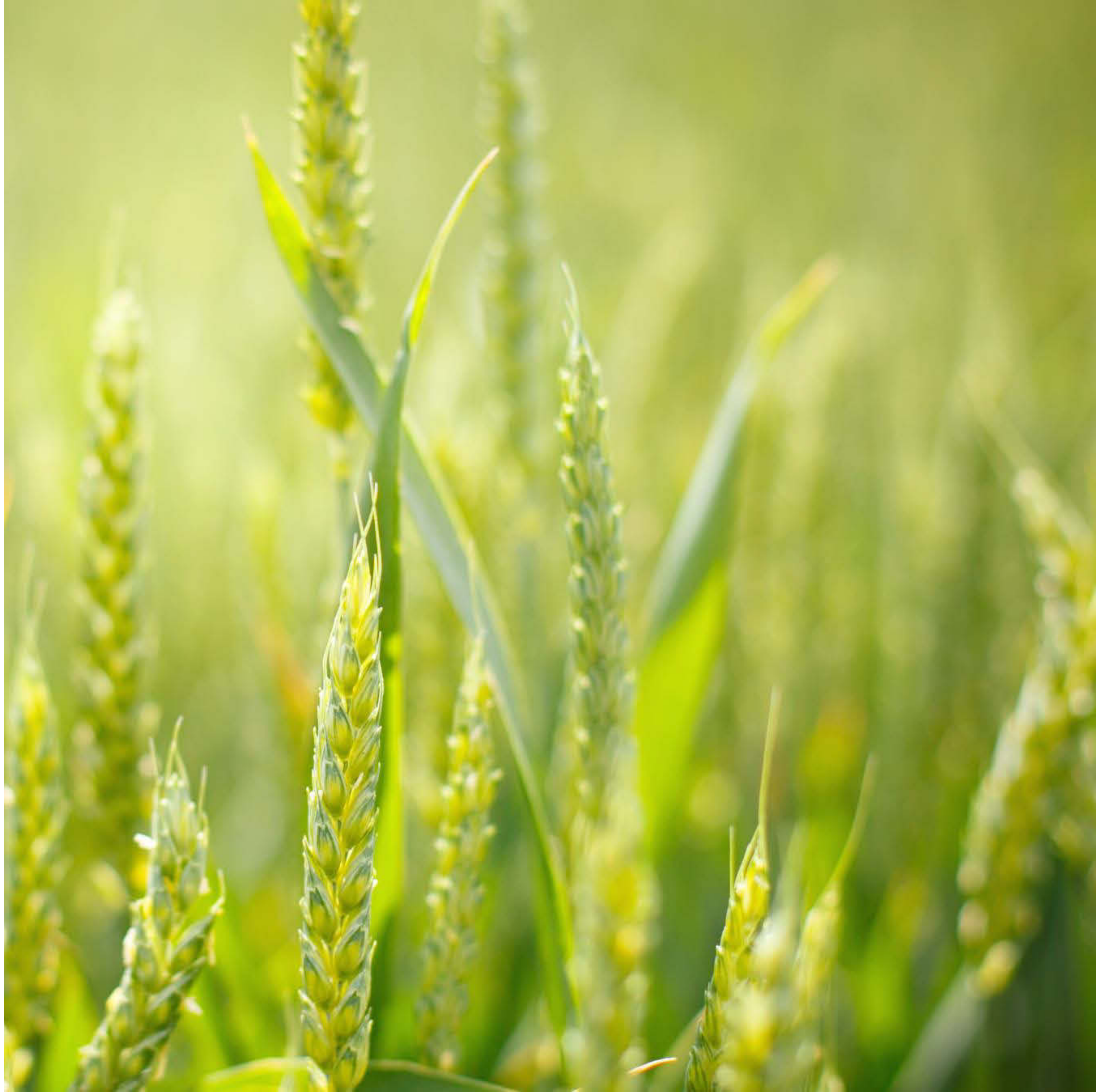
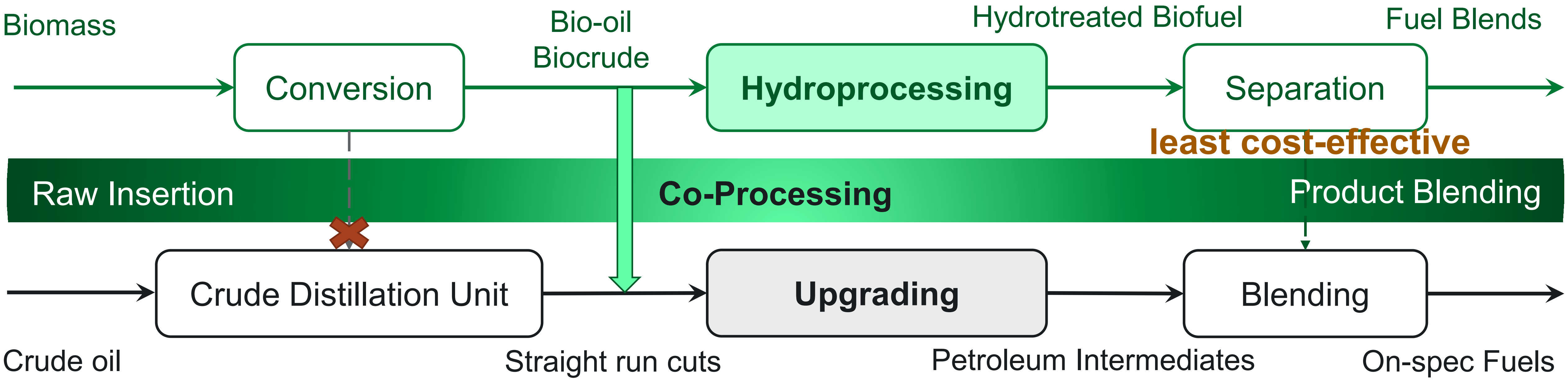


Outline

- Introduction
- Refinery LP Model for Refinery Impact Analysis
- Co-Processing at Mild Hydrocracking Unit
- Co-Processing at Fluidized Catalytic Cracking Unit
- Discussions and Future Plan

Co-Processing Value to Bio-Refiner

- **Refinery Integration – Co-Processing**



- **Potential Cost Saving at Bio-Refinery**

(upgrading at a standalone biorefinery vs an existing petroleum refinery)

Cases (2016$)	Catalytic Fast Pyrolysis (2000 dry tonne/day)	Waste Hydrothermal Liquefaction (110 dry tonne/day)
Reduction in MFSP ($/gge)	0.83	0.65
MFSP w/o SCR ($/gge)	4.28	3.11

Co-processing intermediate bio-oil or biocrude at an existing petroleum refinery has the potential to significantly reduce CAPEX and therefore minimum fuel selling price (MFSP) of a bio-refinery.

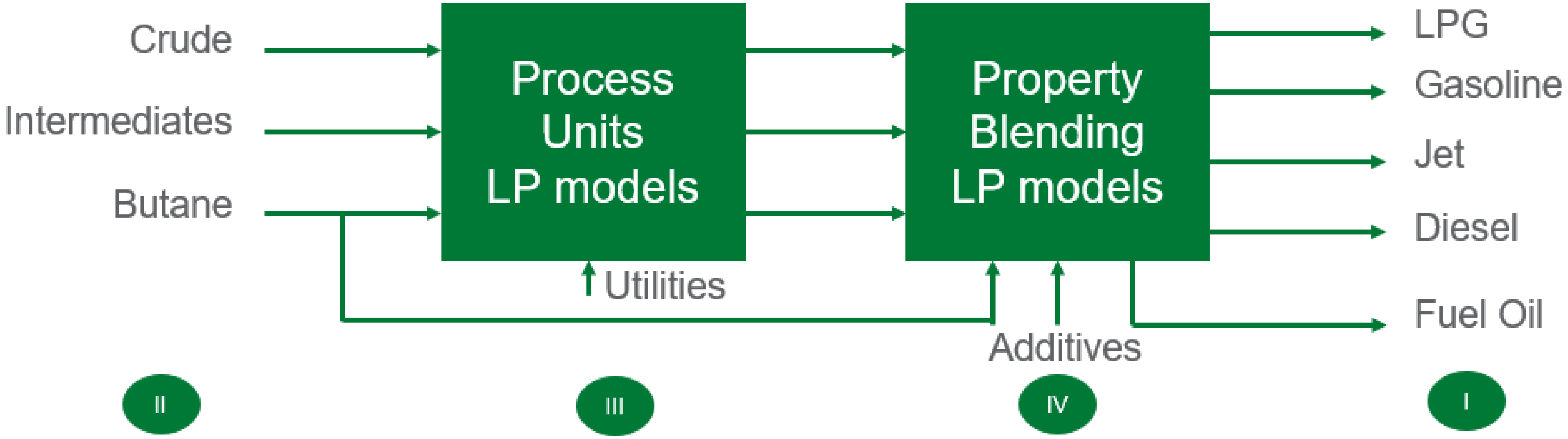
LP Model to Assess Refinery Impacts

✓ Biogenic Carbon ✓ Diesel Production ✓ Less Sulfur ✓ Less Metals

? Stability & Miscibility ? Acidity & Corrosion ? Oxygenates ? CO_2 & H_2O generation ? H_2 Consumption

? Yields & Utilities ? Operating Severity ? Feed & Product Quality ? Up- & Down-streams Operations

➢ **A Bird's Eye View of Full Refinery Linear Programming Optimization in Aspen PIMS**



Objective = Maximize Profits

I.	Sales Revenues	100k
II.	Raw materials	(70k)
III.	Utilities	(10k)
IV.	Additives	(5k)
	Refiner's Margin	15k

➢ The **economic value** of co-processing biomass intermediates can be evaluated by

- comparing the **gross margins** of a petroleum refiner before and after adding bio-oil/biocrude
- comparing the **break-even value** of bio-oil/biocrude to petroleum refiner and its **minimum selling price** at bio-refinery.

LP Model to Assess Refinery Impacts

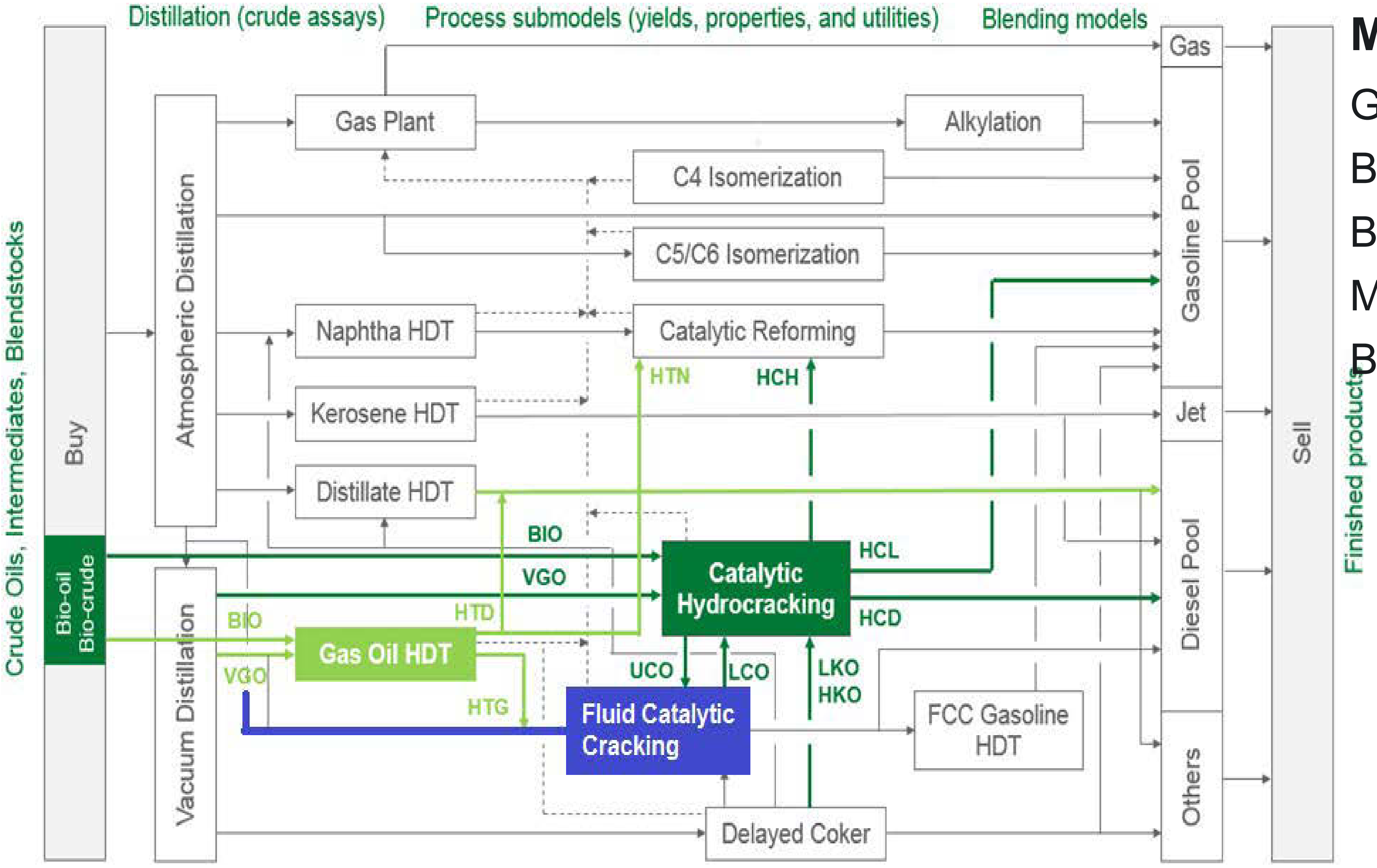
✓ Biogenic Carbon ✓ Diesel Production ✓ Less Sulfur ✓ Less Metals

? Stability & Miscibility ? Acidity & Corrosion ? Oxygenates ? CO_2 & H_2O generation ? H_2 Consumption

? Yields & Utilities ? Operating Severity ? Feed & Product Quality ? Up- & Down-streams Operations

Model Inputs

- **Mass balance** and **key properties** of **co-processing** from experimental data
- **Process model** and assay data of petroleum refinery from Aspen PIMS Gulf Coast Example
- **Process constraints**
- **Fuel specification**
- Feed and Product Slates
- Unit capacity



Model Outputs

Gross margin

Break-even value

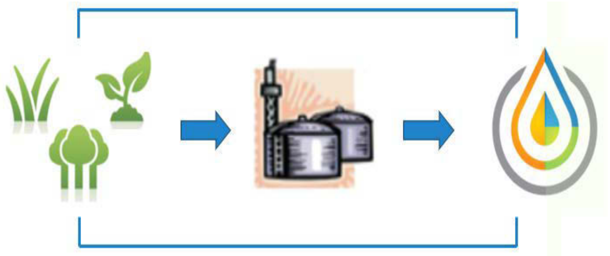
Blending constraints

Mass/Energy Balance

Basis for LCA

Refinery Analysis Inputs for SCR Project

Refinery configuration and unit capacity basis from EIA.



Bio-intermediate costs and refinery yields from SCR project experiments.

ASTM finished fuel specifications are consistent with industry.

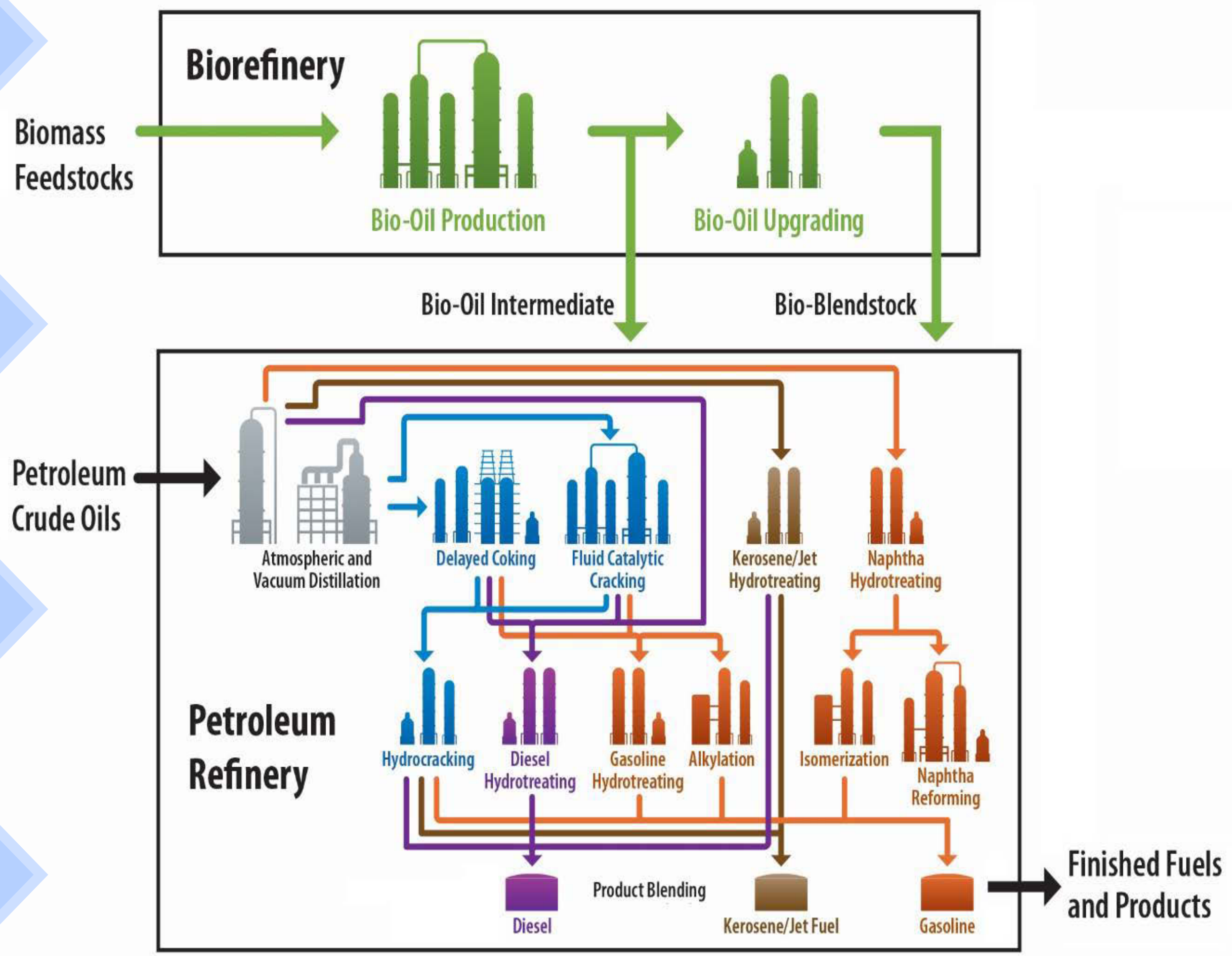
Crude and product pricing data from OPIS by IHS Market.

Fuel market projections from EIA, OPIS and ADOPT.

ADOPT

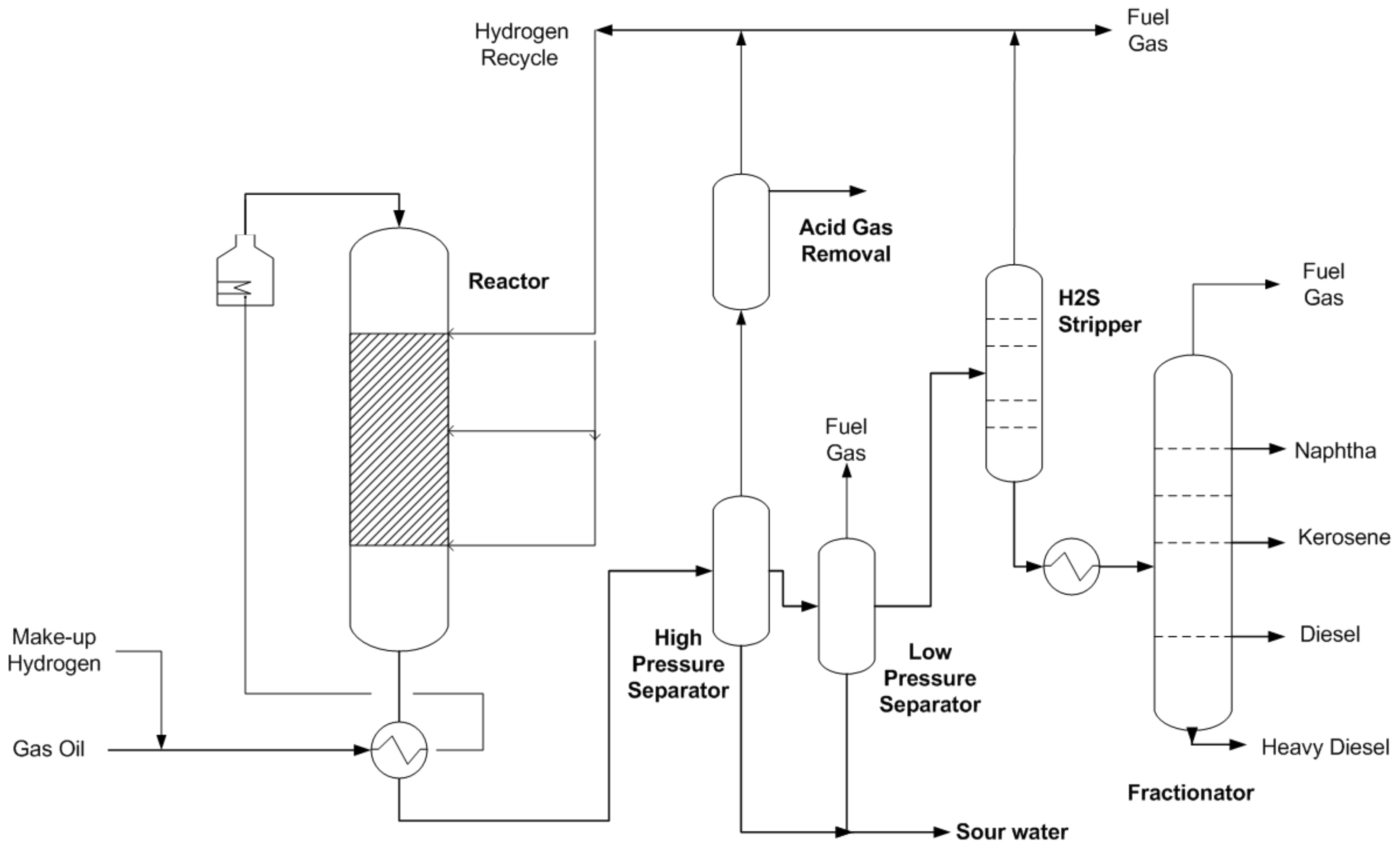
Aspen PIMS

By AspenTech



Process Model for Mild Hydrocracker Co-Processing

- Preliminary Aspen Plus & TEA models have been developed for single-stage fixed-bed mild hydrocracker



Assumptions in preliminary model

- One-stage HDC for bio-oil
- Similar yield as VGO HDC
- O removed via H_2O and CO_2
- No combination effects (either deleterious or synergistic)

To be updated in new model

- Yield
- Gas phase
- Combination effects
- Two-stage HDC for biocrude

- Detailed process model will be updated based on the coming co-processing experimental data
- Results from Aspen Plus model will be leveraged in the full refinery LP model

LP Model for Mild Hydrocracker Co-Processing

- Base-Delta Model in Refinery LP model

$$y_i = y_i^{base} + \sum a_k(q_{f,k} - q_{f,k}^{base}) + \sum a_j(z_j - z_j^{base})$$

Subject to $q_{f,k}^L \leq q_{f,k} \leq q_{f,k}^U,\ z_j^L \leq z_j \leq z_j^U,\ f^L \leq f \leq f^U$

y = yield, product quality; q_f = feedstock quality, z = operating condition, a = parameter ($\Delta y/\Delta q_f$, $\Delta y/\Delta z$), f= capacity

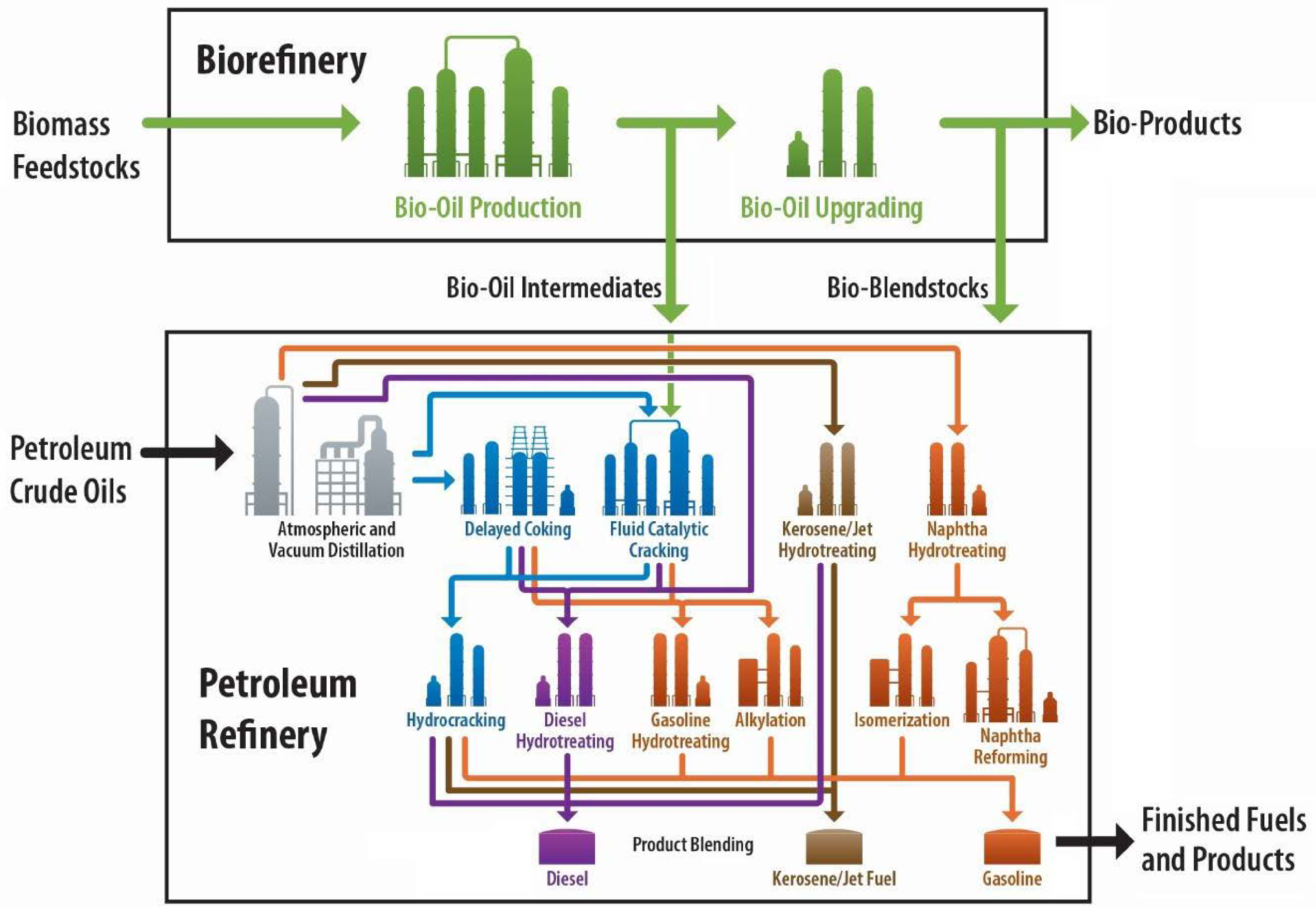
- Base-Delta Model for Mild Hydrocracker

y	q_f	z
Hydrogen consumption Product Yield H_2S, **CO_2**, **H_2O**, Fuel Gas, C_3, C_4, Light Naphtha, Heavy Naphtha, Kerosene, Diesel, Unconverted Oil Product Qualities Required by downstream upgrading, or fuel blending (i.e. Cetane Index) Utility Consumption	Specific Gravity Sulfur, wt% 50% ASTM Distillation Temp, ^oF Basic Nitrogen, ppmv **Oxygen, wt%**	Feed Rate Conversion (%) Recycle (% of fresh feed) Catalyst Age (% used)

LP structure has been modified in Aspen PIMS to **adopt bio-oil/biocrude**; Value of parameter ***a*** will be updated based on the coming **experimental data** and **Aspen Plus model** in Q3 &Q4

Pyrolysis Oil Co-Processing in FCC

- NREL is focused on developing full refinery optimization models with integrated co-processing of pyrolysis oil intermediates in the Fluid Catalytic Cracking unit.
- Initially building models based on Petrobras-NREL CRADA project (Pinho et al, 2017) and prior Strategic Analysis / TC Platform Analysis work.
- Model design methodology to enable quick incorporation of SCR project results.



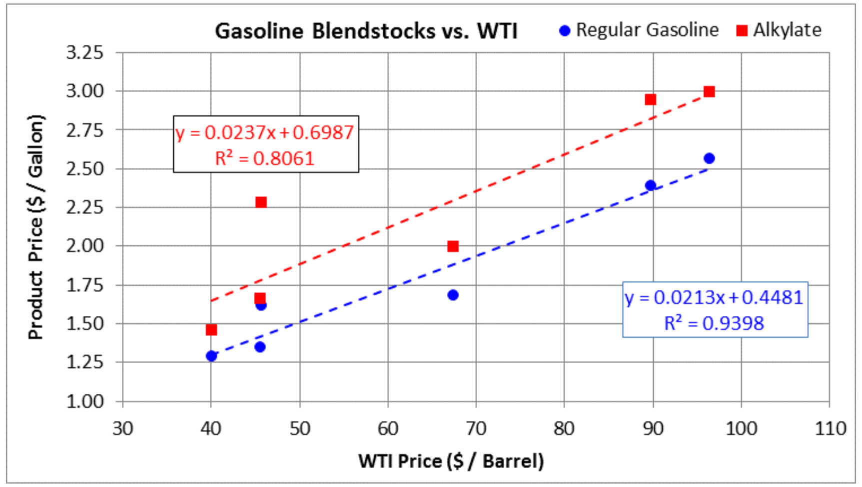
FCC Co-Processing Analysis in FY2020

- Applied initial yield basis for FCC co-processing of pyrolysis oil from Petrobras-NREL CRADA.
- Improved yield model to allow user to assess pyrolysis oils of varying quality based on prior co-processing work in Strategic Analysis and TC Platform Analysis tasks.

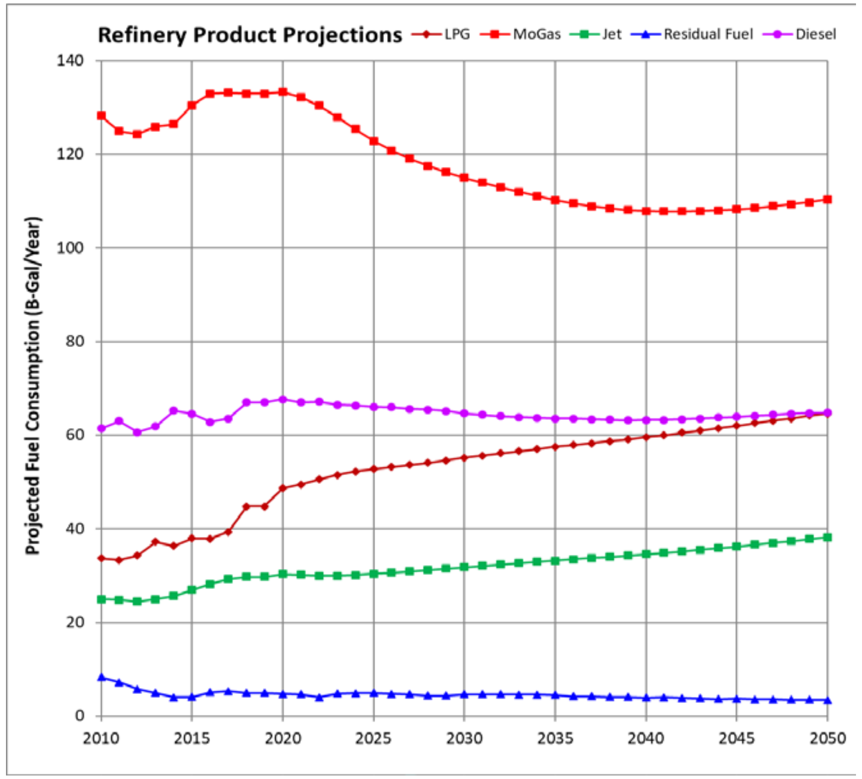
  FCC Product X Yield = f (oxygen content, % FP oil in FCC feed, FCC operating conditions)

- Leveraging refinery impact and co-processing work from (1) Co-Optima ASSERT and (2) TC Platform Analysis.
  - Refinery configuration and unit capacity basis per region.
  - Variable crude and product pricing structure from OPIS.
  - Finished product specifications from ASTM international.
  - Fuel market projections from EIA, OPIS and ADOPT model.

Example of Gasoline Pricing Model

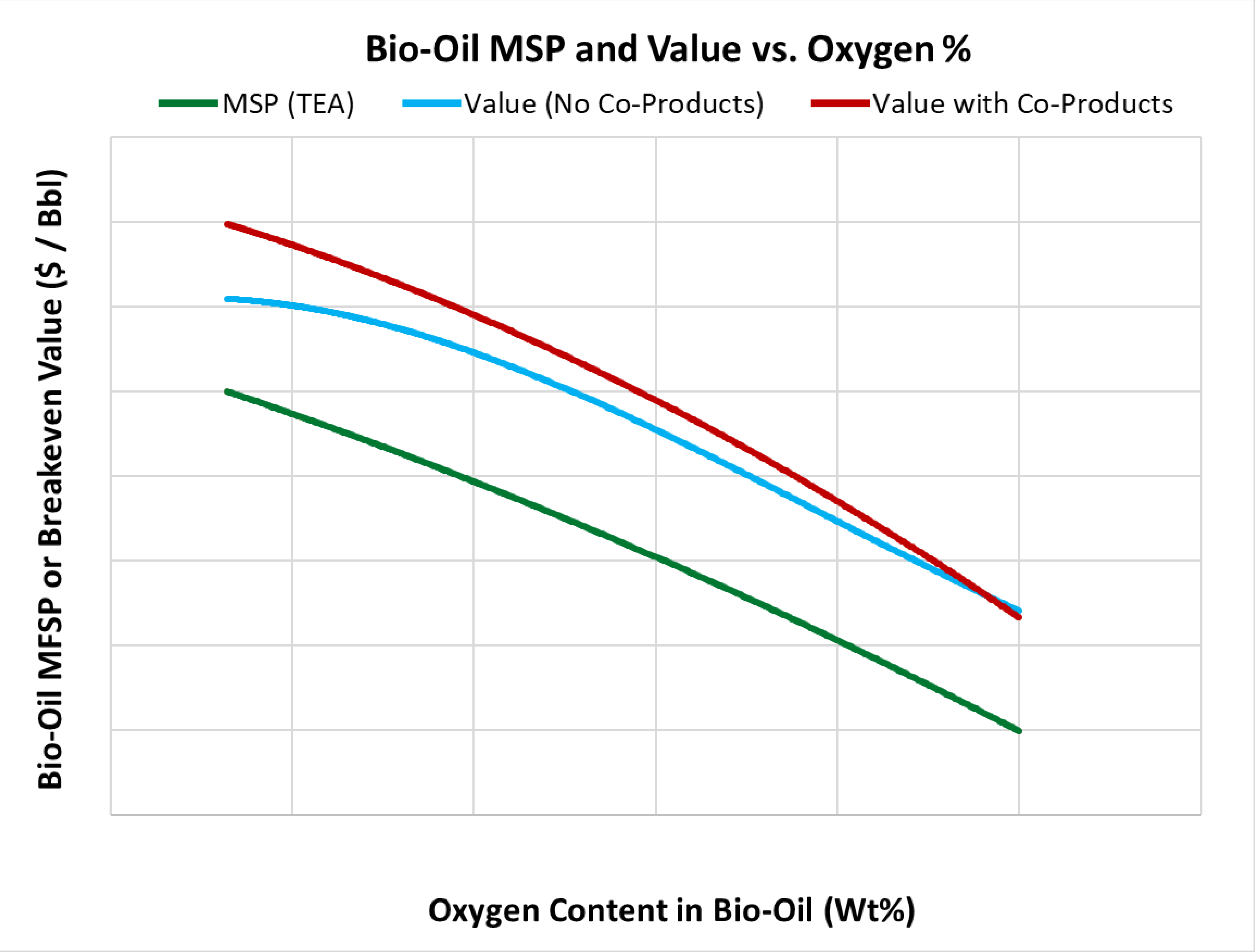


Example of Refinery Product Demand Projections



Preliminary FCC Co-Processing Analysis

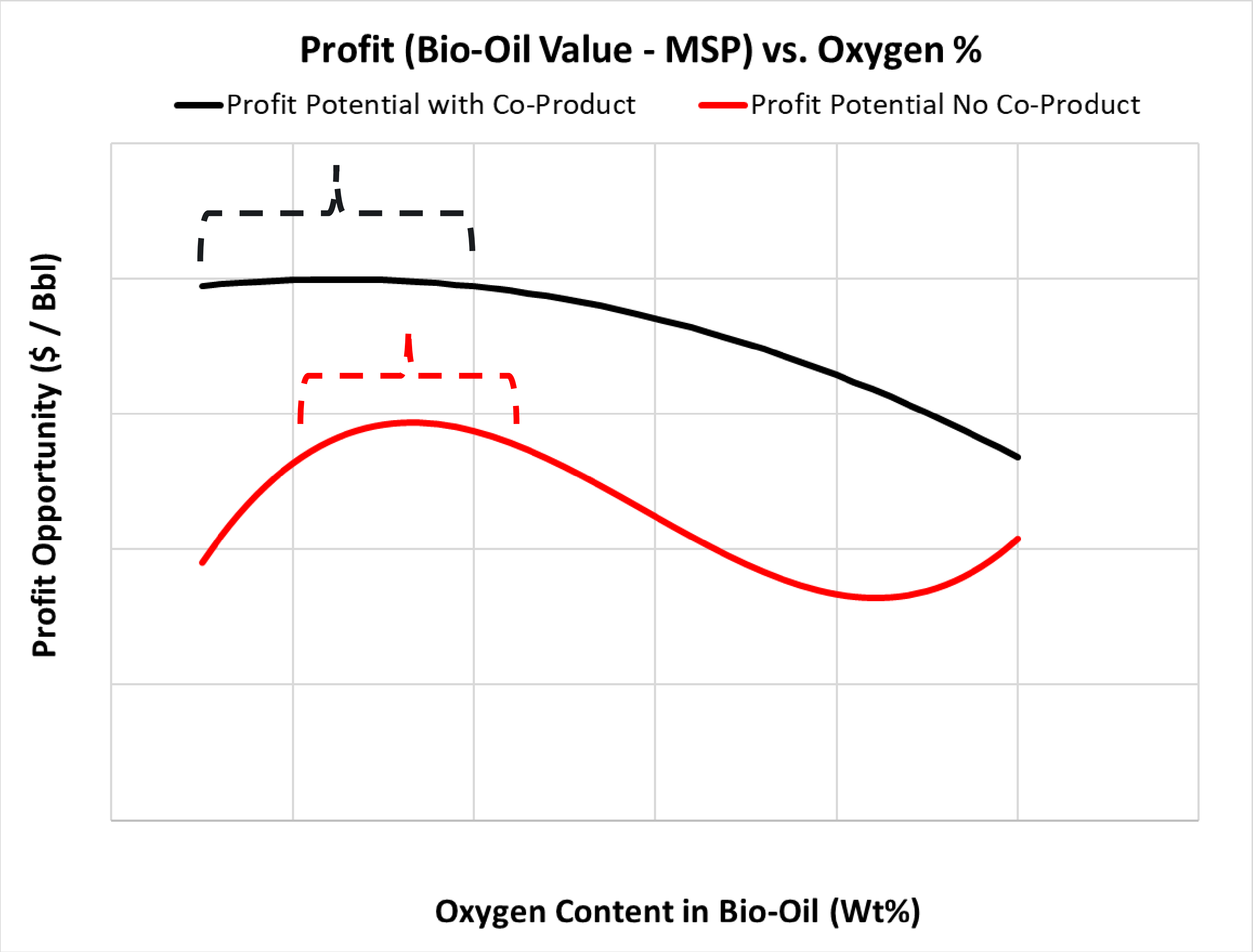
- Develop understanding of the optimal co-processing strategy:
  - Reduce bio-intermediate MSP by avoiding Biorefinery upgrading capital and operating costs.
  - Determine bio-intermediate values to refineries through Aspen PIMS models.
  - Valuation of high-value co-products from catalytic pyrolysis processes.



Preliminary example. Please do not cite or distribute.

Preliminary FCC Co-Processing Optimization

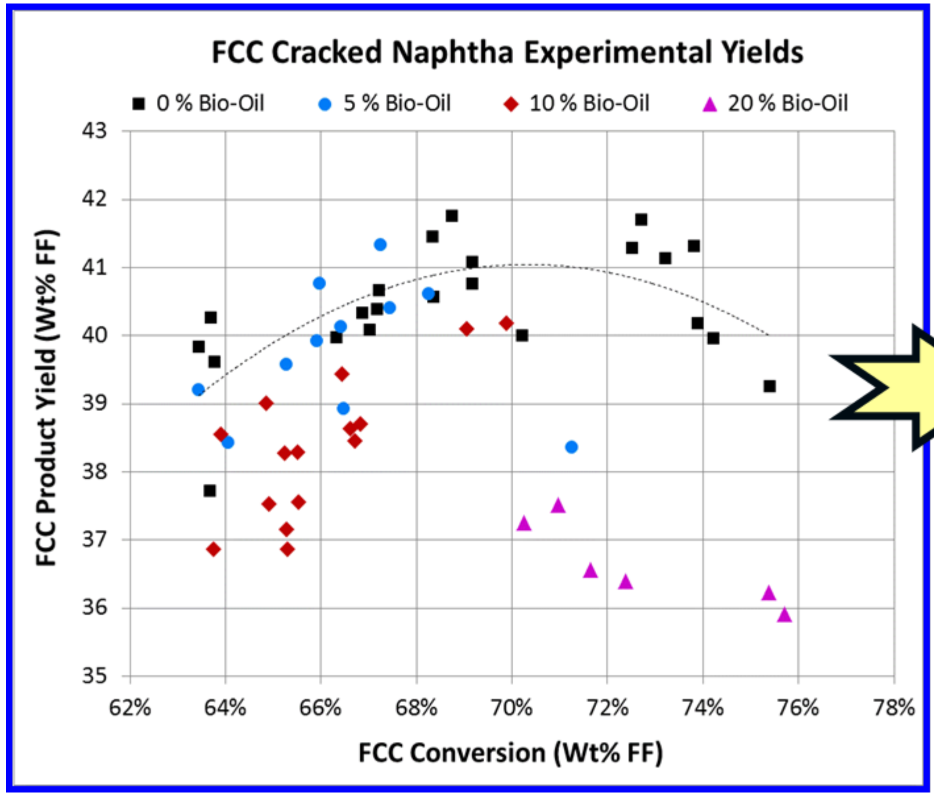
- Optimized scenarios have maximum delta between “Total Value” and “Total Cost”.
- Refinery analysis can help direct R&D.
- Preliminary insights:
  - Maximize yields.
  - Maximize co-product value.
  - Analysis can help optimize.

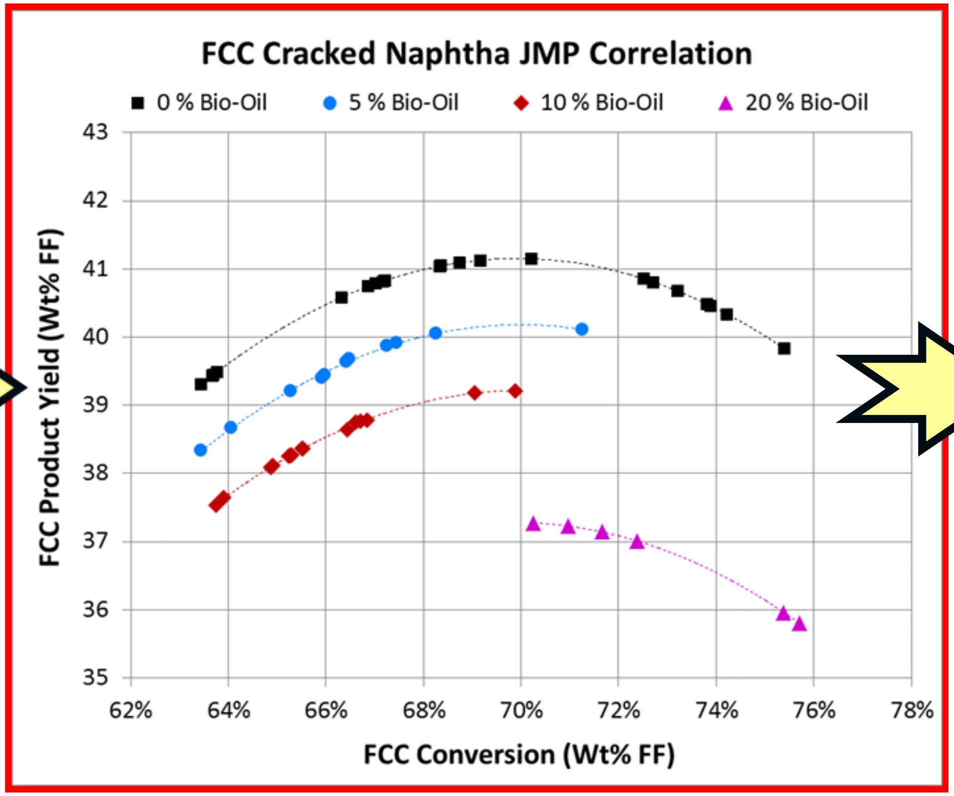


Preliminary example. Please do not cite or distribute.

Next Steps for SCR Co-Processing Analysis

- Experimental **yield data**
  - Develop statistical yield models
  - Incorporate yields into refinery LP models
  - Develop basis for process models
  - Derive basis for environmental analysis





Aspen PIMS By AspenTech

Aspen Plus

aspentech Aspen HYSYS

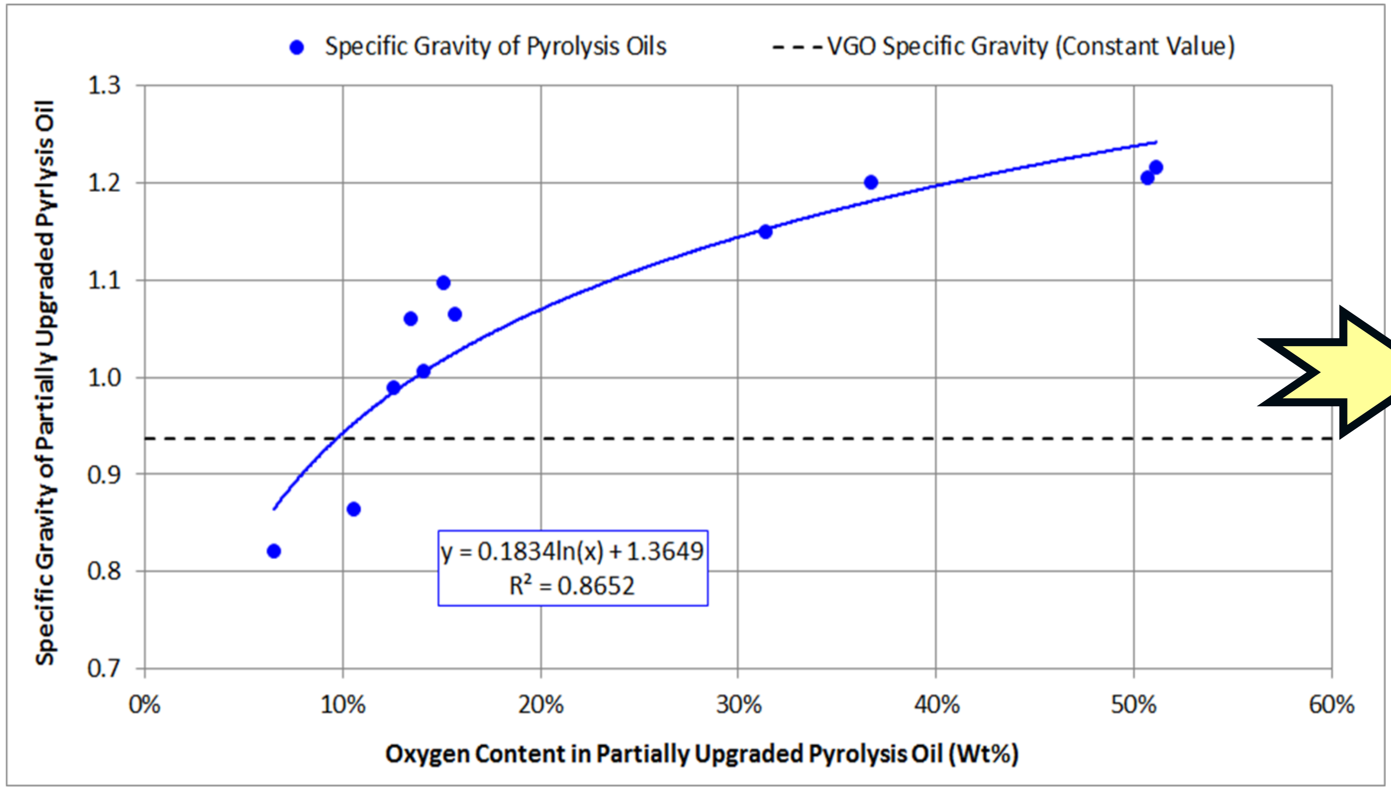
Oxygen Species	Refinery Fuels	LPG Products	Distillate Products
CO CO_2 Water	Dry Gas (C_2-)	Propane Propylene	Cracked Naphtha
	Coke	i-Butane n-Butane Butenes	Light Cycle Oil Resid Fuel Oil

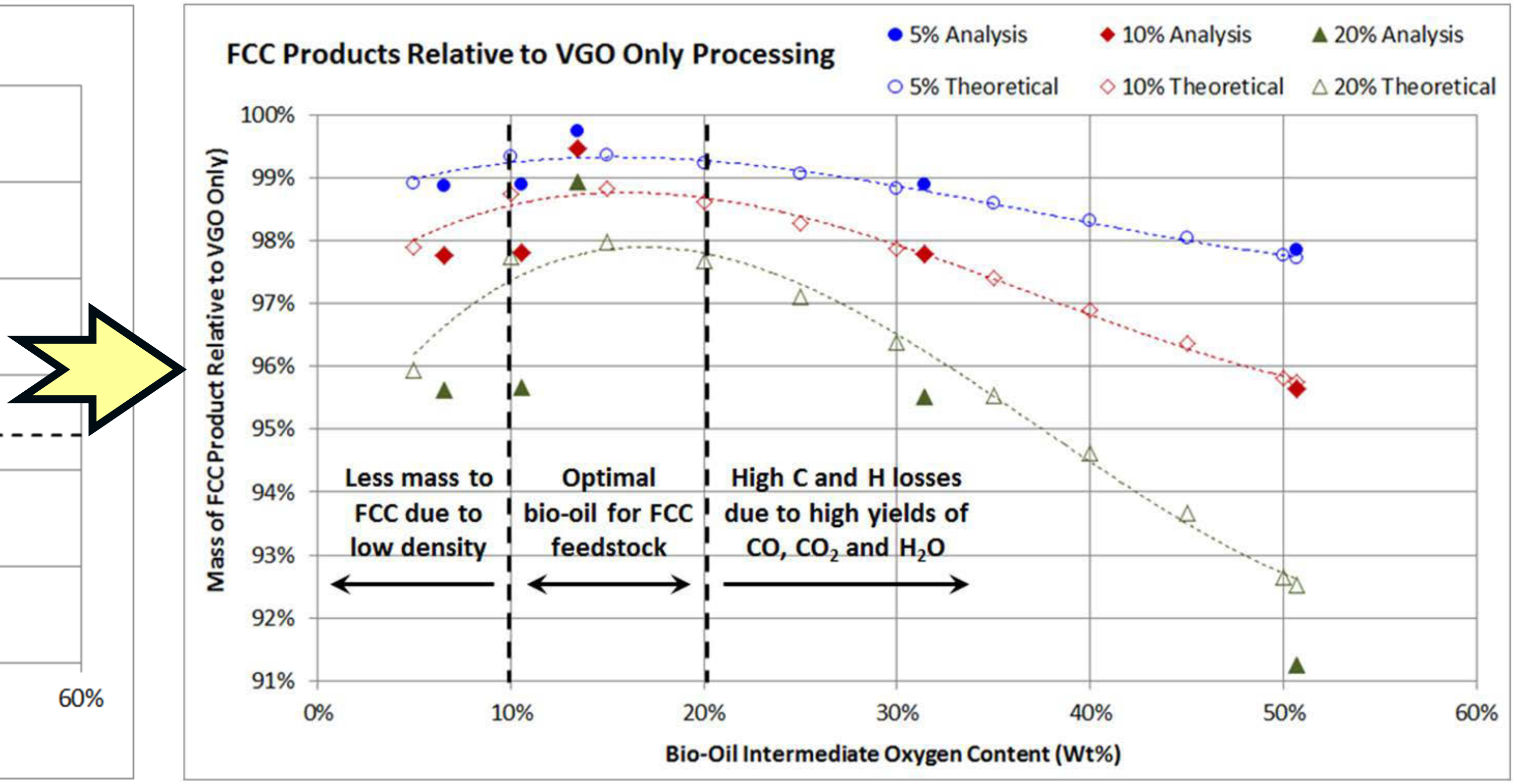
Graphs from TCS 2016, Chapel Hill, NC, November 1, 2016

Next Steps for SCR Co-Processing Analysis

- Feed and product **properties**
  - Empirical physical property models
  - Product allocation analysis
  - Blending and fuel quality analysis
  - ASTM certification and spec development
  - LCA / GHG analysis
  - Inconsistencies in valuation / allocation

Example of insights developed from bio-oil physical property data.





Graphs from NREL TC Platform Analysis Q4 FY16 milestone

Downstream Refinery Impact Assessments

Assist in assessing co-processing topics outside of modeling scope:

- Blendstock quality impacts resulting from co-processing.
- Bio-intermediate logistics costs, challenges and constraints.
- Operational reliability impacts to downstream and ancillary unit operations:

  Managing low bio-oil thermal stability, managing immiscibility of bio-oils with refinery streams, acidity and corrosion potential, alkali and alkaline earth metals, unconverted oxygenated species, H_2O, CO and CO_2 in refinery light end / fuel gas streams, analysis methods for renewable allocations.
- Potential benefits to refiners from co-processing:

  Biofuels tax incentives, crude distillation capacity, FCC regenerator air blower capacity, FCC wet gas compressor, main fractionator flooding in FCC or Hydrocracker, reduced vanadium and nickel, low sulfur to sulfur plant and low nitrogen to sour water stripper.

Thank you!

Questions?

NREL

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