

DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

Refinery Integration 4.1.1.31 NREL 4.1.1.51 PNNL

March 24, 2015 Analysis and Sustainability

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Goal Statement



Petroleum

Crude Oil

NAPHTHA HYDROTREATER

UNIT

Atmospheric distillation uses heat to separate

crude oil into naphtha, light oils, and heavy oils.

Leveraging existing refining infrastructure potentially reduces costs for biofuel production but we first need to understand the impacts

ATMOSPHERIC

VACUUM

DISTILLATION

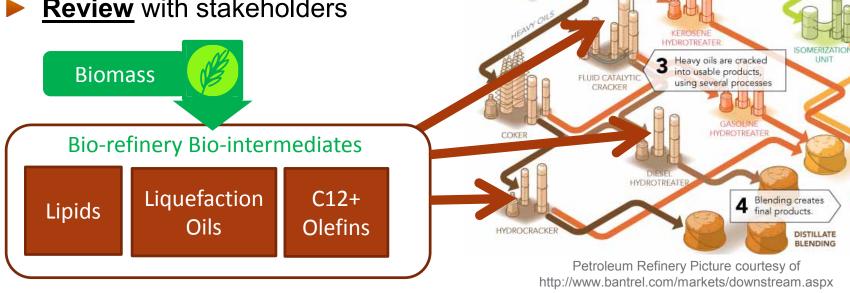
DISTILLATION

Atmospheric residue is

further distilled to extract oil under vacuum conditions

GOALS:

- **Model** bio-intermediates insertion points to better define costs & ID opportunities, technical risks, information gaps, research needs
- **Publish** results
- **Review** with stakeholders



NAPHTHA

REFORMER

GASOLINE

BLENDING

Quad Chart Overview





Timeline

- Start: October 1, 2012 (PNNL only)
- Start: October 1, 2014 (NREL+PNNL)
- End: September 30, 2016
- Completion: 50% for joint project starting in 2014

Budget

DOE Funded	Total Costs FY 10 – FY 12	FY 13 Costs	FY 14 Costs	Total Planned Funding (FY 15 -16)
NREL	\$0	\$0	\$128k	\$422k
PNNL	\$65k	\$195k	\$228k	\$487k

Barriers

- Barriers addressed
 - At-A lack of transparent and reproducible analysis
 - At-C Inaccessibility and unavailability of data
 - Tt-S Petroleum Refinery integration of Bio-Oil intermediates

Partners

- Partners:
 - For joint portion of project: NREL (44%), PNNL (56%)
- External Reviewers:
 - Refining catalyst vendor (2)
 - Refinery #1 modeling contact (2)
 - Refinery #2 modeling contact
 - Refining industry independent contractor

Project Overview

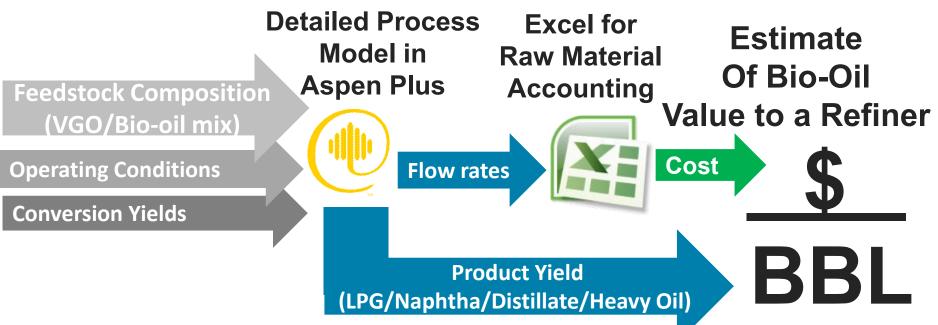


- History: Joint Lab FY14 start builds on previous work at both labs
 - NREL refinery blending models for the NABC
 - PNNL high level survey of refinery integration potential (AOP project FY12-13)
 - Complements separate NRELAOP project for refinery blending
- Context: Economic deployment of biofuel
 - Understand how bio-fuels can replace entire barrel of oil
 - Understand how existing infrastructure can best be used
- Objective: FCC and HCK model development to understand impacts, opportunities and gaps
 - Develop first-of-a-kind process models to enable consistent modeling framework for economic and sustainability assessments
 - Understand and review current state of technology and information
 - ID risks, research needs, and cost drivers
 - Review with key industrial stakeholders
 - **Publish** results and findings

Approach (Technical)







- Potential Challenges & Risk Mitigation
 - Consistent and appropriate assumptions: defined technical basis and economic assumptions at start of project & reviewed with BETO
 - **Data availability**: engage researchers at both labs + literature data to estimate yields and product distribution
 - **Meaningful cost impacts**: estimate value of bio-oil relative to crude oil from a refiner's perspective when considering quality, yield and process impacts

Approach (Technical)





Critical success factors: Stakeholder Review

4 separate <u>refining related entities</u> agreed to assist with project

- FCC catalyst vendor (2 contacts from same company: 1 with refining technologies and renewables expertise; 1 with expertise in FCC evaluations focusing on catalysts and feedstocks)
- Refiner #1 (2 contacts from same company one with FCC expertise and one with HCK expertise)
- **Refiner** #2 (17 years in refining processes modeling research)
- Retired refiners now working as independent consultants
- FY14:
 - Sent the FY14 report document to all and Aspen models to those interested
 - Compiled feedback for use in revising models and methods (details in upcoming slides)

Approach (Management)





Approach structure

- Joint NREL and PNNL effort to leverage capabilities at both labs
- Project Management Plan (PMPs) indicating scope, budget, schedule

Annual Operating Plans (AOPS) prepared prior to each fiscal year

- Details quarterly <u>milestones</u> and <u>deliverables</u> (see additional slides)
- Go/No-go point May 2015 to assess project value and direction
- FY15-16 AOP passed Merit Review July 2014
- **Quarterly reporting** to BETO (written and regularly scheduled calls)

Potential Challenges and Risk Mitigation

- Researcher proximity: we have regularly scheduled calls & data exchanges
- Data compatibility: use same software platforms & exchange models for cross-check review

Critical success factors

- Engage stakeholders
- Make results public
- Deliver product on-time, on-budget

Technical Progress & Results: intermediates





Currently Identified Bio-Oil Intermediates*

	# Properties						Co-processing		#Independent	HDO
Bio-intermediates	Found	CHNOS	Density	Viscosity	TAN	Composition	data		Sources	Data
							FCCU	HCK		
Algae HTL	5	٧	٧	٧	V	GC/MS			3	٧
Algal LE	2	٧				% acids, triglycerides			1	
Wood HTL	5	٧	٧	٧	V	SimDis			3	٧
Stover HTL	4	٧	٧	٧	V				1	٧
НҮР	4	٧	٧		V	GC/MS, SimDis			3	٧
СРО	5	٧	٧	٧	V	GC/MS	٧		14	٧
HDO (partial)	5	٧	٧	٧	٧	GC/MS,SimDis	٧		4	٧
Biological Conv	4	٧	٧	٧		SimDis			1	

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

Petroleum Intermediates

VGO	Vaccuum gas oil			
VBGO	Visbreaker gas oil			
AGO	Atmospheric gas oil			
DAO	De-asphalter oil			
LCO	FCC light cycle oil			
НСО	FCC heavy cycle oil			
Resid	Residual oil			
H+LCGO	Heavy coker gas oil, light cycle gas oil			

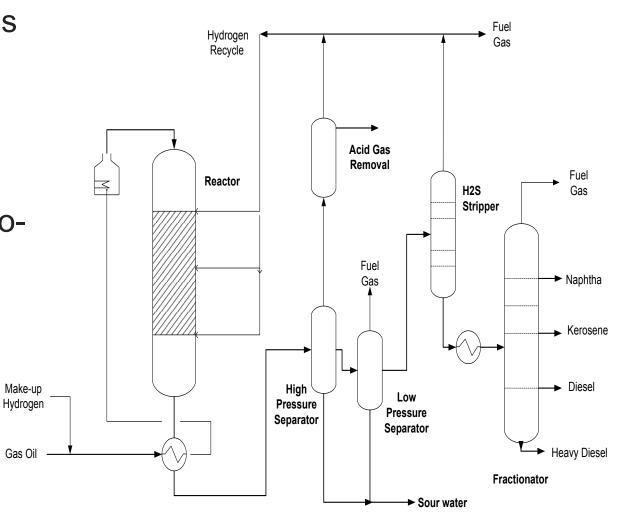
52 references: literature and experimental data

Initial Intermediates chosen:

- Partially hydrotreated pyrolysis oil (fair amount of information available regarding FCC co-processing; some hydroprocessing data)
- VGO as conventional feed

Technical Progress & Results: HCK Model

- Modeled reactor, gas separation and H2 recycle, product separation
- Pure compounds used (versus pseudocomponents)
- Stoichiometric Reactor Model
- Aspen model flowsheet shown in additional slides





Technical Progress & Results: HCK Model

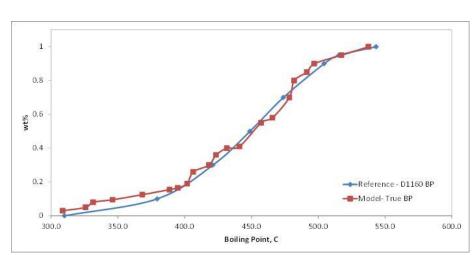
100% VGO feed model

- Back blended distilled products distillation curves* in Excel to estimate HCK effluent
- Model check: Compared resulting utilities and HCK model product distillation compared to literature

* Parkash Refining Processes Handbook, 2003

Blended feed models

- Used best judgment for HCK products of blended feed based on experience with hydrotreating pyrolysis oils; some lit on HCK of VGO with vegetable oils
- 90/10 wt% and 80/20 wt% VGO/bio-oil
- Consistent throughput and reactor inlet temperature for all three cases



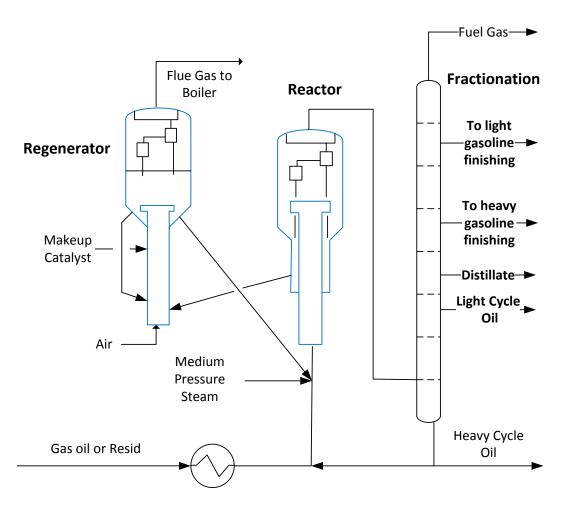


TIONAL RENEWABLE ENERGY LABORATORY

Technical Progress & Results: FCC Model

- Modeled reactor, gas separation and H2 recycle, product separation
- Pure compounds used (versus pseudocomponents)
- Stoichiometric Reactor Model
- Aspen model

flowsheet shown in additional slides





Technical Progress & Results: FCC Model



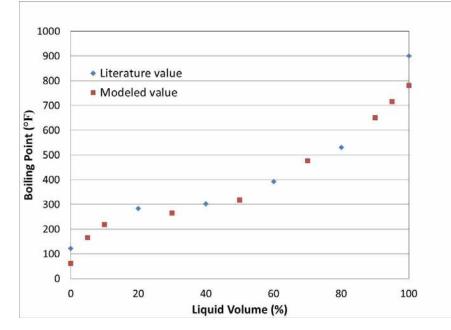
Pacific Northwest NATIONAL LAB Proudly Operated by Battelle Since 1965

100% VGO feed model

- Back blended distilled products distillation curves* in Excel to estimate FCC effluent
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Blended feed models

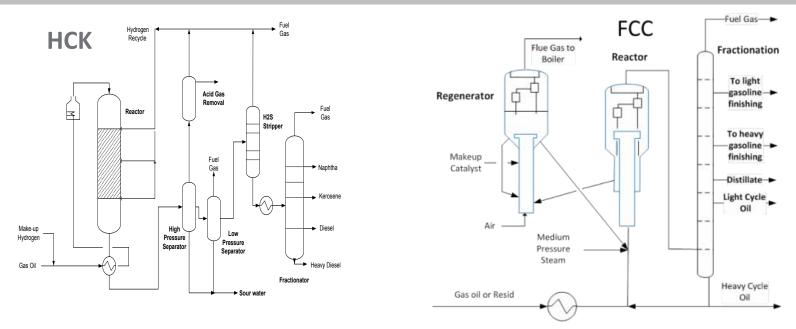


- Overall yields are based on published literature for comparable blends of partially upgraded bio-oil for FCC products
- Oxygen removal is either through the formation of water or CO2 and the yields are consistent with recent experimental results (60-70% of oxygenated species converted)
- 90/10 wt% and 80/20 wt% VGO/bio-oil
- Consistent throughput and reactor inlet temperature for all three cases 12

Technical Accomplishments







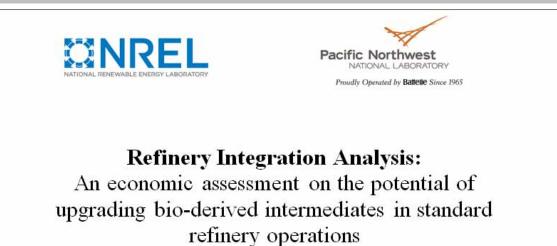
- Developed first of a kind process models for hydrocracker and fluidized catalytic cracker units
- Developed baseline models for traditional petroleum vacuum gas oil (VGO)
- Introduced partially upgraded pyrolysis oil at 10wt% and 20wt% blend
- Performed preliminary economic analysis to estimate the value of bio-oil to a refiner based on set price of crude and process impacts

Technical Accomplishments: Key Milestone





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Mary Biddy (NREL) Susanne Jones (PNNL)

September 30, 2014

Completed report summarizing process design and assumptions and economic analysis of integrating upgraded bio-oil in refinery FCC and HDO processes

Report provided to 4 different external key petroleum refining stakeholder organizations. Feedback received from 5 total independent reviewers.

Technical Accomplishments: Industrial Assistance





General comments:

- Reduce flowrates (or add capital) for blended feeds to account for process constraints such as
 - FCC coke make
 - HCK hydrogen availability
- Heating value vs. volume swell
- Re-evaluate co-product basis (gasoline & diesel fraction, vs offgas, LPG) and consider a range of values
- Consider fixed costs: labor, maintenance, depreciation in addition to variable costs

Unit specific comments

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

Feedback on sensitivities

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

Feedback on data gaps

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

Feedback on data sources: parallels with other work

- Oil shale and tight oil pilot work
- Vegetable oil/triglyceride cc-processing work
- Coal liquid co-processing work

Project Relevance





16

Project directly contributes to BETO goals per 11/2014 MYPP:

- "The market potential of bio-oils as a feedstock for petroleum refineries is largely unknown. There is a need to gather information to understand the technical risks and to illustrate the economics and sustainability of integration so that refineries will consider the bio-oil intermediate an acceptable refinery feedstock." (Thermochemical Conversion)
- Convey the results of analytical activities to a wide audience, including DOE management, Congress, the White House, industry, other researchers, other agencies, and the general public" (Analysis and Sustainability)

Positive impact on commercial biofuel viability:

- Determine bio-fuel production cost reduction opportunities
- Determine realistic estimates of how much biomass could potentially be corefined and the impact on the Renewable Fuels Standards (RFS)

Target Audience: BETO and industrial stakeholders

- Engage key stakeholders in the industry for their review and feedback on underlying assumptions, and share their insight on the issues of risk and technical information needs for risk assessment
- Feed results to **related BETO projects** (experimental and analysis)
- Identify data gaps needed for further consideration to BETO conversion platform

Project Relevance





Expected outcomes and applications

- Understand & review current state of technology and information available to integrate biomass derived intermediates into existing petroleum refineries
- Begin to assess if refinery integration will be successful in the future in terms of economics, sustainability and technical risks. Assess cost requirements from the refiner's perspective
- Identify the technical risks, research needs and primary cost drivers in using biomass derived intermediates in petroleum refinery hydrocracker and fluid catalytic cracker units
- Given the underlying uncertainty in the current data, identify which data gaps are critical to address in the near term to understand the cost implications and/or risk for refinery integration
- Help identify specific properties favorable for integration as well as properties that may limit the ability to integrate biomass intermediates and estimate the economic implications of meeting these desired properties

Future Work



FY15:

- Continue model updates per reviewer feedback; leverage Aspen HYSYS capabilities in addition to AspenPlus
- Begin to identify data needs for Life-Cycle Analysis (LCA)
- Continue stakeholder reviews
- **Stakeholder Dissemination:** Present work to date at **AIChE Spring Meeting**
- **Go/no-Go in May** to determine whether to continue on or change course
- Key Milestone: Complete draft journal manuscript of co-processing information to date

FY16:

- Expand models to consider co-processing of **distilled bio-oil** in **hydrotreaters**
- Potentially work with ANL regarding sustainability assessments
- Investigate supply chain integration (biomass type, location, proximity to petroleum refineries)
- Continue stakeholder reviews
- **Key Milestone:** Summary white paper
- Project ends: Not the last word, results feed into a bigger picture (Refinery Blend LP model for example)

Summary



Overview: Begin to understand co-processing issues

Approach: Iterative, NREL & PNNL **share inputs** & **review results** with external experts

Technical Accomplishments/Progress/Results

- FY14: Completed preliminary FCC and HCK cost and performance models with external review
- **FY15**: received external review feedback & began incorporation
 - Conducting on-going literature search
 - Preparing data requests

Relevance: by assessing use of existing infrastructure, this project **aligns with BETO's mission** to reduce biofuel production costs

Future work: Go/No-go, journal draft, sensitivity analysis, sustainability analysis

Status since 2013 Review: PNNL FY12-13 AOP project had review from one retired refiner. Peer reviewers recommended bringing in additional expertise. Joint NREL/PNNL project started in FY14 and added multiple industrial assistance.





Bioenergy Technologies Office – Alicia Lindauer

NREL TEAM

Mary Biddy Michael Talmadge

PNNL TEAM

Sue Jones Mark Bearden Yunhua Zhu Steve Phillips Asanga Padmaperuma





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Additional Slides

Response to reviewers comments Publications and presentations Project milestones Modelling detail example Abbreviations and acronyms

Responses to Previous Reviewers' Comments





2013 Peer Review of PNNL AOP project from FY12-13:

"Broader engagement with more refineries and with downstream stakeholders is a key factor to make this and follow-up efforts worthwhile"

"Needs much more collaboration with industry and labs"

Response: Per reviewer recommendations, PNNL partnered with NREL to leverage previous and ongoing work at both labs and also increased the number of industry contacts from 1 to 4 separate entities (6 reviewers total)

Go/No-Go Reviews: scheduled for May 31, 2015

Publications and Presentations



PNNL FY12-13 work

- Publications:
 - Freeman C. J.; Jones, S. B.; Padmaperuma, A. B. *et al* Initial Assessment of U.S. Refineries for Purposes of Potential Bio-Based Oil Insertions, April 2013, PNNL-22432

Presentations:

- 2013. Freeman, C. J.; Jones, S. B.; Padmaperuma, A. B. *et al* Initial Assessment of U.S. Refineries and the Potential for Bio-Based Oil Insertions" Presented to the Bioenergy Technologies Office March 22, 2013
- 2013. "Opportunities for Biomass-Based Fuels and Products in a Refinery A Preliminary Investigation" Presented by Corinne Valkenburg (Invited Speaker) at Biomass 2013, Washington, DC on August 1, 2013. PNNL-SA-97258
- 2014. "Preliminary assessment of potential bio-based oil insertions to US refineries" Presented by Asanga Padmaperuma at 2014 Spring Meeting and 10th Global Congress on Process Safety, New Orleans, LA on March 31, 2014. PNNL-SA-101771
- 2014. "Initial Perspectives on Biomass and Bio-oils in Existing Infrastructure." Presented by Corinne Drennan (Invited Speaker) at Bio-oil Coprocessing Workshop, New Orleans, LA on May 23, 2014. PNNL-SA-102992.

NREL/PNNL FY14-17 work

- Presentation planned for AIChE Spring meeting (April 2015)
- Publication draft planned for Q4FY15

Milestones and Metrics



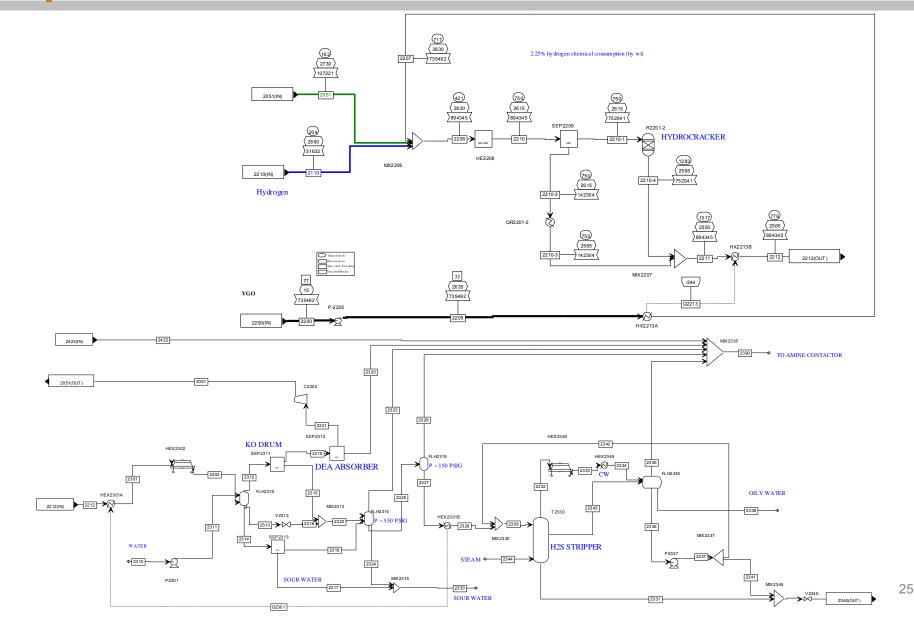


Title/Description	Due Date	Completed
Define conventional feedstocks and up to 5 bio-intermediate streams to feed hydrocracker and FCCU processes (joint PNNL/NREL)	Dec-13	On-time
Complete base Aspen models for the 2 refinery processes (joint PNNL/NREL) to include a stoichiometric based reactor, heat integration and product separation and summarize in a brief (joint PNNL/NREL	Mar-14	On-time
Complete co-processing cost estimates for at least two intermediates (oils with different oxygen contents)	Jun-14	On-time
Complete reviewed hydrocracker models with 2-3 process configurations (PNNL), FCC models with 2-3 process configurations (NREL) and report (PNNL/NREL) summarizing model assumptions, and outcomes identifying gaps, potential issues and opportunities for co-processing ML/DL).	Sep-14	On-time
Revise models (HCK PNNL and FCC NREL primary focus) to incorporate industrial/stakeholder reviewer feedback from FY14 and new literature/ experimental data leading towards the Q2 deliverable and summarize in a brief to BETO	Dec-14	On-time
Define and use models (HCK PNNL primary focus; FCC NREL primary focus) to collect sustainability metrics (e.g. GHG emissions, net fossil energy consumption) that are relevant to BETO's economic and sustainability goals, and summarize in a brief to BETO	Mar-15	
Go/No-Go decision: Model Utility	May-15	
Joint NREL-PNNL publication including a literature review of refinery integration data, and key economic results with a focus on data gaps, roadblocks and opportunities for bio-fuel cost reduction	Sep-15	
Consider alternative biomass derived feedstocks for co-processing, potentially produced from hydrothermal liquefaction or via fermentation, and develop hydrotreating model. Develop list of sustainability metrics to be collected and summarize in a brief to BETO	Dec-15	
Complete base and co-feed hydrotreater models from Q1 FY16 and summarize in a brief to BETO	Mar-16	
Complete biomass availability on a county level and proximity analysis to existing petroleum refineries for current and future scenarios; leverage HCK, FCC and hydrotreater model outputs. Summarize in a brief	Jun-16	
Final deliverable: NREL, PNNL ANL white paper draft for publication	Sep-16	24

Aspen HCK and Gas separation



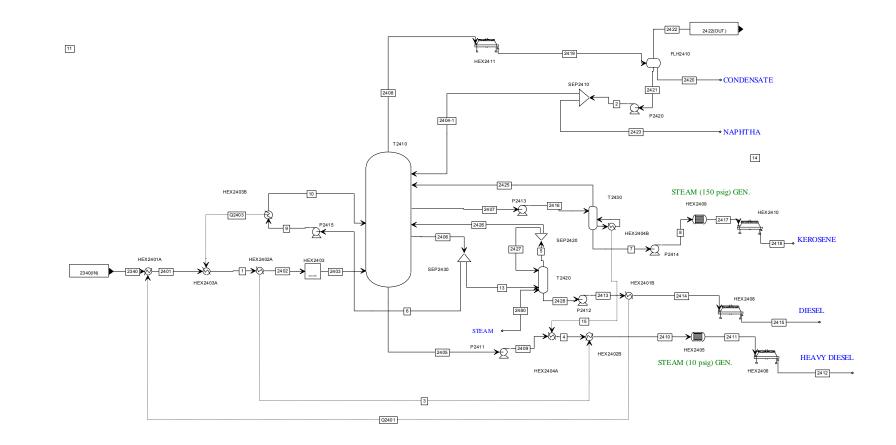




Aspen HCK Product Separation







Abbreviations and Acronyms





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