2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Optimizing Co-Processing of Bio-Oil

Alan Zacher

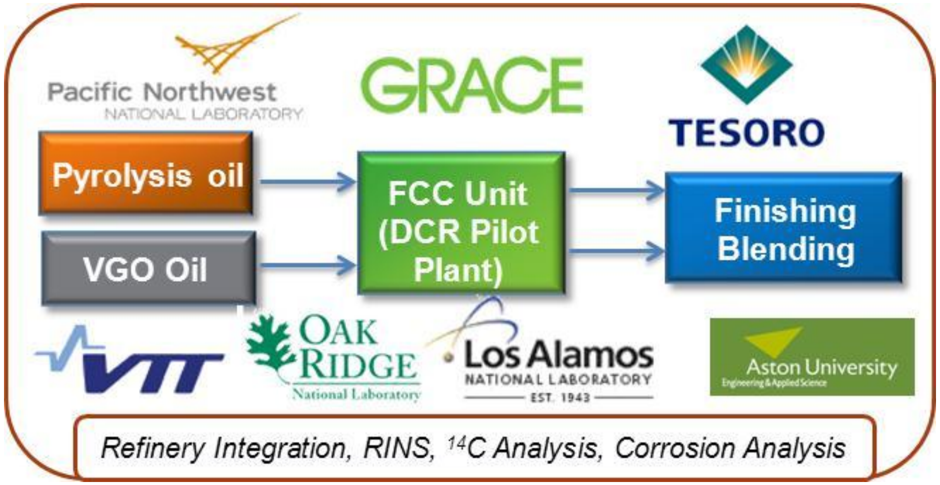
May 21, 2013

Technology Area Review: Bio-oil Technology

Organization: PNNL

PNNL-SA-95398

Goal/Objective Statement



Tesoro Refinery, Anacortes, WA (Scott Butner, PNNL)

- Goal: Understand the minimum stabilization required to co-process bio-oil in a refinery and the quality of co-processing fuel product
- DE-FOA-0000686: Bio-Oil Stabilization and Commoditization
  - Produce bio-oil feed to be used within a petroleum refinery
  - Leverage existing refinery capital
  - Qualify toward EISA RFS advanced biofuel goals

Project Quad Chart Overview

Timeline

- Awarded 10/1/2012
- End 9/30/15
- 0% Complete
- Completing subcontracts prior to start of research

Barriers

- Barriers addressed
  - Tt-E. Pyrolysis/Stabilization of biomass
  - Tt-G. Fuel Synthesis and Upgrading
  - Tt-K. Thermochemical Process Integration

Budget

- Total project funding: $5.0M
- FY 2013: $3.5M

Partners

- W.R. Grace
- Tesoro
- VTT
- ORNL
- LANL
- Aston University

Project Overview

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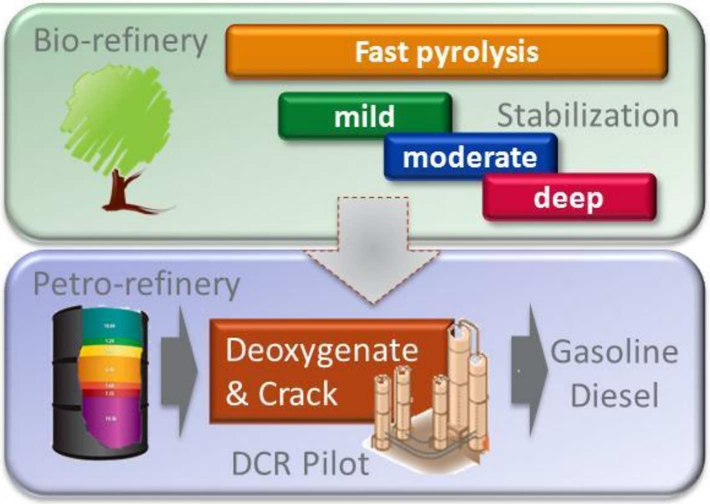

Barrier	Strategy
Need data for "acceptable bio-oil feedstock" and "Yield/quality tradeoff"	Define stabilization/blending envelope and resulting fuel yield specifically applied to FCC unit operation
Market acceptance to biomass insertion	DCR high quality data on range of VGO and bio-oils
Catalyst lifetime during HDO/hydrocracking of raw bio-oil to fuel, catalyst fouling and carbonization	Low severity bio-oil stabilization avoids fouling. Bio-oil cracking and finishing occurs in the FCC reactor where coke mitigation and quick catalyst regeneration is standard industry practice
Hydrogen consumption	Optimize stabilization to minimize hydrogen consumption; FCC unit to complete deoxygenation.

4

1 - Approach

- Task A. Baseline Pyrolysis Oil co-feeds:
  - Obtain two representative bio-oil and VGO oils from three refineries
  - Baseline raw bio-oil co-processing in FCC Pilot Unit (DCR)
- Task B. Catalytic stabilization of bio-oils
  - Stabilized at mild, moderate, and severe catalytic conditions
- Task C. Co-process in refinery unit operations
  - Co-processing of stabilized oils and catalyst development and optimization
  - Analysis of feedstock and refinery products
  - Corrosion and materials of compatibility
  - Biogenic carbon accounting
- Task D. Market Assessments
  - Market assessment and development of licensing path
  - Contribution to the EISA volumetric requirement (RFS)
  - RINS assessments
  - Prepare a co-processing course for the Grace refining series
- Task E. Engineering Assessments
  - TEA refined from current accepted models
  - Life-cycle assessment on the baseline and optimized cases
- Task F: Project Management
  - Project milestones, schedule, and risk mitigation via PMP approved by DOE
  - Weekly telecon meeting with labs and sub-task partners
  - Quarterly reviews

2. Technical Progress

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- New Project for 2013: Technical progress report will consist of detailing the technical approach

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GRACE Enriching Lives, Everywhere.™

PNNL and W. R. Grace will co-manage this project
Project Co-directors: John Holladay & Manoj Koranne
Principal Investigators: Ken Bryden & Alan Zacher

- Pyrolysis oil stabilization (PNNL)
- DCR piloting (Grace)
- Analysis, integration (PNNL/Grace)
- Marketing/Commercialization (Grace)

TESORO

Refinery Lead:
Rick Weyen

- Integration
- RINS

VTT

Aston University Engineering & Applied Science

Pyrolysis — Yrjö Solantausta
Stabilization – Tony Bridgwater

Los Alamos NATIONAL LABORATORY EST. 1943

Biogenic Carbon Analyticals:
Claudia Mora

OAK RIDGE National Laboratory

Materials–
Jim Keiser

Integrating Biomass into Petroleum Refineries

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Insertion Point 1
- Virgin/straight Run Streams
- Not suitable for biomass

Insertion Point 2
- FCC
- Coker
- Hydrotreaters/ hydrocrackers

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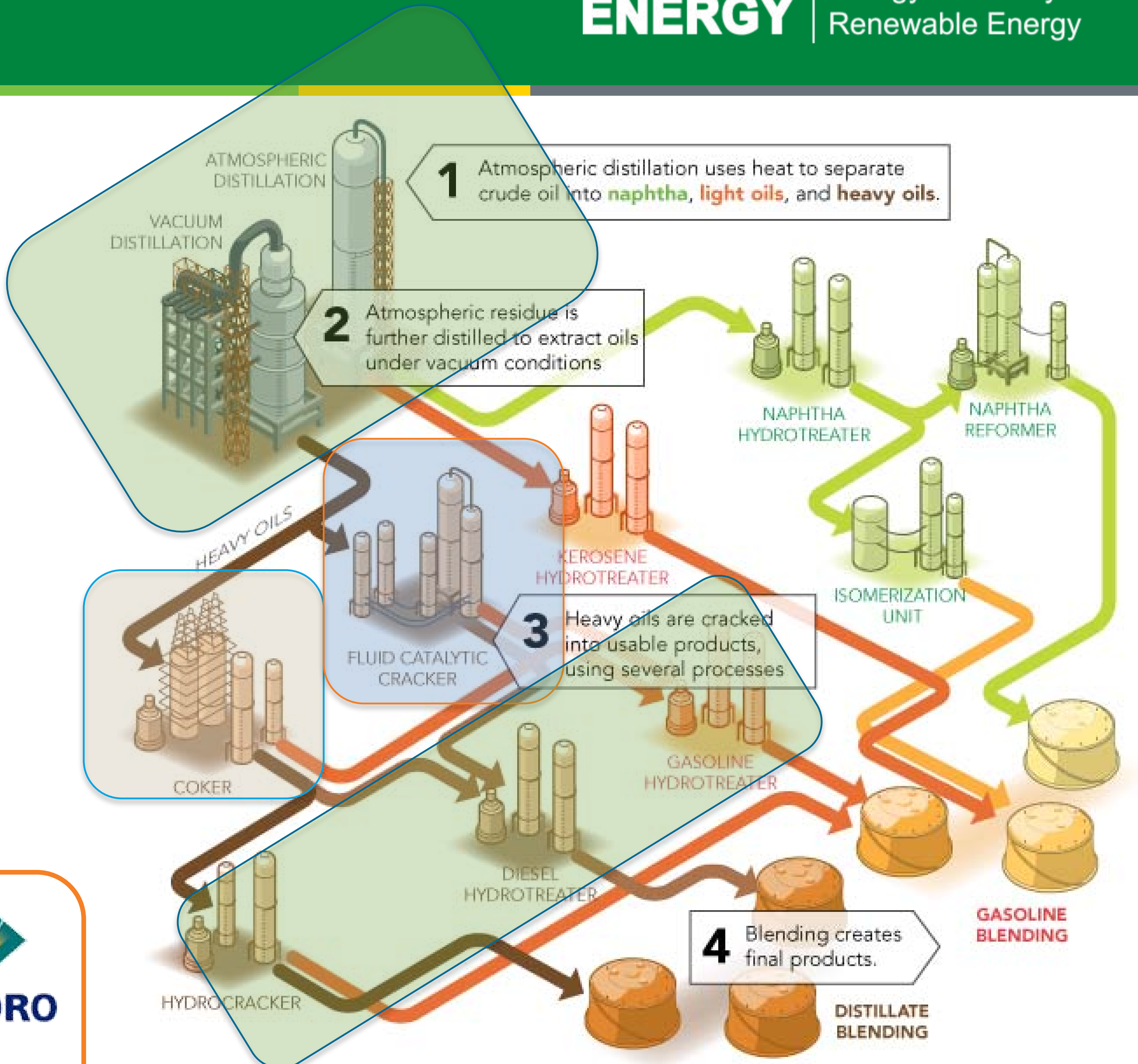

Picture courtesy of http://www.bantrel.com/markets/downstream.aspx

Co-processing Challenge

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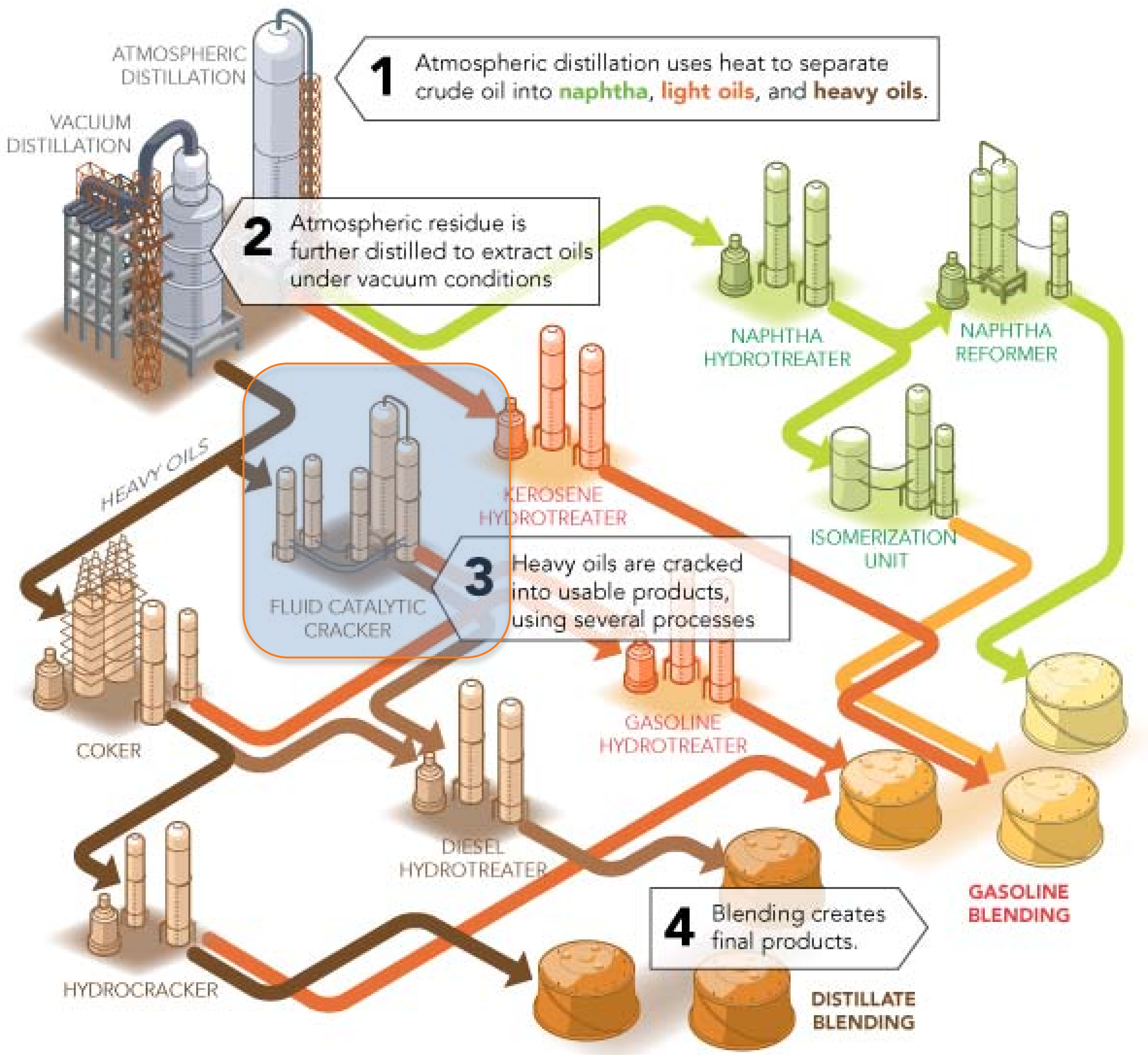
- Baseline bio-oil upgrading strategies do not sufficiently leverage existing refinery capacity
- Oxygen content of raw bio-oil makes it unsuitable for straight run insertion
- The FCC is one of the most flexible refinery unit operations
- Bio-oil will require some stabilization prior to co-processing



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Comparison of Bio-Oil and Heavy Petroleum Characteristics

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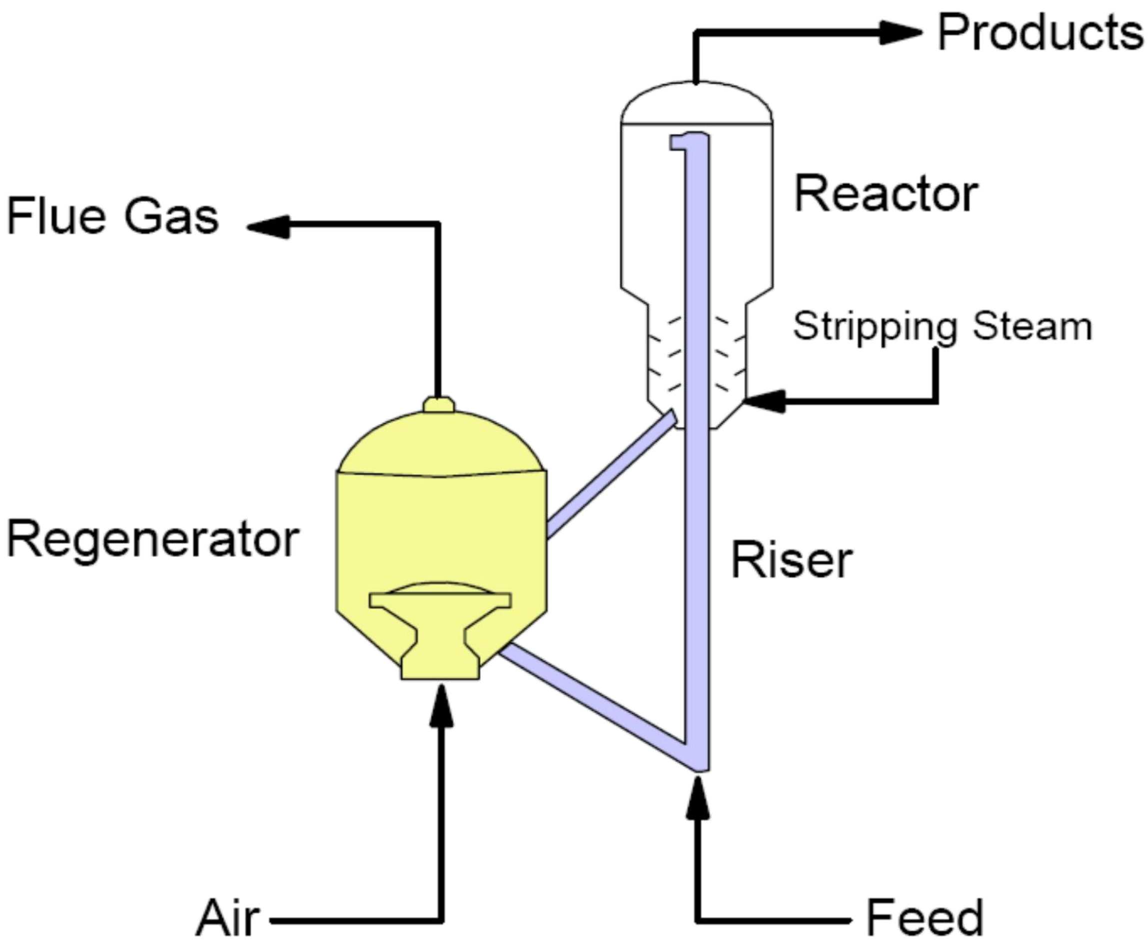
Characteristic	Fast pyrolysis Bio-oil	Heavy petroleum fuel
Water content, wt%	15-25	0.1
Insoluble solids, %	0.5-0.8	0.01
Carbon, %	39.5	85.2
Hydrogen, %	7.5	11.1
Oxygen, %	38-53	1.0
Nitrogen, %	<0.1	0.3
Sulfur, %	<0.05	2.3
Ash %	0.2-0.3	<0.1
HHV, MJ/kg	17	40
Density, g/ml	1.23	0.94
Viscosity, cp	10-150@50ºC	180@50ºC

Simplified FCC Unit Diagram



Simplified diagram of a generic FCC unit. Catalyst circulates from the regenerator to the bottom of the riser, where it mixes with feed, flows up the riser into the reactor, and is separated from the products by cyclone separators. Stripping steam removes entrained hydrocarbon vapors, and the catalyst flows back to the regenerator where air is injected to burn off the coke. The cycle then repeats.

Davison Circulating Riser

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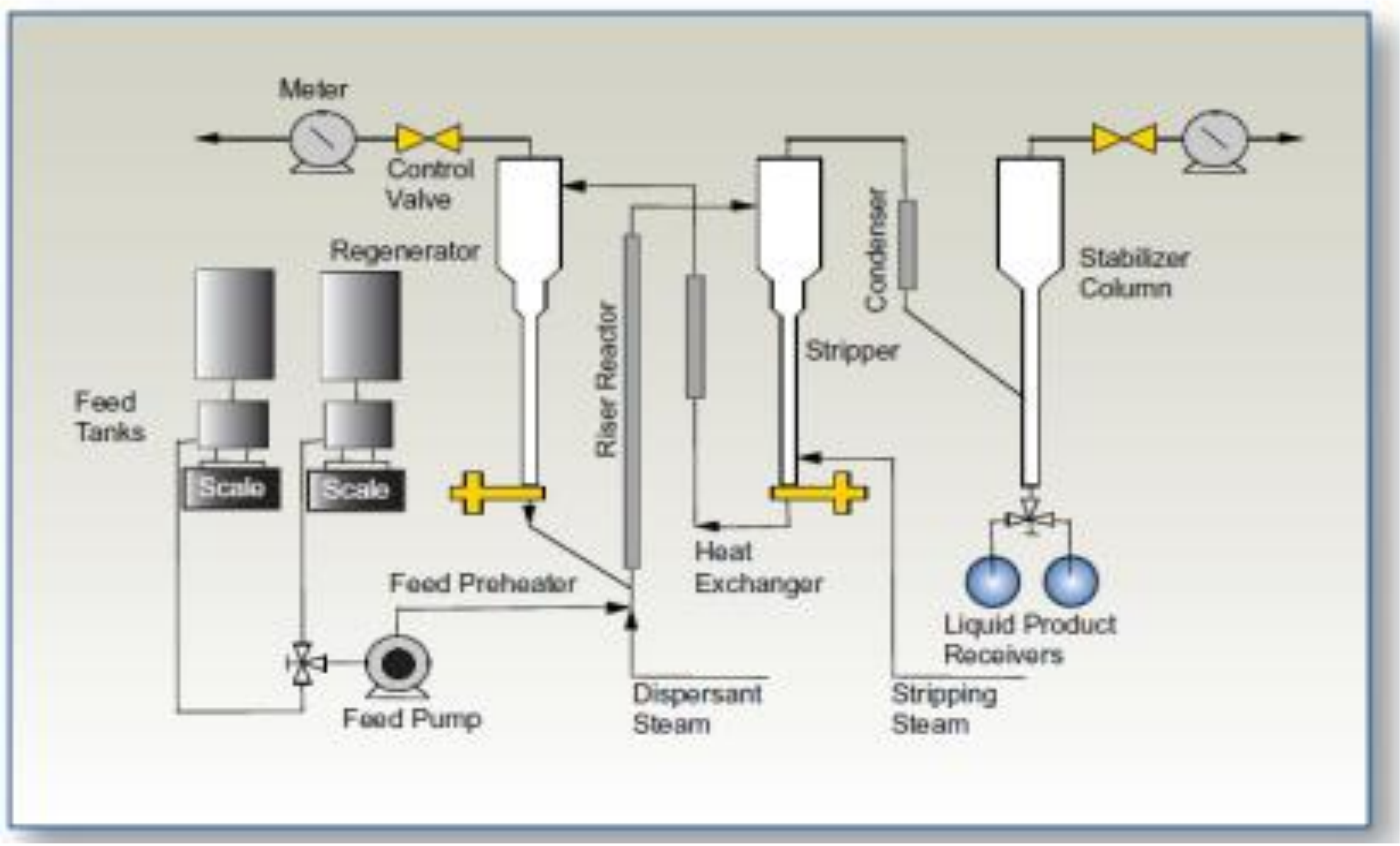

The Davison Circulating Riser is the industry standard for FCC pilot development

Davison Circulating Riser

- Fast turnaround, allows 4 - 5 mass balance tests per 2 shift day
- Complete flue gas analysis, batch collection of liquid and gas products
- Dual feed handling system and capability for blended feeds
- Extensive analytical capabilities to support DCR operations

A view of the Davison Circulating Riser

Fixed Bed Reactor

A view of the fixed bed reactor and distillation column used to make stabilized oils

Milestones/Deliverables

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Task	Outcome	Due Date
A	3 barrels of VGO sourced, 300kg of bio-oil	8/30/13
	Quantify effect of raw bio-oil processing	11/30/13
B	50kg of stabilized bio-oil (severe)	9/31/13
	50kg of stabilized bio-oil (mild)	12/31/13
	50kg of stab. bio-oil (moderate)	6/30/14
	Determine optimal stabilization protocols	9/30/14
C	DCR Campaign 3 completed	5/31/14
	DCR Campaign 5 completed	9/30/14
	All DCR Campaigns completed	11/30/14
	Data package on processing envelope	1/31/15
	Quantify co-processing suite	1/31/15
	Peer reviewed paper on corrosion	1/31/15
	Peer reviewed paper on carbon accounting	1/31/15
D	Document on impact and marketability	1/31/15
	Preliminary design package	3/28/15
E	TEA/LCA package	3/28/15
	Demonstrated 60% GHG reduction	3/28/15

3 - Relevance

- MYPP Barriers addressed
  - Tt-E. Pyrolysis of Biomass and Bio-Oil Stabilization
  - Tt-G. Fuel Synthesis and Upgrading
  - Tt-K. Themochemical process integration

- Applications of the Expected Outputs
  - Preliminary design package will enable pre-commercial trials to be performed at refinery scale
  - Optimal catalyst suite and successful blending envelope will be commercialized to enable refiners to co-process bio-oil at refinery scale
  - Data package will be used to enable refiners with or seeking existing DCR licenses to perform in-house evaluation of co-processing

- Relevance to MYPP Milestones (Bio-Oil conversion)
  - FY15Q4: data to validate bench scale, process via liquefaction
  - BETO Performance Goal: Modeled conversion cost of $1.83/GGE via bio-oil pathway (FY17)

4. Critical Success Factors

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- Critical Success Factors
  - Demonstration of a successful bio-oil co-processing envelope that results in biomass derived fuels to leverage existing refinery infrastructure
  - Development of a RINS approved credit calculation for co-processing by demonstrating the fate of biogenic carbon in the final fuel
  - Market acceptance of co-processing through demonstration on industry standard piloting tools and assessment of fuel product quality impact
- Key Challenges
  - Raw bio-oil is incompatible with existing refinery feeds and equipment
  - Current FCC catalysts are not optimized for biomass requirements (HDO, etc.)
  - Market acceptance will require appropriate RINS credit and thorough evaluation before high value refinery equipment and processing time will be engaged
- Success in this project will:
  - Generate a convincing data package of the required catalysts and conditions for successful co-processing
  - Demonstrate that co-processing can generate RINS credit
  - Provide a path to pre-commercial trials and commercialization

5. Future Work

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- Produce bio-oil
- Baseline raw bio-oil co-processing
- Stabilize bio-oil at three levels of severity
- Co-process stabilized bio-oil
- Perform corrosion and biogenic carbon accounting
- Prepare data package, design package, and market assessment
- Prepare TEA and LCA

5. Future Work

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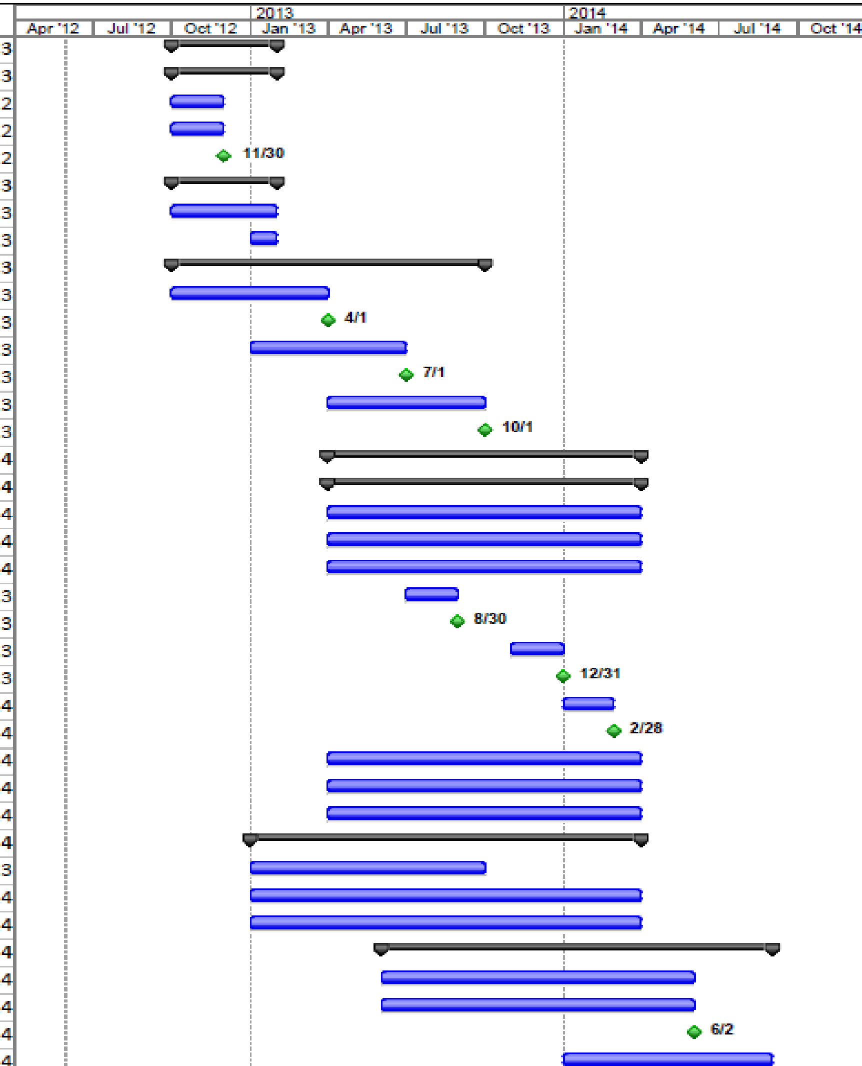
ID	Task Name	Start	Finish
1	**TASK A: Baseline Activities**	**Mon 10/1/12**	**Thu 1/31/13**
2	**Oil Sourcing**	**Mon 10/1/12**	**Thu 1/31/13**
3	Source Bio-Oils	Mon 10/1/12	Fri 11/30/12
4	Source Petroleum Oils	Mon 10/1/12	Fri 11/30/12
5	**Secure 3 Barrels of Different H/C VGO oils and 300 Kg of bio-oil**	Fri 11/30/12	Fri 11/30/12
6	**Processing of Bio-Oil Blends in FCC Pilot Plant (DCR)**	**Mon 10/1/12**	**Thu 1/31/13**
7	Feed Comptability Studies	Mon 10/1/12	Thu 1/31/13
8	Baseline Performance Studies in DCR (Campaign1)	Tue 1/1/13	Thu 1/31/13
9	**TASK B: Produce Bio-Oil with Mild, Moderate, Deep Stabilization**	**Mon 10/1/12**	**Tue 10/1/13**
10	Deeply hydrotreated Bio-Oil Production	Mon 10/1/12	Mon 4/1/13
11	Produce 50Kgs of Hydrotreated Bio-Oil (Deep)	Mon 4/1/13	Mon 4/1/13
12	Mildly Hydrotreated Bio-Oil Production	Tue 1/1/13	Mon 7/1/13
13	Produce 50Kgs of Hydrotreated Bio-Oil (Mild)	Mon 7/1/13	Mon 7/1/13
14	Moderately Hydrotreated Bio-Oil Production	Mon 4/1/13	Tue 10/1/13
15	Produce 50Kgs of Hydrotreated Bio-Oil (Moderate)	Tue 10/1/13	Tue 10/1/13
16	**TASK C: Co-Processing Bio-Oil Blends in FCC Pilot Plant (DCR)**	**Mon 4/1/13**	**Tue 4/1/14**
17	**Parametric Effects (Campaigns 2-6)**	**Mon 4/1/13**	**Tue 4/1/14**
18	Effect of Petroleum Base Feed Type	Mon 4/1/13	Tue 4/1/14
19	Percent Bio-Oil in Feed	Mon 4/1/13	Tue 4/1/14
20	Catalyst Technology	Mon 4/1/13	Tue 4/1/14
21	Campaigns 2-3	Mon 7/1/13	Fri 8/30/13
22	Campaign 3 Completed; Processing Stabilized Bio-Oil in DCR	Fri 8/30/13	Fri 8/30/13
23	Campaigns 4-5	Fri 11/1/13	Tue 12/31/13
24	Campaign 5 Completed	Tue 12/31/13	Tue 12/31/13
25	Campaign 6	Wed 1/1/14	Fri 2/28/14
26	Campaign 6 Completed	Fri 2/28/14	Fri 2/28/14
27	Analyses of Bio-Oil Blends and Refinery Products	Mon 4/1/13	Tue 4/1/14
28	Corrosion and Materials Compatibility	Mon 4/1/13	Tue 4/1/14
29	Biogenic Carbon Accounting - Isotope Studies	Mon 4/1/13	Tue 4/1/14
30	**TASK D: Market Assessments**	**Tue 1/1/13**	**Tue 4/1/14**
31	Refinery Assessment	Tue 1/1/13	Tue 10/1/13
32	Contribution to EISA Volumetric Requirements	Tue 1/1/13	Tue 4/1/14
33	RINS Assessment	Tue 1/1/13	Tue 4/1/14
34	**TASK E: Engineering Assessments**	**Mon 6/3/13**	**Mon 9/1/14**
35	Process Economics (TEA)	Mon 6/3/13	Mon 6/2/14
36	Lifecycle Analysis (CO2)	Mon 6/3/13	Mon 6/2/14
37	60% Reduction in GHG	Mon 6/2/14	Mon 6/2/14
38	Preliminary Design Package	Wed 1/1/14	Mon 9/1/14



Project: Technical Tasks and Milestone
Date: Tue 5/29/12

Task | Split | Progress | Milestone | Summary | Project Summary | External Tasks | External Milestone | Deadline

Summary

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- Relevance: Working to MYPP performance goals, Barriers: Tt-E, Tt-G, Tt-K
- Approach: FCC insertion point 2 of minimally stabilized oils, team with expertise in FCC piloting, hydrotreating, biogenic C accounting, and corrosion
- Technical Accomplishments: New project as of FY13, just starting
- Future Work: Plan designed to shorten discovery phase by interlacing stabilization tests and co-processing results
- Success factors: Will determine co-processing envelope, verify process for RINS credit, and outline a path to pre-commercial trials and commercialization
- Challenges: Bio-oil is not an ideal feed for a petroleum refinery, FCC catalysts need modification, and market acceptance is tough.
- Technology Transfer: Output is a data package for pre-commercial trials
- Other pathways: Process and methodology could be applied for other biomass liquid intermediates

Team is configured to produce a compelling case for commercialization of co-processing

Additional Slides