DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

Optimizing Co-Processing of Bio-Oil in Refinery Unit Operations Using a Davison Circulating Riser (DCR) 2.4.2.402

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Bio-Oil Technology Area

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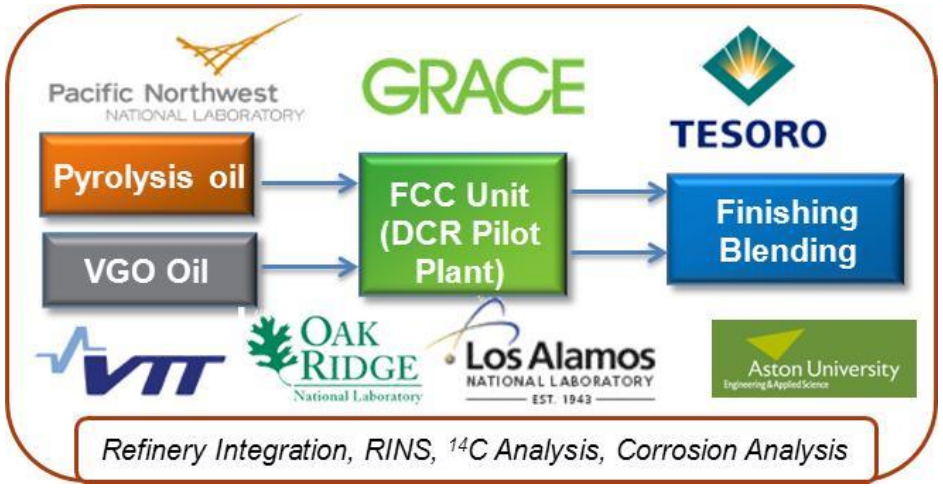
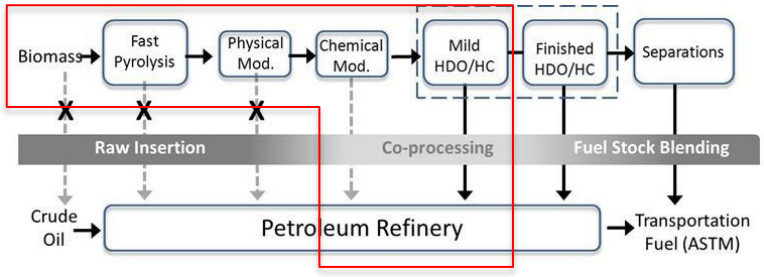
Goal Statement

- Develop a process to produce sustainable bio-fuels through co-processing biomass into a petroleum refinery unit operation.
- There is a need to know:
  - How much stabilization is required to co-process bio-oil into a refinery?
  - What is the quality of fuel product produced?

Impact: This project fulfills the paucity of applied, continuous, pilot scale data evaluating the use of bio-oil as a refinery intermediate.





Quad Chart Overview

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Timeline

- Award: 10/1/2012
- End: 9/30/2015
- 70% complete

Barriers

- Barriers addressed
  - Tt-F Biomass Deconstruction to Bio-oil
  - Tt-H Bio-oil stabilization
  - Tt-R Process Integration
  - Tt-P Materials Compatibility
  - Tt-S Refinery Integration

Budget

FY10-12 Costs	FY13 Costs	FY14 Costs	Planned Funding FY15-End
$0	$251,482	$2,027,483	$1,221,035

Partners

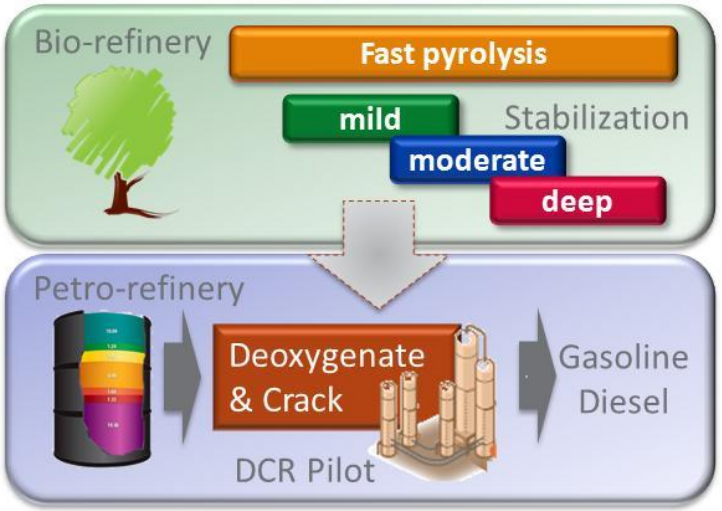
- W.R. Grace
- Tesoro
- VTT
- ORNL
- LANL
- Aston University

1 - Project Overview

DE-FOA-0000686: Bio-Oil Stabilization and Commoditization

- How can bio-oil be co-processed in a refinery that will:
  - Be successfully converted to liquid products
  - Leverage existing refinery capital
  - Qualify toward EISA RFS advanced biofuel goals

- This project is addresses the need for:
  - Data on stabilization/blending envelope of bio-oil/vacuum gas oil (VGO) coprocessing in an FCC
  - High quality pilot FCC data with bio-oils
  - Structural material performance data
  - Develop method for tracking of biogenic carbon to the liquid product

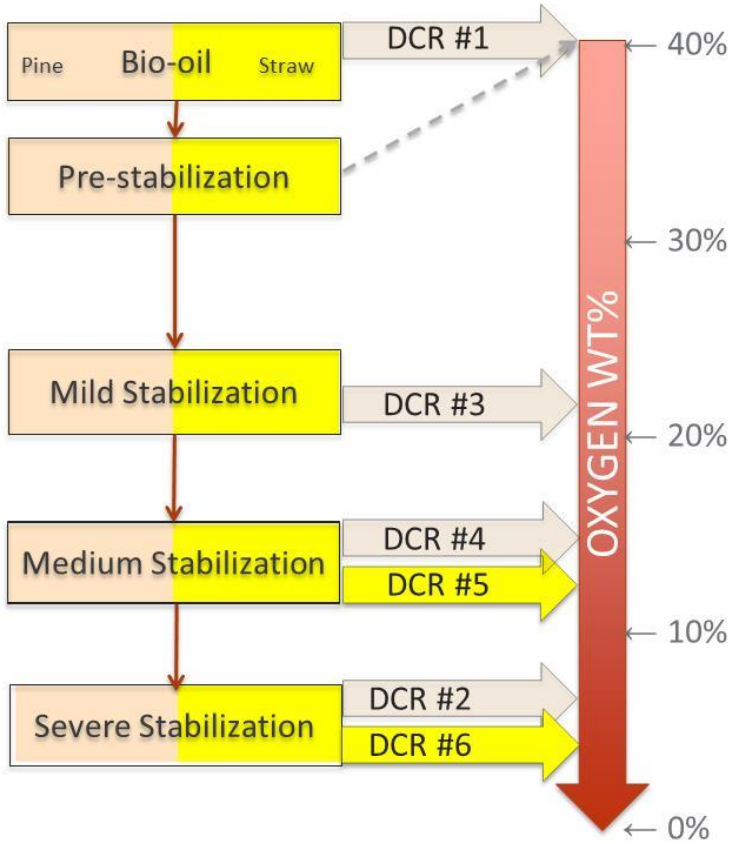


Fluid Catalytic Cracker (FCC)

2 – Approach (Technical)

- Stabilize bio-oil to varying levels of oxygen (wood and crop residue)
- Co-process with vacuum gas oil (VGO) in a pilot-scale FCC system
  - FCC is a representative insertion point, and VGO is a typical feed for it
- Evaluate corrosion and develop tracking method for bio-oil carbon
- Compile and assess co-processing data

- Key Challenges
  - Raw bio-oil is incompatible with existing refinery feeds and equipment
  - Current FCC catalysts are not optimized for biomass
  - Market acceptance will require demonstration of positive impact before high value refinery equipment will be engaged



2 – Approach (Management)

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- Critical Success Factors:
  - Demonstrate a successful stabilized bio-oil FCC co-processing envelope
  - Develop method to demonstrate biomass carbon is converted to fuel
  - Provide data from industry standard pilot FCC reactor
- Success in this project will:
  - Produce a data package for bio-oil co-processing
  - Demonstrate a product that meets bio-fuel qualifications
  - Provide a path to pre-commercial trials and commercialization
- Project Management
  - AOP, quarterly reporting, and quantifiable milestones
  - Monthly teleconference with all partners, domestic and international
  - Frequent email communications among task teams
  - Yearly in-person technical meeting to discuss results and project plan

3 – Pyrolysis Progress

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Objective: Produce pyrolysis oils

Accomplishments:

- Woody Biomass: pine (VTT)
- Crop Residue #1: straw (VTT)
- Crop Residue #2: corn stover (PNNL)

- Oil and data for pyrolysis oil production were generated on VTT 20kg/h pilot system

- Crop residues was produced from two sources due to biomass availability and the need for both C3 (wood, straw) and C4 (corn stover) carbon fixation pathways

3 – Stabilization Progress

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Objective: Produce stabilized oils at various oxygen contents
Accomplishments: 6 DCR Feeds produced

- Adapted methods of bio-oil hydroprocessing: used reduced temperatures, different catalysts, partial processing
- Produced feeds at pilot scale (400ml/800ml)
- Stabilization levels were refined iteratively after interpreting each DCR test

Feed	Biomass	Stabilization	Dry wt% O	Conditions
DCR #2	Pine	Severe	1 – 3%	3 bed, sulfided, 140-420C
DCR #3	Pine	Mild	20 – 22%	2 bed, sulfided, 140-190C
DCR #4	Pine	Medium	8 – 12%	3 bed, noble, 140-340C
DCR #5	Straw	Medium	8 – 10%	3 bed, noble, 140-340C
DCR #6	Straw	Severe	1 – 3%	3 bed, sulfided, 140-420C
DCR #6a	Corn stover	Severe	1 – 3%	2 bed, sulfided, 140-420C

3 – DCR Progress

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Objective: Co-process bio-oil with VGO

Accomplishments:

- 4 VGO examples were obtained: 3 from Tesoro and 1 from Grace
- 5 DCR tests performed

Findings

- Mildly stabilized oil more difficult to handle than raw pyrolysis oil
- Medium and severe hydrotreating led to materials that were easier to handle

DCR	Feed bio-oil	Dry wt% O	Max. VGO feed preheat w/o nozzle plugging	% bio-oil co-processed	Yield Observations
1	Pine, raw	38 – 40%	~200°F	up to 5 wt% with difficulty	Increased coke, reduced gasoline
3	Pine, mild	20 – 22%	~200°F	up to 3 wt% with difficulty	Increased coke, reduced gasoline
4	Pine, medium	8 – 12%	Up to 700°F	10 wt%	Yields similar to VGO
2	Pine, severe	1 – 3%	Up to 700°F	10 wt%	Yields similar to VGO
5	Straw, medium	8 – 10%	Up to 700°F	10 wt%	pending
6	Straw/Corn, severe	1 – 3%	pending	pending	pending

OXYGEN WT%

3 – Corrosion Progress - ORNL

Objective: Assess corrosion of bio-oil and coprocessing

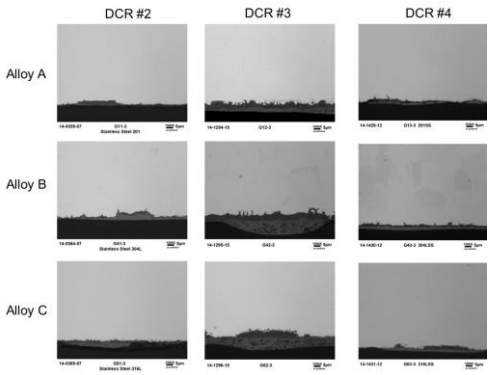
Accomplishments:

- In situ corrosion coupons in DCR 2 – 5 co-processing tests, ~100h
- 1000h ex situ corrosion analysis performed on available stabilized bio-oils

Findings

- In situ DCR corrosion correlates with degree of stabilization

Oil/stab	exposure	C Steel	2¼Cr-1Mo	409 SS	304L SS	316L SS
Pine bio-oil	Vapor	0.20	0.30	<0.01	<0.01	<0.01
	Liquid	2.29	2.71	0.44	<0.01	<0.01
Straw bio-oil	Vapor	0.40	0.36	<0.01	<0.01	<0.01
	Liquid	0.94	2.93	0.33	<0.01	<0.01
Pre-stabilized	Vapor	1.68	1.43	0.04	<0.01	<0.01
	Liquid	1.18	2.07	0.10	<0.01	<0.01
Mild, organic	Vapor	0.59	0.50	<0.01	<0.01	<0.01
	Liquid	0.12	0.70	0.15	<0.01	<0.01
Mild, aqueous	Vapor	1.57	1.89	0.06	<0.01	<0.01
	Liquid	0.35	1.72	0.48	<0.01	<0.01



Calculated corrosion rates in mm/yr based on ex situ tests

3 – Carbon Accounting - LANL

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Objective: Develop stable isotope carbon accounting for bio-oil

Accomplishments:

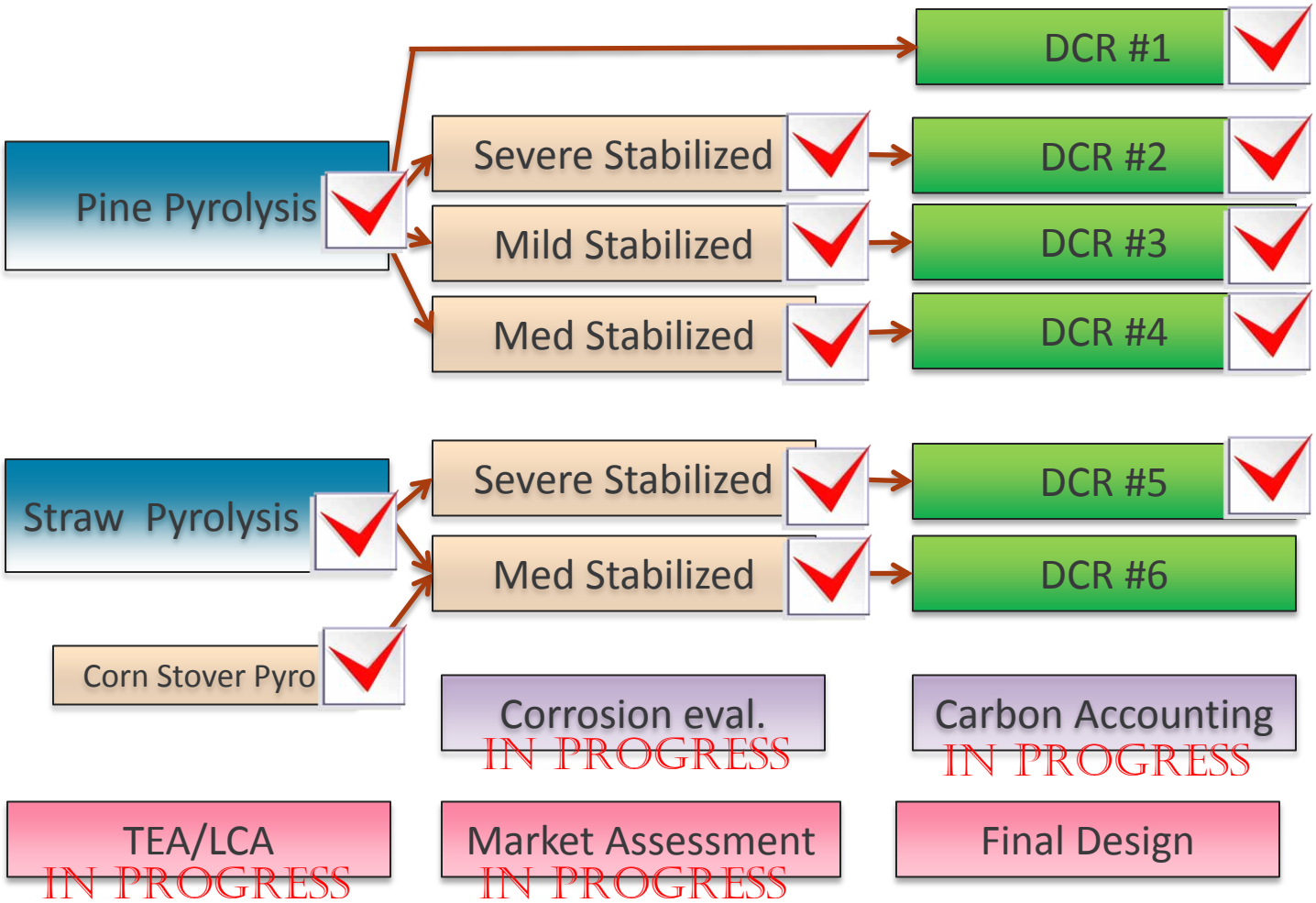
- Stable isotope accounting results have shown great promise for accounting
- Compares well with ^{14}C results
- DCR 1 – 3 gas, liquid, and flue gas samples analyzed for multiple blend rations of bio-oil

Impact: Initial data suggests that stabilized bio-oils may preferentially partition to the liquid fuel products.

Context:

- Radioactive ^{14}C analyses of products are a proven way to follow biogenic carbon, but it is expensive, time consuming, and not readily available to the refiner
- Stable isotopes (C, H, N, O) offer a potentially new way to trace biogenic carbon, it is inexpensive, fast, and performed by readily available equipment

Project Status as of Feb 2015



4 – Relevance

- Addresses the lack of pilot scale data on bio-oil as a refinery intermediate
- Applications of the Expected Outputs
  - Preliminary design package will enable pre-commercial trials to be performed at refinery scale
  - Catalyst suite and blending envelope will be available to commercial refiners to enable bio-oil co-processing at refinery scale
  - Data package will be enable refiners to perform in-house evaluation of co-processing with or seeking existing DCR licenses
- Technology Transfer
  - Involvement of industry partners to keep the results in line with reality
  - Variety of VGO used and pilot scale testing yields industrially relevant data
  - Current industrial partner involvement is a pathway to reach companies interested in in-house evaluation or piloting

5 – Future Work

- All pyrolysis and stabilization tests complete
- Final FCC pilot scale campaign will be performed at Grace upon receipt of samples from PNNL (DCR#6)
- Deliverables
  - Corrosion analysis, manuscript
  - Carbon isotope accounting, manuscript
  - Data package on co-processing, report on refinery impact
  - Preliminary design package
  - TEA and LCA data package
- Project will be completed by September 2015

Summary

- This project addresses the lack of applied, continuous, pilot scale data evaluating the use of bio-oil as a refinery intermediate
- Initial results show that liquid yield from FCC co-processing of stabilized bio-oils is similar to VGO alone
- Information on the performance of structural materials is being collected
- Carbon accounting data shows that stabilized bio-oils may preferentially partition to the liquid products

- Project is on schedule to complete and deliver impactful results by September 2015

Additional Slides

Responses to Previous Reviewers' Comments

"This is more of a matter of establishing a baseline than of real innovation, but since most bio-oil work has focused on hydroprocessing, a baseline is needed for FCC. If this project can just get off the ground, it should be able to accomplish that, as well as some tuning of catalysts and process conditions."

- This project answers the important question if pyrolysis oil can make a meaningful intermediate stream in a refinery. There may be innovation in how this is enabled.

"The project focuses a strong team on the important issue of how to improve FCC of bio-oil. The project, which started very recently, should provide very key data on the suitability of this upgrading approach in a petroleum refinery. The work is very relevant to the DOE program.

- The project team is comprised of noted experts in each of the individual fields, and is well suited to achieving the objectives.

Responses to Previous Reviewers' Comments

"These feeds will likely load up the main column of an FCC and back out feed, as well as adversely affect the unit heat balance. This is unlikely to be attractive unless these feedstocks are very cheap."

- Indeed, this appears to be the experience with raw pyrolysis oil. Stabilization appears to overcome many of the processing issues.

"This project has potential. It has good collaboration, but mostly likely will not be able to integrate with existing refining FCC capacity due to refinery resistance, refinery economics, and availability of spare FCC capacity. However, it will answer some questions."

- There is resistance. This project will generate data that should give a thorough evaluation that will enable refiners to make informed choices about FCC co-processing of bio-oils.