2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

New Technology for Hydroprocessing Bio-oils to Fuels

May 20, 2013
Bio-Oil Technology Area Review

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Grace New Business Development/Catalysts

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Goal/Objective Statement

Goal: demonstrate viability of a new reactor technology and improved-stability catalyst(s) for hydrotreating pyrolysis oils to yield transportation fuels

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Project Quad Chart Overview

Timeline

- Start: October 1, 2011
- End: September 30, 2014
- 50% complete 3-31-2013

Barriers

- Barriers addressed
  - Tt-E (bio-oil stabilization)
  - Tt-G (fuels upgrading)

Budget

- Total project funding $4.0MM
- Funding received in FY 2011: $1.1MM
- Funding in FY 2012: $1.4MM
- Funding for FY 2013: $1.5MM
- ARRA Funding: none
- Funded for 3 years at average of $1.3MM/year

Partners & Roles

- W.R. Grace (lead)-cat. dev.
- PNNL-reactor process development, catalyst testing
- VTT (Finland)-pyrolysis oil (feedstock) production
- ORNL-rxtr corrosion study

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Project Overview

Technical barriers addressed

- Short catalyst lifetime of conventional hydrotreating
- Fixed bed has no mechanism for online catalyst replacement
- Existing EB catalysts are not compatible with bio-oil environment
- Existing EB reactor operation is not designed for bio-oil handling

Approach

- Bio-Oil Production : Fast pyrolysis of high quality bio-oil from wood and crop residue feeds at 1000-L scale (VTT)
- Novel Support Development: Novel hydrotreating supports produced and screened in high throughput, micro-scale stability testing. (Grace and PNNL)
- Novel Catalyst Scale-up: Catalyst are formed/extruded at both lab (100 g) and pilot (1-5 kg) scale for stability and application testing (Grace)
- Ebullated Bed (EB) Testing: Scaled catalysts are performance-tested in EB reactor (~0.5 L catalyst volume) with actual bio-oil (PNNL)
- Corrosion Analysis: Performed both in-situ and ex-situ to evaluate required materials of construction for bio-oil ebullated bed systems (ORNL)
- Process evaluation: Techno-economic and lifecycle analyses to measure improvement over petroleum and fixed bed hydrotreating (PNNL, Grace)
- Progress is reviewed in monthly managerial reviews within each organization, and results are shared in joint quarterly meetings

Major Tasks and Milestones

Task	Task Name	Milestone Description	Start Date	Due Date
A	Catalyst Development	Complete Evaluation of Six (6) Supports in Reactor(s)	10/1/2011	6/30/2013
B	Process Optimization	Complete 100 hours of Operation under Optimal Conditions	1/2/2013	12/31/2013
C	Extended Time Operation	Complete 1000h Extended Test Run	3/1/2013	4/1/2014
D	Points of Insertion in Refinery	Identify two (2) Insertion Points in Refinery	4/1/2014	9/30/2014
D	Points of Insertion in Refinery	Achieve ASTM Fuel Quality	4/1/2014	9/30/2014
E1	Techno-economic Analysis	Determine whether Price Comparable with Gasoline	4/1/2012	7/31/2014
E2	Life Cycle Analysis	Demonstrate GHG Reduction of at least 65% - Goal 85%	4/1/2012	4/1/2014

We have significant progress in Task A and have begun Task B

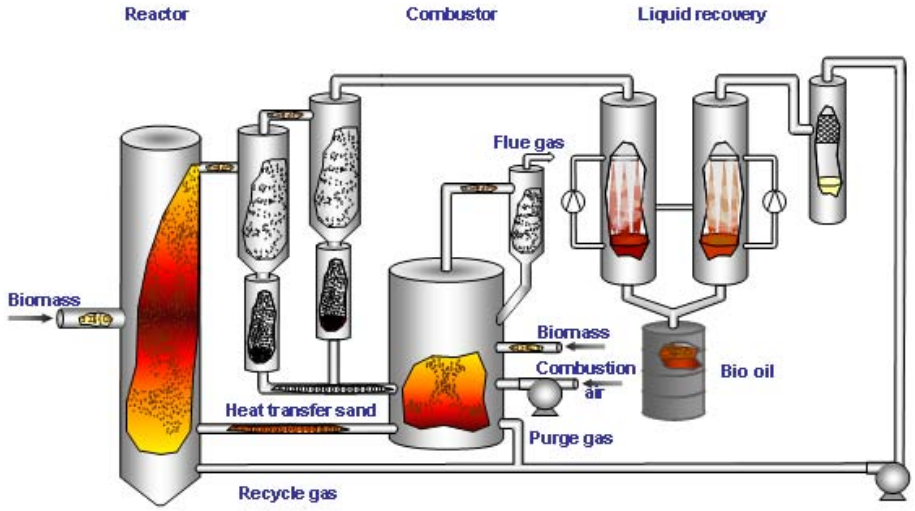
Technical Accomplishments/ Progress/Results

Summary of major tasks and subtasks

- VTT produced /shipped > 100 L of bio-oil (wood and crop residue)
- 193 new and existing supports screened for hydrothermal stability
- Selected first 2 candidates for scaled-up reactor testing
- Performed 9 test runs on ebullated bed reactor
- Extruded 9 most promising oxide supports at 5-kg scale as ebullated bed test candidates
- Corrosion tests underway with *in situ* coupons in reactor
- Initial technoeconomic analysis and lifecycle analysis performed

Technical Accomplishments: Bio-oil Feed Production

Goal: Produce high quality bio-oil for reactor testing



Fast Pyrolysis at VTT Process Dev. Unit: LIifetime Production totals: > 3100 h, > 42 tons liquids to date

Accomplishments:

- Produced representative bio-oil at pilot scale PDU (>100 liter)
- Wood and crop residue oils produced and shipped to partner labs
- Oil is high quality, representative of production scale, and very low in solids

Technical Accomplishments: Support and Catalyst Stability Testing

Goal: Develop and screen supports compatible with biomass upgrading requirements

Accomplishments:

- Hydrothermal stability testing methods developed for high-throughput screening of powders and engineered supports
- 193 samples tested to date
- Analysis by ICP and particle cohesion testing

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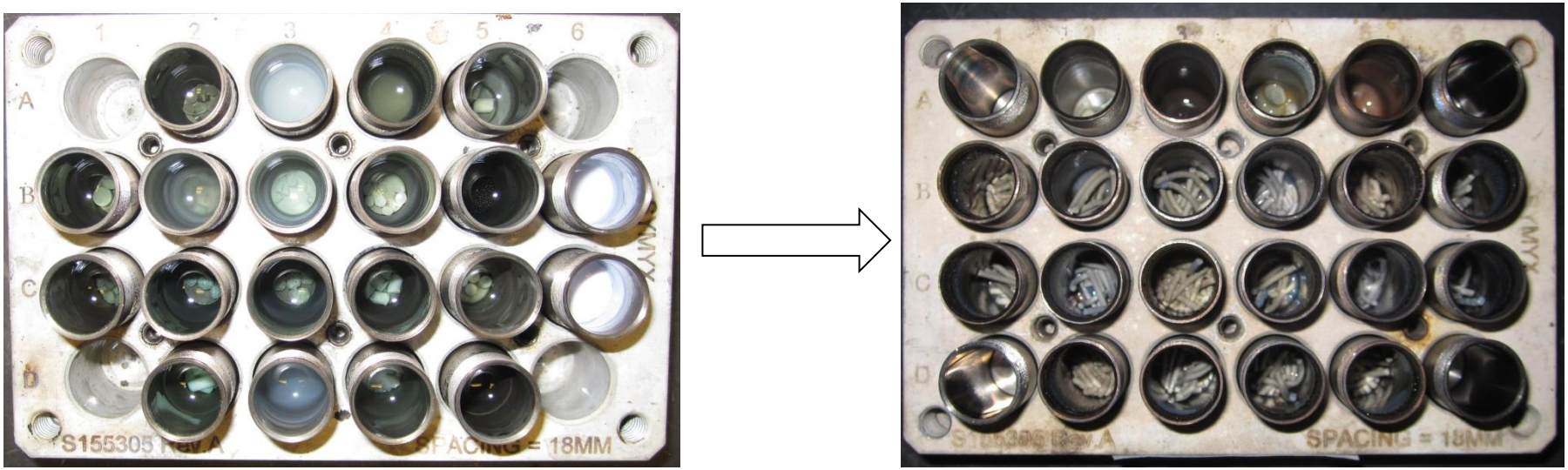
Technical Accomplishments: Support and Catalyst Stability Testing

Goal: Downselect samples for support composition, production techniques, and methods for producing a scaleable engineered form



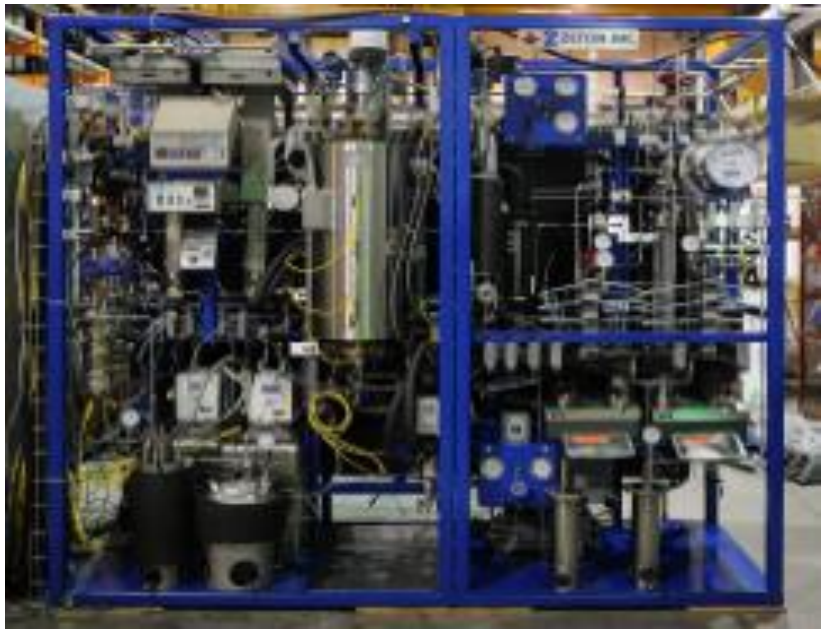
Accomplishments:

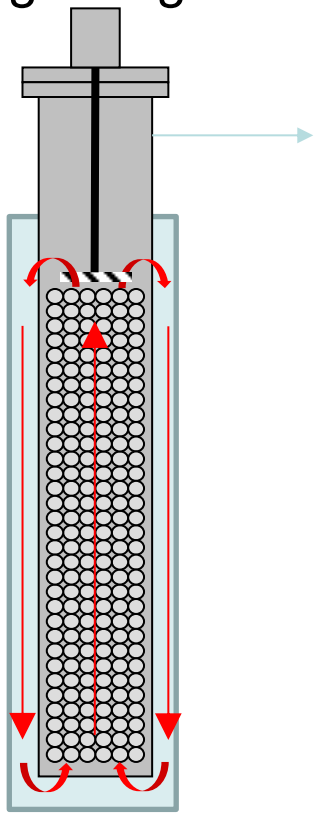
- For existing supports, demonstrated aluminas are not stable due to leaching
- Developed modified support compositions to reduce leaching of support
- Acid leaching of modified supports reduced by >70% (internal target 90%)
- 10 compositions remain as potential candidates

Technical Accomplishments:

Ebullated Bed Shakedown

Goal: Develop and test the ebullated bed concept for bio-oil upgrading





Unique challenges for bio-oil upgrading in ebullated bed

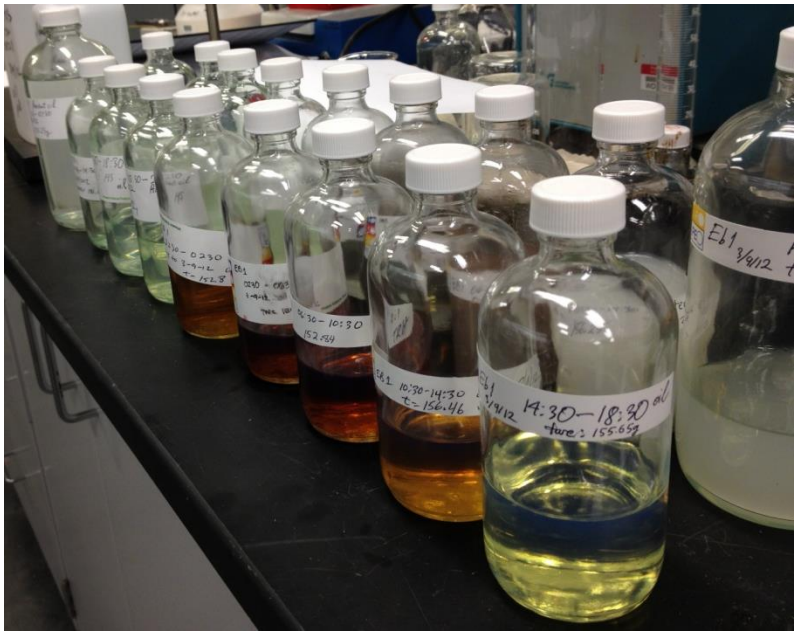
- Existing catalysts are not compatible with bio-oil
- Bio-oil is thermally unstable, dense, and high viscosity
- Polarity change occurs between bio-oil (polar) and upgraded product (non-polar)
- Reactor is highly multi-phasic: solid catalyst, polar and non-polar phases, non-condensible gas, supercritial fluids

Technical Accomplishments:

Ebullated Bed Testing

Goal: Develop and test the ebullated bed concept for bio-oil upgrading

	Temperature	Feed Rate
EB1	400C	50 (ml/hr)
EB2	385C	50
EB3	360C	50
EB4	350C	50
EB5	300C-320C	50
EB6	280C	50
EB7	200C-250C	200
EB8	300C	150
EB9	300C	150



Accomplishments

- Total of 9 ebullated bed tests performed to date, longest test: 48hr on stream
- 2 catalysts tested, range of operating conditions evaluated
- Bio-oil is challenging: Modifications being made to bio-oil feeding system, product recovery system, and operating strategy to extend time on stream

Technical Accomplishments:
Ebullated Bed Product Analysis

Goal: Characterize products from bio-oil upgrading in ebullated bed

GC/MS Analysis									
HOS	MeOH	HCs 3 – 5	HCs 6 – 9	HCs 13+	C5 + subst	C6 + subst	Benz+ subst	indene+ subst	napthalene+ subst
25	11.1	8.3	16.8	0.9	10.8	38.5	3.5	4.8	4.8
33	11.4	9.4	13.1	0.9	11.9	39.6	4.2	4.6	4.2
37	10.7	8.1	11.8	2.3	10.8	39.1	5.7	4.9	4.9

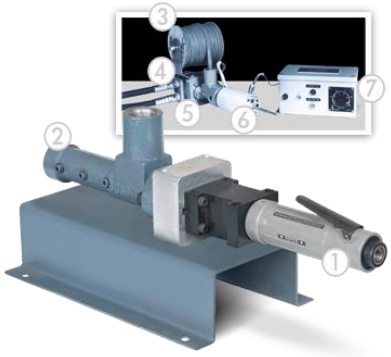
Oil elemental analysis (wet)								
TOS(hr)	Elemental Analysis						K-F	TAN
	C	H	N	O	S	Balance		
Feed	39.5	7.5	0.08	53.0*	0.032	100%*	23.1	74.5
25	82.5	12.9	0	2.0	0	97.4%	0.165	0
33	81.4	12.2	0	1.9	0	95.4%	0.015	0
37	80.0	12.0	0	1.9	0	93.9%	0.010	0
EOR	87.3	10.5	0.14	2.0	0.015	99.8%	n/a	n/a

Accomplishments

- Samples from 48hr test analyzed by GC/MS and elemental analysis
- ~2% Oxygen oil produced
- Predominantly 5-carbon and 6-carbon ring structure in product

Technical Accomplishments: Pilot Scale Extrusion of 9 Candidates

Novel oxide powders → Extrude → Heat-treat Impregnate → Supported Catalyst



Accomplishments

- 5-kg samples made on a pilot extruder
- this equipment is known to be scaleable to commercial quantities
- Provides supports for later milestone of eb bed testing

Technical Accomplishments: Balance of Desirable Support Properties

Properties Normalized to Standard Support					
Support Type	leach rate	Surf. Area	Pore Vol.	APD	Crush Str.
standard support	1.0	1.0	1.0	1.0	1.0
novel 'A'	0.3	1.1	1.0	1.0	1.2
novel 'B'	0.4	1.2	0.9	0.8	1.2

Accomplishments

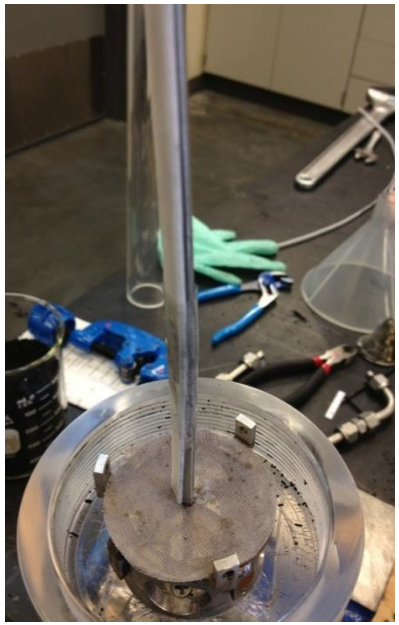
- Identified above from among193 candidates tested to date, including both previous industrial types and (predominantly) novel bench scale preparations
- Devised new synthetic routes to supports
- Lowered support leaching rate in acidic stability test by up to 70%
- Retained or improved upon several desired features of std. support

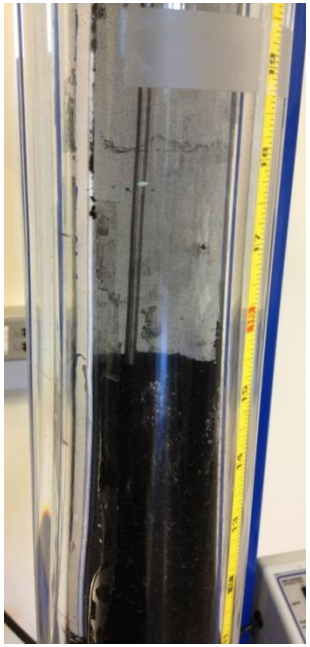
Technical Accomplishments:

Corrosion analysis underway

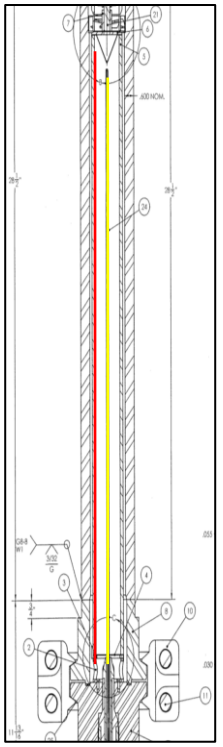
Goal: Evaluate corrosion in ebullated bed upgrader

Centerline placement





Wall placement



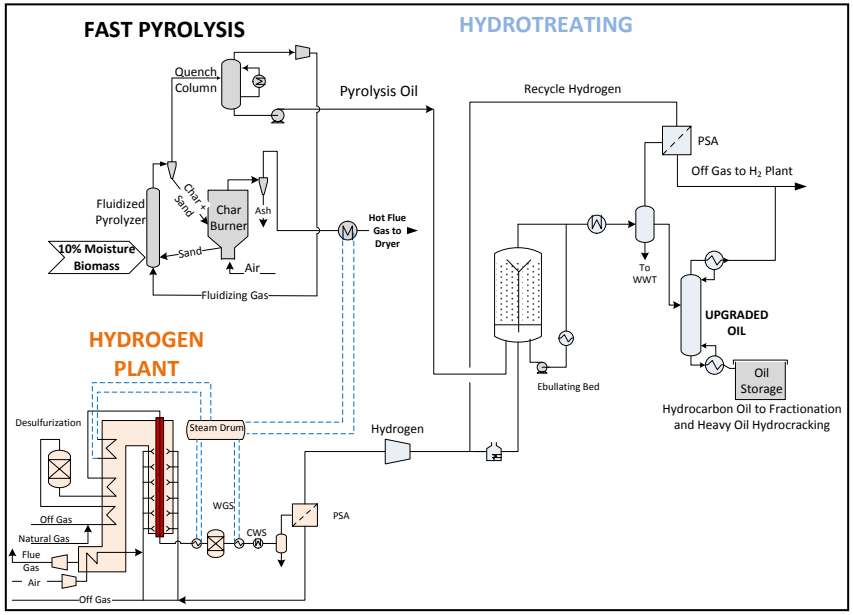
Accomplishments

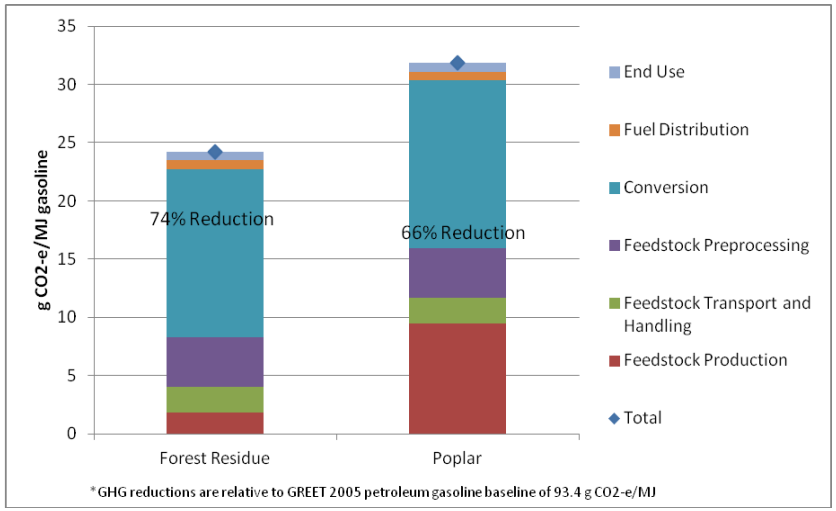
- Downselected metal coupon type to assess full length of reactor
  - Compounds and acid strength predicted to vary widely across bed
- Acrylic demonstration model used for coupon compatibility testing
- Impact on fluid/catalyst flow appeared to be minimized at wall location
- Coupons have been on stream from tests 5 through 9
- Reactor wall thickness measurements completed

Technical Accomplishments:

Initial Techno-economic and life cycle analyses

Goal: Characterize products from bio-oil upgrading in ebullated bed





Accomplishments

- First draft of TEA and LCA complete, based on existing SOT models
- Assumes an intermediate product from ebullated bed followed by finishing
- Catalyst maintenance and finished fuel yield are largest economic drivers
- GHG reduction versus petroleum: 60% from wood, 74% from wood residue

Relevance

- **Supports 2017 pyrolysis targets and themochemical goal**

  "to develop technologies for converting feedstocks into cost competitive commodity liquid fuels, such as ethanol, renewable gasoline, jet fuel, and diesel…."

- **Addresses MYPP Barriers**

  Tt-E Pyrolysis of Biomass and Bio-Oil Stabilization

  Tt-G Fuels synthesis and upgrading of bio-oils

- **International**

  Encourages collaboration between biomass experts (US and Europe)

- **Applications of the expected outputs from this project**

  Use of ebullated bed reactor for biomass processing

  Use of novel acid-resistant supports and catalysts in processing high-oxygen biomass-derived feedstocks and intermediates

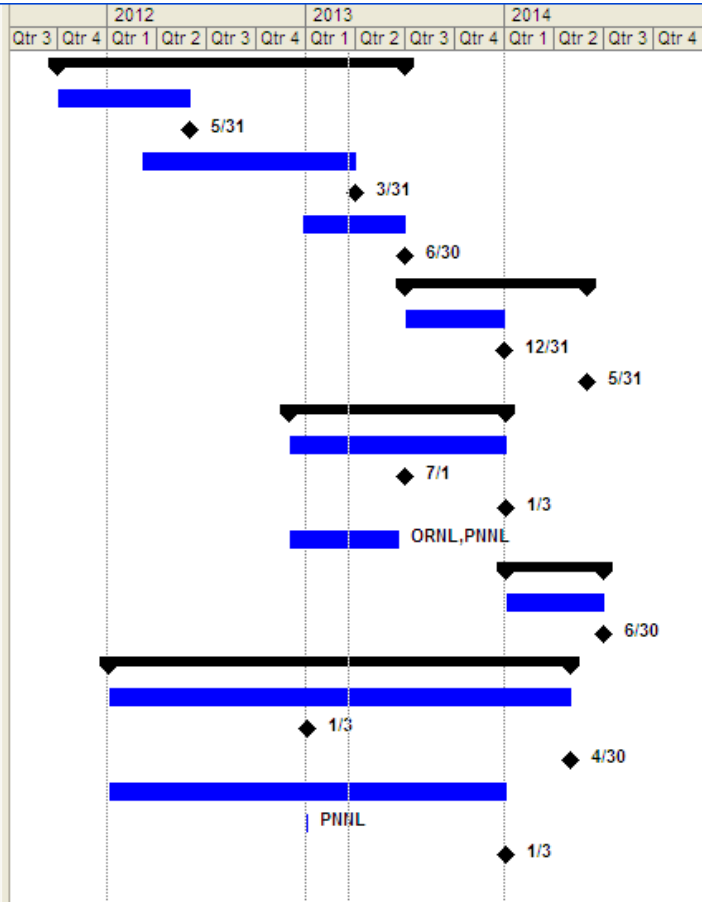
  Bio-oil tolerant catalyst could be useful in other hydrothermal environments and technologies (fixed bed bio-oil upgrading, etc.)

Critical Success Factors

- **Critical success factors**
  - **Technical: 1) robust operation of EB reactor**
    2) demonstrated catalyst life
  - **Market: emergence of pyrolysis vs. other biofuels routes**
  - **Business: competitive affordability of overall route**
- **Top potential challenges**
  - **Technical: 1) reactor compatibility with Bio-oil alone (or with minimal co-processed petroleum feeds)**
    2) balancing catalyst stability and activity requirements
  - **Non-technical: reluctance of refineries to embrace biofuels**
- **Upon successful completion**
  - **1) Higher visibility of EB hydrotreating option for biomass**
  - **2) introduction of next-generation catalysts with improved net economics through longer life (widely applicable)**

Future Work

Task Name	Start	Finish	Resource Names
A. Catalyst Development	**10/1/11 8:00 AM**	**6/30/13 5:00 PM**	**Grace,PNNL,VTT**
Evaluate Existing Formulations	10/1/11 8:00 AM	5/31/12 5:00 PM	Grace,PNNL
Combinatorial Screening	5/31/12 5:00 PM	5/31/12 5:00 PM	PNNL
New Formulation Development	3/5/12 8:00 AM	3/31/13 5:00 PM	Grace
Selection of 6 New Formulations	3/31/13 8:00 AM	3/31/13 8:00 AM	Grace,PNNL
Validation of Formulations	12/24/12 8:00 AM	6/30/13 5:00 PM	Grace,PNNL
Demonstration in Eb Bed	6/30/13 5:00 PM	6/30/13 5:00 PM	Grace,PNNL
B. Process Optimization	**7/1/13 8:00 AM**	**5/31/14 8:00 AM**	**Grace,PNNL**
Test 6 Formulations in Continuous Reactor	7/1/13 8:00 AM	12/31/13 5:00 PM	Grace,PNNL
Confirm Best Formulation	12/31/13 8:00 AM	12/31/13 8:00 AM	PNNL
Complete 100 hour run	5/31/14 8:00 AM	5/31/14 8:00 AM	Grace,PNNL
C. Extended Time Operation (Eb Bed)	**12/1/12 8:00 AM**	**1/3/14 5:00 PM**	**Grace,PNNL,VTT**
Run Extended Time Trials for Bio-Oil Production	12/1/12 8:00 AM	1/3/14 5:00 PM	Grace,PNNL,VTT
Produce 1000L of bio-oil	7/1/13 8:00 AM	7/1/13 8:00 AM	VTT
Complete 1000 hour run	1/3/14 8:00 AM	1/3/14 8:00 AM	PNNL,ORNL
Corrosion Testing	12/1/12 8:00 AM	6/18/13 5:00 PM	ORNL,PNNL
D. Points of Insertion in Refinery	**1/3/14 8:00 AM**	**6/30/14 5:00 PM**	**Grace,PNNL**
Analyze Potential Insertion Points	1/3/14 8:00 AM	6/30/14 5:00 PM	Grace,PNNL
Identify Insertion Points	6/30/14 8:00 AM	6/30/14 8:00 AM	Grace
E. TEA and LCA	**1/5/12 8:00 AM**	**4/30/14 5:00 PM**	**Grace,PNNL**
Techno-economic Analysis	1/5/12 8:00 AM	4/30/14 5:00 PM	Grace,PNNL
Base Case Financial Analysis	1/3/13 8:00 AM	1/3/13 8:00 AM	PNNL
Gasoline Comparable Metric	4/30/14 8:00 AM	4/30/14 8:00 AM	Grace,PNNL
Life Cycle Analysis	1/5/12 8:00 AM	1/3/14 5:00 PM	Grace,PNNL
Baseline GHG Analysis	1/1/13 8:00 AM	1/1/13 5:00 PM	PNNL
Demonstrate GHG Reduction	1/3/14 8:00 AM	1/3/14 8:00 AM	Grace,PNNL



Key upcoming events are selection of eb bed catalysts (Task A) and their use in reactor testing toward optimized process (Task B)

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Summary

- **Relevance**
  - addresses known reactor and catalyst limitations
- **Approach**
  - ebullated bed reactor with non-standard catalyst supports
- **Technical accomplishments**
  - Operation of reactor with real world feeds, yielding low oxygen products
  - Significant reduction in leachability of catalyst supports in acid
  - Pilot-scale synthesis of 9 possible eb bed test candidates
  - Design and early testing of *in situ* corrosion study techniques
  - Preliminary TEA/LCA
- **Future work**
  - Testing of pilot-scale catalysts in eb bed toward robust (1000 hr) process
- **Success factors and challenges**
  - Stability and thereby cost of catalyst and of reactor operation
  - Market readiness for pyrolysis oils in refineries
- **Technology transfer**
  - Existing Grace customers have expressed interest in projected outcomes

Additional Slides

Responses to Previous Reviewers' Comments

- This project was not previously reviewed

Publications and Presentations

- No publications or presentations to date.