2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Upgrading of Biomass Fast Pyrolysis Oil (Bio-oil)

Bio-Oil Technology Area Review

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Goal/Objective Statement

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Develop a hydroprocessing system & catalysts tailored for the Catalytic Bio-Oil produced by Battelle's Ex Situ fast pyrolysis and vapor-phase upgrading system

Addresses all FOA-0000342 Objectives

Supports Bioenergy Technology Office Pathway #3

Supports Battelle's Small Scale Biofuels Production Systems

DE-FOA-0000342

FOA objectives

1. Address bio oil corrosivity;
2. De-oxygenate bio-oil;
3. H/C product 30% blendable with ASTM petroleum fuels
4. Provide data to demonstrate product compatibility with petroleum refining unit operations.

B.T.O. Pathways

1. Fast Pyrolysis;
2. In-situ catalytic fast pyrolysis; Is-situ cat. fast pyrolysis;
3. Ex-situ catalytic fast pyrolysis;
4. Hydropyrolysis;
5. Hydrothermal liquefaction
6. Solvent liquefaction

Industry Needs

1. Drop-in fuel
2. Competitive at market price
3. Low capital needs
4. Scalable
5. Feedstock flexible
6. Environmentally sustainable
7. Near to Mid Term Economic Potential

Project Quad Chart Overview

Timeline

Barriers

Tt-E: Pyrolysis of Biomass:

Development of new methods to control the pyrolytic pathways to bio-oil intermediates in order to increase product yield and quality

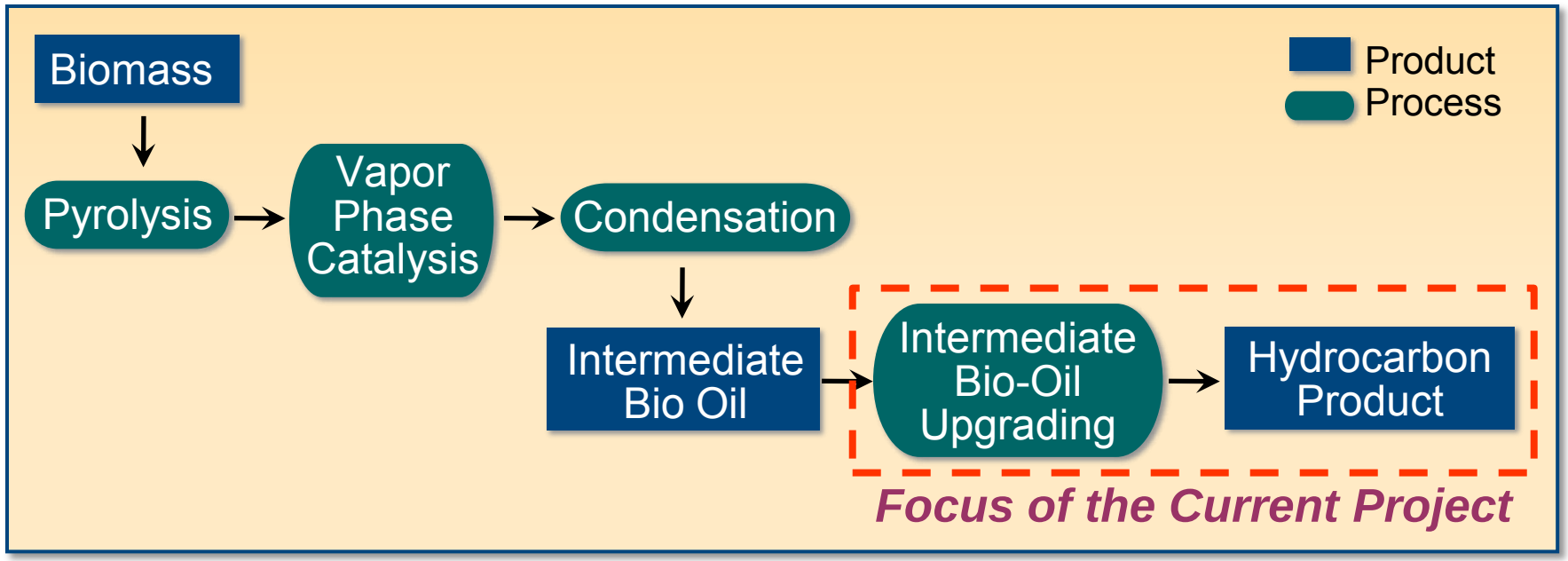
Budget

Year	DOE Funding	Cost Share
FY 2011	$ 60,817	$ 243, 091
FY 2012	$ 811,432	$ 388,710
FY 2013 (to 2/2013)	$ 181,058	$ 136,454
FY 11, 12, 13 Average	$ 360,000	$ 240,000
Total	$2.1 M Battelle $1.1M PNNL	$ 818,200 (20%)

Partners & Roles

Organization	Role(s)
Battelle	PI., PM.
PNNL	H.T. Cat. dev., TEA
Marathon	Fuel assessment
Domtar	Feedstock supply
Praxair	Options for hydrogen
Sud Chemie	Catalyst manufacturer

Project Overview



Key Technical Barriers Addressed by This Project

Technical Barrier	Project Focus to Address technical Barrier
H/T catalyst coking	Development of new catalysts for intermediate bio oil
H/T catalyst coking	Construction of H/T with regeneration capability
Corrosion of materials of const.	Generate data on corrosion due to Intermediate Bio-Oil
Catalyst deactivation preventing long term operation	Demonstration of 1,000 hrs hydrotreater operation on single catalyst charge

1 - Approach

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Technical Approach:

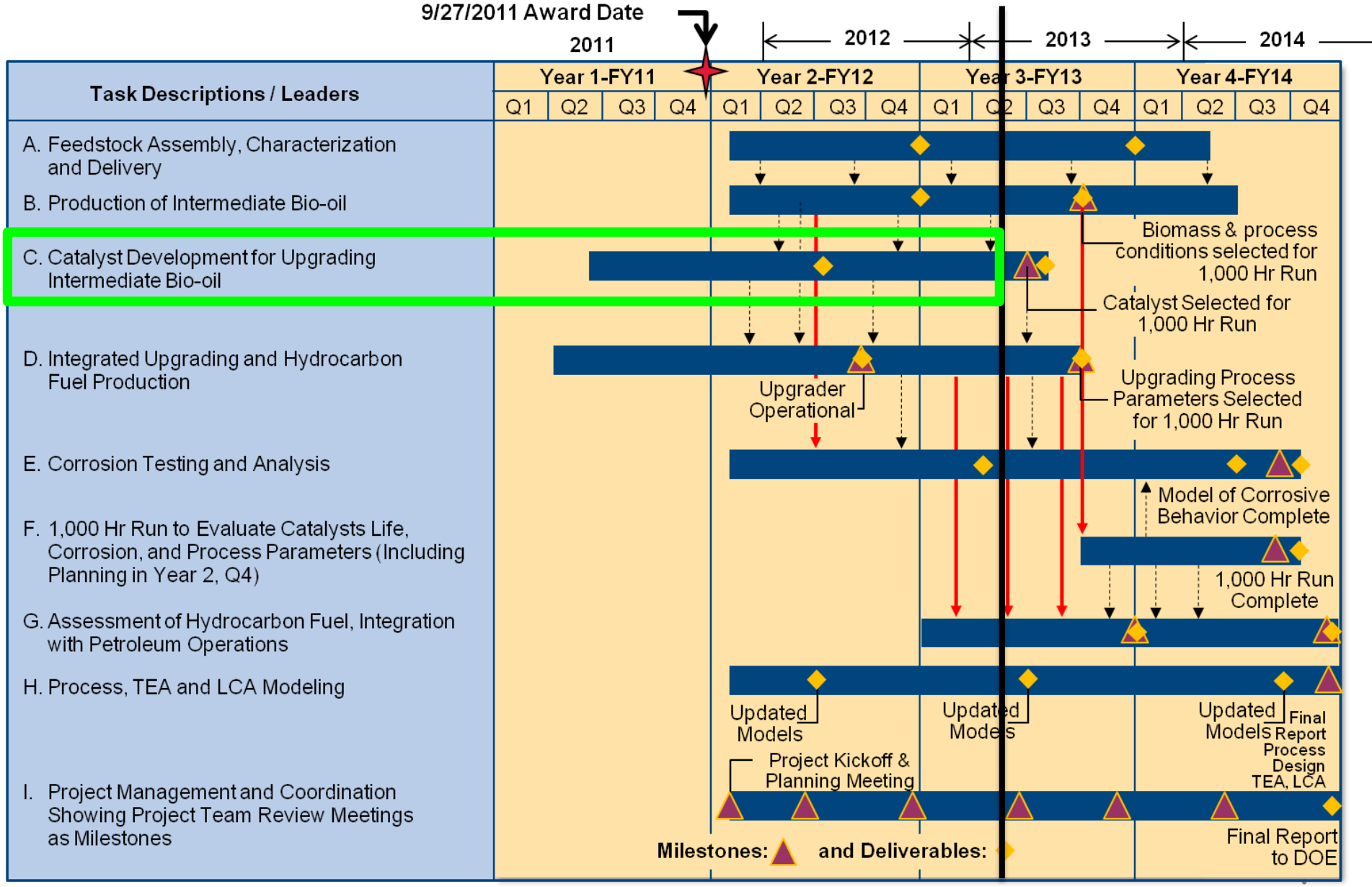
- Catalyst development for upgrading catalytic pyrolysis bio-oil (PNNL)
  - Build Lab-scale hydrotreater
  - Screen catalyst using model compounds
  - Evaluate catalysts with bio oil
  - Establish operating parameters
- Integrated Upgrading & hydrocarbon production (BMI)
  - Build Pilot-scale hydrotreater with catalyst regeneration
  - Test catalysts at pilot scale
  - Conduct 1,000 trial
  - Generate corrosion data & develop corrosion model
- Techno-economic Assessment and Lifecycle Modeling (PNNL)

Management Approach:

Decision points	Go/ No-Go
Hydrotreater operational	☑ ☐
Catalyst demo. lab scale	☑ ☐
Parameter selected 1000 hr run	☐ ☐
Catalyst regeneration demo.	☐ ☐
Successful 1,000 hr run	☐ ☐

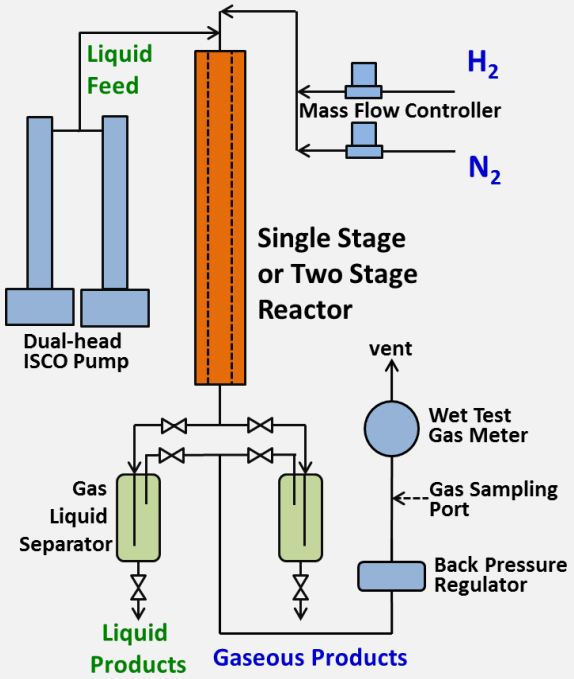
Progress Metric	Basis of Assumption
Demonstrate non carbon non sulfided catalyst	Need for catalyst regeneration
Demonstrate acceptable product quality	Necessary for commercialization
Demonstrate increased TOS	Necessary for commercialization
Demonstrate yield	Commercialization

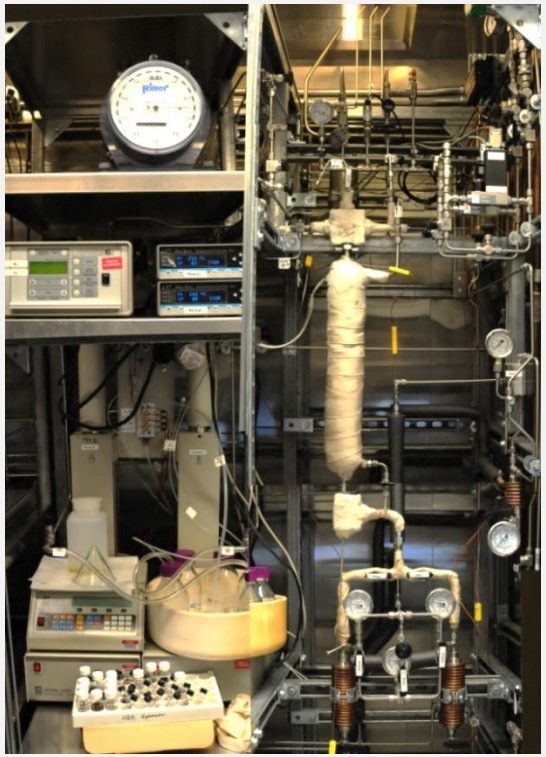
2 - Technical Accomplishments

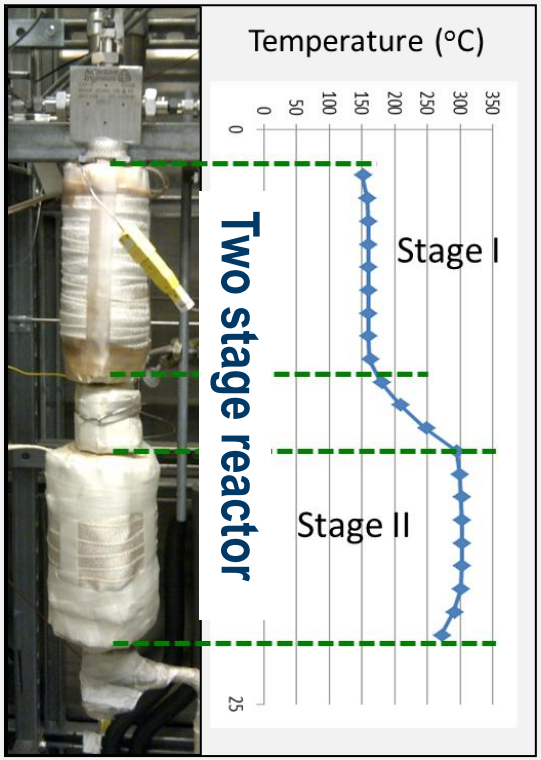


2 - Technical Accomplishments

Task C Accomplishment (1): Built a lab scale hydrotreater for rapid catalyst screening



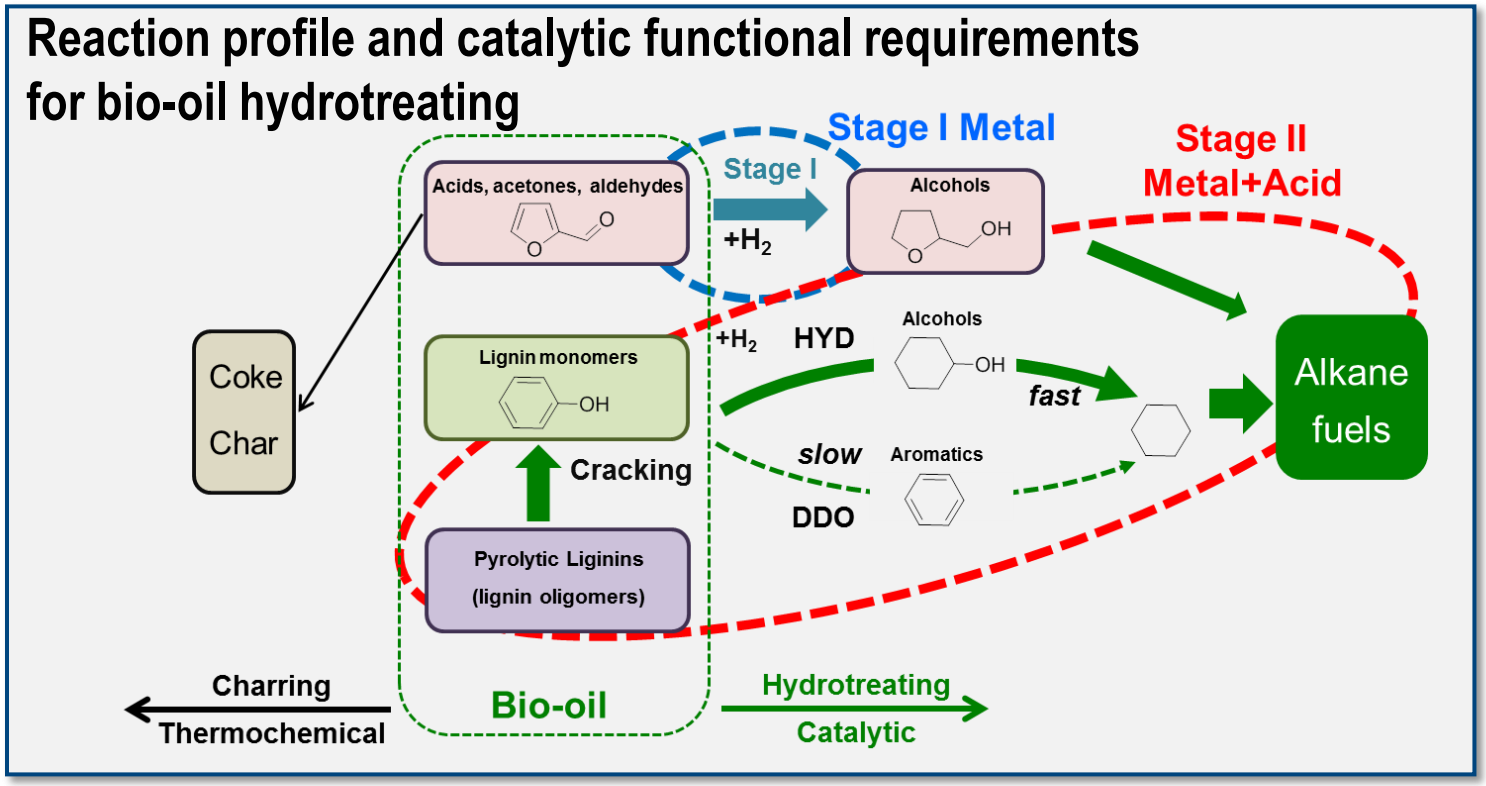




- 30 ml catalyst capacity, T<500 °C, P<15 MPa
- Fast catalyst screening
- One- or two-stage hydrotreating of bio-oil

2 - Technical Accomplishments

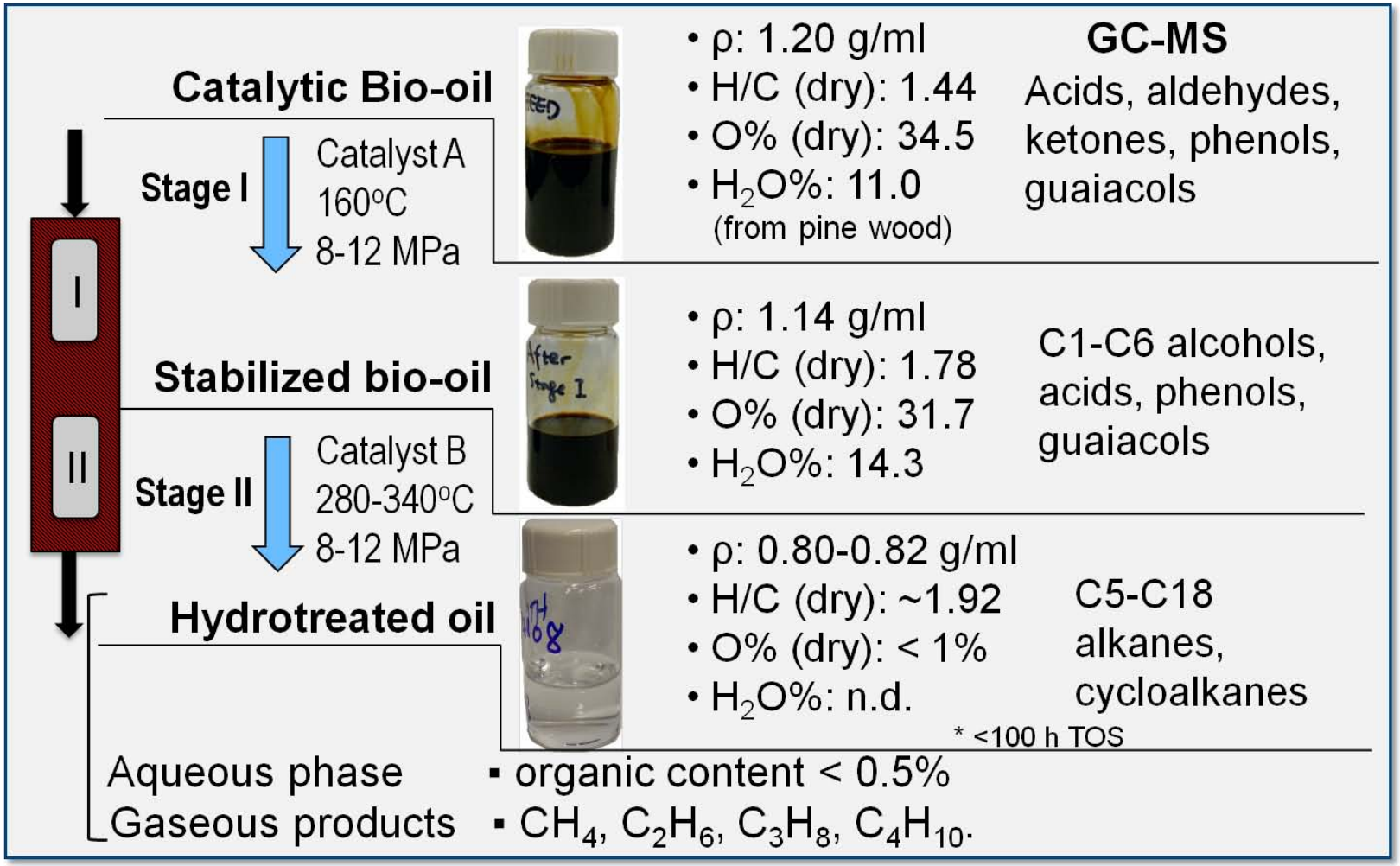
Task C Accomplishment (2): Identified novel non-carbon supported non-sulfide catalysts



- Supported metal with excellent hydrogenation activity as the first stage catalyst to stabilize bio-oil and thus inhibit thermochemical charring
- Bifunctional catalysts with a metal function and a solid acid function as the second stage catalyst for fast HDO and cracking.

2 - Technical Accomplishments

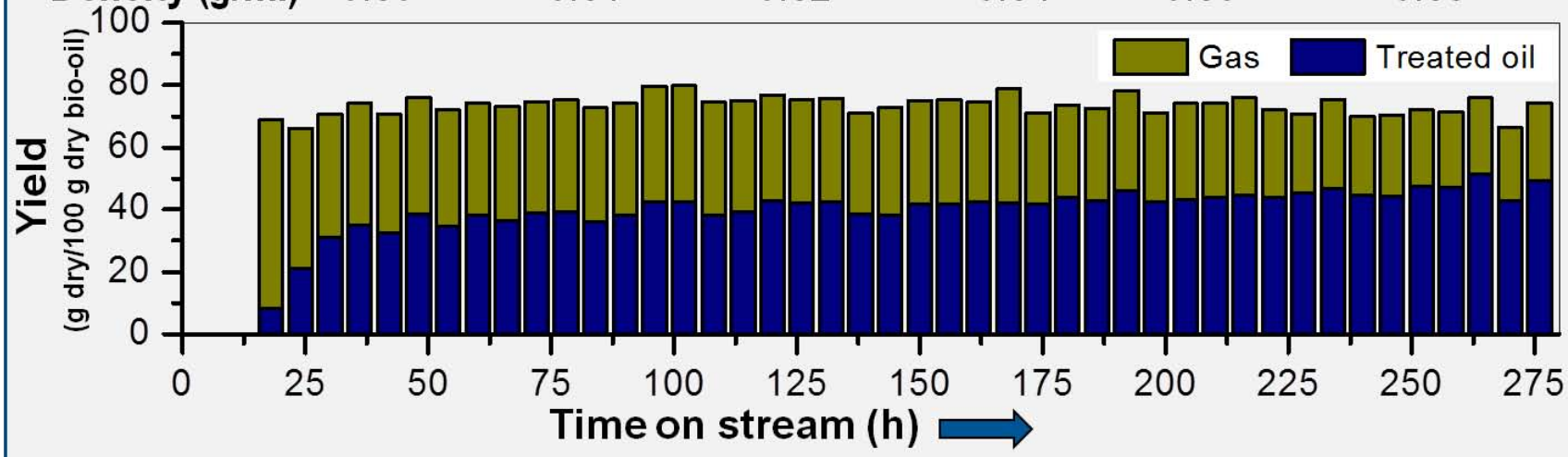
Task C Accomplishment (2): Developed novel non-carbon supported non-sulfide catalysts



2 - Technical Accomplishments

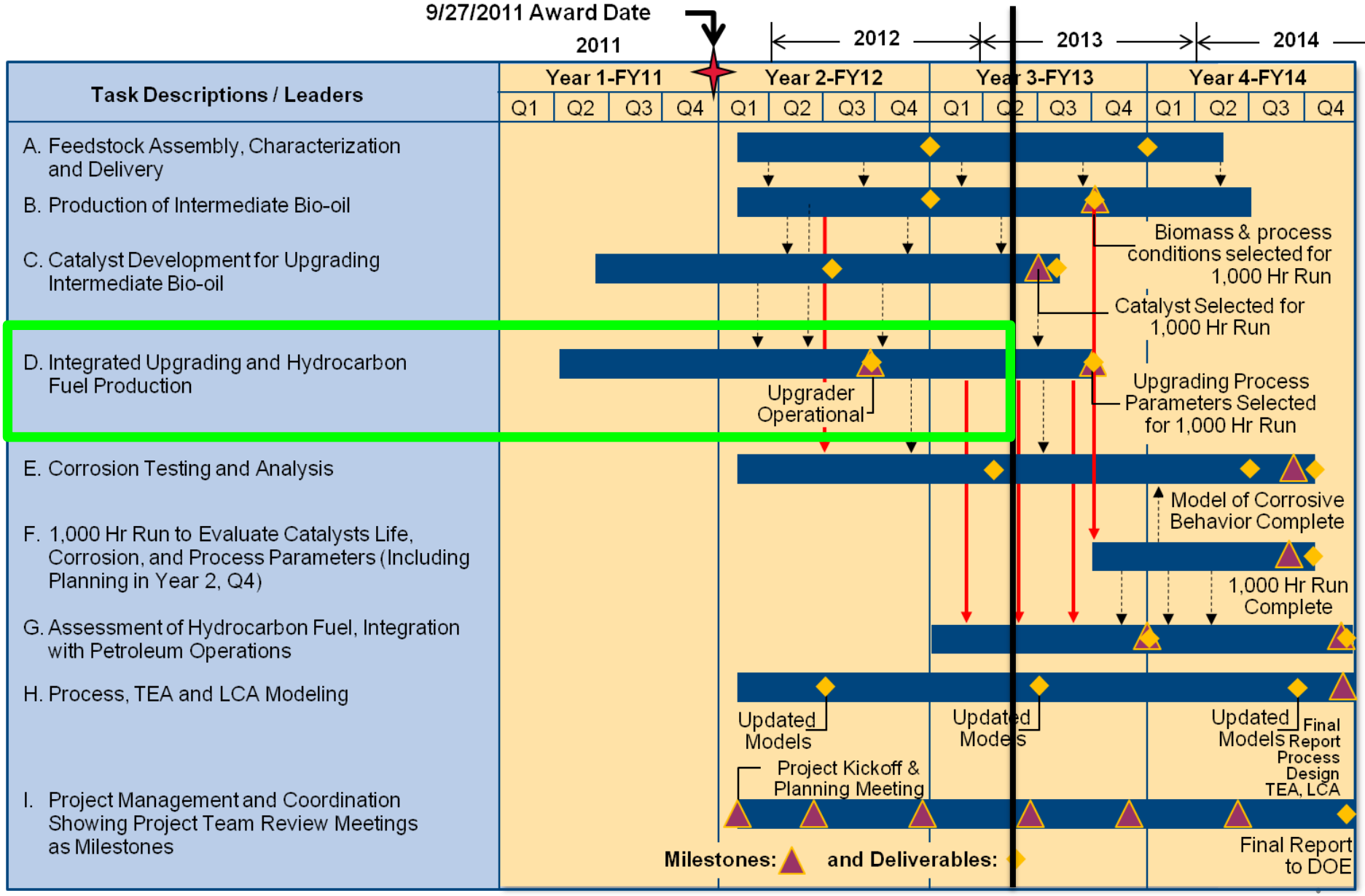
Task C Accomplishment (3): Completed 275 hour time on stream trial at lab scale

TOS (h)	42-54	90-102	138-150	192-204	240-252	264-276
O% (dry)	<0.5	0.56	0.56	0.71	1.27	1.52
H/C (dry)	1.95	1.93	1.95	1.86	1.82	1.84
Density (g/ml)	0.80	0.81	0.82	0.84	0.86	0.85



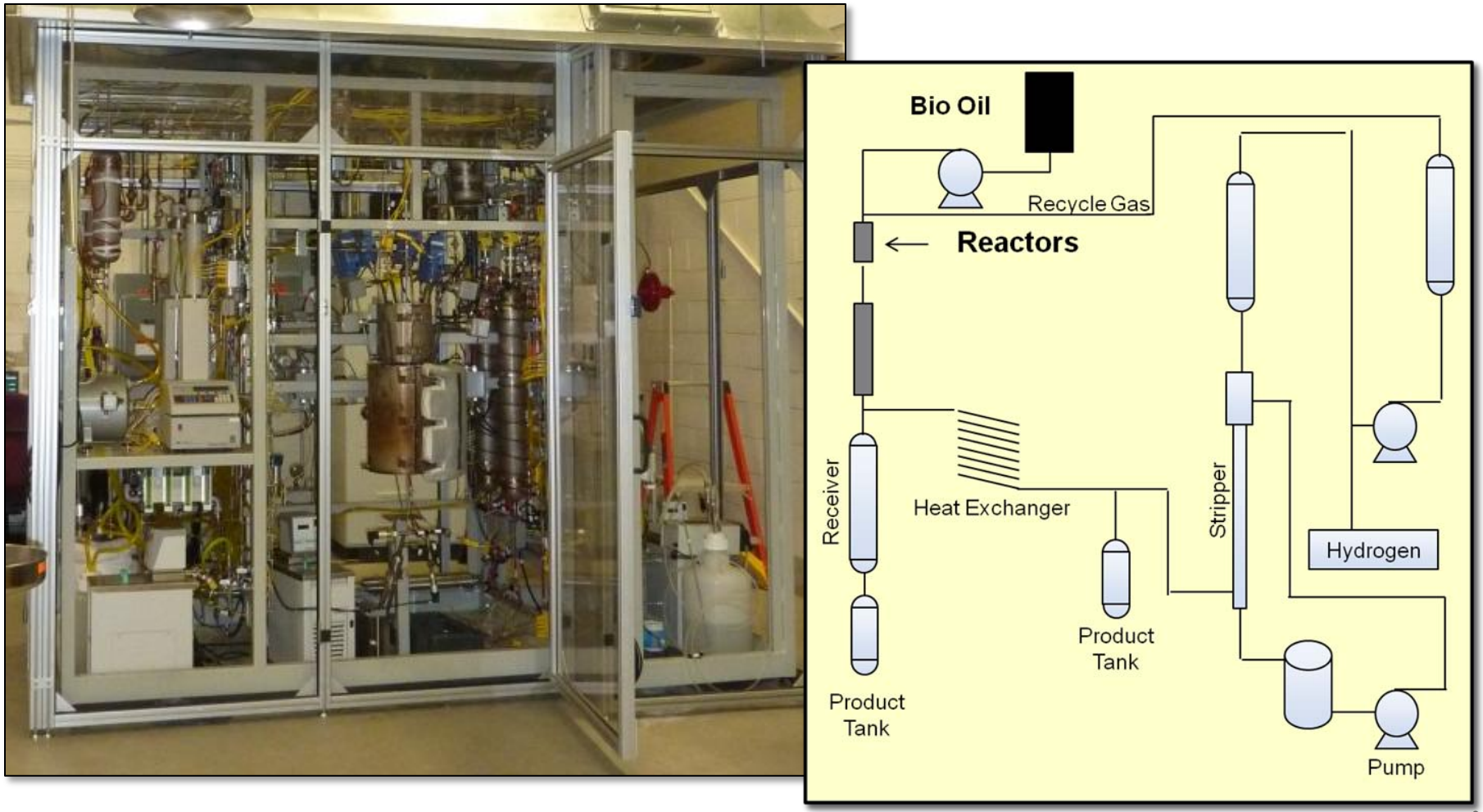
* Feed: non-catalytic bio-oil A; 12 MPa; Stage I: 160 °C, 0.16 LHSV; Stage II: 320 °C, 0.15 LHSV. No char formation.

2 - Technical Accomplishments



2 - Technical Accomplishments

Task D Accomplishment (1): Built & started up a pilot scale hydrotreater with regeneration & hydrogen recycle capabilities



2 - Technical Accomplishments

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Task D Accomplishment (2): Successfully operating the pilot hydrotreater and producing fuel product

Product Properties

- Product composition suitable for blending in gasoline, kerosene, diesel
- RON ~70
- Chain length ~ C6 to C14
- EPA certification process is being started

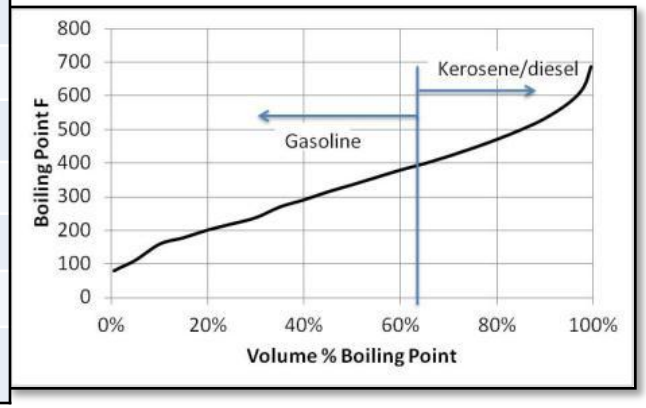
	Catalyst A	Catalyst B
	%Wt	%Wt
Paraffins	23.49	12.19
Total aromatic	12.08	0.17
Total Napththelenes	60.17	84.01
Olefins	3.03	3.30
Unidentified	1.23	0. 33
Total	100	100

Hydrocarbon Aqueous

- Density: 0.79 g/ml
- Less than 1% water by KF
- Hydroxyl value: 0 (NMR)
- Acidity: 0 (NMR)

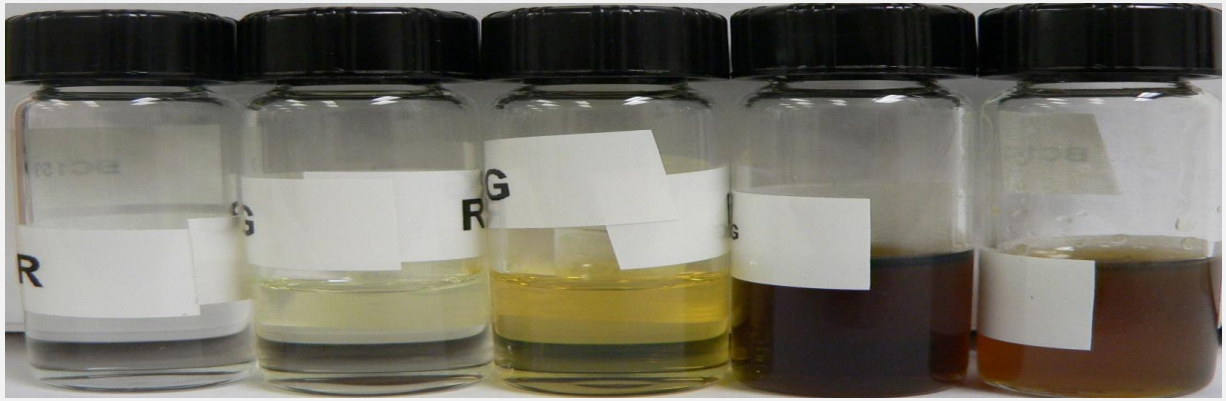
- 0.98 g/ml
- 100% water by KF

	Refinery example	Battelle Results
Density (kg/m^3)	0.8-0.9	0.81-0.9
BSW (wt%)	0.5	NA (<0.5)
Total S (wt%)	0.082	<0.005
Total N_2 (wt%)	0.001-0.015	<0.05
TAN (mg KOH/g)	0.5	<0.5
Pour Point (^{o}C)	21-36	NA(<<20)
Viscosity (cPs)	3-236	NA(1?)

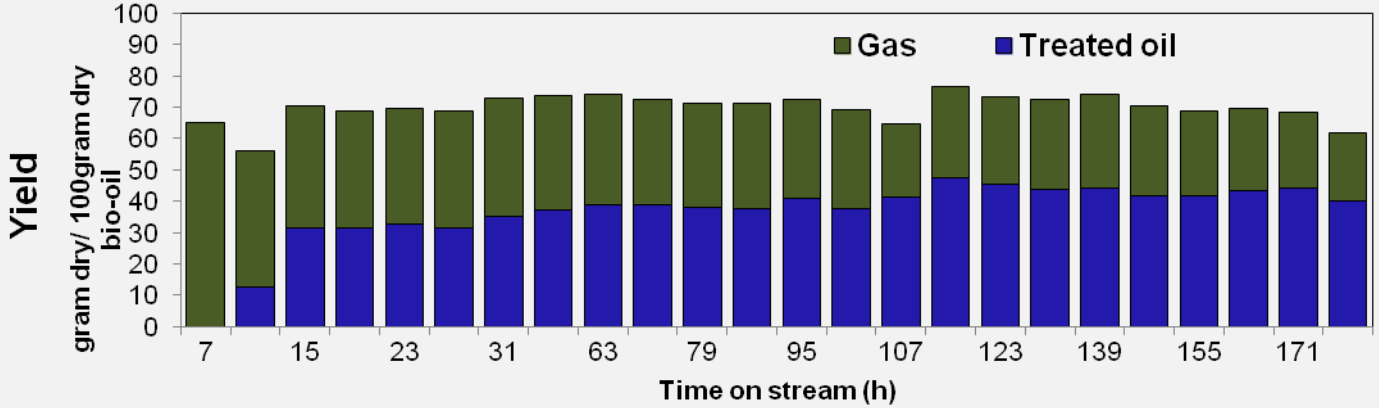


2 - Technical Accomplishments

Task D Accomplishment (3): Scaled up new catalysts by 10x to pilot scale hydrotreater

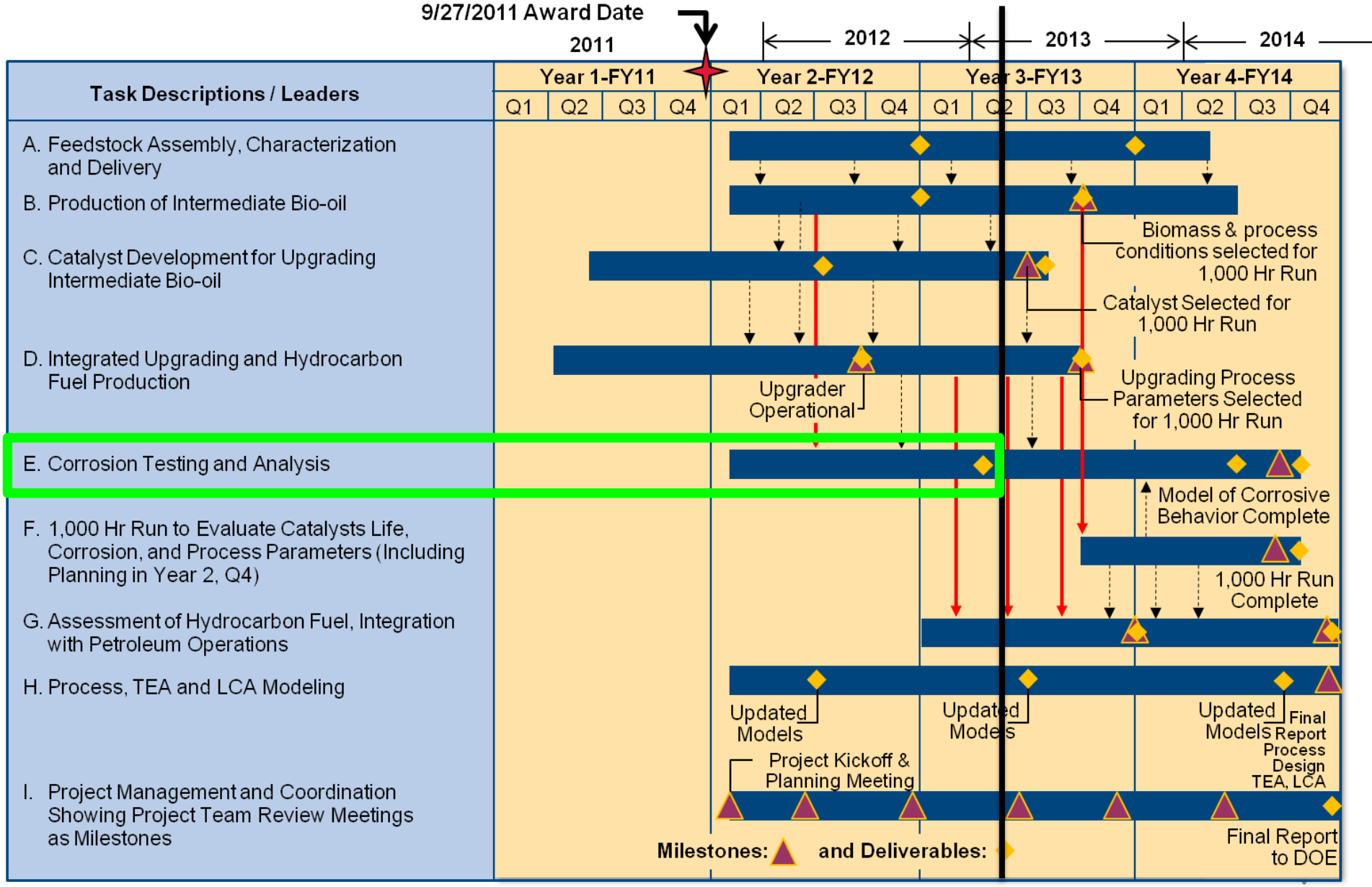


TOS (hrs)	24-32	80-88	148-156	180-188	194-200
Density g/cm^3	0.822	0.841	0.853	0.876	0.897



Feed: catalytic bio-oil, 12 MPa, Stage 1: 150°C, Stage 2 320°C(<110hr) and 340oC(>110h)

2 - Technical Accomplishments



2 - Technical Accomplishments

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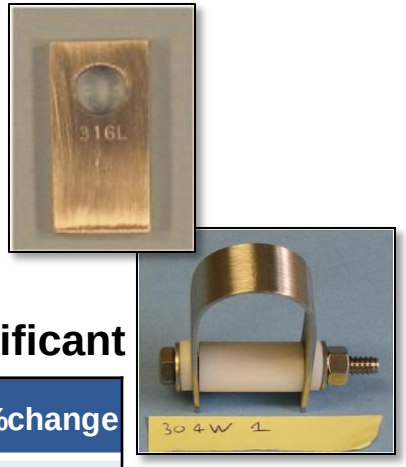
Task E Accomplishment (1):

- Completed low temperature SSC and general corrosion trials.
- High temperature testing started.

Low Temperature Tests showed no significant corrosion:

- Materials: 304L, 316L, 904L, 444, and 2205.
- Samples: U bends (with welds & coupons.
- Exposure time: 1,000 hrs
- Temperature: 50°C

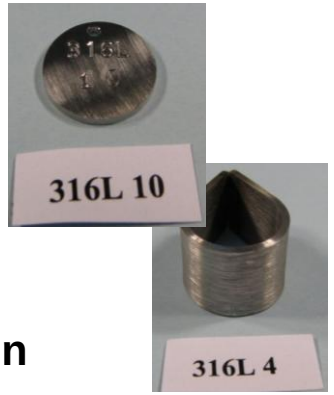


Change in Mass in Not Significant

Alloy	Initial Mass(g)	Final mass (g)	%change
304L	20.713	20.713	.00088
316L	6.3630	6.3635	.00788
904L	4.2992	4.2997	.01144
444	8.0690	8.0690	-0.0001
2205	8.3365	8.3368	0.00352

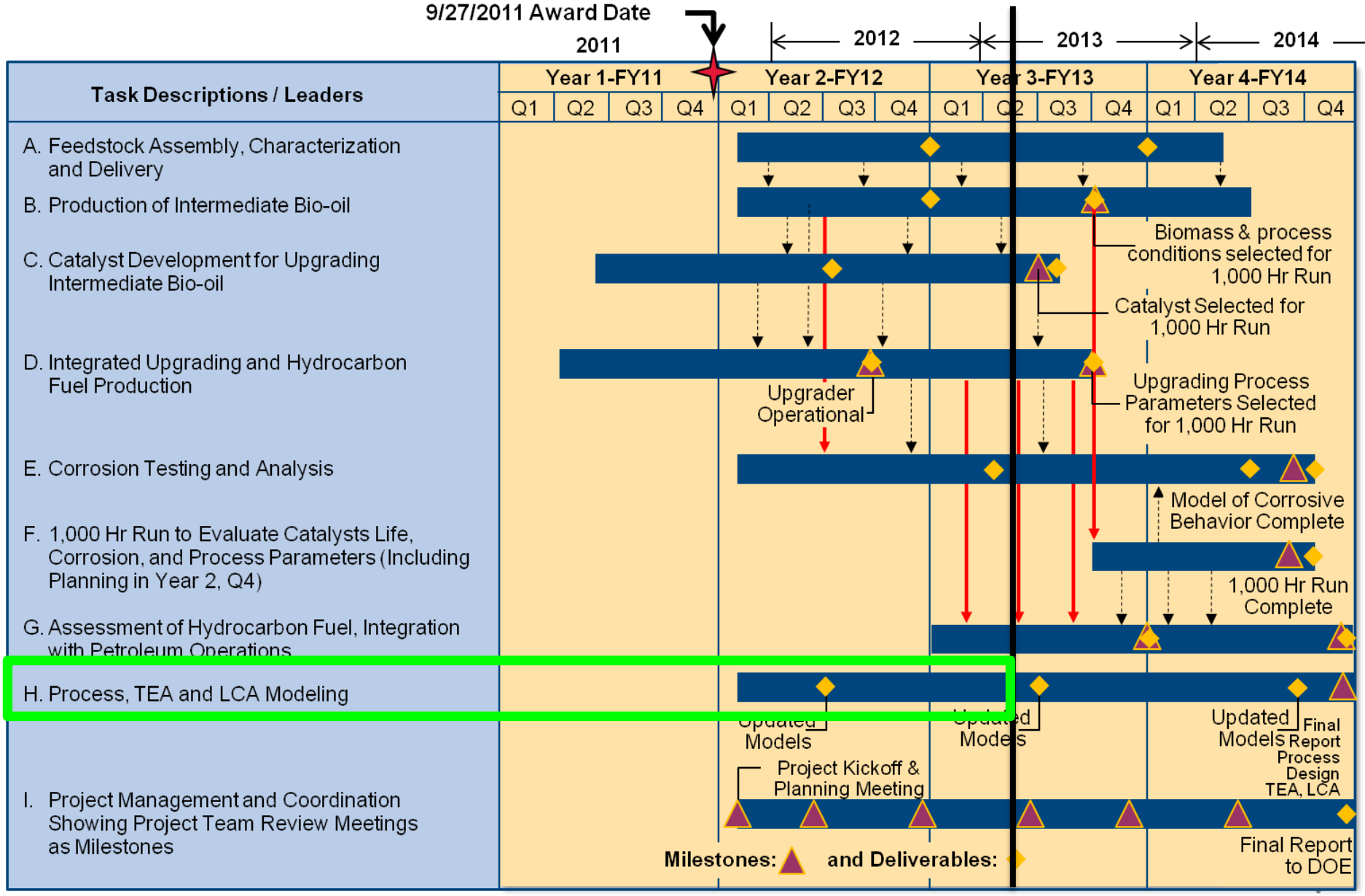
High Temperature Tests Have Been Started

Test stand being used in high temperature autoclave tests



Sample coupons for hot tests

2 - Technical Accomplishments

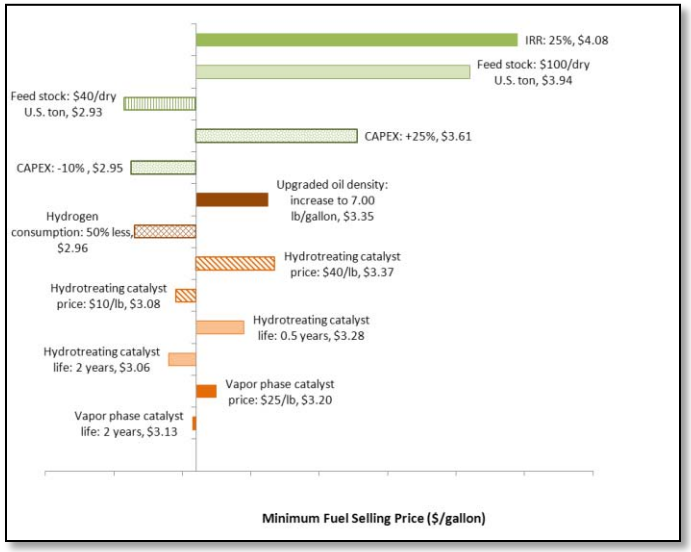


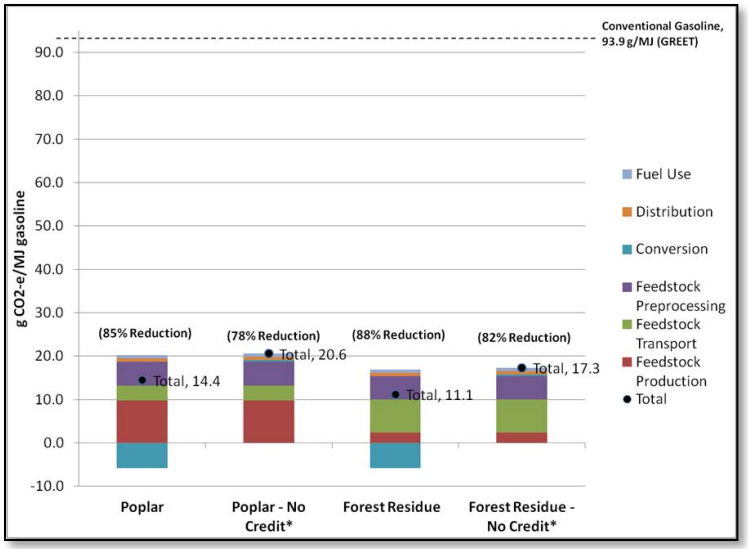
2 - Technical Accomplishments

Task H Accomplishment (1):

- Completed preliminary models March 2012
- Completed updated model using hydrotreatment data March 2013

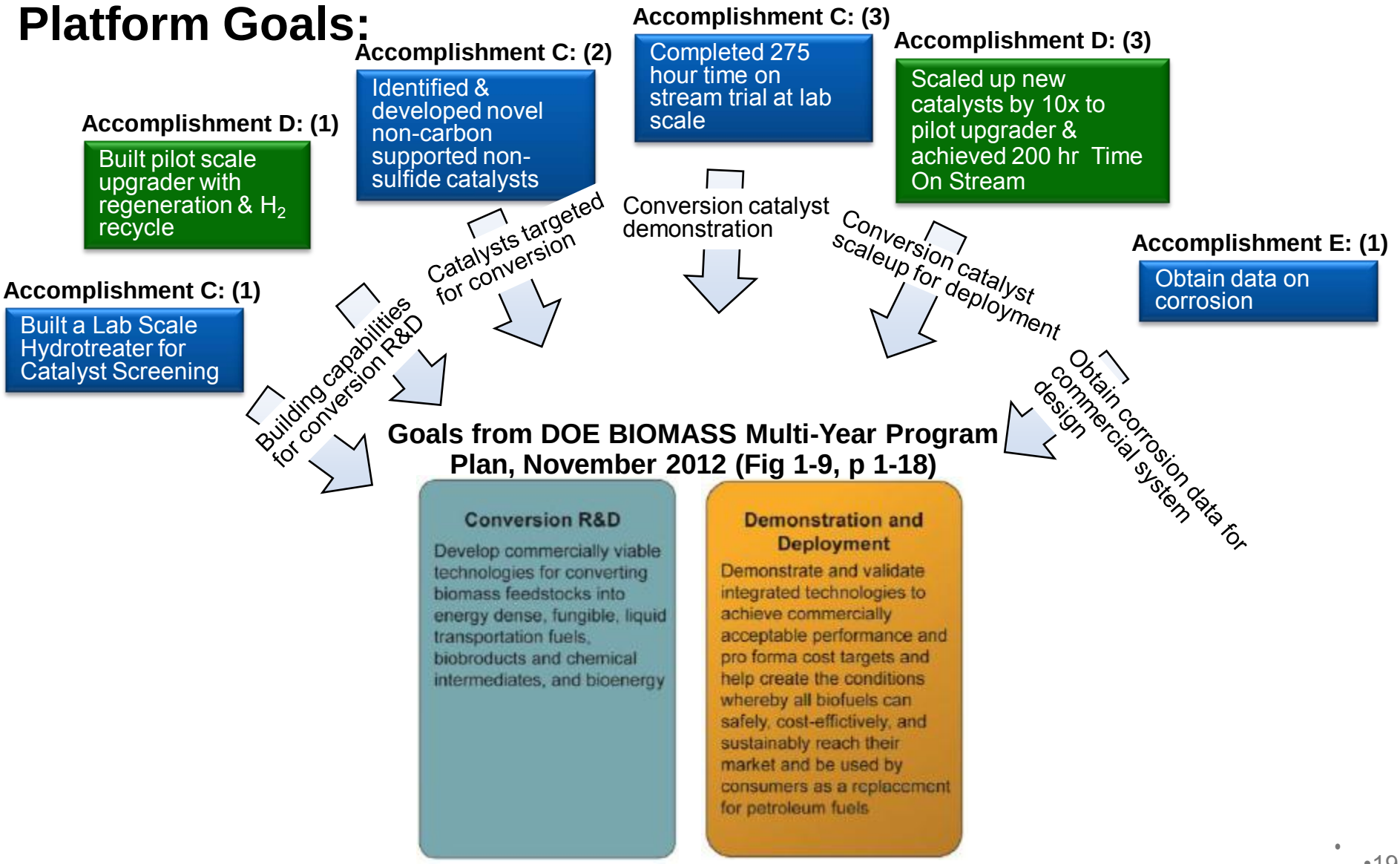
- TEA results essentially unchanged
- LCA results estimated GHG reductions still appear to be well within range of cellulosic biofuels





3 - Relevance

How the Project Accomplishments Contribute to Platform Goals:



3 - Relevance

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Applications of the Project Outputs:

- Battelle is developing small scale (~100 tons/day) biofuels systems based the ex-situ catalytic pyrolysis & hydrotreatment pathway.
- Distributed deployment of a large number of these systems will contribute toward meeting goals & objectives of the Biomass Program
- The technology is expected to be spun off into a separate company FY 2013
- Hydrotreatment catalysts developed under this project will be licensed to the spin-off.

4 - Critical Success Factors

- Critical success factors
  - Technical: Catalysts need to be able to be regenerated , and need to sustain low coking rates and high space velocities.
  - Market: Product quality has to comply with ASTM gasoline fuel standards to be sold as a blendable fuel
  - Business: Capital and operating costs need to be low enough to generate an acceptable IRR at market fuel prices and biomass costs.
- Potential challenges

Technical

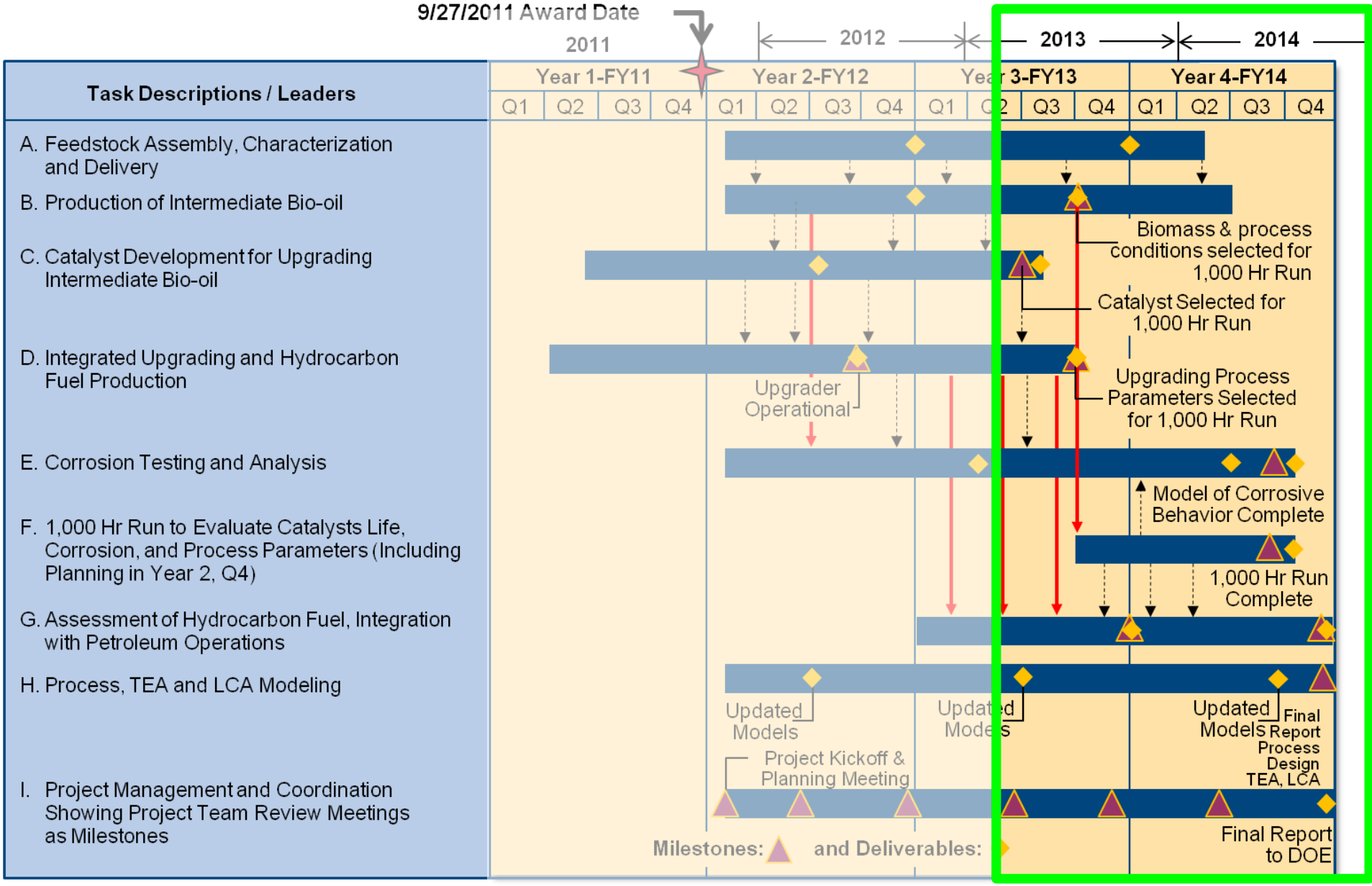
1. Demonstration of 1,000 hours time on stream catalyst life
2. Demonstration of repeated catalyst regeneration to allow extended system operation

Non-Technical

1. Catalyst manufacture at commercially acceptable costs
2. Scale-down of hydrotreater at acceptable capital costs

- Upon successful execution of this project
  - A new generation of hydrotreatment catalysts will be available for catalytic pyrolysis bio oil hydrotreatment.
  - Small scale distributed production of blendable biofuels will be enabled.

5. Future Work



Summary

We are making good progress; our project is on schedule, on budget, aligned with the MYPP goals, and relevant to the bioenergy industry:

- **Relevance**
  - Project is aligned with the MYPP goals and is relevant to the bioenergy industry because it will enable production of biofuels by small systems which will have the same capital effectiveness as that of large systems.
- **Approach**
  - Using an ex situ catalytic pyrolysis process with new non carbon based, non sulfided hydrotreatment catalysts which will be able to be regenerated multiple times to allow long term operation.
- **Technical accomplishments**
  - Demonstrated catalyst performance at the lab scale and pilot scale for 275 hrs and 200 hrs time on stream respectively.
- **Future work**
  - Preparing for and conducting an extended 1,000 hour trial, continue high temperature corrosion tests, conduct TEA, LCA.
- **Success factors and challenges**
  - Ability to regenerate catalyst, achieve long term operation with lower coke production rates.
- **Technology transfer**
  - Planning to license the technology to a spin off company.

Additional Slides

Responses to Previous Reviewers' Comments

- If yours is an on-going project that was reviewed previously, address 1-3 significant questions/criticisms from the previous reviewers' comments (refer to the 2011 reviewer comments if needed)

Note: This slide is for the use of the Peer Reviewers only – it is not to be presented as part of your oral presentation. These Additional Slides will be included in the copy of your presentation that will be made available to the Reviewers.

(Not a template slide – for information purposes only)

- The following slides are to be included in your submission for Peer Evaluation purposes, but will **not** be part of your oral presentation
- You may refer to them during the Q&A period if they are helpful to you in explaining certain points

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Publications and Presentations

- List any publications and presentations that have resulted from work on this project. Use at least 12 point font.

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