2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

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

Direct Liquefaction Aqueous Phase Utilization: Characterization, Upgrading, and Steam Reforming

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Technology Area Review: Bio-Oil Technology

Organization: PNNL
PNNL-SA-95131

Goal Statement

- GOAL: Increase carbon yield to liquid fuels and diminish hydrogen upgrading requirements by utilizing the organics in the aqueous phase produced from a variety of direct liquefaction approaches (e.g. fast pyrolysis, catalytic fast pyrolysis, hydrothermal liquefaction)

Project Quad Chart Overview

Timeline

3 Projects (3.2.2.34, 3.2.2.30, 3.2.2.33)

- Start: October 2012
- End: September 2015
- 17% complete

Barriers

Barriers addressed

- *Tt-E. Pyrolysis of Biomass and Bio-Oil Stabilization*

Budget

- Total project funding
  - $2.4M/yr
- Funding in FY 2011: $0
- Funding in FY 2012: $0
- Funding for FY 2013
  - Characterization $700K
  - Upgrading $1000K
  - Reforming $700K

Partners & Roles

- PNNL

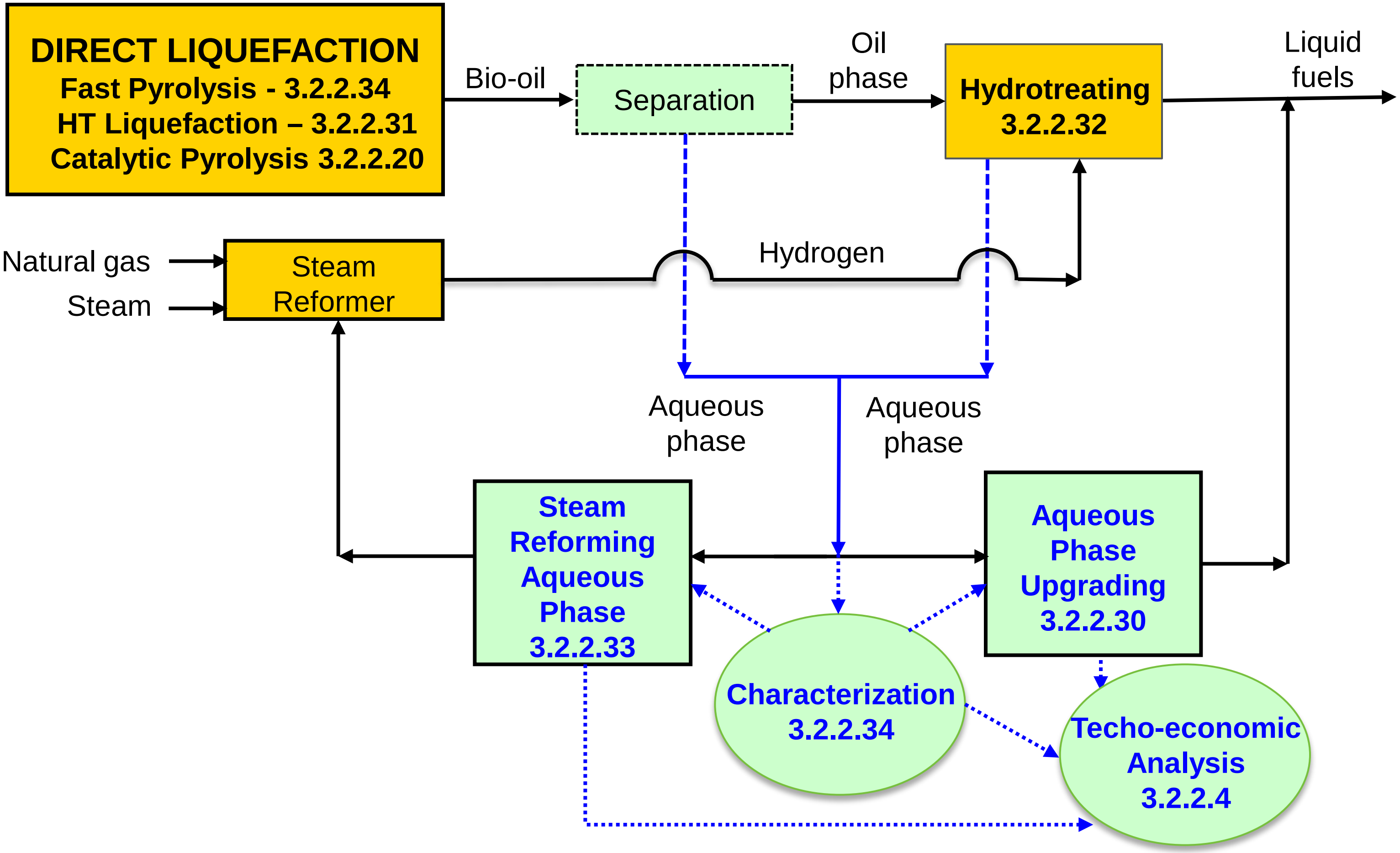
Project Overview

- Characterization and Treatment of Aqueous Products from Direct Liquefaction Processes (3.2.2.34)
  - Characterize multiple direct liquefaction aqueous phase streams
  - Produce and evaluate the effect of process conditions on fast pyrolysis bio-oil product composition/phase separation
- Conversion of Direct Liquefaction Process Aqueous Phase Organic Products into Liquid HC fuels (3.2.2.30)
  - Catalytically upgrade aqueous oxygenates to fuel range hydrocarbons
  - Identify any aqueous stream processes required for successful operation
- Steam Reforming of Aqueous Fraction from Bio-oil to produce H_2 (3.2.2.33)
  - Develop catalysts and process for reforming aqueous phase organics in order to provide supplemental H_2 required for hydrotreating bio-oils
- Technical Barrier: - Tt-E. *Pyrolysis of Biomass and Bio-Oil Stabilization*

Project Overview

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

Conceptual Block Flow Diagram



- Multiple sources of aqueous phase streams containing organics
- Two alternatives for utilizing aqueous stream organics

1 – Approach: 3.2.2.34 Characterization of Aqueous Products

- Overall Technical Approach
  - Characterization
    - Develop a suite of characterization methods relevant for all aqueous streams
    - Analyze both legacy PNNL samples and newly produced samples
  - Modification of PNNL bench scale gasifier to a high-temperature pyrolyzer
    - Investigate the effect of higher temperatures and different quench methods on fast pyrolysis bio-oil and aqueous streams
    - Investigate the effect of different quench methods on the recovered products
- Technical metrics for measuring progress
  - Fraction of total organic carbon identified and quantified in aqueous streams
  - Successful and regular operation of the high-temperature pyrolyzer
- Management Approach – Approved Project Management Plan
  - Regular Milestones (1/Quarter) and Deliverables (Annual Reports)
  - Go/No Go in Q2FY14 to asses the functionality of the high temperature fast-pyrolysis system

1 – Approach: 3.2.2.30
Aqueous Organics to Hydrocarbon Fuels

- Overall Technical Approach
  - Lab scale fixed-bed continuous flow reactor testing
  - Model compounds/synthetic mixtures and real feeds
  - Parametric studies
  - Evaluation of catalyst deactivation trends
- Technical metrics for measuring progress
  - Carbon conversion/yield to liquid fuel-range hydrocarbons
  - Catalyst lifetime/regeneration frequency
- Management Approach – Approved Project Management Plan
  - Regular milestones (1/Quarter) and deliverables (Annual Reports)
  - Go/No Go in Q2FY14 to asses the merit for further development of a catalytic process for one or more of the aqueous process feedstocks

1 – Approach 3.2.2.33
Steam Reforming of Aqueous Phase

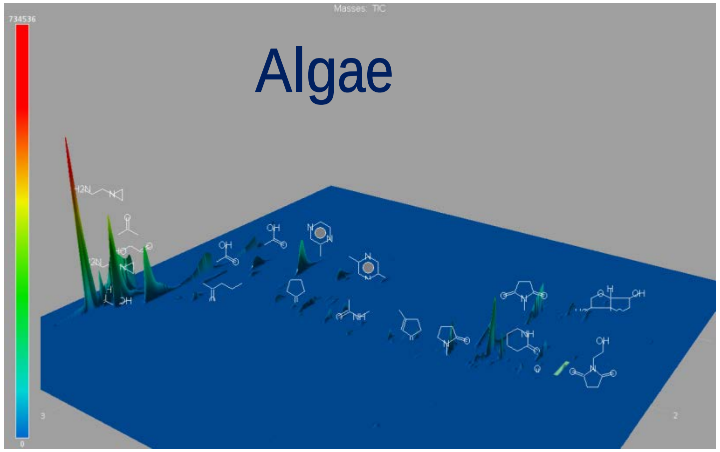
- Overall Technical Approach
  - Lab scale continuous flow reactor for catalyst and process development
  - Conventional versus novel steam reforming catalysts
  - Parametric studies (e.g. temperature, steam:carbon ratio)
  - Techno-enonomic analysis
- Technical metrics for measuring progress
  - Carbon conversion, and H_2 yield
  - Catalyst lifetime/regeneration frequency
- Management Approach
  - Quarterly milestones aimed at evaluating process and catalyst performance and techno-economics
  - Go/No Go in Q3FY14 project based on experimental and techno-economic findings

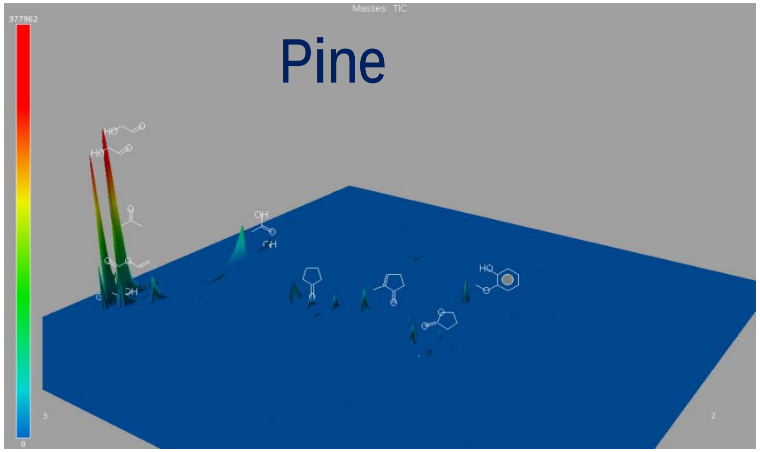
2- Technical Progress Roadmap

- 3.2.2.34 – Characterization
- 3.2.2.30 – Upgrading
- 3.2.2.32 – Reforming

2 – Technical Progress: Characterization

- 2D GCxGC TOF-SIMS and LC-MS used to identify major compounds present in legacy aqueous phases from Hydrothermal Liquefaction (HTL) and Fast Pyrolysis (FP)
- Commercial calibration standards ordered for quantification of identified major species via GC-FID and HPLC
- ICP-AES and IC used to quantify inorganic concentrations
  - >200ppm halogens observed
- Over 200 individual compounds identified, most minor





2 – Technical Progress: Characterization

- In HTL Aqueous phase for lignocellulosics (1-2 wt% TOC), 20 major compounds identified via GC and LC (140%-170% of all area counts)
  - Account for 55%-85% of total GC-MS area count
  - Account for 85% of total LC area count
- Algae results in highly nitrogenated compounds (not shown here)
- In FP Water Extracted Aqueous phase (1-2.5 wt% TOC), 20 major compounds identified via GC and LC (72% - 99% of total area counts)
  - Account for 50% – 67% of total GC-MS area count
  - Account for 22% - 32% of total LC area count
- Fraction of carbon identified currently between 40%-90% based on TOC

Major Compounds Seen in HTL Aqueous Phase		
1,3-butanediol	Acetol	Glycolic acid
Methanol	Cyclopentanone	Acetic Acid
1,2-butanediol	Hydroxy butanone	Ethylene Glycol
Butanoic Acid	2-butanone	Propylene Glycol
Acetone	Ethanol	
1-propanol	Phenol	
Ethyl Acetate	Methyl Acetate	
1-butanol	Propanoic Acid	

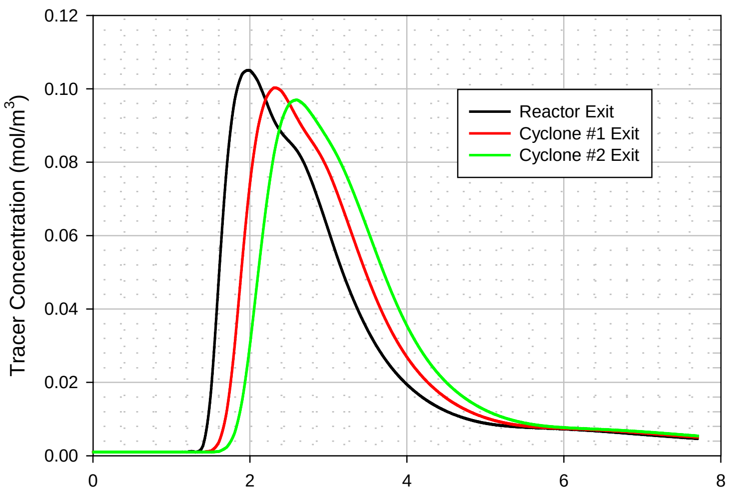
Major Compounds Seen in FP Aqueous Phase		
Formic acid	Acetaldehyde, hydroxy-	Acetic Acid
Glycolic acid	Acetone, hydroxy-	Acetone
Ethylene Glycol	2-Propanone, 1-hydroxy-	
Propylene Glycol	Methylglyoxal	
Acetaldehyde	Ethanedial	
2-Butanol	Acetic acid, hydroxy-	
2-methyl-1-propanol	2(5H)-Furanone	
1-butanol	Ethanol	
Phenol	glyoxal and polymers	

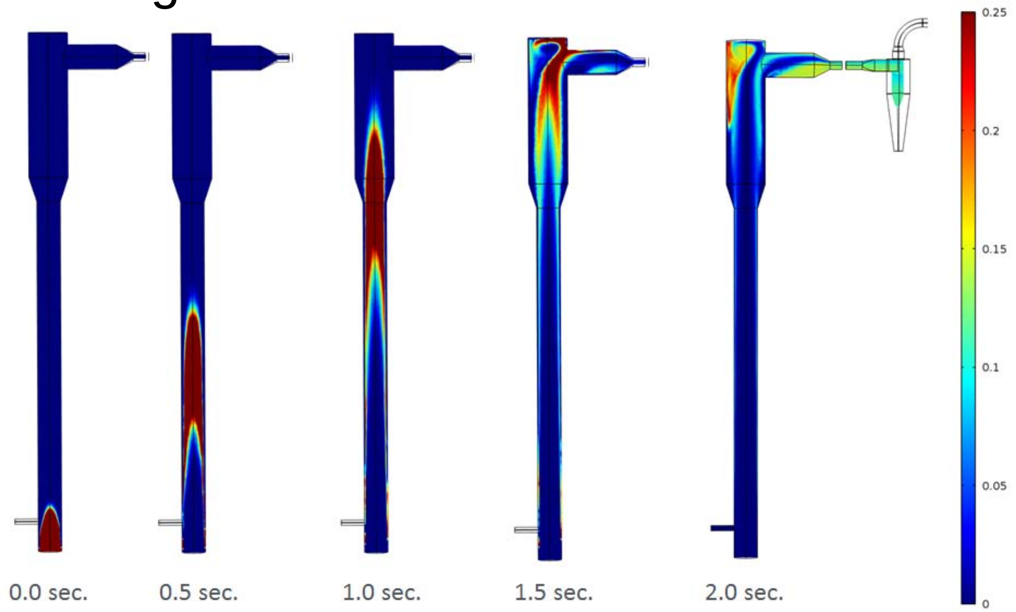
2 – Technical Progress: Characterization

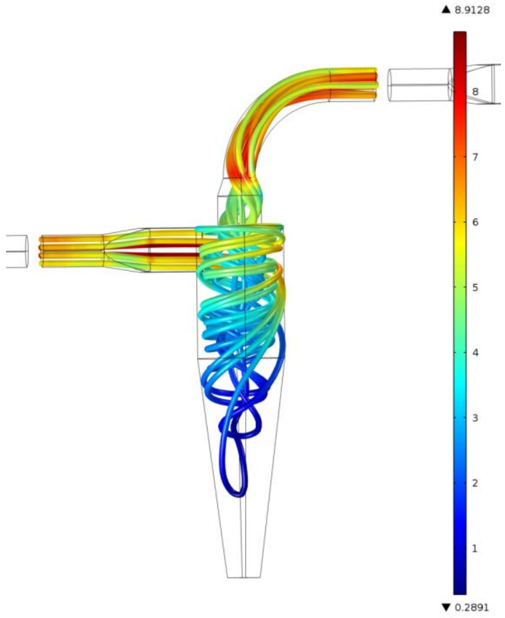
- Gasifier system operated as pyrolyzer in Q1 to serve as benchmark for upgrades
- Existing water spray quench recovery system and solid filters utilized
  - Consistent temperature and pressure profiles
  - >20% of solids passed through existing 20µm filter, needs to be <5%
  - <15% oil recovery efficiency, based on GC analysis of product slipstream and aqueous condensate
    - Large quantities of aerosols observed in demister and outlet gas
- Outcomes
  - Reactor section capable of functioning in fast pyrolysis mode
  - Filters must be replaced with cyclone separators to achieve >95% recovery
  - Single nozzle water quench system highly ineffective in current configuration, should be replaced with organic quench

2 – Technical Progress: Characterization

- Redesign based on COMSOL model used to evaluate potential reactor parameters needed to achieve a nominal residence time = 2s
- Cyclone design parameters based on model
- Parts and equipment specified and on order or being machined

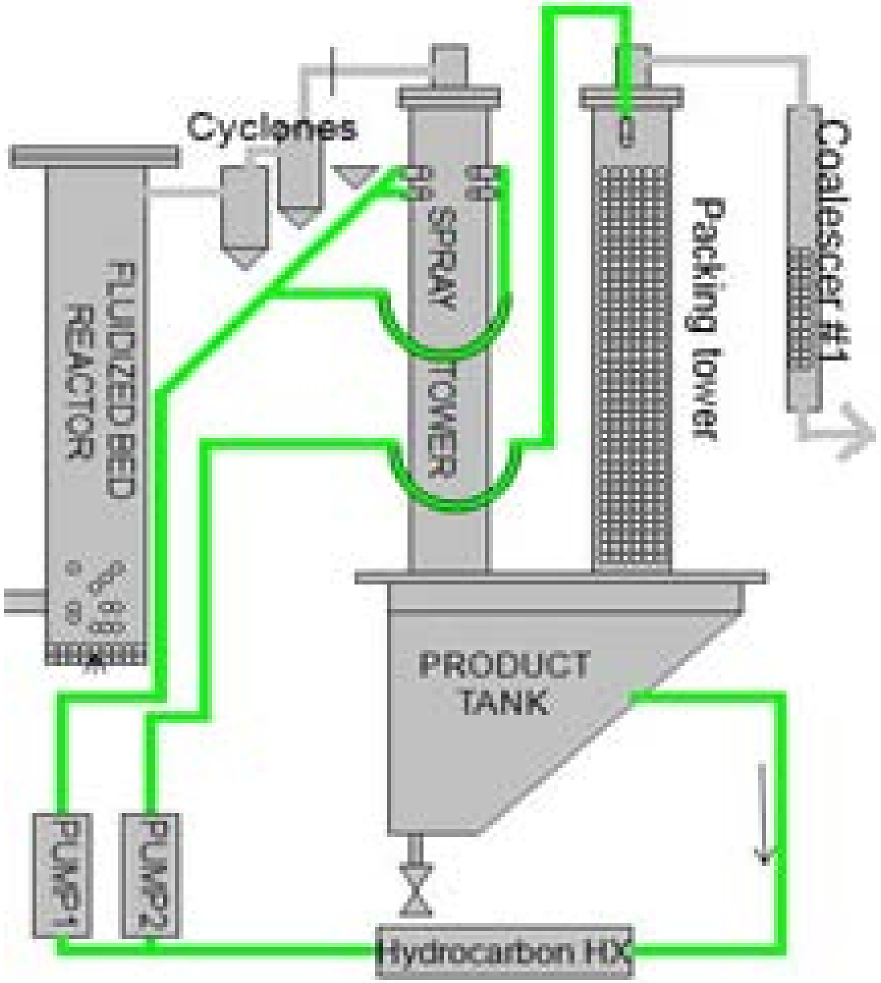






2 – Technical Progress: Characterization

- Organic quench system designed improves upon current PNNL Core Pyrolysis quench system
  - Packing in spray tower
  - Multiple sets of spray nozzles in spray tower
  - Improved packing in demister/coalescer
  - Expected increase in oil capture efficiency



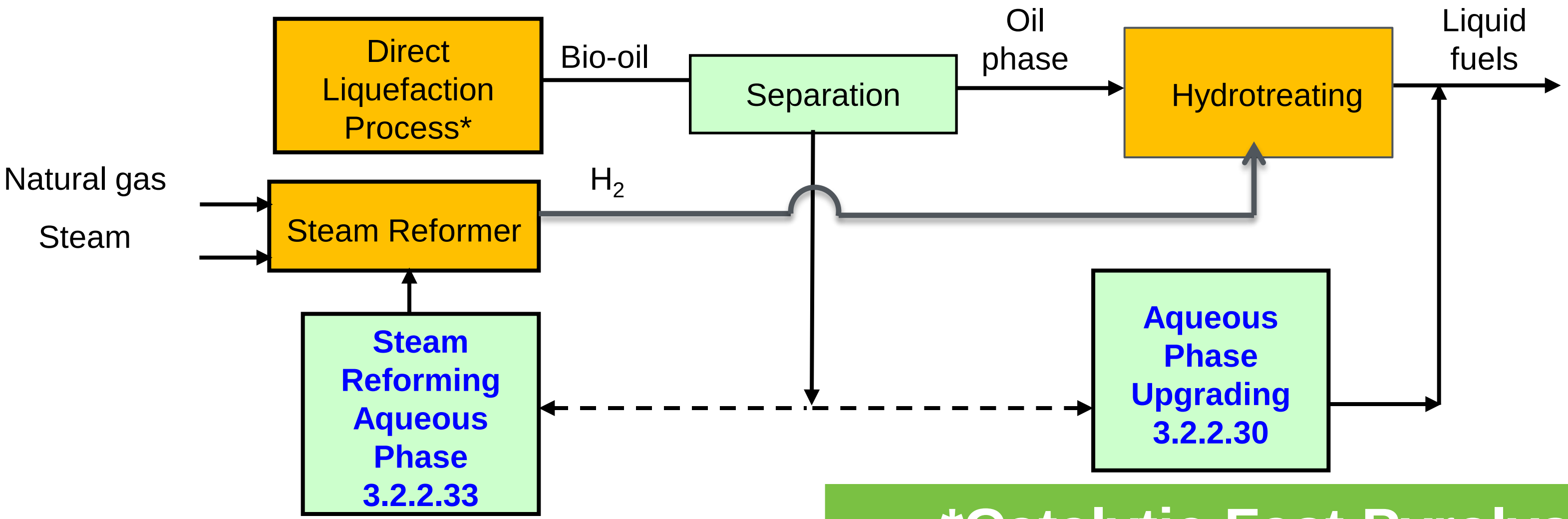
2 – Technical Progress: 3.2.2.34 Characterization

Milestone	Planned Completion Date	Completion
Complete test using current reactor configuration	31 Dec, 2012	✓
Complete reactor and quench system redesign	31 Jan, 2013	✓
Complete characterization method development	31 March, 2013	✓
Complete construction and modification of FP system	31 May, 2013	50%
Complete 2 FP tests using new system	30 Sept, 2013	On schedule

2- Technical Progress Roadmap

- 3.2.2.34 - Characterization
- 3.2.2.30 – Upgrading
- 3.2.2.32 – Reforming

2- Technical Progress: Streams and Constituents



Direct Liquefaction Process*

Bio-oil

Separation

Oil phase

Hydrotreating

Liquid fuels

Natural gas

Steam

Steam Reformer

H_2

Steam Reforming Aqueous Phase 3.2.2.33

Aqueous Phase Upgrading 3.2.2.30

***Hydrothermal Liquefaction** **40-50% Total Carbon Fed** **~5wt % Organics in H_2O**
Methanol
Acetic Acid
Glycolic Acid

*Information leveraging streams from other PNNL projects

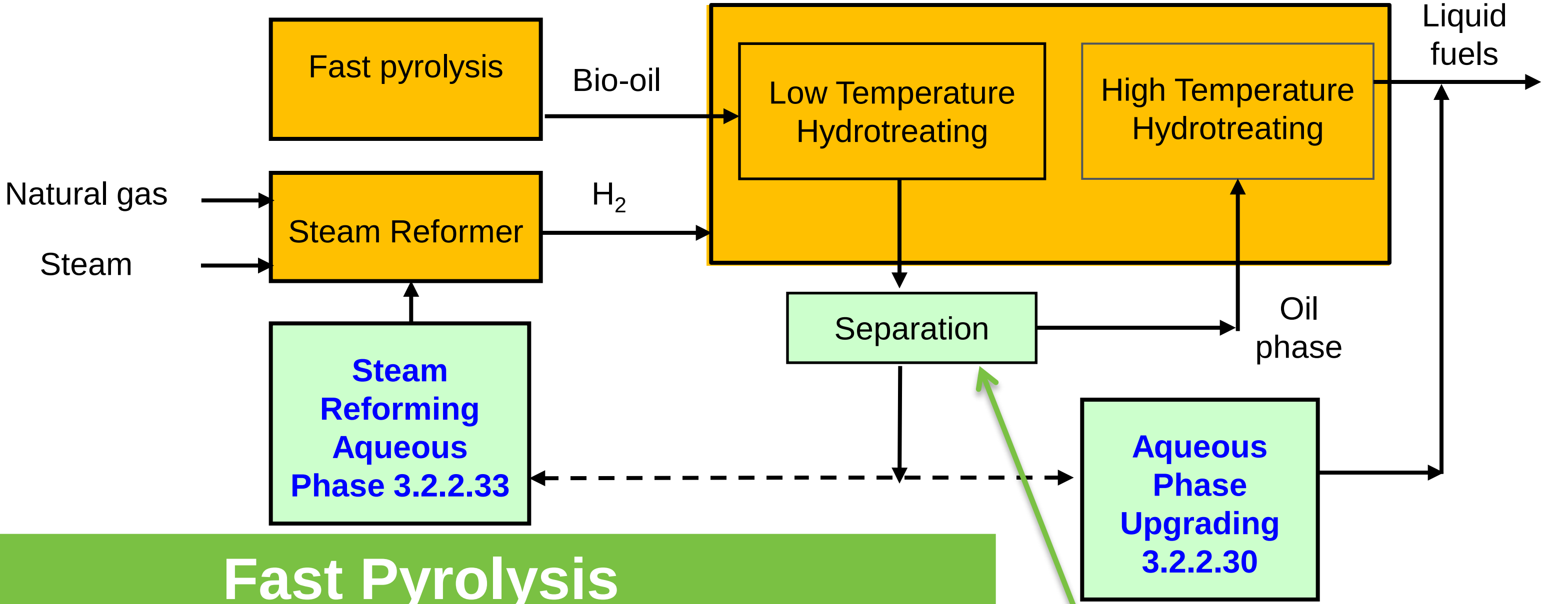
***Catalytic Fast Pyrolysis**

5-10% Total Carbon Fed

~30 wt% Organics in H_2O

Major Compounds	**Minor Compounds**
Acetic Acid	5-methoxyfurfural
Hydroxyacetone	Phenol
Acetaldehyde	Guaiacol

2- Technical Progress: Streams and Constituents



Fast Pyrolysis

5-10% Total Carbon Fed

~45 wt% Organics in H_2O

Major Compounds[1]	**Minor Compounds**[1]
Acetic Acid	Formic Acid
Ethylene Glycol	1,4-butandiol
Propylene Glycol	Tetrahydrofurfuryl Alcohol
Phenol	γ-Butyrolactone

Separating the aqueous phase during upgrading may diminish H_2 requirements

[1] Vispute et al. **2009** Green Chem 11 1433-1455

2 – Technical Progress: Aqueous Organics to Hydrocarbon Fuels

Reactor system construction complete

Currently generating baseline data while refining reactor operation and analytical methods

Compounds and mixtures tested

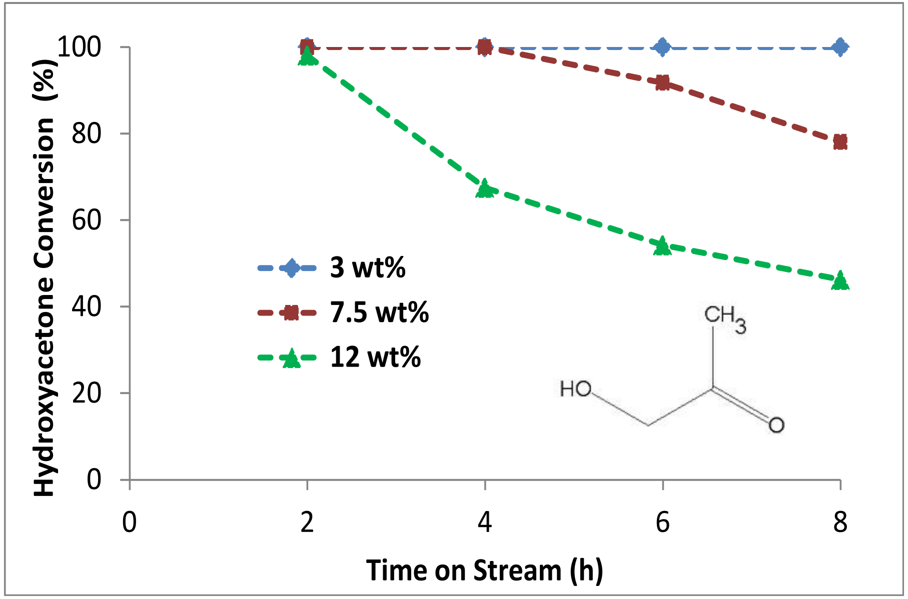
Catalytic Fast Pyrolysis	
Acetic Acid	
Hydroxyacetone	
Hydrothermal Liquefaction*	
Methanol	
Glycolic Acid	
Acetic Acid	
Low Temperature Hydrotreated Fast Pyrolysis	
Ethylene Glycol	Acetic Acid
Propylene Glycol	Tetrahydrofurfuryl Alcohol
Phenol	1,4-Butandiol
γ–Butyrolactone	Sorbitol

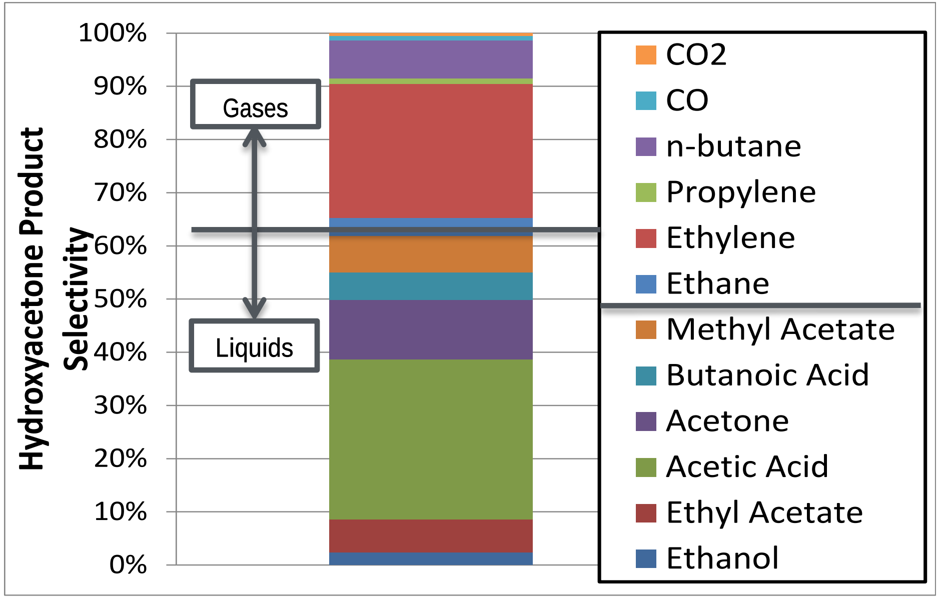
∗Binary and ternary mixtures of HTL compounds have also been completed

2 – Technical Progress:
Aqueous Organics to Hydrocarbon Fuels

Baseline Catalyst Tests with Model Compounds: 350 °C, 300 psig, ZSM-5

Hydroxyacetone: Example of a Catalytic Fast Pyrolysis Model Compound





- Reaction products trend towards other light oxygenates and light olefins
- Catalyst coking/deactivation significant at higher feed concentrations
- **Solution:** Investigate other catalyst classes to improve results
  1. Multi-functional catalysts for **direct conversion** to fuel range carbon molecules (e.g. aldol condensation, ketonization)
  2. Catalysts for the production of **olefins** with a subsequent oligomerization to fuel range hydrocarbons

2 – Technical Progress: 3.2.2.30 Aqueous Organics to Hydrocarbon Fuels

Milestone	Planned Completion Date	Completion
Select feed stock compositions for initial testing	12 Dec, 2012	✓
Complete construction of a catalyst test bed	31 Mar, 2013	✓
Complete a catalyst regeneration test	30 Jun, 2013	Planning Underway
Complete initial set of catalyst experiments	30 Sep, 2013	25%

2- Technical Progress Roadmap

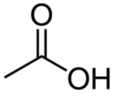
- 3.2.2.34 - Characterization
- 3.2.2.30 – Upgrading
- 3.2.2.32 – Reforming

2 – Technical Progress: Steam Reforming of Representative Compounds

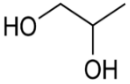
- Initial steam reforming feedstocks evaluated were model compounds found in the aqueous phase of fast pyrolysis bio-oil after low temperature hydrogenation:

Representative Compounds

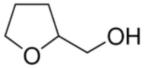
- Acetic Acid



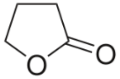
- Propylene Glycol



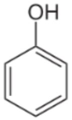
- Tetrahydrofurfuryl Alcohol



- g-Butyrolactone

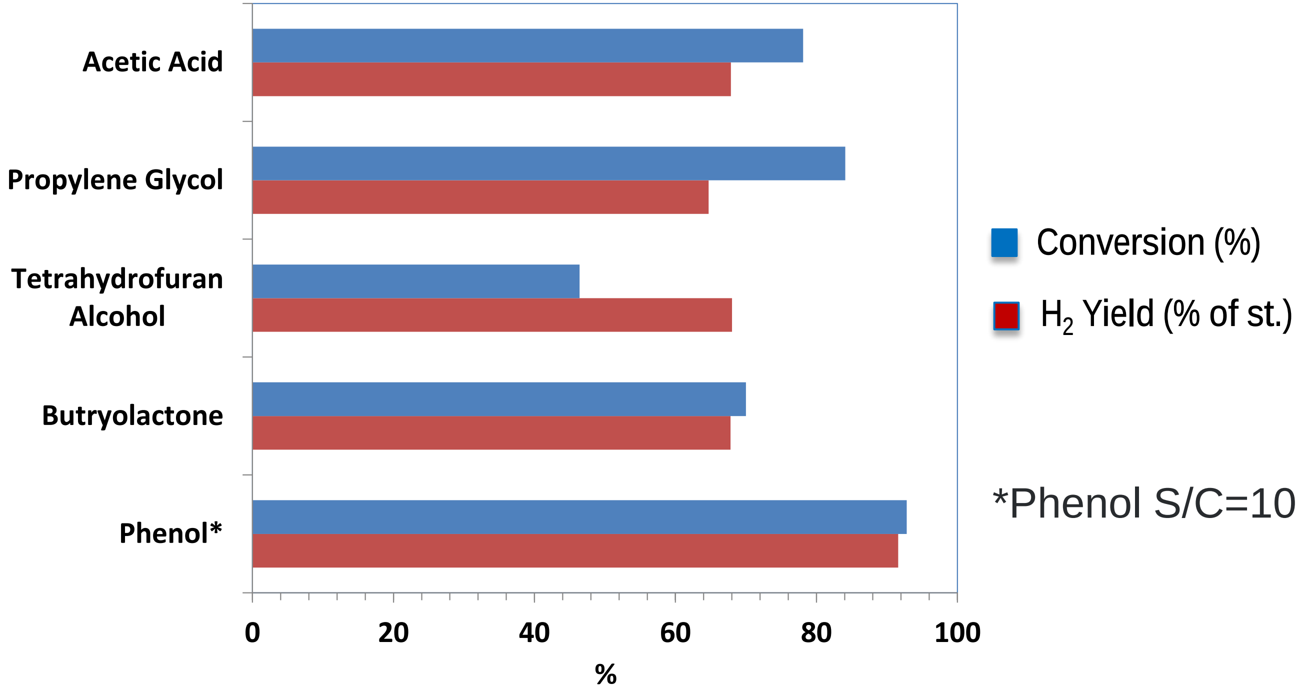


- Phenol



2 – Technical Progress: Steam Reforming of Model Feeds

500 ^{o}C, 1 atm, 30,000 hr^{-1}, S/C=3.0 (mol)*
Noble metal-based catalyst



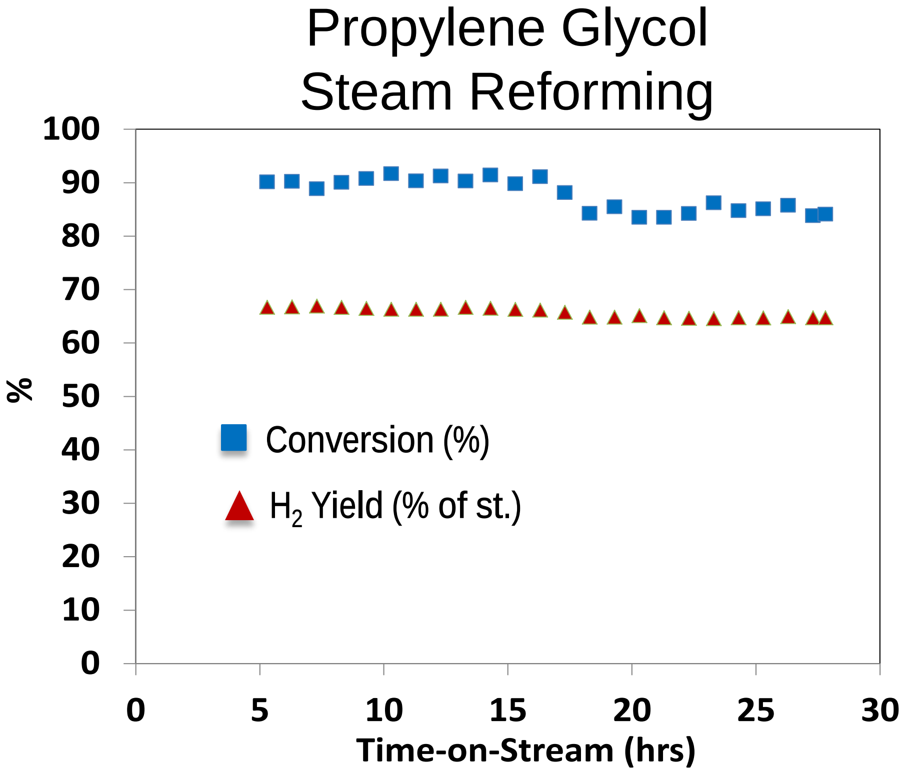
*Phenol S/C=10.7 (mol)

- Model feeds were evaluated for catalytic performance at 500^{o}C using both in-house and commercial reforming catalysts
- Steam:carbon molar feed concentrations were generally representative of the aqueous phase (no additional water would need to be added)
- C Conversion, H_2 Yield, and catalytic stability were assessed under various process conditions (e.g. temperature, space velocity)

2 – Technical Progress: Steam Reforming Catalytic Stability

500 °C, 1 atm, 30,000 hr^{-1}, S/C=3.0 (mol)
Noble metal-based catalyst

- All model feeds evaluated thus far exhibit good stability under these conditions
- Propylene glycol steam reforming shown here, as an example feed, for nearly 30 hours time-on-stream



Accomplishment: Evaluation for several of the model components found in the aqueous phase of fast pyrolysis bio-oil after low temperature hydrogenation exhibited relatively stable conversions under these conditions.

High space velocities used in testing to assess any deactivation (conversion kept below 100% intentionally)

2 – Technical Progress: 3.2.2.33 Steam Reforming of Aqueous Phase

Milestone	Planned Completion Date	Completion
Complete test stand setup & shakedown evaluation	12 Dec, 2012	✓
Complete initial model feed compound evaluations for at least three in-house catalysts and one commercial Ni-based catalyst	31 Mar, 2013	✓
Complete initial TEA review comparing “baseline” and “alternative process with steam reformer” models	30 Jun, 2013	50%
Conduct at least one stability test evaluation of steam reformation using actual bio-oil aqueous fraction for 100 hours' time-on-stream	30 Sep, 2013	Planning underway

3 - Relevance

MYPP Goal: By 2017 achieve $1.83/gal conversion (bio-oil pathway)

Project relevance to Bioenergy Technologies Office goals:

- *"For these (conversion) technologies, processes for recovering carbon and/or hydrogen from aqueous and/or gas phase streams are being developed to maximize energy efficiency." – 2012* MYPP

MYPP Barriers addressed: *Tt-E. Pyrolysis of Biomass and Bio-Oil Stabilization*

MYPP Tasks supported:

- R 3.6.3.2.1 - Develop Fast Pyrolysis Technology
- R 3.6.3.2.2 - Develop bio-oil upgrading and conditioning processes

Applications of the expected outputs from this project:

- Further the understanding of constituents present in different aqueous streams for project utilization and for BETO programmatic economic analyses
- Successful demonstration of aqueous stream processing in support of direct liquefaction pathways using real bio-oils

4 - Critical Success Factors

Critical success factors which will define technical and commercial viability:

1. Improve the overall carbon liquid fuel yield and reduce processing cost for select direct liquefaction processes by upgrading organics in various aqueous streams
2. Reduce H_2 requirements for bio-oil hydrotreating and reduce overall processing costs by reforming organic compounds in the aqueous phase of select direct liquefaction processes

Potential challenges to overcome in order to achieve successful project results:

1. Characterization of aqueous streams for multiple direct liquefaction processes
2. Processing of nontraditional feedstocks (e.g. dilution, specific organic species, presence of inorganics)

With the often costly and limited supply of biomass BETO, and industry will be driven to maximize the usage of the atomic constituents of biomass

4 - Critical Success Factors, cont.

At their conclusion, the successful projects will have:

1. Improved the fundamental understanding of the constituents of the aqueous phases produced by direct liquefaction processes
2. Developed a process and collected relevant data regarding the upgrading of aqueous phase organics to hydrocarbons (catalyst type and stability; processing conditions; hydrocarbon yields)
3. Developed a process and collected relevant data regarding the reforming of aqueous phase organics to hydrogen (hydrogen yield; required steam/carbon ratios; catalyst stability)

Each successful project will produce data that can be implemented into techno-economic analyses for modeling anticipated economic benefits

Prior to these projects a clear knowledge gap has been the identification and manipulation of components in aqueous streams derived from direct liquefaction

5. Future Work: 3.2.2.34 Characterization of Aqueous Products

ML, DL or Go/No Go	Description	FY13 Q3	FY13 Q4	FY14 Q1	FY14 Q2	FY14 Q3	FY14 Q4
ML	Complete construction and modification of new FP system	🟩					
ML	Complete aq phase analyses	🟩					
ML	Complete 2 FP tests using new system		🟩				
DL	Annual Report		🟩				
ML	Complete 2 Catalytic VPU tests using new system			🟩			
ML	Complete 2 direct liquefaction tests with 2 different feedstocks				🟩		
Go/No Go	Go or No Go Decision -- Is the fast pyrolysis system operational and functioning?						

Go/No Go 4/30/2014

5. Future Work: 3.2.2.30 Aqueous Organics to Hydrocarbon Fuels

ML, DL or Go/No Go	Description	FY13 Q3	FY13 Q4	FY14 Q1	FY14 Q2	FY14 Q3	FY14 Q4	FY15 Q1	FY15 Q2	FY15 Q3	FY15 Q4
ML	Complete a catalyst regeneration test	🟩									
DL	Annual Report		🟩								
ML	Complete initial set of catalyst experiments		🟩								
ML	Identify any major technical issues that preclude further development of concept		🟩	🟩							
Go/No Go	A decision regarding the merit of further developing and optimizing a catalytic process for one or more aqueous process feedstocks				**Go/No Go 4/1/2014**						
ML	Identify any preconditioning requirements for select feed streams					🟩	🟩				
DL	Annual Progress Summary Report						🟩				
ML	Complete long-term test with at least one feed stream							🟩	🟩		
ML	Prepare set of operating conditions and feed stream preconditioning requirements for most promising feed stream									🟩	🟩
DL	Annual Progress Summary Report										🟩

5. Future Work: 3.2.2.33
Steam Reforming of Aqueous Phase

	ML, DL or Go/No Go	Description	FY13 Q3	FY13 Q4	FY14 Q1	FY14 Q2	FY14 Q3	FY14 Q4
30-Jun-13	ML	Complete initial TEA review comparing "baseline" and "alternative process with steam reformer" models	🟩					
30-Sep-13	ML	Conduct at least one stability test evaluation of steam reformation using actual bio-oil aqueous fraction for 100 hours' time-on-stream		🟩				
30-Oct-13	DL	Annual Report		🟩				
30-Dec-13	ML	Complete comparative evaluation with a second oxygenate feed with at least one candidate catalyst			🟩			
30-Mar-14	ML	TEA performance and cost evaluation for two models				🟩		
31-May-14	Go/No Go	Go or No Go Decision based on experimental and techno-economic findings			**Go/No Go** **5/31/2014** →			
30-Jun-14	ML	Evaluate at least two oxygenates in model feeds with at least one candidate catalyst and compare to a commercial Ni-based					🟩	
9/30/2014		Determine a preferred catalyst for parametric evaluations.						🟩
30-Oct-13	DL	Annual Report						🟩

Summary

1) Comprehensive and combined approach to improve aqueous phase carbon utilization
    1) Aqueous phase characterization to improve fundamental understanding
    2) Upgrading to improve carbon yield to fuel
    3) Reforming to supplement H_2 requirements
2) Addresses Technical Barriers: *Tt-E*
3) Critical Success Factors
    1) Improve carbon yield
    2) Reduce H_2 requirements
    3) Produce data implementable to techno-economic analyses
4) Future Work
    1) Produce a vapor phase upgrading product utilizing fast pyrolysis system for characterization purposes
    2) Investigate alternative catalysts and processing conditions for improved upgrading and reforming
    3) Evaluate with increasingly complex mixtures and then real bio-oils

Additional Slides

Responses to Previous Reviewers' Comments

- Each of the three projects presented herein (3.2.2.30, 3.2.2.32 and 3.2.2.34) are new projects in FY2013 and were not peer reviewed in 2011

Publications, Presentations, and Commercialization

- Conversion of Direct Liquefaction Process Aqueous Phase Organic Products into Liquid HC fuels (3.2.2.30)
  - Abstract for an Oral Presentation submitted to TCBiomass2013 Sept. 3-6, 2013. Chicago, IL. Pending Acceptance.
  - Abstract for an Oral Presentation submitted to the 246th ACS National Meeting and Exposition. Sept. 8-12, 2013. Pending Acceptance.

- Steam Reforming of Aqueous Fraction from Bio-oil to produce H_2 (3.2.2.33)
  - Abstract submitted to TCBiomass2013 Sept. 3-6, 2013. Chicago, IL. Pending Acceptance.
  - Abstract submitted to the 246th ACS National Meeting and Exposition. Sept. 8-12, 2013. Pending Acceptance.