

2015 DOE Bioenergy Technologies Office (BETO) Project Peer Review

WBS 2.4.1.403 - Improved Hydrogen Utilization and Carbon Recovery for Higher Efficiency Thermochemical Bio-oil Pathways

March 25, 2015
Bio-Oil Technology Area Review
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Goals and Objectives

Objective: Evaluate the potential for improved hydrogen utilization and carbon recovery in a novel, direct biomass liquefaction process.

- 1. Increase hydrogen utilization for hydrodeoxygenation during *in-situ* catalytic biomass pyrolysis to maximize the carbon and energy recovery in a low oxygen content, thermally stable bio-crude intermediate that can be upgraded into a finished biofuel.
- 2. Improve the carbon efficiency of the integrated process by 1) converting carbon in various aqueous streams to methane for hydrogen production, 2) recovering oxygenated hydrocarbons for hydroprocessing, or 3) upgrading aqueous phase carbon to value-added by-products.

Technical goals are to:

- Demonstrate production of bio-crude with less than 10 wt% oxygen
- Greater than 30% of the carbon input from biomass will be recovered in the bio-crude
- Quantify methane produced from AnMBR treatment of aqueous phase and recover 20% of the carbon as methane



Quad Chart Overview

Timeline

- Contract award date: 9/1/2014
- Project kick-off: 01/29/2015
- Budget Period 1 end date: 9/1/2015
- Project end date: 9/30/2017

Barriers Addressed

- Tt-F. Deconstruction of Biomass to Form Bio-Oil Intermediates
- Tt-H. Bio-Oil Intermediate Stabilization and Vapor Cleanup
- Tt-N. Aqueous Phase Utilization and Wastewater Treatment

Partners

- RTI International project lead, CFP technology development, catalyst development, water treatment technology testing, process modeling, project management
- Haldor Topsøe A/S (HTAS) Catalyst development consultant
- <u>Veolia Water Technologies, Inc.</u> Aqueous carbon recovery and water treatment technologies consultants

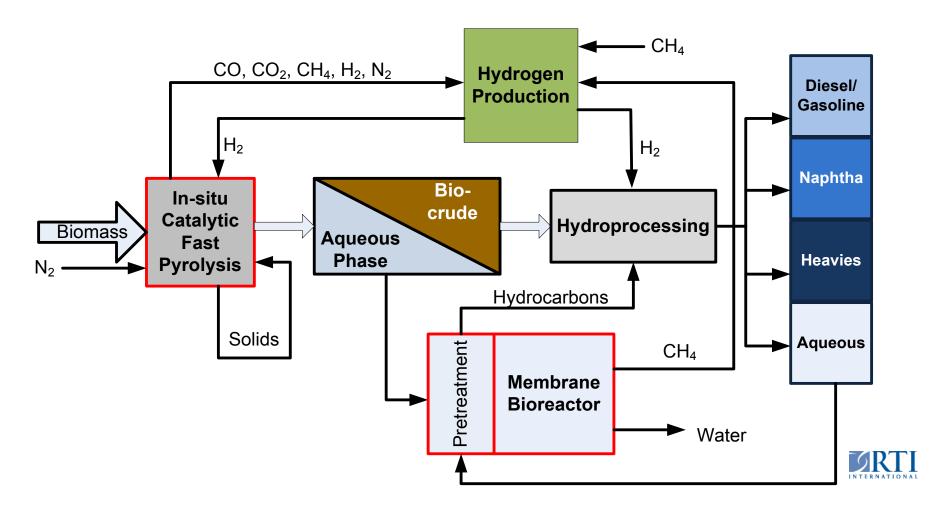
	Total Costs FY 10 –FY 12	_	FY 14 Costs	Total Planned Funding (FY 15-Project End Date)
DOE Funded				\$3,140,526*
Project Cost Share RTI (State of NC) HTAS Veolia				\$605,754 \$25,000 \$154,608



^{*}Approved spend plan for Budget Period 1 is \$1,221,567 (\$977,253 DOE + \$244,314 cost share)

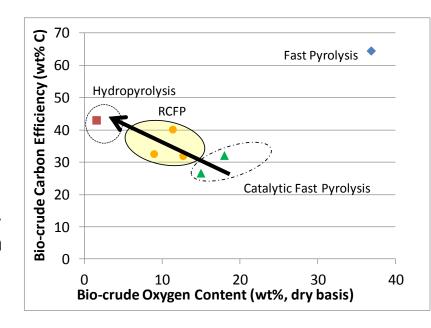
1 – Project Overview

- Improve Hydrogen Utilization
- Enhance Carbon Efficiency by Recovering Carbon from the Aqueous Phase



2 – Technical Approach

- Develop 2nd generation catalysts to enhance hydrodeoxygenation during biomass pyrolysis at low severity process conditions
- 2) Integrate wastewater treatment technology to recover aqueous phase organic compounds to recycle hydrocarbons to hydroprocessing unit or convert hydrocarbons into methane that can be reused to produce hydrogen for bio-crude production and upgrading.



	Theoretical	Hydrogen Demand (g/kg biomass fed)		External CH₄	MBR CH₄
	Fuel yield (gal/dry ton)	Conversion Process	Hydroprocessing	Demand (g/kg fed)	potential (g/kg fed)
In-situ Catalytic Fast Pyrolysis	47-57	0	12-15	8-18	31-45
In-situ Catalytic Fast Pyrolysis w/H ₂	57-71	5	12-16	23-29	16-28



Hydrogen demand for hydroprocessing is calculated based on removing the remaining oxygen and adjusting H/C Theoretical Fuel Yield is based on H/C of 2 and density of 0.8 g/ml, assumes no carbon loss in hydroprocessing

2 – Management Approach

BUDGET PERIOD 1 [Laboratory-scale Evaluations] M1-M12

Task 1.0: Catalyst Development M1-M12

Subtask 1.1: Catalyst Synthesis and Characterization (M1-M6)

Subtask 1.2: Catalyst Screening (M2-M10)

Subtask 1.3: Catalyst Testing (M4-M11)

Task 2.0 Aqueous Phase Carbon Recovery Proof-of-Concept (M1-M12)

Task 3.0: Preliminary Process Design and Integration (M4-M11)

Go/No-Go Decision Point (M12): Correlate catalyst characteristics with HDO activity and coke formation rates measured in 1) model compound experiments and 2) validated with CFP data collected in a 2" FBR system. In parallel, evaluate pretreatment strategies and methane potential of aqueous phase carbon recovery in AnMBR.

BUDGET PERIOD 2 [Scale-up and Process Development] M12-M36

Task 4.0: Catalyst Screening (M13-M24)

Subtask 4.1: Catalyst Scale-up (M18-M24)

Task 5.0: CFP Process Development (M18-M32)

Subtask 5.1: CFP Bio-crude Production (M24-M28)

Subtask 5.2: CFP Bio-crude Upgrading (M28-M32)

Task 6.0 Anaerobic Membrane Bioreactors (AnMBR) for Converting Aqueous Phase Carbon to Methane (M13-M34)

Task 7.0: Process Modeling and Techno-economic Analysis (M24-M36)

Subtask 7.1 Process Modeling (M24-M34)

Subtask 7.2 Life-Cycle Assessment (M32-M36)

Task 8.0: Project Management and Reporting



3 – Technical Accomplishments/Progress/Results

Catalyst Development

- Catalyst preparation and characterization underway (9 materials)
- Catalyst screening with model compounds initiated
- Fluidized Bed Reactor modifications for atmospheric pressure operation complete

Aqueous Phase Carbon Recovery Proof-of-Concept

- AnMBR system preparation
- Aqueous phase sample analyses

Project Management

- Project award signed September 22, 2014
- Project Kickoff Meeting at RTI on January 29, 2015
- Sub-award negotiations with Haldor Topsoe and Veolia are complete and full executed



Task 1: Catalyst Development

Summary: In collaboration with our catalyst development partner, Haldor Topsøe A/S, RTI will develop novel catalyst formulations that activate hydrogen to enhance hydrodeoxygenation (HDO) in an innovative, new in-situ rapid catalytic fast pyrolysis (RCFP) of biomass with higher yields of low oxygen content biocrude and improved carbon efficiency.

- Develop a robust catalyst that efficiently uses hydrogen for HDO and increases the hydrogen to carbon (H/C) ratio in volatile products to limit char and coke formation.
- Selective HDO to remove the more recalcitrant oxygen species will also be investigated.
- Four catalyst classes are being considered with the understanding that different deoxygenation mechanisms may contribute to the activity of each class of catalysts.



Catalyst Development

The goal is to produce a bio-crude intermediate with < 5 wt% oxygen with yields and carbon efficiency comparable to hydropyrolysis (300 psig) but at atmospheric pressure.

Class	Description	Variables
1	Precious metal promoted solid acids	Precious metal loading
	1 st iteration: Pt promoted tungstated zirconia and alumina	Acid strength
	Additional iterations: alternative promoters on additional supports	Surface area
2	Precious metal promoted mixed metal oxides (MMO)	Precious metal loading
	1 st iteration: Pt on MMO	Metal oxide composition
	Additional iterations: alternate promoters with additional metal	Surface area
	oxides	Additional promoters and supports
3	Metal phosphide promoted solid acids	Phosphide loading
	1 st iteration: Ni₂P on tungstated zirconia and alumina	Acid strength
	Additional iterations: alternative phosphides and supports	Surface area
		Additional promoters and supports
4	Metal phosphide promoted mixed metal oxides	Phosphide loading
	1st iteration: Ni ₂ P on MMO	Metal oxide composition
	Additional iterations: alternative phosphides including and metal	Surface area
	oxides	Additional promoters and supports

Catalyst Preparation to date

Class	Type	Description	Amount (g)
	Sold Acid	Al_2O_3	117.75
		Ni_2P on Al_2O_3 - A	20
3		Ni_2P on Al_2O_3 - B	20.92
3		WO_3ZrO_2	10g
		Ni ₂ P on WO ₃ ZrO ₂ - A	15.54
		Ni ₂ P on WO ₃ ZrO ₂ - B	16.49
	BA: BA (MMO1	17.76
4	Mixed Metal Oxides	N _{i2} P on MMO1 - A	14.95
		Ni ₂ P on MMO1 - B	19.94

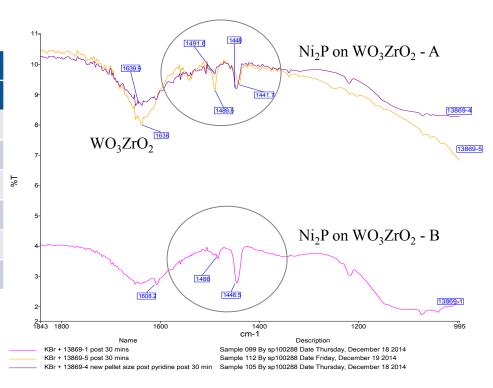
Example preparation method:

$$Ni_{1}(NO_{3})_{2}(H_{2}O)_{6} + (NH_{4})H_{2}PO_{4} + Al_{2}O_{3} \longrightarrow Ni_{3}(PO_{4})_{2}Al_{2}O_{3} + NH_{4}NO_{3}$$
 (Step 1)
$$Ni_{3}(PO_{4})_{2}Al_{2}O_{3} \xrightarrow{500 \text{ C}} 3NiOP_{2}O_{5}Al_{2}O_{3}$$
 (Step 2)
$$3NiOP_{2}O_{5}Al_{2}O_{3} \xrightarrow{600C, H_{2}} Ni_{2}PAl_{2}O_{3}$$
 (Step 3)



Catalyst Characterization

Description	BET Surface	Ammonia TPD	
	Area (m²/g)	°C	ml/g
WO ₃ ZrO ₂	TBD	200.0	6.75
Ni ₂ P on WO ₃ ZrO ₂ - A	204.8	196.8	14.88
Ni ₂ P on WO ₃ ZrO ₂ - B	206.8	102.6	20.20
Al ₂ O ₃	TBD	200.2	9.83
Ni ₂ P on Al ₂ O ₃ - A	114.2	202.8	12.13
Ni ₂ P on Al ₂ O ₃ - B	106.4	146.5	14.01



Pyridine FTIR



Catalyst Screening

Automated microreactor with model compounds

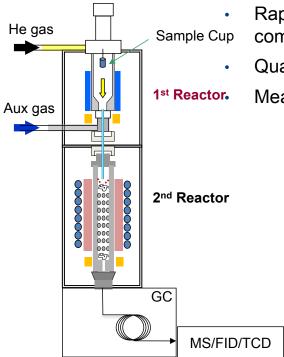
Programmed reaction sequence for unattended operation

Rapid screening to evaluate deoxygenation activity with model

compounds

Quantitative real-time product analysis

Measure regeneration products for coke yield



Screen catalysts for deoxygenation activity to control bio-crude properties and maximize carbon efficiency



MicroPyrolyzer-GC/MS

- Fundamental research to support technology development
- Dual microreactors for in situ or ex situ catalytic pyrolysis studies
- Efficiently screen catalysts and process conditions with real biomass
- Good mass balance (>90%) and excellent reproducibility (s.d.< 2~3%)



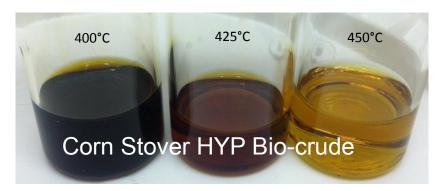
Bio-crude Production





Modified High Pressure System for Atmospheric Pressure Operation

- 2.5" FBR with 4" disengagement zone
- Catalyst Loading: ~250-mL
- Temperature: 350-700°C
- Pressure: 0-75 psig
- Various H₂ partial pressures
- Bio-crude Collection: HX with 3 impingers and ESP





Task 2: Aqueous Phase Carbon Recovery Proof-of-Concept

Summary: The objective of this task is to determine the technical feasibility of biologically converting carbon in the aqueous phase to methane. Less than expected carbon conversion to CH₄ and CO₂ can result from incomplete digestion, production of by-products (such as acetic acid and other acids), and conversion of carbon into cell matter.

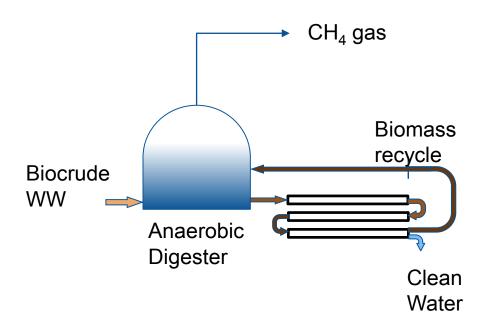
- Detailed chemical analysis of the amount and type of hydrocarbons in aqueous phase samples will be measured.
- Chemical oxygen demand (COD) and biological oxygen demand (BOD) will be compared with the biological methane potential (BMP) to evaluate the recalcitrance of organic compounds in aqueous phase samples.
- Evaluate possible pretreatment technologies that would improve carbon recovery in BP2.
- Proof-of-principle experiments will be performed to demonstrate CH₄
 production from aqueous phase carbon in an anaerobic membrane
 bioreactor (AnMBR).



Aqueous Phase Carbon Recovery

Determine the technical feasibility of biologically converting carbon in the aqueous phase to methane.

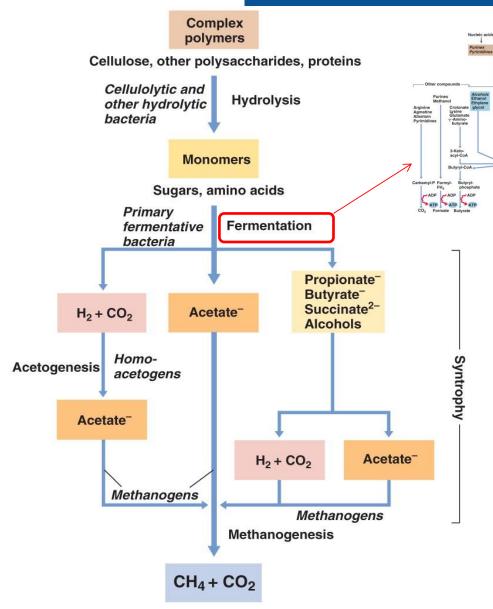
Veolia Water Solutions will support project during Budget Period 1 by characterizing aqueous streams from RTI's biomass conversion process to determine treatment options.



- Test aqueous phase samples for methane potential and toxicity with regards to digestion in bioreactors based on industry relevant test protocols
- Provide a preliminary assessment of treatment needs of water effluent from thermochemical biomass conversion processes and suggest treatment technology options



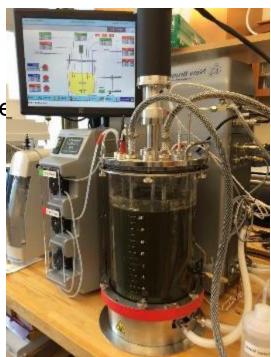
Anaerobic MBR



- Absence of specific microbial populations results in unbalanced anaerobic food web.
- Unbalanced anaerobic food web leads to metabolic imbalance.
- Metabolic imbalance leads to process failure.
- P Balanced anaerobic food web requires the right microbes with the right quantity for each target substrate and intermediate.

AnMBR Reactor Preparation

- Initial Cleaning
 - Collect remaining biomass culture
 - Clean out tank and lines and flush system
 - Clean the membrane clean in place (CIP)
 - Determine the clean water permeability of the membrane
- Re-seed reactor with new sludge from Veolia
 - Make synthetic feed following existing recipe
 - Grow the biomass culture to an optimal Mixed Liquor Suspended Solids (MLSS) level
- Initial Operation
 - Begin filtration, permeate extraction (draw down) and feeding cycle
 - Calculate the sludge and hydraulic retention times (Est. SRT: 60-80d; HRT: 8 15 hr)





4 - Relevance

BETO MYPP: The strategic goal of Thermochemical Conversion R&D is to develop commercially viable technologies for converting biomass into energy-dense, fungible, finished liquid fuels, such as renewable gasoline, jet, and diesel, as well as biochemicals and biopower.

Applicable Thermochemical Conversion Process Steps:

- Deconstruction to Form Bio-Oil Intermediates
- Bio-Oil Intermediate Stabilization and Upgrading
- Balance of Plant: hydrogen generation, emissions abatement, wastewater treatment, heat and power generation, and solid waste disposal.

Performance Milestones for Thermochemical Pathways

- By 2017, achieve an nth plant modeled conversion cost of \$2.50/GGE via a thermochemical pathway. This contributes to a minimum gasoline and diesel blendstock fuel selling price of \$3.50/GGE in 2011 dollars.
- By 2017, validate the R&D performance goal of \$2.50/GGE nth plant modeled conversion cost and thus the Office's performance goal of \$3.00/GGE MFSP by performing integrated operations using on-specification feedstock via a thermochemical pathway that produces gasoline and diesel blendstock fuels.



5 - Future WorkCatalyst Development and Testing

Catalyst preparation

Class 1 and 2 materials synthesis Additional supports and promoters for Class 3 and 4 materials

Catalyst characterization

Acid strength - Ammonia TPD and Pyridine FTIR Surface Area and Porosity Temperature Programmed Reduction/Reaction

Catalyst Screening with Model Compounds and Biomass

Guaiacol, anisole, and furfural conversion over selected catalysts as a function of temperature, hydrogen partial pressure, and space velocity.

Micropyrolyzer studies with biomass (Temperature and H₂ concentration)

Bio-crude Production with Selected Catalysts

Determine material balances, bio-crude yields, and bio-crude oxygen content as a function of catalyst, temperature, and H₂ partial pressure



5 - Future Work Aqueous Phase Carbon Recovery

Test aqueous phase samples for biological toxicity using a respirometer, considering:

Heavy metals

Phenolics, Benzene, Toluene, Ethylbenzene, Xylene (BTEX), etc.

Sanitizers & Detergents

Research solutions to mitigate the effect of toxicity to the biomass, including:

Pre-oxidation, Sonification

Other treatments, e.g., enzyme

Test the genetic composition and diversity of the anaerobic micro-organisms

Community fingerprinting – done at a potential university partner's laboratory

Test the permeate and the sludge for:

Volatile fatty acids (VFAs)

Alkalinity

Chemical oxygen demand (COD)

Total suspended solids (TSS)

Volatile suspended solids (VSS)

Mixed liquor suspended solids (MLSS)

Gas output quantity and composition (CO₂, CH₄, H₂S, H₂, estimate 25 L/d biogas output)



5 - Future Work Go/NoGo Decision Point

Go/No-Go Decision Point (M12):

Correlate catalyst characteristics with HDO activity and coke formation rates measured in 1) model compound experiments and 2) validated with CFP data collected in a 2" FBR system.

Evaluate pretreatment strategies and methane potential of aqueous phase carbon recovery in AnMBR.

- Demonstrate production of bio-crude with less than 8 wt% oxygen
- Greater than 42% of the carbon input from biomass will be recovered in the biocrude
- Quantify methane produced from AnMBR treatment of the aqueous phase and recover 20% of the carbon as methane
- Develop a process model for an integrated direct biomass liquefaction process that utilizes methane produced from carbon recovered from the aqueous phase to generate hydrogen for upstream conversion or downstream upgrading. Estimate advanced biofuel production cost for integrated process and preliminary GHG emissions reduction potential
- Estimate preliminary GHG emissions reduction potential from integrated process with a target of 60% compared to petroleum based fuels

Summary

- This project is focused on improving hydrogen utilization and increasing carbon efficiency by recovering carbon from the aqueous phase in a novel, direct biomass liquefaction process
- New, 2nd generation catalysts are being developed for in situ catalytic fast pyrolysis to optimize hydrodeoxygenation to produced a low oxygen content bio-crude
- Novel water treatment technologies as being applied for aqueous phase carbon recovery
 - Aqueous phase sample characterization for pretreatment strategies
 - Anaerobic Membrane Bioreactors for methane production
- Less than 1 year into this relatively new project
 - Catalyst preparation and characterization underway
 - Catalyst screening underway
 - Aqueous phase sample analysis
 - AnMBR system preparation
- Support BETO goal for developing commercially viable technologies for converting biomass into energy-dense, fungible, finished liquid fuels
- Key near-term milestone: Go/NoGo decision point 9/2015



Acknowldegments









BETO Project Officer: Liz Moore

RTI Contributors

- David C. Dayton (PI)
- Kaige Wang Johnathan Peters
- John Carpenter
- Marty Lail
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Haldor Topsoe

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- Herve Buisson
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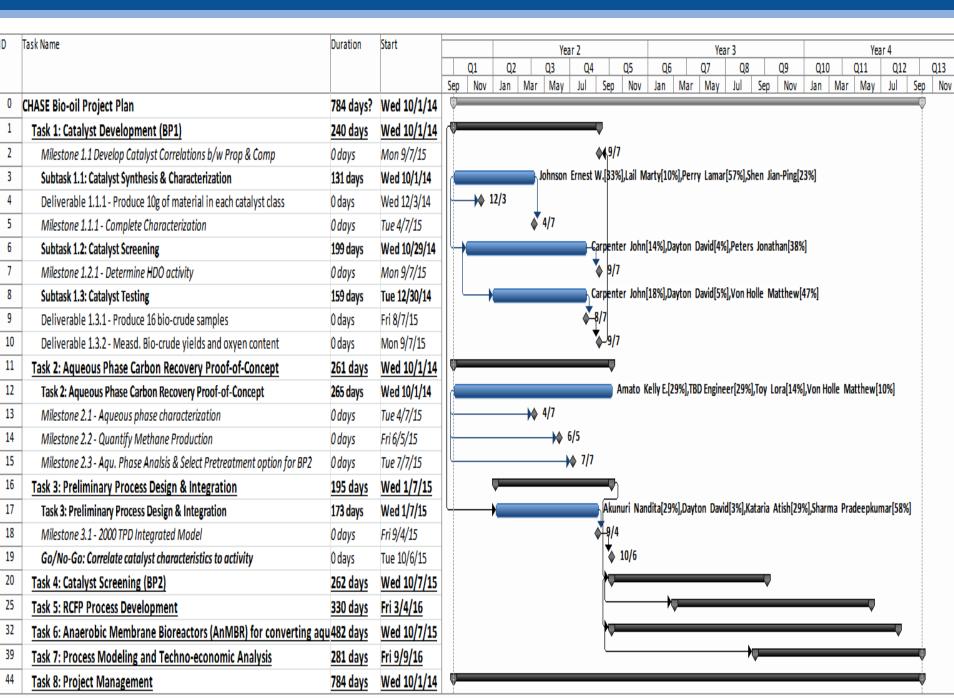


Additional Information

- Publications/Patents/Awards none
- Presentations
- No previous reviewer comments. New project that was not reviewed in 2013.



RTI International



Task 1 Milestones and Deliverables

Milestone Number	Milestone Description	Milestone Verification (What, How, Who, Where)	Date
M1 1	Develop a correlation between specific catalyst characteristics such as catalyst acidity (NH ₃ -TPD and pyridine-FTIR), metal loading and dispersion, and surface area; and catalyst hydrodeoxygenation activity and coke formation rates based on model compound screening in an automated fixed bed microreactor.	RTI Model Compound Screening Results in consult with Haldor Topsøe AS	M11
D1.1.1	Produce 10-g of material in each of the four catalyst classes being considered.	RTI Catalyst Synthesis	M2
M1.1.1	Complete characterization (XRD, BET, NH ₃ -TPD, DRIFTS, and TPR) of catalysts synthesized in subtask 1.1 and determine structure function relationships	RTI catalyst characterization with consult from Haldor Topsøe AS	M6
M1.2.1	Determine HDO activity for catalysts synthesized in subtask 1.1 as a function of temperature and hydrogen partial pressure and correlate with characterization results.	RTI	M11
M1.3.1	Produce at least 16 bio-crude samples in the 1"FBR with at least 90% mass balance for chemical characterization.	RTI laboratory experiments	M10
M1.3.2	Measured bio-crude yields and oxygen content as a function of catalyst, biomass feedstock and process conditions.	RTI analytical capabilities	M11



Task 2 Milestones and Deliverables

Milestone Number	Milestone Description	Milestone Verification Process (What, How, Who, Where)	Date
M2.1	Measure COD, BOD and total organic carbon in selected aqueous phase samples and compare to BNP to estimate microbial toxicity for organic compounds present in the aqueous-phase waste stream.	RTI analytical capabilities	M6
M2.2	Quantify the methane production potential of the AnMBR process for recovering aqueous phase carbon	RTI Water Laboratory Facilities in consult with Veolia Water Solutions and Technologies	M8
M2.3	Preliminary characterization and analysis of RCFP aqueous phase samples; including, acetic acid content, pH, TOC, and BMP in addition to the toxic or recalcitrant components identified will collectively be evaluated to select pretreatment technology options for testing in BP2.	RTI and Veolia Water Solutions and Technologies	M9



Task 3 Milestone

Milestone	Milestone Description	Milestone Verification Process	Date
Number	(Go/No-Go Decision Criteria)	(What, How, Who, Where)	
M3.1	A preliminary process model based on a 2,000 tpd commercial-scale design for an integrated process with aqueous phase carbon recovery.	RTI process modeling capabilities with input from Veolia Water Solutions and Technologies and Haldor Topsøe AS	M11



Task 4 Milestones and Deliverables

Milestone Number	Milestone Description (Go/No-Go Decision Criteria)	Milestone Verification Process (What, How, Who, Where)	Date
M4.1	Optimized catalyst (commercially relevant formulation) to produce bio-crude with less than 8 wt% oxygen with at least 45% carbon efficiency in an integrated process design ased on data from the 1"diameter catalytic biomass pyrolysis system.	RTI Laboratory-scale 1"FBR	M20
M4.1.1	Produce at least 200 kg of attrition resistant catalyst with target performance properties for pilot plant testing in Task 5	RTI spray drier facilities in consult with catalyst vendor	M24



Task 5 Milestones and Deliverables

Milestone Number	Milestone Description (Go/No-Go Decision Criteria)	Milestone Verification Process (What, How, Who, Where)	Date
D5.1.1	Produce at least 25 gallons of aqueous phase by- product for anaerobic membrane bioreactor testing	RTI Energy Technology Development Facility	M25
D5.1.2	Produce at least 10 gallons of RCFP bio-crude from loblolly pine for upgrading	RTI Energy Technology Development Facility	M28
M5.2.1	Upgrade RCFP bio-crude intermediate from loblolly pine for a minimum of 100 hrs and report hydrogen consumption and product fraction yields and compositions	RTI pilot-scale hydrotreater with input from Haldor Topsøe AS	M32



Task 6 Milestones and Deliverables

Milestone Number	Milestone Description (Go/No-Go Decision Criteria)	Milestone Verification Process (What, How, Who, Where)	Date
M6.1	Measure methane concentration as a function of the concentration of identified recalcitrant organic compounds to determine toxicity effects and test pretreatment methods for optimizing methane production.	RTI Water Treatment Lab	M15
M6.2	Develop a model to predict CH ₄ production, effluent quality, and the environmental and economic benefit potential as a function of the organic components in the aqueous phase.	RTI and Veolia Water Solutions and Technologies	M18
M6.3	Demonstrate the potential of an integrated pretreatment process with AnMBR to maximize the production of CH ₄ from aqueous phase organic compounds at the bench-scale	RTI Water Treatment Lab	M32
D6.4	Estimated capital and operating costs associated with this carbon recovery option will be compared to the cost of aqueous phase disposal	RTI ASPEN/Icarus software and vendor quotes with input from Veolia Water Solutions and Technologies	M34
D6.5	Estimate relative GHG emissions for carbon recovery option compared to conventional disposal and waste water treatment.	RTI and Veolia Water Solutions and Technologies	M34



Task 7 Milestones

Milestone Number	Milestone Description (Go/No-Go Decision Criteria)	Milestone Verification Process (What, How, Who, Where)	Date
M7.1.1	Detailed techno-economic analysis of the optimized catalytic biomass pyrolysis process in excess hydrogen integrated with aqueous phase carbon recovery using AnMBR to produce methane. The advanced biofuels production cost target is \$3/gallon	RTI ASPEN software with input from Haldor Topsøe AS and Veolia Water Solutions and Technologies	M34
M7.2.1	Life-cycle assessment of the optimized process design demonstrating 60% GHG reductions compared to petroleum transportation fuels	RTI LCA models based on GREET data with input from Haldor Topsøe AS and Veolia Water Solutions and Technologies	M36

