U.S., Department of Energy (DOE)
Bioenergy Technologies Office (BETO)
2017 Project Peer Review

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

(WBS 2.5.4.405)

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Thermochemical Conversion

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Goal Statement

Evaluate the potential for improved hydrogen utilization and carbon recovery in a novel, enabling technology that combines the best of several direct biomass liquefaction technologies.

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.
3. Improve water quality to reduce fresh water consumption and reduce wastewater treatment costs

Target: nth plant modeled MFSP of $3/GGE (2014$) via RCFP with hydroprocessing to produce hydrocarbon biofuel with GHG emissions reduction of 50% or more compared to petroleum-derived fuel.

Quad Chart Overview

Timeline

- Contract award date: 9/1/2014
- Project kick-off: 01/29/2015
- Budget Period 1 end date: 5/31/2016
- Budget Period 2 approved: 10/14/2016
- Project end date: 9/30/2018
- Project ~60% complete

Barriers

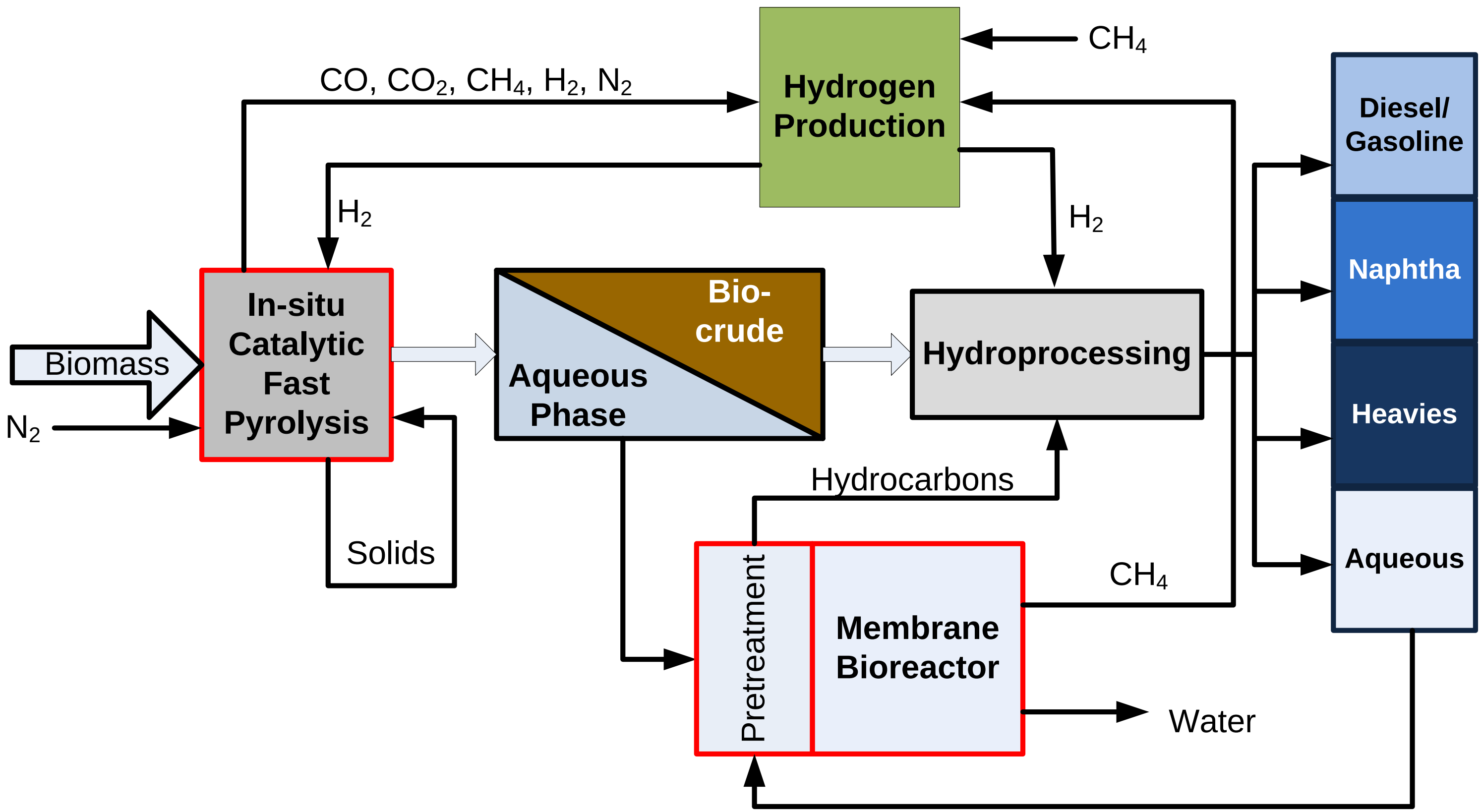
- Ct-F. Efficient High-Temperature Deconstruction to Intermediates
- Ct-H. Efficient Catalytic Upgrading of Bio-Oil Intermediates to Fuels and Chemicals
- Ct-L. Aqueous Phase Utilization and Wastewater Treatment

Partners

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

	FY12 - FY14 Costs	FY15 Costs	FY16 Costs	FY17 - Project End Date Cost
DOE Funded	$426	$578,890	$567,150	$1,994,060
Cost Share - Veolia	$0	$0	$0	$50,000
Cost Share - Haldor Topsoe	$0	$0	$0	$103,072
Cost Share - State of NC	$104	$213,894	$52,439	$365,854
Total	**$530**	**$792,784**	**$619,589**	**$2,512,986**

1- Project Overview



- Develop 2nd generation catalysts to enhance hydrodeoxygenation during biomass pyrolysis at low severity process conditions

- Integrate wastewater treatment technology to recover aqueous phase organic compounds to recycle hydrocarbons to hydroprocessing unit or convert hydrocarbons into methane that can be re-used to produce hydrogen for bio-crude production and upgrading.

2 – Approach (Management) BP1 Laboratory-scale Evaluations

Detailed project plan with quarterly milestones and deliverables and Go/NoGo decision point between budget periods

Task 1.0: Catalyst Development (RTI, Haldor Topsoe)

Subtask 1.1: Catalyst Synthesis and Characterization

Subtask 1.2: Catalyst Screening

Subtask 1.3: Catalyst Testing

Task 2.0 Aqueous Phase Carbon Recovery Proof-of-Concept (RTI, Veolia)

Task 3.0: Preliminary Process Design and Integration (RTI, Haldor Topsoe, Veolia)

Go/No-Go Decision Point: 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.

- 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 bio-crude
- Quantify methane produced from AnMBR treatment of the aqueous phase and recover 20% of the carbon as methane
- Estimate advanced biofuel production cost for integrated process and preliminary GHG emissions reduction potential

Task 8.0: Project Management and Reporting

2 – Approach (Management) BP2 Scale-up and Process Development

Task 4.0: Catalyst Screening (RTI, Haldor Topsoe)

Subtask 4.1: Catalyst Scale-up

Key milestone: Obtain fluidizable catalyst for 1TPD biomass pyrolysis unit based on catalyst screening efforts in BP1 and BP2

Task 5.0: RCFP Process Development (RTI, Haldor Topsoe)

Subtask 5.1: RCFP Bio-crude Production

Subtask 5.2: RCFP Bio-crude Upgrading

Key deliverables: Produce at least 25 gallons of aqueous phase for bioreactor studies and 10 gallons of bio-crude for upgrading

Task 6.0 Anaerobic Membrane Bioreactors (AnMBR) for Converting Aqueous Phase Carbon to Methane (RTI, Veolia)

Key Milestones: Develop an empirical model to describe methane production from aqueous phase; Demonstrate the potential of an integrated pretreatment process for AnMBR and estimate capital and operating costs

Task 7.0: Process Modeling and Techno-economic Analysis (RTI, Haldor Topsoe, Veolia)

Key Milestone: TEA/LCA benefits of AD for aqueous phase carbon recovery compared to alternative wastewater treatment options

Subtask 7.1 Process Modeling

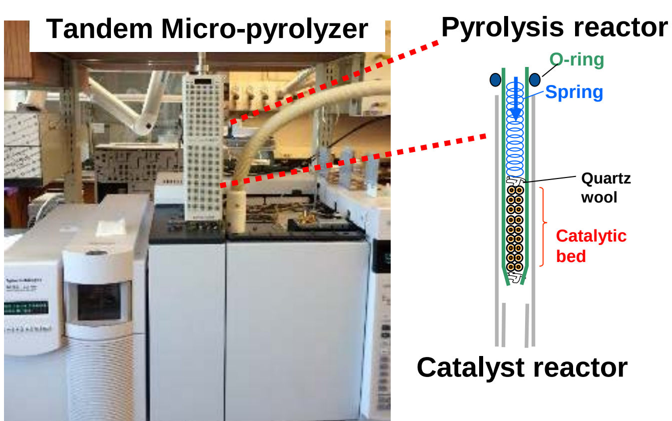
Subtask 7.2 Life-Cycle Assessment

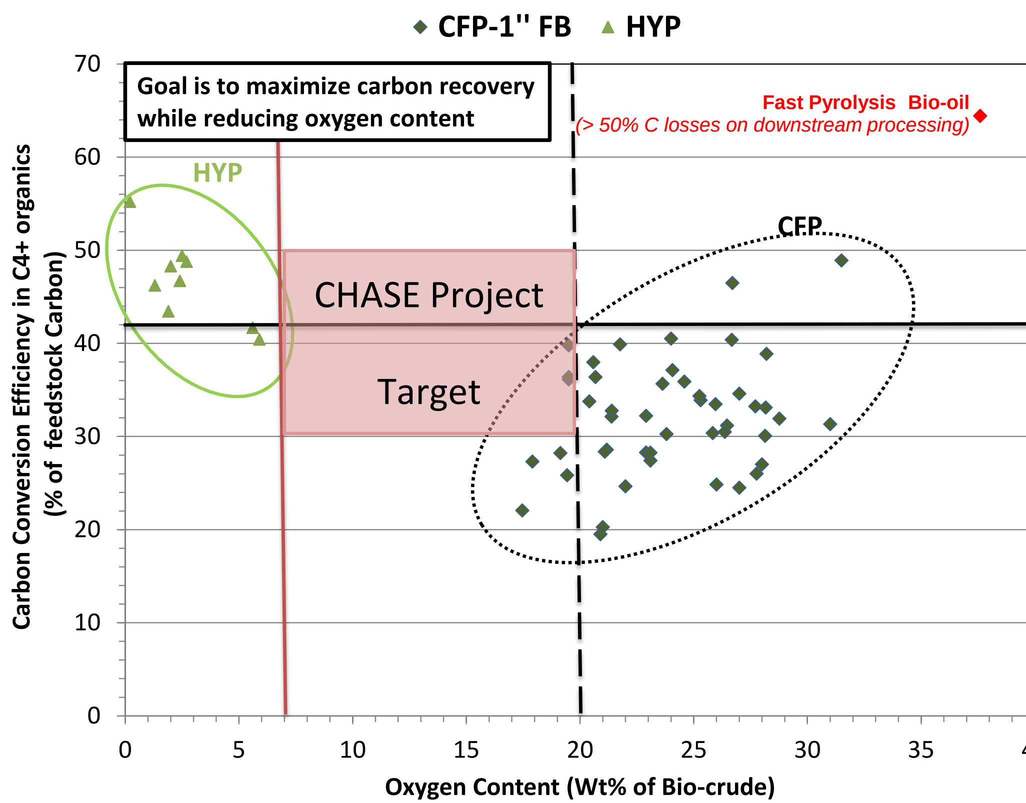
Task 8.0: Project Management and Reporting (RTI)

2 – Approach (Technical) Improving hydrogen utilization

Screening at multiple scales to identify catalysts that maximize biocrude yield and minimize biocrude oxygen content:

- Fundamental micropyrolyzer studies to study HDO as a function of catalyst and process conditions with real biomass
- Automated catalyst screening with model compounds to understand fundamental HDO chemistry and reaction schemes
- Laboratory-scale fluidized bed studies to investigate material balances and bio-crude properties as a function of catalyst and process conditions
- Pilot-scale (1TPD) bio-crude production for process optimization and upgrading studies





3 – Technical Accomplishments/Progress/Results

Catalyst Summary

Consistent results from micropyrolyzer, model compound reactor, and fluidized bed reactor

- Catalyst-to-biomass ratio was a challenge in micropyrolyzer
- Deoxygenation pathways could be interpreted from model compound results
- Hydrogen in the pyrolysis reactor improved yields and reduced coke formation
- SA2 produced high liquid yield (23 mole %C) with reasonable deoxygenation efficiency (14.9 wt% O)
- HT2 had the best deoxygenation efficiency **(7.4 wt% O)** with the highest **C_4^+ yield (43.0 mole %C)**

Anaerobic Digestion of Aqueous Phase

- Based on elemental analysis, the wastewater organics have the chemical composition - $C_{5.88}H_{5.01}O_1$
- Theoretical limit of biogas from anaerobic digestion of biofuel wastewater is 56.5% methane
- Empirically, the nutritious feedstock produces biogas with 65% methane (theoretical maximum is 67%)
  - The theoretical methane content of biogas from a feedstock with 1.2 v% WW is 63.8%
  - Measured methane content of biogas is 63.3%.

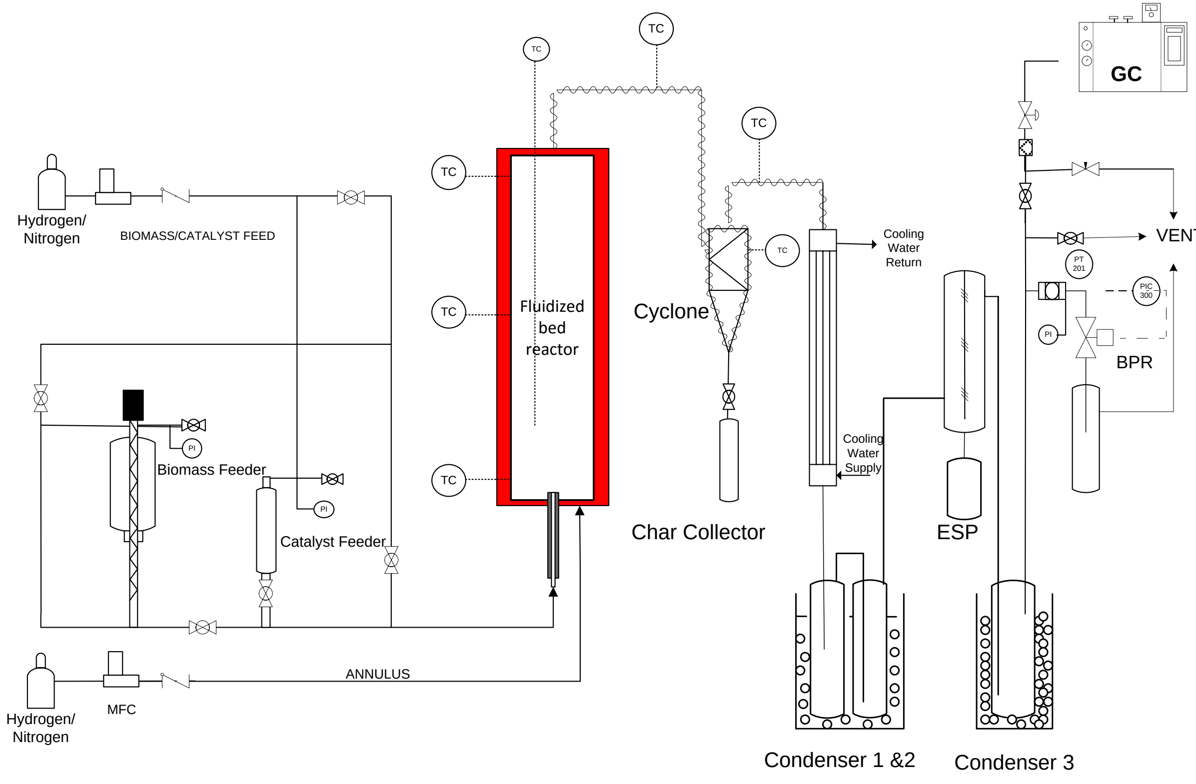
Preliminary TEA and LCA

- Updated CFP process model
- Advanced **biofuel production cost: $2.36-$2.70** (depending on process hydrogen use)
- **GHG reduction: 76.4%-97.7%** (depending on process hydrogen use)

Go/NoGo Criteria Met for BP1

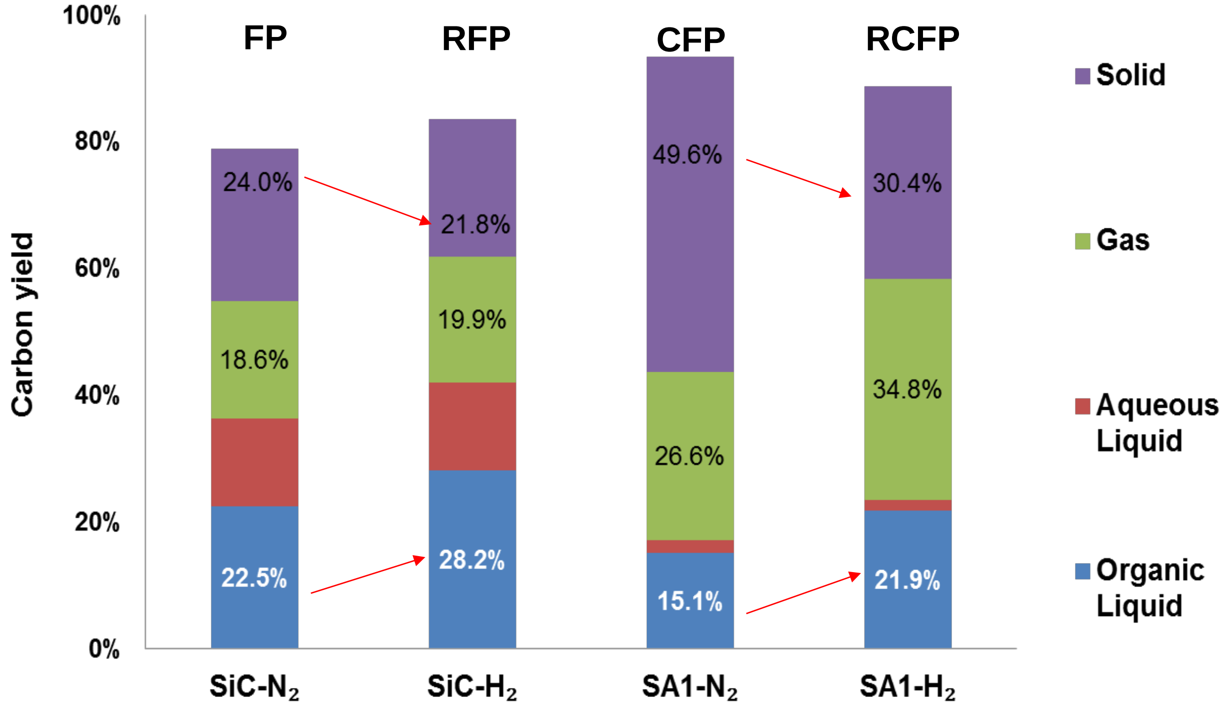
Lab-scale Reactor System – Bio-crude Production

- 2.5'' fluidized bed reactor with 4'' disengagement zone
- Biomass feeding rate: 2-5 g/min
- Liquid collection: 3 condensers and 1 ESP
- Non-condensable gases analyzed by on-line micro GC
- Liquid product analyzed by Karl Fischer titration, elemental analysis, GC/MS, etc..

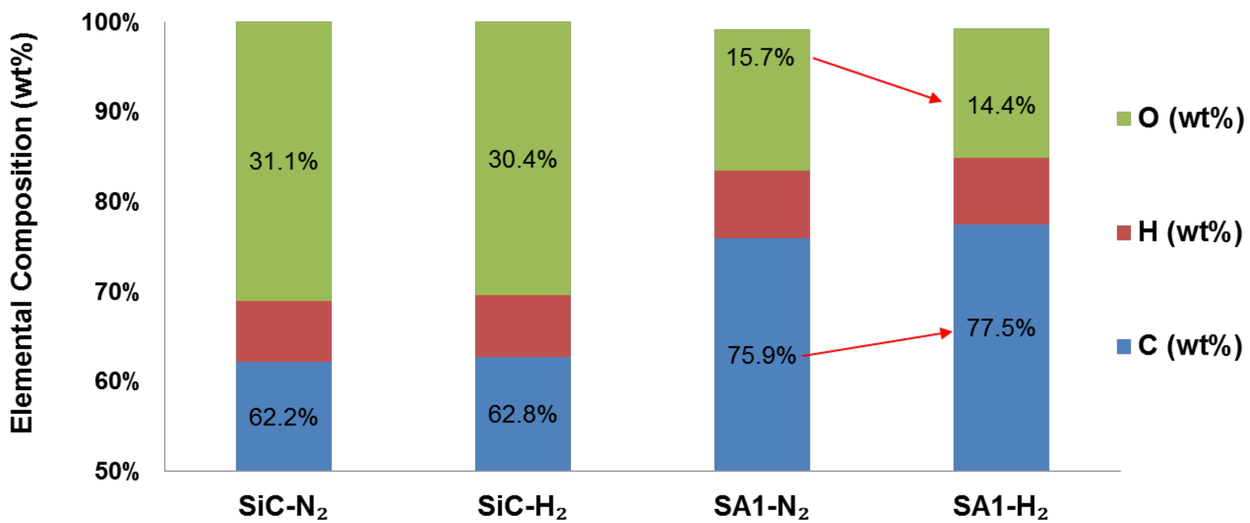


Effect of hydrogen atmosphere

Co-feeding hydrogen reduces solids formation and increases organic liquid yield

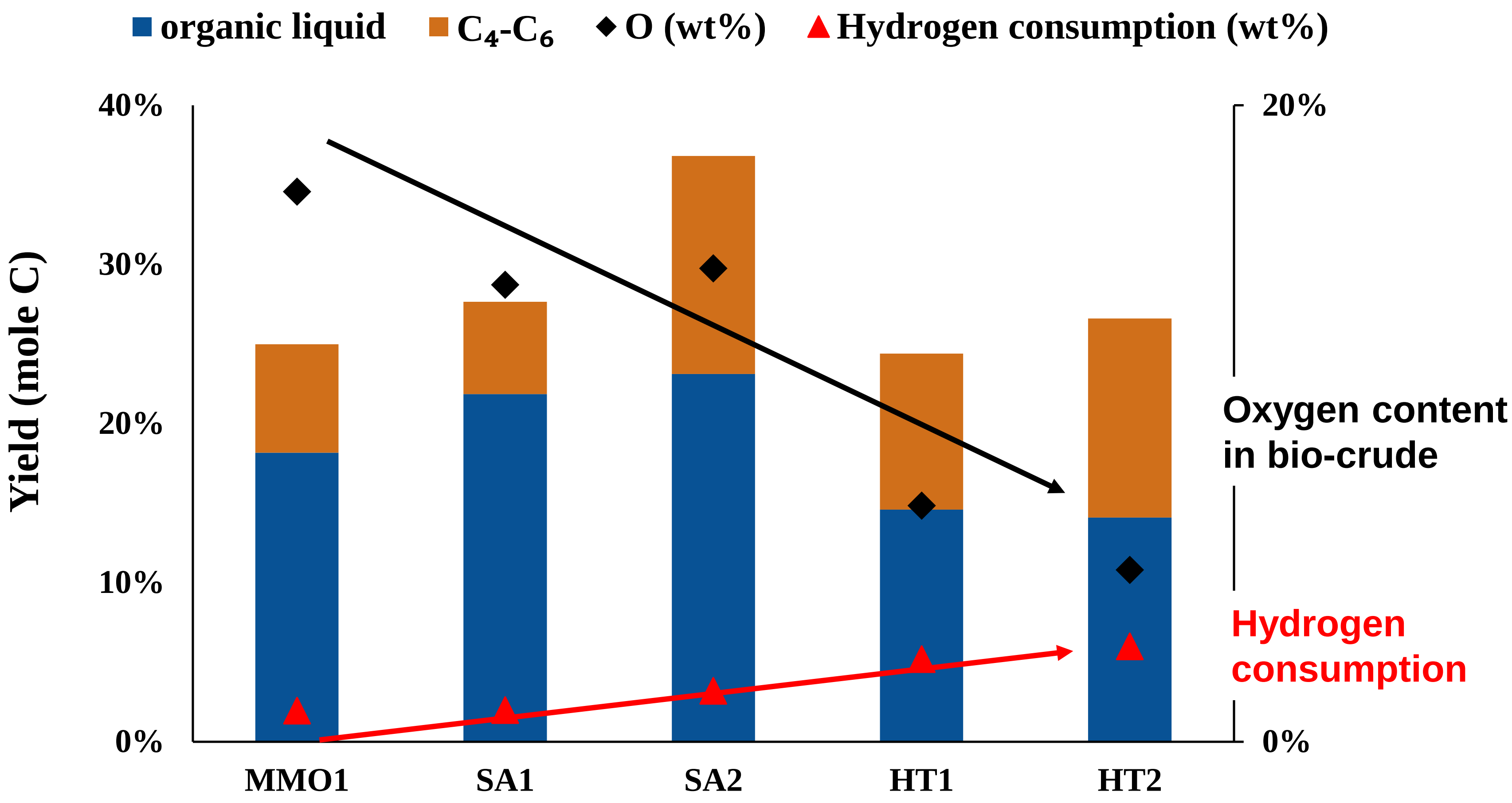


Co-feeding hydrogen decreased oxygen content in the organic bio-crude



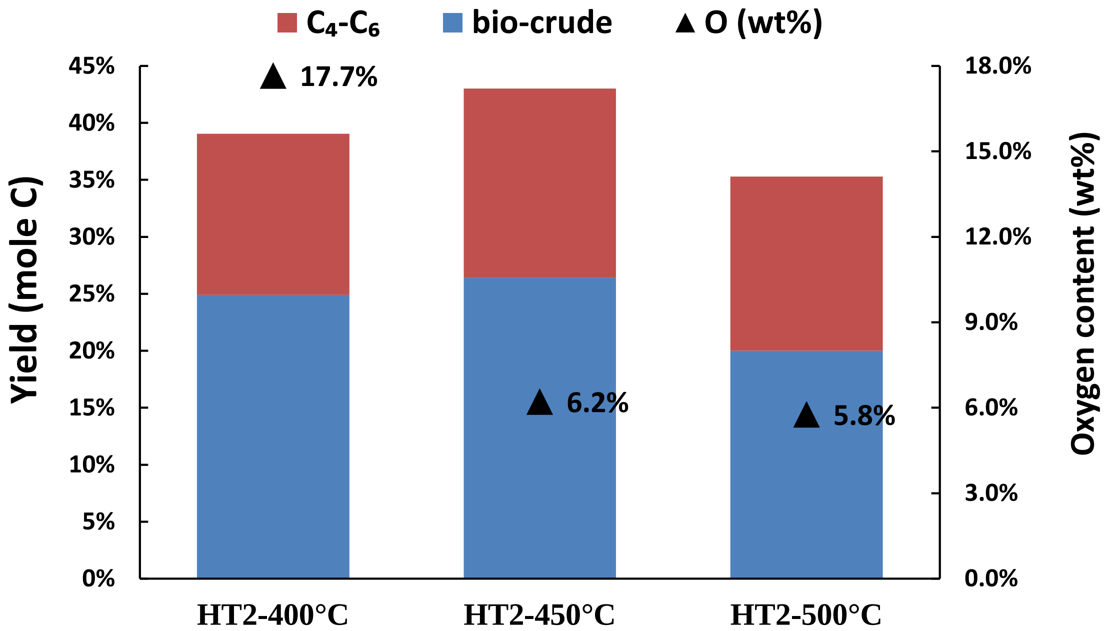
Reaction conditions: **500ºC**; 2:1 SiC and catalyst (SA-1) to biomass ratio; 12 SLPM gas flow rate (100% N_2 and 60% H_2 in N_2)

Catalyst Screening – oxygen content and hydrogen consumption



- Correlation of oxygen content and hydrogen consumption
- HT2 bio-crude contains lowest oxygen content

Influence of Process Conditions



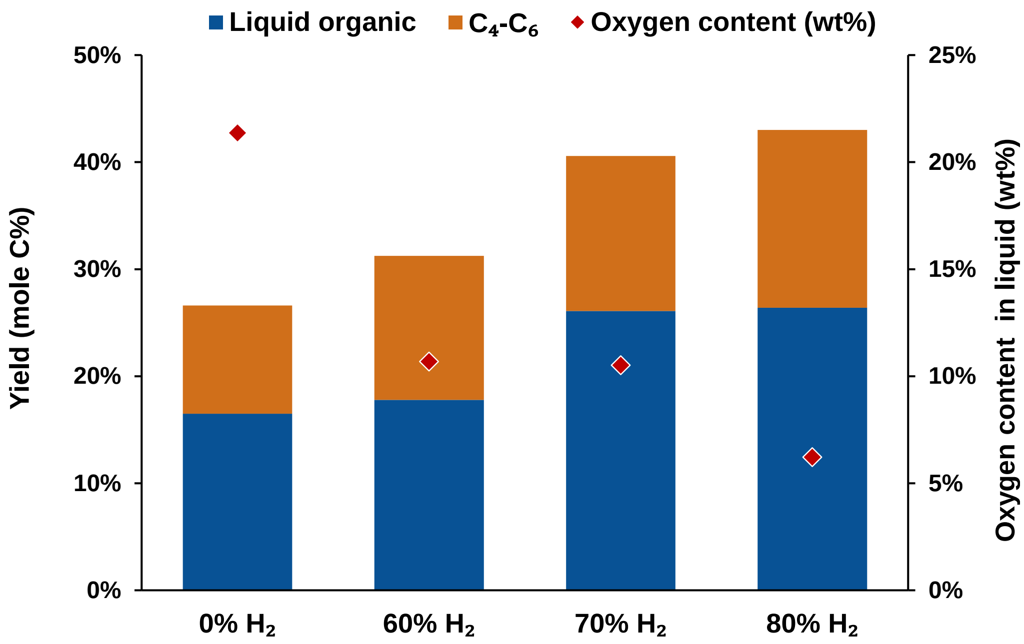
High temperature (500^oC)

Lower solids yield and higher gas yield

- More light gases, especially methane, indicates over-cracking
- Lower C_4^+ organics yield

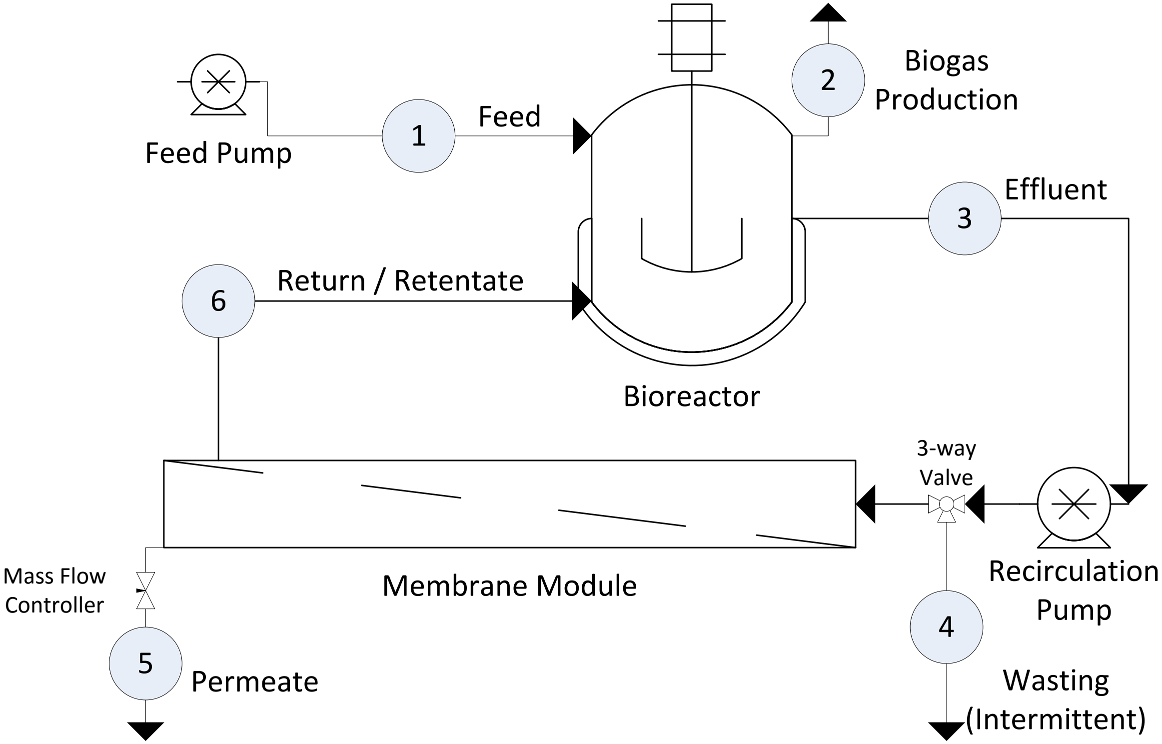
450^oC seems optimal for maximizing deoxygenation and minimizing cracking

Higher hydrogen concentration seems to inhibit coking and increase organic liquid yield while decreasing bio-crude oxygen content



2 – Approach (Technical) Improving carbon efficiency

Determine the technical feasibility of biologically converting carbon in the aqueous phase to methane using anaerobic digestion coupled with membrane distillation.

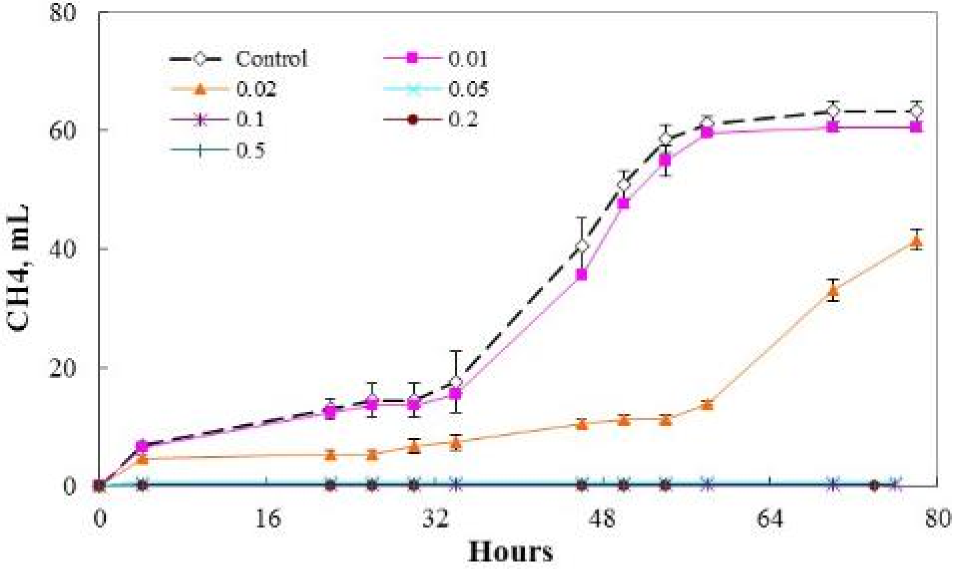


- Test aqueous phase samples for methane potential and toxicity with regards to digestion in bioreactors based on industry relevant test protocols
- Provide a preliminary assessment of treatment needs of water effluent from thermochemical biomass conversion processes and suggest treatment technology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

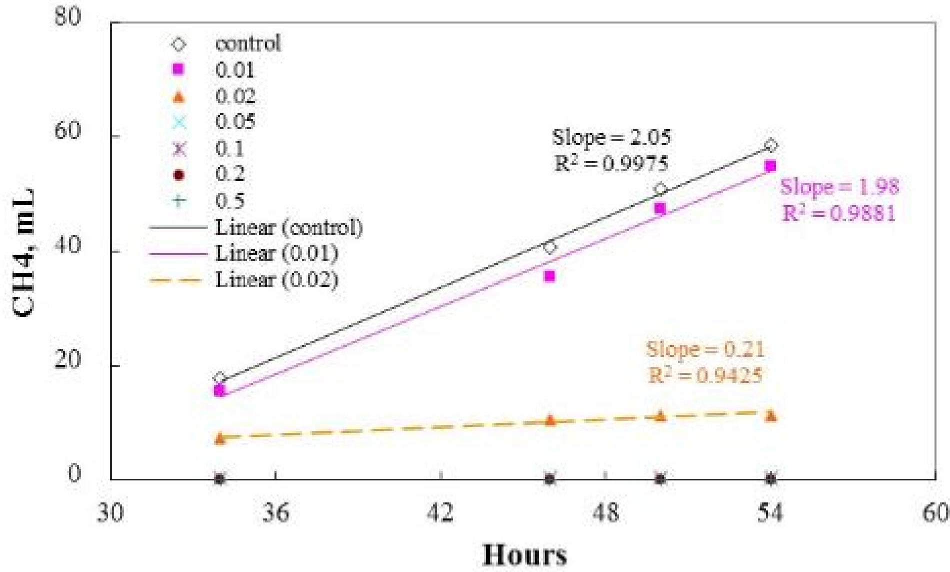
Toxicity and Biodegradability of Bio-crude

Prior to continuous operation of the anaerobic reactor, batch samples were analyzed for toxicity. Initially, the organics in the aqueous phase were very toxic and showed very poor biodegradability in un-acclimated microbial community

Cumulative methane production

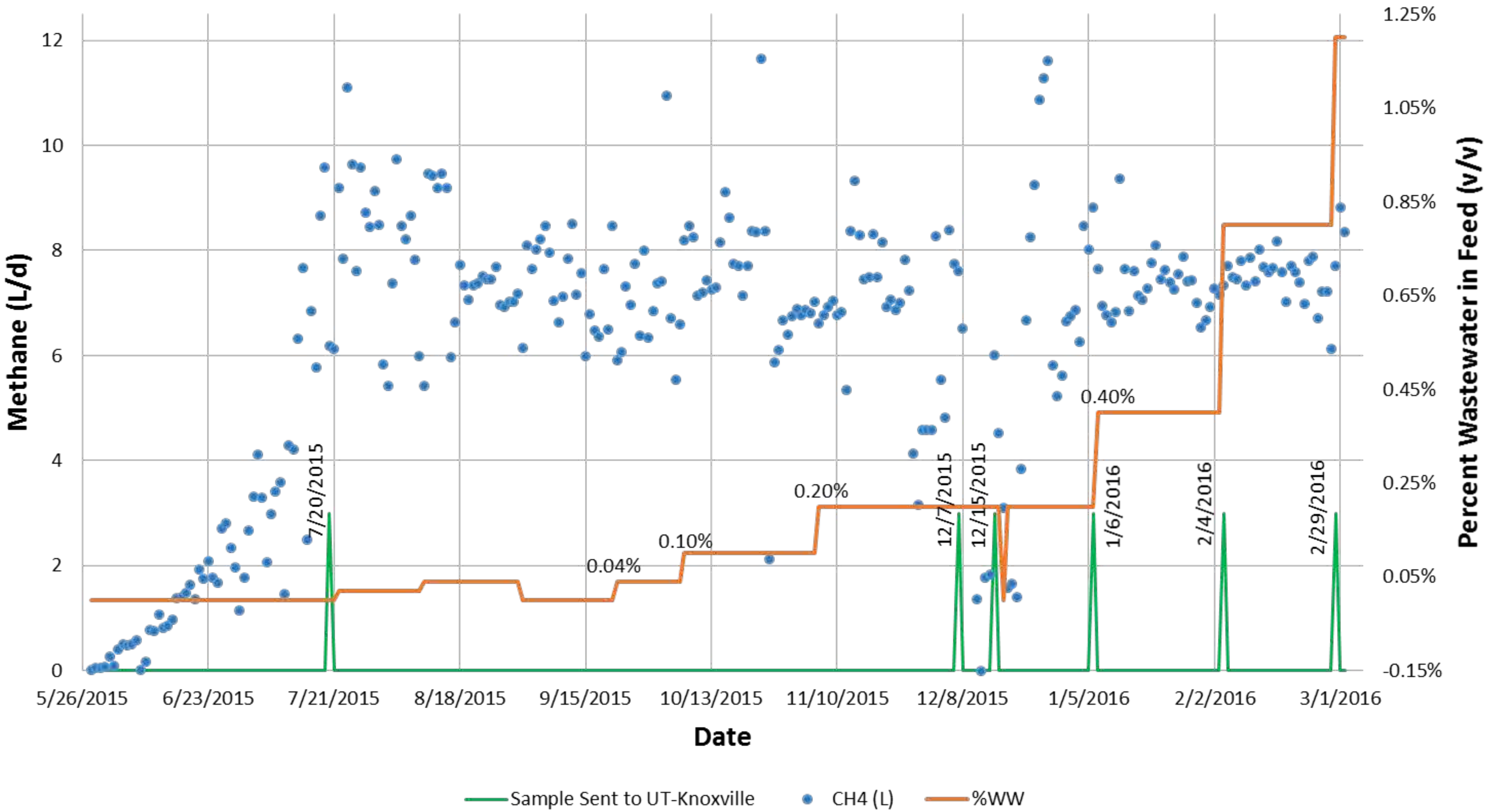


Methane production rates during the exponential phase



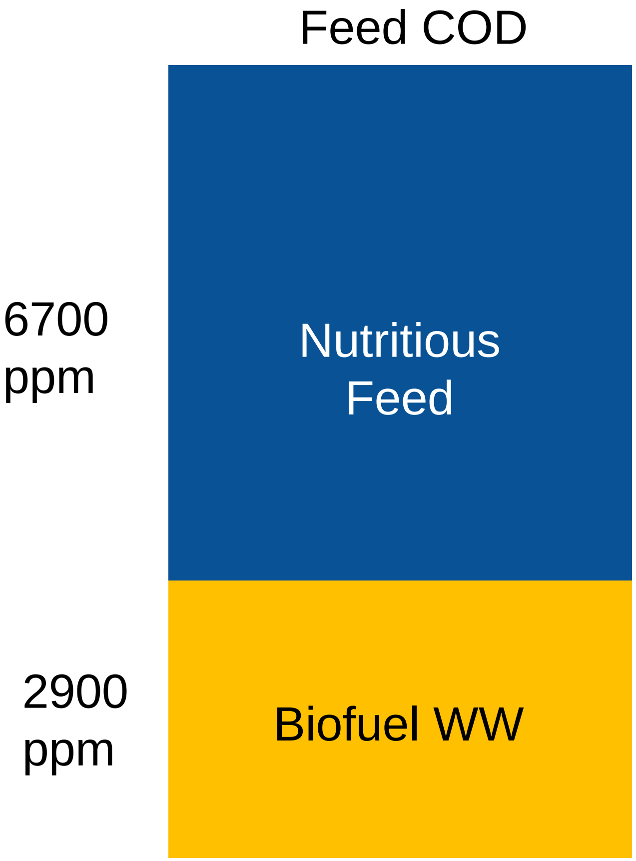
Bio-crude wastewater could cause severe inhibition in methanogenic biomass with loading rates as low as 0.02% and lead to complete inhibition of methanogenesis at loadings of 0.05% or above

Methane Production from Anaerobic Digestion

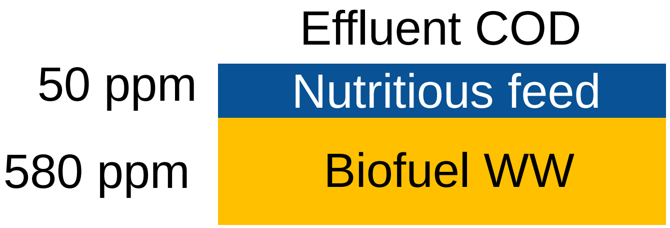


- The biofuel wastewater was added to the AnMBR's feed in steps to achieve a very slow acclimation.
- Currently, the biofuel WW is fed at 2% of the feed volume and the AnMBR is performing well
- Significant improvement compared to the initial results, which showed toxicity at 0.02% feed volume.

Biodegradability

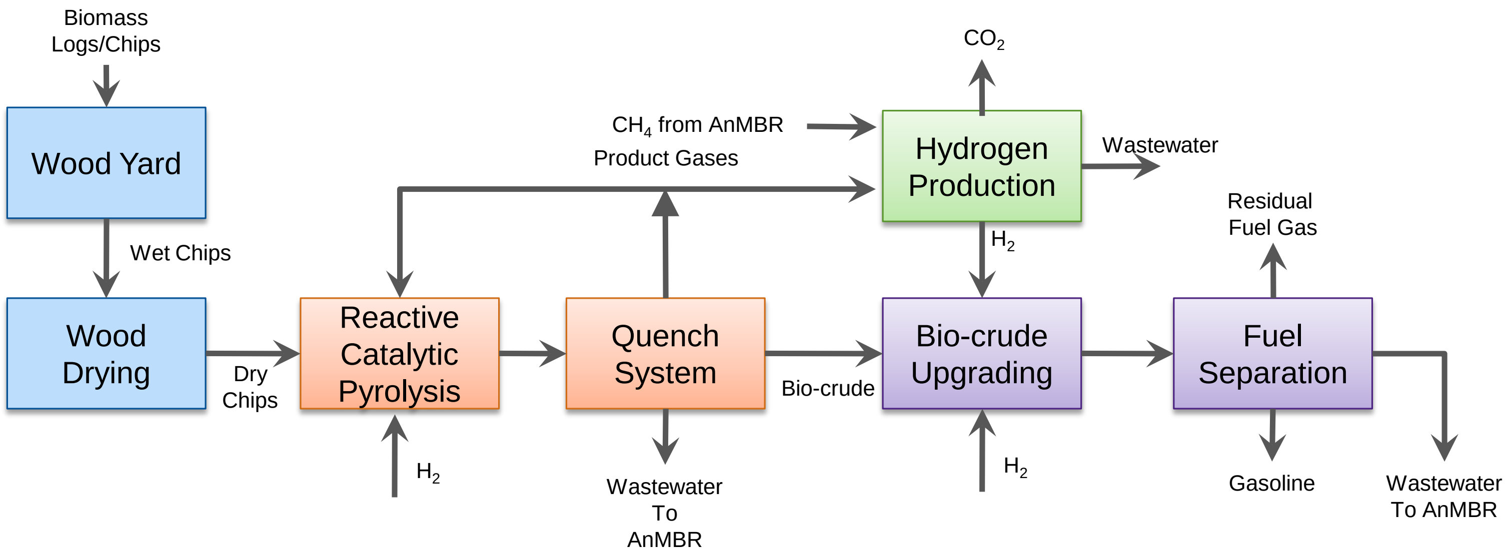


- 80% of wastewater COD in the feed is biodegraded
- 45% of the wastewater COD in the feed is converted to CH_4



The feed's nutritious components are generally biodegraded 95% or higher. The biofuel wastewater was much less biodegradable at the beginning, but it has now increased to 75-80% biodegradation.

Techno-economic Analysis: 2000 DTPD



Wood Yard and Drying

- Logs and chips storage
- Wood chipping
- Wood chips drying
- Dry chips storage

Biomass to Bio-crude

- Reactive Catalytic pyrolysis reactor
- Coolers and quench column
- Electrostatic precipitator
- Bio-crude/water separation

Bio-crude Upgrading

- Bio-crude pump and heater
- Hydrotreater
- Multi-stage H_2 compressor
- Gasoline/water separation

Hydrogen Production

- Steam reformer
- Shift reactor
- Amine scrubber
- Gas furnace

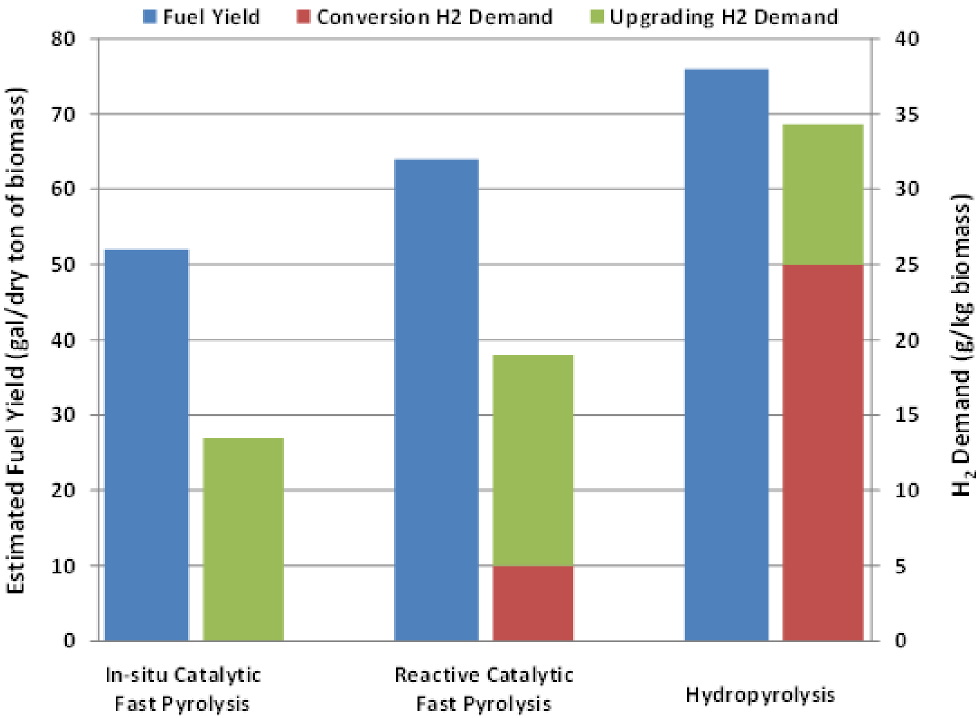
Capital Cost Scenarios	Without H_2 market	With H_2 market	Without H_2
	\$ 501MM	\$ 518MM	\$471MM

- When 7.5% of the pyrolysis gas is combusted for process heat, no additional methane from fossil based sources is required in the process.
- Hydrogen consumption in the pyrolysis reactor alone is 2.3 wt% of biomass fed
- Methane produced during RCFP was higher compared to CFP so more H_2 produced via steam methane reforming with water gas shift.

4 - Relevance

- Hydrogen in the pyrolysis reactor improves bio-crude yield and quality while reducing char and coke formation
- Carbon recovery from the aqueous phase maximizes the renewable carbon efficiency, provides a renewable hydrogen source for the process, and improves water quality so fresh water consumption is reduced.
- Overall hydrogen demand is comparable to other integrated thermochemical conversion processes
- Potential to reduce biofuels production cost with a novel, low-severity *in situ* CFP process to convert lignocellulosic biomass to hydrocarbon fuels.

- Fuel yields estimated from bio-crude yields measured in RTI reactor systems
- H_2 demand for RCFP and HYP measured
- H_2 demand for upgrading a function of bio-crude oxygen content
    - Measured for CFP and calculated for RCFP and HYP



5 - Future Work: Catalyst Screening and Scale-up

Catalyst Screening

- Complete studies on furfural conversion over selected catalysts in model compound reactor
- Evaluate the effect of feedstock on catalyst performance in micropyrolyzer
- Optimize process conditions for down-selected catalysts identified in Task 1
  - Temperature
  - Hydrogen concentration
- Detailed study on catalyst deactivation and hydrogen utilization to maximize carbon recovery in and minimize oxygen content of bio-crude
- Detailed characterization of aqueous product to determine effect on carbon recovery

Catalyst Scale-up

- Work with catalyst suppliers to produce at least 200-kg of fluidizable, attrition resistant catalyst for pilot plant tests
  - Develop formulations at RTI for transfer to partners
  - Verify performance in laboratory fluidized bed reactor

5 - Future Work: Aqueous Phase Carbon Recovery

Continue development of AnMBR technology to biologically convert aqueous phase carbon into methane. Evaluate the impact of various pretreatment, process modification, and additive options to enhance methane production to its highest potential.

- Biochemical Methane Potential (BMP) as a function of aqueous-phase loading (e.g., over 30-day duration) using respirometry
- Characterize bacteria, archaea, and fungi population in the biomass by DNA analysis
- Evaluate pretreatment approaches (UV, sonication, and ozone) for degrading the most inhibitory organics to enhance anaerobic digestion
- Develop empirical model based on experimental data to predict AnMBR performance
- Estimate capital and operating costs of AnMBR process with integrated feed pretreatment for making CH_4 from RCFP aqueous phase
- Estimate carbon and water footprints and air (GHG) emissions of AnMBR process, relative to conventional wastewater handling and treatment practices, for the project’s aqueous phase

5 - Future Work: Process Development

Pilot-scale (1 TPD) catalytic biomass pyrolysis with added hydrogen at atmospheric pressure to produce a bio-crude with less than 8 wt% oxygen with at least 42% carbon efficiency. Updated TEA and LCA.

RCFP Bio-crude and aqueous phase production

- Pilot plant reactor modifications to safely operate with hydrogen
  - Complete safety review
  - Approval from RTI's Risk Management Board
- Produce up to 10 gallon of bio-crude for future upgrading study
- Produce up to 25 gallon of aqueous for carbon recovery in AnMBR

RCFP Bio-crude upgrading

- Validate RCFP bio-crude upgrading to gasoline- and diesel- range hydrocarbons
- Operate hydrotreating unit at RTI with RCFP bio-crude for up to 100 hours
- Determine hydrocarbon yields, hydrogen consumption and product split
- Compare hydrotreating study using RCFP bio-crude and CFP bio-crude

Techno-economic Analysis and Life-cycle Assessment

- *Update integrated process models*
  - *bio-crude yields from pilot plant tests*
  - *bio-crude upgrading results*
  - *carbon recovery from the aqueous phases.*
- *The integrated process will have a minimum 50% carbon efficiency target and a $3.00/gal biofuel production cost target.*

Summary

- Improve hydrogen utilization and carbon recovery in a direct biomass liquefaction technology where hydrogen is added to an atmospheric catalytic biomass pyrolysis process and aqueous phase carbon is converted to methane via anaerobic digestion.
- Catalyst development includes screening at multiple scales to identify catalysts that maximize biocrude yield and minimize biocrude oxygen content.
- Evaluating the technical feasibility of biologically converting carbon in the aqueous phase to methane using anaerobic digestion.
- Experimental results inform TEA and LCA to determine technical and economic feasibility and environmental sustainability of the integrated process
- Go/NoGo Decision Criteria met – project is proceeding into Budget Period 2
- Future work includes catalyst scale up, bio-crude production and upgrading, and continued optimization of aqueous phase carbon conversion.
- Final results will be used to evaluate TEA and LCA of novel, integrated advanced biofuels process

Acknowledgements

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RTI Contributors

- David C. Dayton (PI)
- Young Chul Choi
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- Lora Toy

Haldor Topsoe

- Glen Hytoft
- Jostein Gabrielsen
- Sylvain Verdier

Veolia

- Herve Buisson

Additional Information - Publications

Publications

- Dayton, D.C., O.D. Mante, J.E. Peters, and K. Wang *Chapter 5 - Catalytic Biomass Pyrolysis with Reactive Gases* in *Fast Pyrolysis of Biomass*. 2017, Royal Society of Chemistry.
- Dayton, D. C.; Hlebak, J.; Carpenter, J. R.; Wang, K. G.; Mante, O. D.; Peters, J. E., Biomass Hydropyrolysis in a Fluidized Bed Reactor. Energy & Fuels 2016, 30 (6), 4879-4887
- Black, B. A.; Michener, W. E.; Ramirez, K. J.; Biddy, M. J.; Knott, B. C.; Jarvis, M. W.; Olstad, J.; Mante, O. D.; Dayton, D. C.; Beckham, G. T., Aqueous Stream Characterization from Biomass Fast Pyrolysis and Catalytic Fast Pyrolysis. ACS Sustainable Chemistry & Engineering 2016, 4 (12), 6815-6827
- Peters, J. E.; Carpenter, J. R.; Dayton, D. C., Anisole and Guaiacol Hydrodeoxygenation Reaction Pathways over Selected Catalysts. Energy & Fuels 2015, 29 (2), 909-916

Additional Information - Presentations

Presentations

- K. Wang, D. Dayton, O. Mante, J. Peters. Reactive Catalytic Fast Pyrolysis of Biomass to Produce Hydrocarbon-rich Bio-crude, TCS2016, Chapel Hill, NC. Nov.2016.
- K. Wang, D. Dayton, O. Mante, J. Peters. Reactive Catalytic Fast Pyrolysis of Biomass to Produce High-quality Bio-crude, TCBiomass 2015, Chicago, IL. Nov.2015.
- M. Von Holle, “Small Scale Catalyst Testing with Biomass for Advanced Biofuels Technology Development.” Poster Presentation, TCBiomass 2013 September 3-6, 2013 Chicago, IL.
- J. Carpenter, “Low Oxygen-Content Bio-Crude via Single Step Hydropyrolysis.” Poster Presentation, TCBiomass 2013 September 3-6, 2013 Chicago, IL.
- J. Hlebak, “Experimental Capabilities at RTI International to Support R&D for Direct Biomass Liquefaction Pathways.” Poster Presentation, TCBiomass 2013 September 3-6, 2013 Chicago, IL.
- J. Peters, “Deoxygenation Chemistry of Bio-oil Model Compounds with Selected Catalysts.” Poster Presentation, TCBiomass 2013 September 3-6, 2013 Chicago, IL.

Responses to Previous Reviewers' Comments

Overall Impressions

- Inclusion of Veolia to avoid reinventing past developments is a good idea. Process will likely evolve to many more necessary steps and hence capital complexity.
- This is an interesting new concept to achieve high carbon conversions to fuel. Historically, the in-situ catalytic pyrolysis has low carbon conversion to fuels, so the project needs to maintain the goal of high yields as a primary focus.
- The project involves new catalyst and novel carbon recovery technology. It needs a high level TEA analysis at this point to identify and make sure that the team is working on the critical issues. The project team may want to operate the hydropyrolysis unit at higher pressures than atmospheric to provide an economic driving force and unit sizing through the integrated process.
- The economic impact of this novel approach needs to be assessed to determine how much economic impact it can make.

PI Response to Reviewer Comments

- By the end of the first budget period, a bio-crude intermediate with less than 10 wt% oxygen will be produced and the potential to recover 20% of the aqueous phase carbon as methane will be demonstrated in laboratory reactor systems. These results will be used to 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. The process model will be the basis for a preliminary techno-economic analysis to estimate advanced biofuel production cost for the integrated process.