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

Liquefaction of Forest Biomass to “Drop-In” Hydrocarbon Fuels

Contract DE-EE0005974

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Presenter: Lysle E. Whitmer
Project Personnel: Taylor C. Schulz, Martin R. Haverly, Ryan G. Smith
Principal Investigator: Robert C. Brown
Iowa State University

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Goal Statement

- **Demonstrate solvent liquefaction as viable path to stable intermediates for subsequent upgrading to fuel blendstocks**
- **Funding Opportunity Announcement DE-FOA-00005100**
  - R&D, demonstration, and life-cycle evaluation/optimization of technologies for biofuels and bio-based product generation
- Supports goal of cost-effective biomass liquefaction to intermediates suitable for further upgrading to hydrocarbon transportation fuels

Quad Chart Overview

Timeline

- Project Start: Jan. 1, 2013
- Project End: June. 30, 2017
- Percent Complete: 94%

Budget

	Total Costs FY 10 – FY 14	FY 15 Costs	FY 16 Costs	Total Planned Funding (FY 17- Project End Date)
DOE Funded*	0.71M	0.79 M	0.56 M	1.44M
Project Cost Share*	0.64	0.24 M	0	0

*Provided by Chevron Technology Ventures – $400k for sustainability study, $475k for pilot plant engineering support

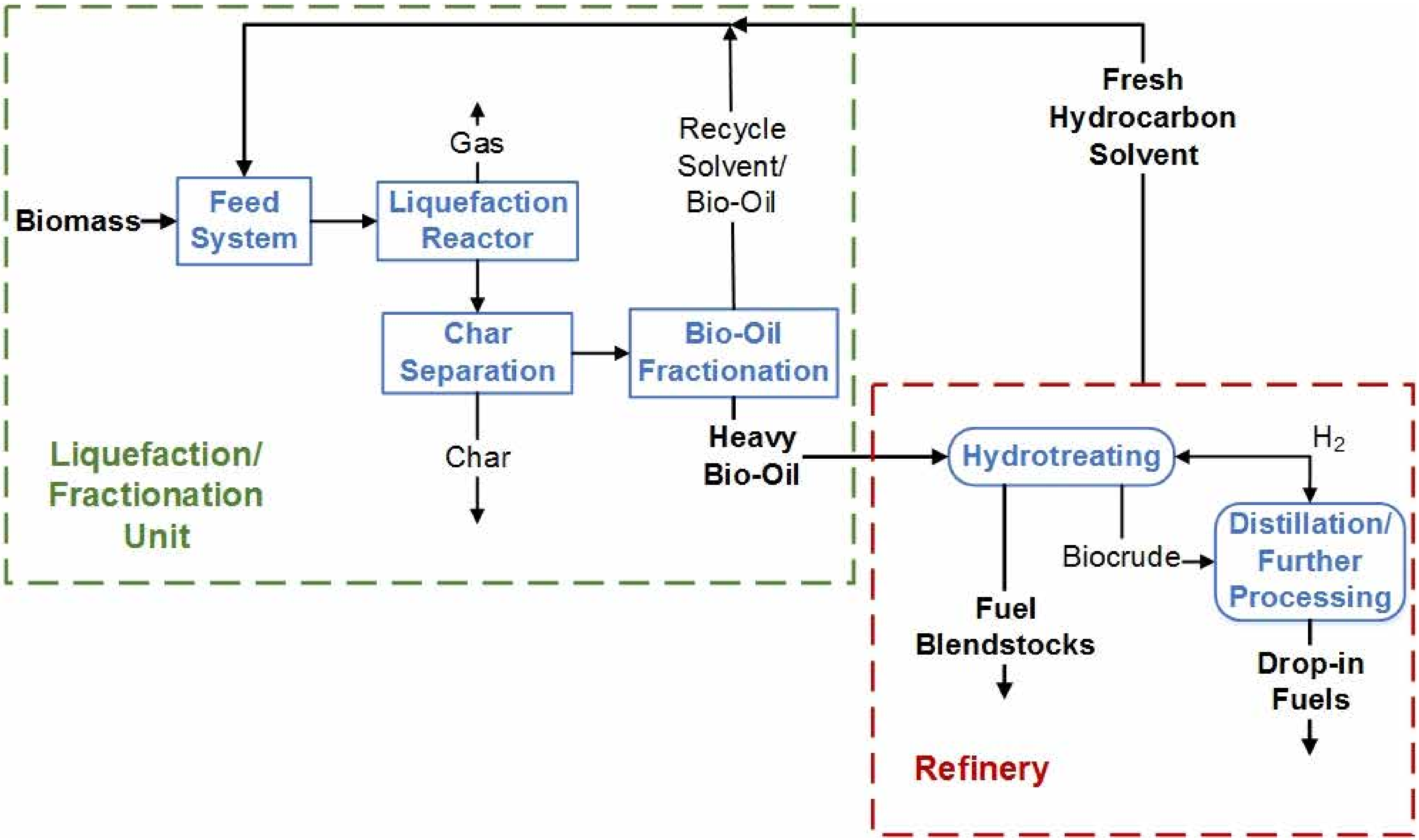
Barriers

- Ct-F: Efficient High-Temperature Deconstruction to Intermediates

Partners

- Chevron Technology Ventures (CTV) has assumed contractual obligations for the project from Catchlight Energy
- CTV received 40% of DOE funding, providing 100% of the cost-share
- As part of CTV cost share, Weyerhaeuser and Mississippi State University contracted to study impact of feedstock production of forest biodiversity

Project Overview



Project Overview

- **Project Goals**
  - Pilot-scale testing for Chevron's solvent liquefaction process with direct solvent/bio-oil recycle
  - Generate stable, deoxygenated bio-oil
  - Explore hydroprocessing conditions for bio-oil upgrading to refinery-compatible biocrude and fuel blendstocks
  - Develop demonstration plant design package and TEA
  - Elucidate impact of biomass production on forest ecosystems
- **Technical Barrier Addressed:** Ct-F: Efficient High-Temperature Deconstruction to Intermediates

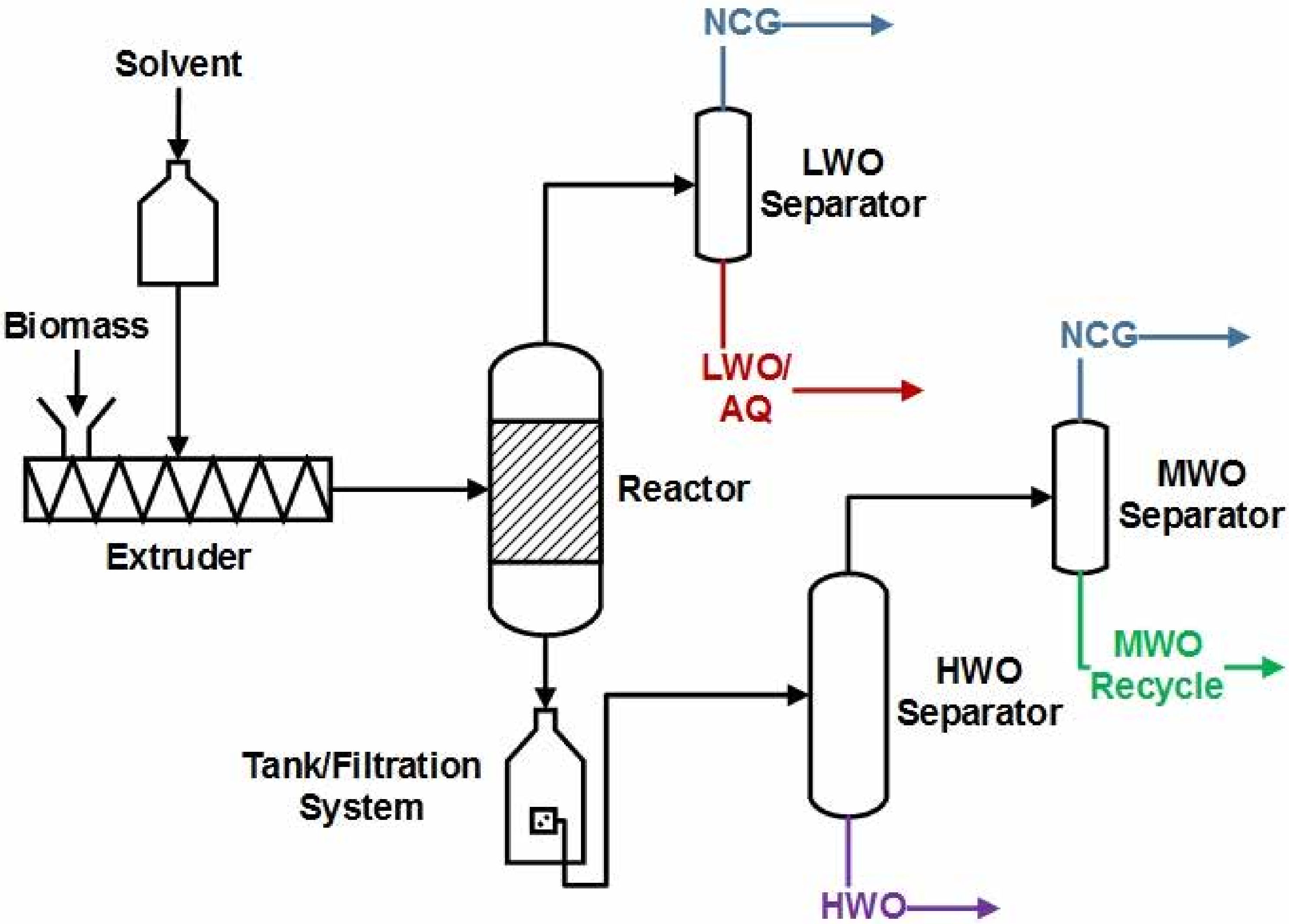
Technical Approach

- **Proof of concept testing using continuous liquefaction unit**
  - Biomass liquefaction at feed rates ~1 kg/h
  - Continuous bio-oil product separation and solvent recycle
- Determine hydroprocessing catalysts and optimal process conditions utilizing bench-scale fixed-bed micro-reactors
- **Operability and product quality targets**
  - 8 h of continuous liquefaction unit operation
  - Bio-oil yield >50 wt. % and <20 wt. % oxygen
  - 15 d bio-oil hydroprocessing to biocrude (<2 wt. % oxygen)

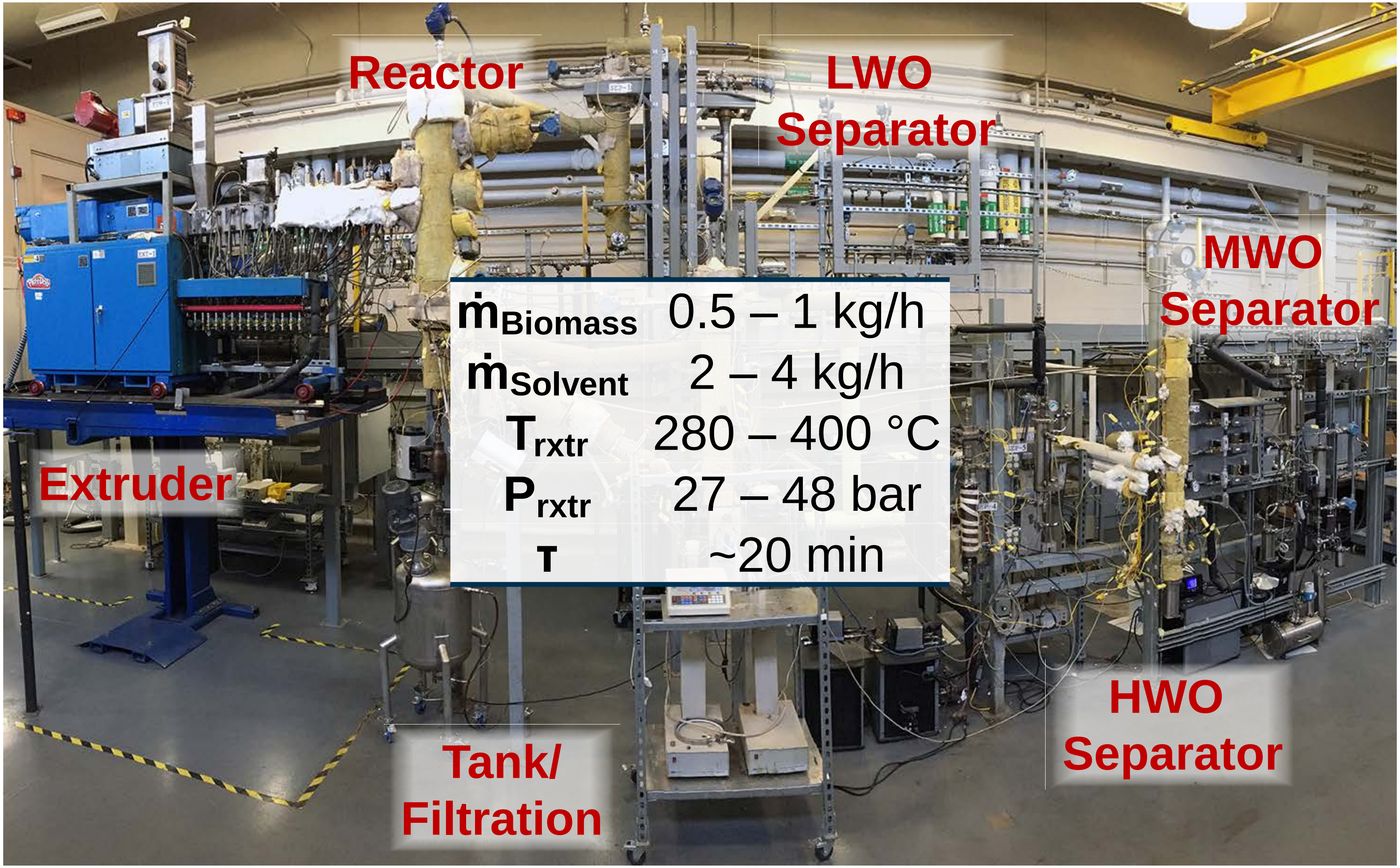
Management Approach

- **Critical Success Factor and Potential Challenges**
  - Production of thermally stable, low oxygen bio-oil
  - Continuous operation of key unit operations
    - Solids removal, bio-oil fractionation, and solvent recycle
    - Cost-effective hydroprocessing to biocrude
    - Sustainable growth/harvest of low-cost biomass
- **Project Approach**
  - Integrate Iowa State engineers with thermochemical pilot plant expertise and CTV personnel with solvent liquefaction experience, hydroprocessing, PHA, TEA

Once-Through Biomass Processing

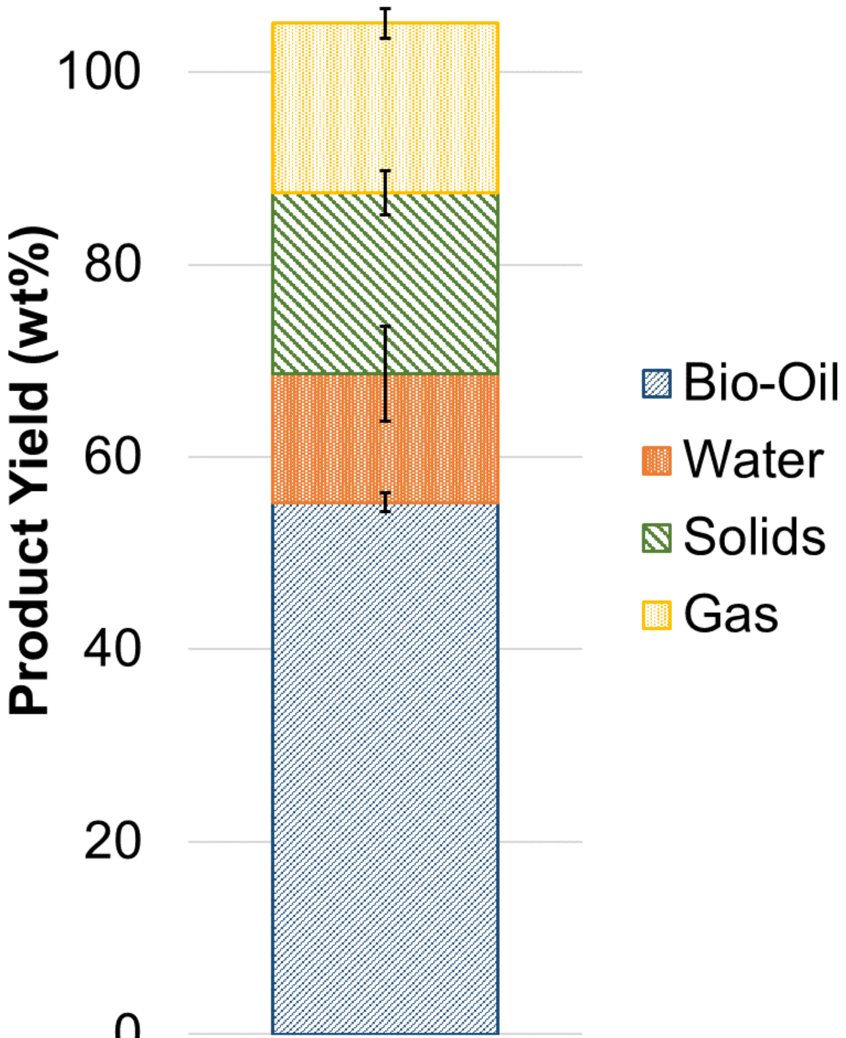


SCLU and Process Conditions



$\dot{m}_{Biomass}$	0.5 – 1 kg/h
$\dot{m}_{Solvent}$	2 – 4 kg/h
T_{rxtr}	280 – 400 °C
P_{rxtr}	27 – 48 bar
τ	~20 min

Hydrocarbon Solvent Processing



*Average of three runs.

- Three continuous liquefaction experiments with fractionation for >4 h
- Retention of char particles in mixing tank via barrier filtration
- Sufficient selectivity to MWO to close recycle loop at 25% makeup solvent – more expensive test case

Liquefaction Metrics	
Bio-Oil Yield (wt. %)[a]	55.3

[a]Solvent-less, dry biomass basis

Hydrocarbon Bio-Oil Analysis

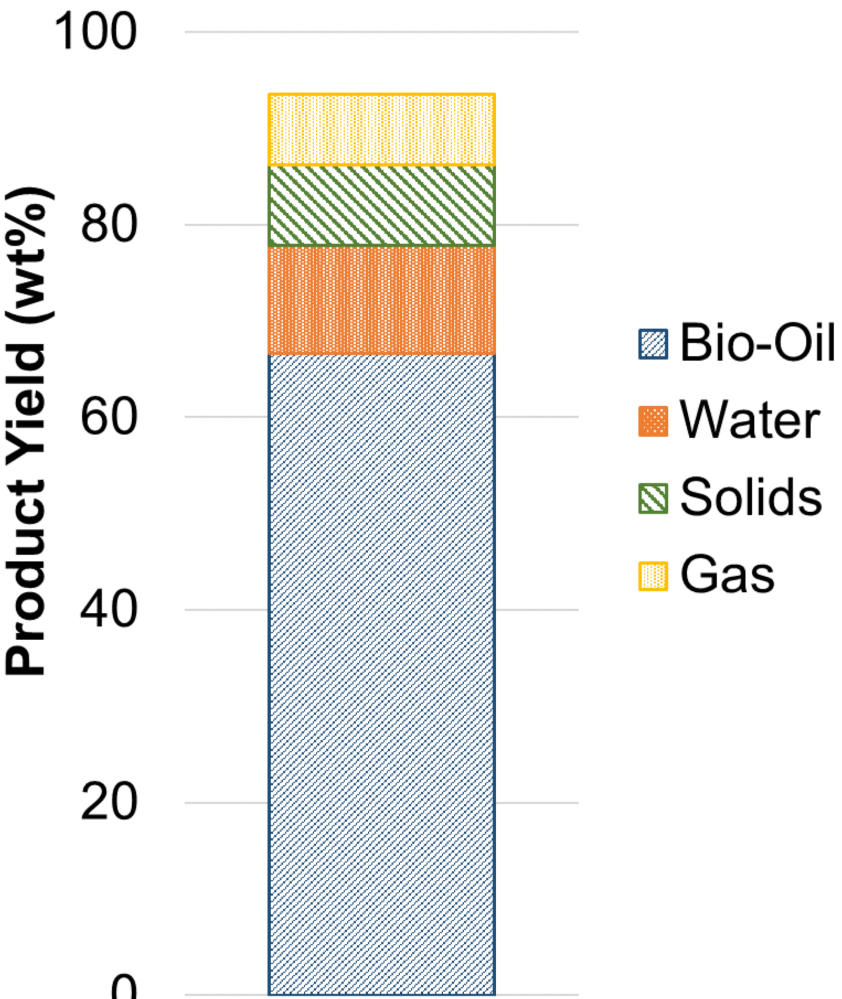
Sample	LWO	MWO	HWO
Moisture (wt. %)	1.08	0.76	0.914
Elemental Analysis (wt. %, MF/AF)			
C	86.4	86.7	88.0
H	7.80	7.25	6.93
O[a]	5.43	5.75	4.69

[a]Determined by difference

- MWO mix of hydrocarbon solvent, phenolic monomers/oligomers, and biopolymers
- HWO viscous liquid at room temperature

MWO Product **HWO Product**

Phenolic Solvent Processing



*Based on single run.

- Solvent mix simulates expected composition for full recycle operation with 5% makeup solvent
- Phenolic solvent generated smaller char particles requiring offline separation
- Insufficient selectivity to MWO to close recycle loop at these conditions

Liquefaction Metrics	
Bio-Oil Yield (wt. %)[a]	66.7

[a]Solvent-less, dry biomass basis

Phenolic Bio-Oil Analysis

Sample	LWO	MWO	HWO
Moisture (wt. %)	1.48	0.208	2.53
Elemental Analysis (wt. %, MF/AF)			
C	73.0	73.3	83.7
H	6.42	5.98	5.76
O[a]	20.2	20.3	10.3

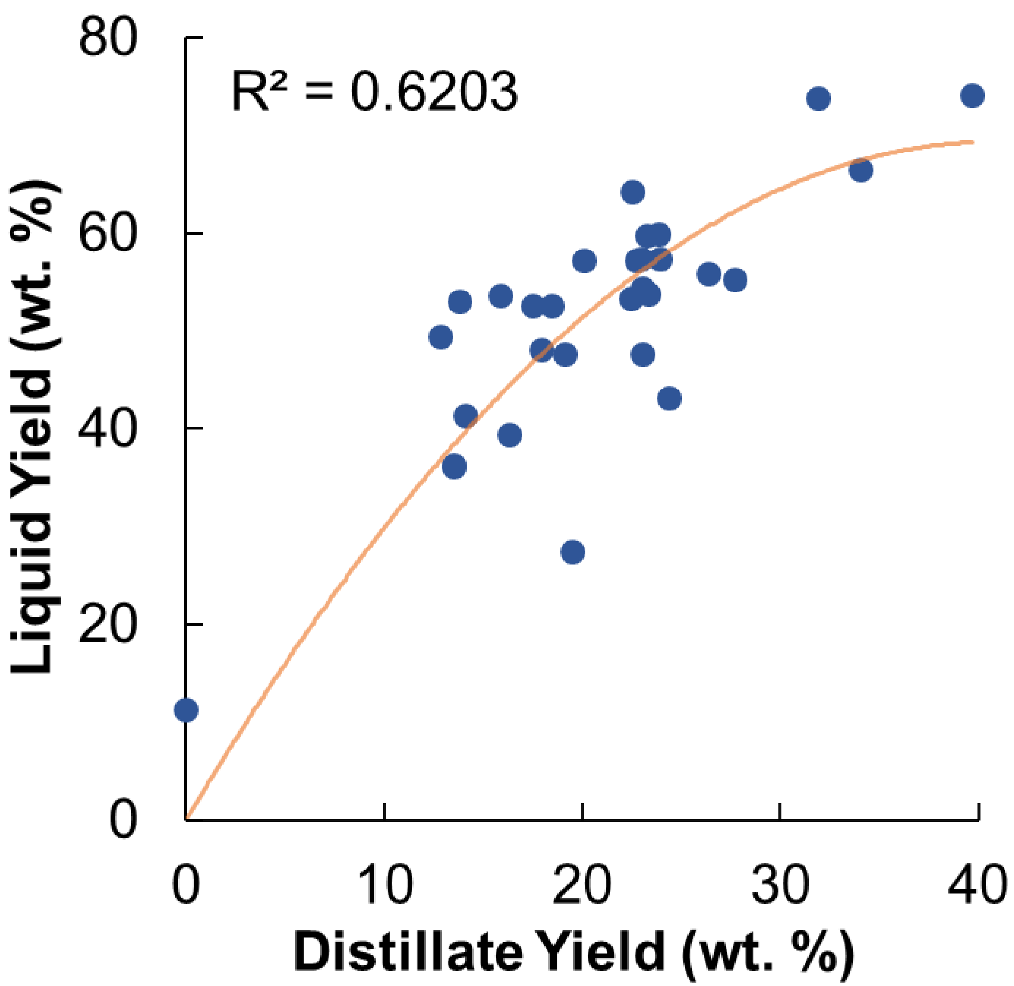
[a]Determined by difference

- MWO mix of phenolic monomers/oligomers and biopolymers
- HWO solid at room temperature with melt point ~80 °C

HWO Product

Batch Liquefaction of Lignin

- Valorization of ethanol plant waste lignin (98,000 tn/y) via liquefaction
- High yield of distillable liquid product containing phenolic monomers suitable for recycle
- Potential use of ethanol as liquefaction solvent



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[Haverly, M.R.; Okoren, K.V.; and Brown, R.C. (2017) *Optimization of phenolic monomer production from solvent liquefaction of lignin.* Manuscript in preparation.]

Relevance

- **Produces deoxygenated, stable bio-oil for upgrading to drop-in transportation fuels (gas/diesel/jet) at <$3/gal**
  - Produce clean, low-cost bio-oil for integration into biorefinery
  - Develop cost-effective hydroprocessing conditions
  - Identify large, sustainable supply of high quality biomass
- Improves commercial prospects of biomass-based transportation fuels
- Continuous bio-oil production with solvent recycle and solids removal critical to technology feasibility

Future Work

- **Explore hydroprocessing catalysts/conditions for bio-oil upgrading**
- **Develop TEA based on results using hydrocarbon and phenolic solvents**
- **Demonstration scale design package**
- **Assess viability of using lignin feedstock**
  - What liquid yields will be achieved in pilot unit?
  - Is solids separation efficient at pilot scale?
  - Will fractionation occur with same product selectivity under similar conditions?

Summary

- **Goal:**
  - Demonstrate pine solvent liquefaction means of producing stable, low oxygen (<20 wt. %) bio-oil for upgrading
- **Approach:**
  - Integrate ISU expertise in pilot-scale thermochemical conversion and Chevron experience in solvent liquefaction, hydroprocessing and TEA
- **Achievements:**
  - Pine liquefaction in hydrocarbon/phenolic solvents, solids separation, and bio-oil fractionation to low-oxygen bio-oil with yield >50 wt. % and high selectivity to MWO

Summary

- **Relevance:**
  - Continuously produces deoxygenated, stable bio-oil for upgrading to drop-in transportation fuels (gas/diesel/jet) at <$3/gal, helping to meet RFS benchmarks
- **Future Work:**
  - Determine hydroprocessing catalysts/optimal conditions and assess process economic viability based on experimental results
  - Explore viability of lignin as alternative feedstock for liquefaction/fractionation process

Publications

- **Papers**
  - Haverly, M. R. , Schulz, T. C. , Whitmer, L. E. , Friend, A. J. , Funkhouser, J. M. , Smith, R. G. , and Brown, R. C. Continuous solvent liquefaction of biomass in a hydrocarbon solvent. In preparation.
  - Haverly, M.R.; Okoren, K.V.; and Brown, R.C. (2017) *Optimization of phenolic monomer production from solvent liquefaction of lignin.* In preparation.
  - Loman, Z. G. , S. K. Riffell, B. Wheat, D. A. Miller, J. A. Martin and F. J. Villela. *In Press* (tentative acceptance). Breeding bird community response to establishing intercropped switchgrass in intensively-managed pine stands. Biomass & Bioenergy.
  - Loman, Z. G. , S. K. Riffell, B. Wheat, D. A. Miller, J. A. Martin and F. J. Villela. Bird community response to establishing intercropped switchgrass in intensively-managed pine stands. Biomass & Bioenergy, in review.
  - Loman, Z. G., S. K. Riffell, D. A. Miller, J. A. Martin and F. J. Villela. 2013. Site preparation for switchgrass intercropping in loblolly pine plantations reduces retained trees and snags, but maintains downed woody debris. Forestry 86: 353-360.

- **Presentations**
  - Schulz, T. C. , Haverly, M. R. , Whitmer, L. E. , Friend, A. J. , Funkhouser, J. M. , Smith, R. G. , and Brown, R. C. 2016. Continuous Pilot-Scale Loblolly Pine Liquefaction to a Partially Deoxygenated Bio-Oil. Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products, Chapel Hill, NC.
  - Loman, Z. G., S. K. Riffell and D. A. Miller. 2013. Effects of switchgrass intercropping in early successional pine plantations on bird communities. American Ornithologists' Union-Cooper Ornithological Society Joint Meeting, Chicago, Illinois.
  - Loman, Z. G., S. K. Riffell, J. Martin and D. A. Miller. 2013. Effects of switchgrass intercropping in early successional pine plantations on bird communities. Mississippi Chapter of The Wildlife Society, Jackson, MS.
  - Wheat, B. R., Z. G. Loman, S. K. Riffell, S. Demarais and D. A. Miller. 2013. Biomass and deer forage response to intercropping switchgrass as bioenergy feedstock in Mississippi. 67th Annual Conference of the Southeastern Association of Fish and Wildlife Agencies, Oklahoma City, Oklahoma.
  - Wheat, B. R., Z. G. Loman, S. K. Riffell, S. Demarais and D. A. Miller. 2013. Biomass and deer forage response to intercropping switchgrass as bioenergy feedstock in Mississippi. Mississippi Chapter of The Wildlife Society, Jackson, MS.
  - Riffell, S., S. P. Rupp (Committee chair), J. Verschuyl, T. B. Wigley, L. Bies, A. Glaser, C. Kowaleski, T. McCoy, T. Rentz and J. Sibbing. 2013. Effects of bioenergy production on wildlife and wildlife habitat: an overview of the TWS Technical Review and implications for forestry in the Southeast. The Role of Natural Renewable Resources in Energy Sustainability and Global Warming Mitigation: A Symposium. Maroon Edition Event, Mississippi State, MS.