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DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

Mild Biomass Liquefaction Process for Economic Production of Stabilized Refinery-Ready Bio-oils

**March 23-27, 2015
Thermochemical Conversion**

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Goal Statement

- **Project Goal**

- Develop a mild thermochemical liquefaction process to convert woody biomass to stabilized refinery ready bio-oils.

- **Project Objectives**

- Develop process at laboratory scale.
- Discuss with refinery/industry to move the technology towards commercialization.

- **FOA: Bio-oil Stabilization and Commoditization (DOE-FOA-0000686)**

- Conduct R&D on conversion of high-impact biomass to bio-oil using thermochemical liquefaction technologies.
- Goal: Utilize bio-oil within a petroleum refinery to leverage its existing capital for further processing to final fuels.

- **Project Goals/Objectives Support**

- The solvent liquefaction pathway.
- BETO's objectives to accelerate the production of transportation fuels from high impact biomass.

Quad Chart Overview

Timeline

- Project start date: Jan. 2, 2013
- Project end date: Jun. 30, 2015
- Percent complete: 95%

Budget

	FY 13 Costs (\$K)	FY 14 Costs (\$K)	Total Planned Funding (FY 15- Project End Date) (\$K)
DOE Funded	302	227	125
Cost Share (SR)	270	0	0

Barriers

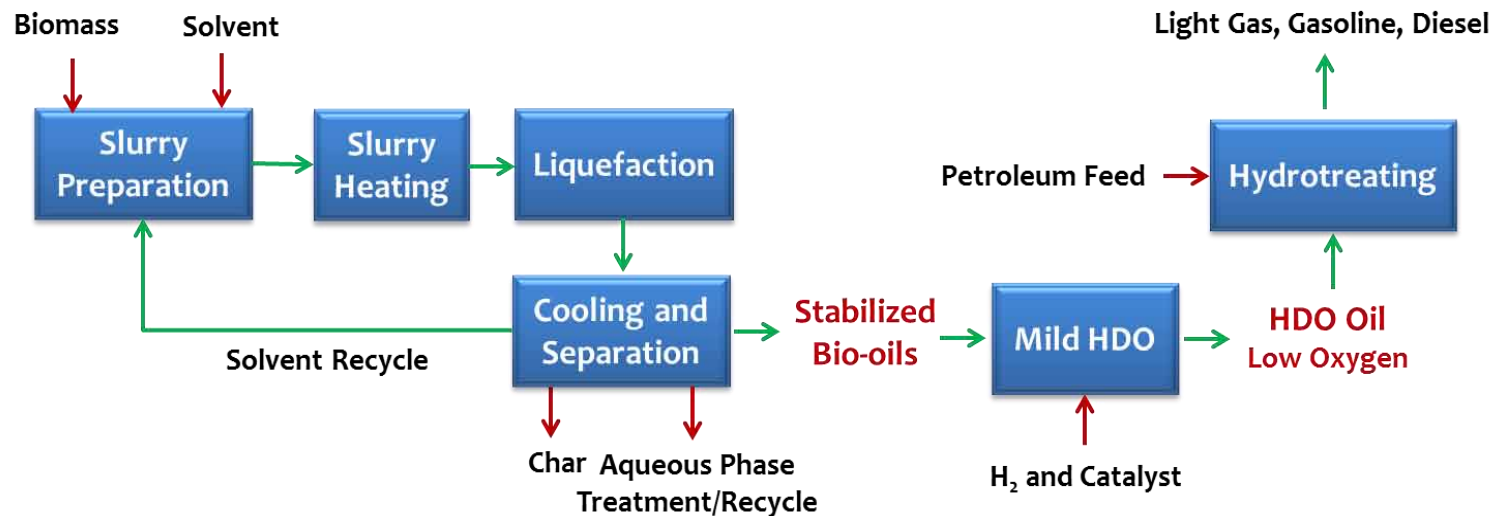
- Barriers addressed
 - **Tt-E.** Liquefaction of Biomass and Bio-Oil Stabilization
 - **Tt-G.** Fuel Synthesis and Upgrading

Partners & Roles

- **Southern Research** – Lead
- Dr. Eric Larson, Princeton University – TEA/LCA
- Catalyst Company – Hydrotreating catalyst supplier

1 - Project Overview

- The project uses a **methanol/H₂O** based solvent liquefaction process that operates under **mild conditions (< 300°C, <2000psi)** compared to hydrothermal liquefaction (**~370°C, 3000psi**) for transportation fuel production.



- **Literature Basis :** Liquefaction of wood using methanol and water is synergistic and efficient at relatively mild conditions (Cheng et al. 2010; Minami et al. 2005)
 - Water potentially hydrolyzes holocellulose and methanol is able to attack lignin, and/or alters the solubility of lignin and allows water to attack lignin
 - Methanol stabilizes bio-oil by converting the carboxylic acids formed to esters

2 – Approach (Technical)

■ Overall Technical Approach

- Solvent liquefaction using MeOH/H₂O for stable bio-oil production
- Bio-oil upgrading via mild HDO for refinery insertion

■ Process development in concert with refinement of commercial embodiment through techno-economic evaluation (TEA) via

- Parametric experimentation in lab-scale liquefaction and HDO reactors
- Evaluation of liquefaction product separation/recovery methods
- Characterization of liquefaction oil for compatibility with HDO process

■ Critical Success Factors

- High liquefaction bio-oil yield and stability
- Oxygen content after HDO allows blending with diesel at 20 %
- Levelized cost of HDO Oil from process < \$3.00 per gallon

■ Challenges

- Sufficient yield of bio-oil to allow cost target to be met
- Production of stable bio-oil from liquefaction
- Minimize HDO severity and hydrogen consumption

2 – Approach (Management)

■ Management Approach

- Periodic review of milestones, schedule and budget
- Early management of critical path requirements
- Use of independent expert for conducting TEA starting early in the project

■ Critical Success Factors

- Physicochemical properties of bio-oil acceptable for insertion into a refinery process step
- Bio-oil projected for commercial production at a cost that is competitive with petroleum based feed

■ Challenges

- Convincing the industrial community that our solvent liquefaction approach is competitive or superior to other approaches
- Keeping experimental development focused to achieve biofuel cost target using techno economic evaluation in concert

3 – Technical Accomplishments/ Progress/Results

Highlights of Accomplishments/Results

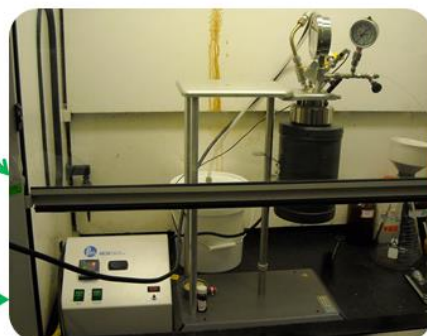
- Batch lab-scale experiments (Parr Reactor) and TEA were successfully carried out in concert to develop an optimized commercial embodiment of the process **yielding 37 % light bio-oil** (free flowing at 40°C) for HDO
- Liquefaction bio-oil was shown to be **stable over several months**
- **Partnership was established with a catalyst company** for HDO catalyst and development of appropriate HDO process for the bio-oil produced to allow refinery insertion
- HDO experiments were carried out to show bio-oil **oxygen reduction down to 1.5 %** at relatively mild conditions with **H₂ consumption of <0.03 g/g oil**
- Discussions are ongoing with selected refinery companies
- TEA/LCA showed that the process could be cost-competitive, and with further improvements the process has the potential to achieve a lifecycle **HDO oil cost of <\$3 per gallon** and **>50 % reduction in GHG emissions** compared to a petroleum baseline

Lab-scale Batch Liquefaction Process

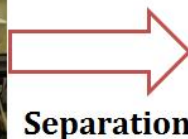


Commercial Pulverized wood

Liquefaction Solvent



Parr Reactor



Bio-oil

Bio-oil characterization



CHN analyzer

GC/MS

Viscometer

KF titrator

TAN

GPC

Parametric Study of Solvent Liquefaction

High conversion/oil yield

Low oxygen content

Parametric Study (45 experiments, 1/4 factorial design)

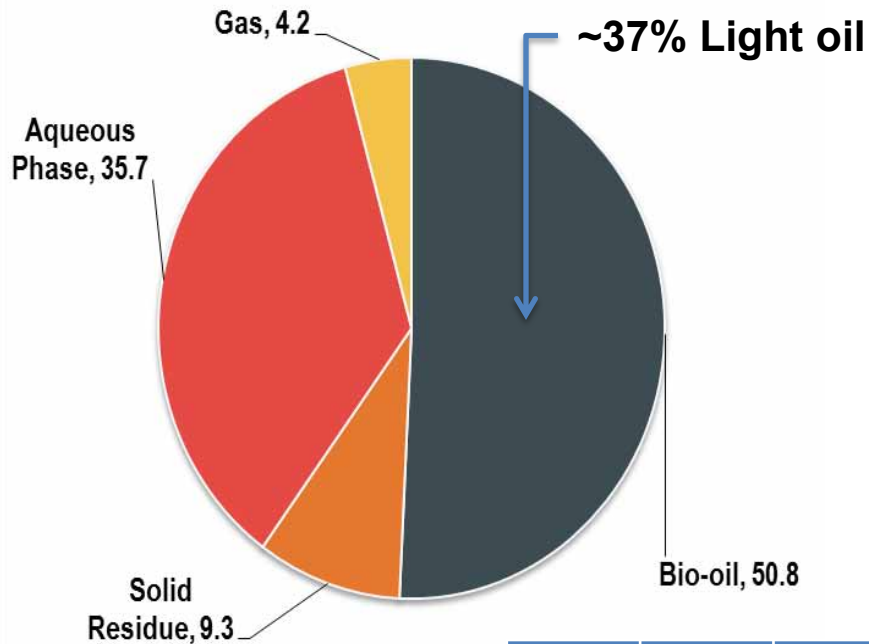
Optimized Conditions	Value
Temperature, °C	200-300
Pressure, psi	1000-2000
Residence time, min	5-30

Liquefaction performance	Value
Conversion of biomass to non-solids %	90.7
Total bio-oil yield, %	50.8
Oxygen content, %	~25.0

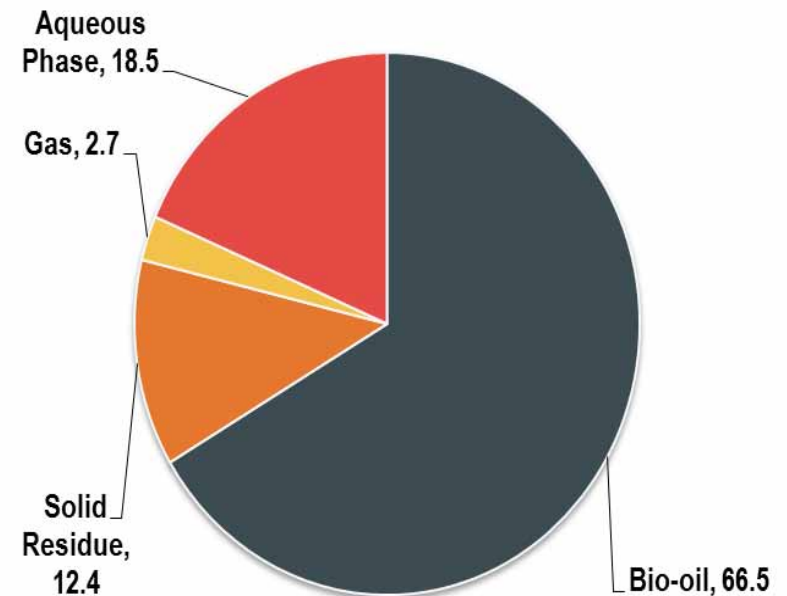
- Statistically designed parametric study was carried out to understand how process parameters affect biomass conversion, oil yield and oxygen content
- High conversion and oil yield were achieved under optimized conditions
- Optimized liquefaction conditions were significantly milder than those used in HTL process

Mass and Carbon Balance

Mass Balance



Carbon Balance



H ₂	CO	CO ₂	CH ₄	MeOH	C ₂₊
4.8	11.3	75.5	0.7	5.1	1.3

- Solvent liquefaction produced good bio-oil yield and minimum gas products
- Aqueous phase (~35%) needs to be recycled to minimize carbon loss (~18.5%)

Characterization of Aqueous Products

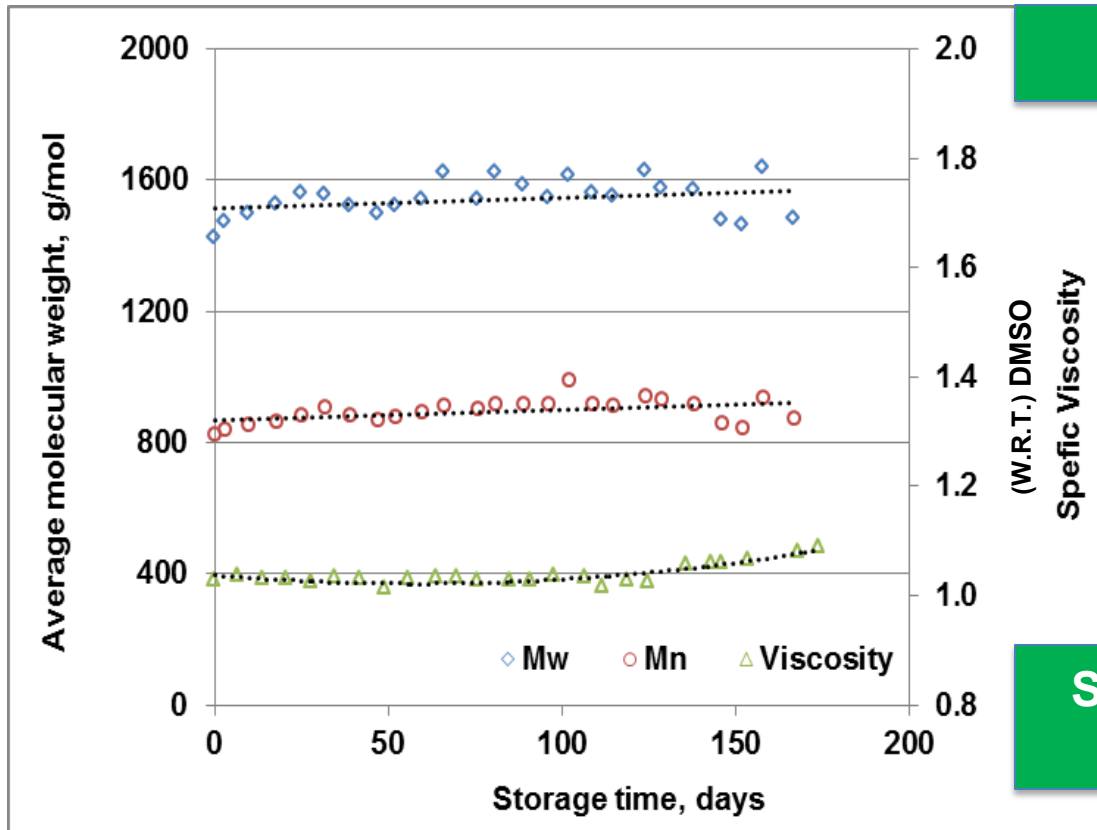
- Aqueous products from biomass liquefaction is mainly derived from holocellulose (cellulose and hemicellulose) decomposition
- HPLC and GC characterization identified sugar and other oxygenates in AP

Aqueous Phase (AP)		
Mass distribution in liquefaction product, wt%	~40	Utilization critical to further increase oil yield and reduce the load on waste water treatment
TAN, mg KOH/g AP	~45	
Chemical Composition (HPLC, GC/MS)	8.3% sugar; 91.7% other light oxygenates, e.g. acetic acid, HMF	

- Recycling aqueous phase back to fresh wood liquefaction may further increase bio-oil yield through condensation reaction, e.g. Aldol condensation

Physicochemical Properties of Bio-oil

Physicochemical Properties	Liquefaction oil	Pyrolysis oil	Petroleum oil
Oxygen Content, wt%	~25	35-40	~1.0
Moisture Content, wt%	~1.0	~25	< 0.1
TAN, mg KOH/g bio-oil	~1.0	~100	< 1.0



Highly viscous bio-oil



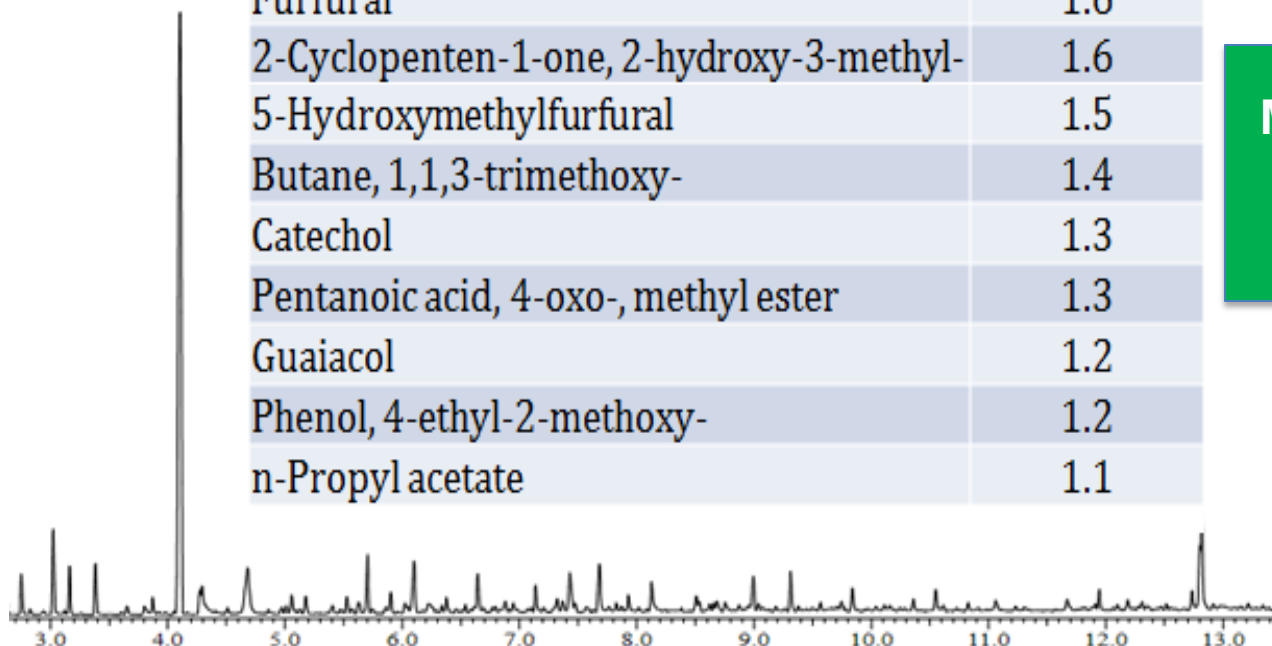
Superior stability: stable Mw and viscosity

Chemical Composition of Bio-oil

Top 15 compounds detected by GC-MS*	Content, %
6-Octadecenoic acid, methyl ester, (Z)-	3.2
2-Propanol, 1-ethoxy-	2.4
2-Propanone, 1-hydroxy-	2.2
Furfural	1.6
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	1.6
5-Hydroxymethylfurfural	1.5
Butane, 1,1,3-trimethoxy-	1.4
Catechol	1.3
Pentanoic acid, 4-oxo-, methyl ester	1.3
Guaiacol	1.2
Phenol, 4-ethyl-2-methoxy-	1.2
n-Propyl acetate	1.1

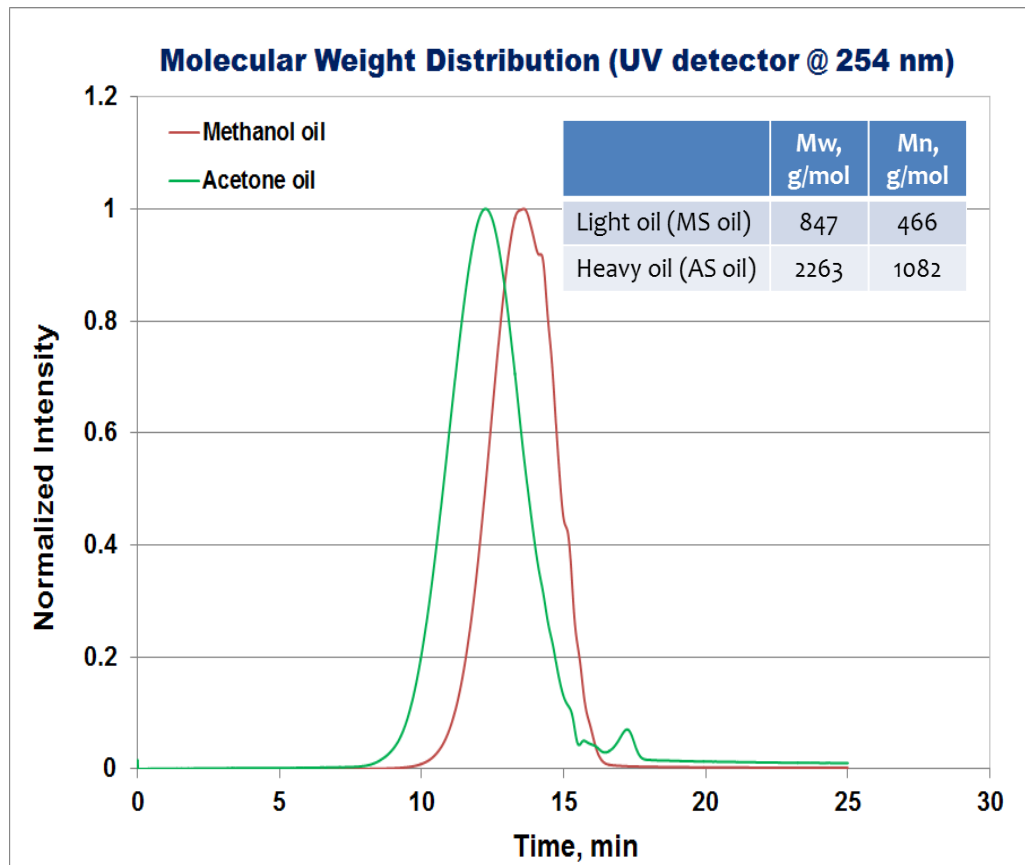
Complicated chemical composition

Methanolysis occurred (methyl ester was identified in oil)



Physicochemical Property of Bio-oil

- Bio-oil with distinct molecular weights was identified and a cost-effective process was established to separate the light and heavy oil



	Light oil	Heavy oil
C, %	68.9	75.9
H, %	6.8	5.6
O, %	23.4	18.5
N, %	ND	ND



Light oil flows freely upon 40 °C heating



Heavy oil appears to be solids

Collaboration with Refinery and Catalyst Partners

- Stabilization of bio-oil using our process was considered highly desirable by refinery companies we contacted
- However, 25 % oxygen in bio-oil prevented direct blending in a refinery stream
- Mild HDO was needed to reduce oxygen to <10 % before sending to refinery
- Experiments were carried out using catalyst supplied by our catalyst partner at conditions they suggested in a ½ inch OD trickle bed reactor
- Three proprietary HDO catalysts tested; results are under evaluation by catalyst supplier

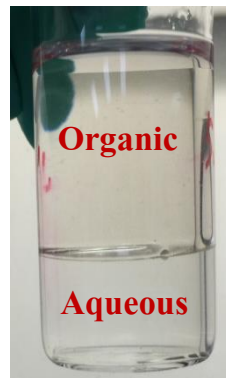
HDO Results

- HDO process development was carried out in collaboration with a catalyst partner using their proprietary process and catalyst.

HDO Feed



HDO Product

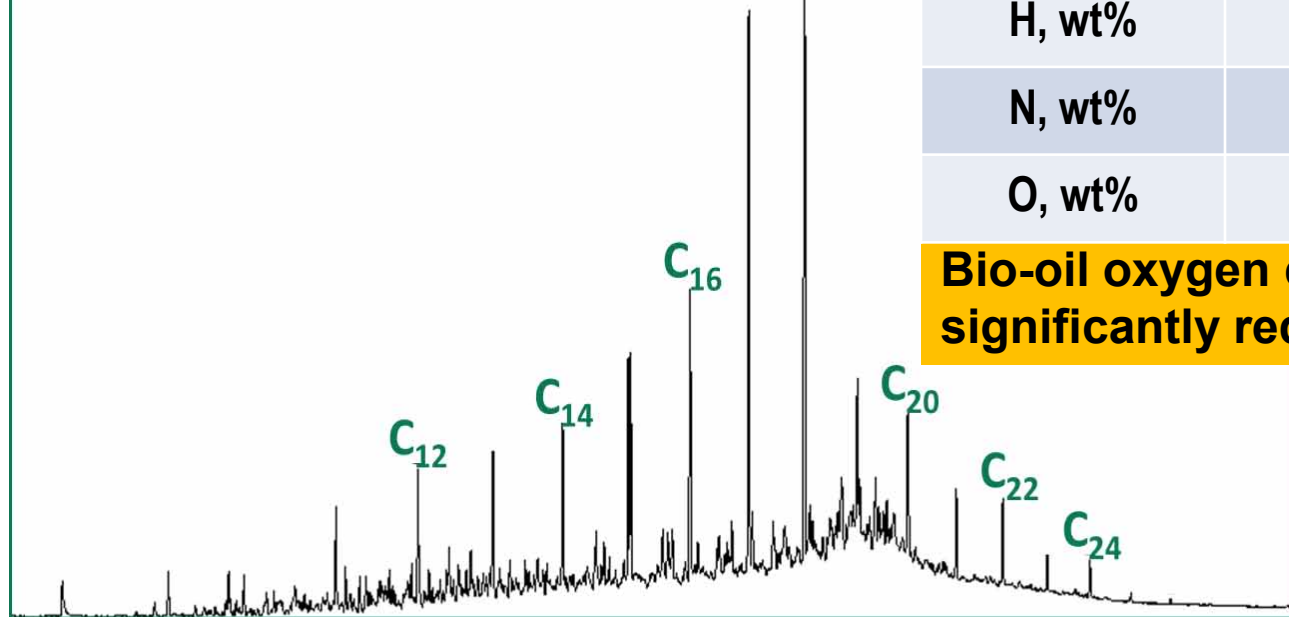


Mass Balance	Yield, %
Hydrotreated Bio-oil yield, wt%	73.7
Carbon yield, wt%	85.4
Coke, wt%	6.5
H ₂ O, wt%	20.4
Gas, wt%	3.5
H ₂ consumption, g/g dry oil	0.02

- Complete oil color change was observed after HDO and the upgraded oil phase separated into two layers
- HDO H₂ consumption is 50% lower than literature data for HTL oil upgrading (~0.04 g/g oil)

Elemental/Chemical Composition of HDO Oil

HDO oil has carbon number falling in diesel fuel range



Bio-oil Composition	Raw oil	HDO oil
C, wt%	70.6	85.1
H, wt%	7.0	13.4
N, wt%	0.27	N.D.
O, wt%	22.2	1.5

Bio-oil oxygen content was significantly reduced after HDO

GC/MS characterization of HDO oil

Preliminary TEA Results

System Performance

Biomass liquefaction	SR_SOT	Target
Raw Material		
Biomass input, dry metric ton/day	1000	1000
Overall Process Yields		
Raw bio-oil production rate, ton/day	355	449
Hydrocarbon production rate, ton/day	245	306
Hydrogen consumption, g H ₂ /g oil	0.02	0.02
Carbon Efficiency		
Liquefaction, %C based on biomass	50.0	62.5
HDO, %C based on bio-oil	85.4	85.4
Liquefaction+HDO, % C based on biomass	42.7	53.3

Cost Estimates by Dr. Eric Larson (2013\$)

Biomass liquefaction	SR_SOT	Target
Capital Cost, \$/gal	2.44	1.95
O&M, \$/gal	0.56	0.45
Biomass, \$/gal	0.55	0.50
Methanol, \$/gal	0.20	0.05
Hydrogen, \$/gal	0.19	0.21
Electricity, \$/gal	0.12	0.10
Light gas credit, \$/gal	(0.00)	(0.00)
RIN credit, \$/gal	(0.40)	(0.40)
Levelized Cost of Oil Production, \$/gal	3.66	2.86
Minimum Fuel Selling Price, \$/gal	3.78	2.95

- SR liquefaction process is cost-competitive vs HTL process that has minimum fuel selling price of \$4.88/gallon

Preliminary LCA

Conventional Petroleum Baseline

LC emissions	Kg CO ₂ /GJ finished fuels LHV
Extraction	6.84
Transport to refinery	1.40
Refining	8.78
Transport to user	0.87
Combustion	72.78
Total emission	90.7

~66% GHG emission benefits is achievable with SR's solvent liquefaction process

Biomass solvent liquefaction and HDO

LC emissions	Kg CO ₂ /GJ finished fuels LHV
Photosynthesis	-120.4
Upstream biomass	19.2
Hydrogen supply	10.3
Makeup MeOH	1.9
Makeup Solvent	0.1
Solids	21.2
Liquid plant effluents	0.1
Gas effluents	14.4
Bio-oil transport to refinery	1.4
Refinery emissions	8.8
Finished fuel transport to user	0.9
Finished fuel combustion	72.8
Total net LC GHG emission	30.6

4 – Relevance

- Project supports BETO's bio-oil pathway and objectives to accelerate the production of transportation fuels from high impact biomass
- Project is attempting to develop a cost-competitive commercially viable process for producing stabilized refinery-ready bio-oils;
- Process could be adapted by refineries to obtain RIN credits, thus giving a boost to biofuels production.
- Project enhances the state of the art for solvent-based biomass liquefaction technology
- Successful demonstration at lab-scale will encourage government agency and private industry to support larger scale demonstration and final technology deployment for producing transportation fuels from biomass
- Project encourages bio-oil utilization within a petroleum refinery to leverage its existing capital for further processing to final fuels.

5 – Future Work

- Fine tune TEA model
 - Capital cost
 - Utility costs
- Finalize LCA of proposed process
- Continue discussion with potential refinery partners on inserting bio-oil produced by the process into petroleum refinery infrastructure
- Complete final project report
- Work with NREL to complete data mining

Summary

- Mild methanol/H₂O-based biomass liquefaction process integrated with an HDO process was demonstrated at lab-scale
- Stabilized bio-oil produced and upgraded from ~25 % oxygen to ~1.5% oxygen content
- TEA was iteratively used to guide process development and experiments and experimental data was obtained to support TEA for the final commercial embodiment
- TEA of the final commercial embodiment showed that a cost <\$3.00 per gallon for upgraded bio-oil for refinery insertion is achievable with >50 % GHG reduction over a petroleum baseline

Additional Slides

Responses to Previous Reviewers' Comments

- The 2013 peer review was conducted with the project in very early stages. Thus it was not possible to efficiently separate the non-proprietary information from proprietary information.
- The project has been extended at no additional cost from 1 to 2.5 years. This has allowed us to develop a viable commercial embodiment of the process through experimental work and TEA in concert.
- More non-proprietary data and information has been provided so that the reviewers can better gauge the project's accomplishments.

Publications, Patents, Presentations, Awards, and Commercialization

- Poster Presentation: Bio Pacific Rim Summit on Industrial Biotechnology & Bioenergy, San Diego, 2014
- Poster Presentation: Bio International Convention, Philadelphia, 2014
- Oral Presentation: AIChE Annual Conference 2013, San Francisco, 2013
- Poster Presentation: TC Biomass, Chicago, 2013