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

Novel Electro-Deoxygenation for Bio-oil Upgrading

09 March 2017
Thermochemical Conversion Session

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Ceramatec, Inc.

Pacific Northwest NATIONAL LABORATORY
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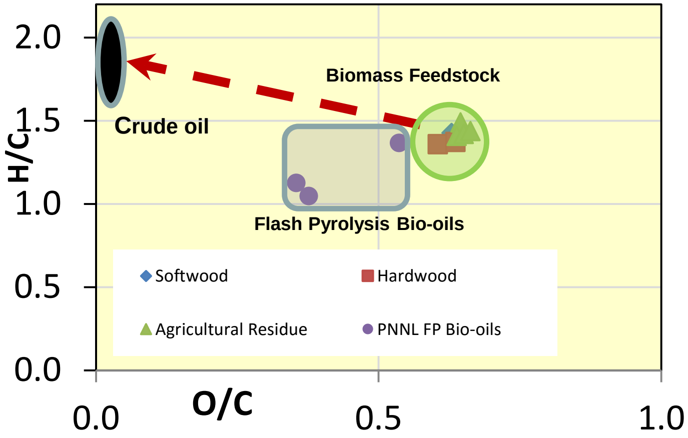
Drexel UNIVERSITY

Project

- CHASE
  - CARBON, HYDROGEN AND SEPARATION EFFICIENCIES IN BIO-OIL PATHWAYS
- Bio-oil Challenges in Direct Use

Low heating value, incomplete volatility, acidity, instability, and **oxygenated organic compounds**



Problem Statement

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- Upgrading is required to lower oxygen content of bio-oil
- Barriers
  1. Carbon efficiency: developing selective fractionation and separation systems in bio-oil processing;
  2. Hydrogen efficiency: improving H_2 production, use, and transfer in biomass liquefaction and bio-oil upgrading; and
  3. Separations efficiency: developing technologies for use and mitigation of the **aqueous fraction of bio-oil**.

CHASE FOA to focus on moving knowledge and understanding of basic or fundamental principles observed at Technical Readiness Level (TRL) 1 into practical, applied research and development at TRLs 2-3 or beyond

Current & Proposed Approach

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- Current processes (e.g. Hydro-deoxygenation) are inefficient
  - Requires large quantities of hydrogen
  - Amenable to only centralized processing
- Proposed Electrochemical Deoxygeneation (EDox) work when successfully demonstrated
  - Smaller processing plant to match biomass gathering radius, pyrolysis unit size
  - Very low hydrogen requirement
  - Use of electricity (distributed availability)
  - Integrated with pyrolyzer (direct feed of pyrolysis vapor - does not exclude aqueous fraction)

Goal Statement

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- **Goal**: Demonstrate techno-economic feasibility of upgrading biomass derived pyrolysis oil using electro-deoxygenation process. A ceramic membrane that selectively transports oxygen under an applied electric potential is integrated with a fast pyrolysis unit for in-situ removal of oxygen to stabilize bio-oil.
- **Objective**: Move technology from concept stage (TRL 1) to practical, applied R&D at TRL 2-3

Technical Area Objective	Relevance of Innovation
Carbon Efficiency	Deoxygenation of both organic & aqueous phases of bio-oil
Hydrogen Efficiency	In-situ hydrogen generation from steam present in bio-oil

- Advance DOE-BETO goal of producing bio-oils with desirable qualities for making hydrocarbon transportation fuels
- **Outcome**: Produce bio-oils with desirable qualities for making hydrocarbon transportation fuels
  - Decentralize bio-oil upgrading process
  - Low requirement for hydrogen gas for upgrading

Quad Chart Overview

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Timeline

- Project start date: Sep. 30, 2013
- Project end date: Mar 31, 2018
- Percent complete: 80%

Budget

	Total Costs FY 12 – FY 14	FY 15 Costs	FY 16 Costs	Total Planned Funding (FY 17-Project End Date)
DOE Funded	642,503	735,957	724,997	500,705
Cost Share (Ceramatec)	169,044	400,675	107,433	73,708
Cost Share (Drexel)		14,541	29,964	31,271

Barriers

- Understanding of coking and contamination issues within process
- Improved (electro)catalysts for deoxygenation
- Processing inline with fast pyrolysis
- Technical target: High C and H efficiency

Partners

- **PNNL** (20%):
  - Pyrolysis Integration
- **Drexel University** (10%):
  - LCA, TEA
- **Technology Holding, LLC**:
  - TEA consultancy

1 - Project Overview

– This project has **demonstrated the feasibility of electrochemical deoxygenation** using solid oxide electrolysis cell in

1. Small cells,
2. Multi-cell stacks, and
3. An integrated test with a fast pyrolysis unit
4. LCA & TEA in progress

Project Goals

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1. Demonstrate technical feasibility of electrochemical deoxygenation (EDOx) reactor at bench scale
2. Integrate the EDOx reactor with a bench scale pyrolysis reactor
3. Perform overall process simulation
4. Perform life cycle and overall techno-economic analyses
5. Prepare a preliminary commercialization plan

2 – Approach (Management)

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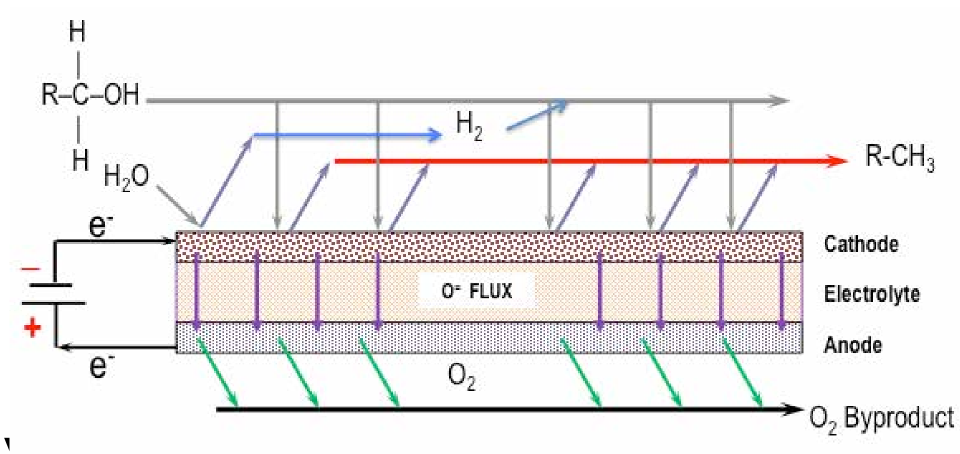
- Communication of Critical Success Factors
  - Demonstration of bio-oil deoxygenation using EDOx process and achieve high C and H efficiency
- Updating Project Status
  - Monthly teleconference among team members
  - Monthly update to DOE technical and contracting officer
  - Quarterly milestone updates to DOE
  - Involvement of multidisciplinary team of materials scientists, chemical process model engineers, pyrolysis professionals, LCA experts, graduate students
- Project structure
  - **Ceramatec**: EDOx process verification via cell and stack testing
    PNNL: EDOx stack test using slip stream from pyrolyzer
    Drexel: LCA and TEA aspects of overall process

2 – Approach (Technical)

- Use of **oxygen ion conductor based membrane** electrolyzer for bio-oil deoxygenation
- Unique Aspects:
  - Direct removal of oxygen from bio-oil compounds



  - In-situ generation of hydrogen from steam electrolysis for indirect deoxygenation
  - Oxygen is transported across the membrane and is a high purity valuable by-product
  - Operating temperature nearly match pyrolysis process

2 – Approach (Technical)

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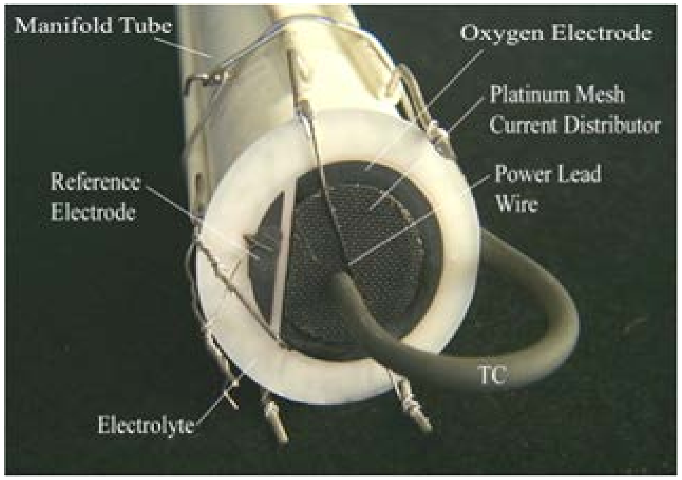
- ***Challenges***
  - *Use of solid oxide cell to remove oxygen from complex hydrocarbon has not been demonstrated in the past*
  - *Commonly used fuel electrode is Ni based and can be prone to formation of coke from hydrocarbon.*
  - *Sufficient current for high level deoxygenation as solid oxide cells are designed to operate at 800 C.*
    - *Pyrolysis temperature max 550 °C*
    - *Electric current is proportional to oxygen flux*
- ***Critical Success Factors***
  - *Demonstration of deoxygenation of bio-oil to produce stable intermediates*
  - *Experiments and process analysis shows a reduction in hydrogen requirement relative to HDO process*
  - *LCA shows GHG emission lower than HDO process*

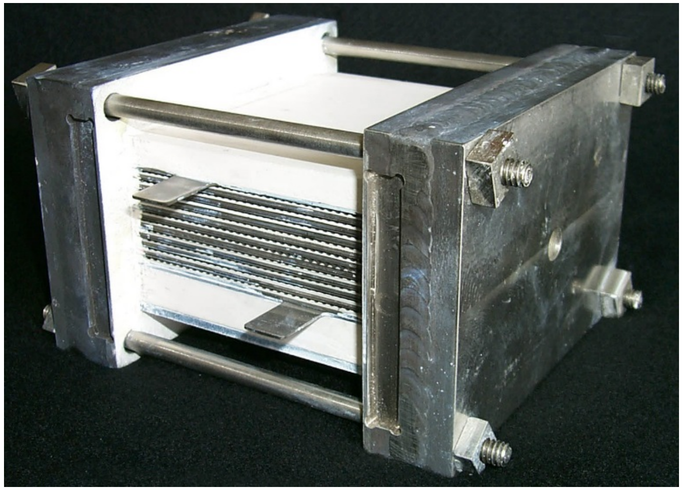
3 – Technical Accomplishments/ Progress/Results

- ***Three levels of tests conducted***



1. Electrochemical Button Cell

- Screening of deoxygenation capability
- ~ 2 cm^2 electrode active area
- Stirred reactor configuration
- Evaluation of operating conditions



2. Electrochemical Stack

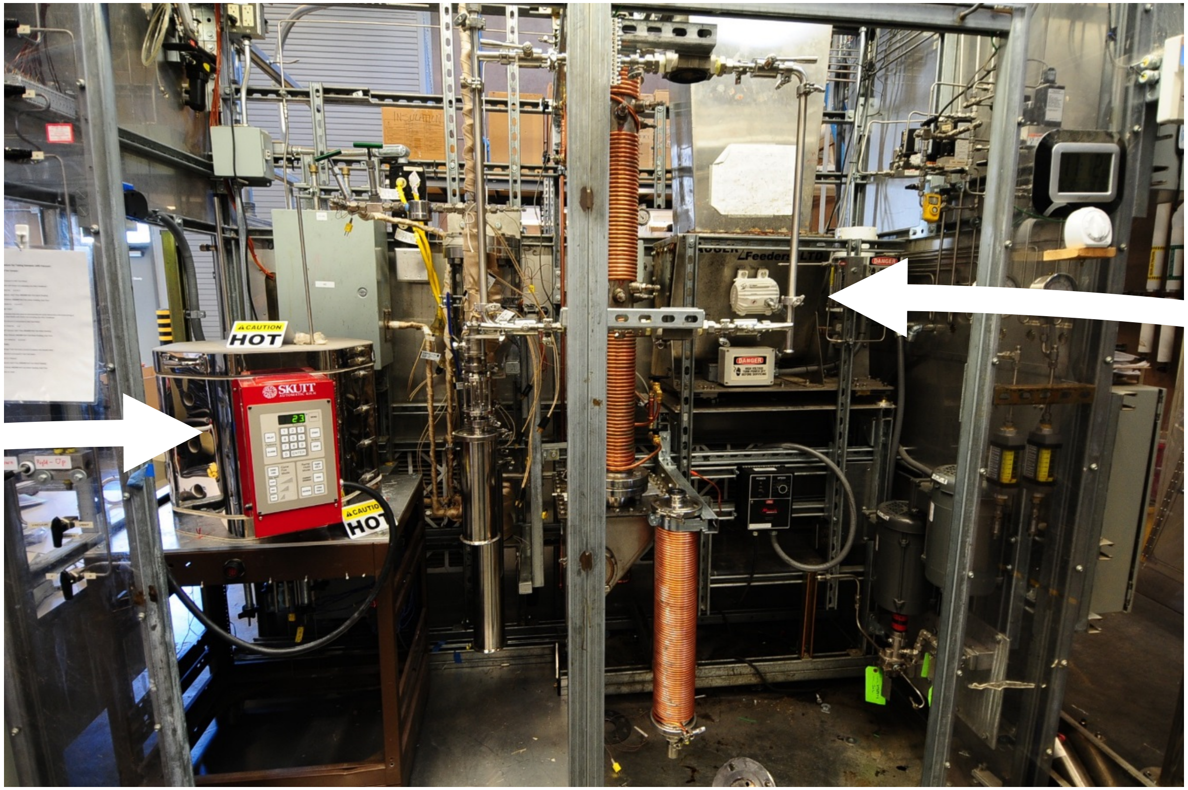
- Larger scale testing ~50 cm^2 active area
- Typically 10 cell stacks
  - longer residence time
  - No mixing of fresh inlet and product stream

3 – Technical Accomplishments/ Progress/Results

3. Integrated Testing at PNNL

- *Slip stream pyrolysis vapor fed to DeOx Stack*

EDox Stack
in Furnace
10-cells
Total area
~500 cm^2



Pyrolysis
Unit

3 – Technical Accomplishments/ Progress/Results

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- *Button Cell Test Feed*
  - *Syringol*
  - *Guaiacol*
  - *Syringol + Guaiacol Mix*
  - *Aqueous Phase of Bio-oil*
- *Stack Test Feed*
  - *Syringol + Guaiacol*
- *Integrated Test*
  - *Slip stream of Pyrolysis Vapor*

Button Cell Test Schematic

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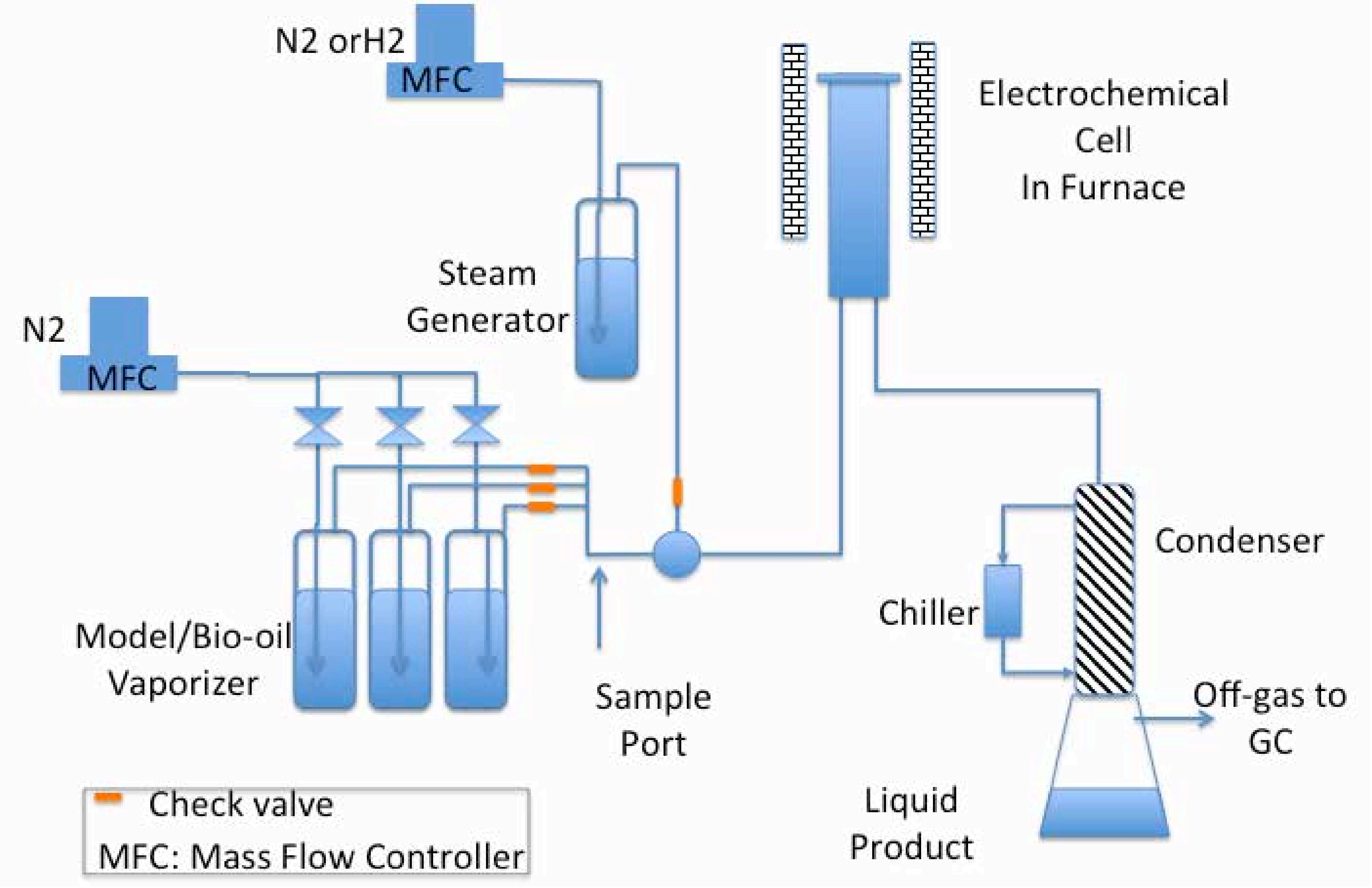

Results-Button Cell: Model Compound Syringol

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Elemental Balance Between Feed and Liquid Products*

Element	Feed wt% By Formula	Liquid Product wt% by GC-MS	Feed to Product wt% Change
Carbon	62.3%	76.9%	+23.3%
Hydrogen	6.5%	6.7%	+2.3%
Oxygen	31.1%	16.4%	-47.2%

Liquid Product showed 47 wt% Oxygen relative to feed
***Gas products not included**

Results-Button Cell: Aqueous Phase Bio-Oil

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Gas Product Micro-GC Analysis

Component	H_2	N_2	CH_4	CO	CO_2	Ethene	Ethane	Propane	Butane
Wt %	0.40%	92.95%	0.15%	2.17%	2.02%	0.09%	0.02%	2.17%	0.02%

Elemental Balance Between Feed and Product

Element	90 ° C Condensate Feed wt% by GC-MS	Liquid Product wt% by GC-MS	Feed to Product % Change
Carbon	60.93%	70.58%	15.8%
Hydrogen	7.42%	5.57%	-24.9%
Oxygen	31.65%	23.85%	-24.6%

Liquid Product showed 25 wt% reduction Oxygen relative to feed
Feed composition likely varied with time
Gas products not included

Summary
Select Button Cell Tests

Mass Balance Between Feed and Product: Button Cell

	Syringol Cell 32	Guaiacol Cell 35	Aqueous phase Bio-Oil Cell 39
Carbon	23.3%	10.1%	15.8%
Hydrogen	2.3%	-3.7%	-24.9%
Oxygen	-47.2%	-25.5%	-24.6%

Mixture of Syringol and Guaiacol shows 30% oxtygen reduction

3 – Technical Accomplishments/ Progress/Results (cont'd)

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- *Year 1: 30% deoxygenation; 75% C and H Efficiency*
  - *Model compounds showed >30% deoxygenation in liquid product*
  - *Complete mass balance and C and H efficiency estimate could not be done due to leak in the system*
- *End of Project target: 60% deoxygenation; 75% C and H Efficiency*

System Configuration and Run Summary

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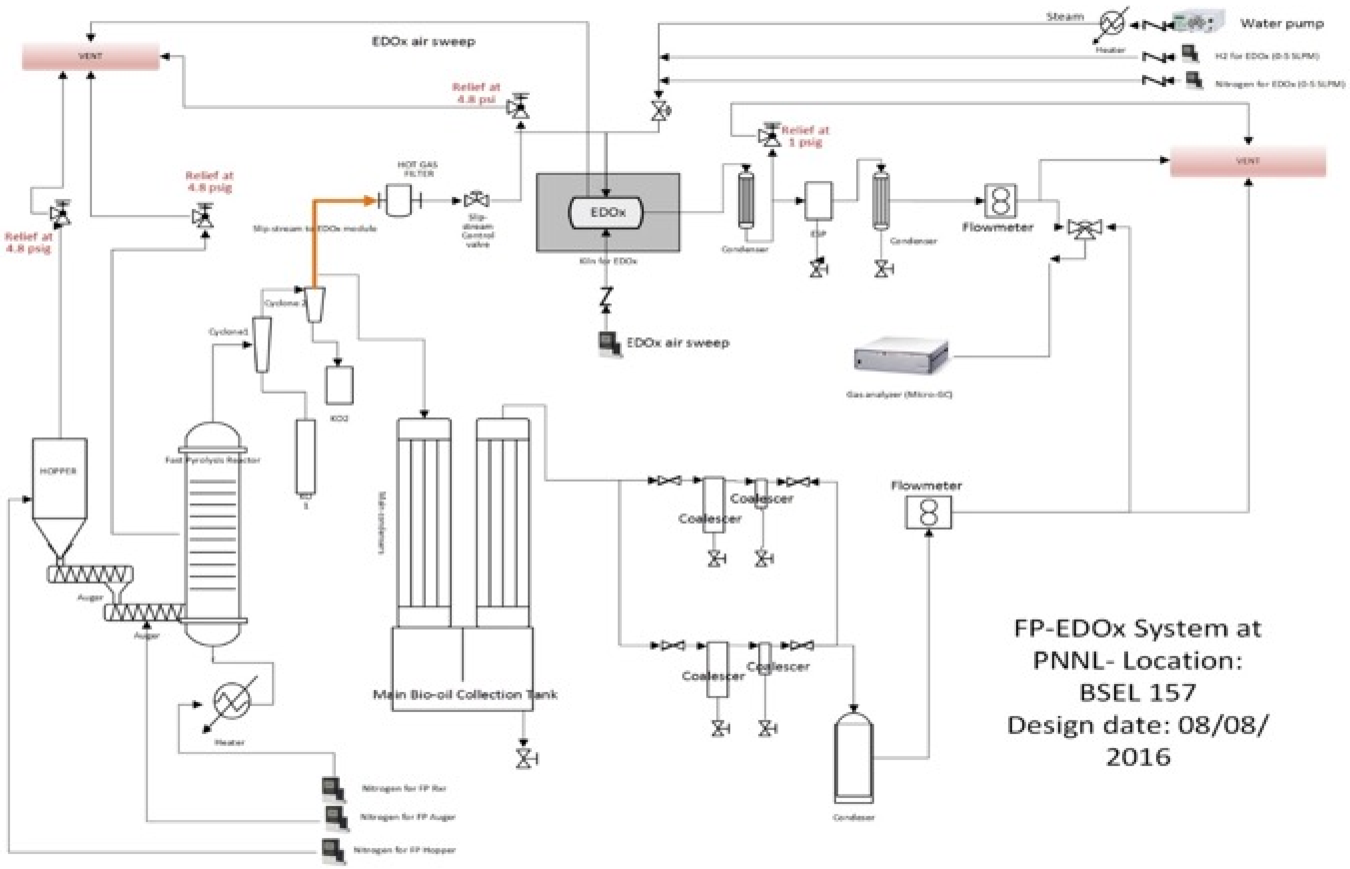

Biomass	Ponderosa Pine (American Wood Fiber), fines removed
Fast pyrolysis temperature	480°C
EDOx temperature	550 and 600°C
dP across reactors	not detected
Biomass Feed rate	0.9 kg/h

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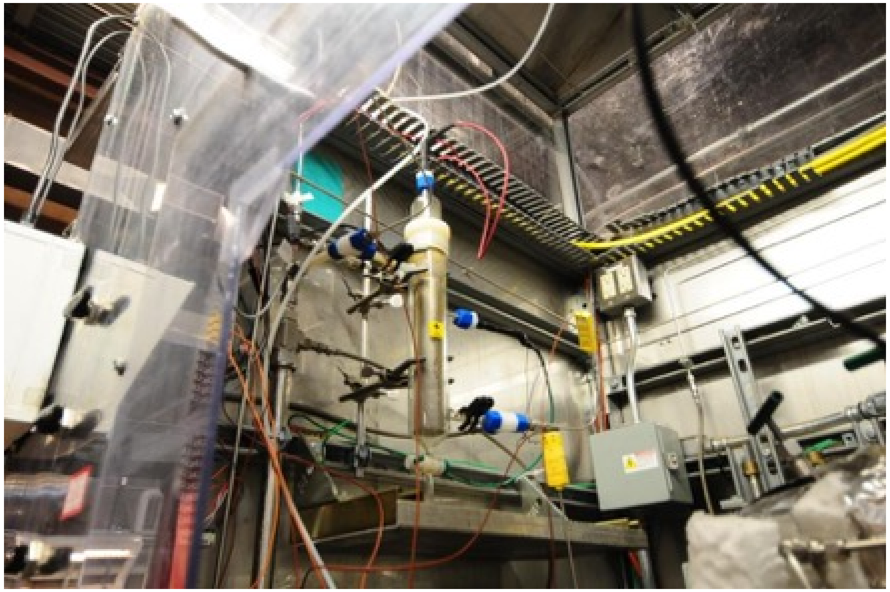
Integrated Testing

- First ever integration of FP and EDOx
- Analysis on the liquid product were done:
  - GC-MS
  - C13 NMR (carbon functionalities)
- Valuable input to run strategy for the next test.
  - Need stable Cv on the main slip-stream valve
  - Needs low back-pressure condenser after the ESP for improved volatile product recovery



Liquid Product of EDOx is being collected at the Electrostatic Precipitator (ESP)

GC-MS- 600 deg C

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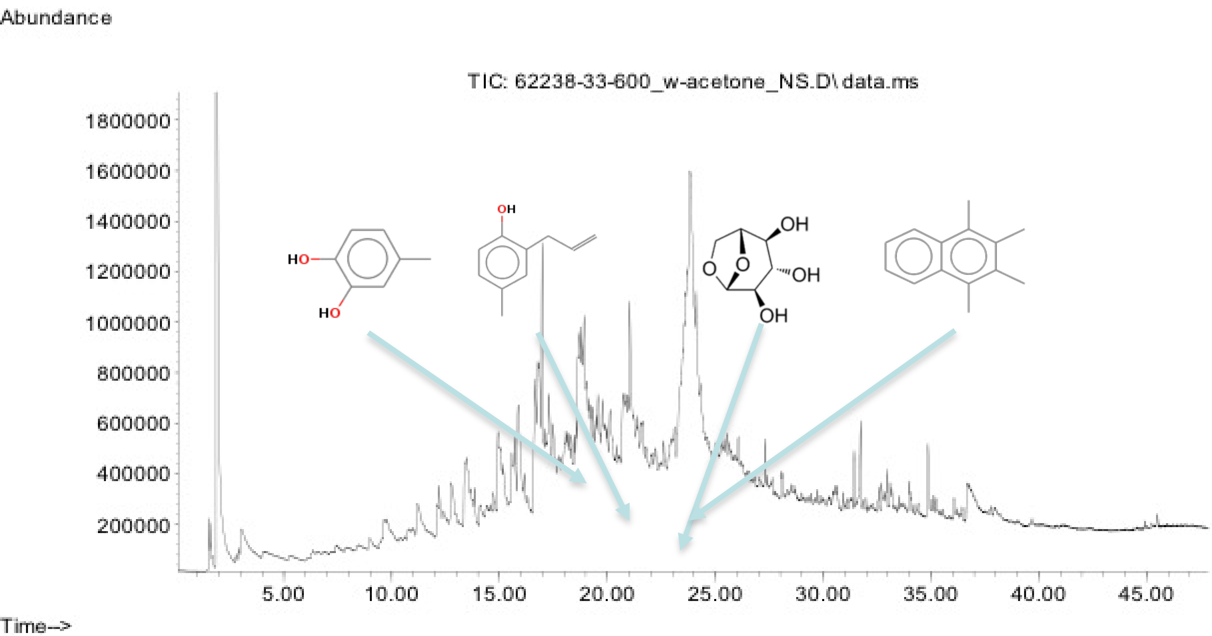

Ret Time	Top 10 species detected with the GC-MS, %agreement to NIST library
23.8	beta.-D-Glucopyranose, 1,6-anhydr 96%
24.1	Naphthalene, 1,2,3,4-tetramethyl- 89%
18.7	1,2-Benzenediol, 4-methyl- 97%
21.0	2-Allyl-4-methylphenol 84%
14.9	Phenol, 2,4-dimethyl- 96%
17.3	1,2-Benzenediol 42%
13.5	Phenol, 3-methyl- 94%
18.8	1,2-Benzenediol, 4-methyl- 96%
23.0	Benzenemethanol, 4-amino- 46%

- Initial GC-MS analysis shows highly aromatic products
- Naphthalene (hydrocarbon product not seen in regular raw pyrolysis oil)
- Depolymerized lignin products: Monomeric-phenolic

C13 NMR Summary

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^{13}C Chemical shift - Functional Groups	Raw Bio-oil	Stabilized Bio-oil	HDO of Bio-oil	FP-EDOx	Catalytic Fast Pyrolysis Oil
Carbonyl (aldehyde ketone)	3.6	1.6	Neg	1.8	2.5
Carbonyl (ester acid)	9.1	5.8	Neg	2.45	5.2
Aromatics olefins	14.9	3.9	13.2	65.8	61.1
Anomeric Carbon Sugars	11.5	3.2	Neg	Neg	Neg
Methoxy/hydroxyl-alcohol, ethers	42.7	57.5	Neg	11.6	11.5
Alkyl/aliphatic carbons	18.3	28.1	82.6	18.4	19.7

- **Low Carbonyl content** in the FP-EDOX product (**lower acidity**) and higher stability
- Dominated by Aromatics olefins (Ring products)
- **Negligible amount of Anomeric carbon-sugars –correlates to higher stability, similar to both CFP and HDO oil.**
- **Similar functionalities to Catalytic Fast Pyrolysis oil**: highlighted in red (below).

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Supply Logistics

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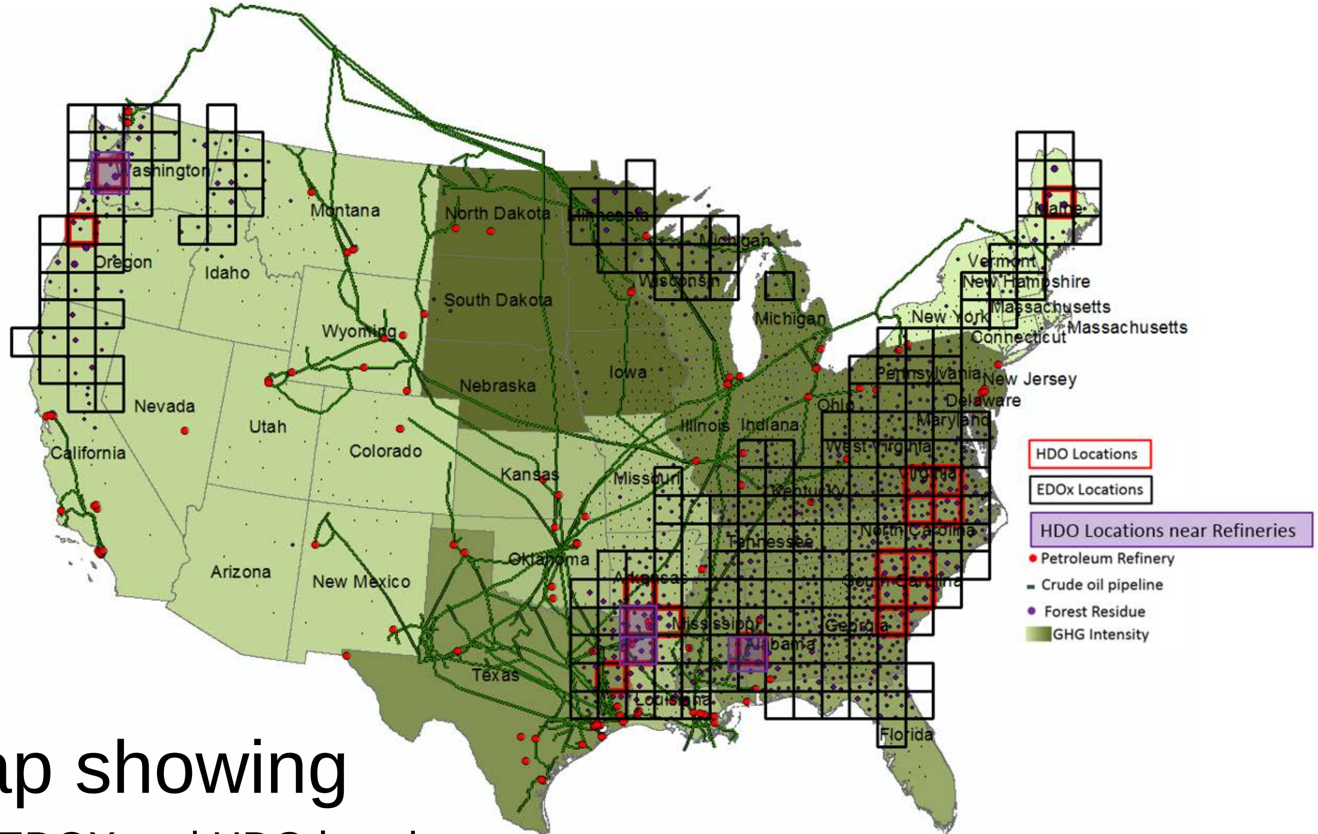
- GIS tools to evaluate biomass supply at two scales for EDOx relative to HDO



- Map showing
  - EDOX and HDO locations
  - GHG intensity in CO_2 eq. varying by the different electricity grids
  - Forest residue availability in billion dry tons per year (bdtpy)
  - Petroleum refineries and pipeline locations.

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Life Cycle Assessment and Cost Estimation

- Investigation of Biomass supply logistics for Electrochemical deoxygenation (EDOx)
  - Compare to Hydrodeoxygenation (HDO)
  - 300 mtpd for EDOx and 2000 mtpd for HDO
- Explore the cost of total energy input needed
  - Proposed partial EDOx process vs. the cost of full EDOx and full HDO

Process Model

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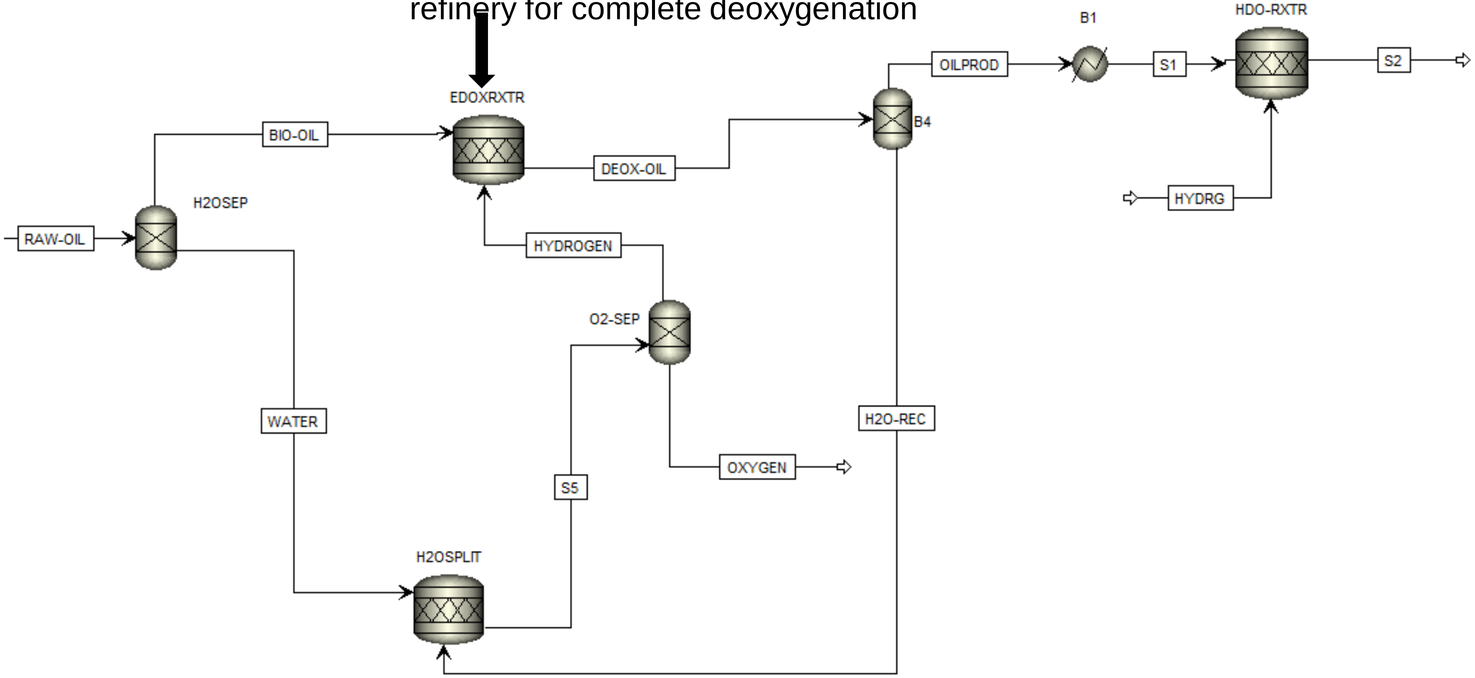
EDOx reactor for partial deoxygenation (67%) of bio-oil to stable oil before transportation to refinery for complete deoxygenation

HDO reactor for complete deoxygenation of bio-oil



Completely deoxygenated bio-oil

On-going research: Aspen plus is used to model the proposed process of partial electrochemical deoxygenation

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Energy Input Cost and GHG Emissions from Process Simulation

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	External Hydrogen (lb./h)	Electricity (kWh)	Energy Cost/unit	Total ($/hr.)	GHG Emissions (Kg CO_2 eq.)
[1]Full EDOx	110	6660	90 cents/lb.+ 11.96 cents /kWh	797	0.58
[2]Full HDO	1296	0	90 cents/lb.	1166	0.25
[3]Partial EDOx	588	1465	90 cents/lb.+ 11.96 cents /kWh	704	0.20

The proposed process (Partial EDOx) has the lower cost of energy and GHG emissions in the three processes

[1]Full EDOx represents complete deoxygenation with Electrochemical deoxygenation reactor
[2]Full HDO- complete deoxygenation with Hydrodeoxygenation reactor
[3]Partial EDOx- use of an EDOX reactor deoxygenating the oil to point of stability (23% deoxygenation) followed by complete deoxygenation with hydrotreating. External Hydrogen is not needed in first deoxygenation with EDOx but 588 lb./hr. of external hydrogen is needed for the remaining deoxygenation with HDO.

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Data used for Process Model

Proposed Process ↓

Input		Hydrotreating	Partial EDOx
Pressure	psi	2000	
Heat content of py oil in	MJ/kg HHV (wet)	16 - 19	35.5
Moisture content of py oil in	wt%	20 - 30	23%
Pyrolysis oil density	g/ml	1.2	0.86
Heat content of hydrogen in	MJ/kg HHV	142	142
Typical hydrogen consumption	g H2/ 100 g pyrolysis oil (dry basis)	4-6	4
Output	**Notes**	**Value**	
Heat content of upgraded hydrocarbons	MJ/kg HHV	44-47	35
Yield of upgraded hydrocarbons - nominal	g hydrotreated oil/dry gr of pyrolysis oil	0.41	0.74
Hydrotreated oil density - nominal	g/ml	0.8	0.93

4 – Relevance

- *Electrochemical deoxygengation of bio-oil*
  - *Supports BETO mission of enabling commercial viability of biomass based fuels*
- *Addresses BETO target in Bio-oil Pathways R&D in lowering conversion cost*
- *This project investigates an alternative to hydro-dexoygenation process of bio-oil that is more economical and amenable to distributed processing*
- *Project combines technical feasibility demonstration, analysis of supply logistics and process economics to guide towards commercial viability of biofuels*

5 – Future Work

- Higher performance stack for integrated test planned late Q1-2017
  - Cathode modification to reduce coking
  - Improved seal for better mass balance
    - Stack performance on steam showed 4X amperage at the same voltage
  - Improved product collection for integrated test
- *Upcoming key milestones*
  - *Integrated Pyrolyzer-EDox test using improved stack and producrt collection system*
- Completion LCA and TEA
  - Using experimental data
  - Using projected performance data
- *Remaining budget of $600k (DOE share $500k) is adequate to complete the tasks*

Summary

- A novel electrodeoxygenation process is investigated
- A solid state electrochemical device isused to remove oxygen from bio-oil
- Model compounds tests demonstrated deoxygenationof
- Integrated test with a slip stream of bio-oil vapor showed reduction in carbonyl groups and elimination of carbohydrates
- LCA analysis shows supply chain logistics
- Partial EDox shows the lowest hydrogen use and cost relative to HDO
- Integrated testing with improved stack and system will allow completion of mass balance to estimate C and H efficiency and deoxygenation in a bench scale system

Additional Slides

Responses to Previous Reviewers' Comments

- **Comments**: Remove oxygen rather than adding hydrogen. Something does not feel right from a thermodynamic standpoint, which should be addressed up front.
- **Response**: Thermodynamic basis of electrolysis is well established. Under an applied potential across an oxygen conducting membrane, the oxygen from the molecule (H2O or CO2) is first ionized and then transported through the membrane to the opposite side where it becomes neutral oxygen. Similar principle is expected for oxygenated compounds. When steam present in the feed it can provide protons as they lose the oxygen electrochemically and react with the radicals and original molecules.
- Comments: Removing oxygen as O2 would benefit yields, but might have an energy penalty
- Response: Generating oxygen and hydrogen from steam using high temperature membrane process can be done at 100% electrical efficiency. Bio-oil deox efficiency will be lower because of lower temperature, but still expected to be high.

Responses to Previous Reviewers' Comments

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- **Comments**: Investigators need to carry out poisoning experiments with H_2S & NH_3 to determine if Ni catalyst is stable.
- **Response**: In the final deliverable, a deoxygenation unit will receive all vapors from a pyrolyzer that includes potential poison such as NH_3 and H_2S. Similar devices running at somewhat higher temperature in fuel cell mode have shown resistance to sulfur poisoning and can utilize ammonia as a fuel. Inorganic ash, and halogen containing compounds could potentially require upstream removal systems.

Highlights from any Go/No-Go Reviews

Memo dated June 1, 2015

- Overall the project continues to make good progress and the recipient is on target to enter Budget Period 2 of the project.
- Technical Highlights include: The recipient redesigned the test rig to remove leaks and improve product collection. The test rig improvements will allow collection of data to close the mass balance. Project partner PNNL prepared their pyrolysis unit to provide aqueous and heavy oil phases to the recipient for testing during the next quarter. The expansion of the process model with actual experimental data by project partner Drexel introduces the possibility of utilizing the model for scale-up. The process model will also provide insight into the electrochemical (hydro) deoxygenation mechanism.
- DOE held a Stage Gate Review on March 2, 2015 to determine if the project is ready to enter Budget Period 2 (BP2). The project passed with a Go decision and the award modification to approve the start of BP2 is in progress.

Publications, Patents, Presentations, Awards, and Commercialization

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Presentations

1. S. Elangovan et al. (Jan. 2017), “Electrochemical In-situ Upgrading of Bio-oil Using Solid Oxide Electrolysis Stack,” 14th International Symposium on SOFC: Materials, Science and Technology, 41st International Conference and Exposition on Advanced Ceramics and Composites, Daytona, FL.
2. S. Elangovan, “Electrochemical deoxygenation of bio-oil,” Proceedings of the 12th European SOFC & SOE Forum , 5 - 8 July 2016, Lucerne Switzerland.
3. Billen et al. (Nov. 2015), “First principle investigation of mechanisms for electrochemical deoxygenation of model compound guaiacol, and the implications for the life cycle environmental impact,” American Chemical Society annual meeting, Salt Lake City, UT
4. S. Elangovan et al. (Nov. 2015), Electrochemical Upgrading of Bio-oil, tcbiomass2015, Chicago, IL.
5. S. Elangovan et al., (May 2015), “Electrochemical Upgrading of Bio-oil, Electrochem. Synthesis of Fuels 3, 227th ECS Meeting, Chicago, IL.

Publications, Patents, Presentations, Awards, and Commercialization

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Publications

1. S. Elangovan et al., "Electrochemical deoxygenation of bio-oil," Proceedings of the 12th European SOFC & SOE Forum , 5 - 8 July 2016, Lucerne Switzerland.
2. S. Elangovan et al., Electrochemical Upgrading of Bio-Oil, ECS Transactions, 2015, 66, 3,1.

Patent Application

1. S. Elangovan and M. Karanjikar., US Patent Application No. 61872184 (Publication No. 20150060296), "Hydrogen Utilization and Carbon Recovery," Aug. 2013.