DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

Novel Electro-Deoxygenation Process for Bio Oil Upgrading

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TOMORROW'S CERAMIC SYSTEMS

March 24, 2015
Thermochemical Conversion

S. (Elango) Elangovan

Goal Statement

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- Demonstrate the techno-economic feasibility of upgrading biomass derived pyrolysis oil using electro-deoxygenation process
- 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 and aqueous phase of bio-oil prior to phase separation
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
- Enable acceptance of widely varied non-food, “high impact” biomass based bio-oil feedstocks to produce fuels that are similar to those found in crude oil derived products.

Quad Chart Overview

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Timeline

- **Project start date**: October 1, 2013
- **Project end date**: September 30, 2016
- **Percent complete**: 33%

Budget

	FY 14 Costs	Total Planned Funding (FY 15-Project End Date)
DOE Funded	$ 485,820	$ 2,118,326
Cost Share (Ceramatec)	$ 169,044	$ 581,456
Cost Share (Drexel Univ)		$ 75,776

Barriers

- Bio-Oil stabilization and improved catalysts for deoxygenation
- Removal of hydroprocessing steps with processing inline with fast pyrolysis
- Understanding of coking and contamination issues within process
- High C efficiency by utilization of aqueous phase of bio-oil
- Technical target: Integration of deoxygenation process and pyrolysis unit

Partners

PNNL (20%):

Pyrolysis Integration

Drexel University (10%):

LCA

Technology Holding, LLC:

TEA consultancy

Project Overview

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Bio-Oil as a fuel Source

– Low heating value, incomplete volatility, acidity, instability, and incompatibility due to <u>oxygenated organic compounds</u>
– Elimination of oxygen by current processes is inefficient; requires hydrogen; amenable to only centralized processing
– Ceramatec has demonstrated oxygen removal from CO_2/steam mixture and proposed extending the concept to deoxygenation of bio-oil

Program Objectives

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 analysis and overall techno-economic modeling
5. Prepare a preliminary commercialization plan

Approach (Technical)

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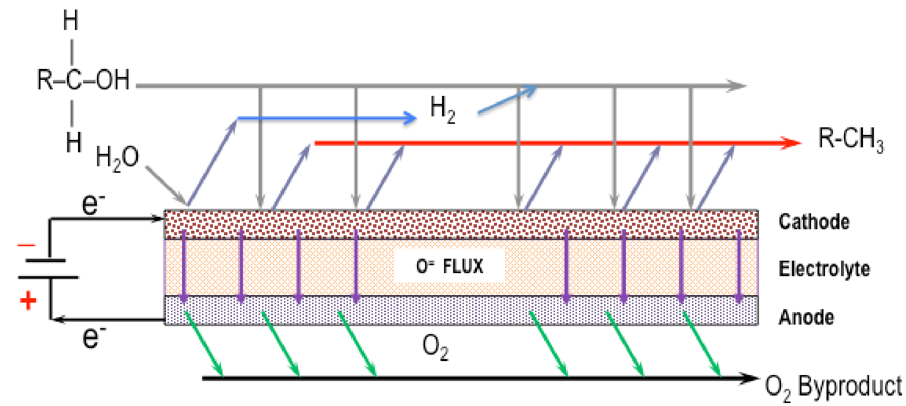
- Oxygen ion based membrane electrolyzer
  - Technology has been demonstrated for electrolysis of CO_2–steam mixture to produce CO+H_2 mixture by using electric energy
- Unique Aspects:
  - Direct removal of oxygen from bio-oil compounds
  - In-situ generation of hydrogen from steam electrolysis for indirect deoxygenation
  - Removed oxygen is electrochemically transported across the membrane and is a high purity valuable by-product



- Y1 Go/No-Go Decision Points to show Proof of Concept
  - 60% efficiency of deoxygenation using model compounds
  - 30% efficiency of deoxygenation and 75% C and H efficiency using aqueous fraction of bio-oil

Approach (Management)

- Critical success factors
  - *Technical*: Demonstration of bio-oil deoxygenation at high (85%) C and H efficiency
  - *Market*: Adaptation of distributed pyrolyzers with economical access to bio-mass
  - *Business*: Investment in manufacturing infrastructure for large scale production of electrolysis units
- Potential challenges
  - Direct integration of EDOx units with a pilot scale pyrolyzer
  - Electrode poisoning from contaminants in pyrolysis vapors
- Project structure
  - **Ceramatec**: Leading R&D company in solid oxide electrolysis
    PNNL: A national lab with extensive pyrolysis experience
    Drexel: University to evaluate LCA and TEA aspects of overall process
  - Monthly teleconference among team members and quarterly milestone updates to DOE

Technical Accomplishments/Progress/Results

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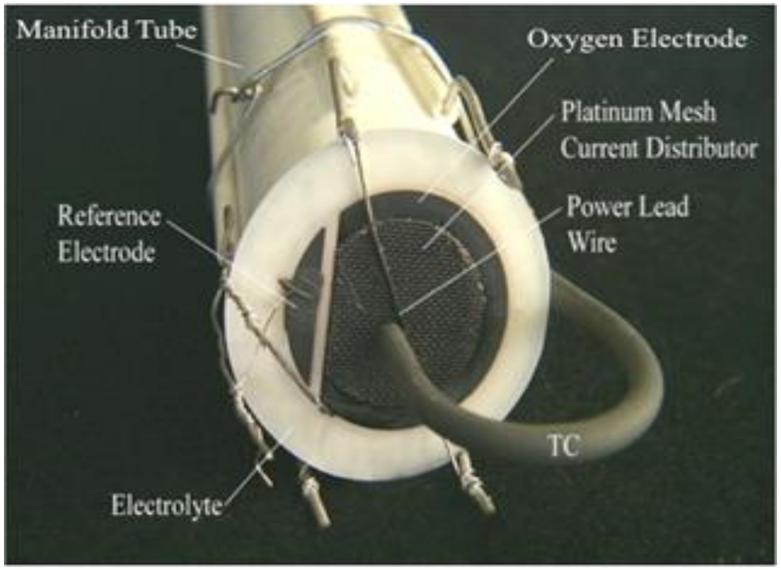
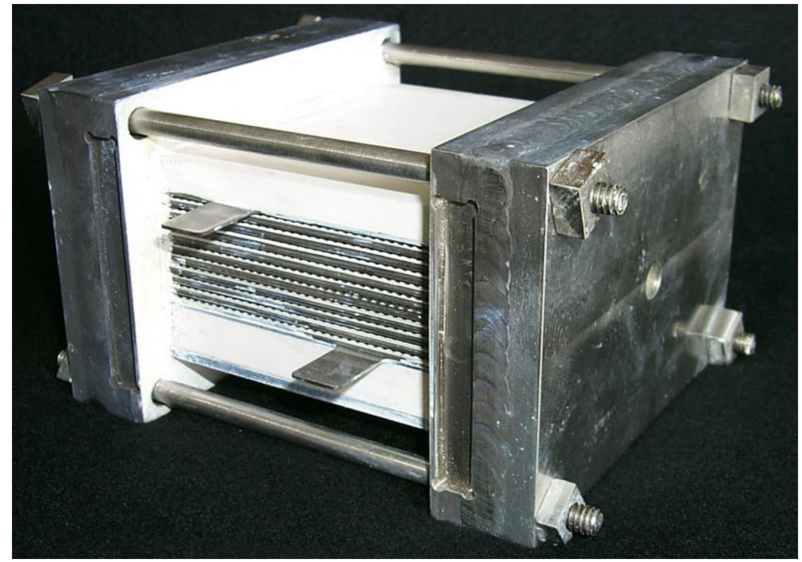
Test Set-up



Electrochemical Button Cell

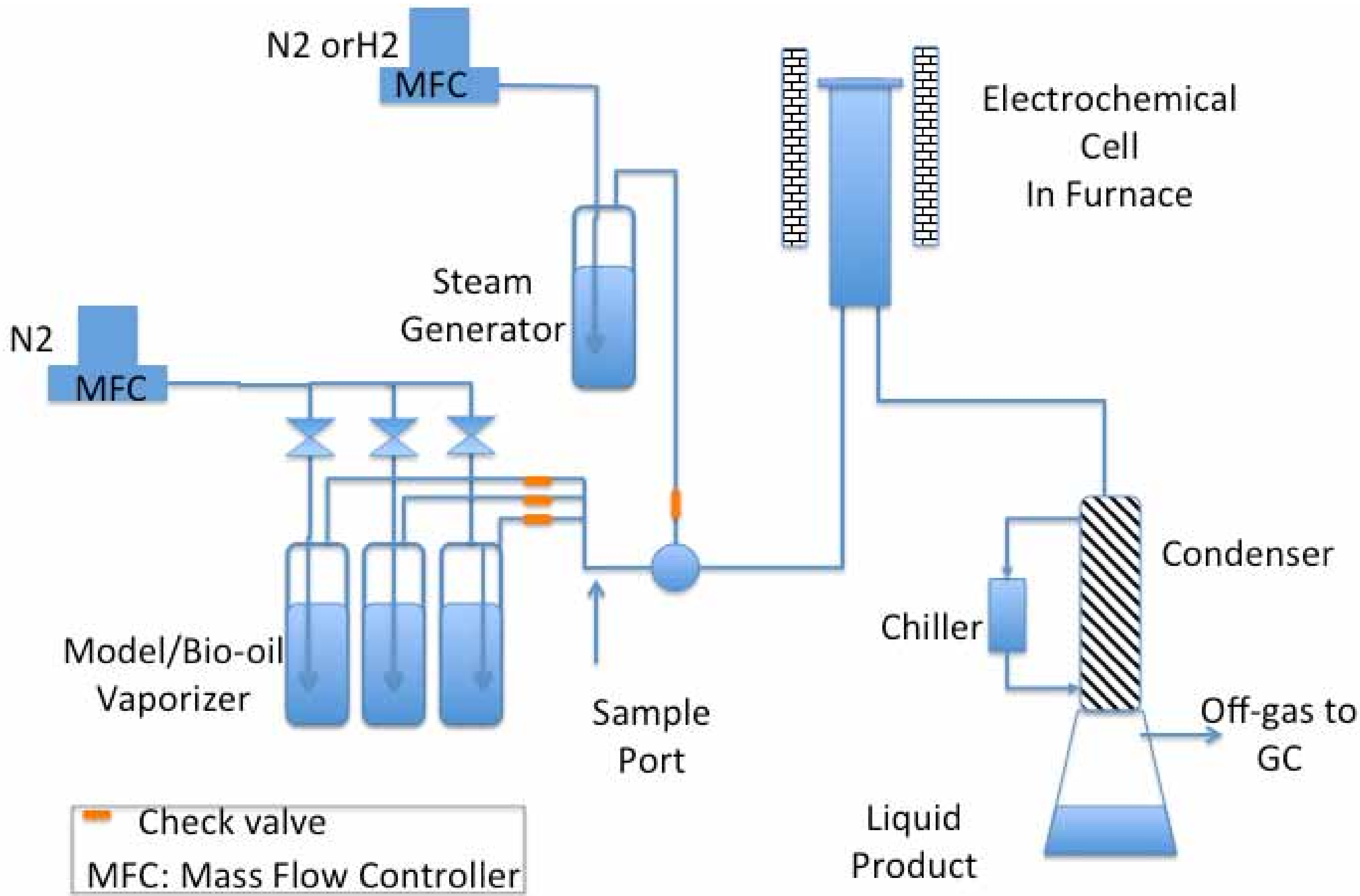
- Preliminary screening of deoxygenation capability
- ~ 2 cm^2 electrode active area
- Stirred reactor configuration
- Evaluation of operating conditions



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

Test Apparatus Schematic



Selected Model Compounds

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- Acetic acid
- Acetol (hydroxyacetone)
- Levoglucosan
- Furfural
- Methyl-2-cyclopenten-1-one
- Phenol
- Guaiacol
- Syringol
- Methanol

- Model Compounds:
  - Selected to cover representative compounds from carbohydrate and lignin fractions
- Bio-oil Testing:
  - Only aqueous fraction selected – more stable to reheating
- Integrated DeOX unit will face slip stream entire bio-oil vapor prior to condensation

Electrolysis Tests on Organic Material

Cell #	Electrolyte	Fuel side CC	Air side CC	Feed Material	Temperature	Coke Formation	Comments
27	*YSZ*	*Ni*	*Ag*	*Acetic Acid*	*800C*		*steam H2 performance increased post test with acetic acid*
28	YSZ	Ni	Ag	Acetic Acid, Acetone	700C,800C		Voltage vs Gas Phase Composition sweeps
29	SDC	Ni	Ag	Acetone, Furfural	550C, 600C, 800C	carbon build up	Voltage vs Gas Phase Composition sweeps
30	SDC	Ni	Ag	Furfural	550C	carbon formation on fuel exhaust tubes and cell in hot zone	Voltage vs Gas Phase Compostion sweeps, poor collection
31	SDC	Ni	Ag	Guaiacol, furfual, phenol, syringol	550C	carbon formation on fuel exhaust tubes in hot zone	Voltage vs Gas Phase Compostion sweeps, and long term condensate collection for GCMS, cell cracked
32	SDC	Ni	Ag	Syringol	550C	carbon formation on fuel exhaust tubes and cell in hot zone	Low collection due to possible condensation in test fixture, cell cracked and internally shorted
33	SDC	Ni	Ag	Guaiacol	550C	Chort test time no coke noticed	New bubbler cart used, Cooled due to leaky exhaust lines
34	SDC	Pt	Pt	Guaiacol	550C	Come coke or residue	
35	SDC	Pt	Pt	Guaiacol	550C	Come coke or residue	
39	SDC	Pt	Pt	PNNL Aq Bio-O	550C	Some coke or residue	operated until power outage terminated test, little sample collected
stack 541	ScSZ	Ni	Ag	guaiacol, PNNL BO	550C	Pending analysis	impingers added to collect vapor during BO run but added too much back pressure
46	ScSZ	Pt	Pt	Levoglucosan	550C	Pending anlaysis	dilute mix of levoglucosan and water 1 : 33.3, glassed cell

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Technical Accomplishments/ Progress/Results: Model Compounds

Button Cell: Syringol Results

Feed and Liquid Product Comparison (GC-MS Results)

Feed					Liquid Products				
Compound	C	H	O		Compound	C	H	O	wt %
Syringol	8	10	3		Phenol	6	6	1	76%
					o-cresol	7	8	1	22%
					p-cresol	7	8	1	0%
					m-cresol	7	8	1	0%
					2,6-xylenol	8	10	1	1%
					2-ethylphenol	8	10	1	1%

Gas Product Micro-GC Analysis

Component	H_2	N_2	Methane	CO	CO_2	Ethene	Ethane	Propane
wt%	0.01%	93.7%	0.1%	0.9%	3.8%	0.1%	0.1%	1.4%

Technical Accomplishments/ Progress/Results

Model Compound: Syringol

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

Technical Accomplishments/ Progress/Results

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Model Compounds

Button Cell: Guaiacol Results

Feed and Liquid Product Comparison (GC-MS Results)

Feed					Liquid Products				
Compound	C	H	O		**Compound**	C	H	O	wt %
Guaiacol	7	8	2		2,3-dihydrofuran	4	6	1	0.14%
					Unknown C6H8O	6	8	1	1.54%
					2-cyclopenten-1-one	5	6	1	0.68%
					Phenol	6	6	1	48.76%
					2-methyl-2-cyclopenten-1-one	6	8	1	0.51%
					Benzaldehyde	7	6	1	0.93%
					4,4-dimethyl-2-cyclopenten-1-one	7	10	1	0.56%
					o-cresol	7	8	1	18.02%
					Salicylaldehyde	7	6	2	28.47%
					2,5-xylenol	8	10	1	0.39%

Gas Product Micro-GC Analysis

Component	H_2	N_2	CH_4	CO	CO_2	Ethene	Ethane	Propane	Butane	Pentane
wt %	0.05	95.7	0.17	0.00	2.27	0.04	0.06	1.71	0.01	0.02

Technical Accomplishments/ Progress/Results

Model Compound: Guaiacol

Elemental Balance Between Feed and Product

Element	Feed wt% by Formula	Liquid Product wt% by GC-MS	Feed to Product % Change
Carbon	67.7%	74.55%	10.1%
Hydrogen	6.5%	6.26%	-3.7%
Oxygen	25.8%	19.19%	-25.5%

Liquid Product showed 26 wt% Oxygen relative to feed
Gas products not included

Technical Accomplishments/ Progress/Results Model Compounds

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Stack: Guaiacol Results

Feed and Liquid Product Comparison (GC Results)

Feed					Liquid Product					Liquid Product				
Compound	C	H	O		Compound	C	H	O	wt %	Compound	C	H	O	wt %
Guaiacol	7	8	2		Toluene	7	8	0	0.04	Guaiacol	7	8	2	2.47%
					Styrene	8	8	0	0.05	2,3-dihydrobenzofuran	8	8	1	0.66%
					Anisole	7	8	1	0.43	Naphthalene	10	8	0	0.57%
					1,2,4-Trimethylbenzene	9	12	0	0.34	1,2-dimethoxybenzene	8	10	2	1.89%
					2-cyclopenten-1-one	5	6	1	0.20	Catechol	6	6	2	39.81%
					Phenol	6	6	1	11.07	3-methylcatechol	7	8	2	2.78%
					Methyl Anisole	8	10	1	0.13	4-methylcatechol	7	8	2	2.22%
					Benzofuran	8	6	1	0.85	α-cedrene?	15	24	0	0.10%
					2-methyl-2-cyclopenten-1-one	6	8	1	0.25	o-anisaldehyde	8	8	2	0.07%
					Benzaldehyde	7	6	1	0.13	2,3-dihydro-1H-inden-1-one	9	8	1	0.17%
					o-cresol	7	8	1	8.71	Benzalmalonic dialdehyde?	10	8	2	0.04%
					p-cresol	7	8	1	0.57	o-bidiphenylol?	10	12	1	0.05%
					m-cresol	7	8	1	0.30	Dibenzofuran	12	8	1	0.15%
					Salicylaldehyde	7	6	2	20.65	4-ethyl-3-methylphenol	9	12	1	0.04%
					2,6-xylenol	8	10	1	0.22	2-methylbenzofuran	9	8	1	0.07%
					2-ethylphenol	8	0	1	4.96					

Technical Accomplishments/ Progress/Results

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Model Compounds

Gas Product Micro-GC Analysis

Stack: Guaiacol Results

Component	H_2	N_2	CH_4	CO	CO_2
wt %	0.05%	95.3%	0.18%	0.00%	2.46%
Component	Ethene	Ethane	Propane	Butane	Pentane
wt %	0.05%	0.07%	1.85%	0.01%	0.02%

Elemental Balance Between Feed and Product

Element	Feed wt% by Formula	Liquid Product wt% by GC	Feed to Product % Change
Carbon	67.7%	70.58%	4.2%
Hydrogen	6.5%	5.57%	-14.2%
Oxygen	25.8%	23.85%	-7.5%

Liquid Product showed 7.5 wt% Oxygen relative to feed
Inadequate stack seal caused product loss
Gas products not included

Technical Accomplishments/ Progress/Results

PNNL's Aqueous Phase Bio-Oil (Yellow Pine)

Button Cell Bio-Oil Feed and Liquid Product (cell 39) Comparison

*In Feed Only, In Product Only

Compound	C	H	O	Bio Oil Feed (90 °C evaporation and condensation as reference feed) wt %	Cell 39 Liquid wt %
2,3-dihydrofuran	4	6	1		3.12%
Acetic Acid	2	4	2	11.34%	
2-methoxytetrahydrofuran	5	10	2	0.09%	
2,3-butanedione	4	6	2	0.48%	
2-Butenal	4	6	1	0.28%	
Hydroxyacetone	3	6	2	16.14%	19.48%
Acetoin	4	8	2	2.42%	2.20%
3-penten-2-one	5	8	1	1.44%	2.21%
1-hydroxy-2-butanone	4	8	2	6.02%	
Cyclopentanone	5	8	1	1.76%	7.28%
3-Furaldehyde	5	4	2	0.86%	1.93%
2-Butoxyethanol	6	14	2	4.36%	
Furfural	5	4	2	9.85%	24.20%
2-cyclopenten-1-one	5	6	1	13.82%	18.58%
Phenol	6	6	1	3.07%	3.41%
2-methyl-2-cyclopenten-1-one	6	8	1	4.64%	10.86%
Acetylfuran	6	6	2	1.05%	1.82%
2,3-dimethyl-2-cyclopenten-1-one	7	10	1	0.18%	
o-cresol	7	8	1	2.64%	
Acetol acetate	5	8	3	2.62%	2.21%
p-cresol	7	8	1	0.40%	
m-cresol	7	8	1	0.48%	
5-methyl-2-furancarboxaldehyde	6	6	2	1.57%	1.96%
5-methylfurfural	6	6	2	1.57%	
Xylenol	8	10	1	0.03%	
3-methyl-1,2-cyclopentadione	6	8	2	0.66%	
Unknown C6H8O	6	8	1	1.90%	
Unknown C7H10O	7	10	1	0.89%	
1-(acetyloxy)-2-butanone	6	10	3	0.40%	
Guaiacol	7	8	2	6.19%	
2,3-dimethyl-2-cyclopenten-1-one	7	10	1		0.73%
5-methyl-2(5H)-Furanone	5	6	2	0.54%	
2,5-dihydro-3,5-dimethyl-2-furanone	6	8	2	0.64%	
3-ethyl-2-cyclopenten-1-one	7	10	1	0.16%	
Creosol	8	10	2	1.48%	

Technical Accomplishments/ Progress/Results: Aqueous Phase Bio-Oil

Button Cell Aqueous Phase Bio-Oil

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

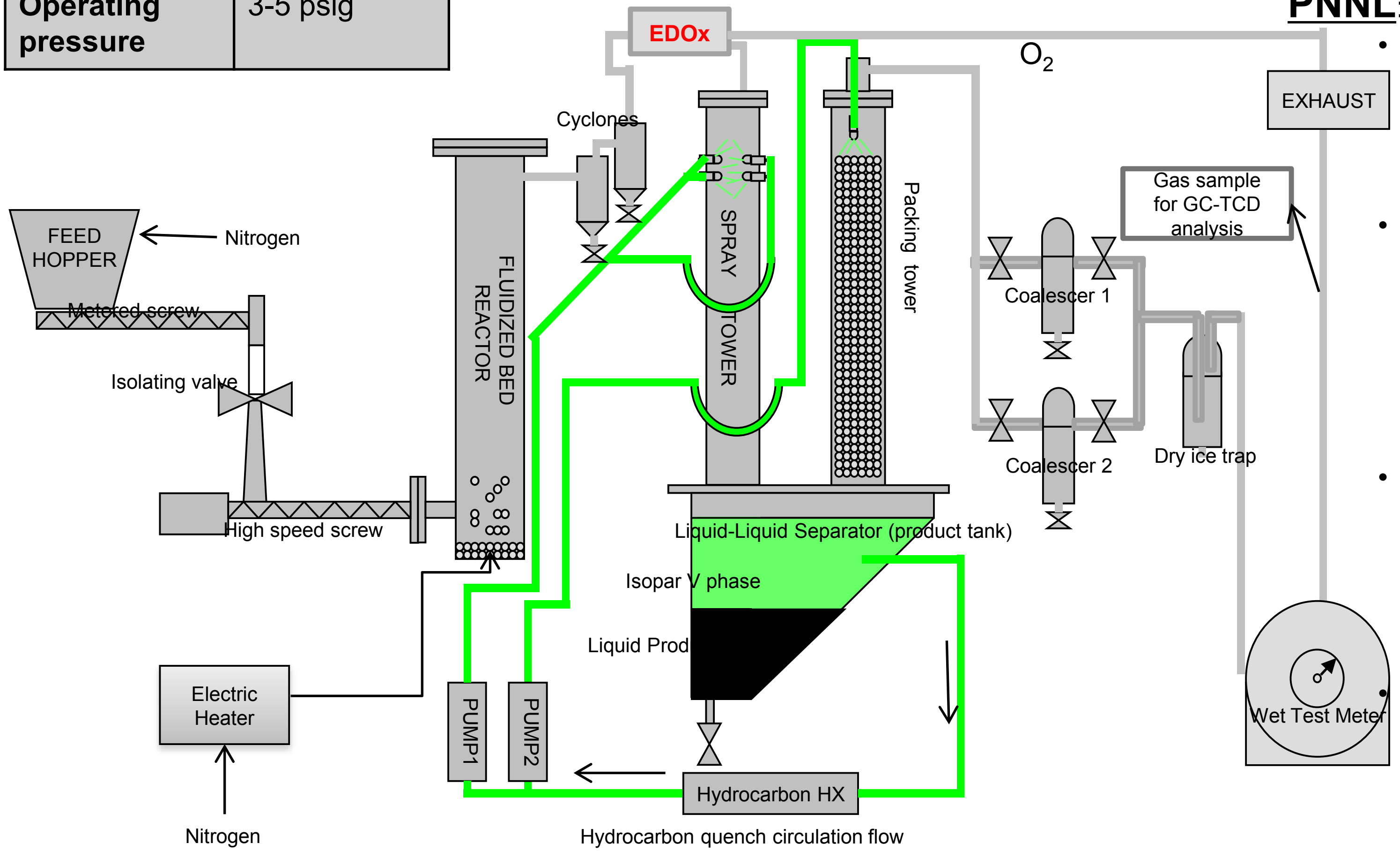
Element	90 ° C Condensate Feed wt% by GC-MS	Liquid Product wt% by GC-MS	Feed to Product % Change
Carbon	60.93%	70.58%	15.8%
Hydrogen	7.42%	5.57%	-24.9%
Oxygen	31.65%	23.85%	-24.6%

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

Bench-Scale Continuous-flow Fast pyrolysis System at PNNL

Reactor type	**Bubbling fluidized bed**
Operating Temperature	450-500 ° C
Biomass flow rate	1-1.5 kg/h
Operating pressure	3-5 psig

Vapor Residence time	**<2 sec**
Biomass used/Size	Softwood, hardwood, grass/ <2mm
Liquid collection strategy	Dry quench, Hydrocarbon quench, or Electrostatic Precipitator (ESP).



Planned activity at PNNL:

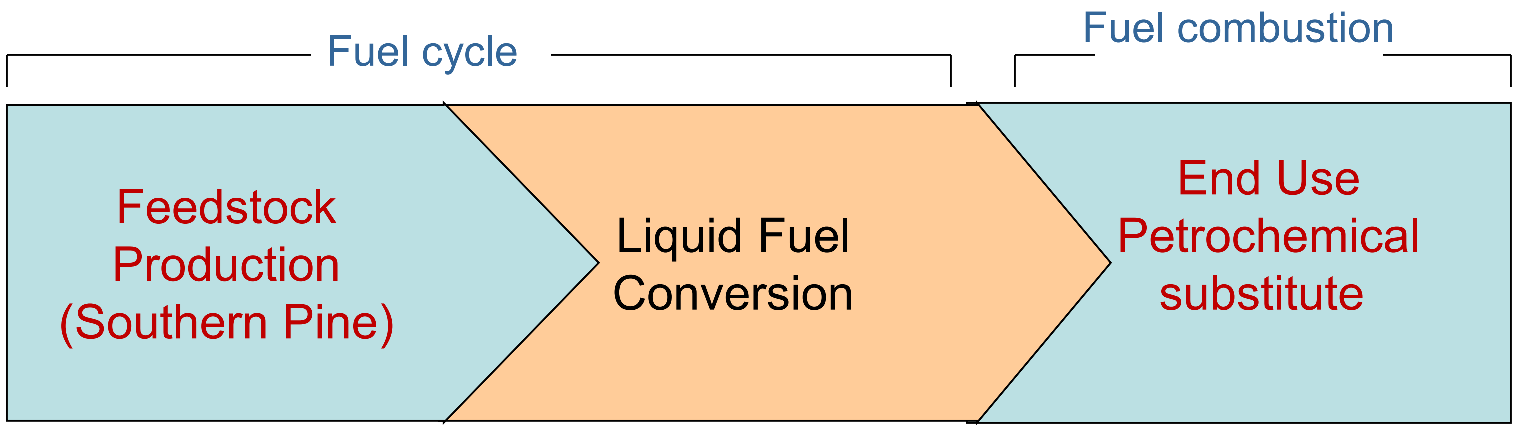
- Reactor modification: reduce effective volume and thus reduce vapor residence time-> **Improve liquid yield**.
- Add another cyclone unit to allow capture of fine particulates leading to the EDOx reactor-> **Reduce fouling of the reactor membrane by particulates**
- Potential addition of electrostatic precipitator to capture aerosol products-> **Improve liquid product capture and achieve better mass balance.**
- Re-piping to accommodate the EDOx reactor

Pacific Northwest NATIONAL LABORATORY

Technical Accomplishments: LCA/Process Modeling

- Life Cycle Inventory:
  - Forest residue harvest and farmed tree harvest (Southern Pine) as feedstock
  - Completed for feedstock, additional computation being finalized to complete fuel conversion segment of the fuel production LCI model
- ASPEN+ Modeling:
  - Material and energy balance modeling of fast pyrolysis to bio-oil
  - Model Compounds: Fufural and levoglucosan

Advanced Bio-oil Markets



- Harvesting equipment and energy
- Transportation steps

Feedstocks:
- Woody biomass (Forest residues)

- Electricity
- Feedstock provides thermal energy

Technologies:
- Fast Pyrolysis
- Electro de-oxygenation

- Petroleum blendstock
- Bio-char (co-product)

Transportation fuel market:
-Substitute for gasoline, diesel, or petroleum blendstock
-Co-products may be land applied (sequestration)

Technical Accomplishments/ Progress/Results
Summary

– Year 1 Technical Objectives/Results
  - 60% efficiency of deoxygenation from mixtures of model compounds
  - 30% efficiency of deoxygenation and 75% C and H efficiency using aqueous fraction of bio-oil

Elemental Balance Between Feed and Product

	Syringol Cell 32	Guaiacol Cell 35 1.3 V	BioOil Cell 39
Carbon	23.3%	10.1%	15.8%
Hydrogen	2.3%	-3.7%	-24.9%
Oxygen	-47.2%	-25.5%	-24.6%

Relevance

- BETO Multi-Year Program Plan of Using Bio-oil as source of fuel
  – Project demonstrated feasibility of deoxygenation of bio-oil.
  – Both model compounds and aqueous phase of pinewood pyrolysis oil showed oxygen loss via electrochemical means
  – High C and H efficiency was indicated
- EDOx unit can be potentially integrated to pyrolysis unit to stabilize bio-oil prior to cooling
- Project objective is to demonstrate integrated operation of EDOx with pilot scale pyrolysis unit at PNNL
- Successful project will enable hydrogen-free, integrated operation of pyrolyzer to provide stable pyrolysis oil product
- Ceramatec's parent company CoorsTek is the largest technical ceramics manufacturer. Ceramatec will seek to team with a bio-oil producer to demonstrate the technology at TRL 4 – 5.

Future Work

- Process improvement to reach project milestone of 60% efficiency of deoxygenation and 85% C and H efficiency using aqueous phase of bio-oil
  - Evaluation of catalyst with high selectivity for non-oxygenated compounds
  - Improved feed system to introduce entire aqueous phase of bio-oil vapor
  - Elimination of system leaks through improved seals and product collection
  - Integration of gas product in overall mass balance

- Engineering prototype of integrated Electro-EDOx design
  - Final stack design integrated at PNNL

- Completion of TEA and Modeling Efforts
  - ASPEN+ and LCA

Summary

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1. A novel electrochemical means of deoxygenation demonstrated
   1. No external hydrogen feed
   2. Electric input allows distributed, small scale operation
   3. Integration with pyrolyzer will allow upgrading prior to bio-oil cooling
2. Feasibility demonstrated with button cells and stacks using standard electrolysis electrodes
   1. Model compounds showed 25 to 47% oxygen removal
   2. Bio-oil showed 25% oxygen removal
3. When matured, electrochemical process will addres techno-economic challenges of upgrading of bio-oil
4. Integrated testing of EDOx unit with PNNL's pilot scale pyrolyzer planned

Additional Slides

Ceramatec Technology Focus in Fuels

– Fuel Synthesis/Processing
  - Biofuels (Production of Na-methylate reactant)
  - Methane to Liquid fuels
  - Heavy oil upgrading
  - Direct methane to chemical
  - Biogas clean up

Project Status: Fuel Synthesis/Ugprading

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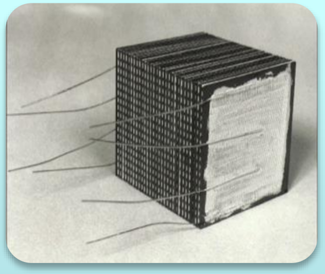
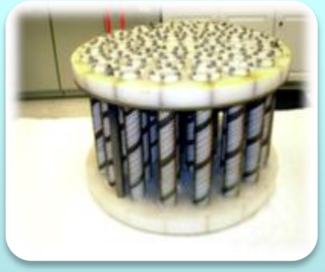


Electrochemical Deoxygenation of Pyrolysis Oil

- DOE CHASE Project
- Electric Energy input, No hydrogen
- TRL 2



Electrochemical Hydrocarbon Coupling

- USDA (Biomass R&D Initiative)
- Electric Energy input, No hydrogen, Hydrogen byproduct
- TRL 3 - 4

Biogas and Coal-gas to Liquids

- DOE/ONR/Private
- Biogas tar clean up, Fischer Tropsch (Gas to Liquids)
- TRL 6

Publications, Patents, Presentations, Awards, and Commercialization

- A provisional patent application was filed on August 30, 2013, titled "Hydrogen Utilization and Carbon Recovery", with the application number 61/872,184.
- On September 2, 2014, the non-provisional patent application was filed, titled "Hydrogen Utilization and Carbon Recovery", with the application number 14/474,843.
- A manuscript was submitted to Electrochemical Society Transactions (Title: Electrochemical Upgrading of Bio-Oil)