Electrochemical Deoxygenation Process for Bio-oil Upgrading

CAAFI R&D Webinar Series

S. (Elango) Elangovan

Joseph Hartvigsen

Lyman Frost

Ceramatec Overview

- Founded 1976
- *Subsidiary Company* of Keystone Holdings (Coors Family owned)
- 140,000 ft^2 R&D and Manufacturing Facility
- 150 Employees
- Concept to commercialization
  - R&D --> prototype --> pilot scale fabrication
- Core competencies:
  - Electrochemistry, Ionic conducting ceramics, & Advanced Materials
- Customers
  - 50% Fortune 100/500 Companies
  - 50% Govt.

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Ceramatec Technology Focus

- Combining Electrochemistry, Ceramics, Advanced Materials, and Novel Fabrication:
  - Energy Conversion/Storage
    - Solid Oxide Fuel Cells/Electrolyzer
    - Batteries
  - Chemical Synthesis
    - Na, Li metal
    - Na methylate, Na hypochlorite
    - High purity oxygen, hydrogen

Ceramatec Technology Focus

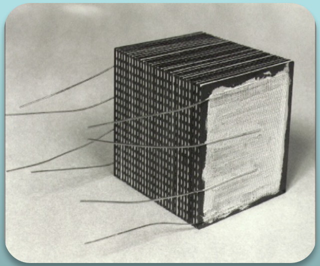
- Fuel Synthesis/Processing
  - Biofuels and Methane to Liquid fuels
  - Heavy oil upgrading
  - Direct methane to chemical
  - Biogas clean up
- Environmental
  - Fly ash treatment
  - Na removal from radioactive waste

Recent Project Awards

- ARPA-E
  - Intermediate Temperature Fuel Cell (2012)
  - Direct Conversion of Natural Gas to Chemical (2012)
  - Li-S Battery (2013)
- USDA
  - Biomass to Fuel
- DOE
  - Bio-oil Upgrading
- State of Wyoming/Office of Naval Research (2011/2013)
  - Modular Fischer Tropsch Demonstration

Overview of Biofuel Technologies

Biofuel Synthesis

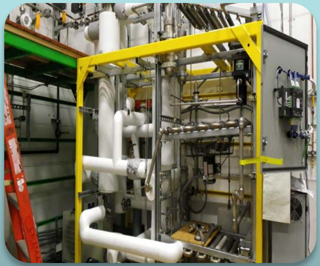


Electrochemical Deoxygenation of Pyrolysis Oil

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

Electrochemical Hydrocarbon Coupling

- USDA
- Electric Energy input, No hydrogen, Hydrogen byproduct
- TRL 3 - 4



Biogas to Liquids

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

CHASE Project Team

- Ceramatec
  - Electrochemical Technology Development
    - Dr. S (Elango) Elangovan – PI
    - Mr. Joseph Hartvigsen – Chemical Engineer
- Pacific Northwest National Laboratory
  - Bio-oil Expertise and DeOx Integration test
    - Mr. Douglas Elliott
- Drexel University
  - Lifecycle Analysis
    - Dr. Sabrina Spatari

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

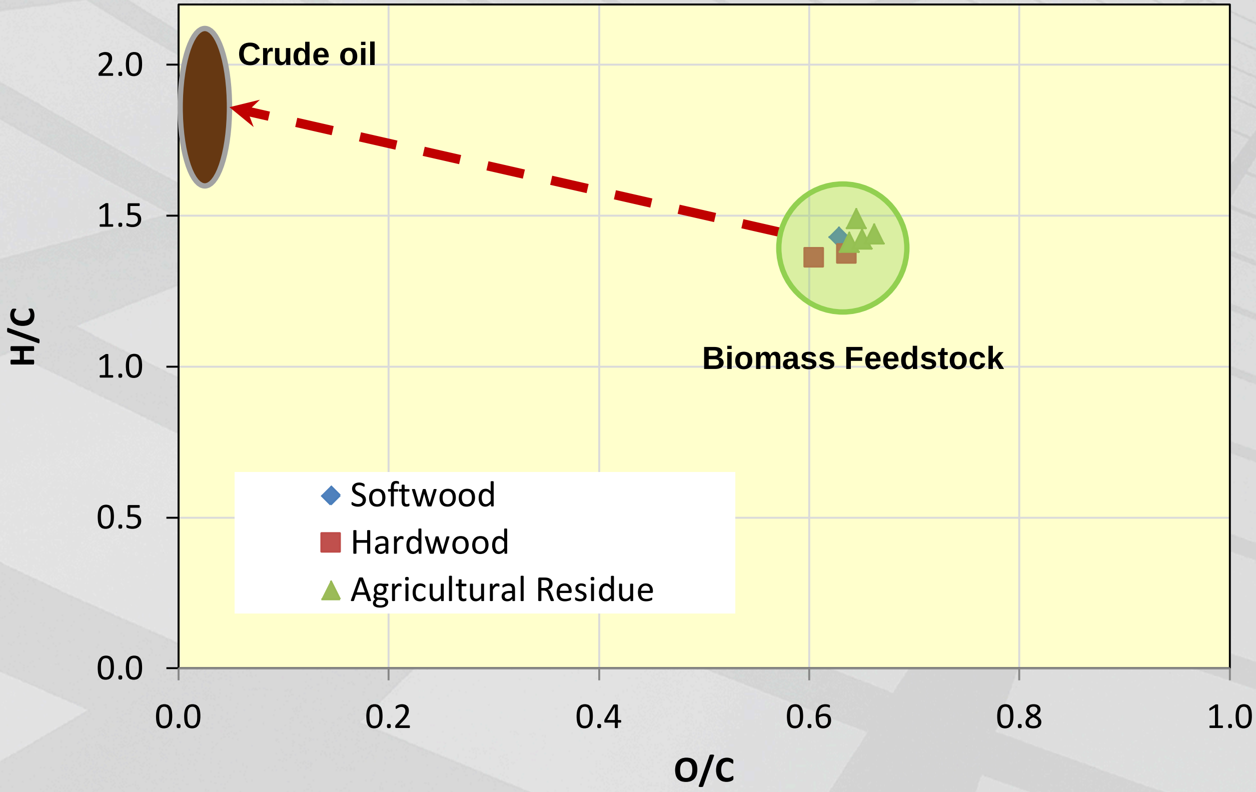
Fast Pyrolysis of Biomass to Bio-oil for Liquid Fuels Production

DOUGLAS C. ELLIOTT

Pacific Northwest National Laboratory

Ceramatec
Salt Lake City, Utah
December 6, 2013

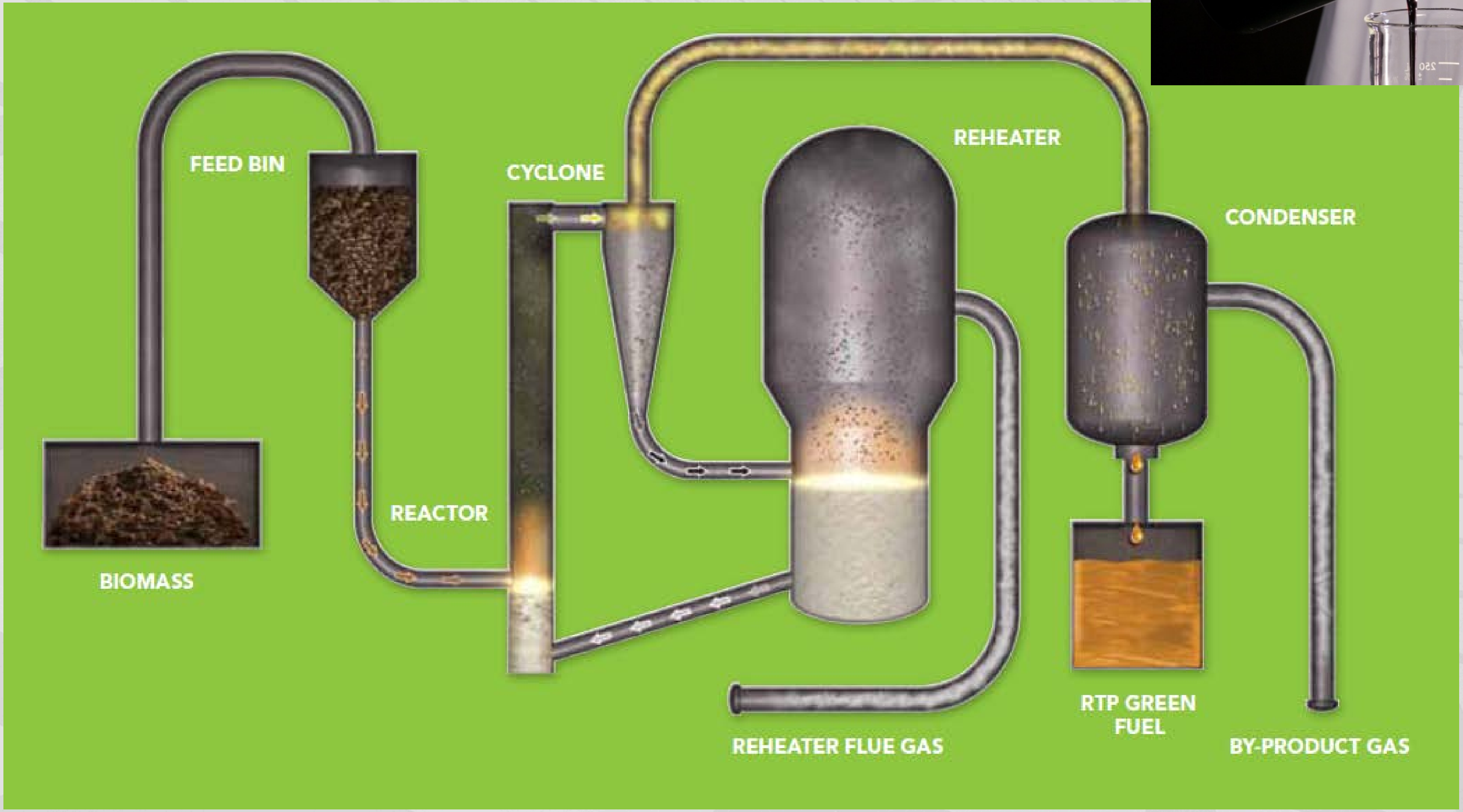
Relationship of Fuel Compositions



<u>Targets:</u>

- ❑ H/C = 1.6 – 2.1
- ❑ O/C = 0.02 – ?

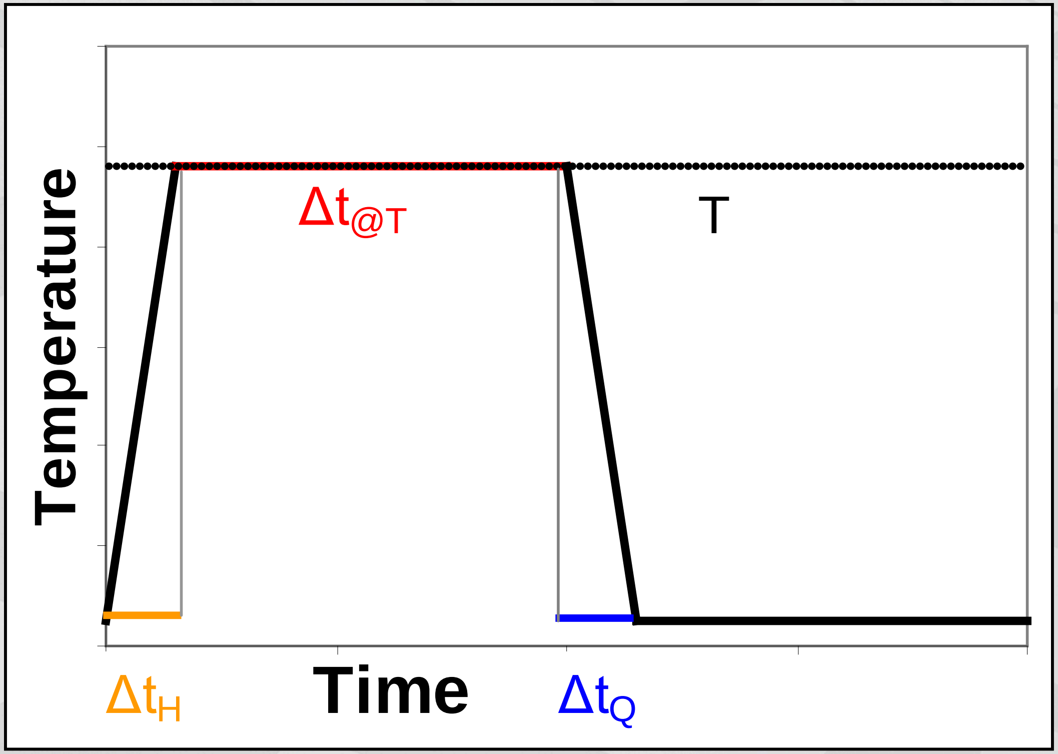
Typical Pyrolysis Process



www.honeywellnow.com
The Practical, Proven Path to Green Energy. 2010. Envergent Technologies.

Conditions to Maximize Bio-oil Production

- Liquid intermediates from the degradation of hemicellulose, cellulose, and lignin in particles of 2-4 mm, <10% moisture
- Fast Pyrolysis: 450°C < T < 550°C, $t_{@T} < 2$ sec



- As $\Delta t_{@T}$ ↑: Gas ↑ Oil ↓
- As Δt_{H} ↑: Char ↑ Oil ↓
- As Δt_{Q} ↑: Gas ↑ Oil ↓

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Comparison of Wood-Derived Bio-oils and Petroleum Fuel

Characteristic	Fast pyrolysis Bio-oil Wet --------- Dry		Heavy petroleum fuel
Water content, wt%	15-25		0.1
Insoluble solids, %	0.5-0.8		0.01%
Carbon, %	39.5	55.8	85.2
Hydrogen, %	7.5	6.1	11.1
Oxygen, %	52.6	37.9	1.0
H/C	2.3	1.3	1.6
O/C	1.0	0.5	0.01
Nitrogen, %	<0.1		0.3
Sulfur, %	<0.05		2.3
Ash	0.2-0.3		<0.1
HHV, MJ/kg	17		40
Density, g/ml	1.23		0.94
Viscosity, cp	10-150@50ºC		180@50ºC

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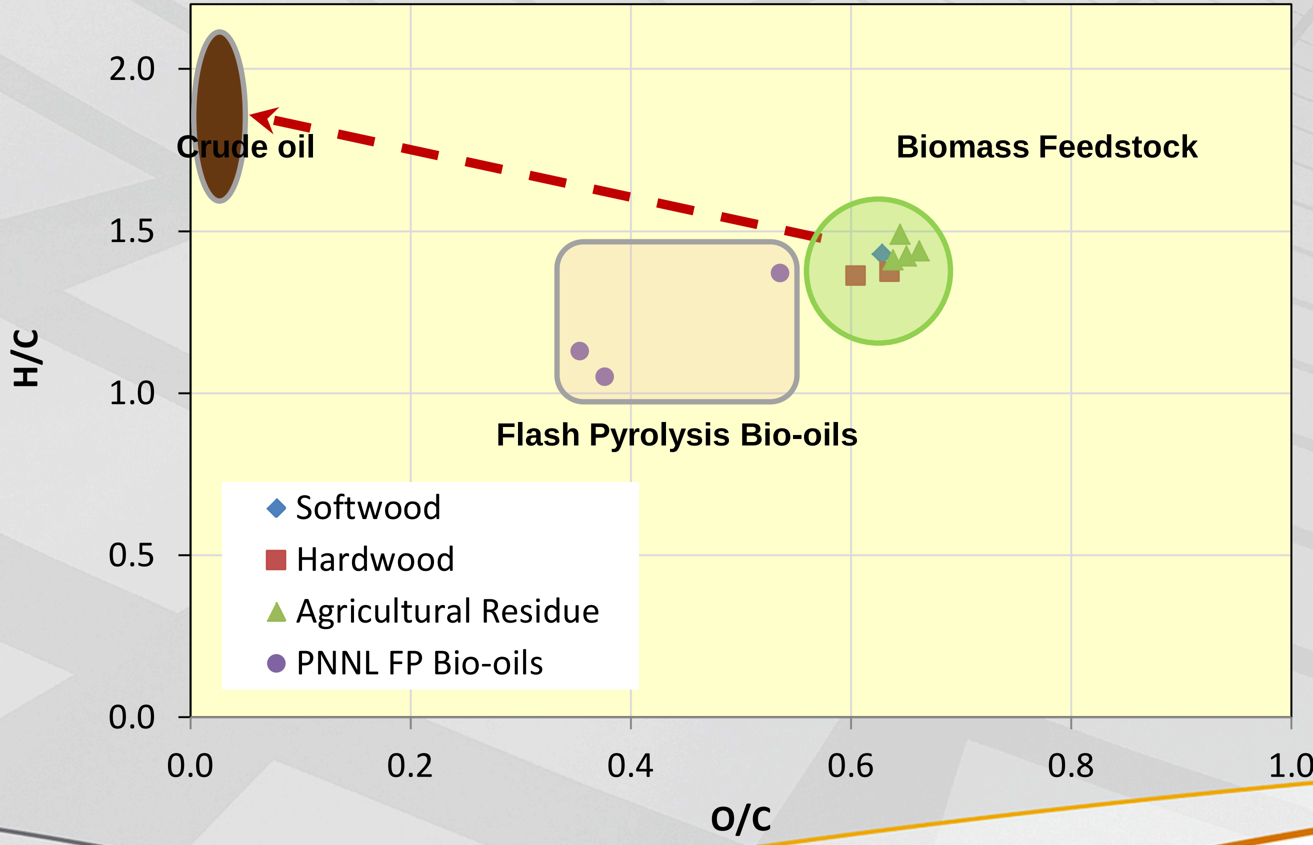
Bio-oil Composition Quick Check

Feedstock	H/C	O/C
Softwood Forest Residue	1.05	0.38
Mtn Pine Beetle Killed	1.37	0.54
Hog Fuel	1.13	0.35



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Unwanted Characteristics of Bio-oil

Attribute	Problem
Low pH	Corrosion
High viscosity	Handling, pumping
Instability	Storage, phase separation, polymerization, viscosity increase
Solids content	Combustion problems, equipment blockage, erosion
Alkali metals	Deposition of solids in boilers, engines, and turbines
Water content	Complex effect on heating value, viscosity, pH, homogeneity, etc.

Bio-oil Components—Essentially all oxygenates

- Carbohydrate fragments
  - Anhydrosugars
  - Sugar fragments
    - Carbonyls
    - Hydroxyaldehydes
  - Furfurals
  - Alcohols
  - Acids
    - Acetic
    - Formic
    - Sugar acids
- Lignin fragments
  - Phenolics
  - Aromatic ethers
  - Methanol
  - Oligomers

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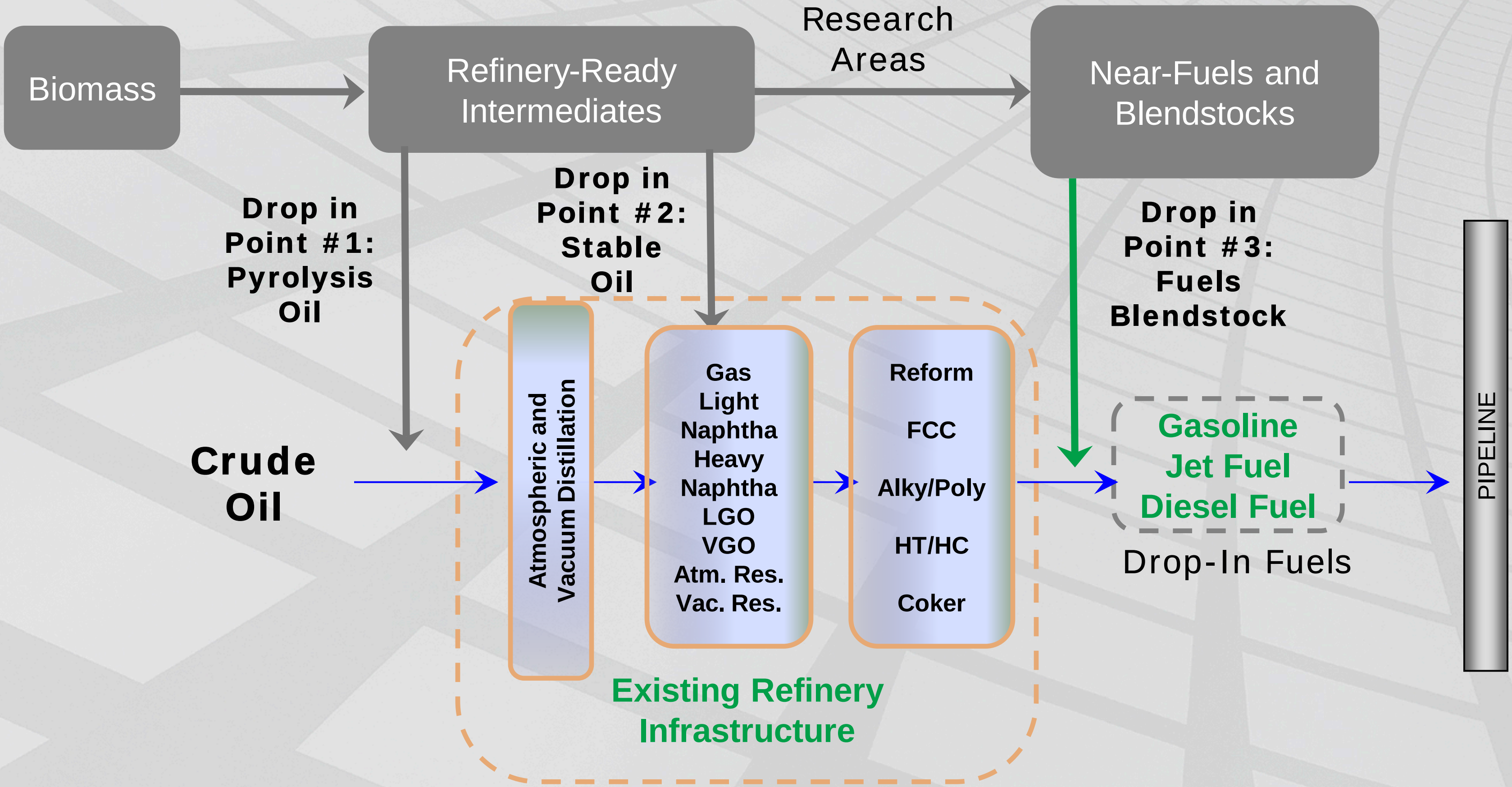
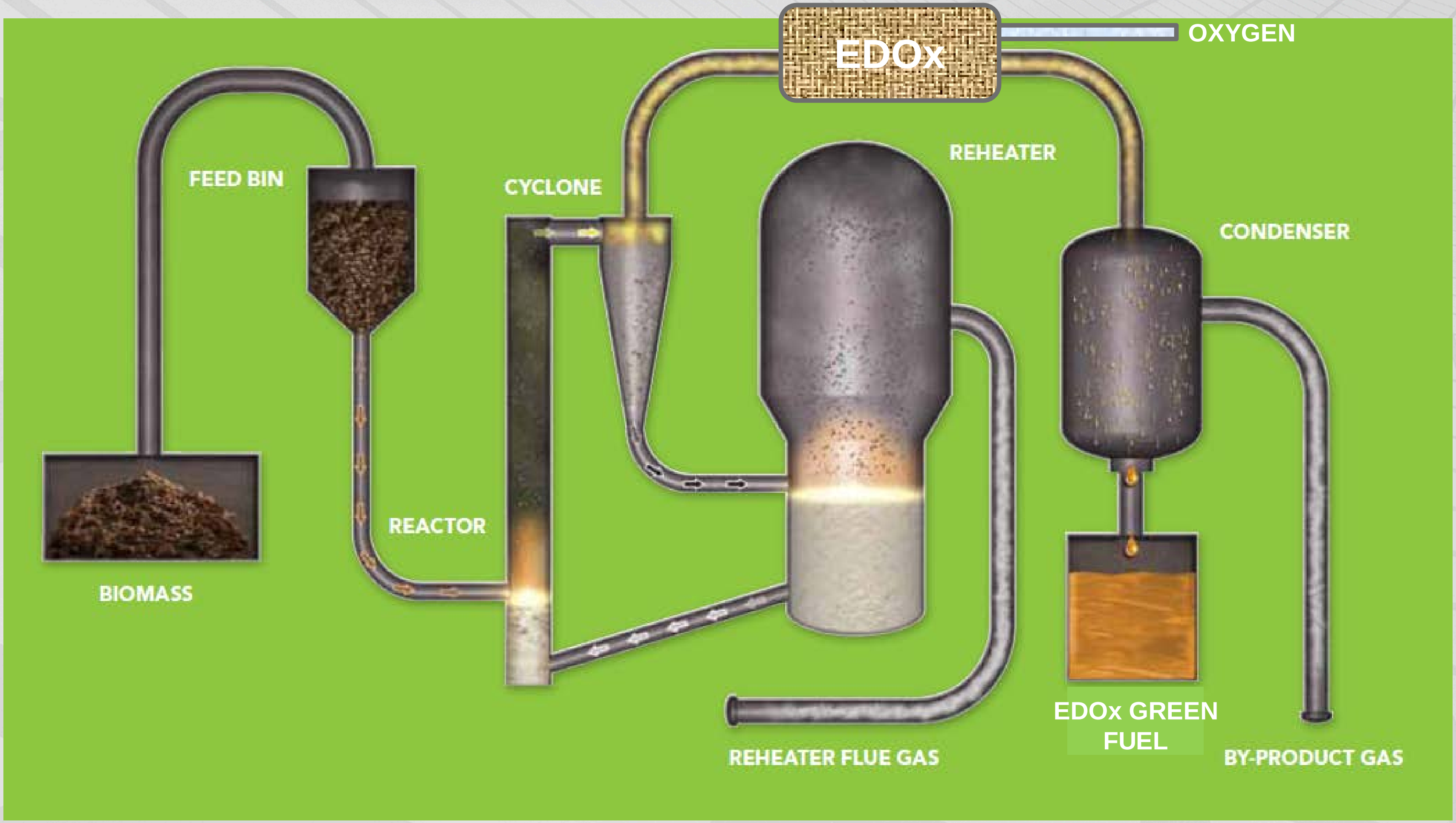
Refinery Drop-in points for Bio-Oil



EDOx Pyrolysis Process



Modified from www.honeywellnow.com

Path Forward-Ceramatec/PNNL project

- Bio-oil vapor conversion to liquid fuels via EDOx process needs to be demonstrated
  - Appropriate model compounds
  - Mixed model compounds
  - Bio-oil vapor components
- Process design for bench-scale demonstration needs to be developed
- Bench-scale processing of hot vapor from fast pyrolysis by EDOx needs to be evaluated

Deox Process Overview

“Deoxygenation” Background

- 25 Years of Solid Oxide Fuel Cells
  - Fuel: hydrogen, syngas from reformed methane, JP-8
  - kW class demonstration
- 10 Years of Solid Oxide Electrolysis Cells
  - Electrolysis of steam to generate hydrogen
  - Co-electrolysis of steam, carbon dioxide mixture to generate syngas
  - 17 kW demonstration at Idaho Natl Lab.

Deoxygenation Process

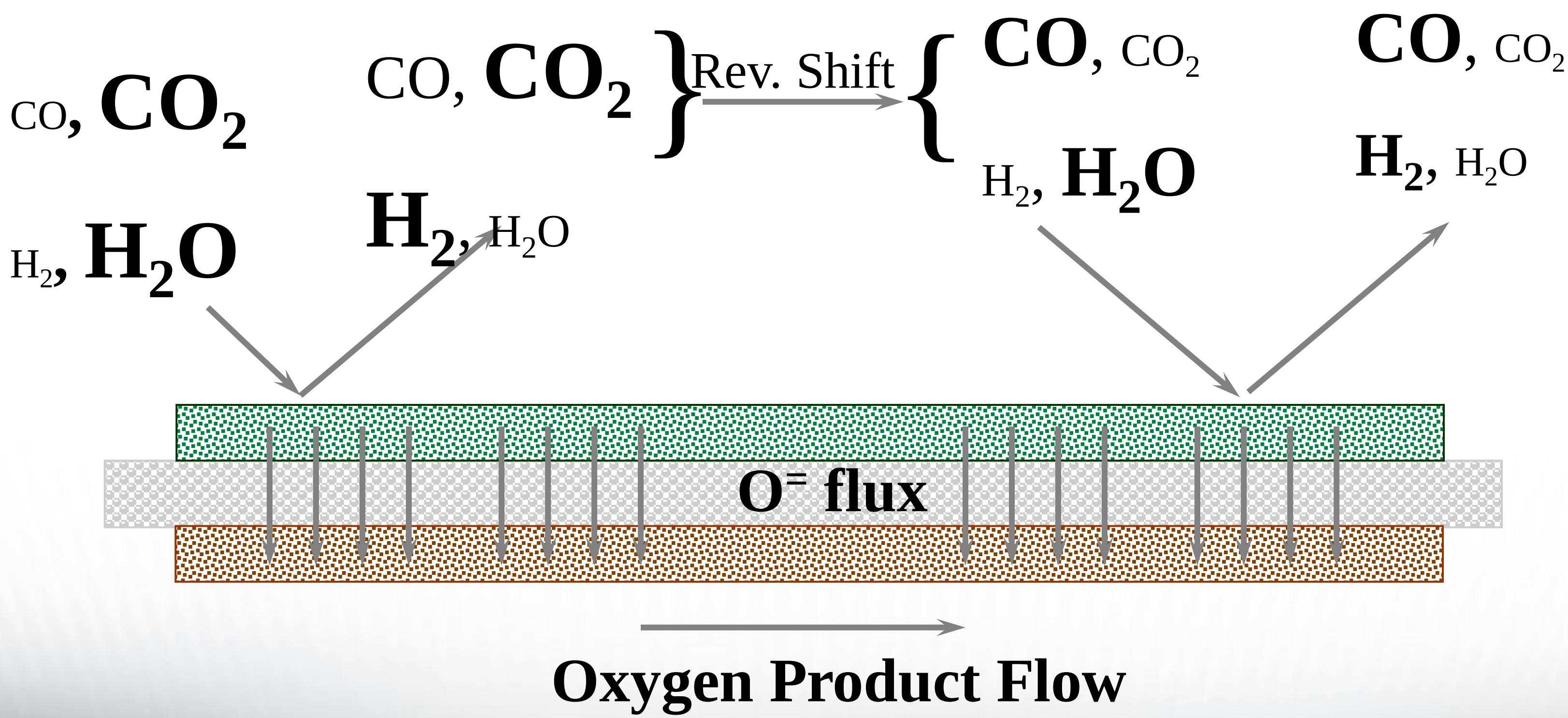
- Doped (Y or Sc) Zirconia membrane
  - Oxygen ion conductor
  - No other ions move through
  - 100% of current is from oxygen transport
    - 100% Current (Faradaic) efficiency
- Air electrode (Perovskite)
- Fuel electrode (Ni-Ceria cermet)

Electrolysis Of CO_2

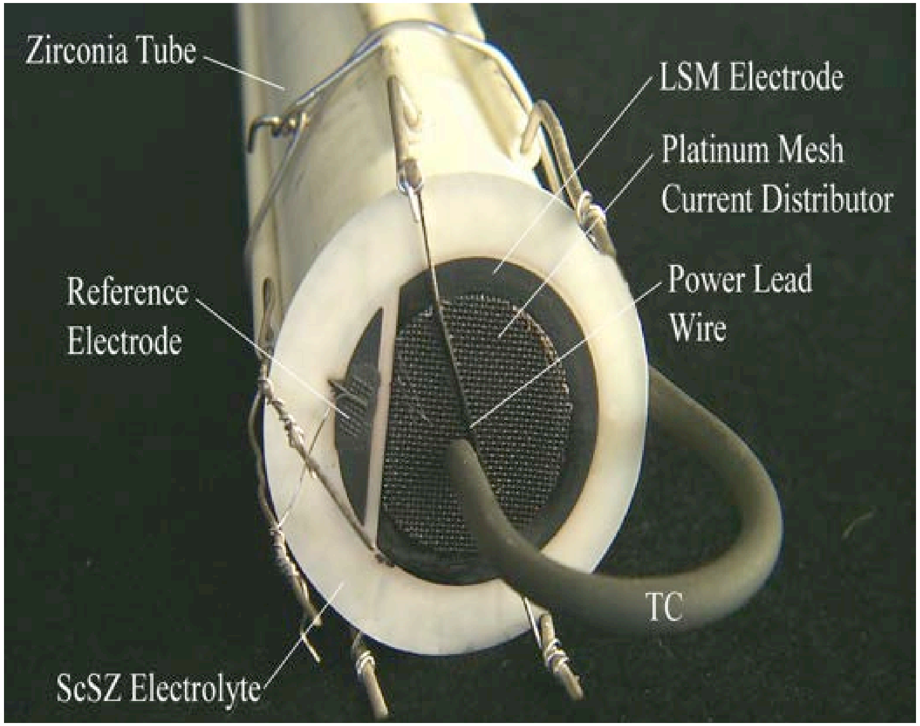
Feed: H_2O, CO_2, (minor H_2, CO)

Reactions: Oxygen removal from steam, CO_2, and Reverse Shift

Reverse Shift Reaction: CO_2 + ⇑ H_2 <==> CO + ⇓ H_2O



Button Cell



Reactor for feasibility tests

- Single Cell (Anode/Electrolyte/Cathode)
- Oxygenated Species on cathode side (inside the tubular manifold)
- Air flow on the anode side

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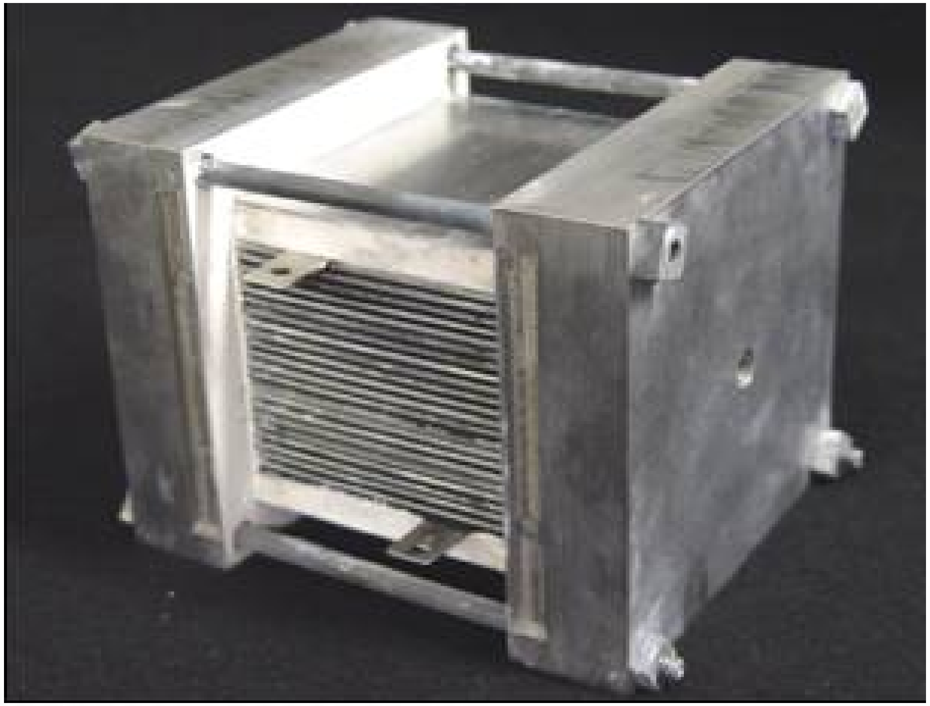
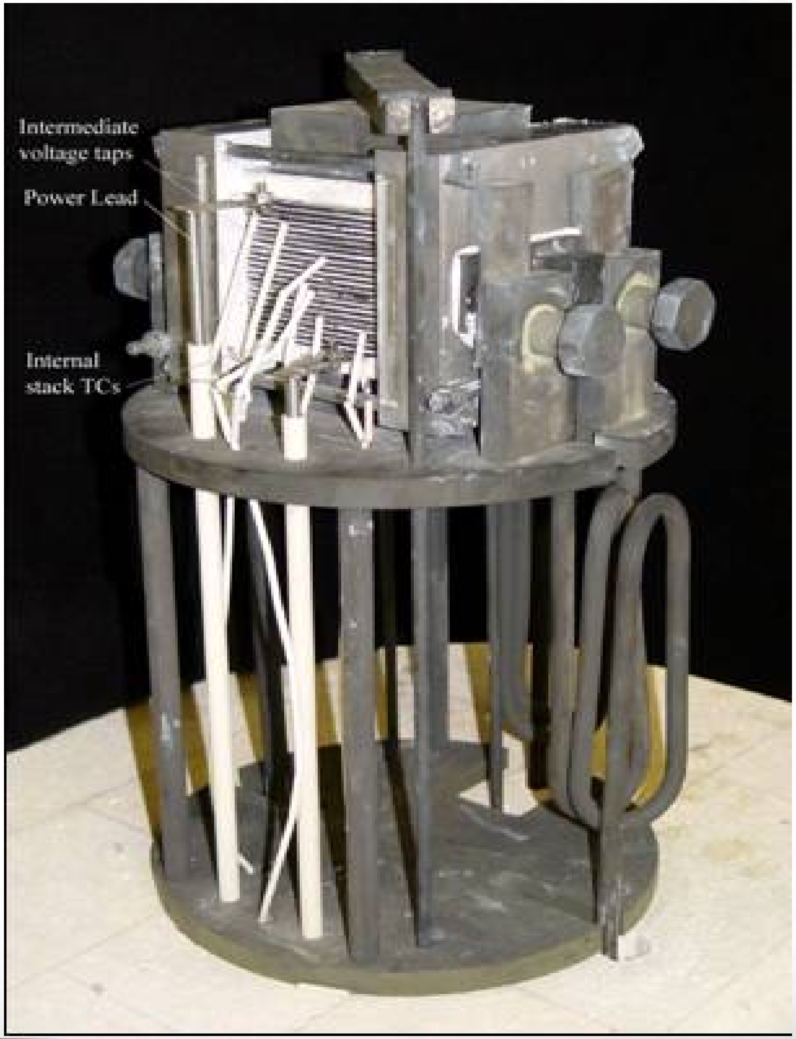
Short Stack Configuration

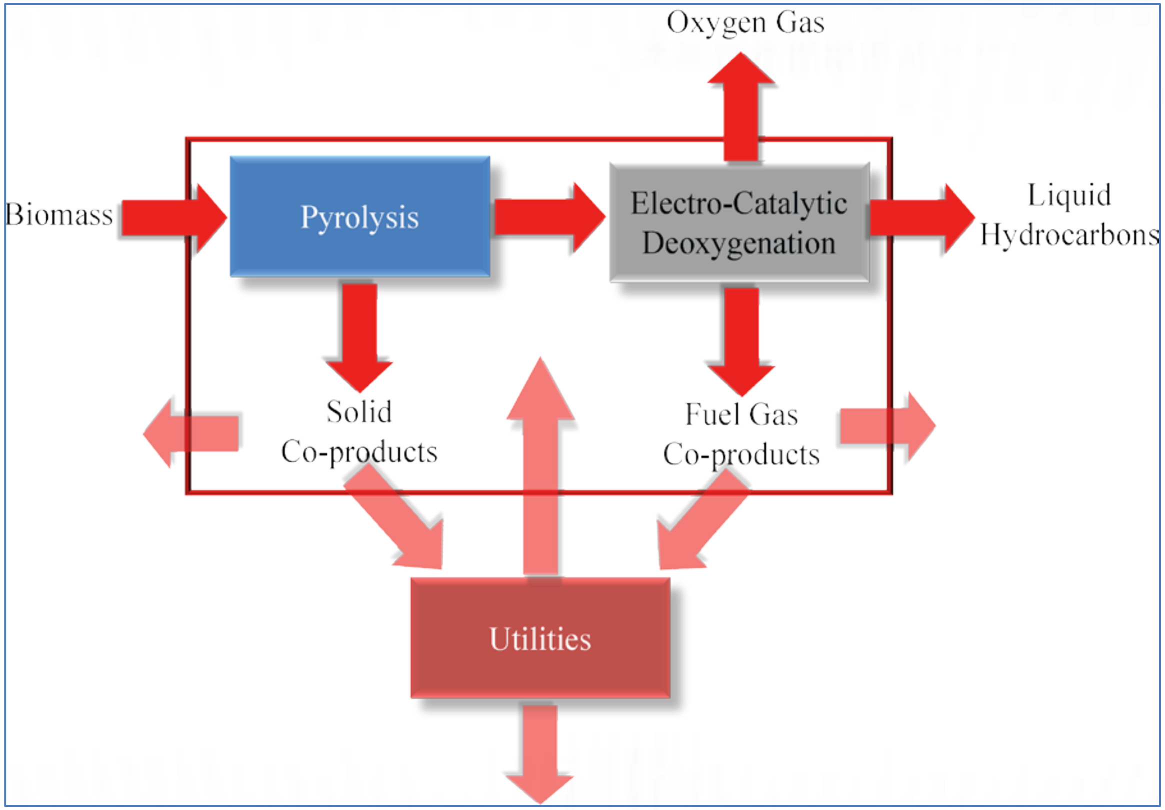




Possible Scale up options

720 Cell System at INL
5.7 Nm^3/hr - 17.5kW H_2 Production

Overall Process Schematic



The overall pyrolysis oil to liquid hydrocarbons system without using hydrogen

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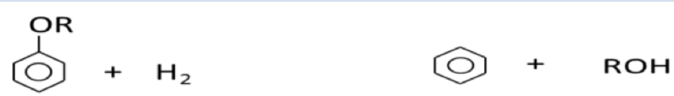
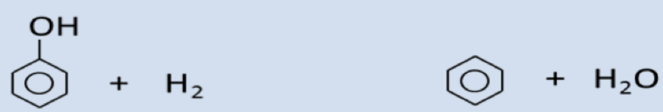
Hypothesis

- Can we remove oxygen from oxygenated hydrocarbon directly or indirectly?

Table 1: Hydrocarbons from Py-oil

Acids	R-COOH + $3H_2$	→	RCH_3 + $2H_2O$
Acids	2R-COOH	→	R-R + 2CO2
Aldehydes	R-CHO + $2H_2$	→	R-CH_3 + H_2O
Aldehydes	2R-CHO +$3H_2$	→	R-CH_2-CH_2-R + 2H2O
Ketones	R-CO-R + $2H_2$	→	R_2CH_2+ H_2O
Ketones	2R-CO-R' + $3H_2$	→	RR'CH-CHR'R + $2H_2O$
Alcohols	R-CH_2OH + H2	→	R-CH_3 + H_2O
Ethers			
Phenols			

Direct: Electrochemical transport of oxygen directly

Indirect: Electrochemical transport of oxygen from water to create hydrogen in-situ to deoxygenate hydrocarbon

Benefits

- Deoxygenation prior to cooling of bio-vapors
- Electrochemical reaction only removes oxygen (every 4 electrons in the circuit removes one molecule of oxygen)
  - All C and H are retained on the fuel side
  - Lighter HC with fuel value as co-product
- No hydrogen required
- Temperature compatibility (EDOx ~ 650-700°C)

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Initial Experiment

- Model Compound Acetone
  - Dilute Acetone vapor (N_2 bubbled through acetone liquid)
  - Hydrogen bubbled through water (to keep Ni reduced)
- Test Condition: 650 °C, 30 to 50 mA/cm^2
- Under current the exit gas contained methane (~70%), other hydrocarbon – ethane mainly, and some evidence of octane - (10%)

Challenges

- Would Ni promote coking, formation of large amount of syngas?
  - Will investigate coke-resistance cathode compositions
- Regeneration of electrode after fouling
- Conversion at ambient pressure, and recycle requirements
- Module design
- Separator/current collector (protective layer for metal plates?)

Model Compound Selection

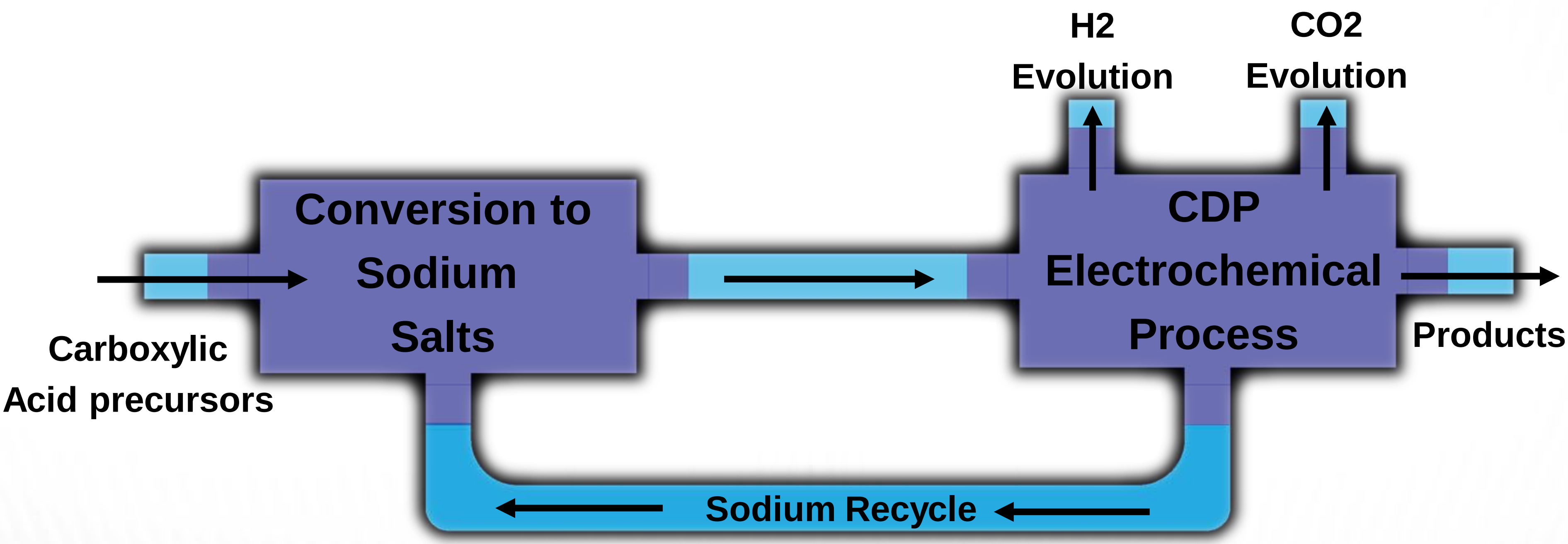
- Simple to Complex
  - Aldehydes, Ketones, Acids, Phenol
  - Mixtures
  - Bio-oil vapor
- Button Cell to multi-cell reactor
- Integrated test at PNNL

Other Fuel Synthesis Projects

Ceramatec's Decarboxylation Process

Modified Kolbe Electrolysis

$$2RCO_2Na \rightarrow R-R+2CO_2+2e^-+2Na^+$$



- No hydrogen addition
- Enables distributed manufacturing

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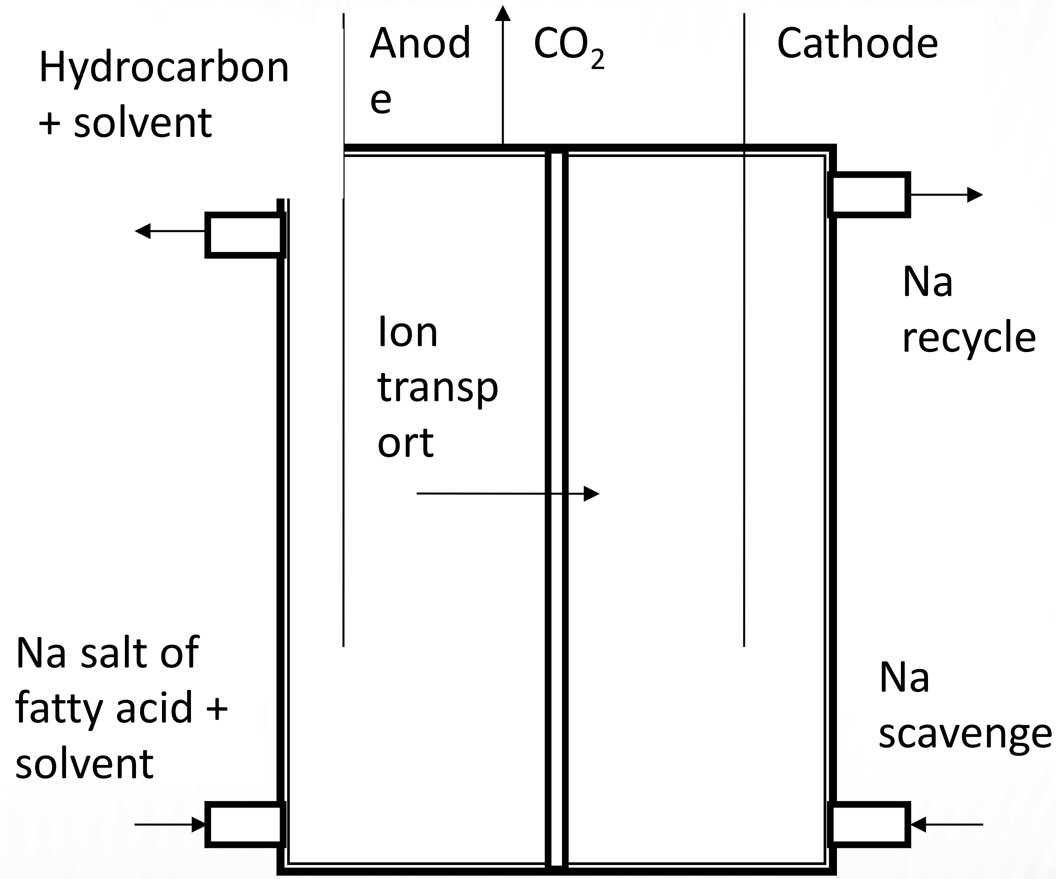
Decarboxylation Technology

- Description:
  - NaSICON electrolytic cell used to produce hydrocarbons from fatty acids
- Applications:
  - Chemicals production
  - Lubricant production
  - Fuels production
- Status:
  - Laboratory investigation on-going

$$2R\text{-}COONa \text{ --------- } > \mathbf{R\text{-}R} + 2CO_2 + 2e^- + 2Na^+$$



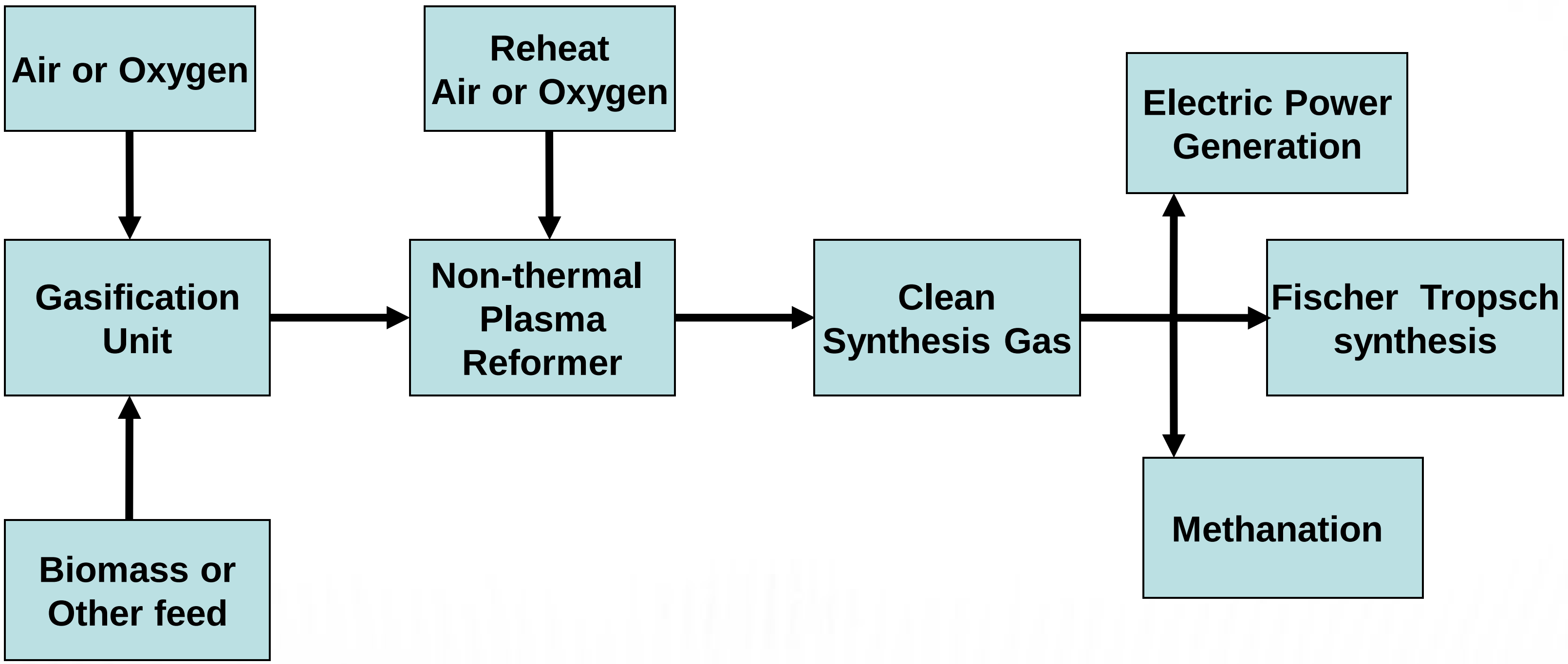
Decarb Module

- Currently testing single membrane
  - Vary starting hydrocarbon
  - Product Selectivity
  - Yield
  - Operating conditions
  - Lifetime

Other Fuel Synthesis Projects

Reformation of Tars & Oils from Biogas

Directly reform tars & oils



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Laboratory scale plasma reformer

Simulated gasifier stream

- Bottled syngas
- Toluene injection
- Steam, O_2, or air to obtain temperature
- GC analysis of toluene destruction and CGE

Best combination

	Dry Gas	Air In	O_2 In	H_2O In	Toluene In
Run	**L/min**	**L/min**	**L/min**	**g/min**	**g/min**
4	50	52	0	1.7	5.9

			Mole %	Output			
Run	H_2	N_2	**CO**	CO_2	**Toluene**	CH_4	H_20
4	12	54	21	7	0	.3	6

	LHV Gas In	LHV Gas Out	Thermal Eff	Toluene
Run	**kW**	**kW**	**Percent**	**% Destroyed**
4	5.02	5.87	117	100

- Run 4 had good destruction and good efficiency

Excellent Conversion Obtained

- Conversion of BTX and other hydrocarbons very good
  - 92% methane (near equilibrium limit)
  - 96% ethane
  - 100% (to detection limit) of other C2-C4
  - 98% benzene
  - 99% toluene
  - 100% (to detection limit) of xylenes

Process design basis

- Basis process feed: 500 SCFM
- Gasifier product composition from Emery Energy
- Ability to add O_2 or air
  - to provide heat of reformation
  - raise temperature to 850ºC
  - 17.9 SCFM of O_2 required to raise T from 504ºC to 850ºC
- No coke is detected (sufficient steam present)

Reformer installation

- Assembled 3-stage reformer
- At Western Research Institute – Laramie, WY
- Installed and tested

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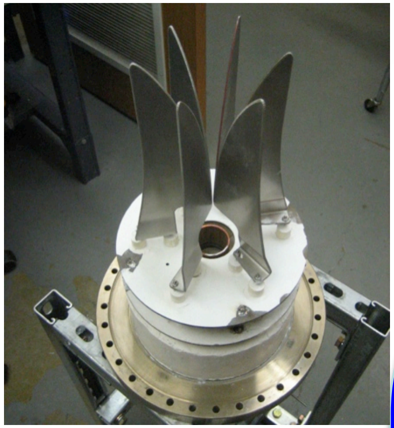
Other Fuel Synthesis Projects

Syngas to Liquid

Biogas to Fuel Capabilities



Sulfur Tolerant Reformer

Syngas

Compression & Storage

Biogas

Fischer-Tropsch

Transportation Fuels

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Ceramatec Laboratory FT System

Capacity: 3 to 4 liters/day

Single tube FT reactor
42.7mm ID, 2.0 m length, ~2.9 liters

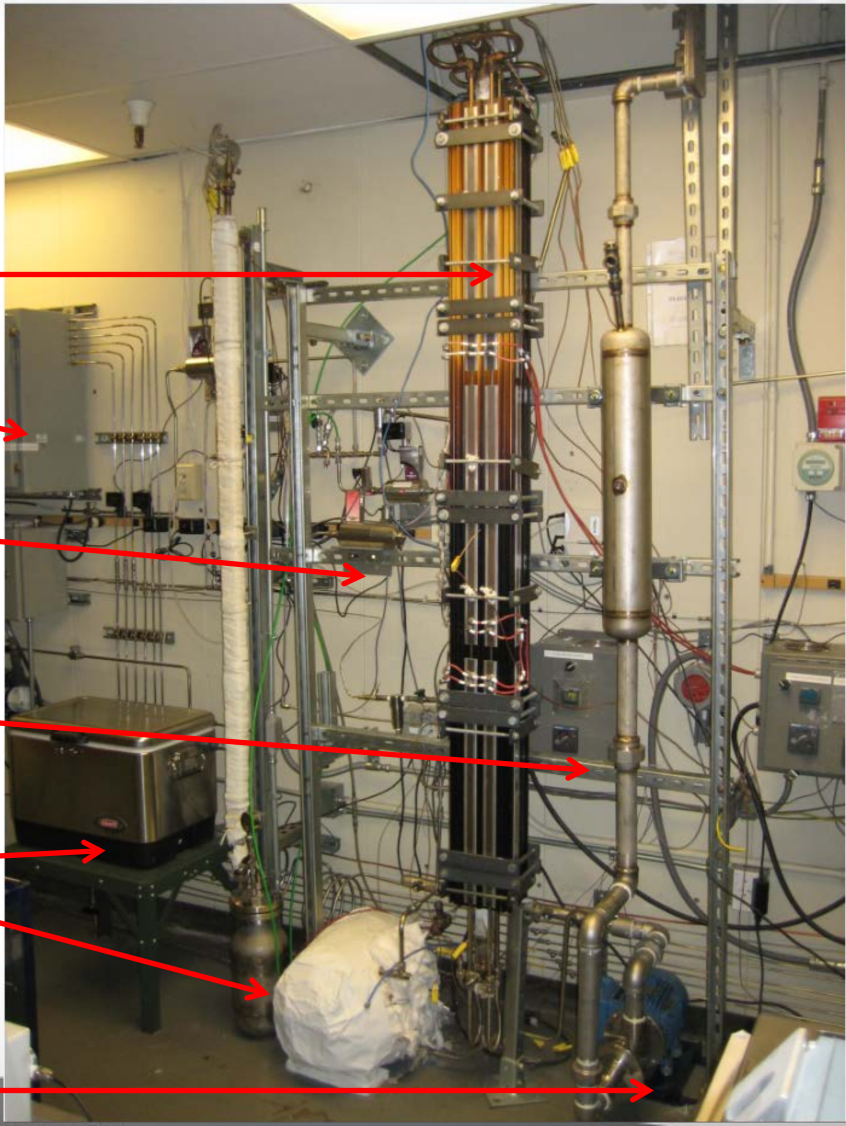
Backpressure regulation system, 20-30 barg

High pressure mass flow controllers (low/high range)

Temperature controllers for reactor and collection system

Hot and cold product collection vessels

Recycle pump
&
Cooling system



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Ceramatec FT Product From 1-1/2" Reactor

- Production rates up to 4 liter/day
- 2200 hour run
- FT 46.5 MJ/kg, diesel 46 MJ/kg, 40 MJ/kg B100 FAME
- Cetane 60.2 by ASTM D613

Pre-pilot Plant Scale up

4” Reactor Tube - Fischer Tropsch Skid

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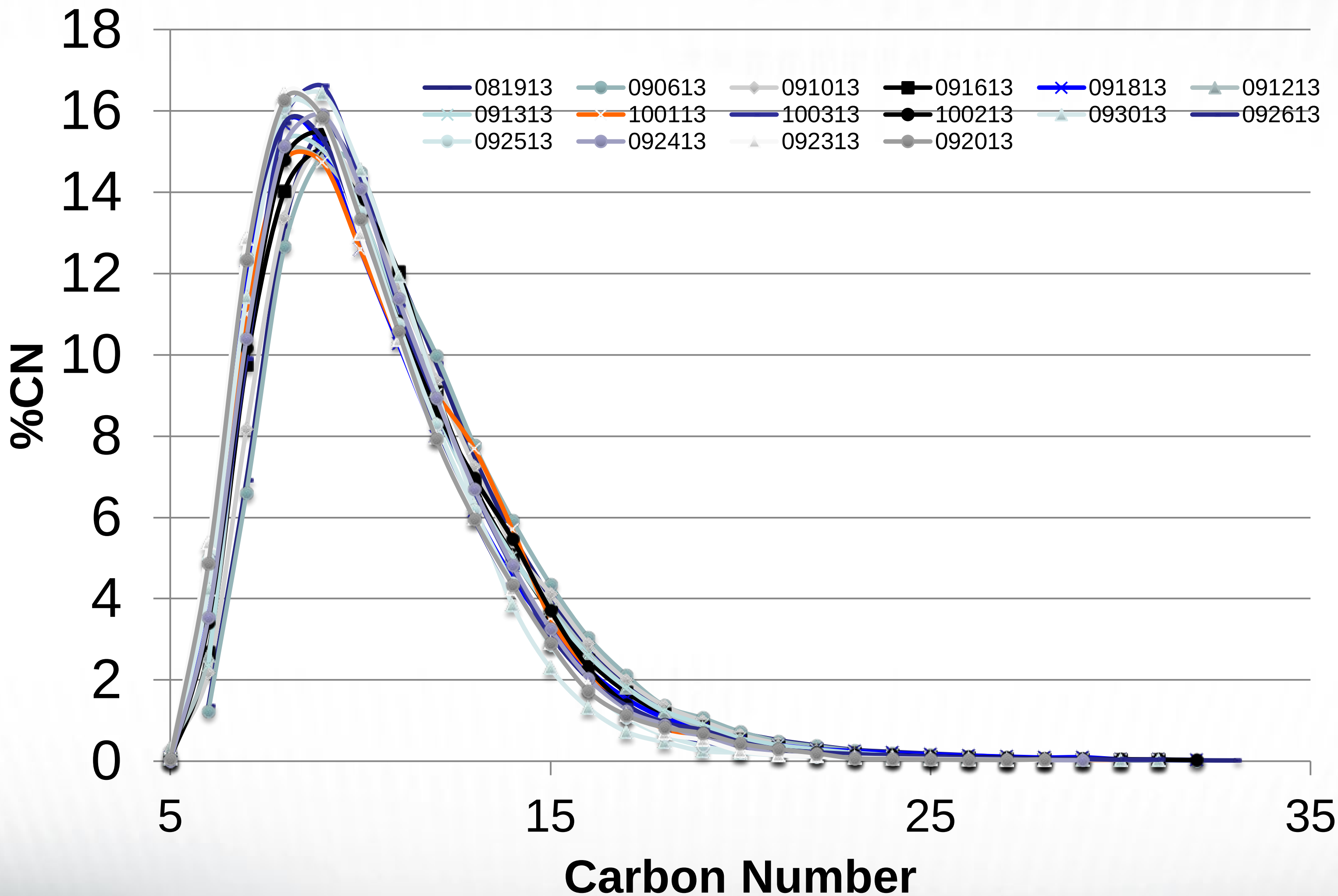
FT Demonstration

Product Collection

30 liters/day FT Production Demonstrated

FT Product Analysis



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Summary

- Ceramatec has been investigating transportation fuel synthesis options for over a decade
- Currently three major projects at various TRL underway
  - Deoxygenation of Bio-oil
  - Decarboxylation of fatty acids from bio-source
  - Biogas clean up and FT conversion to liquids