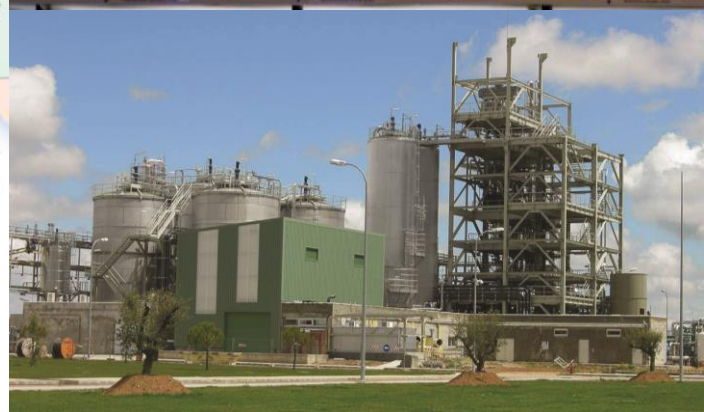


# 2015 DOE Bioenergy Technologies Office (BETO) Project Peer Review



**2.3.1.311:**  
**Reforming Pyrolysis Aqueous  
Waste Streams to Process  
Hydrogen and Hydrocarbons**

**March 27, 2015**

**Kim Magrini**

***Program Mission:** Transform our renewable biomass resources into commercially viable, high-performance biofuels, bioproducts, and biopower through targeted research, development, demonstration, and deployment supported through public and private partnerships.*

**Task Goal:** Develop, evaluate and characterize reforming and upgrading catalysts that produce hydrogen and hydrocarbons from biomass-derived aqueous pyrolysis fractions.

- Increase H<sub>2</sub> efficiency > 90% stoichiometric
- Decrease catalyst coking < 10%
- Explore oxygenate upgrading to HC fuels, products

**Task Objective:** Develop and optimize an integrated process and associated catalysts for producing hydrogen and possibly fungible hydrocarbon blend-stocks from aqueous pyrolysis liquids contained in pyrolysis plant waste water (and related streams – biochemical).

# Project Quad Chart Overview

## Timeline

- Project start date: 10/2013
- Project end date: 9/2017
- Percent complete: 24%

## Barriers

- Tt-E. Liquefaction of Biomass and Bio-Oil Stabilization
- Tt-E. and Tt-G. Conversion and Conversion Enabling Technologies

## Budget

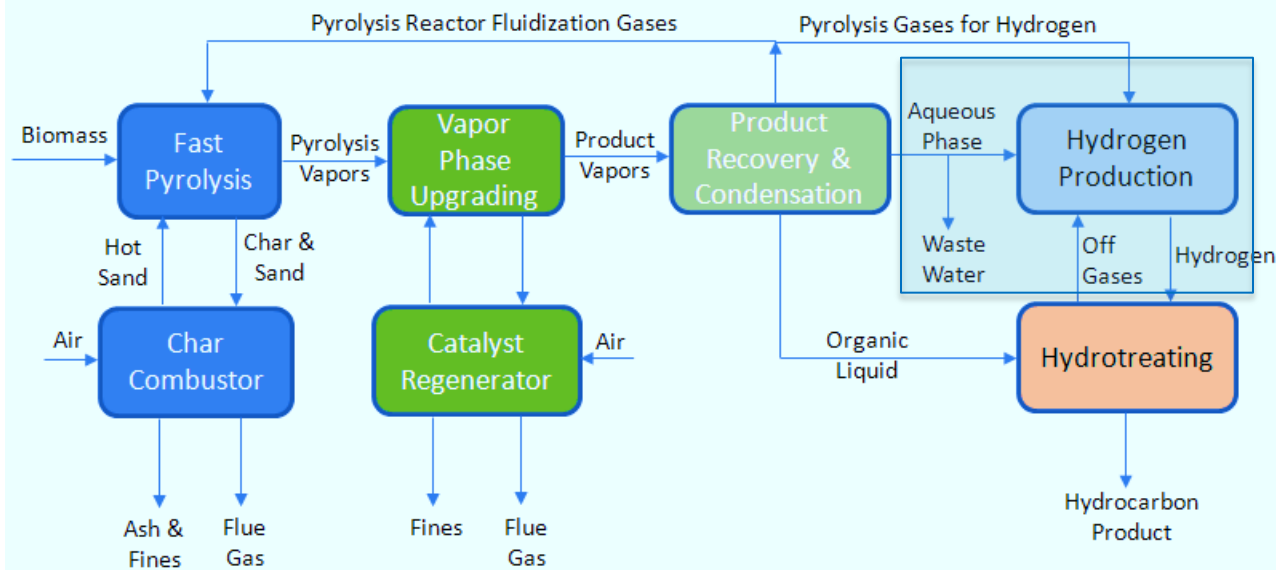
Total Costs FY10 – FY12	FY13 Costs	FY14 Costs (\$)	Total Planned Funding (FY15-end) (\$)
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DOE Funded	0	0	196,427	303,573
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## Partners & Roles

- NREL: catalyst development, evaluation/characterization
- PNNL: aqueous fraction upgrading
- Johnson Matthey: upgrading catalyst development
- CoorsTek – catalyst supports

# 1 - Project Overview



Dutta et al., 2015  
NREL/TP-5100-62455,  
PNNL-23823

Schematic of vapor phase upgrading of biomass fast pyrolysis products to fuel intermediates.

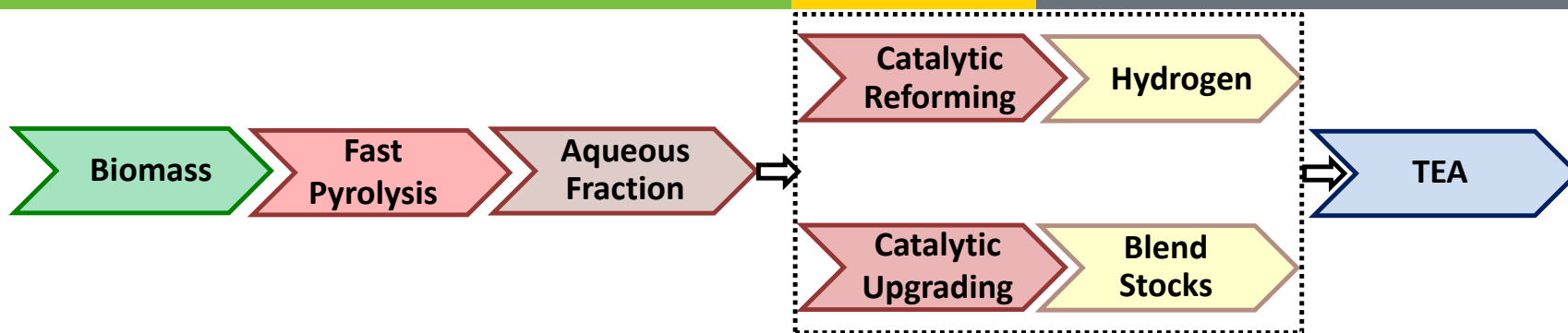
State of Technology and 2022 Targets for *Ex Situ* and *In Situ* Vapor Upgrading

Process Parameter	Ex Situ		In Situ	
	2014 SOT	2022 Target	2014 SOT	2022 Target
Vapor Products (wt.% dry biomass)				
Non-Condensable Gases	35	23	31	23
Aqueous Phase (% C Loss)	25 (2.9)	30 (1.3)	26 (3.2)	29 (2.1)
Solids (Char + Coke)	12 + 11	12 + 8.0	12 + 12	12 + 8.1
Organic Phase	17.5	27.2	19.5	28.3
H/C Molar Ratio	1.1	1.6	1.1	1.5
Carbon Efficiency (%)	27	44	29	44
Oxygen Content (% of organic)	15.0	6.4	15.6	10.5

Carbon loss with vapor upgrading

Higher losses with less upgrading

# 1 - Project Overview



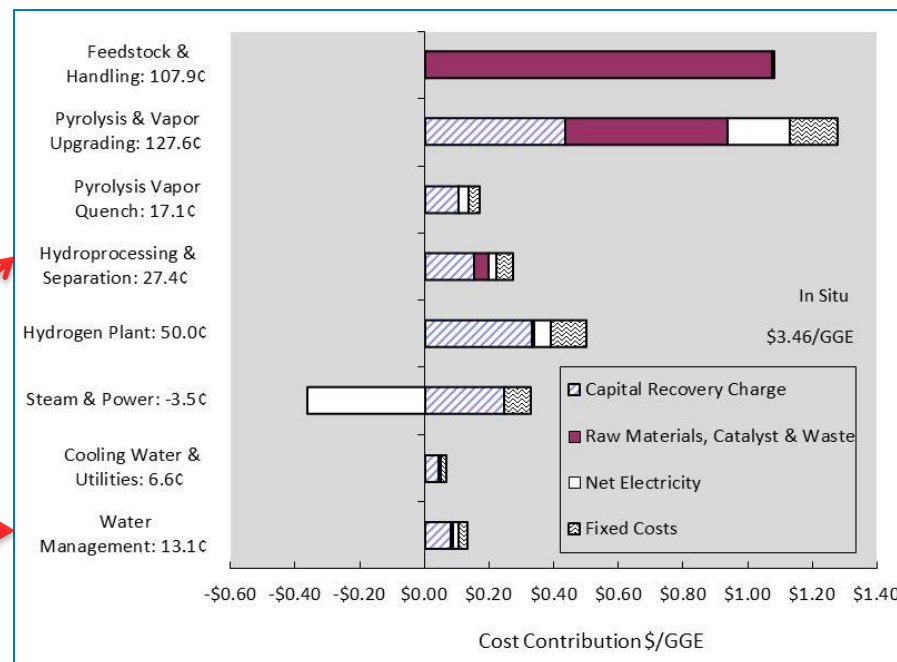
Robust reforming catalysts for H<sub>2</sub> production  
Oxygenate upgrading catalyst to hydrocarbons  
Comprehensive fraction analysis

### Catalyst Targets

Coking ≤ 10%  
Hydrogen ≥ 90%

**Project rationale:**  
*Waste water management from a pyrolysis plant likely a significant cost*

*Work on valorization instead of destruction (oxidation) of carbon in the aqueous phase.*



*In Situ* 2022 cost target from NREL/TP-5100-62455, 2015.  
Assumes thermal oxidation of aqueous carbon.



# 2 – Technical Approach

## Task Structure

- 1) Produce and characterize biomass pyrolysis derived aqueous fractions (plant waste water not yet available)
  - Aqueous fraction used for H<sub>2</sub>, hydrocarbons (HC)
  - Lignin fraction to be used for upgrading by Enerkem-CRB, NRCan
- 2) Screen and characterize reforming catalysts for hydrogen production
  - Fixed, fluid bed micro-reactors, small pilot fluid bed reactor
- 3) Screen and characterize upgrading catalysts for oxygenate conversion
  - Fixed, fluid bed reactor coupled with MBMS product analysis
- 4) Modify existing TEA model and assess process data for:
  - H<sub>2</sub> and product cost
  - Down select best process
  - Waste water treatment cost reduction
- 5) Process TEA Data Needs:
  - Estimate aqueous fraction processing time
  - Quantify chemicals from VPU with other catalysts
  - Seek high value chemical production from VPU
  - Characterize steam condensate after VPU
  - Consider steam generation duty within plant heat integration

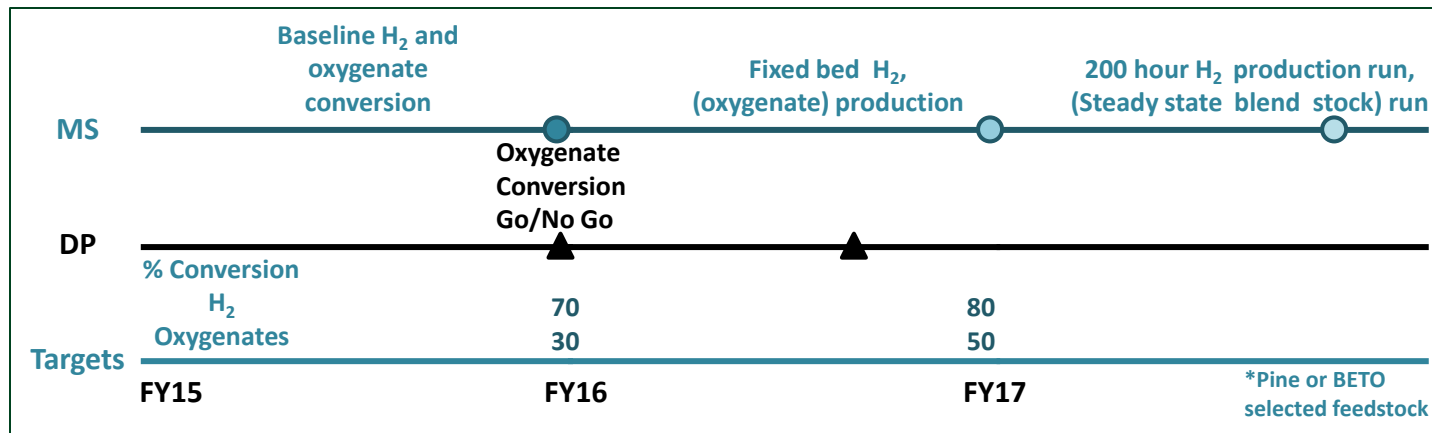
# 2 – Management Approach

## Critical Success Factors

**Technical:** Develop/identify/evaluate 1) reforming catalysts that maximize **H<sub>2</sub> yield (100% stoichiometric)**; 2) are selective for fungible hydrocarbon intermediate production at (g-kg scale) with < 10% coking

**Market:** Produce H<sub>2</sub> for upgrading and possibly hydrocarbon intermediates that can be processed in a conventional refinery with acceptable cost (**\$3.31/gal**)

**Challenges:** Develop efficient 1) reforming catalysts and 2) aqueous oxygenate conversion to products



Project milestones (MS), decision points (DP), and technical targets for hydrogen and blend stock production from aqueous pyrolysis oil fractions.

# 2 – Management Approach

## Critical Success Factors

### Hydrogen:

- Achieve stoichiometric yields (100%) with < 10% coking
- Demonstrate extended production (200 h)
- Mitigate water reboiling in pyrolysis plant TEA

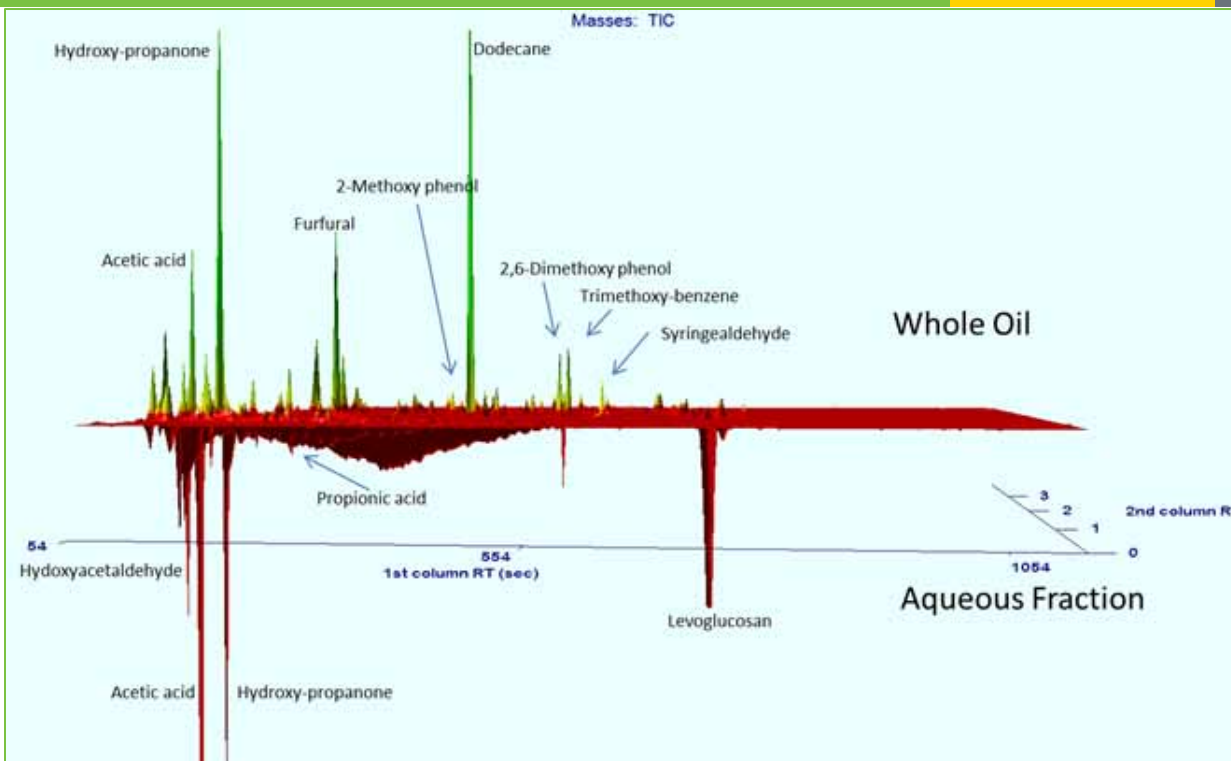
### Hydrocarbons:

- Quantify aqueous phase [C] >16 wt%
- Characterize phase separated lignin: less oxygenates reduce impact on hydrotreating catalysts
- Choose best HC products – maximize yield, selectivity
- Assess options/cost reduction for water reboiling in pyrolysis plant TEA

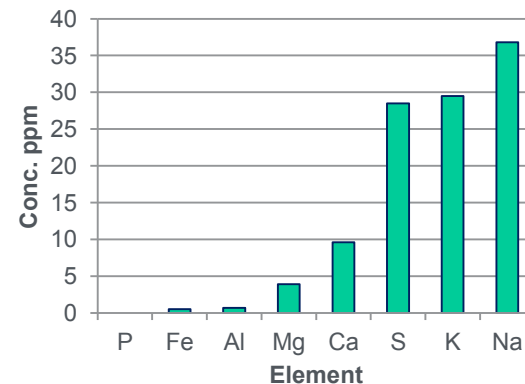


# 3 – Progress

## Oil Fractionation and Characterization



Difference chromatogram of whole oil and aqueous fraction oil produced from oak fast pyrolysis by 2D-GCMS.



Elemental analysis of oak-derived aqueous fraction pyrolysis oil as determined by inductively coupled plasma spectroscopy (ICP).

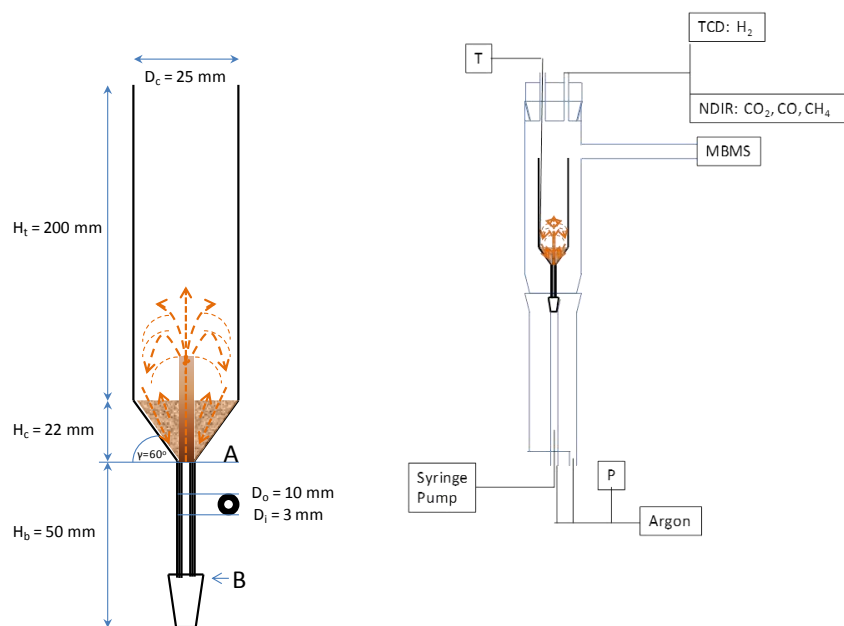
**Deutch, Olstad, Starace, Black**

- Aqueous fraction enriched in low molecular wt. hydrocarbons (acetic acid, levoglucosan, HAA) candidates for upgrading

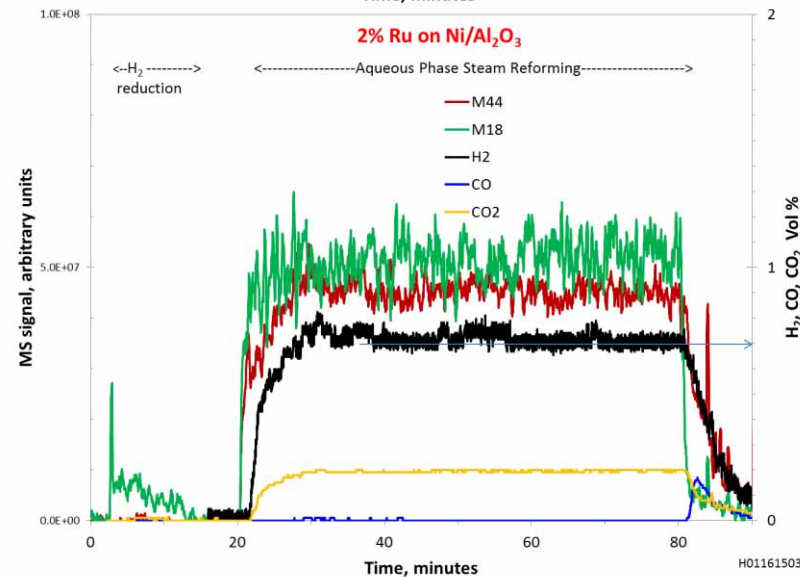
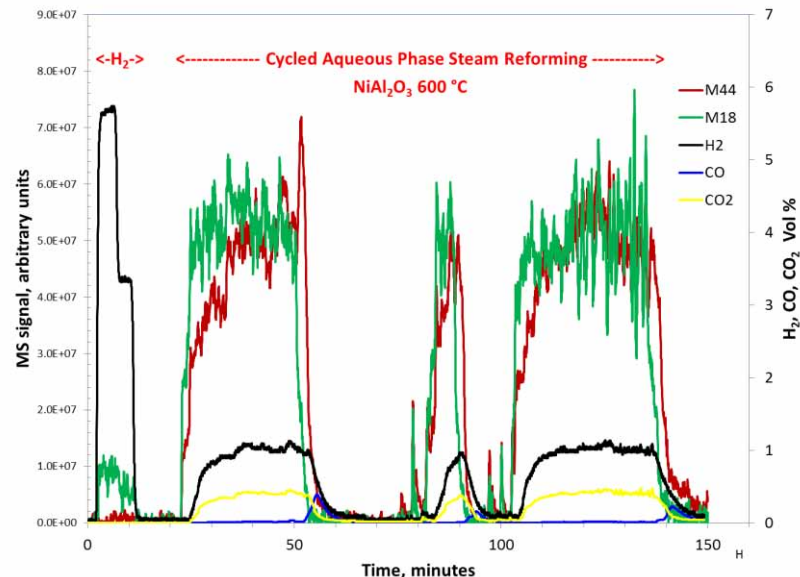
Sample ID	KF water%	Total COD (g/L)	Organic Content Wt%	H <sub>2</sub> production potential (g/L)
Oak Oil S1	83.3	309.6	16	38.7
Oak Oil S2	83.9	268.0	16	33.5

# 3 – Progress

## H<sub>2</sub> Production Spouted Bed Reactor (1 g catalyst)



Schematic of the spouted bed reactor used H<sub>2</sub> production from aqueous fraction reforming.

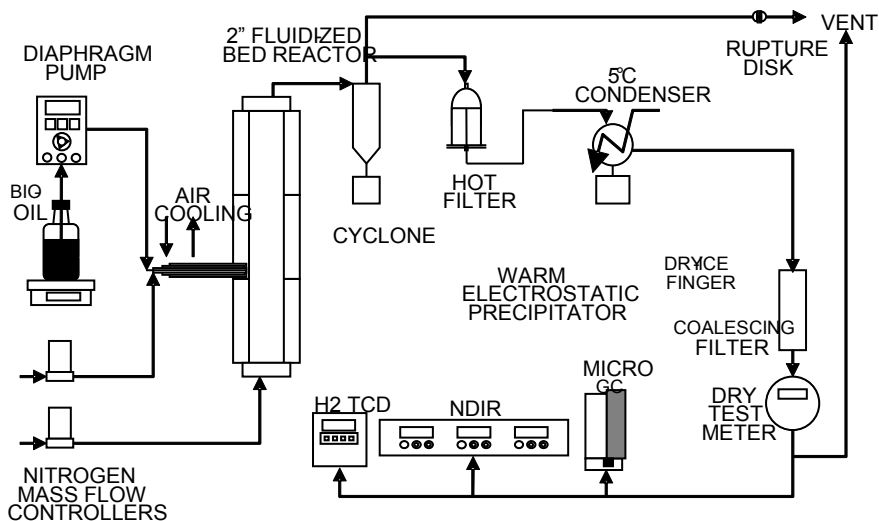


	Cat51	Cat51	Au/Cat51	Ru/Cat51	Rh/Cat51
Feed	Ethanol	Aq. Frac.	Aq. Frac.	Aq. Frac.	Aq. Frac.
Temperature, °C	600	600	600	600	600
H <sub>2</sub> O/C molar	6.7	6.7	6.7	6.7	6.7
WHSV, hr <sup>-1</sup>	0.2	0.2	0.2	0.2	0.2
run length, minutes	60	64	63	60	60
% of stoic H <sub>2</sub>	88.8	92.2	92.6	106.5	95.4
% of C reformed	99.8	94.2	93.3	95.5	96.4
% of C Deposited on catalyst	0.2	5.8	6.7	4.5	3.6

P. Kechagiopoulos et al., *Ind. Eng. Chem. Res.* **2009**, *48*, 1400–1408

# 3 – Progress

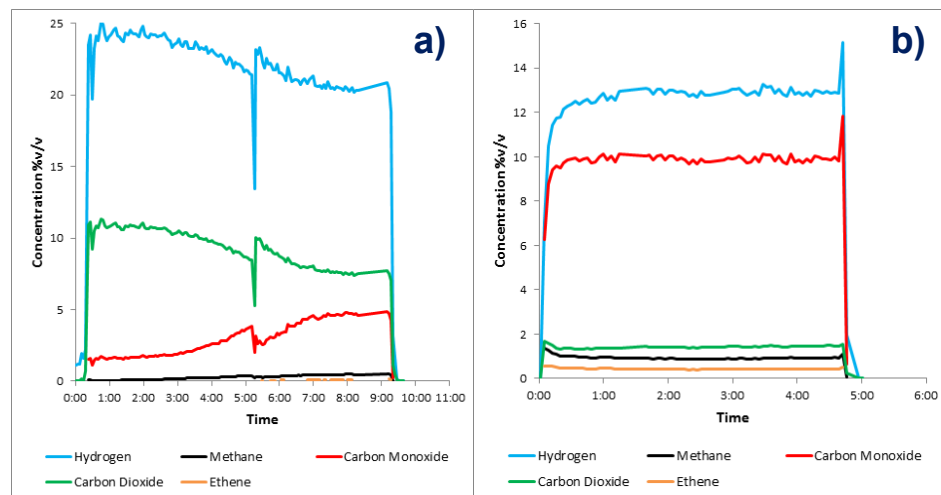
## H<sub>2</sub> Production Fluid Bed Reactor (300 g catalyst)



2-inch Diameter Fluidized-Bed Reactor System.

### Hydrogen Yields and Potential Hydrogen Yields

	NREL 60			Nickel Ceria
	Total	Hour 1	Hour 8	Total
Feed Mass	5	232.0	234.6	1101.7
Cond Mass	4015.			
Feed COD H <sub>2</sub>	79.3	8.6	8.73	34.1
H <sub>2</sub> Produced	56.0	6.7	5.45	15.0
CO Produced	104.9	6.1	17.5	161.3
CH <sub>4</sub> Produced	5.4	0.1	1.0	8.8
C <sub>2</sub> H <sub>4</sub> Produced	0.7	0.0	0.045	7.1
<b>H<sub>2</sub> Yield</b>	<b>71</b>	<b>78</b>	<b>62</b>	<b>44</b>
CO potential yield	9	5	14	34
H <sub>2</sub> +CO potential	80	83	77	78
CH <sub>4</sub> , C <sub>2</sub> H <sub>4</sub> pot. yield	4	1	6	22
<b>Total H<sub>2</sub> pot. yield</b>	<b>84</b>	<b>84</b>	<b>83</b>	<b>100</b>



Gas composition during aqueous phase reforming with a) NREL60 Ni-K-Mg catalyst and b) Ni-Ce-La-Cr catalyst as determined by rapid scan GC, balance nitrogen

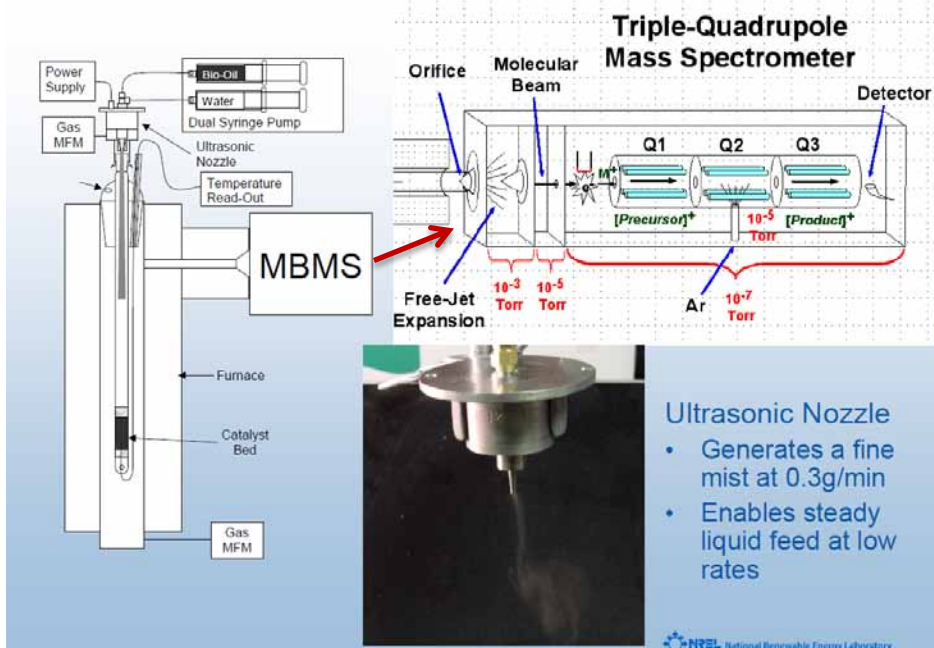
- The NREL Ni catalyst had high initial H<sub>2</sub> production which decreased to a lower steady level. Not all of the COD could be accounted for, suggesting the formation of char, coke or heavy tars.
- The nickel-ceria catalyst had a lower initial H<sub>2</sub> yield but was more stable and all of the COD could be accounted for, suggesting that this material is resistant to coking.
- Future work will 1) combine the two formulations to achieve higher stable H<sub>2</sub> conversion and 2) add a downstream WGS catalyst to shift to maximize H<sub>2</sub> yield (approach used for naphtha reforming to H<sub>2</sub>).

- Stoichiometric H<sub>2</sub> yields achievable with fluidized reforming catalysts
- Longer duration H<sub>2</sub> production achieved (8 h TOS)
- Combining increased yield (Ru) with anti-coking properties (La) in one catalyst is achievable
- Process steam reduces catalyst coking
- Alkali's remain in aqueous phase and enhance oxygenate gasification to H<sub>2</sub>

# 3 – Progress

## HC Production Fixed Bed Reactor (1 g catalyst)

### Aqueous Oil Upgrading System



Investigate different catalysts for their ability to upgrade oxygenated species in bio-oil aqueous fraction to form **hydrocarbons** and **value added chemicals** (cyclopentenones and phenols).

Catalysts: HZSM-5,  $\beta$ -zeolites, silica alumina and hydrotalcites.

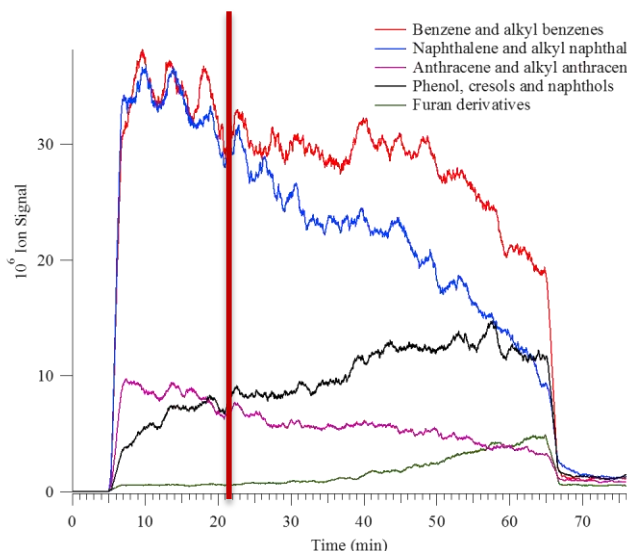
Experiment:

- MBMS: real-time deactivation of the catalysts
- GCMS: Identify and quantify products
- TGA analysis: coking extent
- XRD/NMR Investigate dealumination

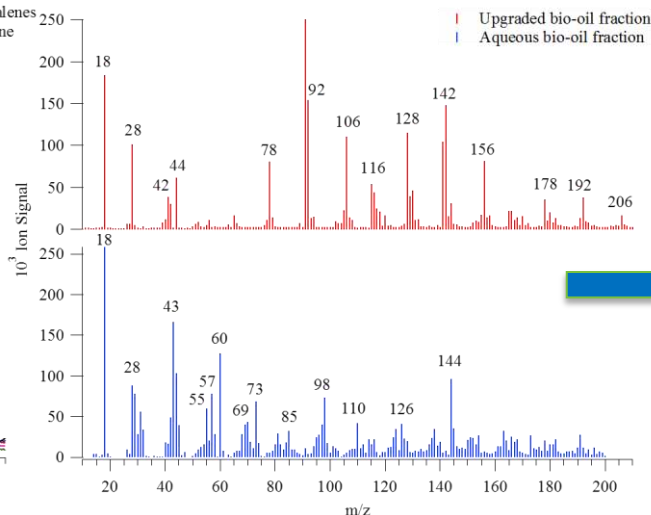
Catalyst: HZSM-5,  $\beta$ -zeolite, silica alumina, hydrotalcite  
Temperature: volatilization = upgrading = 500 °C  
WHSV: 1 hr<sup>-1</sup>

# 3 – Progress

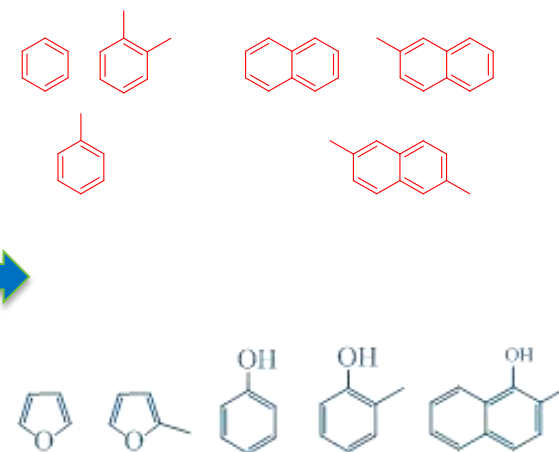
## HC Production Fixed Bed Reactor (1 g catalyst)



Ion count profiles of species produced from upgrading the aqueous bio-oil fraction using HZSM-5 at 500°C.



The lower panel shows the composition of the aqueous bio-oil fraction and the upper panel shows the products obtained by upgrading the oil with HZSM-5 at 500 °C.



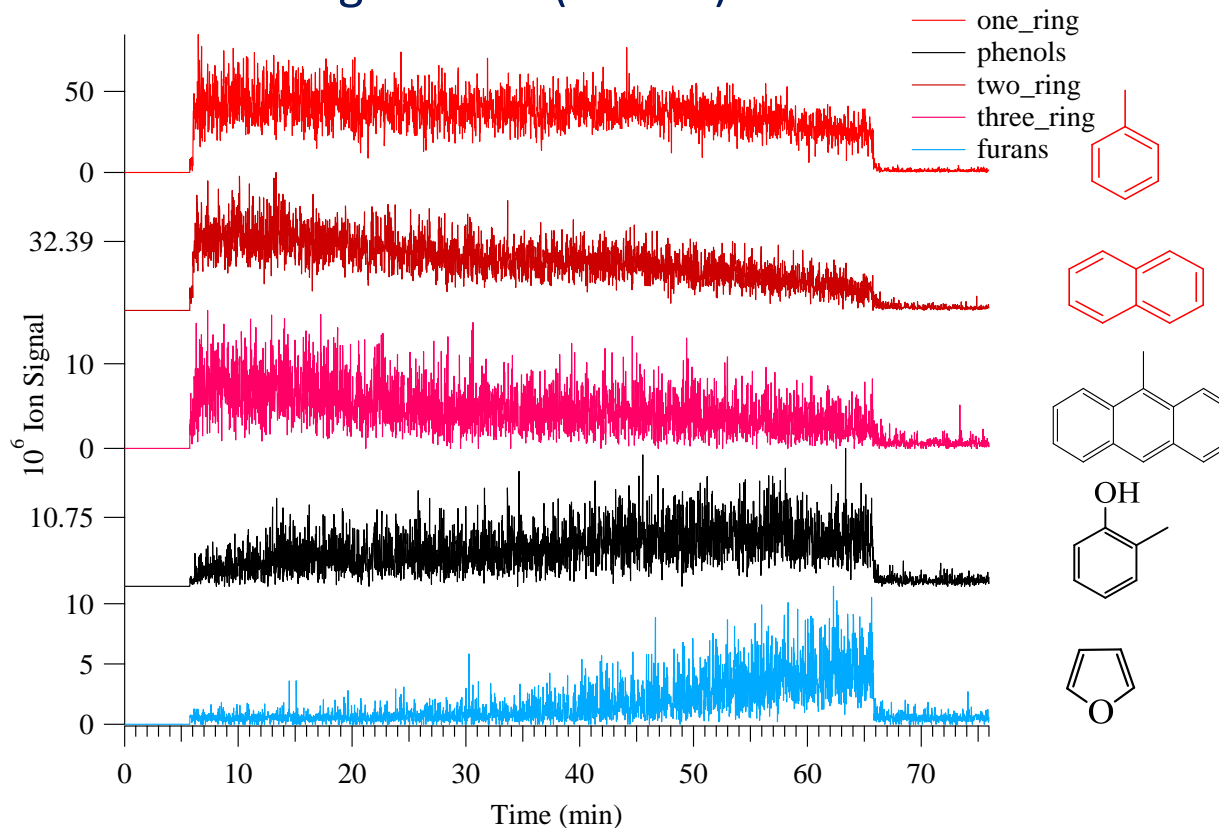
Time Interval, min	CO	CO <sub>2</sub>	C <sub>2</sub> -C <sub>4</sub>	BTX	Furans	phenolics	naph	total
10-20	40.7	21.9	4.2	16.0	1.0	3.3	4.5	91.7
20-30	54.1	26.4	5.3	12.2	3.8	4.3	2.8	108.9
30-40	44.8	29.3	7.9	8.1	6.1	4.2	1.8	102.2
40-50	40.3	31.0	9.3	5.2	7.0	3.8	1.2	97.8
50-60	31.7	32.3	11.0	3.5	7.2	3.4	0.9	89.9
60-70	40.8	34.6	11.8	2.6	6.9	3.1	0.7	100.4



# 3 – Progress

## HC Production Fixed Bed Reactor (1 g catalyst)

### Activity of ZSM-5 during Oil VPU (MBMS)

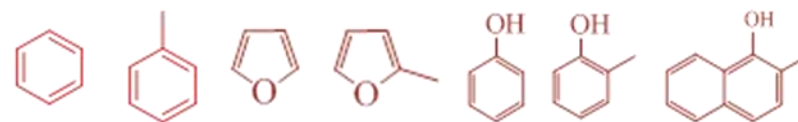
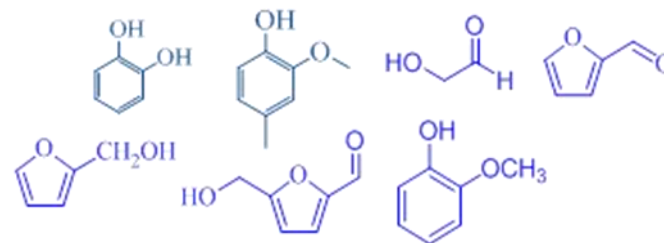
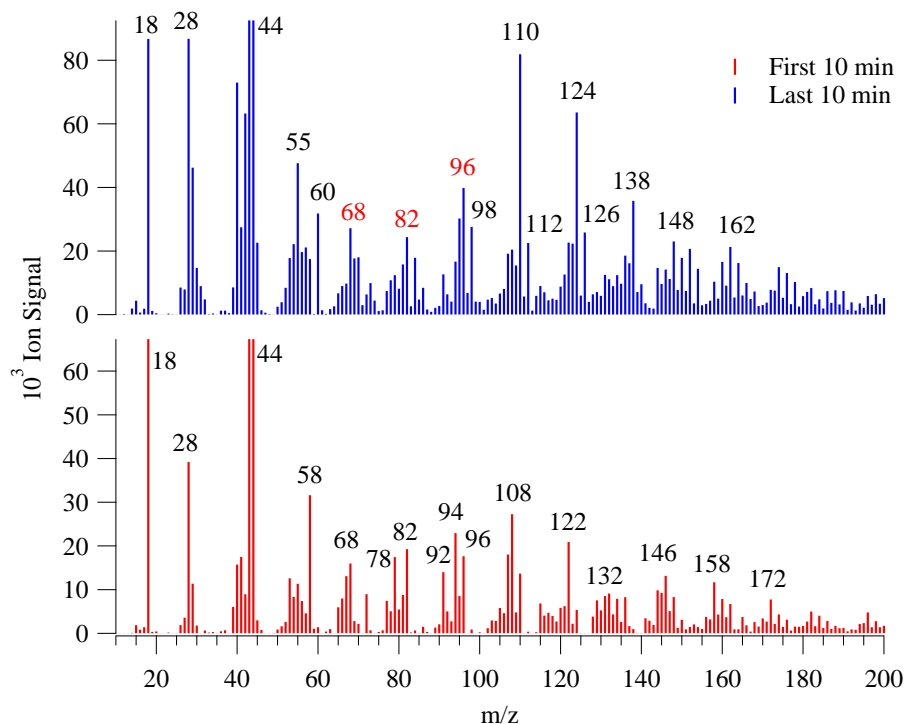


The furans and phenols can be used to determine when catalysts begin to deactivate

# 3 – Progress

## HC Production Fixed Bed Reactor (1 g catalyst)

### Oil VPU using hydrotalcites

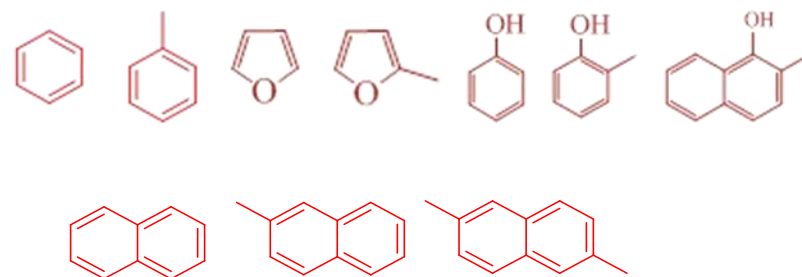
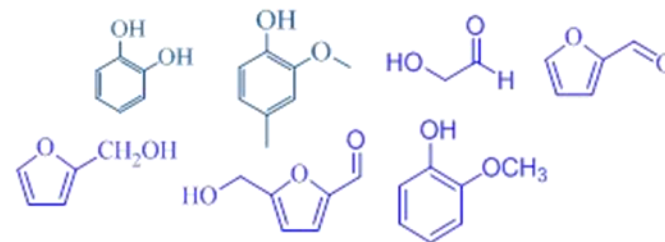
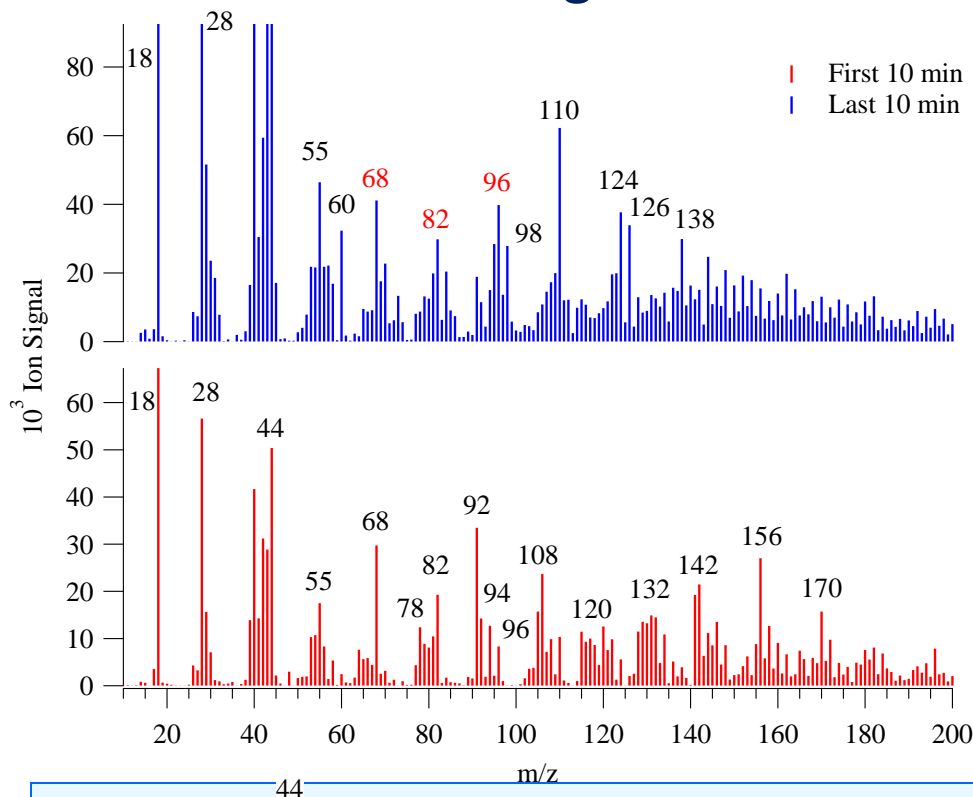


- When the catalyst is fully active, the oil is upgraded to form furans, phenol, cresols, methyl benzofurans and naphthols.
- When the catalyst is partially deactivated, oil upgrading is dominated by furans and catechols. Some aromatics still form.

# 3 - Progress

## HC Production Fixed Bed Reactor (1 g catalyst)

### Oil VPU using silica alumina



- When the catalyst is fully active, the oil is upgraded to form furans, phenol, cresols, methyl benzofurans and aromatics
- When the catalyst is partially deactivated, oil upgrading is dominated by furans and catechols.

- HZSM-5 and  $\beta$ -zeolites upgrade the oil to form hydrocarbons
- As the zeolites catalysts starts to deactivate the oil is initially upgraded to furans, phenol, cresol and naphthols
- Silica alumina upgrades the oil to form furans, phenol, cresols and aromatic hydrocarbons
- Hydrotalcites upgrades the oil to form furans, phenol, cresol, naphthols, benzofurans.

Catalyst	Products	Uses
<b>HZSM-5</b>	Olefins and aromatic hydrocarbons	Gasoline precursors
	Phenols, cresols and naphthols	Chemicals and polymers
<b><math>\beta</math>-zeolite</b>	Olefins and aromatic hydrocarbons	Gasoline precursors
<b>Silica alumina</b>	Furans, cyclopentenones, aromatic hydrocarbons	Diesel/jet fuel precursors
	Phenol, cresol and naphthols	Chemicals and polymers
<b>Hydrotalcite</b>	Furans and cyclopentenones	Diesel/jet fuel precursors
	Phenol, cresols and catechols	Chemicals and polymers

- Project supports the production of hydrogen (for hydrotreating) and hydrocarbons from biogenic hydrogen and carbon contained in aqueous pyrolysis waste streams.
  - *Yields, products to be evaluated in a pyrolysis plant TEA for cost and potential use for treating plant waste water (and other process streams).*
- For the Bioenergy Industry:
  - *Contribute to the expansion of the biomass pyrolysis industry by converting pyrolysis waste streams to higher value products (H<sub>2</sub>, hydrocarbons) while reducing water treatment costs.*

# 5 - Future Work

## H<sub>2</sub> Production and Hydrocarbons

### Hydrogen

- Evaluate bifunctional catalysts (high yield, anti-coking properties)
- Long duration runs of best catalysts for TEA analysis
- Evaluate aqueous fractions as a function of pyrolysis conditions
- Evaluate best process in DCR
- Complete process TEA and economics

### Hydrocarbons

- Measure coke and hydrocarbon yields
- Improve product yields
- Evaluate other emerging catalysts (selectivity, yield, steam resistance).
- Change conditions (temperature, WHSV, etc.)



This project develops and optimizes an integrated process and associated catalysts for producing hydrogen and possibly fungible hydrocarbon blend-stocks from aqueous pyrolysis liquids contained in pyrolysis plant waste water (and related streams – biochemical).

## Hydrogen

- Stoichiometric H<sub>2</sub> yields achievable with fluidized reforming catalysts for > 8 h TOS
- Combining increased yield (Ru) with anti-coking properties (La) in one catalyst is achievable
- Process steam reduces catalyst coking and inherent alkali species enhance oxygenate gasification to H<sub>2</sub>.
- Evaluate bifunctional catalysts (high yield, anti-coking properties)
- Complete process TEA and economics

This project develops and optimizes an integrated process and associated catalysts for producing hydrogen and possibly fungible hydrocarbon blend-stocks from aqueous pyrolysis liquids contained in pyrolysis plant waste water (and related streams –biochemical).

## Hydrocarbons

- HZSM-5 and  $\beta$ -zeolites upgrade the oil to form hydrocarbons
- Silica alumina upgrades the oil to form furans, phenol, cresols and aromatic hydrocarbons
- Hydrotalcites upgrades the oil to form furans, phenol, cresol, naphthols, benzofurans

## Future Work

- Measure coke and hydrocarbon yields
- Improve product yields
- Evaluate other emerging catalysts (selectivity, yield, steam resistance)
- Change conditions (temperature, WHSV, etc.)

*Adam Bratis*  
*Robert Dagle (PNNL)*  
*Mark Davis*  
*Steve Deutch*  
*Robert Evans*  
*Tabitha Evans*  
*Calvin Mukarakate*  
*Rick French*  
*Scott Palmer*

*Matthew Seabaugh (Nexceris)*  
*Steve Landin (CoorsTek)*  
*Jacques Monnier (NRCan)*  
*Mike Watson and Andrew Heavers (Johnson Matthey)*



Johnson Matthey

Canada



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## **PUBLICATIONS**

C. Mukarakate, K. Magrini, R. Evans, S. Deutch, T. Evans, Developing and evaluating upgrading catalysts for producing hydrocarbons from biomass-derived aqueous pyrolysis fractions, to be submitted to *Applied Catalysis A* in 2015.

K. Magrini, R. French, R. Evans, C. Mukarakate, T. Evans, S. Deutch, M. K. McKinney, S. Palmer, Developing and evaluating fluidizable bimetallic reforming catalysts to produce hydrogen from reforming oak derived aqueous fractions, *Applied Catalysis A*, submitted March 2015.

## **MILESTONE REPORTS**

C. Mukarakate, R. Evans, S. Deutch, T. Evans, K. Magrini, “Assess at least two upgrading catalysts for aqueous fraction oxygenate conversion, BETO Milestone Report, September 30, 2014.

M. Oddo, R. Evans, R. French, C. Mukarakate, K. Magrini, “Identify and test upgrading catalysts to establish baseline activity for hydrocarbon production from aqueous pyrolysis fractions”, BETO Milestone Report, March 31, 2014.

K. Magrini, R. French, R. Evans, T. Evans, Produce bimetallic reforming catalysts: Ni-Ru, Ni-Au, Ni-Fe on fluidizable CoorsTek alumina and compare with base line Ni catalyst to select best composition that meets or exceeds 70% hydrogen yield from reforming oak derived aqueous fractions, BETO Milestone Report, December 30, 2014.

M. Jarvis, S. Deutch, K. Magrini, Produce liter quantities of aqueous fraction oils from pine in the DCR and establish fraction chemistry and any variance with pyrolyzer temperature and residence time with GCTOFS and NMR analysis, BETO Milestone Report, March 31, 2015 – in progress

## **INVENTION RECORDS**

K. Magrini, C. Mukarakate, R. Evans, T. Evans, “Upgrading aqueous fraction oxygenates to fungible hydrocarbons and chemicals with zeolites in fixed bed and Davison circulating riser (DCR) systems, NREL ROI-15-04, October 2014.