Reforming Pyrolysis Aqueous Waste Streams to Process Hydrogen and Hydrocarbons
**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 $\text{H}_2$ 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).
**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**

<table>
<thead>
<tr>
<th>FY10 - FY12 Costs ($)</th>
<th>FY13 Costs ($)</th>
<th>FY14 Costs ($)</th>
<th>Total Planned Funding (FY15-end) ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE Funded</td>
<td>0</td>
<td>0</td>
<td>196,427</td>
</tr>
</tbody>
</table>

**Partners & Roles**

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

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

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

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

<table>
<thead>
<tr>
<th>Process Parameter</th>
<th>Ex Situ</th>
<th>In Situ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2014 SOT</td>
<td>2022 Target</td>
</tr>
<tr>
<td>Vapor Products (wt.% dry biomass)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-Condensable Gases</td>
<td>35</td>
<td>23</td>
</tr>
<tr>
<td>Aqueous Phase (% C Loss)</td>
<td>25 (2.9)</td>
<td>30 (1.3)</td>
</tr>
<tr>
<td>Solids (Char + Coke)</td>
<td>12 + 11</td>
<td>12 + 8.0</td>
</tr>
<tr>
<td>Organic Phase</td>
<td>17.5</td>
<td>27.2</td>
</tr>
<tr>
<td>H/C Molar Ratio</td>
<td>1.1</td>
<td>1.6</td>
</tr>
<tr>
<td>Carbon Efficiency (%)</td>
<td>27</td>
<td>44</td>
</tr>
<tr>
<td>Oxygen Content (% of organic)</td>
<td>15.0</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Carbon loss with vapor upgrading  
Higher losses with less upgrading
Project Overview

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.

2 – Technical Approach

Task Structure

1) Produce and characterize biomass pyrolysis derived aqueous fractions (plant waste water not yet available)
   - Aqueous fraction used for H₂, 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:
   - H₂ 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
Critical Success Factors

Technical: Develop/identify/evaluate 1) reforming catalysts that maximize $\text{H}_2$ yield (100% stoichiometric); 2) are selective for fungible hydrocarbon intermediate production at (g-kg scale) with < 10% coking.

Market: Produce $\text{H}_2$ 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.

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

### Sample ID

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>KF water%</th>
<th>Total COD (g/L)</th>
<th>Organic Content Wt%</th>
<th>H₂ production potential (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oak Oil S1</td>
<td>83.3</td>
<td>309.6</td>
<td>16</td>
<td>38.7</td>
</tr>
<tr>
<td>Oak Oil S2</td>
<td>83.9</td>
<td>268.0</td>
<td>16</td>
<td>33.5</td>
</tr>
</tbody>
</table>

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

Deutch, Olstad, Starace, Black
3 – Progress

H₂ Production Spouted Bed Reactor (1 g catalyst)

Schematic of the spouted bed reactor used for H₂ production from aqueous fraction reforming.

<table>
<thead>
<tr>
<th>Feed</th>
<th>Cat51</th>
<th>Cat51</th>
<th>Au/Cat51</th>
<th>Ru/Cat51</th>
<th>Rh/Cat51</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td>H₂O/C molar</td>
<td>6.7</td>
<td>6.7</td>
<td>6.7</td>
<td>6.7</td>
<td>6.7</td>
</tr>
<tr>
<td>WHSV, hr⁻¹</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>run length, minutes</td>
<td>60</td>
<td>64</td>
<td>63</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>% of stoic H₂</td>
<td>88.8</td>
<td>92.2</td>
<td>92.6</td>
<td>106.5</td>
<td>95.4</td>
</tr>
<tr>
<td>% of C reformed</td>
<td>99.8</td>
<td>94.2</td>
<td>93.3</td>
<td>95.5</td>
<td>96.4</td>
</tr>
<tr>
<td>% of C Deposited on catalyst</td>
<td>0.2</td>
<td>5.8</td>
<td>6.7</td>
<td>4.5</td>
<td>3.6</td>
</tr>
</tbody>
</table>

3 – Progress

H₂ Production Fluid Bed Reactor (300 g catalyst)

2-inch Diameter Fluidized-Bed Reactor System.

Hydrogen Yields and Potential Hydrogen Yields

<table>
<thead>
<tr>
<th>NREL 60</th>
<th>Nickel Ceria</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
</tr>
<tr>
<td>Feed Mass</td>
<td>2170.</td>
</tr>
<tr>
<td>Cond Mass</td>
<td>4015.</td>
</tr>
<tr>
<td>Feed COD H₂</td>
<td>79.3</td>
</tr>
<tr>
<td>H₂ Produced</td>
<td>56.0</td>
</tr>
<tr>
<td>CO Produced</td>
<td>104.9</td>
</tr>
<tr>
<td>CH₄ Produced</td>
<td>5.4</td>
</tr>
<tr>
<td>C₅H₁₀ Produced</td>
<td>0.7</td>
</tr>
<tr>
<td>H₂ Yield</td>
<td>71</td>
</tr>
<tr>
<td>CO potential yield</td>
<td>9</td>
</tr>
<tr>
<td>H₂+CO potential</td>
<td>80</td>
</tr>
<tr>
<td>CH₃C₂H₄ pot. yield</td>
<td>4</td>
</tr>
<tr>
<td>Total H₂, pot. yield</td>
<td>84</td>
</tr>
</tbody>
</table>

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 H₂ 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 H₂ 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 H₂ conversion and 2) add a downstream WGS catalyst to shift to maximize H₂ yield (approach used for naphtha reforming to H₂).
Summary: H₂ Production

- Stoichiometric H₂ yields achievable with fluidized reforming catalysts

- Longer duration H₂ 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 H₂
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, β-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, β-zeolite, silica alumina, hydrotalcite
Temperature: volatilization = upgrading = 500 °C
WHSV: 1 hr⁻¹
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.

<table>
<thead>
<tr>
<th>Time Interval, min</th>
<th>CO</th>
<th>CO2</th>
<th>C2-C4</th>
<th>BTX</th>
<th>Furans</th>
<th>phenolics</th>
<th>naph</th>
<th>total</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-20</td>
<td>40.7</td>
<td>21.9</td>
<td>4.2</td>
<td>16.0</td>
<td>1.0</td>
<td>3.3</td>
<td>4.5</td>
<td>91.7</td>
</tr>
<tr>
<td>20-30</td>
<td>54.1</td>
<td>26.4</td>
<td>5.3</td>
<td>12.2</td>
<td>3.8</td>
<td>4.3</td>
<td>2.8</td>
<td>108.9</td>
</tr>
<tr>
<td>30-40</td>
<td>44.8</td>
<td>29.3</td>
<td>7.9</td>
<td>8.1</td>
<td>6.1</td>
<td>4.2</td>
<td>1.8</td>
<td>102.2</td>
</tr>
<tr>
<td>40-50</td>
<td>40.3</td>
<td>31.0</td>
<td>9.3</td>
<td>5.2</td>
<td>7.0</td>
<td>3.8</td>
<td>1.2</td>
<td>97.8</td>
</tr>
<tr>
<td>50-60</td>
<td>31.7</td>
<td>32.3</td>
<td>11.0</td>
<td>3.5</td>
<td>7.2</td>
<td>3.4</td>
<td>0.9</td>
<td>89.9</td>
</tr>
<tr>
<td>60-70</td>
<td>40.8</td>
<td>34.6</td>
<td>11.8</td>
<td>2.6</td>
<td>6.9</td>
<td>3.1</td>
<td>0.7</td>
<td>100.4</td>
</tr>
</tbody>
</table>

Mukarakate, Evans
Activity of ZSM-5 during Oil VPU (MBMS)

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

Mukarakate, Evans
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.
Summary
Hydrocarbon Production

- HZSM-5 and β-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.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Products</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-5</td>
<td>Olefins and aromatic hydrocarbons</td>
<td>Gasoline precursors</td>
</tr>
<tr>
<td></td>
<td>Phenols, cresols and naphthols</td>
<td>Chemicals and polymers</td>
</tr>
<tr>
<td>β-zeolite</td>
<td>Olefins and aromatic hydrocarbons</td>
<td>Gasoline precursors</td>
</tr>
<tr>
<td>Silica alumina</td>
<td>Furans, cyclopentenones, aromatic hydrocarbons</td>
<td>Diesel/jet fuel precursors</td>
</tr>
<tr>
<td></td>
<td>Phenol, cresol and naphthols</td>
<td>Chemicals and polymers</td>
</tr>
<tr>
<td>Hydrotalcite</td>
<td>Furans and cyclopentenones</td>
<td>Diesel/jet fuel precursors</td>
</tr>
<tr>
<td></td>
<td>Phenol, cresol and catechols</td>
<td>Chemicals and polymers</td>
</tr>
</tbody>
</table>
4 - Relevance

- 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 ($H_2$, hydrocarbons) while reducing water treatment costs.
5 - Future Work
H₂ 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 $\text{H}_2$ 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 $\text{H}_2$
- Evaluate bifunctional catalysts (high yield, anti-coking properties)
- Complete process TEA and economics
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- HZSM-5 and β-zeolites upgrade the oil to form hydrocarbons
- Silica alumina upgrades the oil to form furans, phenol, cresols and aromatic hydrocarbons
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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.


MILESTONE REPORTS


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.