This presentation does not contain any proprietary, confidential, or otherwise restricted information.
Goal Statement

The goal of this project is to design and develop scalable and cost-effective next generation catalysts for ex-situ catalytic fast pyrolysis (CFP) to improve the fuel quality and stability of the resulting bio-oil by reducing oxygen content, increasing hydrogen content, and increasing carbon number to a range suitable for gasoline, diesel, or jet fuel. These catalysts must achieve the following intermediate technical targets for upgraded oils at the large-bench scale (~200g catalyst) in 2017:

- H/C molar ratio of 1.3
- Carbon efficiency of 34%
- Oxygen content of 12.5wt%

Near-term Impact:
- Ex-situ CFP catalysts that outperform SOT materials
- In-house data collection and validation for ex-situ CFP pathway

Long-term Impact:
Catalysts developed within this project, when integrated with upstream and downstream processing, can be scaled to commercial size and yield a drop-in hydrocarbon fuel at a minimum selling price of $3.30/GGE by 2022.
Quad Chart Overview

**Timeline**
- **Project start date:** 10/1/2012
- **Project end date:** 9/30/2017
- **Percent complete:** 50%

**Budget**

<table>
<thead>
<tr>
<th></th>
<th>Total Costs FY10–FY12</th>
<th>FY13 Costs</th>
<th>FY14 Costs</th>
<th>Total Planned Funding (FY15-Project End Date)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE Funded</td>
<td>$0</td>
<td>$1.52M</td>
<td>$2.0M</td>
<td>$7M</td>
</tr>
</tbody>
</table>

**Barriers addressed**
- Tt-E. Liquefaction of Biomass and Bio-Oil Stabilization
- Tt-G. Fuel Synthesis and Upgrading
- Conversion enabling technologies through *development of next generation catalysts*

**Partners**

**Key Collaborators**
- **Internal**
  - Computational Pyrolysis Consortium (2.5.1.302)
  - Catalytic Pyrolysis Science (2.3.1.313)
- **External**
  - Dr. Levi Thompson, University of Michigan (SUB)
  - Dr. Will Medlin, University of Colorado-Boulder (SUB)
  - Dr. Richard Brutchey and Dr. Noah Malmstadt, University of Southern California
Design and development of *ex-situ* CFP catalysts using a “Bottom Up” approach combined with validation of improvement in downstream processing.
Project Overview: Ex-situ CFP Conditions

Temperature (°C)

Pressure (psia)

High

Hydrotreating

Metal hydrogenation catalysts (Ru, Pd)
Removal of O as H₂O
High H₂ P and condensation required

Vapor Phase

Low H₂ P
Moderate T

Ex-situ CFP

Catalytic Cracking

Zeoites and reducible metal oxides
Removal of O as CO and CO₂ (H₂O)
High rate of coking and deactivation

In FY13, we evaluated the SOT and identified promising catalysts for ex-situ CFP through a critical lit review:


- **Bifunctionality is essential**
  - Hydrogenation (metallic) and dehydration (acid or oxygen-vacancies)
  - Bifunctional active phase or active phase/support combination
- **Metals and metal phosphides/carbides**
**Project Overview: Platform Integration**

**Catalytic Pyrolysis Science**

Pyrolysis science fundamentals, catalyst modeling
Lab scale

**Catalytic Upgrading of Pyrolysis Products**

*Ex-situ, in-situ* Catalyst
development/evaluation
Lab scale

**Biomass Deconstruction: Catalyst Development/Testing**

*Ex-situ* catalyst
evaluation/characterization
Lab-small pilot

**Engineering Integration and Scale-up**

*Ex-, in-situ* TCPDU pilot scale
demonstration
Pilot scale

**Thermochemical Platform Analysis: TEA**

*Ex-, in-situ*, product/process costs at Pilot scale

---

**Near-term emphasis:** Zeolites and modified zeolites (2.3.1.313 and 2.3.1.315)

**Long-term emphasis:** Next-generation catalysts (2.3.1.314)

---

### Process Parameter

<table>
<thead>
<tr>
<th>Parameter</th>
<th>2017 Target</th>
<th>2022 Target / Design Case</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vapor Products</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-Condensable Gases</td>
<td>30</td>
<td>23</td>
</tr>
<tr>
<td>Aqueous Phase (% C Loss)</td>
<td>26 (2.3)</td>
<td>30 (1.3)</td>
</tr>
<tr>
<td>Solids (Char + Coke)</td>
<td>12 + 10 2</td>
<td>12 + 8.0</td>
</tr>
<tr>
<td>Organic Phase</td>
<td>22.0</td>
<td>27.2</td>
</tr>
<tr>
<td>H/C Molar Ratio</td>
<td>1.3</td>
<td>1.6</td>
</tr>
<tr>
<td>Carbon Efficiency (%)</td>
<td>34</td>
<td>44</td>
</tr>
<tr>
<td>Oxygen Content (% of organic)</td>
<td>12.5</td>
<td>6.4</td>
</tr>
<tr>
<td>Diesel-Range Product (% GGE basis)</td>
<td>14</td>
<td>55</td>
</tr>
<tr>
<td>Minimum Fuel Selling Price ($ / GGE)</td>
<td>$4.58</td>
<td>$3.31</td>
</tr>
</tbody>
</table>

---

**Yield/C Efficiency**

**Catalyst Cost**

**Catalyst Lifetime**

---

% Change to MFSP from the ex situ base case ($3.31/GGE)
Project Overview: Objectives

The primary objectives of this project are:

• Design and develop scalable and cost-effective next generation ex-situ CFP catalysts which outperform commercial and SOT materials for hydrogen incorporation, deoxygenation, and C-C coupling.

• Provide in-house data for technoeconomic analysis to guide the selection of the optimal process design for producing liquids fuels at ~$3/GGE via biomass pyrolysis.

• Validate that ex-situ CFP reduces the severity, cost, and/or unit operations for down-stream hydroprocessing.

• Demonstrate catalyst performance at the large-bench scale (~200g cat) with real pyrolysis vapors in 2017.
Technical Approach

Combine **experimental** and **computational** efforts to drive catalyst discovery and development through theoretical modeling, advanced synthetic techniques, rigorous catalyst characterization, and reaction testing with model compounds and real pyrolysis vapors.

**Synthesis/Characterization**
- Colloidal solution-phase synthesis
- Support independent
- Metrics:
  - Cost
  - Scalability
- Catalyst down-selection
- Metrics:
  - Extent of deoxygenation
  - Extent of $H_2$ incorporation
  - C efficiency
  - Stability

**Catalytic Testing**
- Testing with model compounds and real pyrolysis vapors

**Computational Pyrolysis Consortium (2.5.1.302)**
- Mechanisms
- Performance Descriptors
- Predictive Capability
Management Approach

Peer-reviewed 3-year AOP

**FY13**
- Review of ex-situ CFP conditions and catalysts, and identification of preliminary materials of interest

**FY13-FY17**
- Catalyst Development and Refinement
  - Yearly milestones tied to catalyst performance
  - Quarterly progress updates
  - Joint milestones

**Catalytic Testing with Model Compounds (mg-g scale)**
- Targets achieved?
  - Yes (Y)
  - No (N)
  - Targets guided by TEA analysis
    - FY16 Go/No-Go Decision on catalyst feasibility
      - Ex-situ CFP performance
      - Cost
      - Scalability

**FY16-FY17**
- Catalyst Scale-up

**FY17**
- Large-bench scale demonstration of ex-situ CFP with real pyrolysis vapors

Technology Validation

**Computational Modeling (2.5.1.302)**
- Fundamental

**Catalytic Testing with Real Pyrolysis Vapors (2.3.1.313)**
- Applied
Challenges and Success Factors

**Grand Challenges**

- **Activation and incorporation of** $H_2$ **at moderate T (300-500°C) and low** $H_2$ **P to achieve** **selective hydrogenation** **of specific functional groups**
- **Removal of O via** $H_2O$ **instead of CO/CO$_2$ (C-O vs. C-C bond cleavage)**
- **Increase product carbon number** (**C$_{8+}$**) **via C-C coupling while minimizing deactivation due to carbon deposition**
- Achieve this functionality with **cost-effective, scalable materials**

**Critical Success Factors**

- Achieve 2017 targets for ex-situ CFP at large-bench scale:
  - H/C molar ratio = 1.3, C efficiency = 34%, and O content = 12.5wt%
- Minimize catalyst cost by using low-cost metals and precursors and achieving high dispersion of the active phase
  - Target: scaled catalyst cost < $50/lb
- Demonstrate that ex-situ CFP reduces cost of downstream hydrotreating

**Go/No-Go Decision Point - March 2016**

- Commercial feasibility assessment of colloidal nanoparticle catalysts
- Metrics: Cost, scalability, and ex-situ CFP performance
Support-independent synthesis with precise control over the size, shape, and composition of the active phase accelerates catalyst development and facilitates direct linkages to theory.
Research Progress: NP Surface Chemistry-Ligands

- Organic ligands (e.g., alkylamines) stabilize NPs and control features (size, shape, composition)

- Investigated the effect of ligands on NP surface chemistry and reactivity
  - As-prepared NPs are resistant to ligand exchange with phenolic but not acidic compounds
  - Thermal transformation of organic ligands leads to an accessible amorphous carbon shell

- Beneficial catalytic effects
  - Active site geometric/electronic structure
  - Active phase-support interface

Tailored carbon coating for enhanced catalytic performance

Understanding ligand effect on reactivity will help us design improved catalysts
Research Progress: Model Compound Upgrading

Catalytic upgrading of guaiacol was used to evaluate and down-select active phase materials

- Colloidal NP catalysts outperformed incipient wetness materials
- Catalysts down-selected for further study: NP-Ni/SiO₂, NP-Pt/SiO₂, and NP-Rh₂P/SiO₂

350°C, 0.5MPa, WHSV 5 h⁻¹, 12:1 H₂:guaiacol
Catalytic upgrading of guaiacol over NP-Ni and NP-Rh₂P dispersed on selected supports was used to evaluate and down-select active phase-support materials.

### Mechanistic Insights

- **Best performing materials:**
  - NP-Rh₂P/TiO₂, NP-Ni/SiO₂, NP-Ni/TiO₂

- Combining upgrading results with computational efforts to determine dominant reaction mechanism under ex-situ CFP conditions:
  - Ring hydrogenation
  - Tautomerization
  - Direct Deoxygenation

### Catalysts and Deactivation Rates

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Deactivation Rate Constant (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP-Ni/Al₂O₃</td>
<td>0.0007</td>
</tr>
<tr>
<td>NP-Rh₂P/TiO₂</td>
<td>0.0007</td>
</tr>
<tr>
<td>NP-Rh₂P/Al₂O₃</td>
<td>0.0008</td>
</tr>
<tr>
<td>NP-Ni/SiO₂</td>
<td>0.0011</td>
</tr>
<tr>
<td>NP-Ni/TiO₂</td>
<td>0.0014</td>
</tr>
</tbody>
</table>
Research Progress: Preliminary Catalyst Cost

- Processing costs for metals and metal phosphides are similar.
- Materials for NP catalysts are the greatest contributor to cost.
- Opportunities to reduce cost exist through:
  - Alternative metal precursors
  - Elimination of TOP

**Total Catalyst Cost**

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP-Rh$_2$P/SiO$_2$</td>
<td>$2515</td>
</tr>
<tr>
<td>IW-Rh$_2$P/SiO$_2$</td>
<td>$709</td>
</tr>
<tr>
<td>NP-Ni$_2$P/SiO$_2$</td>
<td>$151</td>
</tr>
<tr>
<td>NP-Ni/SiO$_2$</td>
<td>$72</td>
</tr>
<tr>
<td>IW-Ni$_2$P/SiO$_2$</td>
<td>$13</td>
</tr>
<tr>
<td>IW-Ni/SiO$_2$</td>
<td>$12</td>
</tr>
</tbody>
</table>

**Materials**

- Ni(acac)$_2$ comm. $\rightarrow$ $18$
- Ni(acac)$_2$ synth. $\rightarrow$ $7$
- Ni(acac)$_2$ hydrate synth. $\rightarrow$ $4$
- Ni(NO$_3$)$_2$ hydrate comm. $\rightarrow$ $3$
- Ni(ac)$_2$ hydrate comm. $\rightarrow$ $1$

**Alternative precursors**

- Acetone
- Isopropanol
- Support
- Chloroform
Research Progress: NP Synthesis-Carbides/Nitrides

High temperature decomposition of metal-urea gel

\[ \text{MCl}_x + \text{EtOH} + \text{H}_2\text{NCONH}_2 \xrightarrow{\text{Mix at RT, dry}} \text{Metal-urea gel} \]

- MCl\(_x\) + EtOH + \text{H}_2\text{NCONH}_2 \xrightarrow{T > 700^\circ\text{C}} \text{M}_x\text{N} \text{ metal nitride}
- MCl\(_x\) + EtOH + \text{H}_2\text{NCONH}_2 \xrightarrow{T > 700^\circ\text{C}} \text{M}_x\text{C} \text{ metal carbide}

Novel Hard-template Method

- Impregnated SBA-15 silica
- Encapsulated \(\text{Mo}_2\text{C} nps\)

- Successfully synthesized nanoparticles of metal carbides (\(\text{Mo}_2\text{C}, \text{W}_2\text{C}, \text{VC}\)) and metal nitrides (\(\text{Mo}_2\text{N}, \text{W}_2\text{N}, \text{VN}, \text{Mo}_x\text{V}_y\text{N}\))
- Developed a hard-templating method
Research Progress: Mo$_2$C-Acetic Acid Upgrading

**Experimental Results**

1bar, H$_2$/AA = 4

- Acetaldehyde
- Ethylene
- Ethane
- Ethanol

**Modeling Results**

XPS Elemental Estimates

<table>
<thead>
<tr>
<th>XPS depth, Å</th>
<th>Exp.</th>
<th>Theor.</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.62</td>
<td>0.52</td>
</tr>
</tbody>
</table>

**Reaction pathways and energetics**

• At T<400°C, Mo$_2$C favors hydrogenation-dehydration products (C-O bond cleavage)
• Mo$_2$C surface and sub-surface contains oxygen even after pretreatment in H$_2$
• Good agreement between experiment and theory

Joint with Computational Pyrolysis Consortium (2.5.1.302)
Tested the ex-situ CFP performance of Mo$_2$C with real biomass pyrolysis vapors using a py-GC system.

Preliminary results indicate that Mo$_2$C is a promising material for ex-situ CFP.
Compared the hydrotreatability of surrogate mixtures representing catalytically upgraded and raw pyrolysis oils over Pd/C at 250-360°C

- Catalytically upgraded oils result in lower oxygen content in the final product and reduced H₂ consumption
- Oxygenates remaining in catalytic pyrolysis oil are recalcitrant and require temperatures in excess of 350°C for deoxygenation
Relevance

Decreasing Biomass Conversion Costs through Catalyst Development

- Directly supports BETO’s mission:
  “Develop and transform our renewable biomass resources into commercially viable, high performance biofuels”
- Addresses BETO’s 2017 target for Bio-Oils Pathways R&D of a conversion cost of $1.83 per gallon of total blendstock
  - Project fulfills a critical need for Conversion Enabling Technologies:
    “The need to develop the next generation of catalysts for conversion of biomass and conditioning of bio-oils is critical in the advancement of biomass processing technologies.”
- Project metrics and technical targets are driven by TEA
- Reduction in conversion costs through improvements in:
  - $H_2$ incorporation
  - Deoxygenation
  - C efficiency/yield
  - C-C coupling

[Graph showing production cost per GGE of fuel product (2015)]

<table>
<thead>
<tr>
<th>Year</th>
<th>Production Cost per GGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>2014 State of Technology</td>
<td>$6.17</td>
</tr>
<tr>
<td>2015 Target</td>
<td>$5.92</td>
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<tr>
<td>2016 Target</td>
<td>$5.24</td>
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<tr>
<td>2017 Target</td>
<td>$4.58</td>
</tr>
<tr>
<td>2018 Target (Interpolated)</td>
<td>$4.83</td>
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<tr>
<td>2019 Target (Interpolated)</td>
<td>$4.07</td>
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<tr>
<td>2020 Target (Interpolated)</td>
<td>$3.82</td>
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<tr>
<td>2021 Target (Interpolated)</td>
<td>$3.57</td>
</tr>
<tr>
<td>2022 Target (Interpolated)</td>
<td>$3.31</td>
</tr>
<tr>
<td>2022 Target / Design Case</td>
<td>$3.12</td>
</tr>
</tbody>
</table>
Future Work

- **Continue catalyst development**
  - *Increase extent of hydrogenation and deoxygenation by 15%* in 2016 compared to FY15 guaiacol upgrading results
  - Evaluate catalyst performance with *model compound mixtures of increasing complexity*
    - Leverage mechanistic insights from computational modeling to design next-generation catalysts
      - Modification of Mo$_2$C to enhance H$_2$ incorporation
      - Tune active phase-support interface to drive chemistry towards specific reaction pathways
- **Demonstrate C-C coupling** with model compounds
  - *Methyl/Alkyl Transfer*
  - *Ketonization*
  - *Aldol Condensation*
  - *Hydroalkylation*
- **Validate** reduction in H$_2$ consumption and oxygen content during hydrotreating with real upgraded oils
- **Demonstrate scale-up** of colloidal NP catalysts from 5g to 200g per batch using micro-fluidic flow reactors

Summary

- Ex-situ CFP conditions (vapor phase, low H₂ P, moderate T) lie outside of those typically explored for hydrotreating and catalytic cracking
  - *Multi-functional catalytic materials* need to be developed specifically for these conditions
- This project focuses on *developing next generation catalysts for ex-situ CFP through a combined experimental-computational approach* which leverages theoretical modeling, advanced synthetic techniques, rigorous catalyst characterization, and reaction testing with model compounds and real pyrolysis vapors
  - Catalysts are designed and evaluated based on *metrics derived from TEA*
  - *Collaborative* research across multiple projects
  - *Commercial viability* is assessed through catalyst cost calculations and scale-up of synthesis methods
- Results suggest that *NP-Ni and Mo₂C are promising catalysts* for ex-situ CFP
- *Further catalyst advancements* will be driven by mechanistic insights and will reduce conversion costs to *achieve our 2017 targets at the large-bench scale*
Acknowledgements

NREL
Dan Ruddy  Adam Bratis  Jason Thibodeaux  Levi Thompson (UM)
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Mike Griffin  Asad Sahir  Xerxes Steirer  Allison Robinson (CU)
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Jun Wang  Jared Clark  Jack Ferrell  Noah Malmstadt (USC)
Ming Pan  Gregg Beckham  Matt Yung
Jesse Hensley  David Robichaud  Mark Nimlos
Kristiina Lisa  Tabitha Evans  Jeff Blackburn
Rick French  Calvin Mukarakate  Jim Stunkel
Luc Moens

External

Image of a group of people standing together.

U.S. DEPARTMENT OF ENERGY
Energy Efficiency & Renewable Energy

NATIONAL RENEWABLE ENERGY LABORATORY
2.3.1.314
Catalytic Upgrading of Pyrolysis Products

March 24th, 2015
Thermochemical Conversion

Josh Schaidle
NREL
Nomenclature

AA: Acetic Acid
CFP: Catalytic Fast Pyrolysis
CU: University of Colorado
GGE: Gasoline Gallon Equivalent
IW: Incipient Wetness
MFSP: Minimum Fuel Selling Price
NP: Nanoparticle
SOT: State of Technology
SUB: Subcontract
TCPDU: Thermochemical Process Development Unit
TEA: Technoeconomic Analysis
TOP: Triocetylphosphine
UM: University of Michigan
USC: University of Southern California
Presentations

- R. French, Hydrotreating Pyrolytic Lignin to Produce a Refinery Feedstock, TCBiomass 2013, Chicago, IL, September 3-6, 2013.
Publications, Patents, and Awards

Publications


• M. Griffin, F. Baddour, S. Habas, J. Hensley, D. Ruddy, J. Schaidle, An Investigation into the vapor phase deoxygenation of guaiacol over metal and metal phosphide catalysts, Topics in Catalysis, manuscript in preparation.

Patents/ROIs

• D. Ruddy, J. Schaidle, J. Blackburn, Synthetic routes for shape- and composition-controlled metal carbide and metal nitride nanocrystal catalysts, NREL ROI-12-00034.

• D. Ruddy, S. Habas, J. Schaidle, M. Griffin, Novel pretreatment procedure for the activation of supported colloidal nanoparticle catalysts, NREL ROI-14-11.


Awards

• J. Schaidle, NREL Chairman’s Award for Exceptional Performance, September 2014.
Milestones
## Milestones-FY15

<table>
<thead>
<tr>
<th>Level</th>
<th>Performance Measure</th>
<th>Planned Completion Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deliverable</td>
<td><strong>Characterization and Evaluation of Colloidal Ligand-capped Nanoparticles:</strong> Determine the key physical and/or chemical attributes of colloidal ligand-capped nanoparticles that provide their superior upgrading performance compared to standard incipient wetness, bulk catalysts. This study will determine these attributes using two (2) probe tests: transformation of the ligands under pre-treatment and reaction conditions and external ligand exchange. These tests will be combined with CO or H₂ chemisorption, DRIFTS, XPS, <em>in-situ</em> NMR, and/or thermogravimetric analysis. Results from this milestone will be used to guide catalyst selection and activation procedures for the FY15 Q2 milestone.</td>
<td>12/31/2014</td>
</tr>
<tr>
<td>Regular</td>
<td><strong>Catalyst Screening for <em>Ex-situ</em> CFP:</strong> Evaluate a series of at least ten (10) active phase-support combinations for high temperature (300-500°C), low pressure (&lt;1MPa) <em>ex-situ</em> CFP of at least one (1) model pyrolysis compound. The active phase materials will be selected from our FY14 Q2 milestone and from materials predicted by the Computational Pyrolysis Consortium (WBS 2.5.1.302) to have high performance. Support materials will be selected from our FY14 Q3 milestone. Active phase-support combinations will be ranked for performance in terms of i) their abilities to increase the ratio of H:C and decrease the ratio of O:C from reactants to products, ii) higher selectivities to larger carbon number products, and iii) relative deactivation rates. Catalyst rankings will inform the down-selection of two (2) to three (3) catalysts for further study. These down-selected materials will be identified as the state-of-the-art materials in 2015 and will be given to the Catalytic Pyrolysis Science project (WBS 2.3.1.313) for evaluation under real pyrolysis vapors in FY15 Q3.</td>
<td>3/31/2015</td>
</tr>
<tr>
<td>Deliverable</td>
<td><strong>Demonstrate C-C Coupling Capability:</strong> Demonstrate the coupling of at least two (2) model <em>ex-situ</em> CFP intermediates over at least two (2) commercial or in-house catalysts under conditions relevant to <em>ex-situ</em> CFP. The model <em>ex-situ</em> CFP intermediates will be selected based on the results from the FY15 Q2 milestone.</td>
<td>6/30/2015</td>
</tr>
<tr>
<td>Deliverable</td>
<td><strong>Hydrodeoxygenation of Catalytically Upgraded Bio-oils:</strong> Compare the hydrotreating severity required to deoxygenate three (3) upgraded whole bio-oils collected from <em>ex-situ</em> CFP over the catalysts down-selected in the FY15 Q2 milestone or over HZSM-5. The results for the upgraded oils will be compared with those of representative whole non-upgraded pyrolysis oil. The evaluation metrics will be temperature and H₂ consumption.</td>
<td>9/30/2015</td>
</tr>
</tbody>
</table>
## Milestones-FY16

<table>
<thead>
<tr>
<th>Level</th>
<th>Performance Measure</th>
<th>Planned Completion Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deliverable</td>
<td><strong>Demonstrate Scale-up of the Colloidal Nanoparticle Synthesis Method:</strong> Demonstrate the scale-up of our colloidal nanoparticle synthesis method from 5g of supported catalyst (5wt% active phase) per batch to 200g per batch while maintaining similar physical properties (i.e., particle size and shape, phase purity, crystallinity). Provide an estimate of synthesis method costs and potential pathways to reduce cost.</td>
<td>12/31/2015</td>
</tr>
<tr>
<td>Regular</td>
<td><strong>Advanced Catalyst Testing for Ex-situ CFP:</strong> Evaluate a series of at least six (6) advanced catalysts for ex-situ CFP of at least two (2) model pyrolysis compounds. These catalyst formulations will be guided by results from the FY15 Q2 and Q3 milestones, the Computational Pyrolysis Consortium (WBS 2.5.1.302), and selective hydrogenation studies at the University of Michigan. The target for this milestone is to improve the extent of hydrogenation and deoxygenation by 15% and the extent of C-C coupling by 30% compared to the state-of-the-art catalysts down-selected in FY15.</td>
<td>3/31/2016</td>
</tr>
<tr>
<td>Go/No-Go</td>
<td><strong>Feasibility Assessment of Colloidal Nanoparticle Catalysts:</strong> Based on results from the FY16 Q1 and Q2 milestones, determine the feasibility of using colloidal nanoparticle catalysts in a commercial-scale process. The metrics for evaluating feasibility will be cost ($/kg-catalyst), scalability (compared to common bulk synthesis methods), and ex-situ CFP performance (compared to similar materials synthesized using bulk methods). Provide cost estimates to TC Analysis team (WBS 2.1.0.302).</td>
<td>3/31/2016</td>
</tr>
<tr>
<td>Deliverable</td>
<td><strong>Evaluation of Bench-Scale Ex-Situ CFP Performance with Complex Model Compound Feed Mixtures and Real Biomass Pyrolysis Vapors:</strong> Down-selected catalysts from the FY16 Q2 milestone will be tested at the bench-scale (~1g) for ex-situ CFP with (i) a mixture containing at least two (2) pyrolysis model compounds and steam and (ii) real biomass pyrolysis vapors. The effect of steam and additional compounds with increased functionality will be established, and the relationship between model compound experiments and real pyrolysis vapor experiments will be elucidated.</td>
<td>9/30/2016</td>
</tr>
</tbody>
</table>
## Milestones-FY17

<table>
<thead>
<tr>
<th>Level</th>
<th>Performance Measure</th>
<th>Planned Completion Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deliverable</td>
<td><strong>Catalyst Scale-Up for Large Bench-Scale Experiments:</strong> Produce ~200g of each of the catalysts down-selected in the FY16 Q2 milestone. These materials will be used for tests in FY17 Q2 and Q4 milestones.</td>
<td>12/3/2016</td>
</tr>
<tr>
<td>Regular</td>
<td><strong>Generation of Ex-situ CFP kinetic data for Process Models:</strong> Generate a set of kinetic expressions (e.g., power laws) for ex-situ CFP of model compound mixtures over the down-selected catalysts in FY16 that capture deactivation and the effects of temperature, pressure, steam concentration, and hydrogen concentration. Provide these kinetic models to the TC Analysis team (WBS 2.1.0.302).</td>
<td>3/31/2017</td>
</tr>
<tr>
<td>Deliverable</td>
<td><strong>Evaluation of Reactor Configuration and Design:</strong> In conjunction with the TC Analysis team (WBS 2.1.0.302), evaluate reactor configurations (e.g., fixed bed, fluidized bed, circulating bed) based on reactor cost and properties of the down-selected catalysts (e.g., attrition resistance, surface area, deactivation rate), and identify two (2) configurations to be further investigated.</td>
<td>6/30/2017</td>
</tr>
<tr>
<td>Regular</td>
<td><strong>Ex-Situ CFP of Real Pyrolysis Vapors at the Large-Bench Scale:</strong> Demonstrate ex-situ CFP of real biomass (pine) pyrolysis vapors at the large-bench scale (~200g of catalyst) over one (1) of the advanced catalysts developed during FY14-FY17 for 24 hours on stream while achieving our 2017 intermediate technical targets of 34% carbon efficiency to the organic phase and 12.5wt% oxygen content in the oil.</td>
<td>9/29/2017</td>
</tr>
</tbody>
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