

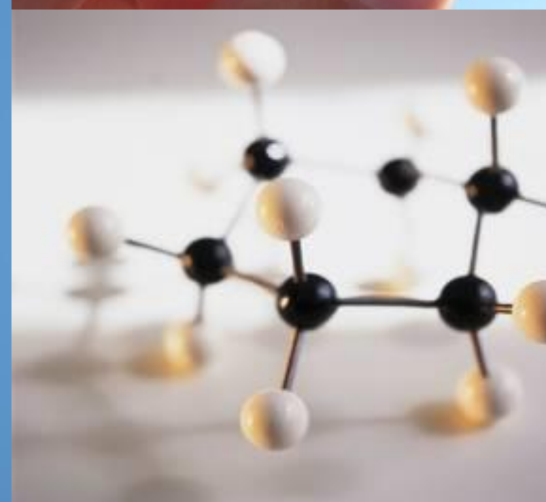


2013 DOE Bioenergy Technologies Office (BeTO) Bio-Oil Technology Area Review

–WBS 3.3.1.12 Catalytic Upgrading of Pyrolysis Products–

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Goal Statement

Project Goal – Develop catalysts and processes for high-yield upgrading of pyrolysis vapors

- Invent novel and effective catalysts **informed by first principles** and **structure-function relationships**

- **Provide data and validation** for Bio-Oil platform TEAs

Quad Chart Overview

Timeline

- Project start: 2012
- Project end: 2022
- 5% complete

Barriers

- **Tt-E** pyrolysis of biomass and bio-oil stabilization
  - Ex-situ catalytic fast pyrolysis
  - Oil deoxygenation and stabilization
- Process and market-driven attributes (achieve MFSP ≤ $3/gal)
  - Produce HC fuels that are ‘substantially similar’ to petroleum HC fuels
  - Maximize bio-oil yield
  - Minimize hydrogen requirements

Budget

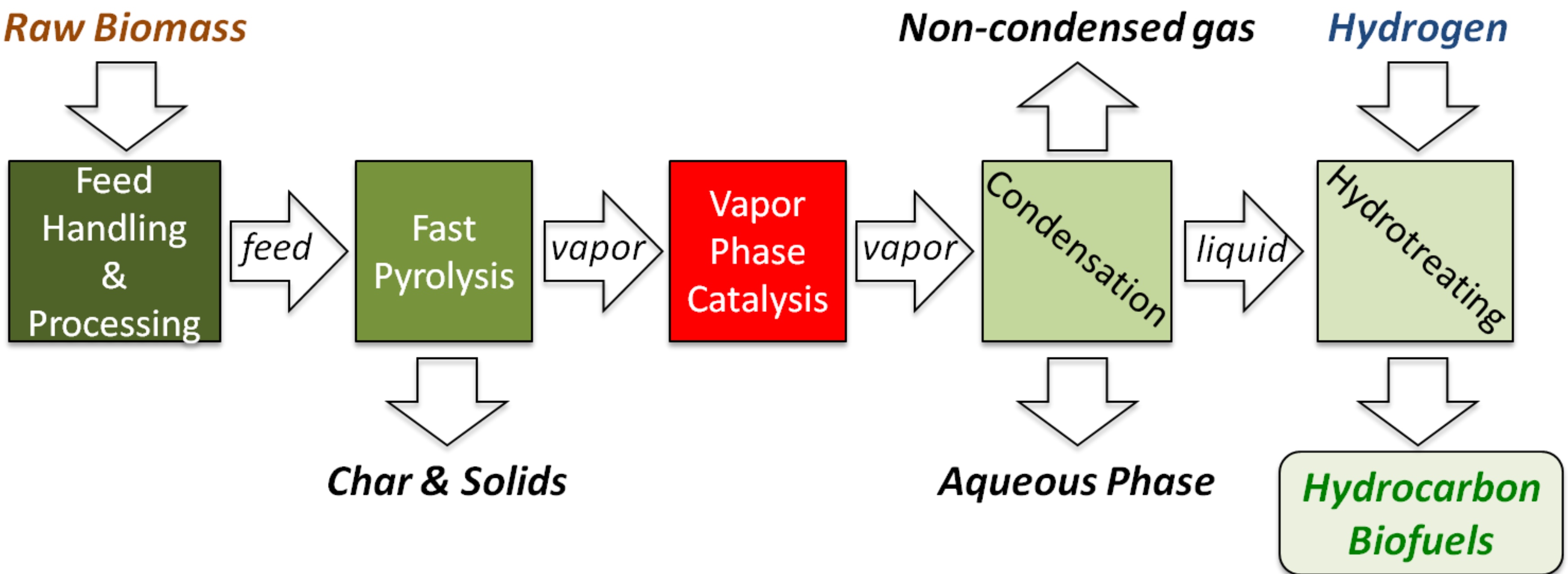
- Total project funding to date
  - $2 MM DOE
- FY13 funding $2 MM
- Project has been funded for 0.65 y

Partners & Roles

- Thermochemical Platform Analysis [WBS 3.6.1.1, 3.6.1.3]
- Integration & Scale up [WBS 3.3.1.13]
- Pyrolysis Science [WBS 3.6.1.6]
- Catalyst Development/Testing [WBS 3.3.1.14]

Project Overview

Ex-situ Upgrading



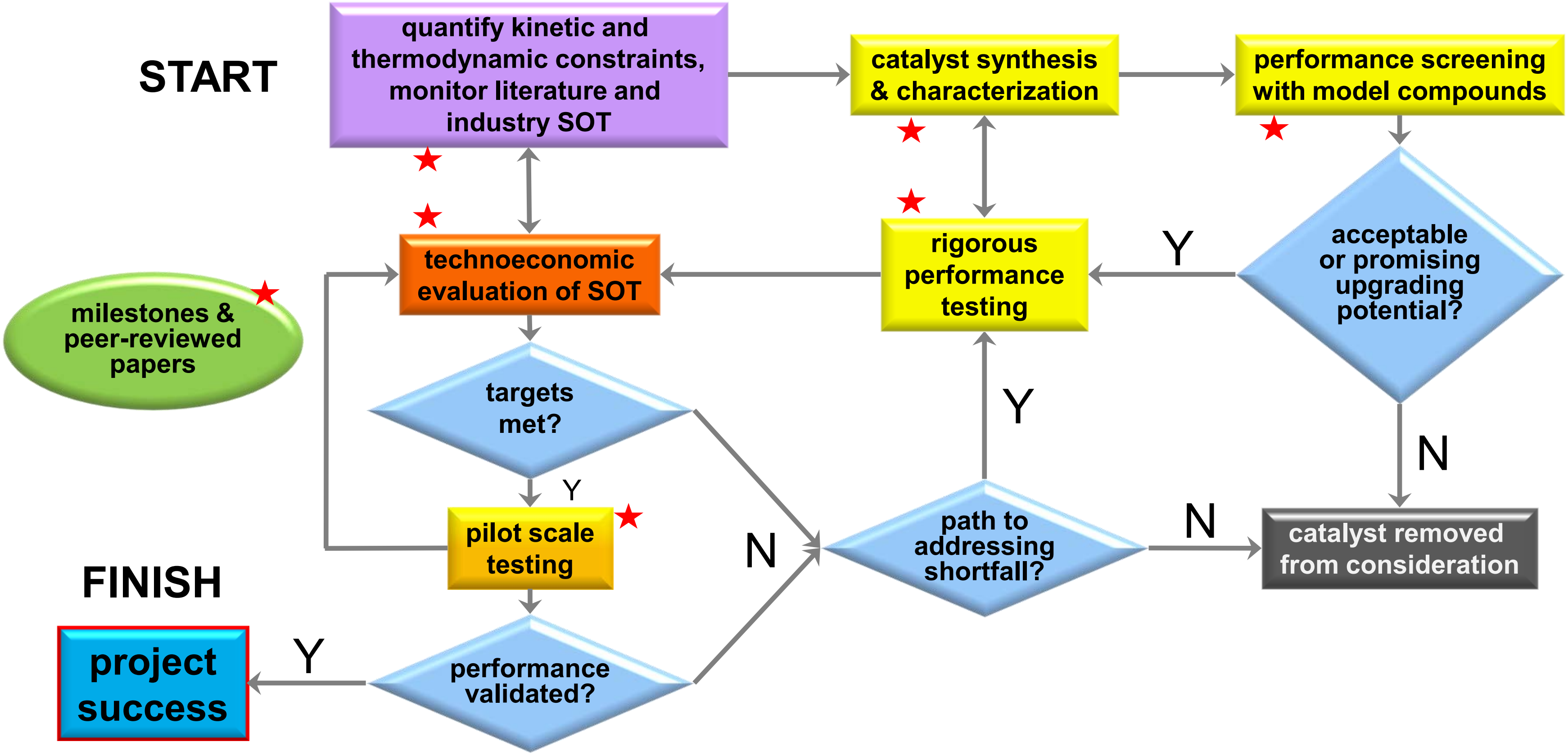
Technical Goals

- Contribute to cost target: $3/gal HC fuel by 2022
- Impact areas: product yield, capital cost, operating cost
- Preferred products: diesel and jet fuels

Approach

Target: modeled and pilot-validated MFSP of $3/gal

Catalyst development informed by literature SOT, TEA, and directed by progress, go/no-go decision points, etc.



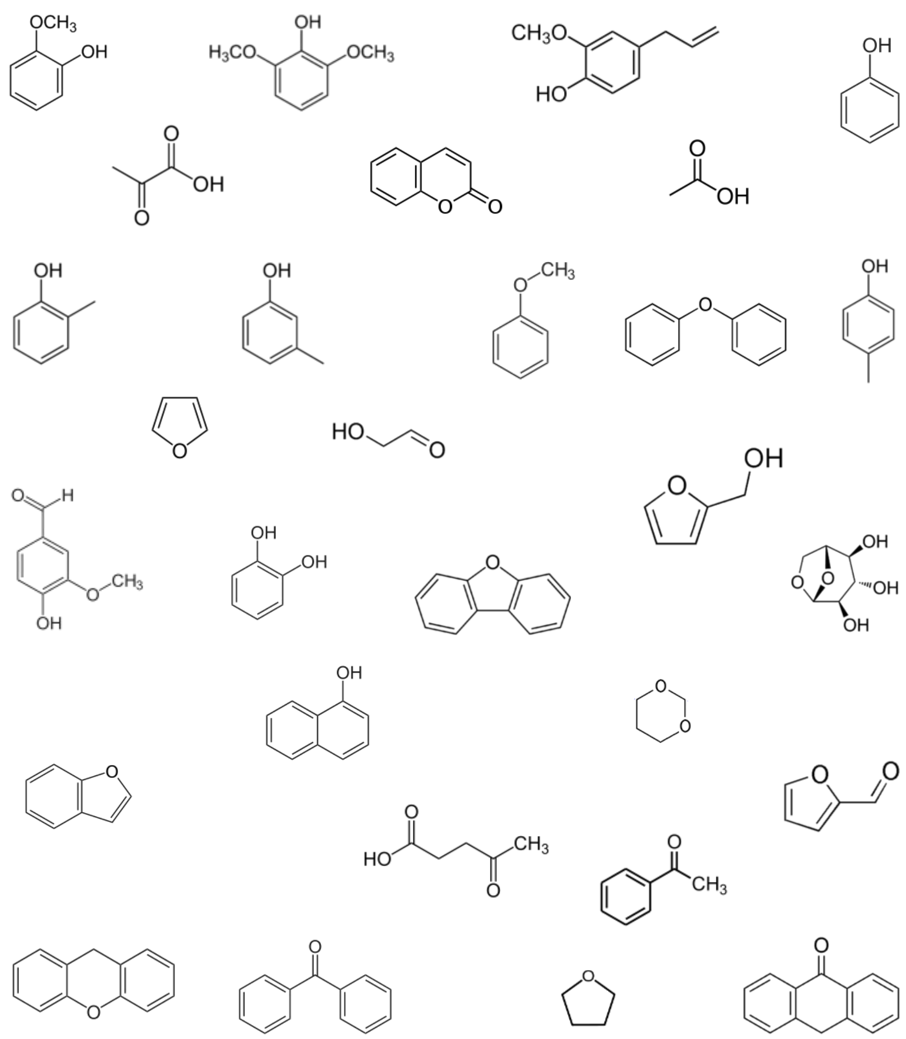
Technical Approach: *Develop novel catalysts for ex-situ catalytic pyrolysis*; provide data for TEA using model compounds; interface with integration task for testing in raw pyrolysis vapor; scale and demonstrate

Management Approach: DOE-approved Project Management Plans detail schedules/milestones/risk abatement

Key Accomplishments

- Established framework for addressing out-year cost targets:
  - Established the role of this task within the NREL thermochemical platform—development of novel catalysts for ex-situ pyrolysis vapor upgrading
  - Developed a focus on process-relevant model compounds, catalyst synthesis, and comparison to literature state of the art
  - Interface with other pyrolysis tasks:
    - TC Analysis for guidance on TEA, yield and upgrading requirements, etc [WBS 3.6.1.1]
    - In-situ upgrading for information on vapor composition and conditions [WBS 3.6.1.6]
    - Catalyst testing for extension of model compound studies to whole pyrolysis vapor studies [WBS 3.3.1.14, 3.5.1.6]
    - Integration to inform process requirements for pilot-scale validation [WBS 3.3.1.13]
- Completed a review of upgrading SOT
  - Indentified promising and problematic technologies for *ex-situ* CFP
  - Used learnings to inform FY14 AOP and to ensure minimal duplication of past effort
- Reviewed product analysis methods
  - Assures that data to be collected shall meet or exceed norms and be readily accepted by the pyrolysis community
  - Physical inventory of capabilities and future needs

Indentifying the Problem:
Complexity of Reactant Pool



Objectives

- Deoxygenate vapors before condensation to reduce downstream processing duty
- Eliminate unstable functionalities that complicate fractionation and/or hydrotreating of condensed pyrolysis oils
- Oligimerize molecules to improve carbon number and reduce losses to light gases in hydrotreating
- Limit loss of carbon to coke through catalyst design
- Utilize H_2 at lower P, higher T than in hydrotreating

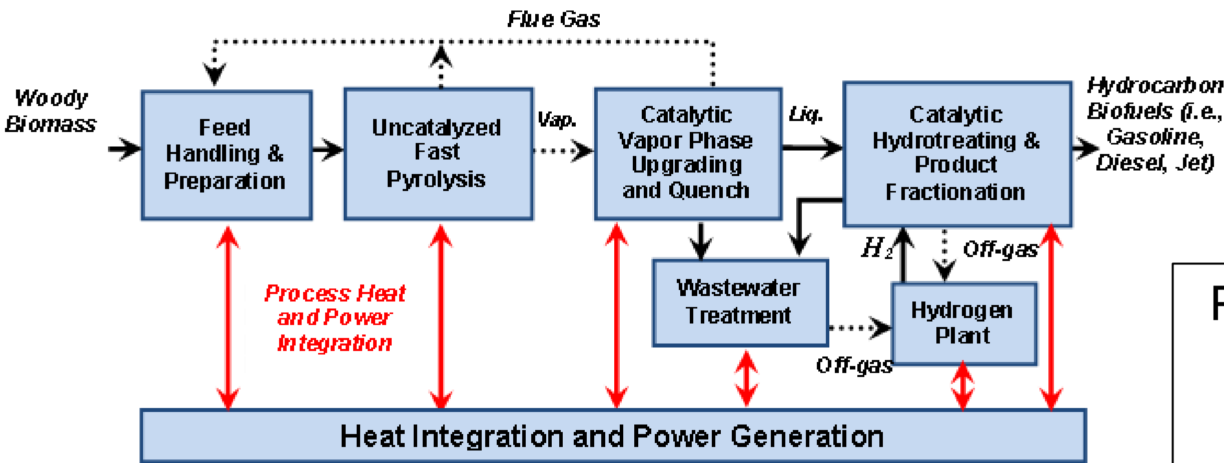
Indentifying Areas of Maximum Impact:
Requirements of End Product

oxygen content, fuel components' incompatibilities

- **Aviation Fuels**
  - Jet A (most common commercial fuel)
  - Jet B (cold regions)
  - JP-X (military grades)
  - Requirements:
    - Essentially zero O, S
    - C_8-C_{16}
    - Very low freeze point = branching and unsaturation (≤ - 40°C)
    - High auto ignition temperature (≥ 210°C)
    - Aromatics ≤ 20%
- **Diesel**
  - Requirements:
    - high cetane (≥ 40 required) = minimal branching
    - High energy density = some aromatics (≤ 30% allowed)
    - Low cloud point = branching
    - C_8-C_{21}
    - Low S (≤ 15 ppm, may get lower with new fuel standards)
    - No O allowed for non-FAME blends without EPA register/waiver/E-tests (big $)
- **Gasoline**
  - Requirements:
    - High octane (≥ 87) = branching, low MW
    - C_4-C_{12}
    - High energy density = more aromatics
    - Aromatics ≤ 40% (Europe), similar regulations coming for US
    - Low O, S (≤ 3.7%, 80ppm, may get lower with new fuel standards)
    - Required ranges for boiling, vapor pressure
    - Stable, no crystallization (durene +) or phase separation in water

cost of production and sale value

Indentifying Research Needs:
TEA Technologies Pathways Exercise



Biddy, M & Dutta, A. **2013** *NREL/TP-5100-58050*

Formal design and technical targets to be developed in FY14

Preliminary design to define semi-quantitative technical targets, suggest process configurations

Expected Conditions & Targets

- Reactor T < 500 °C
- catalyst life: ≥1 year
- Net increase in oil yield over current SOT

Data Gaps

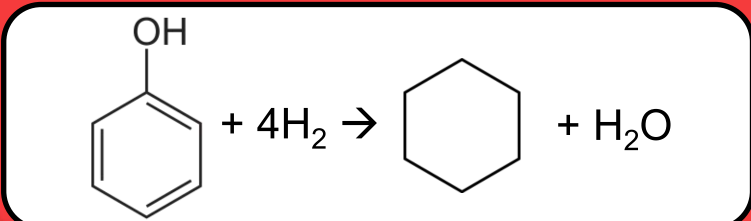
- Demonstrate and optimize VPU yield
- Develop and optimize VPU catalysts
- Develop VPU reactor design data

Ex-situ Upgrading Approaches:
Processing Options

Popular Upgrading Methods

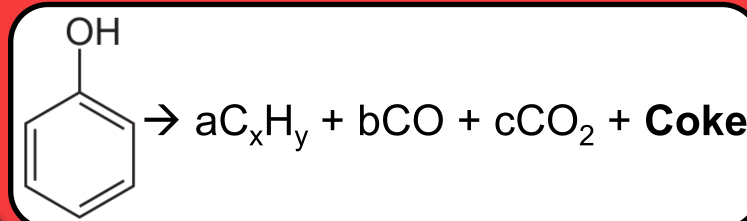
Hydrodeoxygenation

- Sulfided NiMo or CoMo catalysts
- 250-450°C, 20-100 atm
- High partial pressures of H_2
- Energy and H_2 intensive process



Cracking

- Acid zeolite catalysts
- 300-600°C, 1 atm
- No H_2 addition resulting in low liquid yields
- Char, coke and tar formation → catalyst deactivation



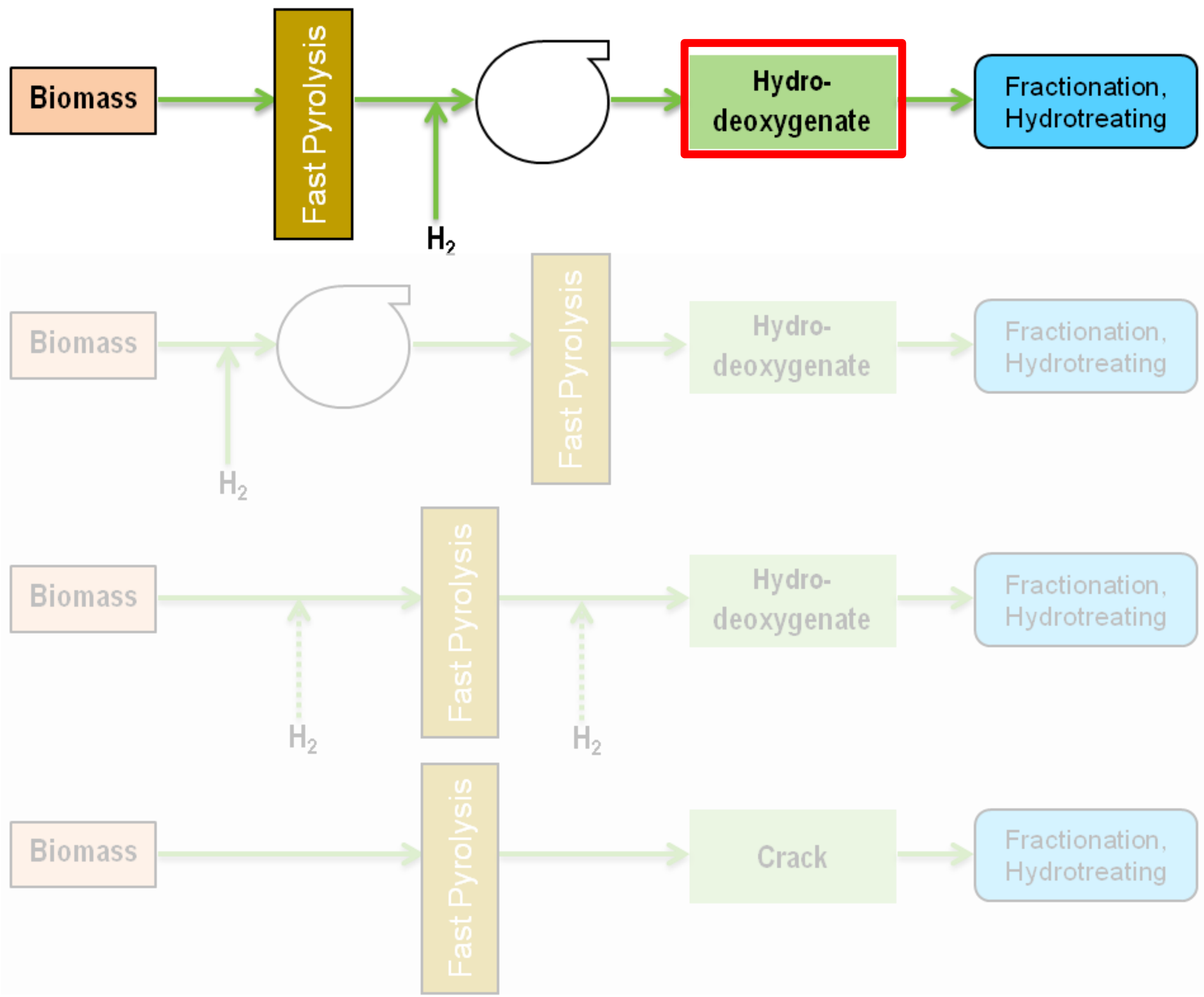
The temperature of pyrolysis vapor effluent is appropriate for both processes

To improve yield, low-pressure HDO may be required –our focus–

Ex-situ Upgrading Approaches:
Vapor-Phase Hydrotreating

- Pro
  - Known catalysts and chemistries
  - Kinetics favor high T
  - Use in place of stabilization step for hydrotreating
- Con
  - How to compress hot pyrolysis vapors?
  - Complicated solids removal?
  - More capital-intensive upgrading reactor
  - Use of large H_2 excess

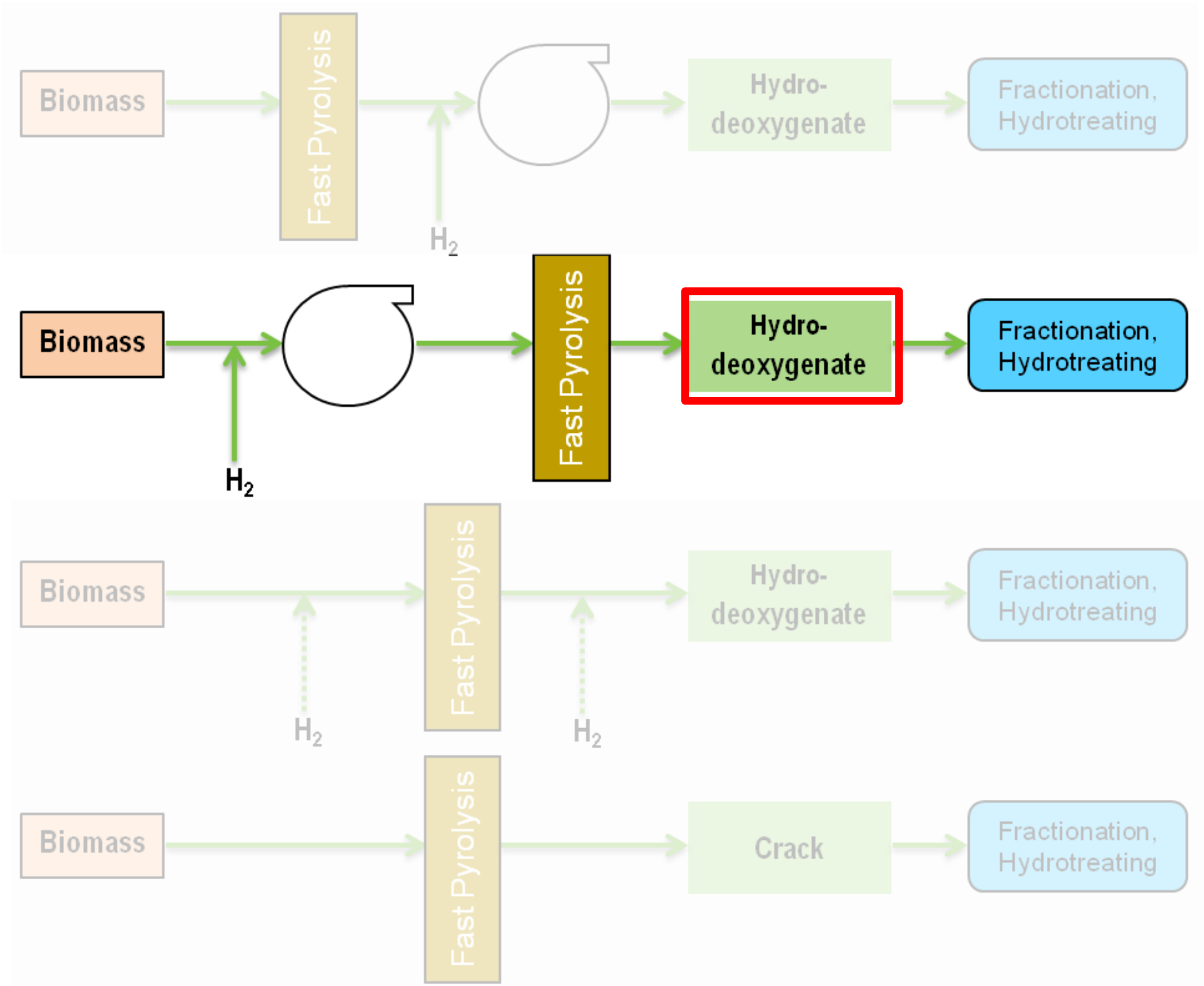
Potential Process Strategies



Ex-situ Upgrading Approaches:
Pressurized Hydropyrolysis

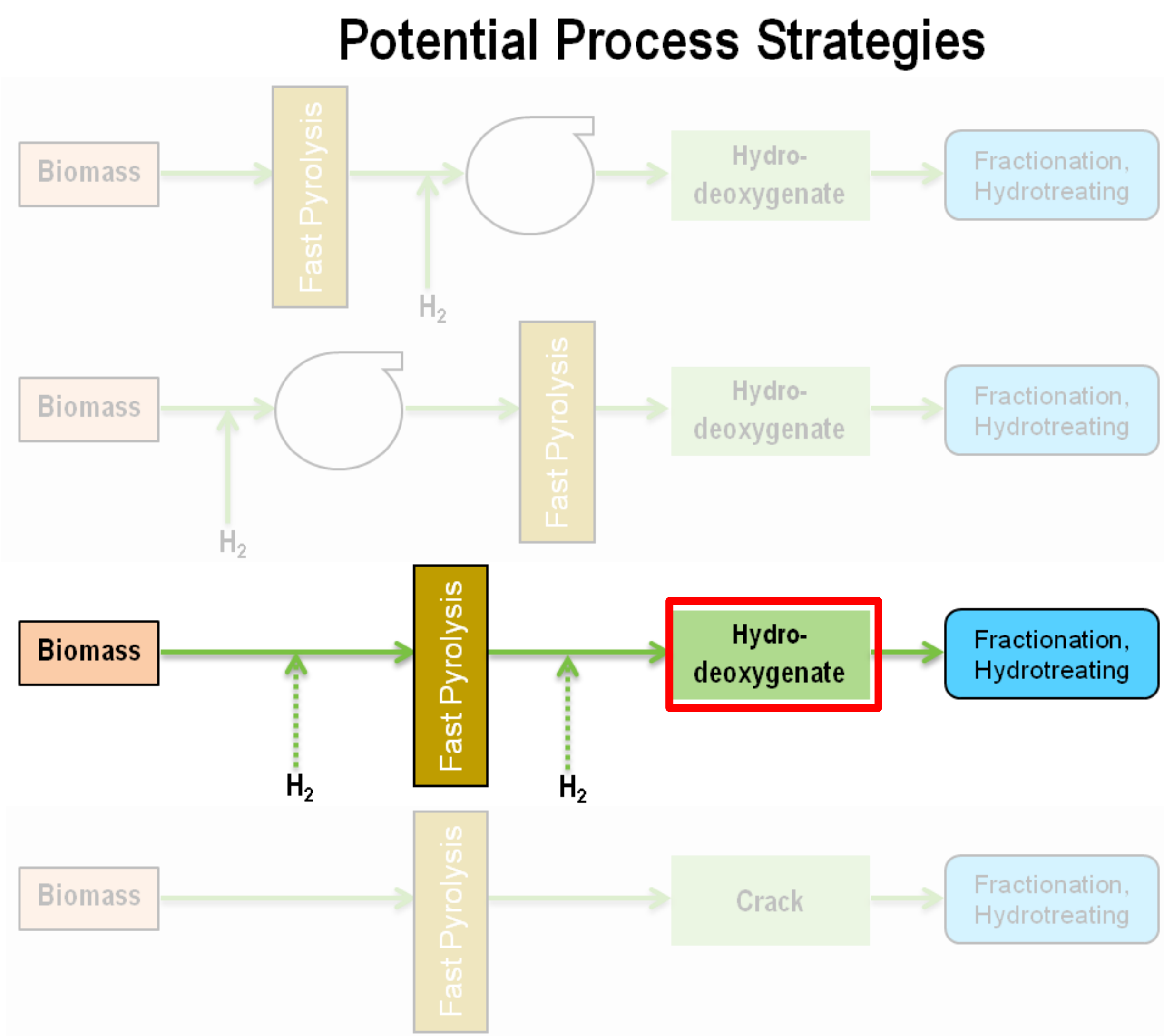
- Pro
  - Pyrolysis vapors potentially partially ‘upgraded’ before reaching reactor
  - Pyrolysis vapor already at P – easier to feed solids + H_2 at pressure than to compress vapors
  - Same kinetic pros as for VP hydrotreating
- Con
  - More complicated, capital-intensive pyrolysis
  - Use of large H_2 excess

Potential Process Strategies



Ex-situ Upgrading Approaches: *Atmospheric Hydropyrolysis*

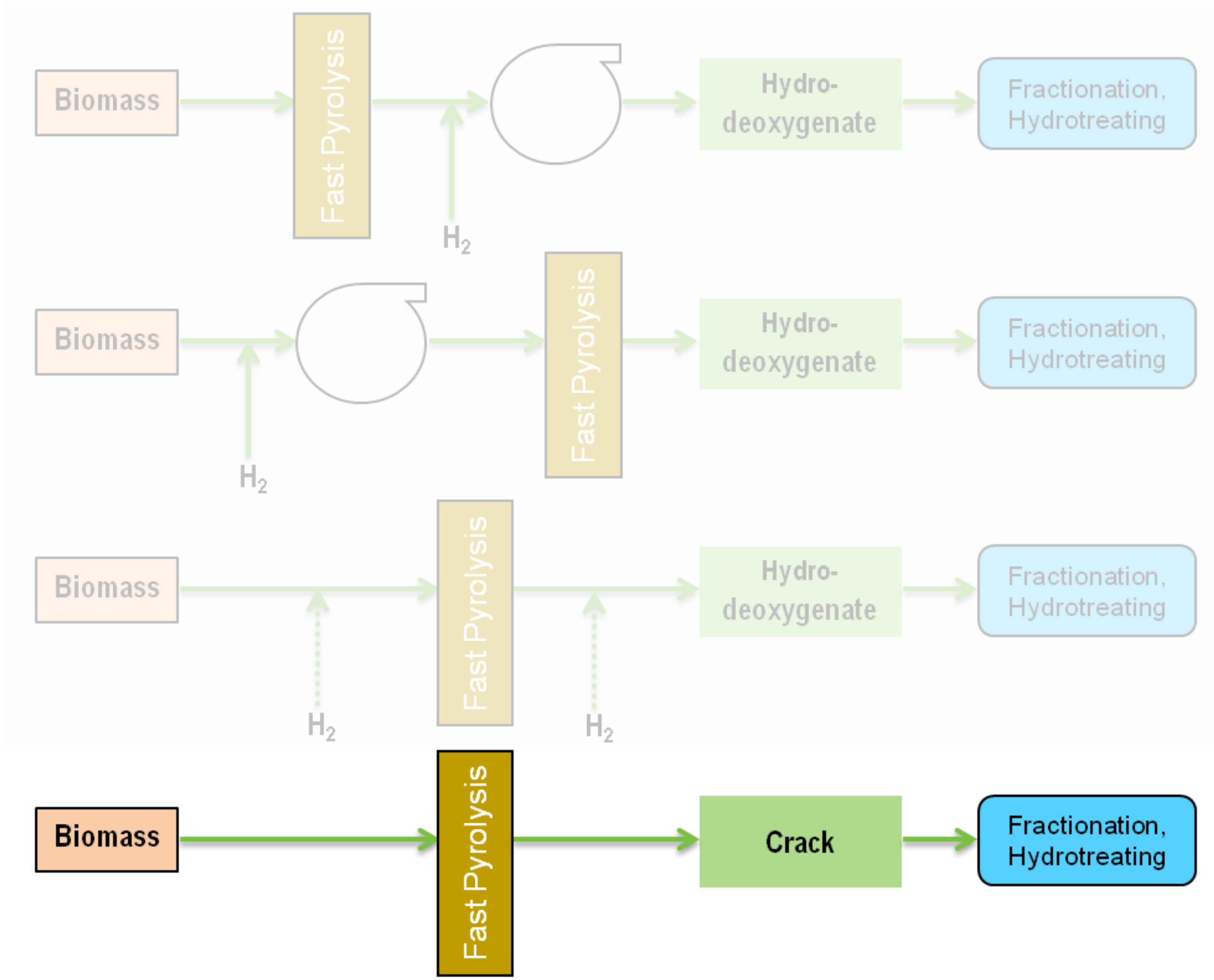
- Pro
  - Combine pros of pressurized hydro-pyrolysis and fast pyrolysis
  - No compression required
  - Less excess of H_2
- Con
  - Deoxygenation kinetics poor at low pressure
  - H_2 as fluidizing gas may have unintended consequences for fast pyrolysis



Ex-situ Upgrading Approaches:
Fast Pyrolysis and Catalytic Cracking

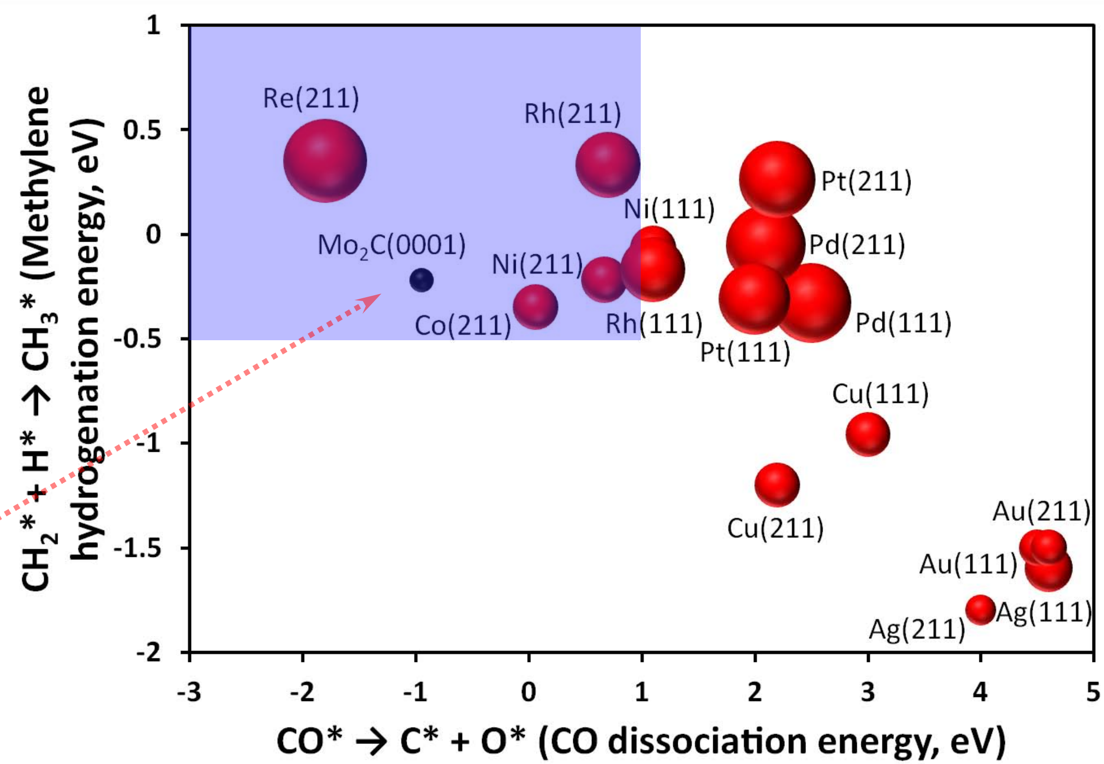
- Pro
  - No H_2 needed in these sections
  - Leverage technology developed for fluidized bed tar reforming (reactor)
  - Regeneration and replacement of catalyst easier
- Con
  - Significantly faster catalyst deactivation
  - Minimal fuel *yield* due to C lost to coke

Potential Process Strategies



Catalyst Development:
Targeting Deoxygenation Functionality

- “Norskov” type plots show energies of dissociation and association
- Materials with **favorable C—O dissociation** (negative eV) and less-favorable hydrogenation (positive eV) may promote deoxygenation with reduced H_2 consumption
- Transition metal carbides, nitrides, etc fall into this region
- **Nano-crystalline materials** may improve density of high-activity sites and impact selectivity

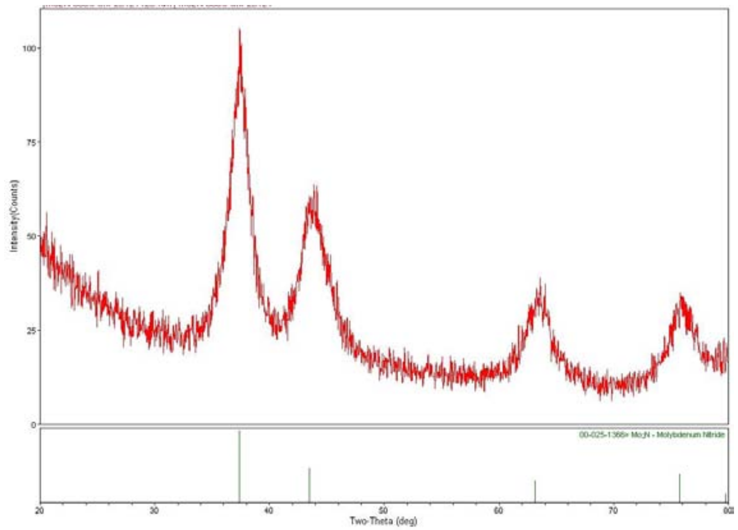


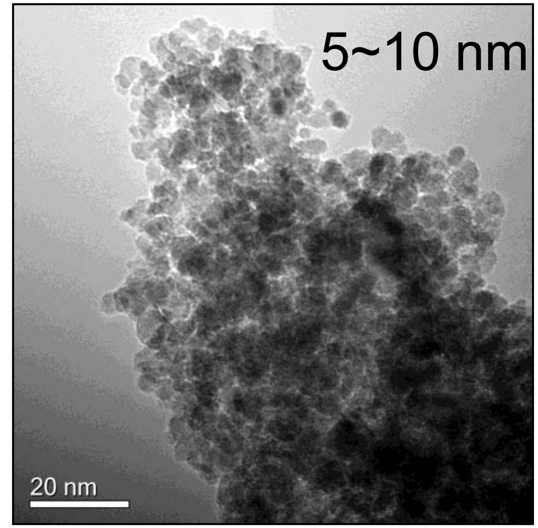
e.g. Medford, AJ *et al.*, **2012**, *J. Catal.*, 296, 175

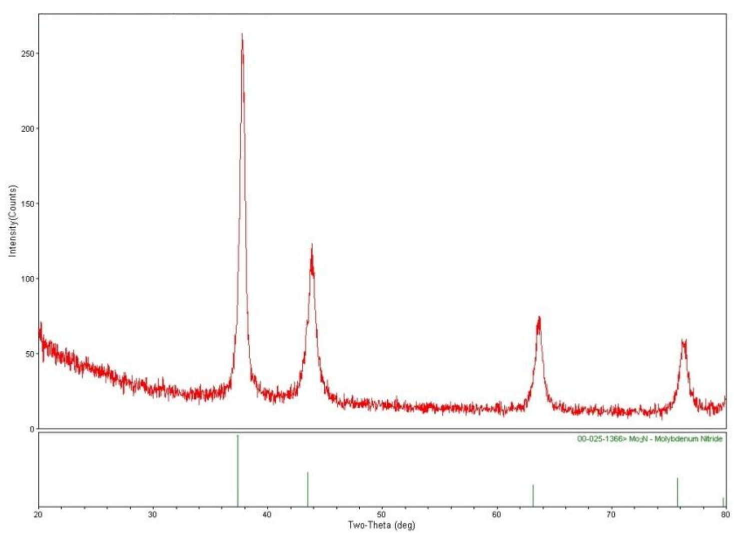
Catalyst Development:
Example—Nano-crystalline Metal Nitride Synthesis

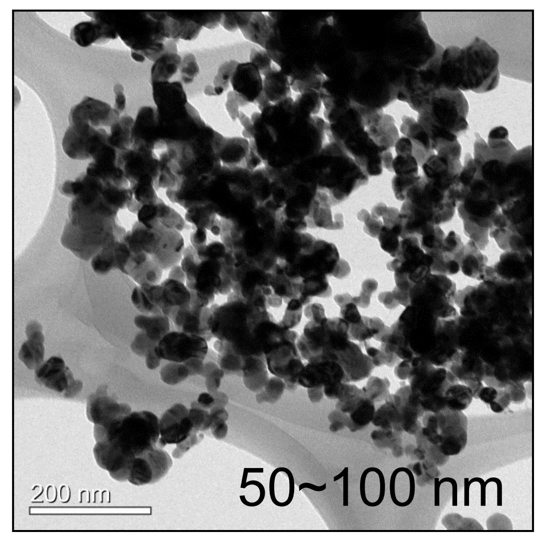
XRD

TEM









Relevance

- Addresses Thermochemical Conversion R&D Strategic Goal:
  "Develop technologies for converting feedstocks into ***cost-competitive*** *commodity liquid fuels such as renewable* ***gasoline, jet fuel, and diesel****."*
  - **Fundamental + applied approach** for efficient production of hydrocarbons via catalytic fast pyrolysis
  - Research and development **guided by technoeconomic feedback**
  - **Application specific catalyst development** instead of catalyst specific application development
    - Different reactant pool and chemistry than petroleum refining processes
    - Catalysts optimized for bio-oil upgrading, not petroleum upgrading
- Project addresses a biomass conversion pathway in the MYPP:
  - M X.17: Demonstrate and validate bio-oil production to a stable intermediate (X = feedstock pathway number)
- Contributes to BeTO portfolio of biomass conversion pathways:
  - Hydrocarbon synthesis from biomass via fast pyrolysis
  - Integrated with upstream and downstream R&D activities
  - **Lowers overall risk of meeting MFSP goals**

Success Factors

- Maximize Bio-Oil Yield
  - **Minimize carbon losses** associated with this upgrading step
- Upgrade and Stabilize Bio-Oil
  - **Low pressures**
  - Efficient utilization of H_2
- Develop Robust, Active, and Cost-Effective Catalysts
  - Upgrading of **model pyrolysis compounds**
  - Extend to whole pyrolysis vapor
  - Understand and address issues around catalyst deactivation
- Validate upgrading performance at scale with whole biomass vapors

Challenges

- Catalyst stability
  - Avoid rapid coke formation and frequent regeneration
  - **Resistance to oxidation in high steam environments**
  - Indifference to inorganic contaminants

- Catalyst and operating costs
  - Use of non-precious metals
  - Robust and/or regenerable materials
  - **Minimal need for excess H_2**

- Product yield
  - Oligimerize molecules with low carbon number
  - **Minimize carbon loss to coke, light hydrocarbons, and CO_2**
  - Produce molecules that are suitable as diesel and jet

Future Work

- Develop catalyst materials for **low pressure HDO**
  - Impacts of catalyst particle size on activity and selectivity
  - Transition metal C/N/S/P
  - Comparison to commercial hydrogenation catalysts

- Evaluate **catalyst supports** for ex-situ vapor phase upgrading
  - Stability in high temperature steam
  - Coking potential and catalytic activity

- **Extension to whole pyrolysis vapor**
  - Joint with other tasks, test catalysts that show good performance with whole or filtered pyrolysis vapor
    - Micro-scale testing with in-situ vapor generation (WBS 3.6.1.6)
    - Pilot-scale testing with dual-bed regenerating recirculating system (DCR) (WBS 3.3.1.14)
  - Explore impacts of inorganic contaminants

- **Rigorous characterization** of novel catalysts
  - Develop structure-function relationships
  - Determine deactivation modes

Summary

- The "Catalytic Upgrading of Pyrolysis Products" task has been initiated
- Reviews of literature and technology have been conducted for:
  - Determination of critical success factors
  - Identification of opportunities for innovation
  - Semi-quantitative definitions of technical targets
- Frameworks for collaborative research have been established:
  - Validation of model compound results using whole pyrolysis vapor
  - Technoeconomic analysis
  - Scale-up and demonstration
- Short, medium, and long-term research strategies have been developed:
  - Short: novel low pressure HDO catalyst development
  - Medium: achievement of performance targets on model compounds
  - Long: demonstrate ex-situ upgrading at the pilot scale

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Jessica Olstad

DOE Contract
DE-AC36-08-GO28308

Questions

Additional Slides

Glossary of Terms

AOP	Annual Operating Plan
DOE	Department of Energy
HC	hydrocarbons
MFSP	Minimum Fuel Selling Price - the sale price of fuel at which a net present value of zero is achieved for a plant with 20 year life and 10% internal rate of return
MYPP	Multi-Year Program Plan
NREL	National Renewable Energy Laboratory
P	Pressure
SOT	State of Technology
T	Temperature
TEA	Techno-Economic Analysis - includes mechanical process design, cost and revenue estimates, and sensitivity analysis
BeTO	BioEnergy Technologies Office
TC Analysis	Thermochemical process design and analysis task
CFP	Catalytic Fast Pyrolysis
MW	Molecular Weight
WWT	Wastewater Treatment
PSA	Pressure Swing Adsorber
FY	Fiscal Year
VPU	Vapor-Phase Upgrading
HDO	Hydrodeoxygenation
VP	Vapor Phase
R&D	Research and Development

Detailed Milestones for FY13, FY14

Due Date	Milestone Type	Milestone Title	Comments
2/28/13	D	Compare H-donor cofeeds	Complete
3/29/13	E	Review of state of the art analytical tools for pyrolysis oil speciation	Complete
6/30/13	D	Upgrading SOT (review paper)	In-progress, on track
8/30/13	D	Coprocessing of bio-oil via hydrotreating	In- progress, on track
12/20/13	D	Screen nano catalysts for low pressure HDO of model compounds	Preliminary
3/31/14	D	Evaluate catalyst supports for coking potential	Preliminary
6/30/14	D	Demonstrate oligimerization of pyrolysis vapor model compounds	Preliminary
9/19/14	E	Hydrotreating of model 'upgraded' bio oil and comparison to traditional fast pyrolysis oil	Preliminary

Additional Required Slides for Peer Evaluation

Responses to Previous Reviewers' Comments

New Project – Not Applicable

Recent Publications and Presentations

Publications

- Ruddy, DR; Schaidle, JA; Ferrell, JR; Moens, L; Wang, J; Hensley, JE, **2013** "Recent Advances in Heterogeneous Catalysts for Bio-oil Upgrading via "Ex-situ Catalytic Fast Pyrolysis": Catalyst Development through the Study of Model Compounds" *Green Chemistry*, submitted for review.

Presentations

- Schaidle, JA; Habas, S; Ruddy, DR; Yung, M; Hensley, JE, "The Effect of Hydrogen Donors on the Vapor-Phase Deoxygenation of Creosol over HZSM-5." Presented by JA Schaidle at *Western States Catalysis Club annual meeting*, **April 19, 2013**, Provo UT.

Reports

- Biddy, M; Dutta, A, (NREL); Jones, S; Meyers, A. (PNNL) **2013** "Ex-Situ Catalytic Fast Pyrolysis Technology Pathway," NREL/TP-5100-58050 (PNNL-22317), National Renewable Energy Laboratory, Golden, CO, http://www.nrel.gov/docs/fy13osti/58050.pdf.
- Schaidle, JA, **2012** "Comparison of H-Donor Cofeeds for the Upgrading of Creosol," *NBC-11137*, National Renewable Energy Laboratory, Golden, CO.
- Ferrell, JR; Jablonski, WS, **2013** "Review of State of the Art Analytical Tools for Pyrolysis Oil Speciation," *NBC-11149*, National Renewable Energy Laboratory, Golden, CO.