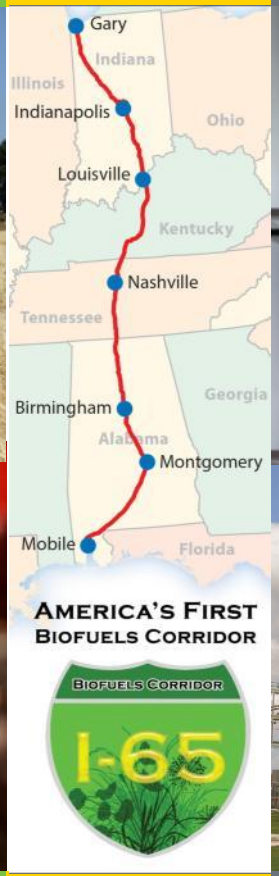
2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

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



CATALYTIC DEOXYGENATION OF PYROLYSIS OILS

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Co-PI: Mariefel V. Olarte

20 May 2013

Technology Area Review: Bio-Oil and Upgrading

Organization: PNNL

Goal Statement

Project Goal

Reduce the costs associated with catalytic upgrading of pyrolysis oil by

- Increasing liquid fuel yield by improving carbon utilization
- Improving H_2 efficiency
- Lowering operating temperatures and pressures

Selected under DE-FOA-0000342, having following objectives:

- **Demonstration of capability of long term processing to address corrosivity issues associated with stabilized bio-oil**
- **Catalytic deoxygenation of the many molecular fragments that collectively comprise bio-oil**
- **Demonstration of the ability to produce a final liquid transportation hydrocarbon fuel that may be blended at up to 30 wt% with ASTM petroleum fuels OR production of an upgraded bio-oil that is compatible with existing petroleum refining unit operations**
- **Provision of extensive supporting data on the physical and chemical property requirements of the petroleum operations to demonstrate the compatibility of the resulting liquid hydrocarbon product with petroleum refining unit operations**

Supports the Fast Pyrolysis followed by Catalytic Upgrading pathway and the BETO target of ~$3/gge by 2017

Quad Chart Overview

Timeline

- Project Start Date: December 2010
  - Rescope: February 2013
  - Restart: May 2013
- Project End Date: December 2015
- Percent Complete: 7%

Budget

- Funding for FY11: $1300k
- Funding for FY12: $891k/11k
- Funding for FY13: $797k
- Average annual funding: $996/year

Barriers

- **Tt-E. –** Liquefaction of Biomass and Bio-Oil Stabilization
- **Tt-G. –** Fuel Synthesis and Upgrading
- **Tt-K –** Bio-Oil Pathways Process Integration

Partners

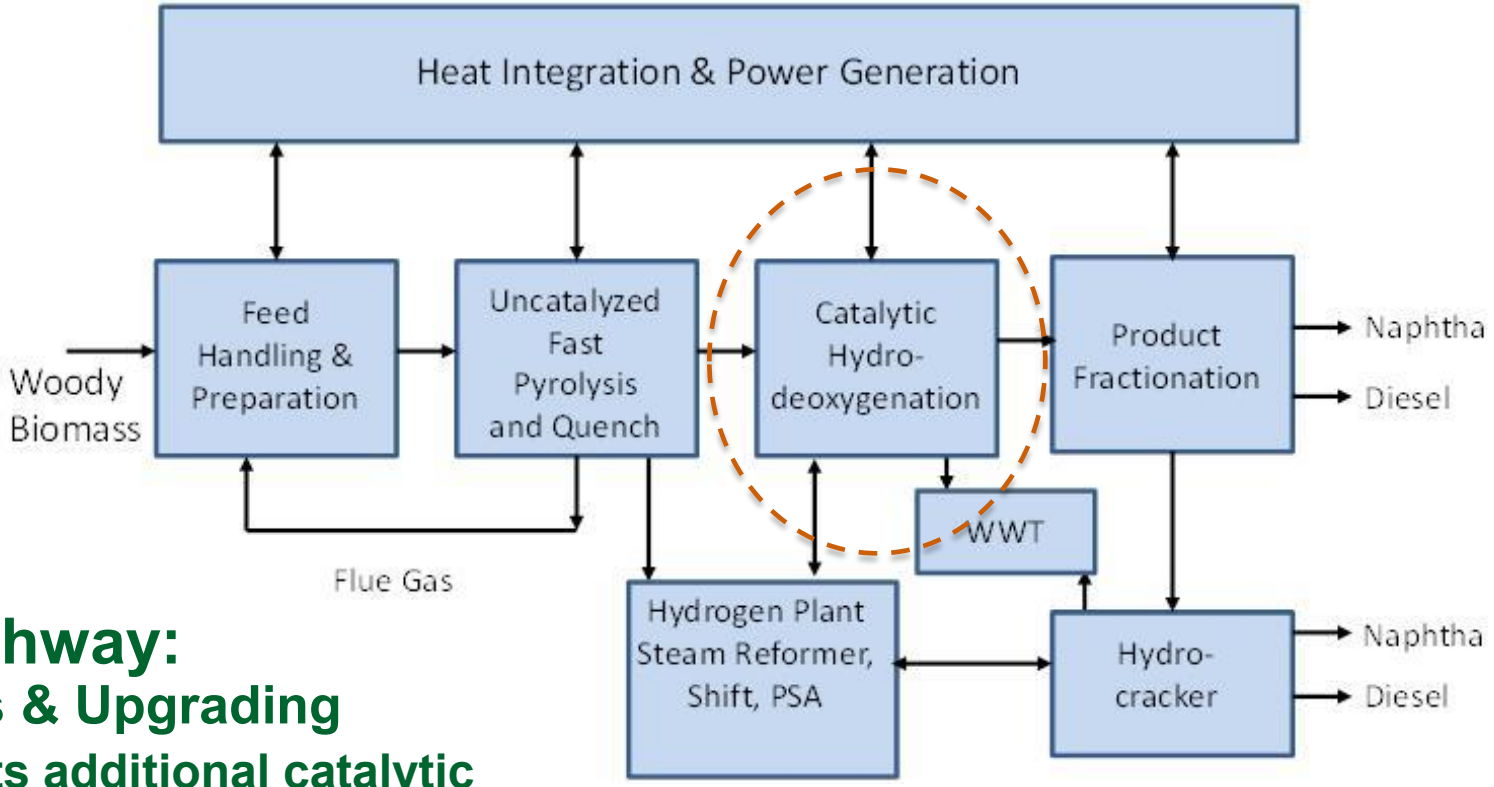
- UOP LLC
  - Ensyn
  - Michigan Technical University (MTU)
- Technische Universität München (TUM)
- W.R. Grace

UOP A Honeywell Company

GRACE Enriching Lives, Everywhere.®

Technische Universität München

Project Overview

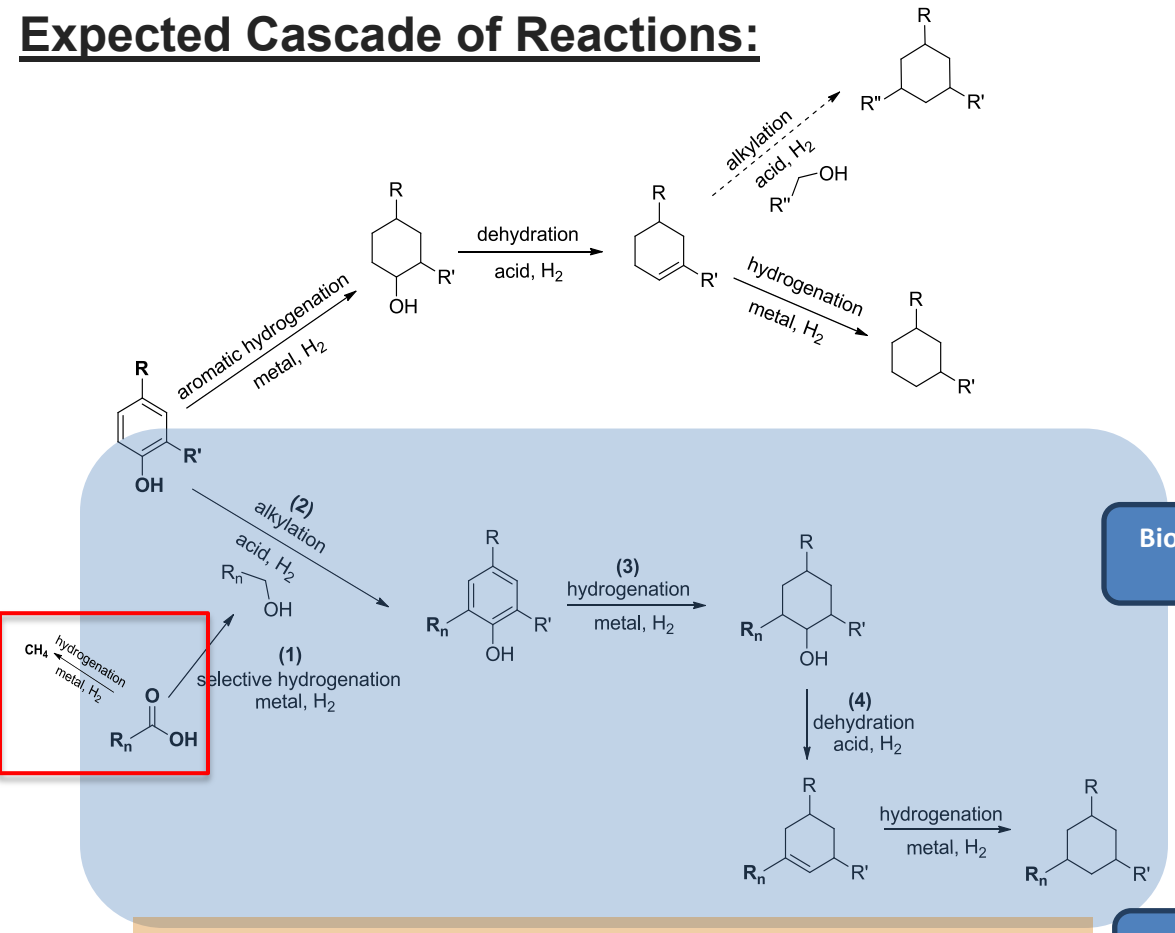


Primary Pathway:
Fast Pyrolysis & Upgrading

- **Work supports additional catalytic processing**

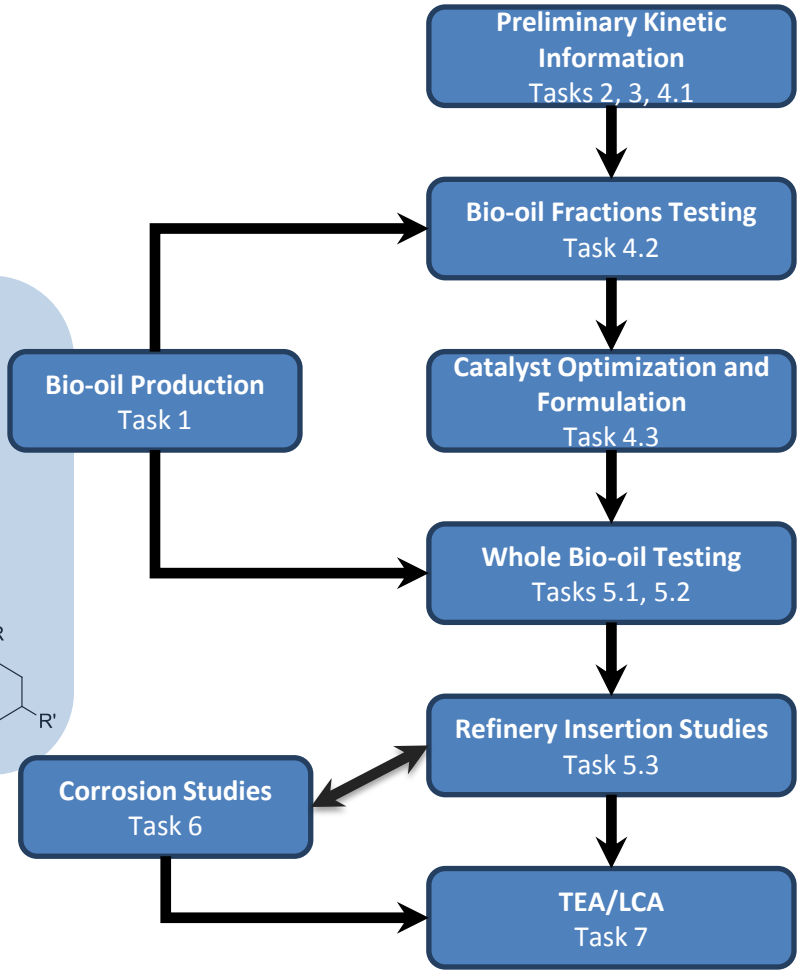
Objective: Develop a low cost catalytic system for stable upgrading to produce gasoline-diesel range hydrocarbons

Expected Cascade of Reactions:



A specific sequence of reactions is necessary (shaded portion)

Project Work Flow



Zhao and Lercher. 2012. *Angew. Chem. Int. Ed., (51) 5935-5940.*

Zhao et. al. 2010. *Chem. Commun., (46) 412-414.*

Zhao et. al. 2012. *J. Catal., (288) 92-103.*

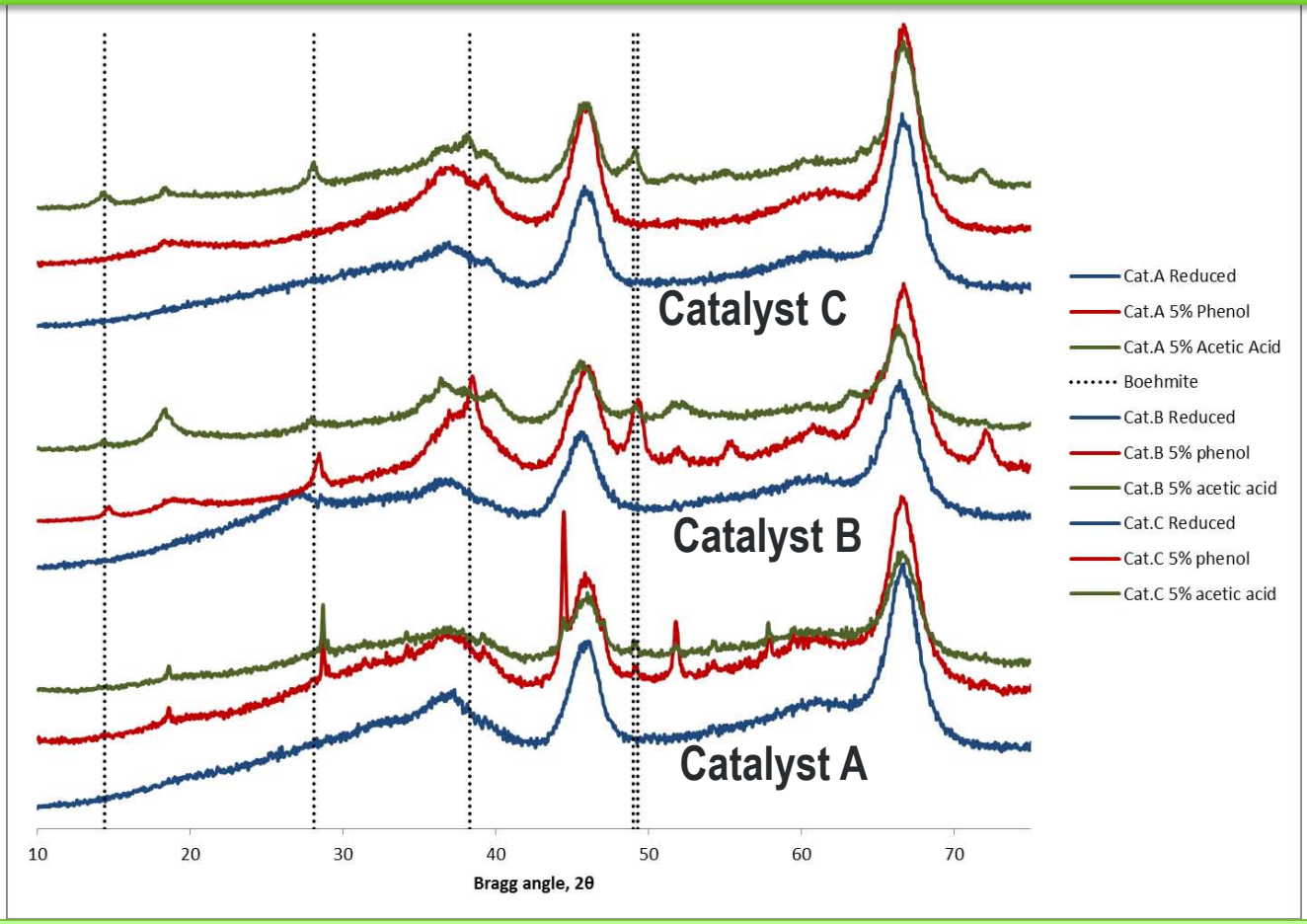
Initial Catalyst Screening: Batch Combinatorial Testing

- Experiments with several catalyst and catalytic supports in batch condition, under 200 ^{0}C and initial 700 psig H_2
- Satisfied milestone of the *original project scope** on narrowing down list of viable catalysts
- ***Relevance***: Unlike petroleum hydrotreating (HT) catalysts, bio-oil HT catalysts are exposed to much larger amounts of H_2O. Thus, catalyst stability and integrity are important for sustainable operation

* Project was re-scoped after: (1) UOP achieved long-term processing success, (2) Corporate structural changes led to re-direction of partner strategies outside of renewable energy

2 – Technical Accomplishments / Progress / Results (cont'd)

Able to identify an Al_2O_3 support that was less susceptible to formation of boehmite (AlO(OH)) in the presence of aqueous feeds



Catalyst A contained a component not found in the other Al_2O_3-support catalysts tested

Rescope approved by BETO February 2013

- Required provisions
  - Updated PMP (status)
  - Budget justification PMC 123.1 for contracts of $100k or more (status)
  - Commitment letters from all partners, on letterhead, confirming cost share contributions (status)
  - Plan for meeting 20% cost share requirements

Plan for expediting 20% cost share requirement & improved communication/collaboration amongst partners

- Alternatively Sponsored Fellow (ASF) program
  - PNNL to host TUM post doctoral researcher, sponsored by TUM
- Task 1 is for UOP to produce pyrolysis oil and subcontract vendor for pyrolysis oil fractionation

Moving Forward – Within the Rescope

Graded Approach to Bring Fundamental Learnings Into Empirical Space (the final frontier)

- **Model Compounds:** Acetic acid, Furfural, Phenol, Guiacol, Ethyl phenol, Ethanol, Furfural alcohol, Syringol
- **Fractionated Pyrolysis Oil:** Solvent extracted fractions to validate model compounds findings
- **Whole Pyrolysis Oil & Long-Term Demonstration of Stable Operation**

Targeted Reaction Chemistries & Cascade

- **Selective Hydrogenation** of the light acids and aldehydes to alcohols;
- **Alkylation** of the aromatic molecules (mostly substituted phenols) by the alcohols;
- **Hydrogenation** of the aromatic rings; and,
- **Hydrodeoxygenation** of oxygenated compounds. Hydrodeoxygenation by the proposed route occurs during alkylation as well as during hydrolysis and ***dehydration*** reactions in the presence of acidic sites

3 - Relevance

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Process Parameter	Baseline	Proposed Process	
		Target	Best Case
Operating Temperature, ^{0}C	< 200	< 250	< 250
	< 400	< 400	
Operating Pressure, bar	~140	<50	<50
Improvement in H_2 Efficiency, H_2 consumed/g liquid fuel produced	-	7.85	15.5
Liquid Yield Increase, %	-	3.7	7.4

Alignment with Bioenergy Technologies Office (BETO)

- **Reducing cost of catalytic processing may be achieved by lowering operating temperatures and pressures, minimizing number of processing units, lowering H_2 requirements, and improving liquid yields**
- **Catalyst development that is applicable to multiple bio-oil pathways**
- **Potential step changes in-route to BETO 2017 target of ~$3/gge for finished hydrocarbon blendstocks**

MYPP Barriers addressed:

- Tt-E. Liquefaction of Biomass and Bio-Oil Stabilization
- Tt-G. Fuel Synthesis and Upgrading
- Tt-K. Bio-oil Pathways Process Integration

4 - Critical Success Factors

Catalyst/Process Stability Challenge	Approach
Loss of small molecular weight bio-oil components (small acids)	• Develop catalytic systems capable of capturing these small molecular weight compounds through alkylation of phenolic groups • Generate kinetic information for individual reaction steps as basis for catalyst design
Fouling of catalyst	• Fractionate bio-oils and identify the fraction/components that cause catalyst fouling
High operating temperatures and pressures	• Development of very active catalyst systems
Sulfur management	• Understand opportunity space for using sulfided and non-sulfided noble and base metal catalysts

Key Milestones

- **Validating reaction chemistry cascades observed using model compounds in bio-oil fractions**
- **Demonstration of long-term processing in minimal stages, at lower temperatures and pressures**

Go/no-go critical decision point after testing of surrogate mixtures

Partnership with technology provider and catalyst manufacturer; both very active in the petroleum refining industry

5. Future Work

ML or DL or Go/No Go	Description	FY13 Q3	FY13 Q4	FY14 Q1	FY14 Q2	FY14 Q3	FY14 Q4	FY15 Q1	FY15 Q2	FY15 Q3
ML	Bio-oil production	■								
ML and Go/No Go	Complete kinetic studies of the key reactions in bio-oil surrogate mixtures		■	■	■					
ML	Processing of actual bio-oil fractions				■	■				
ML and Go/No Go	Long term whole bio-oil upgrading						■	■	■	
ML	Refinery compatibility studies								■	
ML	Corrosion studies								■	
ML	Final TEA and LCA									■
DL	Final Report									■

Clear path forward with 2 Go/No-Go decision points

- **Measure of success for both critical decision points = conversion of target compounds**

Summary

Relevance: Supports the Bioenergy Technologies Office's Multi Year Program Plan (MYPP)

Approach: Graded approach to bring fundamental learnings into empirical space

Technical accomplishments: Promising catalysts were identified; Rescope has approved plan to move forward

Success factors and challenges: Validate chemistry of model compounds to bio-oils; demonstrate long-term processing at lower temperature and pressure

Future work: Improve cost share requirements and closer collaboration with partners; Initiate planned experiments under the approved project rescope

Additional Slides

Acknowldegments

- BETO: Melissa Klembara, Liz Moore, Nichole Litvinas, Prasad Gupte, Kevin Craig

- PNNL: Doug Elliott, Vanessa Lebarbier, Mariefel Olarte

Responses to Previous Reviewers' Comments

This project was not reviewed in 2011

Publications, Presentations, and Commercialization

- Submission of a pre-print and presentation at the 8th International Symposium on Hydrotreating/Hydrocracking Technologies of the 244th ACS National Meeting on Aug. 20, 2012 in Philadelphia, Pennsylvania

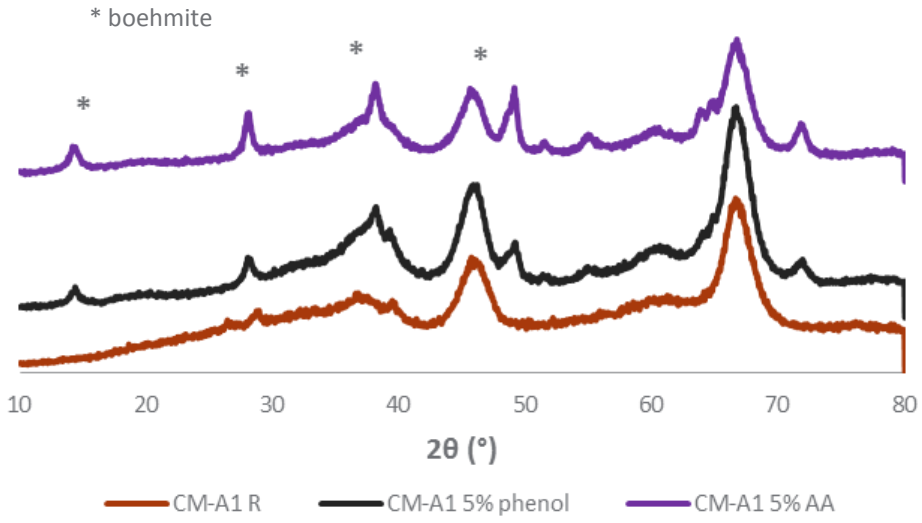
Partial Catalyst Screening: Batch Combinatorial Testing

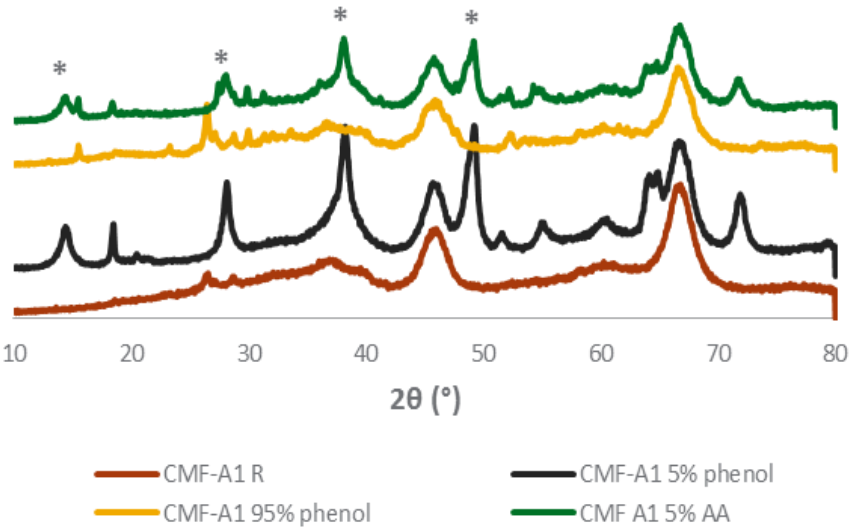
Catalyst designation	Description
RU-C1	Ru/C; 7 wt% Ru; commercial
PD-C1	Pd/C; 2.5 wt% Pd; lab-synthesized
RU-T1	Ru/TiO_2; 3 wt% Ru; commercial
NM-A1	$NiMo/Al_2O_3$; commercial
CM-A1	$CoMo/Al_2O_3$; 2-5 wt% CoO, 12-16 wt% MoO_3; commercial
NM-A2	$NiMo/Al_2O_3$; 5-8% NiO; 25-30% MoO_3; commercial
CMF-A1	$CoMoF/Al_2O_3$; commercial

Partners and Roles

- PNNL – Project lead, Responsibilities: Catalyst selection, screening and validation, process stability and corrosion testing, extended integrated process tests, TEA and LCA
- UOP – R&D support and commercializing partner via Ensyn, Responsibilities: Production, fractionation, and analysis of bio-oils and products, preliminary process design and costing, TEA and LCA (with MTU), refinery compatibility studies
- W.R. Grace – Catalyst supplier, Responsibilities: Provide catalysts, refinery compatibility studies input
- TUM – R&D support, Responsibility: Catalyst selection, screening and validation

Co-Mo-based alumina-supported catalysts

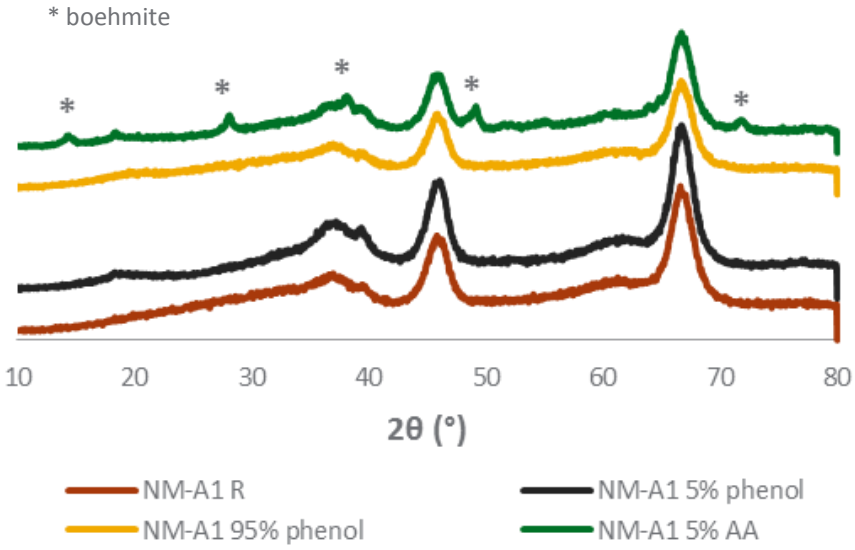


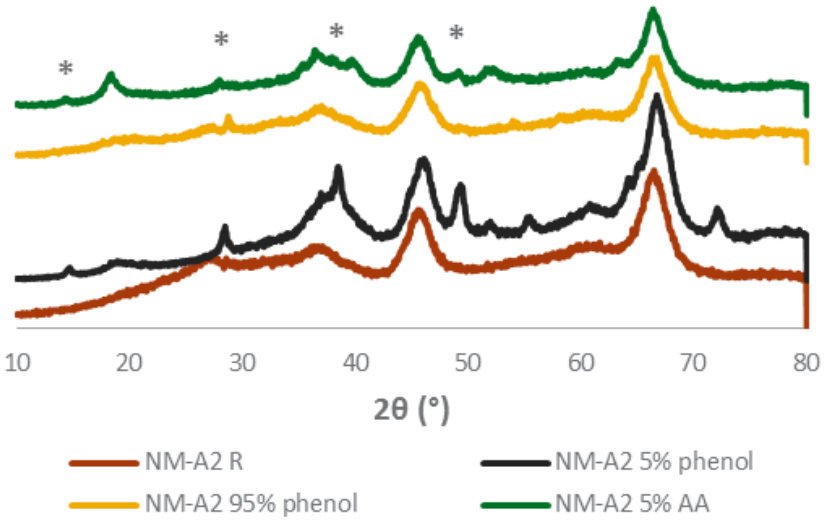


	% Conversion (by GC-MS of liquid)		
	5% Phenol	95% Phenol	5% Acetic Acid
CM-A1	4.3	not tested	7.6
CMF-A1	7.9	18.8	1.8

- Boehmite formation seen in the presence of 95% water and 5% phenol and acetic acid

Ni-Mo-based alumina-supported catalysts

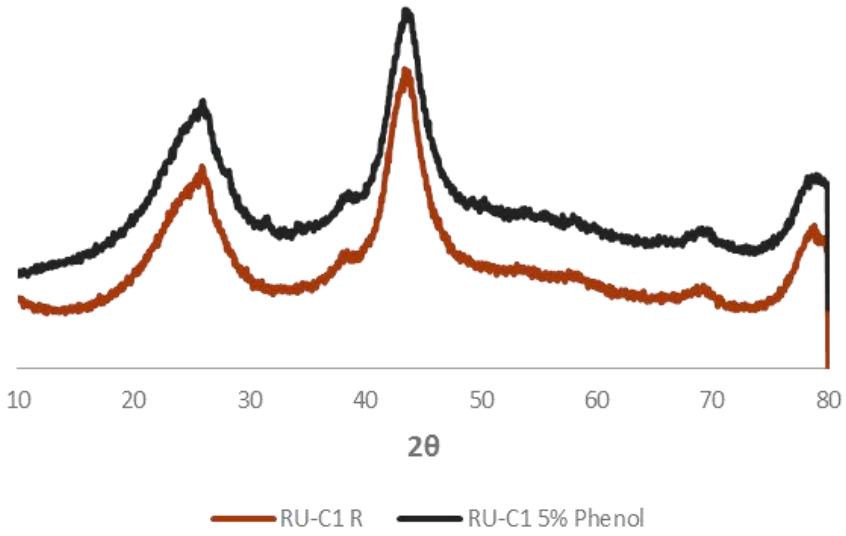


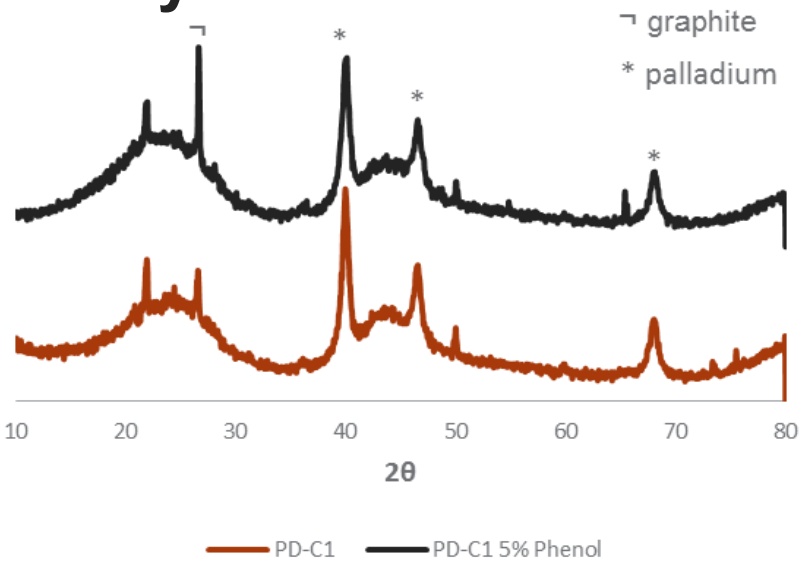


	% Conversion (by GC-MS of liquid)		
	5% Phenol	95% Phenol	5% Acetic Acid
NM-A1	11.1	19.1	17.0
NM-A2	14.6	17.1	17.5

- Phenol and acetic acid conversion almost similar. However, support stabilities are different

Carbon-supported noble metal catalysts





	% Conversion (GC-MS of liquid)		
	5% Phenol	95% Phenol	5% Acetic Acid
RU-C1	100.0	84.6	100.0
PD-C1	100.0	93.6	40.1

- Ru/C and Pd/C both gasified 5% phenol
- Conversion differs at higher organic content but both have cyclohexanol as major product