

Biomass-derived Liquids Distributed (Aqueous Phase) Reforming

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Project ID # PD002

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Overview

Timeline

- ▶ Project start date: Oct. 1, 2004
- ▶ Project end date: October 1, 2011*
- ▶ Percent complete: TBD

Budget

- ▶ Total project funding (starting 2004) : \$3,250K
- ▶ Funding received in FY10: \$450K
- ▶ Funding for FY11: \$450K

* Project continuation and direction determined annually by DOE

Barriers

- A: Reformer Capital Cost
- D: Feedstock Issues
- E. Greenhouse Gas Emissions
- Target: Hydrogen Production Cost
 - 2012: \$3.80/gge delivered
 - 2017: <\$3.00/gge delivered

Collaborations

- ▶ Washington State University (Yong Wang) — catalyst characterization studies
- ▶ Brookhaven National Laboratory (Anatoly Frenkel)—deployment of in situ EXAFS cell
- ▶ Virent Energy Systems (Randy Cortright)—collaboration on findings from in situ EXAFS data

Project Objectives

Relevance

► Over-Arching Objective

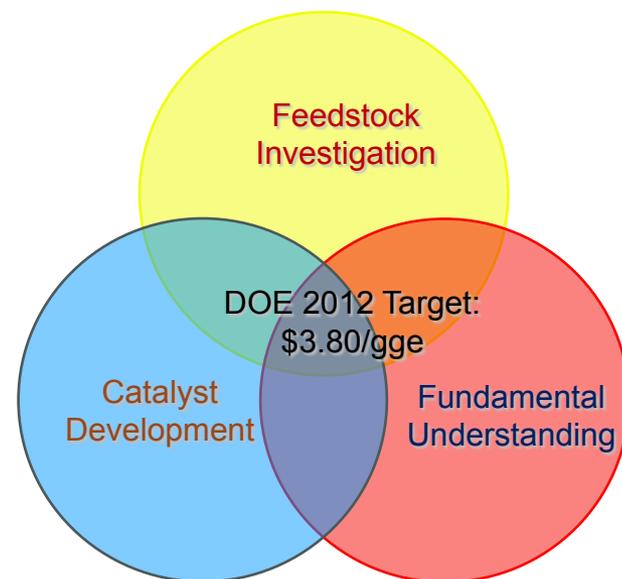
- Develop bio-derived liquids aqueous phase reforming technology for hydrogen production that can meet the DOE 2012 cost target of \$3.80/gge, verified by H2A analysis

► Reduce Reformer Capital Cost

- Maximize catalyst activity and hydrogen selectivity to reduce reactor volume and associated purification steps
- Develop new techniques to characterize the catalyst, especially under operating conditions, in order to understand catalyst functions and improve performance
- Develop understanding of competing reaction pathways to guide the design of improved catalysts

► Feedstock Issues

- Examine efficacy of aqueous phase reforming of (aqueous soluble) bio-oil as means to significantly reduce feedstock costs for hydrogen production



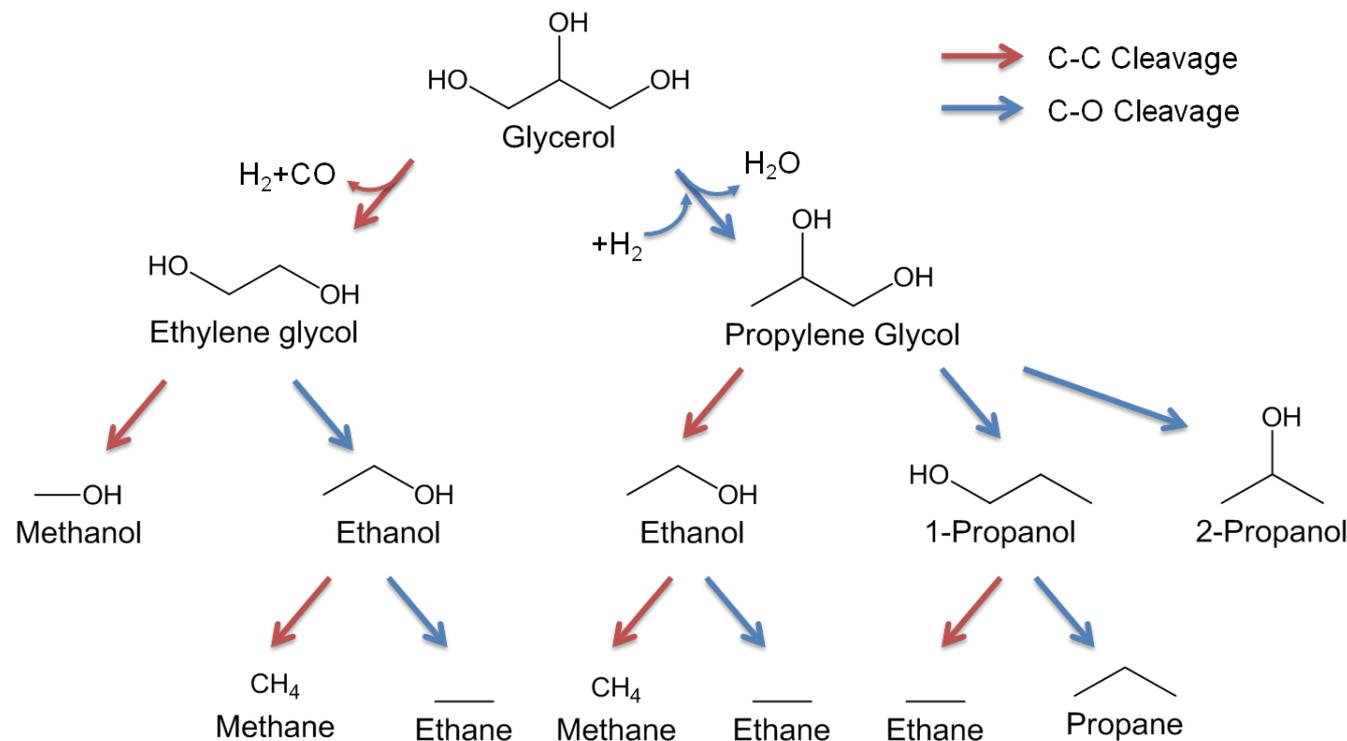
Technical Approach

- ▶ Identify means to facilitate preferred reaction pathways to increase hydrogen selectivity for the APR of glycerol, sorbitol, and glucose with Pt-based catalysts (FY10) (Reduce reformer capital cost)
- ▶ Characterize and modify catalyst formulations and/or pretreatment to improve catalyst activity and hydrogen selectivity, based on reaction pathway analysis (FY10 and FY11) (Reduce reformer capital cost)
- ▶ Carry out H₂A analysis for APR of bio-oil showing that H₂ production targets can plausibly be met and justifying experimental program (FY11) (Feedstock Issues)
- ▶ Select 10 representative compounds present in bio-oil and measure their individual performance in APR testing (FY11), identifying specific hurdles or technical issues needing addressing (Feedstock Issues)
- ▶ Carry out APR of mixture of bio-oil components as well as whole aqueous soluble bio-oil (FY11) and compare performance against H₂A analysis targets (Feedstock Issues)

Following Preferred Reaction Pathways is Key to Hydrogen Production

Approach

Reduce Reformer Capital Cost



- ▶ C-C scission leads to production of H_2 and CO_2 (desired)
- ▶ C-O cleavage, facilitated by catalyst acidity, leads to production of diols, alcohols, and alkanes (not desired)
- ▶ A competition ratio can be defined as $[\text{sum (C-O events)}/\text{sum C-C events}]$
- ▶ Avoidance of catalyst acidity is key to controlling selectivity for H_2 production

Project Milestones

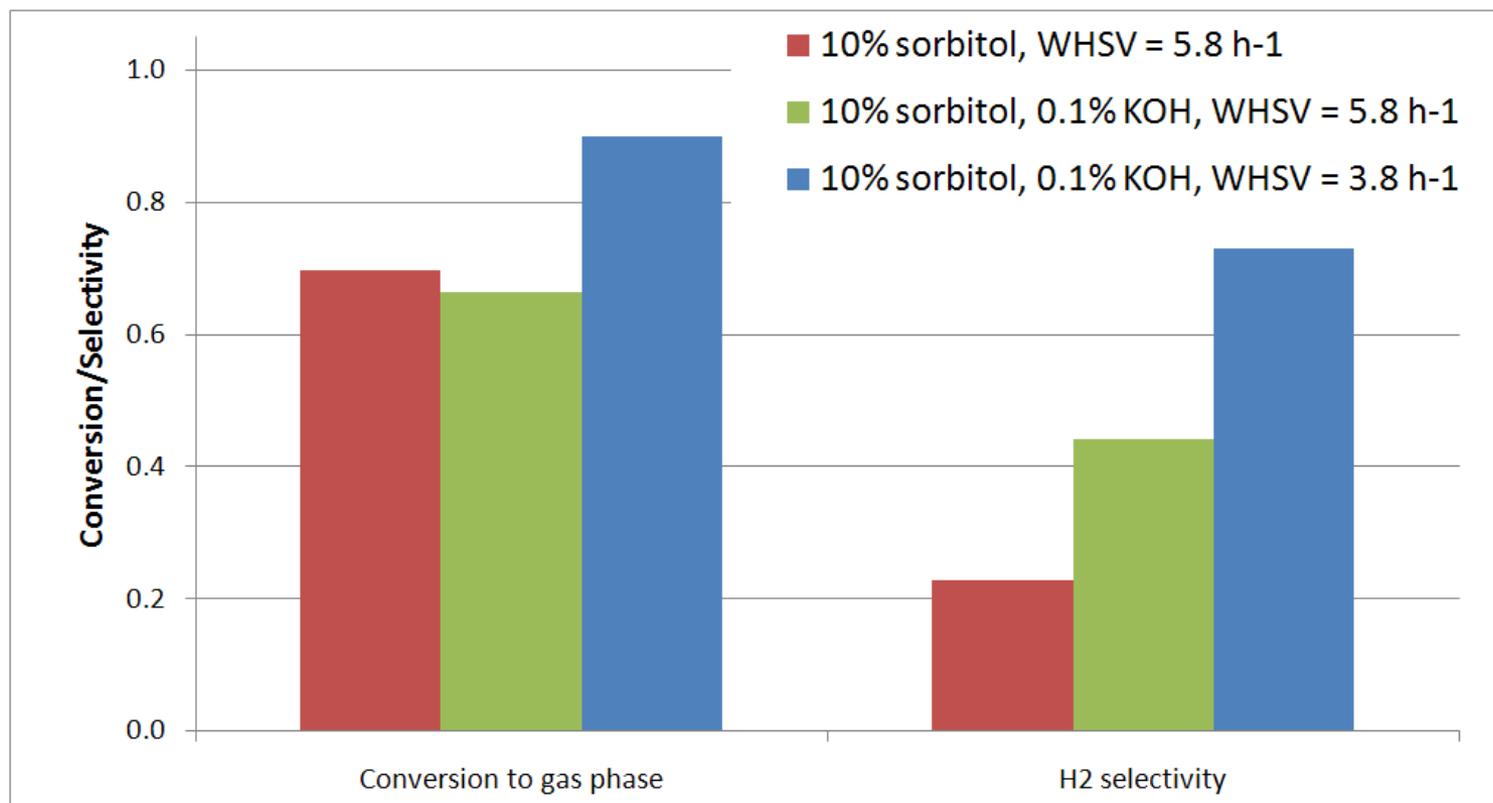
Approach

FY10 Milestones (After June Review)	Completion Date
<i>Aqueous Phase Reforming of glycerol/glucose/sorbitol</i>	
5. Demonstrate full conversion of glucose/sorbitol with <5% carbon retained as C ₂ + oxygenated product	9/30/2010 (90% gas phase product achieved)
FY11 SMART Milestones	
<i>Aqueous Phase Reforming of Pyrolysis Oil (bio-oil)</i>	
1. Show through H2A analysis of APR of bio-oil reforming that the 2017 target of \$3.00/kg H ₂ can be achieved using realistic performance assumptions and published feedstock costs.	3/31/2011 (completed)
2. Complete APR testing of 10 representative bio-oil compounds, and quantify conversion and H ₂ yields as a function of temperature and residence time. Compare actual vs. predicted performance with an aqueous solution of all 10 bio-oil compounds.	6/30/2011
3. Identify through H2A analysis the hydrogen yield and reactor productivity values needed to meet the 2012 cost target of \$3.80/kg H ₂ , and demonstrate through APR testing of aqueous soluble bio-oil feedstock that these values can be achieved.	9/30/2011

Progress vs. 2010 End Year Milestone

Technical accomplishments

Milestone: Demonstrate full conversion of glucose/sorbitol with <5% carbon retained as C₂+ oxygenated product



- Total sorbitol conversion is almost 100% for all cases
- Conversion to gas phase refers to carbon ending up in CO₂, H₂, and alkanes
- H₂ selectivity is based on the total sorbitol conversion and not on conversion to gas phase products

▶ Go/no go decision 1:

- H2A analysis of APR of bio-oil reforming indicates that the 2012 target of \$3.80/kg H₂ can be achieved using realistic performance assumptions and published feedstock costs

▶ Go/no go decision 2:

- Experimentally meet the hydrogen yield and reactor productivity values required by the H2A analysis for aqueous phase bio-oil to meet the 2012 cost target of \$3.80/kg H₂

or

- Have a credible forward plan to meet the targets

Technical Progress and Accomplishments

- ▶ Studies quantifying acidity and structure of Pt-Re/C under APR conditions (Reduce reformer capital cost)
 - Titration of acid sites and correlations with product selectivity
 - X-ray Adsorption *in-situ* studies under reaction conditions to elucidate metal interaction (alloy formation and stability) following reduction and water oxidation
- ▶ H₂A Analysis of bio-oil feasibility for H₂ production (Feedstock Issues)
- ▶ Selection and testing of representative bio-oil aqueous phase components for activity and hydrogen selectivity (Feedstock Issues)

Interaction Between Pt and Re: Reduction Produces a Strong Interaction

Technical accomplishments

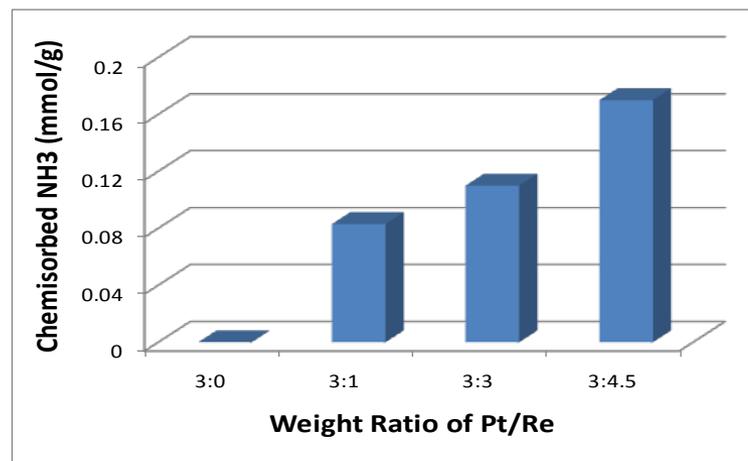
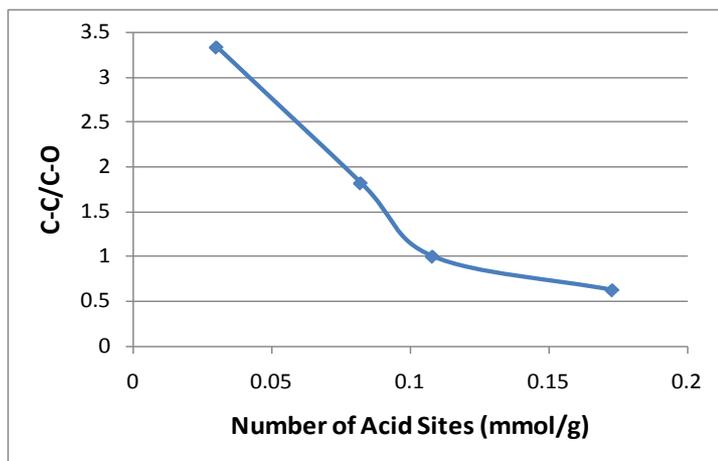
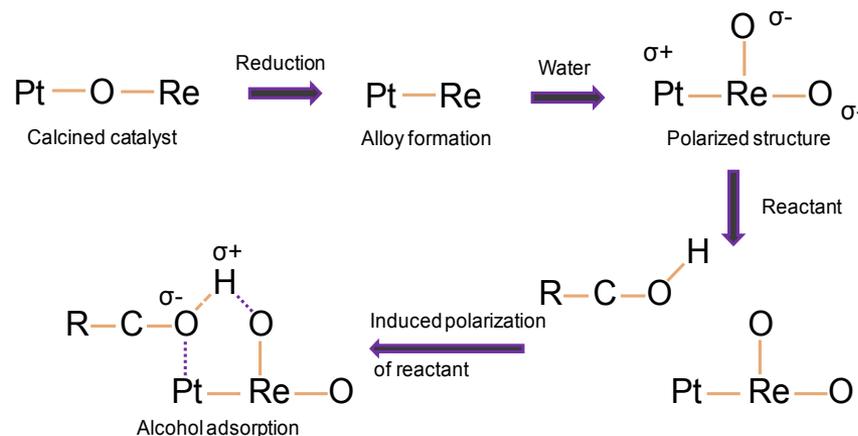
	3%Pt/C Unreduced	3%Pt/C Reduced	3%Pt3%Re/C Unreduced	3%Pt3%Re/C Reduced	Physical Mix Reduced	3%Re/C Reduced
Conversion	8.2%	7.4%	6.7%	68.2%	10.1%	2.6%
C-O/C-C	0.59	0.56	0.52	1.10	1.00	33.83
H ₂ /CO ₂	2.28	2.29	2.33	1.97	1.8	

Glycerol APR @ 225 °C, 420 psig, WHSV = 6 hr⁻¹

- Low activity for both monometallic Pt/C and Re/C
- Both C-O and C-C breaking with Pt/C, mainly C-O breaking (dehydration) on Re/C
- Strong interaction between Pt and Re following reduction of the metal oxides results in dramatic change in activity and selectivity
- Indicative that structural modification and increasing Pt-Re interaction occurs after reduction

Role and Origin of Acidity from Pt-Re

Technical accomplishments

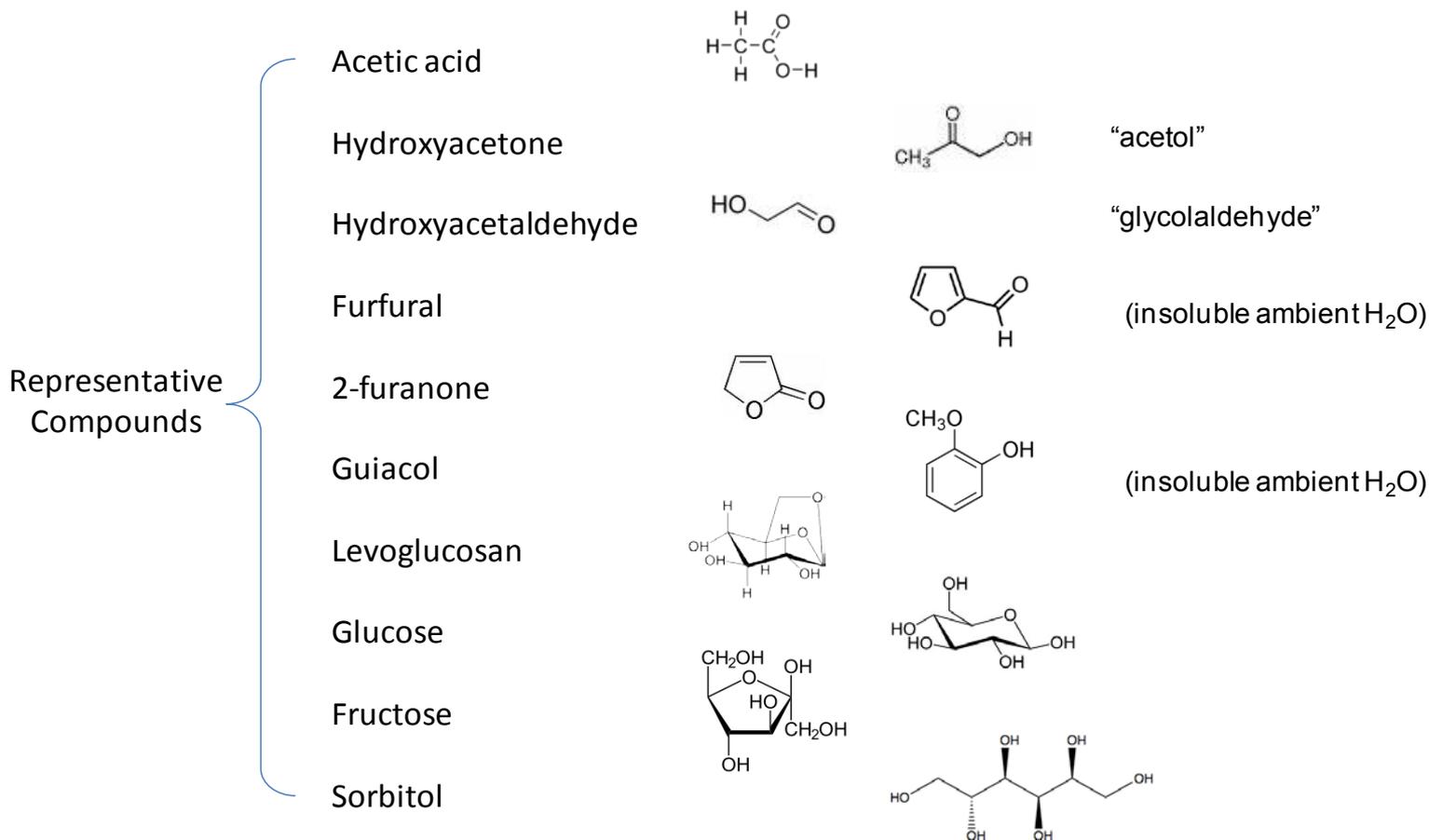


- Acidity develops from Pt-Re interaction following reduction and subsequent water oxidation
- Polarity at the surface may explain strong interaction with ROH and polyols, oxygen end down
- Stronger binding to surface facilitates cleavage of C-O bond primarily, but possibly also the C-C bond, which may explain overall activity increase as well as change in selectivity
- Acidity must be avoided, either by base neutralization or stabilization of Re to oxidation

Bio-oil (Pyrolysis oil) Studies

Initial APR Tests Focus on Selected Representative Compounds

Technical accomplishments

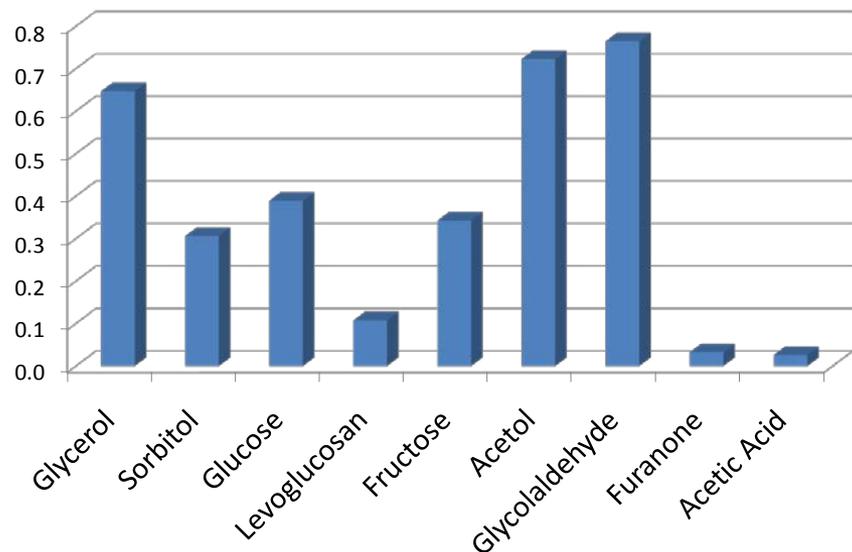


Each molecule poses special reforming requirements
Acetic acid is especially prevalent in aqueous bio-oil and must be reformed

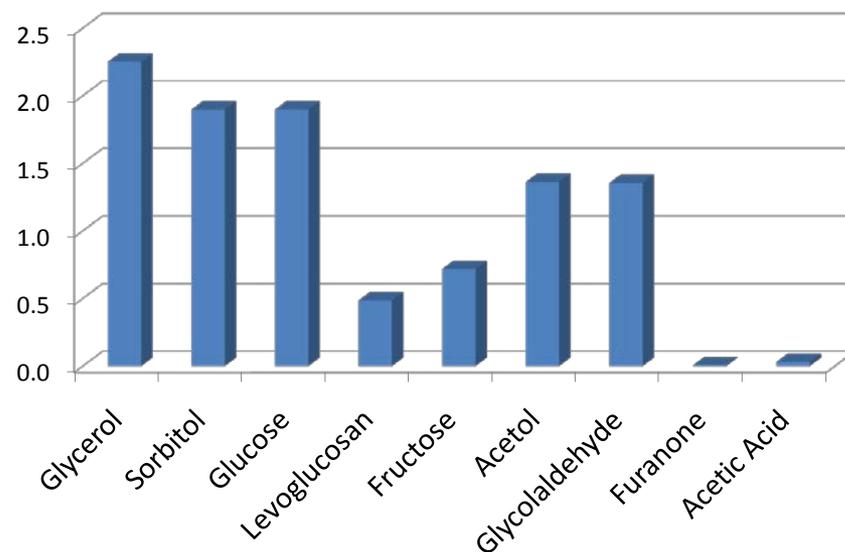
APR of Bio-oil Components Under Standard Reaction Conditions

Technical accomplishments

Conversion to CO₂ (carbon based)



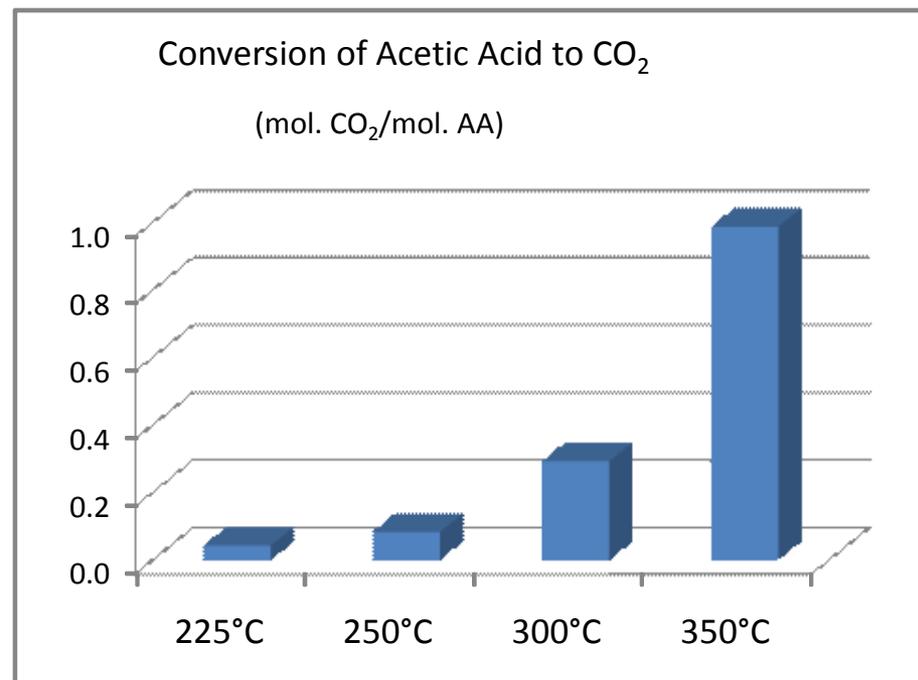
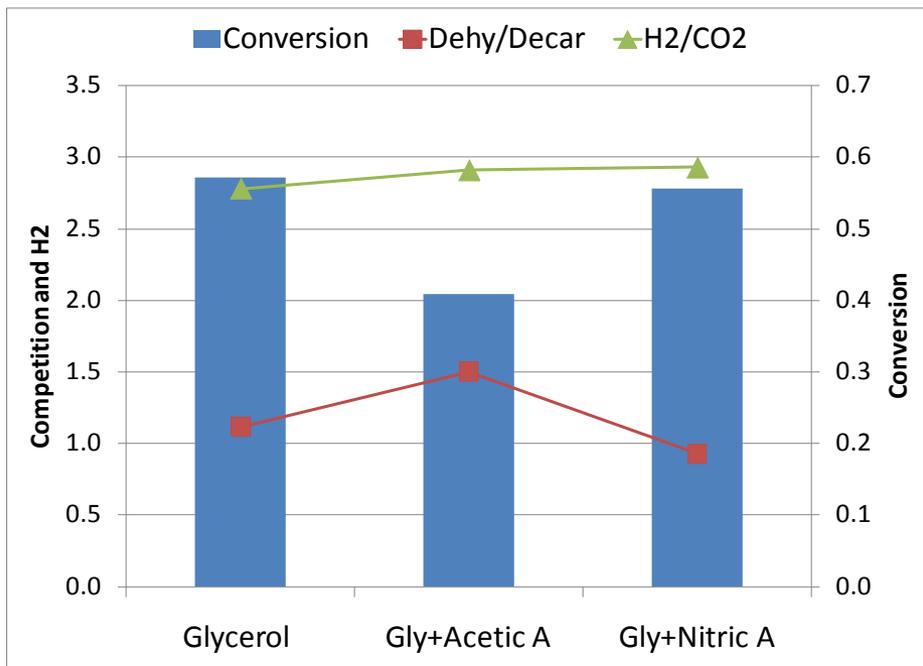
H₂ Yield (mol. H₂/mol. Feed)



- Conditions: 225°C, 420psig, 0.1mL/min, all feeds with the same molar concentration
- Variability in reactivity is clearly demonstrated
- Furanone and acetic acid are especially unreactive at 225°C and have low available H₂ content

Further Studies of Acetic Acid APR

Technical accomplishments



- ▶ Low conversion activity of acetic acid is not a result of an acidic medium affecting the catalyst
- ▶ Reduced activity may be due to carboxylic acid moiety bonding strongly to surface
- ▶ Acetic acid conversion can be significantly increased with increasing temperature, but best performance is at temperatures exceeding those possible with APR (gas phase reforming)

H2A Analysis of Bio-oil Aqueous Phase Reforming

Modeling Assumptions

Technical accomplishments

► Bio-oil feed

- \$0.65/gallon bio-oil delivered (\$0.50-0.80 range)*
- Mol fraction of bio-oil components based on Huber and Vispute. (2009) "Production of hydrogen, alkanes, and polyols by aqueous phase processing of wood-derived pyrolysis oils." *Green Chem.* **11**, 1433-1445.
- Assume bio-oil is composed completely of compounds defined in Huber and Vispute 2009, non-identified fraction ignored

* S. Jones, private communication

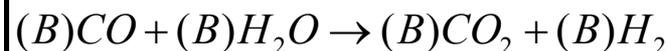
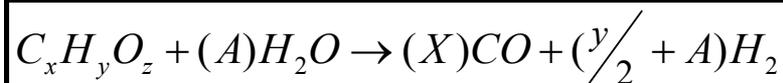
Water soluble bio-oil (WSBO) components	Defined % Total Carbon	Assumed wt% Total Carbon	Molecule	Bio-oil Mol Fraction
<i>Unit</i>	<i>[% out of 60]</i>	<i>[% out of 100]</i>		<i>[molX/mol bio-oil]</i>
Hydroxyacetone	6.5	10.8	C3H6O2	0.15
Hydroxyacetaldehyde	1.4	2.3	C2H4O2	0.05
Guaiacols and derivatives	1.5	2.5	C7H8O2	0.01
Sugars	18.2	30.3	C6H12O6	0.21
Levogluconan	18.8	31.3	C6H10O5	0.21
Acetic Acid	8.8	14.7	C2H4O2	0.30
Furfural and 2-furanone	4.8	8.0	C5H4O2	0.07
TOTAL	60	100		1.00

▶ APR Reactions

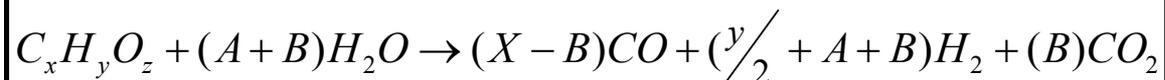
- For optimal case, conversion is to CO and H₂ followed by WGS, with no side reactions
- “Current conversion” case is based on single component data shown previously, excluding glycerol and sorbitol results
- Acetic acid inhibition applied to all reactions in “current conversion” case, based on its mol fraction in the feed and experimental data
- No change in conversion or reactivity with mixed component feed

▶ Water Concentration

- Bio-oil and water fed on a 1:1 mole basis for experimental model
- Stoichiometric amount of water assumed for both full conversion models, since slightly more than 1:1 required.



Overall:



Economics Based on Bio-oil Conversion Level

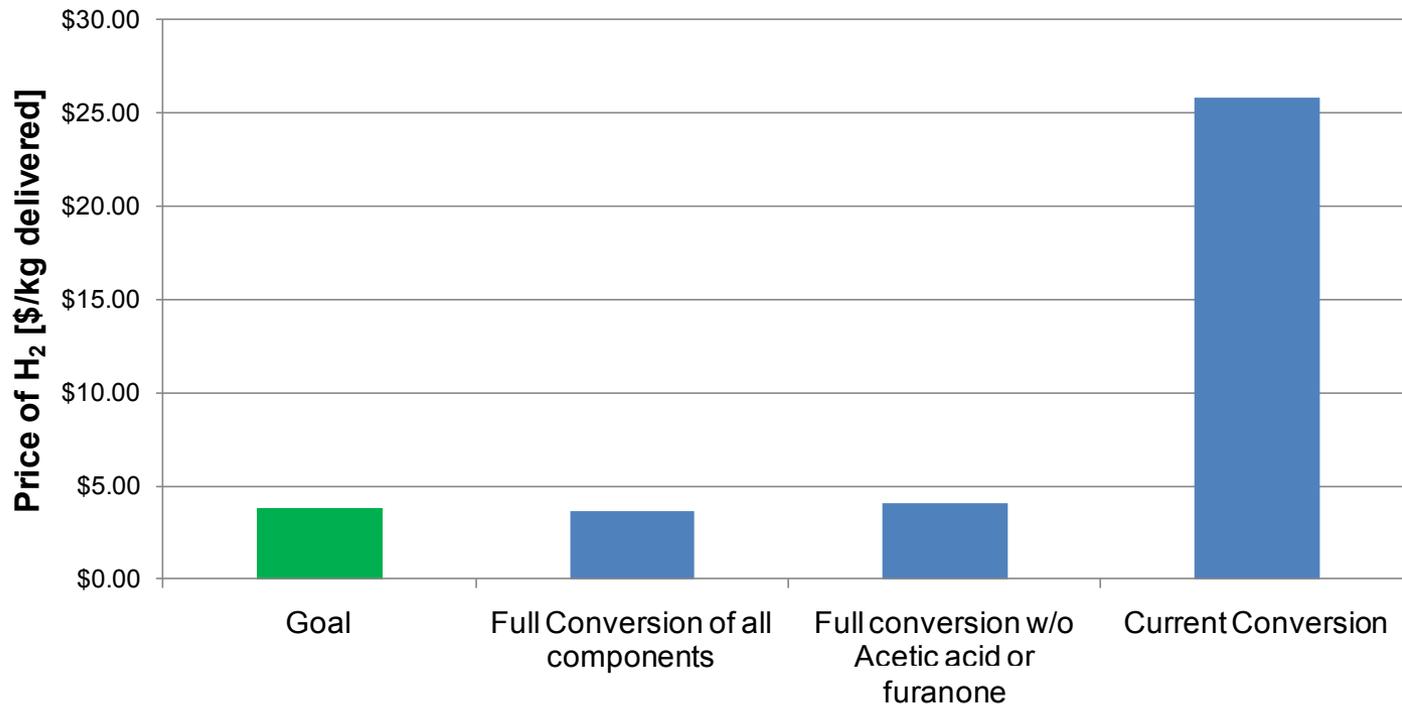
	<i>Units</i>	Full Conversion of all components	Full conversion of readily reactive components	Current conversion
Flow Rate	<i>[kg/day]</i>	1,500	1,500	1,500
Annual Flow Rate	<i>[kg/yr]</i>	517,500	517,500	517,500
Price based on Raw Materials & Utilities	<i>[\$/kg]</i>	2.69	3.00	19.22
Price Including Capital Cost	<i>[\$/kg]</i>	3.65	4.10	25.84
Annual Raw Materials Cost	<i>[\$/yr]</i>	\$582,233	\$748,245	\$9,131,665
Annual Utilities Cost	<i>[\$/yr]</i>	\$807,679	\$799,211	\$815,412
Fixed Capital Investment	<i>[\$]</i>	\$585,220	\$735,971	\$3,845,592
Steam credit	<i>[\$/day]</i>	-\$11.11	-\$8.77	\$2.54

Notes:

- Conversion means conversion of C in feed molecules to CO₂
- “Readily reactive components” are all bio-oil components except acetic acid and furanone/furfural
- Negative steam credit shows the need to purchase steam for those cases
- Some components of bio-oil appear to be resistant to APR and have low available H₂ content

Cost of Hydrogen From Bio-oil Conversion (Relative to 2012 Target of \$3.80/kg H₂)

Technical accomplishments



Conversion means amount of C in feedstock converted to CO₂

Key Factors Relative to \$3.80/kg H₂ Goal

Technical accomplishments

- ▶ High bio-oil conversion levels
 - Full conversion of all components to CO and H₂ and WGS is necessary to meet price targets
 - Proposed solution: increase residence time, improve catalyst formulations
- ▶ Key challenges
 - High concentration of acetic acid in feed that reduces overall catalyst activity
 - Reforming of more “hydrocarbon-like” molecules is difficult under APR conditions
 - Consumption of produced hydrogen by other molecules present in the feed
- ▶ To meet 2017 cost target of \$3.00/kg H₂, bio-oil cost must be priced at \$0.50/gal (with all other assumptions the same)

Collaborations

- ▶ Washington State University (WSU)
 - Sub-contractor
 - Also operates separately within the DOE Hydrogen and Fuel Cells Program
 - PNNL is supporting work at WSU for graduate student/postdoctoral training and use of complementary facilities
 - Work is focused on catalyst characterization techniques (temperature program methods, *in-situ* infrared spectroscopy)
- ▶ Brookhaven National Laboratory
 - DOE user facility
 - Promotes research collaboration on development of *in situ* cell for XAS studies
 - Has provided beam time and consultation for development of tool and data analysis
- ▶ Virent Energy Systems
 - Private company, previously supported in DOE Hydrogen and Fuel Cells Program
 - Previous collaborations on catalyst characterization (not in place in 2010) were re-initiated in FY11, primarily to review and discuss XAS results

Proposed Future Work

- ▶ Further detailed evaluation with H₂A analysis to adjust performance targets
- ▶ Extended testing with bio-oil surrogates and authentic aqueous soluble bio-oil under the conditions compatible with the H₂A analysis
 - Measure H₂ productivity and selectivity, identify undesirable side reactions
 - Determine catalyst life
 - Identify feed clean-up requirements, effect of inorganic impurities
- ▶ Extended catalyst characterization and modification studies
 - Support modification by basification of carbon support to counteract acidity and retain Re
 - Develop methods aimed at stable alloy formation, minimizing subsequent ReOx formation
 - Long term test for quantification of loss of Re from 3%Pt-3%Re/C
 - Evaluate alternate catalyst formulations (both Pt-based and Pt-free) with focus on minimizing PM content of the catalyst

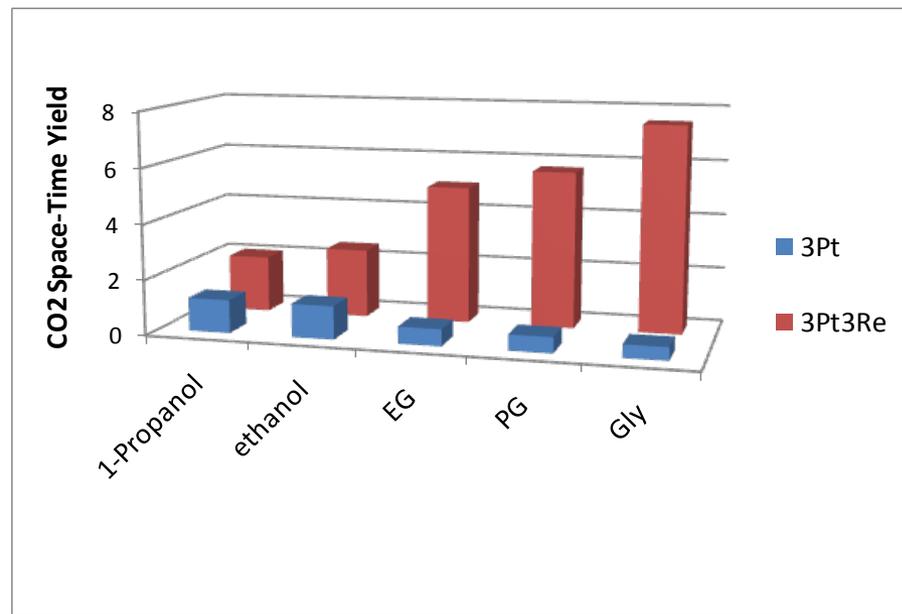
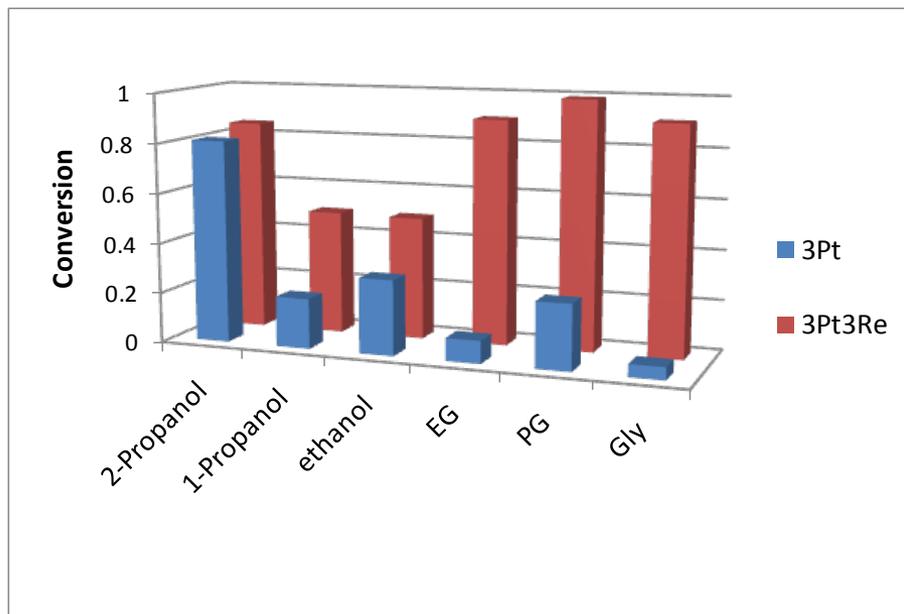
Summary

- ▶ Reforming of many bio-liquids is challenged by the high cost of feedstock, especially sugars and sugar alcohols from purified cellulose
- ▶ As a result, the project switched in FY11 to the water soluble fraction of bio-oil as APR feedstock. The new challenge will be to determine if sufficient hydrogen can be produced from this less expensive feedstock to meet economic targets defined by H₂A analysis.
- ▶ The different feedstocks face different challenges in APR for H₂ production
 - Sugar and sugar alcohols: dehydration (C-O cleavage) competitive pathway, which makes less reactive by-products and consumes the hydrogen that was produced by the desired C-C cleavage reactions
 - Aqueous soluble bio-oil has a diverse set of components, some of which are very resistant to APR and have low available H₂ content
- ▶ Progress has been made in understanding the nature of the acidity of our current most active catalyst Pt-Re/C
 - Acidity generated by ReO_x has been quantified
 - Acidity must be avoided, either by base neutralization or stabilization of Re to oxidation
 - Alternative catalysts aiming at providing both lower cost and improved performance relative to Pt-Re/C should be prepared, characterized, and tested

Technical Back-up Slides

Comparison of 3%Pt/C With 3%Pt-3%Re/C For APR of Alcohols and Diols

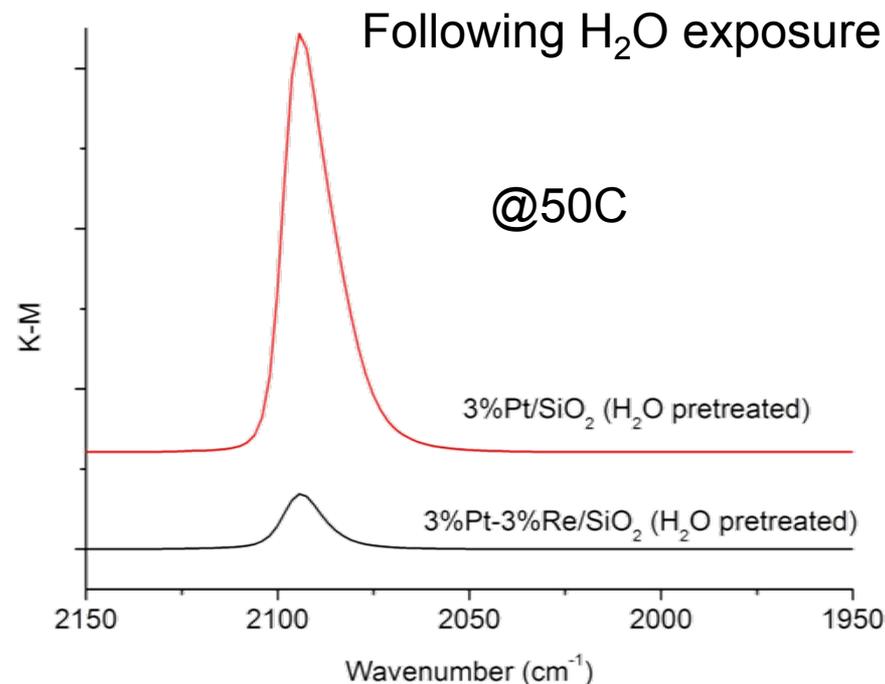
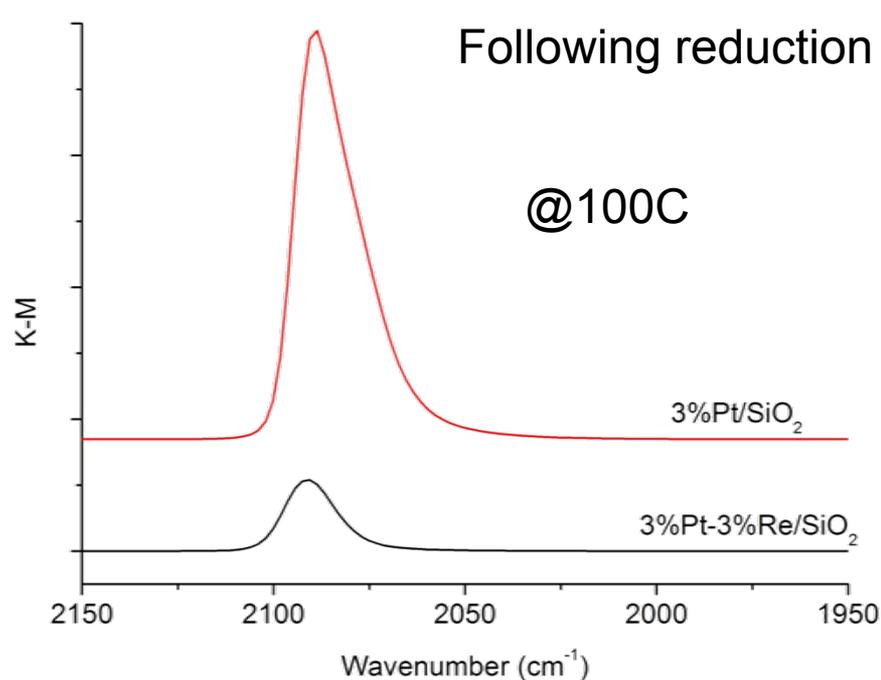
Technical Back-up Slide



Difference in activity between two catalysts is most pronounced with diols, less so with alcohols

CO-FTIR Characterization of Pt and Pt-Re Catalysts

Technical accomplishments

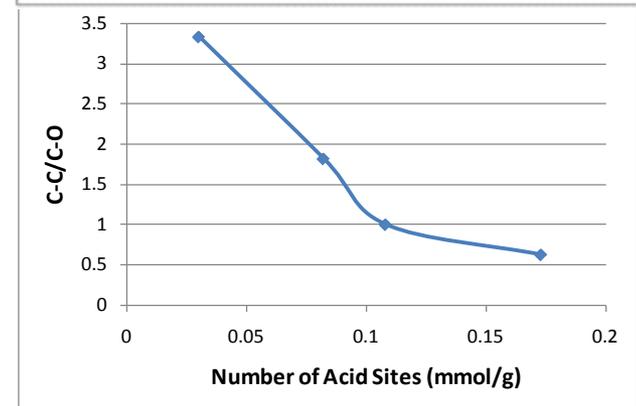
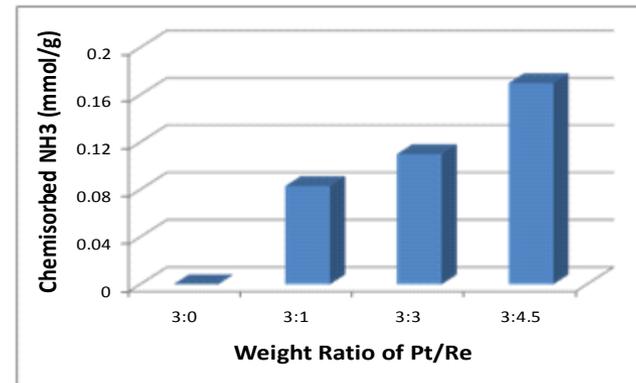
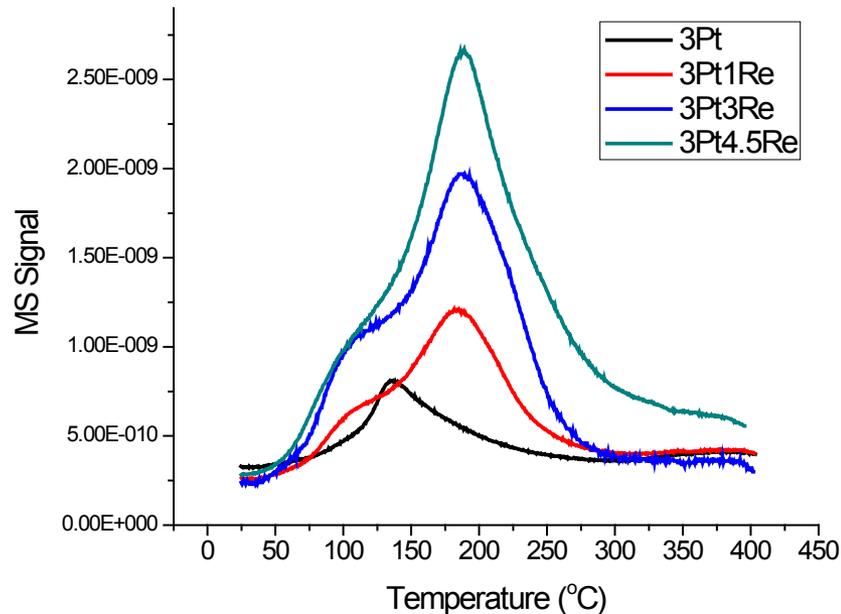


- Re addition reduces the amount of CO adsorbed on reduced catalyst surface
- H₂O exposure affects CO adsorption on Pt/SiO₂ minimally, but reduces CO uptake on Pt-Re/SiO₂ catalyst

Quantification of Acidity with Pt-Re/C

Technical accomplishments

Surface Chemistry Probed by NH₃ TPD

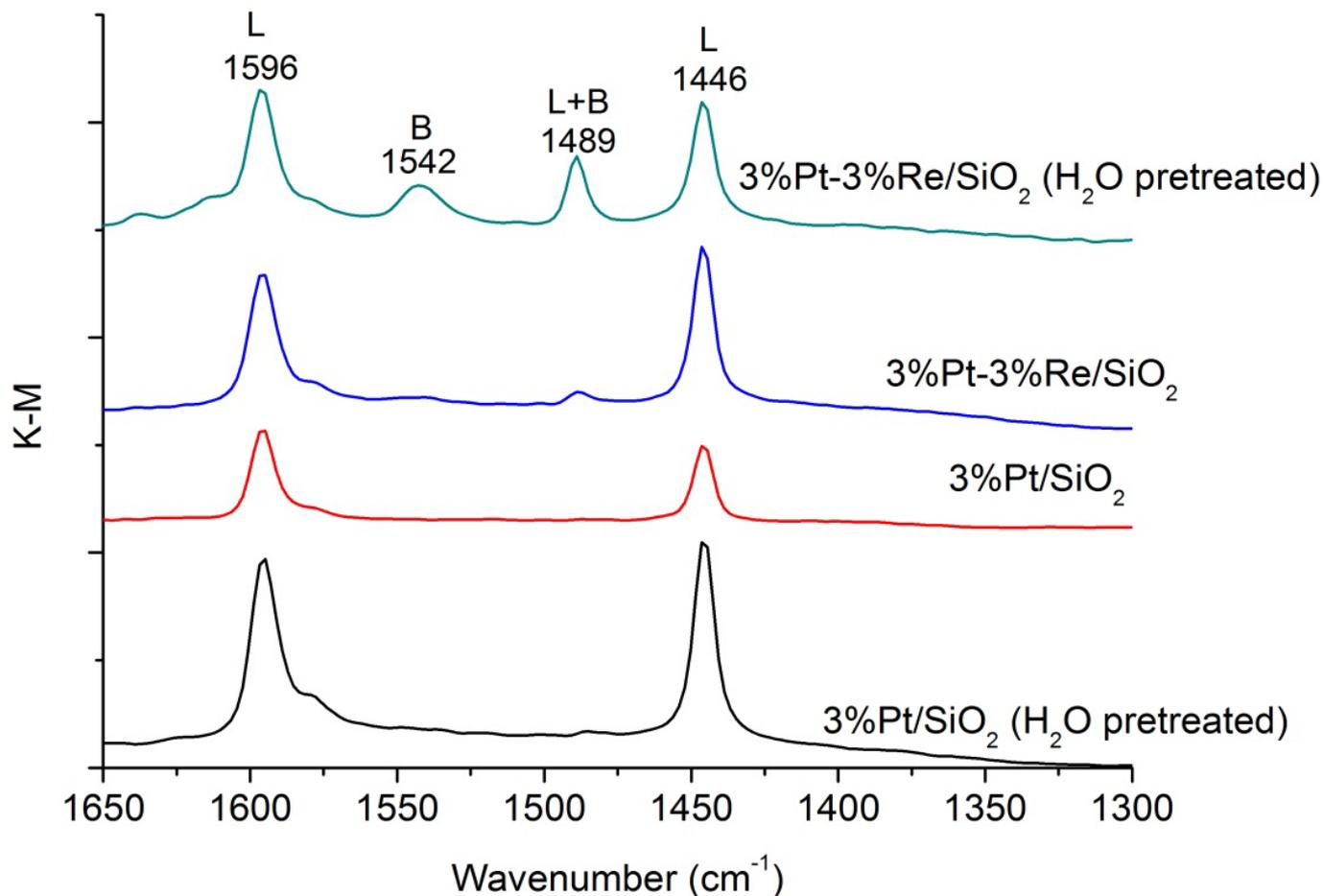


Samples were first exposed to water prior to NH₃ measurements

- ▶ Surface acid sites are generated after water exposure (representative of APR conditions)
- ▶ Acidity of Pt/C lower than Pt-Re/C
- ▶ Acid site strength associated with Re does not vary with different Pt/Re ratio
- ▶ Increasing number of acid sites are generated with increasing Re loading

Pyridine Adsorption Shows Development of Bronsted Acidity on Pt-Re/SiO₂ Catalyst

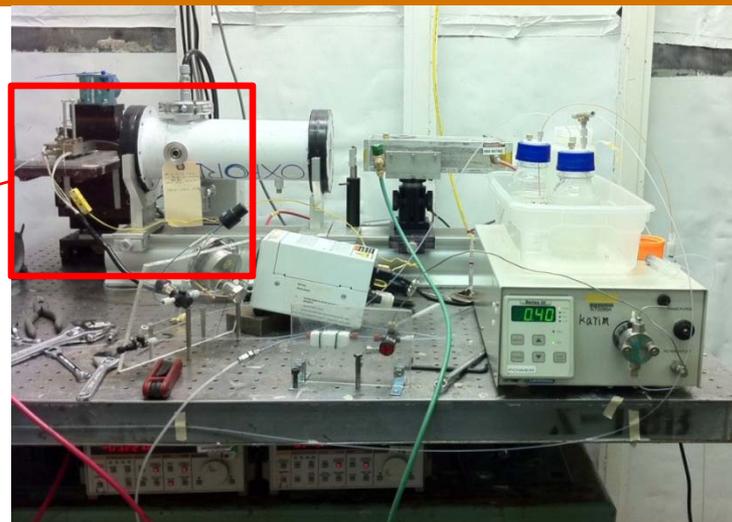
Technical accomplishments



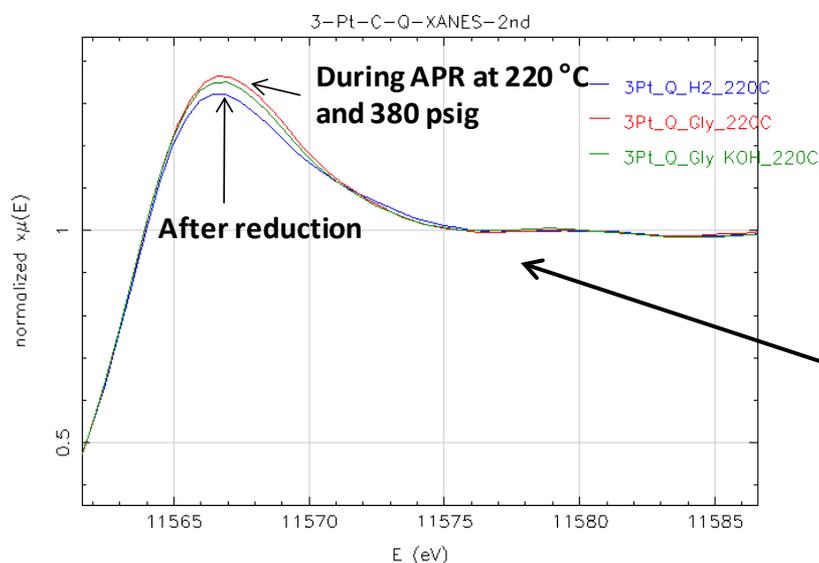
Bronsted acidic sites appear on the 3%Pt-3%Re/SiO₂ catalyst after exposure to H₂O

X-ray Absorption Spectroscopy *in-situ* Cell

Technical accomplishments



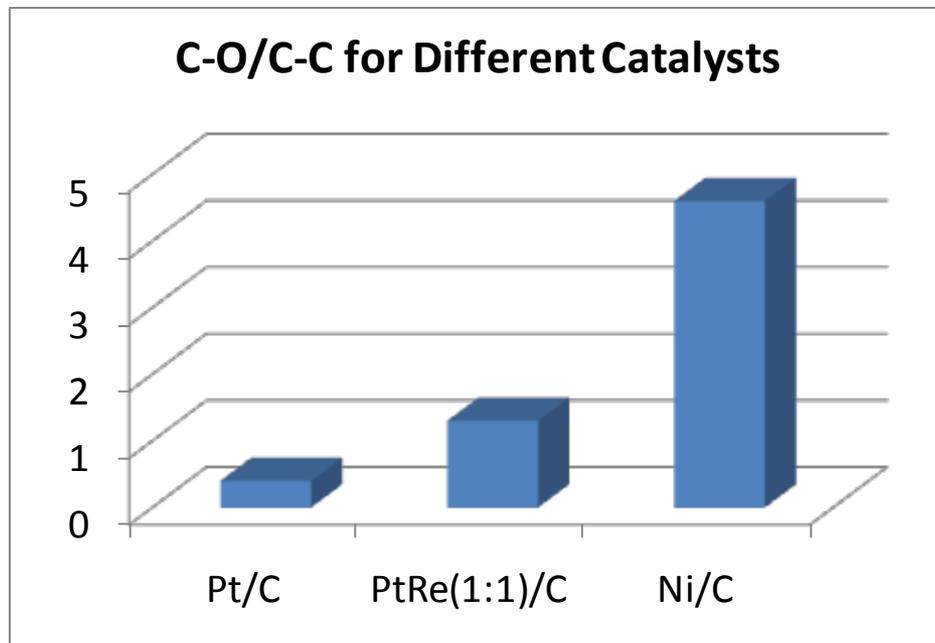
National Synchrotron Light Source (NSLS) beamline X18B at Brookhaven National Laboratory



- High P *in situ* cell developed by PNNL staff
- Design has been made available to other researchers
- Pt oxidation state as well as the local structure can be followed under reaction conditions
- The Pt L3 edge white line intensity increases under glycerol aqueous phase reforming reaction conditions
- Results indicate that Pt gets partially oxidized independent of KOH addition

Comparison of Pt, Pt-Re with Ni Catalyst

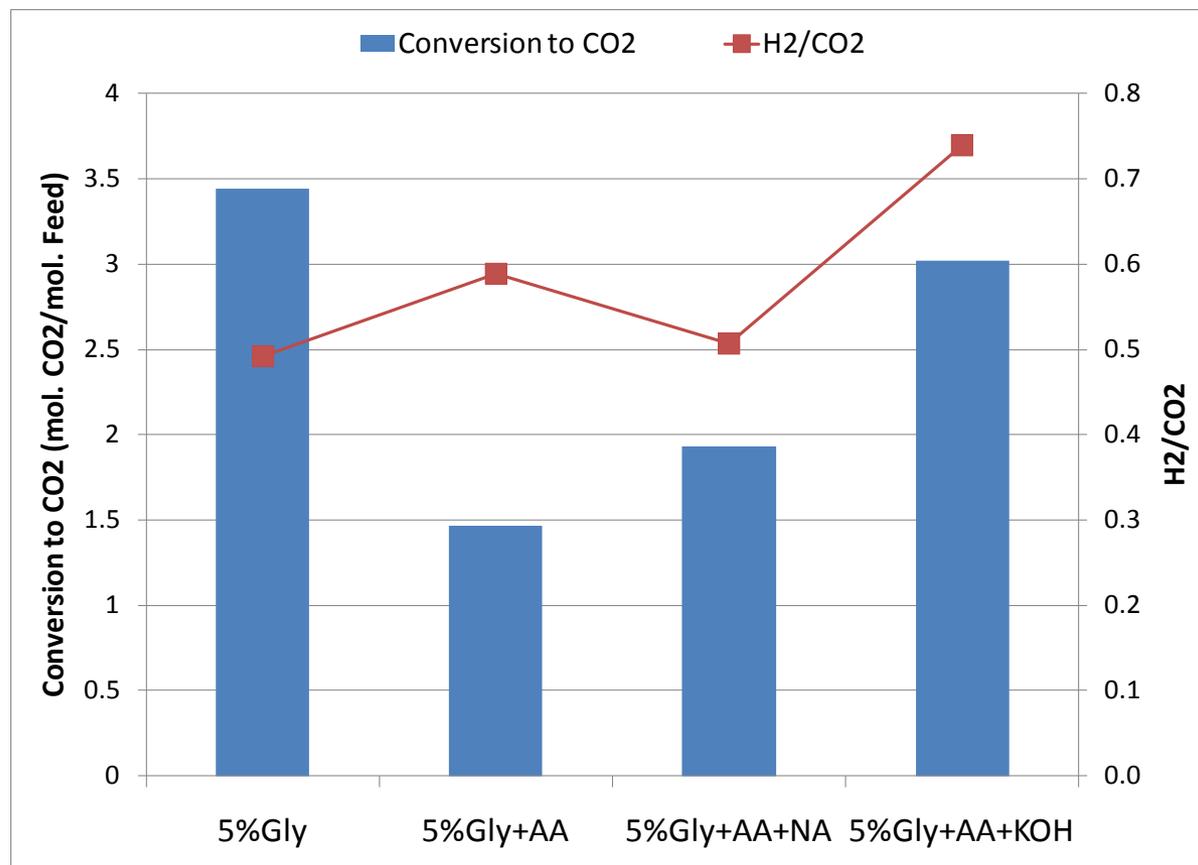
Technical Back-up Slide



- ▶ Ni is leading candidate for lower cost APR of polyols
- ▶ Reduced Ni is subject to oxidation by water, leading to NiO
- ▶ High fraction of C-O bond cleavage is evidenced with Ni/C
- ▶ Comparison is made at similar conversion (5%)

Effect of Acid-Base on Glycerol Conversion

Technical Back-up Slide



- Acetic acid (AA): 3.26 wt.%; nitric acid (NA): 0.062 wt.%; KOH: 3 wt.%
- Addition of KOH neutralizes acidity of acetic acid, recovers activity of catalyst, and increases H₂ selectivity

APR bio-oil Process Flow Diagram

