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Biomass-derived Liquids Distributed (Aqueous Phase) Reforming

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2012 DOE Hydrogen and Fuel Cells Program Review
May 17, 2012

Project PD002

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Timeline

- ▶ Project start date: Oct. 1, 2004
- ▶ Project end date: September 30, 2012
- ▶ Percent complete: 90%

Budget

- ▶ Total project funding (starting 2004) : \$3,250K
- ▶ Funding received in FY11: \$450K
- ▶ Planned funding for FY12: \$400K

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

Partners

- ▶ Washington State University

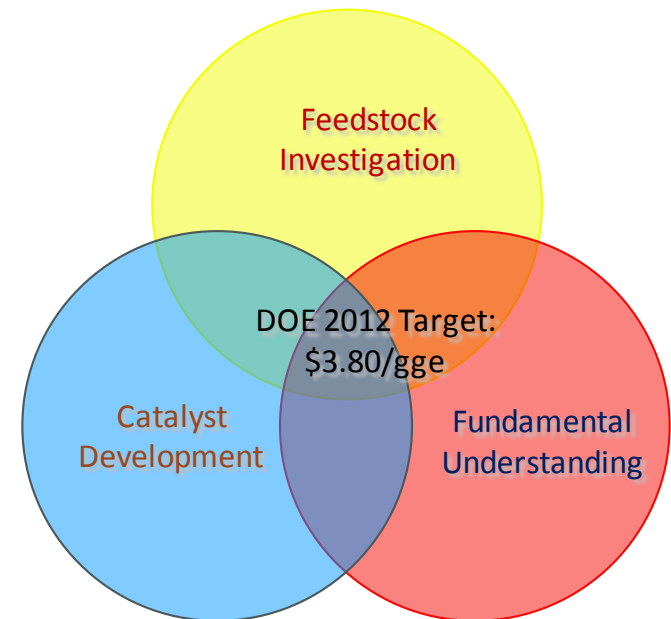
Project Objectives

▶ Primary Objective

- Develop aqueous phase reforming catalysts and technology to convert bio-derived liquids to hydrogen that meets the DOE 2012 cost target of \$3.80/gge, verified by H2A analysis

▶ Objectives -- feedstock

- Identify primary compounds in bio-oil that are extractable into an aqueous phase
- Determine the effectiveness of aqueous phase reforming in producing hydrogen from these water-soluble compounds
- Estimate cost of hydrogen production using best catalytic results, as function of feedstock cost



- ▶ Extended aqueous phase reaction (APR) testing with bio-oil surrogates and authentic aqueous soluble bio-oil
 - Obtain a source of non-stabilized bio-oil
 - Prepare water-soluble fraction and identify major compounds (or compound classes)
 - Build a list of representative compounds from water soluble fraction that have specific bond activation/bond breaking requirements
- ▶ Catalyst screening and characterization
 - Develop a list of catalyst candidates, aiming at improved performance
 - Carry out a preliminary evaluation of catalyst performance in a high throughput combinatorial reactor
 - Support screening studies with additional single unit reactor testing
 - Identify, utilize best catalyst(s) for subsequent testing for H₂ production from aqueous soluble bio-oil
- ▶ Apply results to H₂A analysis and determine H₂ production cost

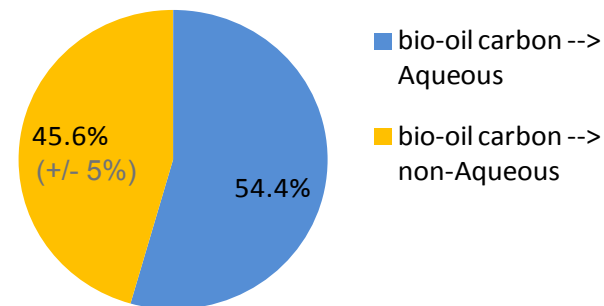
Project Milestones

SMART Milestones	Completion Date	Progress and Comments	Percent Complete
Demonstrate that an aqueous-soluble bio-oil feedstock can be reformed under aqueous phase reforming conditions to H ₂ and CO ₂ , with a carbon-based selectivity of 80%	9/30/2012	<ul style="list-style-type: none">▪ Identified major compounds in water soluble bio-oil▪ Identified a number of promising catalysts that favor C-C over C-O bond cleavage▪ Verified that molecules with lower oxygen content are more difficult to reform to H₂ and CO₂ than poly-oxygenates	60
Demonstrate through H2A cost analysis that H ₂ production from aqueous phase reforming of aqueous soluble bio-oil can meet the threshold cost goal of <\$4.00/kg produced and dispensed	9/30/2012	In progress	75

Bio-oil: Production and Generation of Aqueous Phase Fraction

- ▶ Bio-oil production
 - Source: pine saw dust
 - Pyrolysis conditions: 480°C, 1.6s residence time (vapor)
- ▶ Generation of a water-soluble fraction
 - Water dilution: 1:4 bio-oil in water (by weight)
 - Shake vigorously to form single phase (emulsion)
 - Centrifuge at 5,000 rpm for 30 min

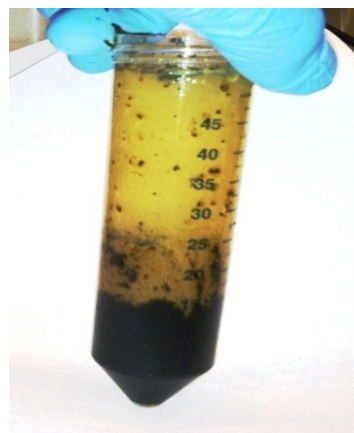
Segregation of bio-oil carbon, by phase (wt% C in raw bio-oil)



H₂O/bio-oil = 4 (wt/wt)



Raw bio-oil



Bio-oil plus H₂O



Shaken and centrifuged

Major Species Identified in the Aqueous Fraction of Bio-oil by High Performance Liquid Chromatography (HPLC) Analysis

Poly-oxygenates	Mono-oxygenates	Carboxylic acids
glycerol	1-butanal	acetic acid
glycolic acid	isobutanol	propionic acid
ethylene glycol	1-butanol	
glycolaldehyde	ethanol	
levoglucosan	propanol	
sorbitol		
glucose		
xylose		

- Approximately 70% of total carbon is accounted for in the analysis
- The majority of compounds are oxygenates having 4 or fewer carbons
- Levoglucosan is the most prominent species identified
- Acetic acid and propionic acid are two species anticipated to be difficult to convert via APR

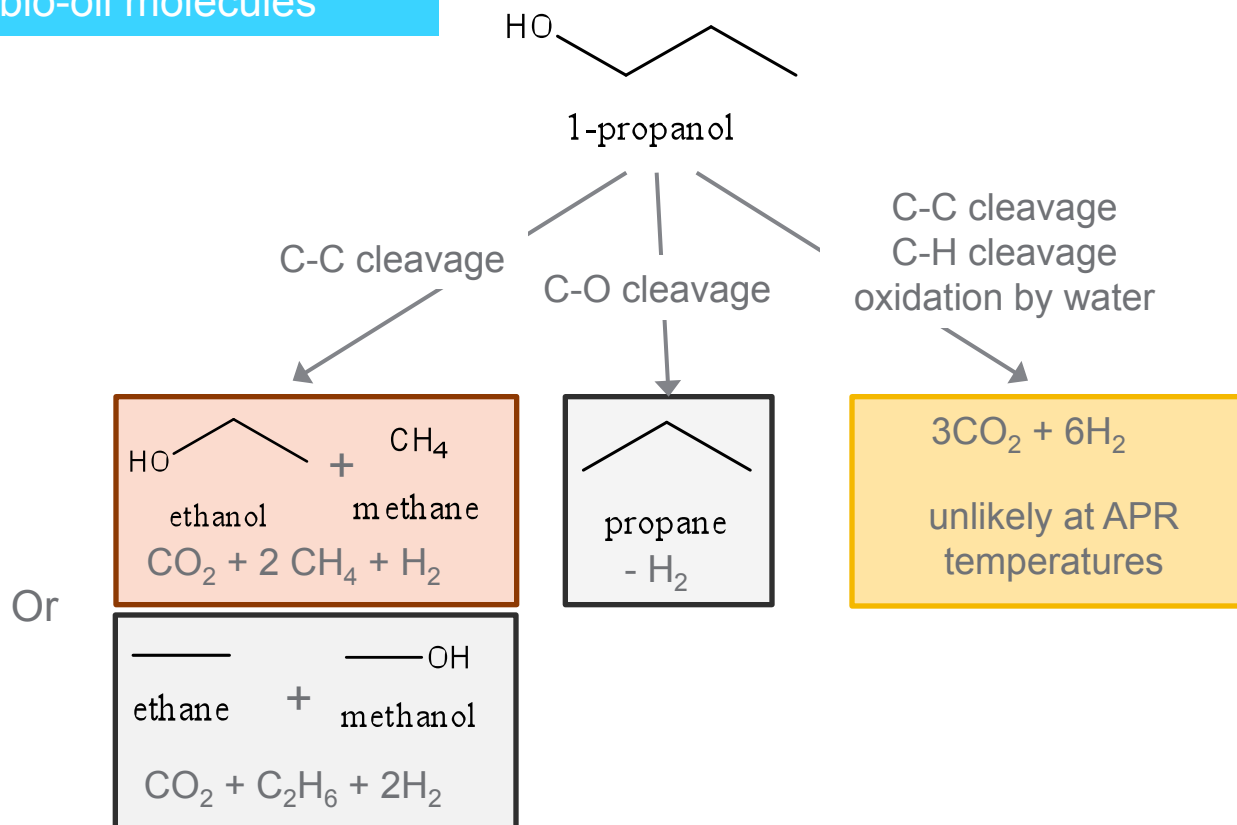
Combinatorial Catalyst APR Studies

- ▶ 16 reactor flow system
- ▶ Catalysts (supported on C and ZrO₂)
 - Pt, Ni, Co, Ru and their bimetals
 - Additional bimetals incorporating Re, Zn, Mo
- ▶ Feedstocks
 - 1-propanol (representative mono-oxygenate)
 - Glycerol (representative poly-oxygenate)
 - Acetic acid (representative carboxylic acid)
- ▶ Conditions
 - 245°C, 600 psi and 300°C, 1350 psi
 - WHSV = 25 h⁻¹
- ▶ Liquid product collected over several hours of run time (no deactivation data)



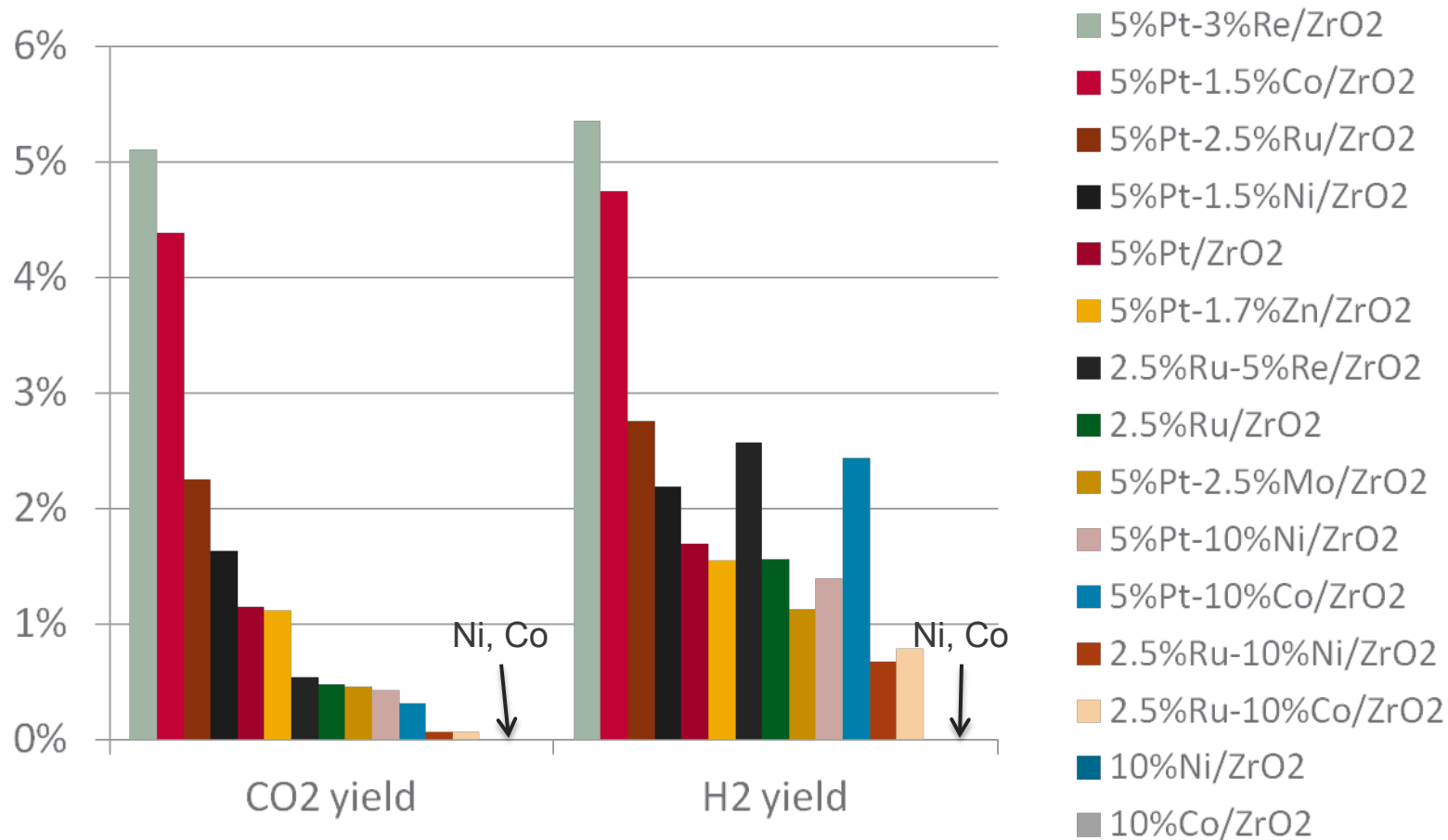
APR of Mono-oxygenates: 1-Propanol

Probe reaction for low oxygen content bio-oil molecules



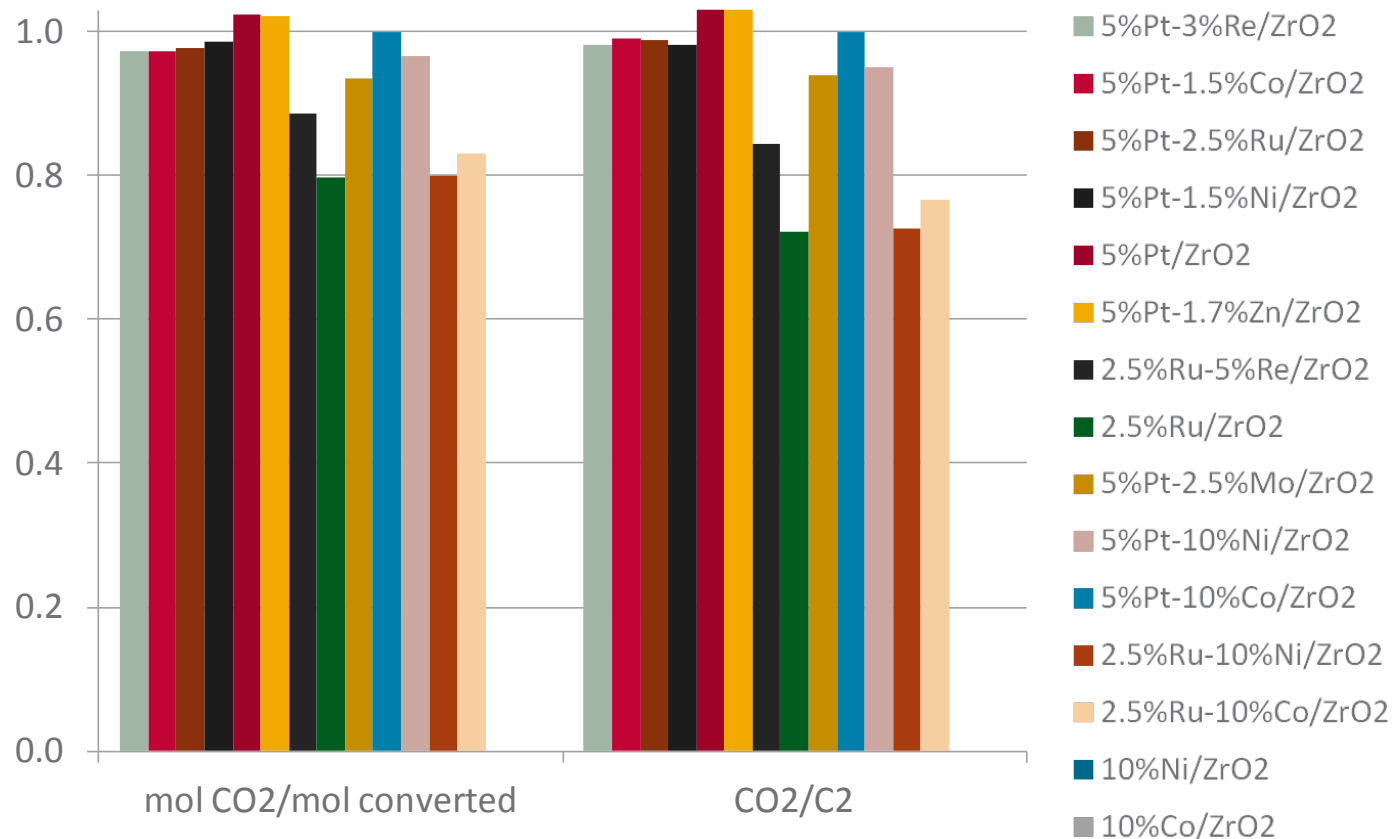
Product distribution depends upon C-C vs. C-O bond cleavage and location of C-C bond cleavage

1-Propanol APR (Combinatorial Testing)



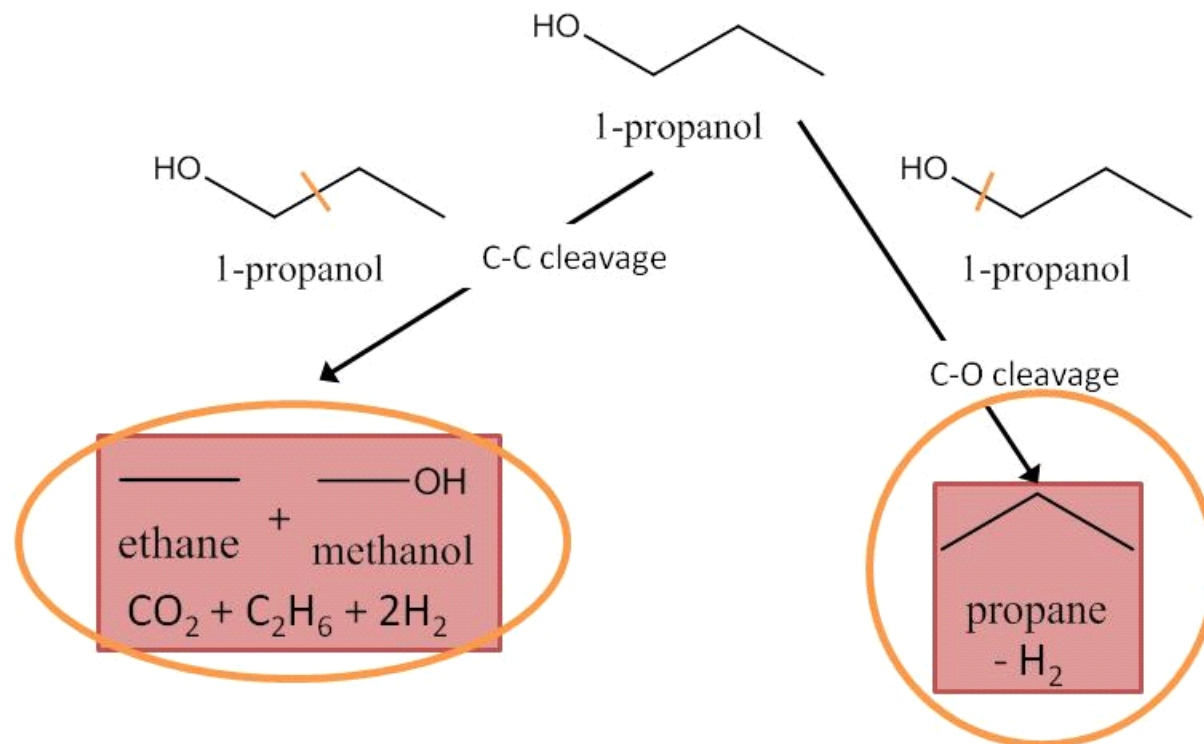
Single, non-precious metal catalysts show virtually no activity
Pt-containing catalysts show best performance

1-Propanol APR (Combinatorial Testing)



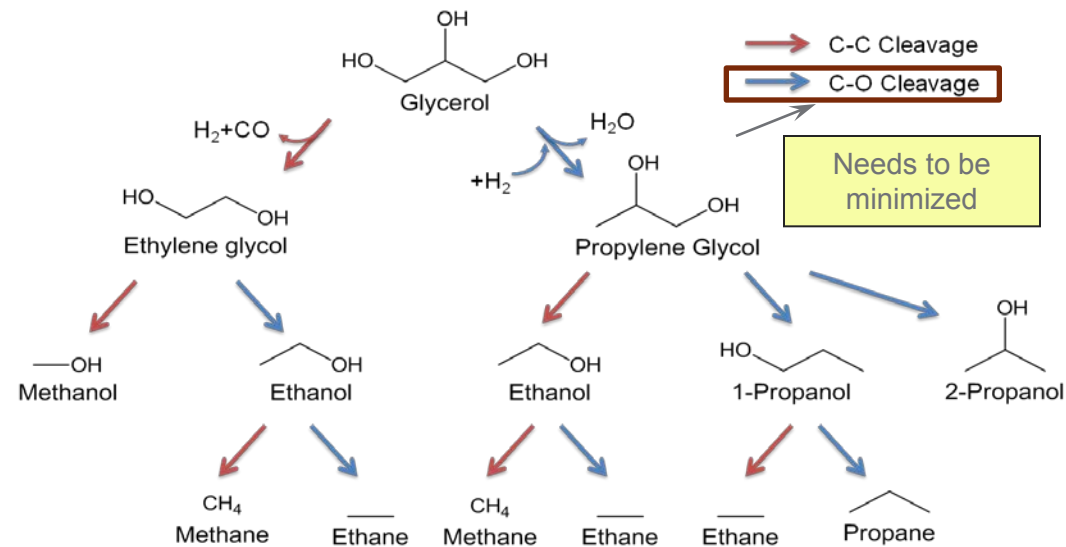
Conditions: 245°C, 600 psi; WHSV = 25
 Ratio of "1" indicates single C-C cleavage event
 Mol CO₂/mol converted <1 indicates C-O bond cleavage

APR of 1-Propanol: Reaction Pathways

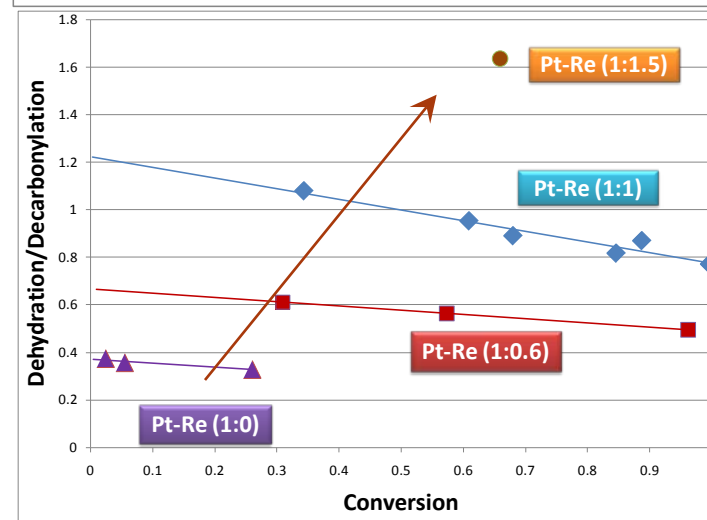
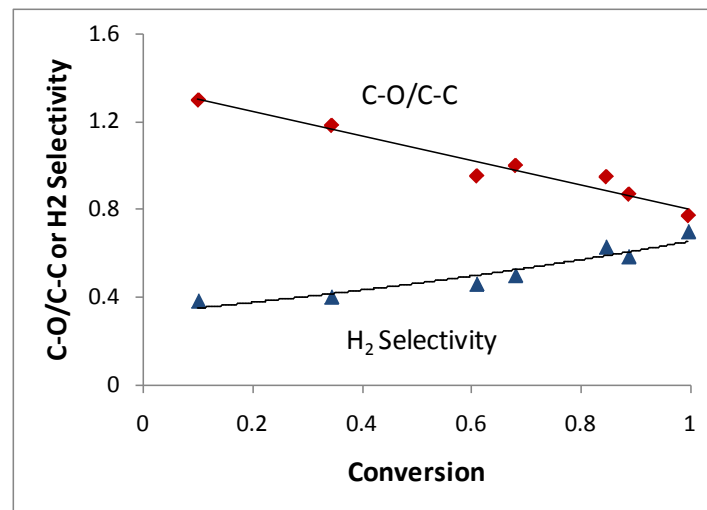


- Only these two pathways proceed under APR conditions
- Efficient production from mono-oxygenates is challenging
- C-O cleavage of poly-oxygenates to mono-alcohols would be detrimental to H_2 selectivity and needs to be minimized.

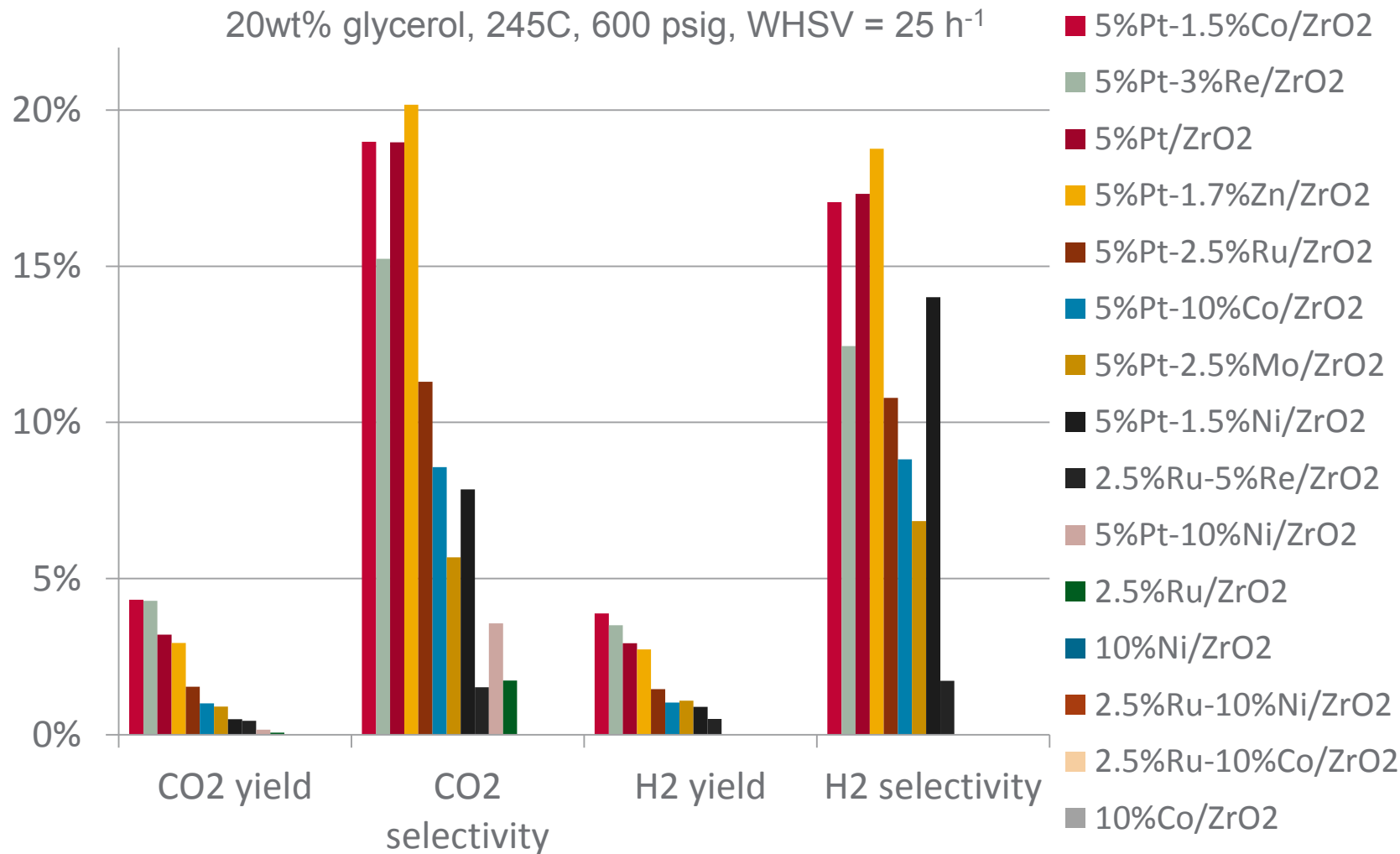
Facilitating C-C Bond Breaking is Key to Hydrogen Production From Glycerol (Surrogate for Poly-oxygenates)



- C-C scission leads to production of H₂ and CO₂ (preferred)
- C-O cleavage leads to production of olefin plus water
- No olefin products are detected: H₂ is consumed to saturate the C-C bond (internally consumed)
- C-O cleavage needs to be minimized, even at the expense of total catalyst activity

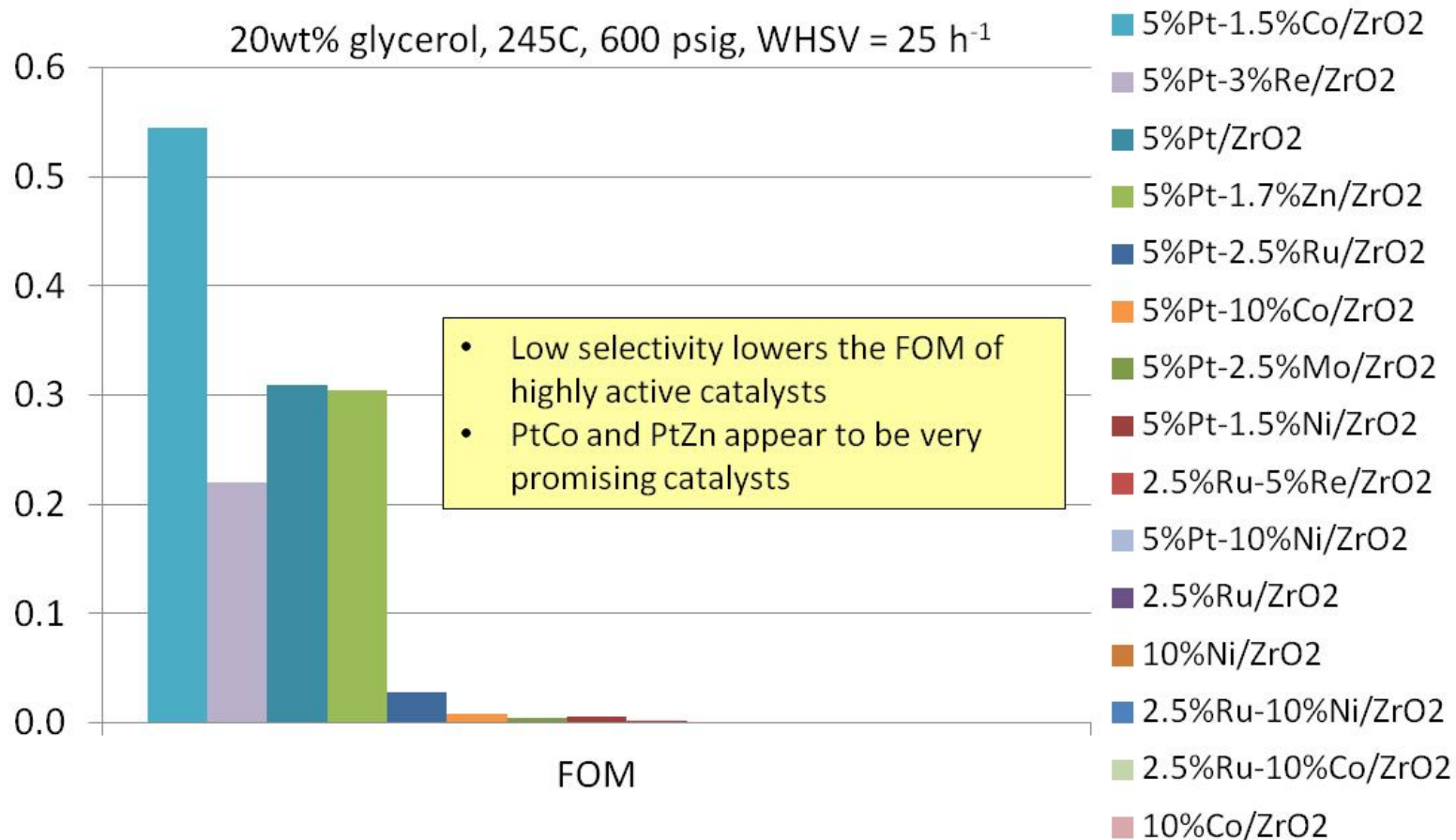


Catalyst Combinatorial Screening for Maximum Activity and C-C/C-O Cleavage: Glycerol APR



Catalyst Combinatorial Screening for Glycerol

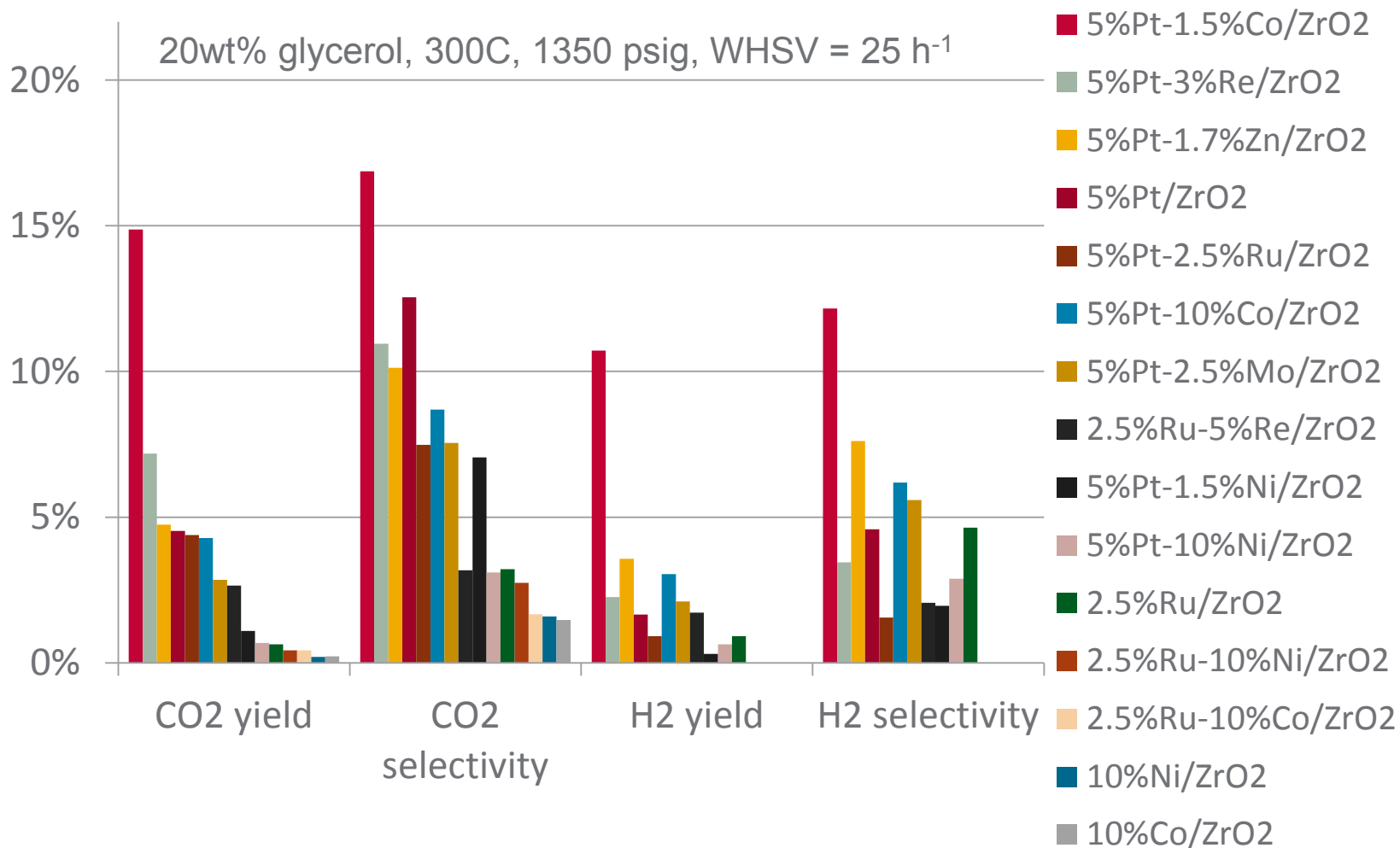
APR: Best ZrO₂-Supported Catalysts



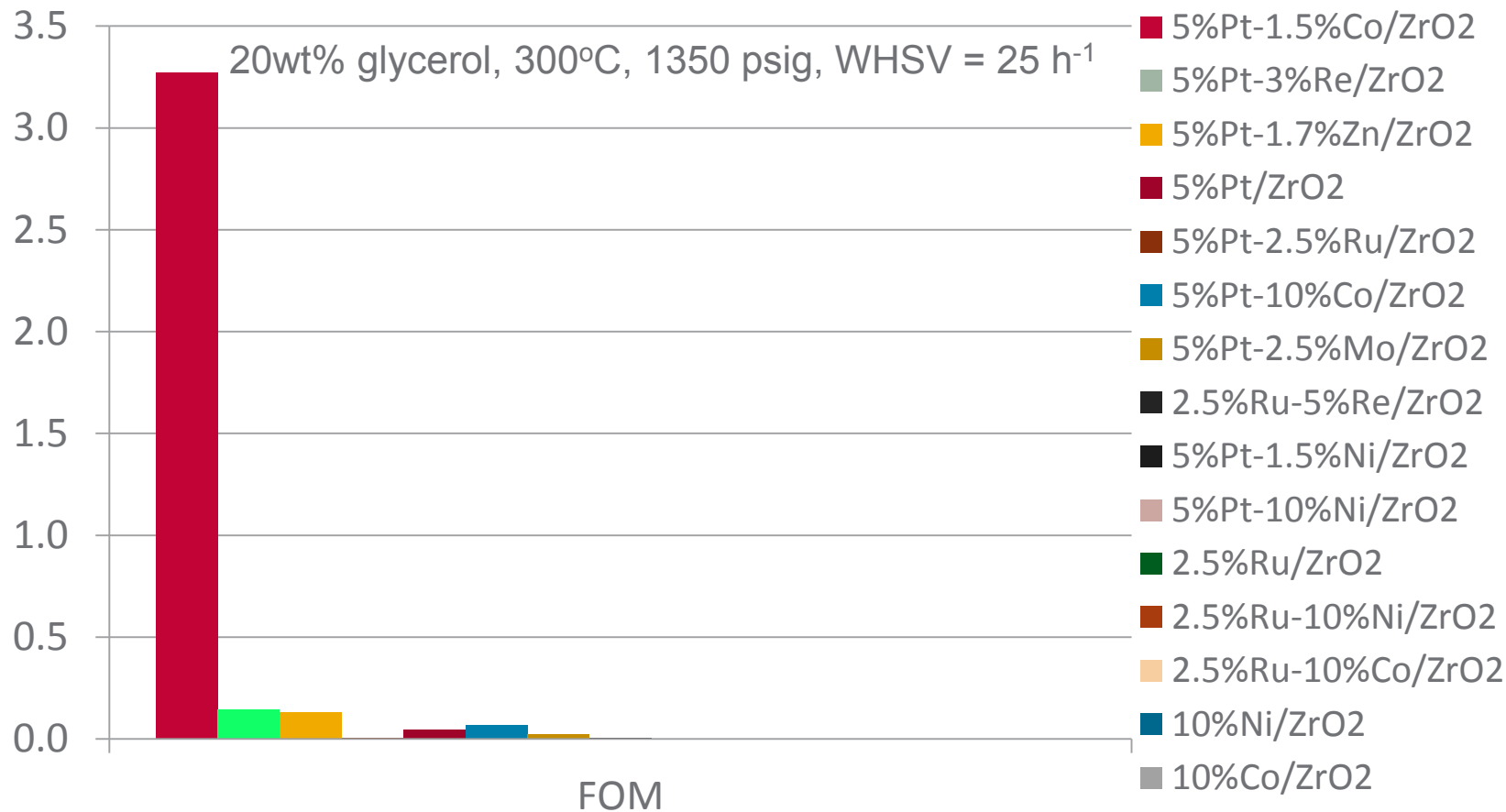
FOM = CO₂ yield x CO₂ selectivity x H₂ yield x H₂ selectivity

Pt-Co and Pt-Zn are new metal combinations meriting further investigation

Glycerol APR: Combinatorial Screening at 300°C with ZrO₂ Supported Catalysts



Glycerol APR Combinatorial Screening at 300°C With ZrO₂ Supported Catalysts: Best Catalysts

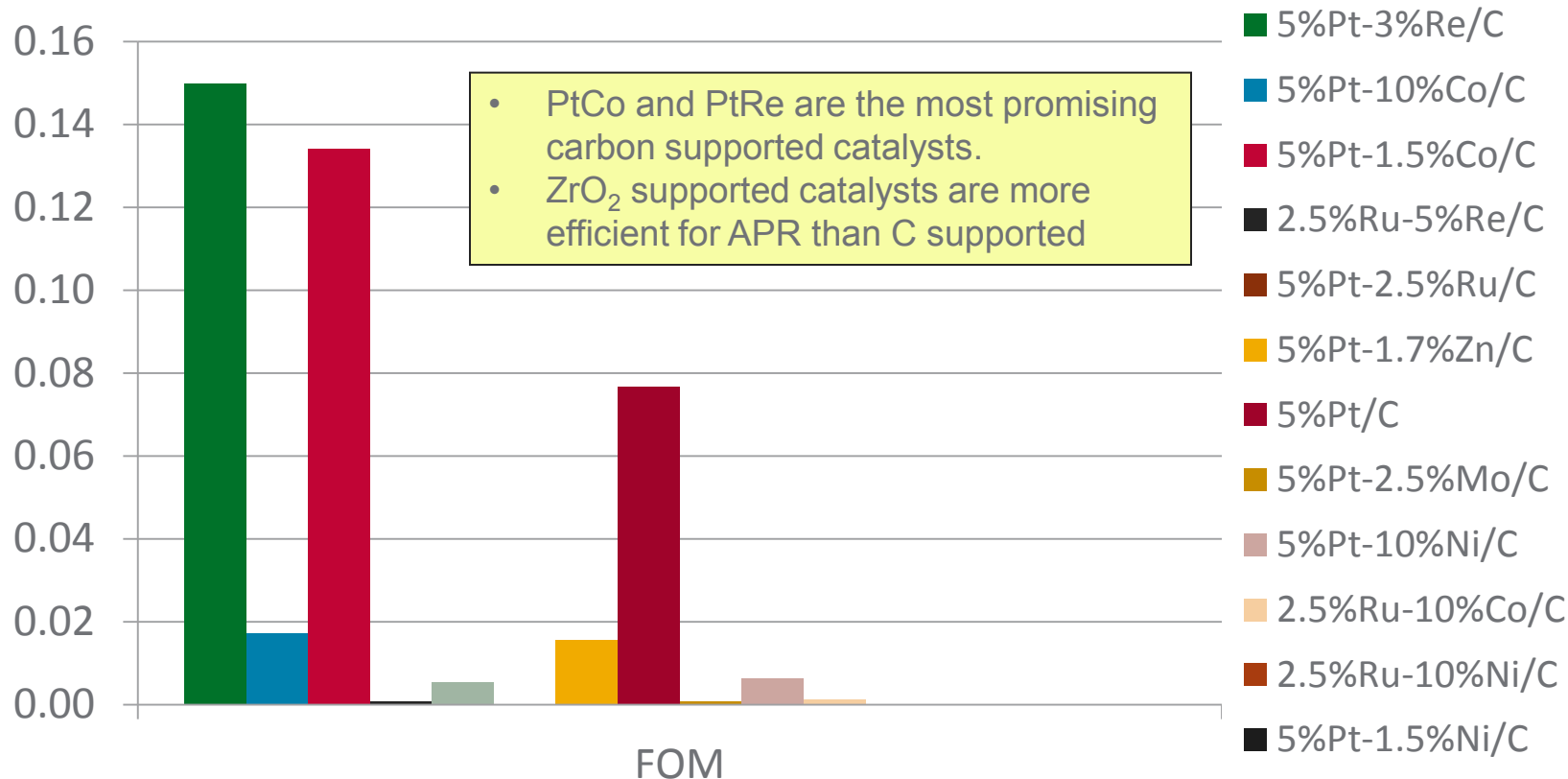


FOM = CO₂ yield x CO₂ selectivity x H₂ yield x H₂ selectivity

- Higher temperature and pressure result in lower selectivity (except PtCo)
- Significant deactivation observed as result of 300°C operation

Glycerol APR Combinatorial Screening: Carbon Supported Catalysts

20wt% glycerol, 245C, 600 psig, WHSV = 25 h⁻¹



FOM = CO₂ yield x CO₂ selectivity x H₂ yield x H₂ selectivity
Pt-Re and Pt-Co are best performing carbon-supported catalysts

H2A Analysis of Bio-oil Water Soluble Fraction Aqueous Phase Reforming

Aqueous Phase Product Distribution Allows Prediction of Maximum H₂ Yield

- ▶ Bio-oil feed composition can be used to predict maximum H₂ yields
 - Mono-oxygenates: 2 mole H₂, 1 mole CO₂
 - Poly-oxygenates (n OH groups): 2n moles H₂, n moles CO₂
 - Carboxylic acids: 1 mole alkane, 1 mole CO₂ (no H₂)
- ▶ Maximum H₂ yield and actual H₂ yields are compared and provided to H2A model
 - Our feedstock analysis and test data are pending
- ▶ Interim approach: re-examine FY11 H2A analysis, update with 2012 H2A inputs, and examine sensitivities

To be updated once quantitative analysis of our bio-oil sample is completed



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
Levoglucosan	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

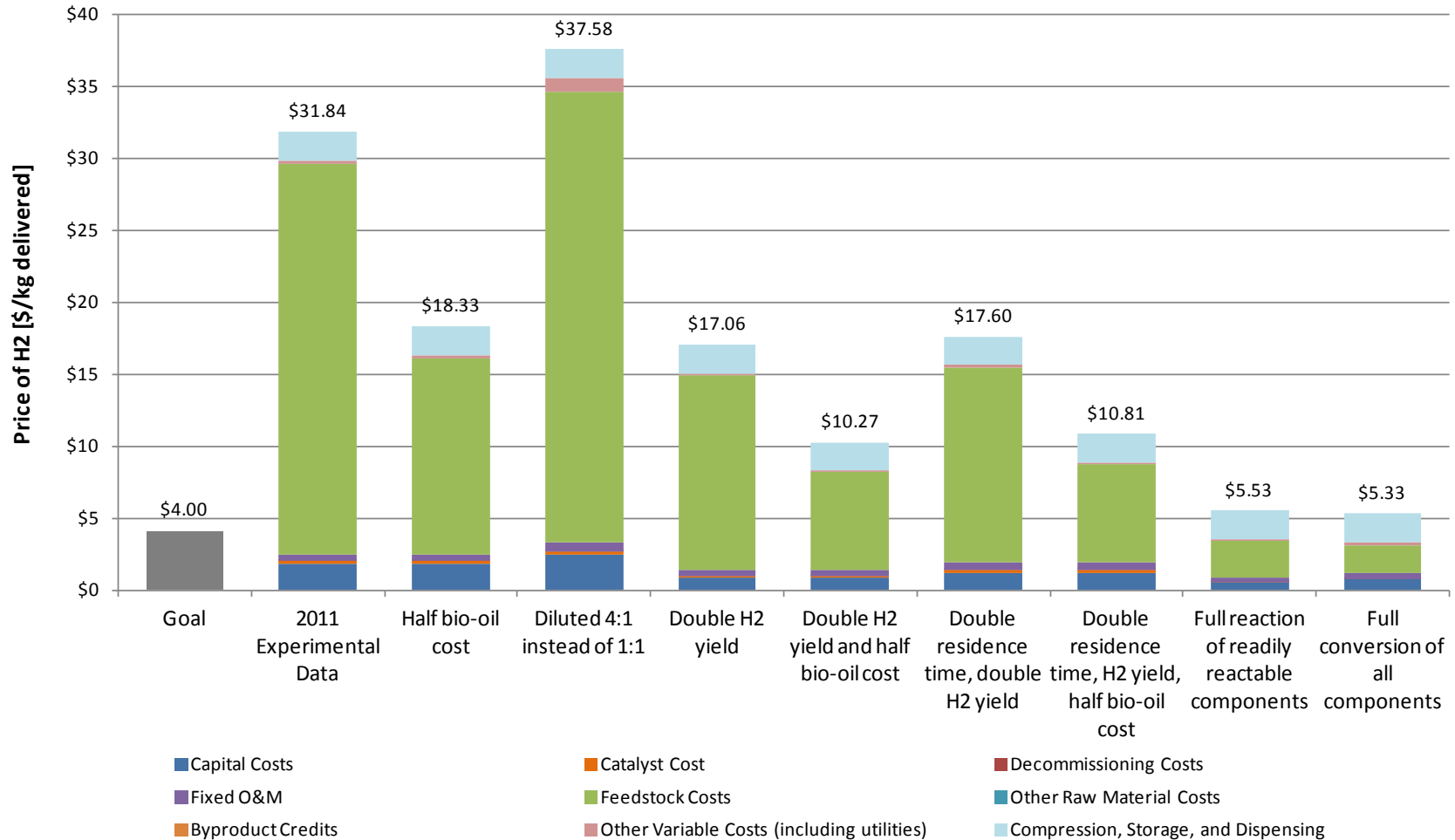
H2A Analysis and Cost Sensitivities Based on Bio-oil APR Performance

H2A Values

Scenario	Units	2011 Experimental Data	Half bio-oil cost	Diluted 4:1 instead of 1:1	Double H2 yield	Double H2 yield and half bio-oil cost	Double residence time, double H2 yield	Double residence time, H2 yield, half bio-oil cost	Full reaction of readily reactable components	Full conversion of all components
Capital Costs	[\$/kg H ₂]	\$1.77	\$1.77	\$2.40	\$0.88	\$0.88	\$1.14	\$1.14	\$0.56	\$0.74
Catalyst Cost	[\$/kg H ₂]	\$0.24	\$0.24	\$0.27	\$0.12	\$0.12	\$0.24	\$0.24	\$0.018	\$0.015
Decommissioning Costs	[\$/kg H ₂]	\$0.01	\$0.01	\$0.02	\$0.01	\$0.01	\$0.02	\$0.02	\$0.01	\$0.01
Fixed O&M	[\$/kg H ₂]	\$0.44	\$0.44	\$0.65	\$0.36	\$0.36	\$0.51	\$0.51	\$0.30	\$0.42
Feedstock Costs	[\$/kg H ₂]	\$27.08	\$13.57	\$31.20	\$13.57	\$6.78	\$13.57	\$6.78	\$2.48	\$1.94
Other Raw Material Costs	[\$/kg H ₂]	\$0.00	\$0.00	\$0.00	\$0.00	\$0.00	\$0.00	\$0.00	\$0.00	\$0.00
Byproduct Credits	[\$/kg H ₂]	\$0.00	\$0.00	\$0.00	\$0.00	\$0.00	\$0.00	\$0.00	\$0.00	\$0.00
Other Variable Costs (including utilities)	[\$/kg H ₂]	\$0.29	\$0.29	\$1.03	\$0.12	\$0.12	\$0.12	\$0.12	\$0.17	\$0.20
Compression, Storage, and Dispensing	[\$/kg H ₂]	\$2.00	\$2.00	\$2.00	\$2.00	\$2.00	\$2.00	\$2.00	\$2.00	\$2.00
Total	[\$/kg H₂]	\$31.84	\$18.33	\$37.58	\$17.06	\$10.27	\$17.60	\$10.81	\$5.53	\$5.33

FY11 value: \$25.84/kg H₂

Sensitivity Analysis: Cost of Hydrogen From Aqueous Bio-oil APR Under Different Scenarios



Major changes for 2012 were an increase in the estimated bio-oil cost from \$0.65/gallon to \$1.12/gallon, and increases in estimated costs of cooling water, process water, and steam.

H₂ Cost Sensitivity Analysis

▶ Bio-oil cost

- This is the most important factor affecting H₂ production cost
- Bio-oil feedstock must cost a fraction (<50%) of H₂A assumption to be economical
- Aqueous fraction of bio-oil has low value as a transportation fuel
 - Should be valued at less than \$1.12/gallon, which would favorably affect economics

▶ Catalyst performance

- Bio-oil conversion level and catalyst selectivity most impactful variable (that we can control) affecting cost of H₂
- If residence time increases in order to increase conversion, a penalty is paid in capital costs (including catalyst), but tradeoff may be acceptable

▶ Bio-oil/water ratio

- Amount of water used in extraction is significant, due to energy costs of heating to reaction temperature; also impacts equipment sizing
- 1:4 dilution (compared to 1:1 base case) negatively impacts the economics; lower dilution is necessary

- ▶ Washington State University (Prof. Yong Wang)
 - Project is supporting a post-doctoral fellow full time
 - Batch APR system studies, primarily examining higher T, higher P regimes for conversion of intractable molecules such as acetic acid
 - ATR-FTIR (attenuated total reflectance) studies of catalysts in aqueous phase
- ▶ Virent Energy Systems (Randy Cortright)
 - ▶ Collaboration on combinatorial studies
- ▶ Brookhaven National Laboratory (Anatoly Frenkel)
 - ▶ Deployment of *in situ* EXAFS cell
- ▶ University of Delaware (Prof. Jingguang Chen, Dion Vlachos)
 - ▶ Collaboration on *in situ* EXAFS studies

FY12

- ▶ Complete studies of acetic acid APR
 - Can conversion to CH_4 and CO_2 be obtained?
 - Are the leading catalysts insensitive to poisoning by acetic acid?
- ▶ Test best catalysts for APR of full aqueous bio-oil
 - Work with minimal water dilution (near 1:1)
 - Measure H_2 selectivity and yield and compare with predictions based on feedstock composition
 - Determine catalyst stability over extended time (50 hours)
- ▶ Produce report on APR of bio-oil: research results, conclusions, and recommendations
- ▶ Complete H₂A analysis to finalize cost of production of H_2 from APR of water-soluble bio-oil

FY13

- ▶ Examine feasibility of single step routes to H_2 from cellulose

- ▶ Aqueous fraction of bio-oil has been examined as low cost bio-liquid feedstock for APR
 - Comprises poly-oxygenates, mono-oxygenates, carboxylic acids, predominantly C₆ or lower
 - Poly-oxygenated components have greatest potential for hydrogen production
 - Mono-oxygenates (alcohols) produce a maximum of 2 moles H₂/mole feed
 - Carboxylic acids have shown low reactivity, may produce no H₂
- ▶ New catalyst leads, especially Pt-Co/ZrO₂, have been identified and have significant potential to improve H₂ yield and economics compared with FY11 results
 - We will predict maximum yield of H₂ based on bio-oil composition (analysis pending) and compare with actual performance with Pt-Co/ZrO₂ catalyst
- ▶ Meeting the target <\$4.00/kg H₂ (produced and dispensed) will be very challenging
 - Theoretical best H₂ yield case will likely exceed this target
 - Lower feedstock cost than 2012 H₂A value of \$1.12/gal is required to meet the target



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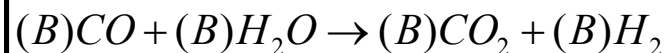
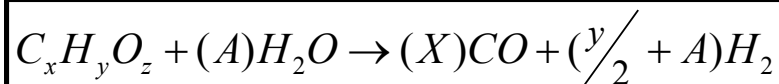
Technical Backup Slides

▶ APR Reactions

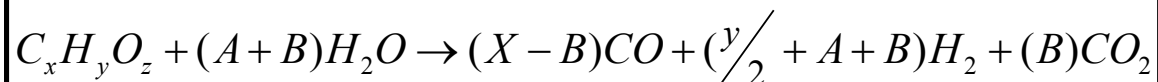
- To model reaction, conversion is to CO and H₂ with no side reactions
- “Experimental data” case is based on single component data shown previously, excluding glycerol and sorbitol results
- Acetic acid inhibition applied to all reactions in “current conversion” case, based on its mol fraction in the feed and experimental data
- No change in conversion or reactivity with mixed component feed
- Kinetics are independent of dilution amount

▶ Water Concentration

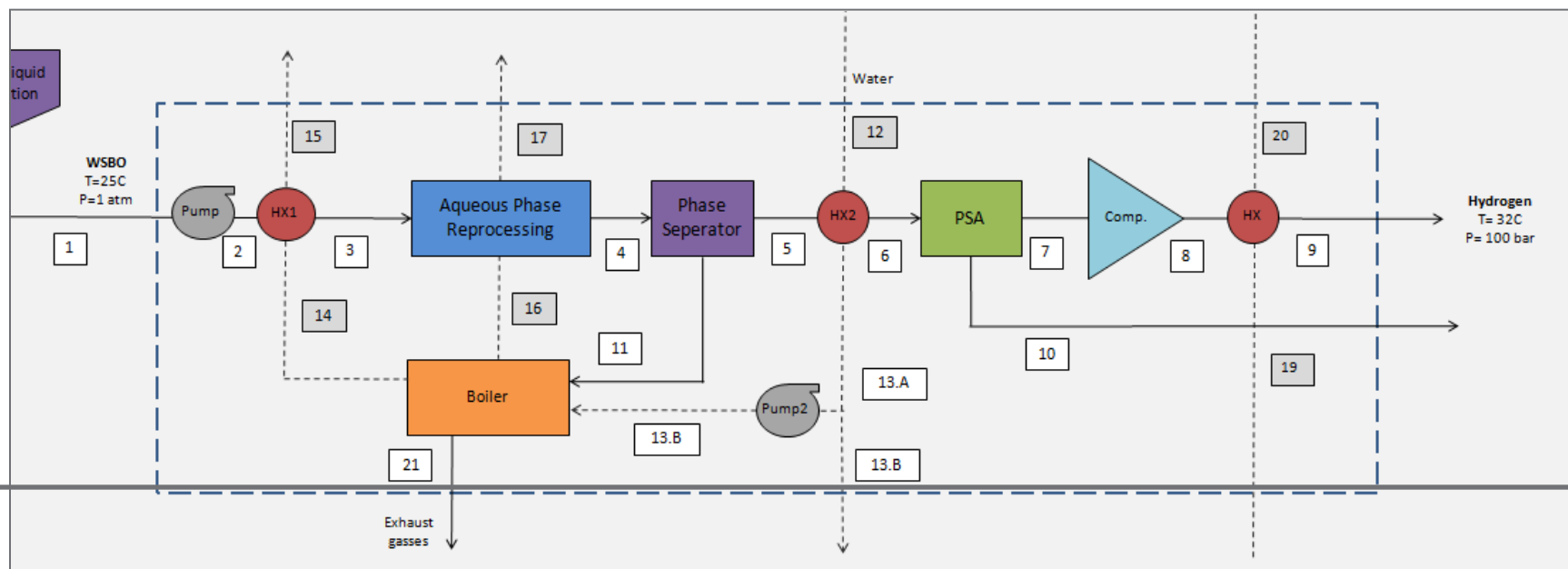
- Bio-oil and water fed on a 1:1 mole basis for experimental model



Overall:

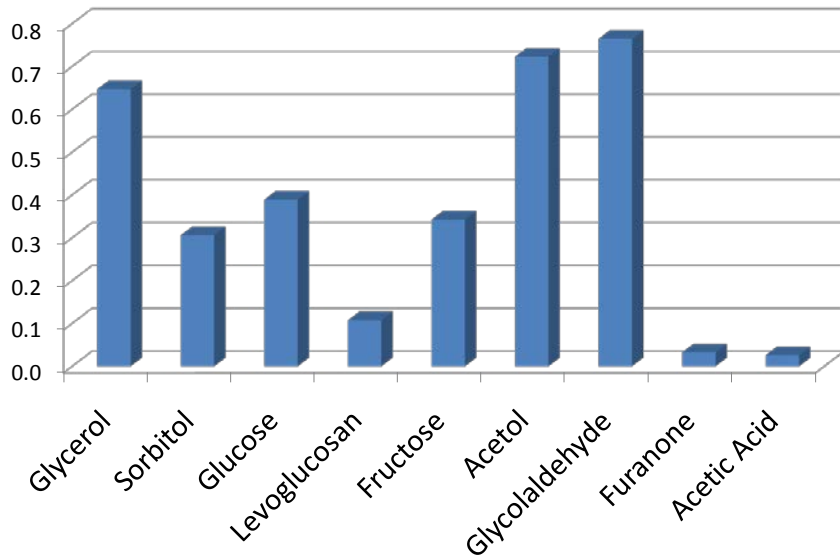


APR bio-oil Process Flow Diagram

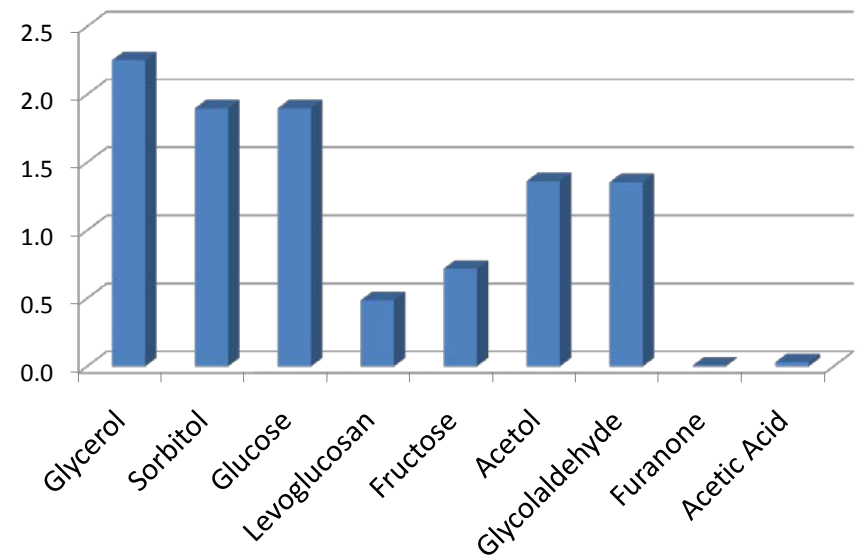


APR of Bio-oil Components (From 2011 Merit Review Presentation)

Conversion to CO₂ (carbon based)



H₂ Yield (mol. H₂/mol. Feed)



- These results need to be improved through better catalyst selection
- Furanone and acetic acid are especially unreactive at 225°C and have low available H₂ content
- Acetic acid depressed conversion of other components with the Pt-Re/C catalyst

ATR-IR setup:

