

Bio-Derived Liquids Reforming

Yong Wang, Dave King, Xianqin Wang,
Gordon Xia, and Tom Peterson

Pacific Northwest National Laboratory

May 15, 2007

Project ID #: PD4

Overview

Timeline

- Project start date: Oct. 1, 2004
- Two projects consolidated in 2007
 - Aqueous phase reforming of sugar and sugar alcohols
 - Vapor phase reforming of ethanol
- Project end date: on-going
- Percent complete: 15%

Budget

- Funding received in FY04: \$100K
- Funding received in FY05: \$500K
- Funding received in FY06: \$0K
- Funding for FY07: \$550K

Barriers

- A: Reformer Capitol Cost
- C: Operation & Maintenance
- D: Feedstock Issues
 - Identify better catalysts to improve yield and selectivity
 - Reduce capital, operation, and maintenance cost, and improve process efficiency
- 2017 target: <\$3.00/gge with 65-75% production unit energy efficiency

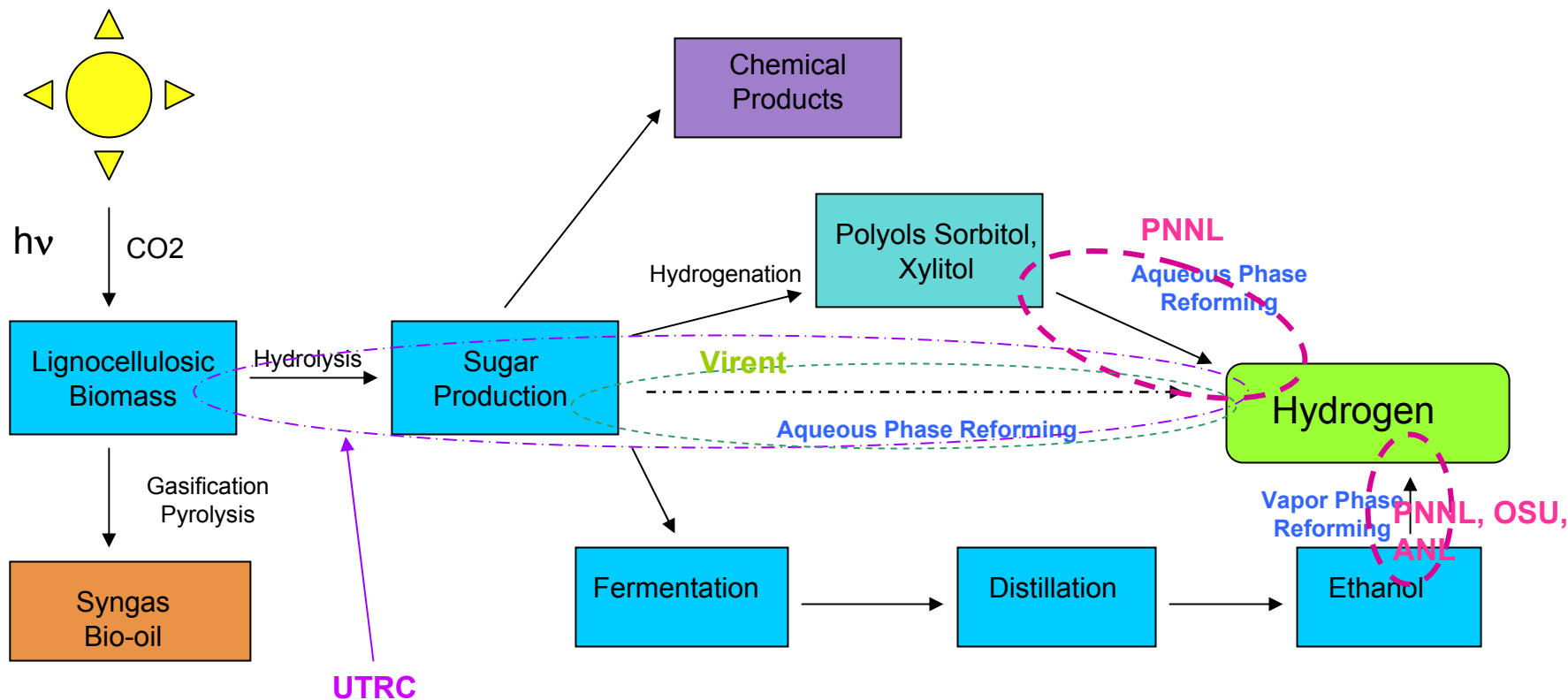
Partners and Collaborators

- Virent Energy Systems - catalyst
- DTI - process economics
- OSU – ethanol vapor phase reforming
- Shell Hydrogen – under discussion
- Ethanol producers - under discussion

Objectives

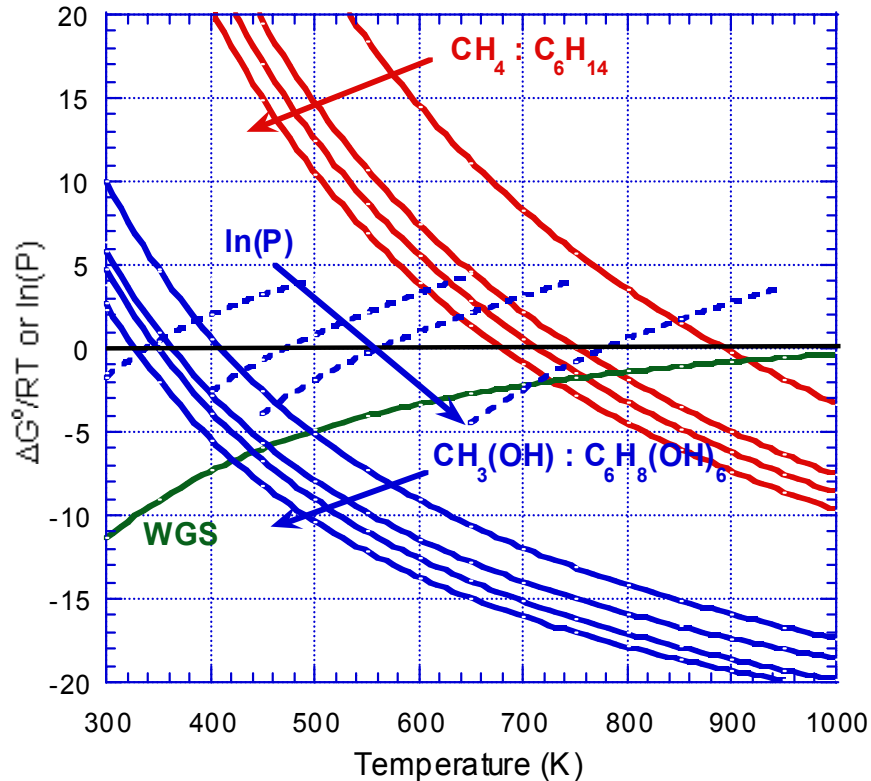
Overall	<ul style="list-style-type: none">• Assist DOE in evaluating and developing alternatives to gasification and pyrolysis of biomass for hydrogen production that can meet the DOE 2017 cost target of <\$3.00 /gge
2007	<ul style="list-style-type: none">• Develop stable and selective catalysts for vapor phase reforming of ethanol to produce hydrogen• Understand the reactivity and selectivity of APR intermediates to enhance the hydrogen productivity
2008	<ul style="list-style-type: none">• Develop catalysts, reaction conditions, and reactors for vapor phase reforming of ethanol to produce hydrogen• Develop APR catalysts, reaction conditions, and reactors to produce hydrogen from sorbitol

Production of Hydrogen in the Bio-refinery



- Vapor phase ethanol reforming:
 - PNNL: low temperature catalyst, catalyst stability, reaction engineering
 - OSU: Co based catalysts for superior selectivity
 - ANL: high pressure membrane reactor
- Aqueous phase reforming
 - PNNL: mechanistic understanding of intermediates, reaction engineering
 - Virent: glucose, glycerol, catalyst, small scale demonstration
 - UTRC: slurry phase hydrolysis + aqueous phase reforming of raw biomass

Reforming Thermodynamics



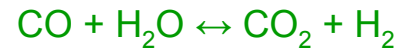
Reforming of Hydrocarbons



Reforming of Oxygenated Compounds



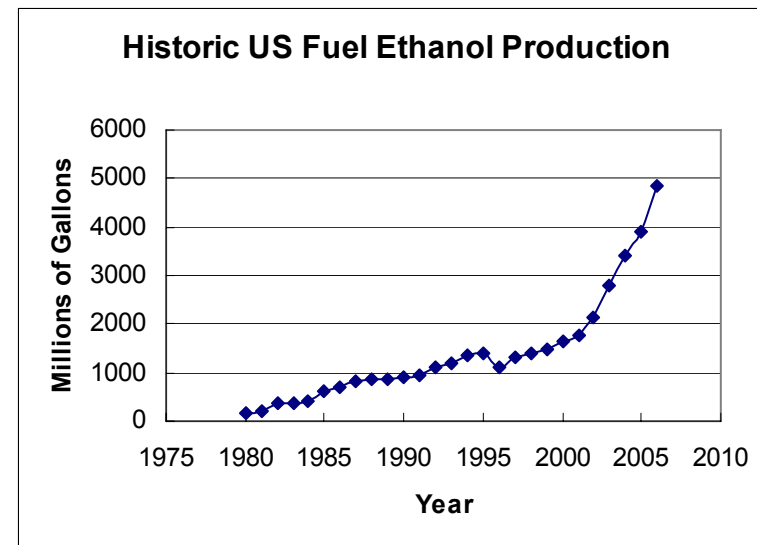
Water-Gas Shift



- Equilibrium is favorable for reforming of oxygenated compounds at low temperatures

Biomass Feedstocks

- Biomass can not meet all of the energy needs, but can provide a major contribution.
 - U.S. consumes 7×10^9 bbl/yr
 - Equivalent to 3.8×10^9 boe/yr (barrels of oil energy equivalent) biomass could be produced in U.S. (1.3×10^9 metric tons of dry biomass/year)
- Ethanol
 - An infrastructure fuel
 - Rapid expansion in production capacity in U.S (as of April, 2007)
115 plants with 5750 mgy production capacity
86 new plants under construction with additional 6337 mgy capacity
 - Competitive price with gasoline (US average on April 23, 2007)
Ethanol: \$2.42/E-100 gal
Gasoline: \$2.87/gal
 - Additional cost saving
 - No need for ethanol-water zeotropic separation
 - Breakthroughs in cellulose ethanol
 - Efficient in retaining hydrogen via sugar fermentation
 - Higher energy density
 - Transportable with minimal new delivery infrastructure
 - Solving near term hydrogen delivery issues



Advantages of Vapor and Aqueous Phase Reforming

- Vapor phase reforming
 - Provides high productivity
 - Has been conventionally practiced in steam reforming of natural gas
 - Less issues with the hydrothermal stability of catalyst supports
- Aqueous phase reforming
 - Allows processing of less refined and less expensive biomass feedstocks (sorbitol, glucose, etc) that are difficult to vaporize without decomposition
 - Compatible with processing wet feedstocks, eliminating energy required to vaporize excess water
 - Operates at low temperatures compared with conventional reforming, reducing energy costs and also favoring water gas shift reaction
 - Pressurized product is compatible with membrane or pressure swing H₂ purification

Vapor Phase Ethanol Reforming Options

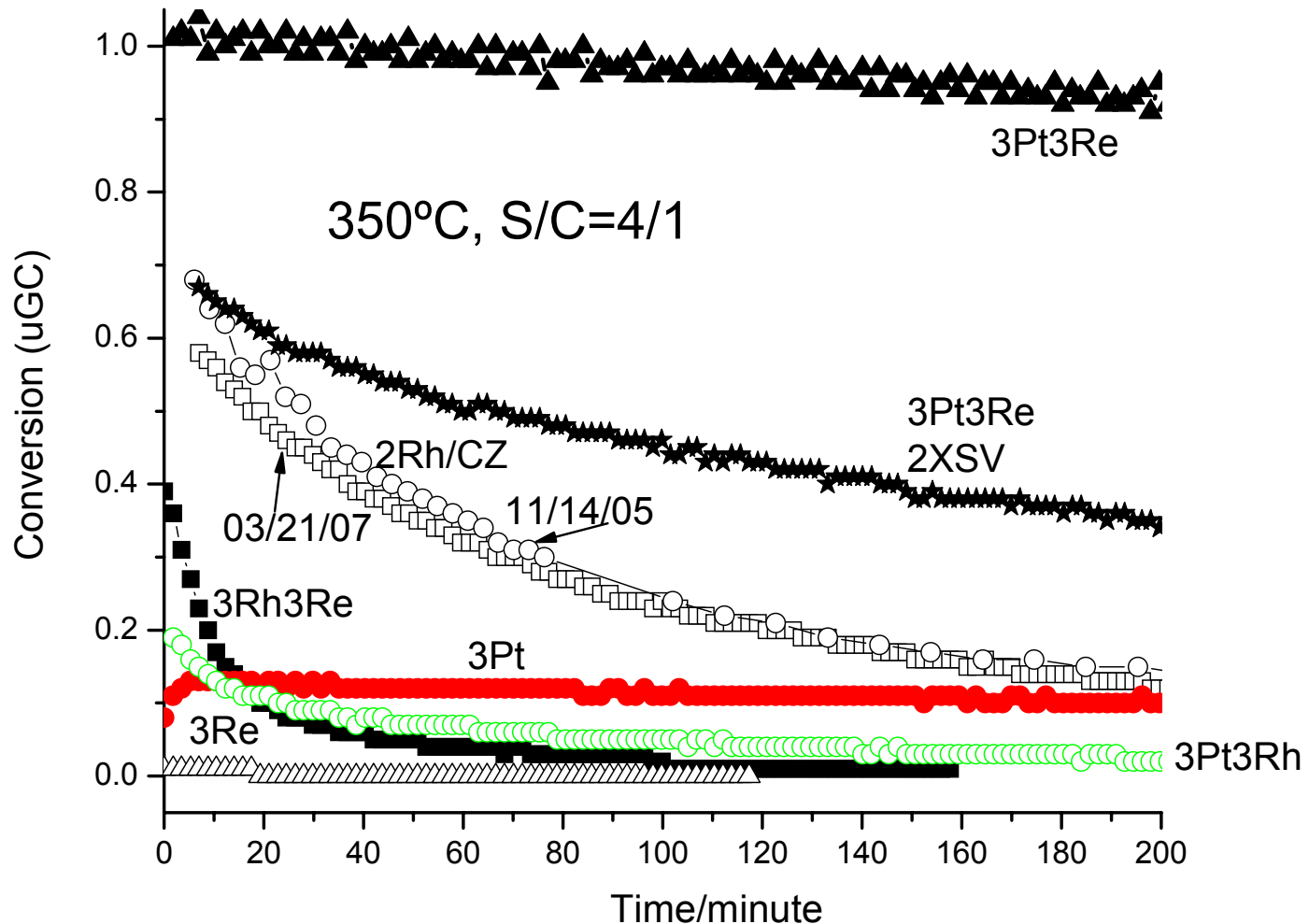
- Low temperature SR (<500°C)
 - Potentially less energy intensive
 - Matches with membrane separation
 - Rapid catalyst deactivation (except the work at Monsanto on Cu-Ni which only facilitates ethanol dehydrogenation and acetaldehyde decomposition, yielding one mole H₂/mole ethanol converted)
- High temperature SR (>500°C)
 - High temperatures facilitates subsequent conversion of parallel product methane
 - Less favored WGS, needs CO clean up unless for SOFC
 - Catalyst deactivation could be masked by excess activity
- Oxidative SR (e.g., work at U of Minnesota and Penn State)
 - Stable catalyst life
 - Complex with O₂ addition and dilution of N₂ in reformat

A Highly Selective and Active 2wt%Rh on CeO₂-ZrO₂ Was Previously Developed at PNNL

Catalyst	X _{EtOH} (%)	H ₂ /EtOH (m/m)	S _{CH₄} (%)	S _{CO} (%)	S _{CO₂} (%)
2%Rh/Ce_{0.8}Zr_{0.2}O₂	100	4.3	25	11	64
2%Rh/Ce _{0.6} Zr _{0.4} O ₂	100	4.0	26	18	56
2%Rh/Ce _{0.4} Zr _{0.6} O ₂	100	4.0	27	20	53
2%Rh/Ce _{0.2} Zr _{0.8} O ₂	95	3.6	28	21	50
2%Rh/CeO ₂	53	1.9	22	32	39

450°C, SV: 133,000 ml/g-h; H₂O/EtOH/N₂ = 8/1/10.6, Data obtained at 10 h TOS

Improved Catalyst Activity and Stability



- Rapid catalyst deactivation on 2wt%Rh/CeO₂-ZrO₂ due to soft carbonaceous deposit
- 3%Pt3%Re/C exhibits improved stability with higher activity

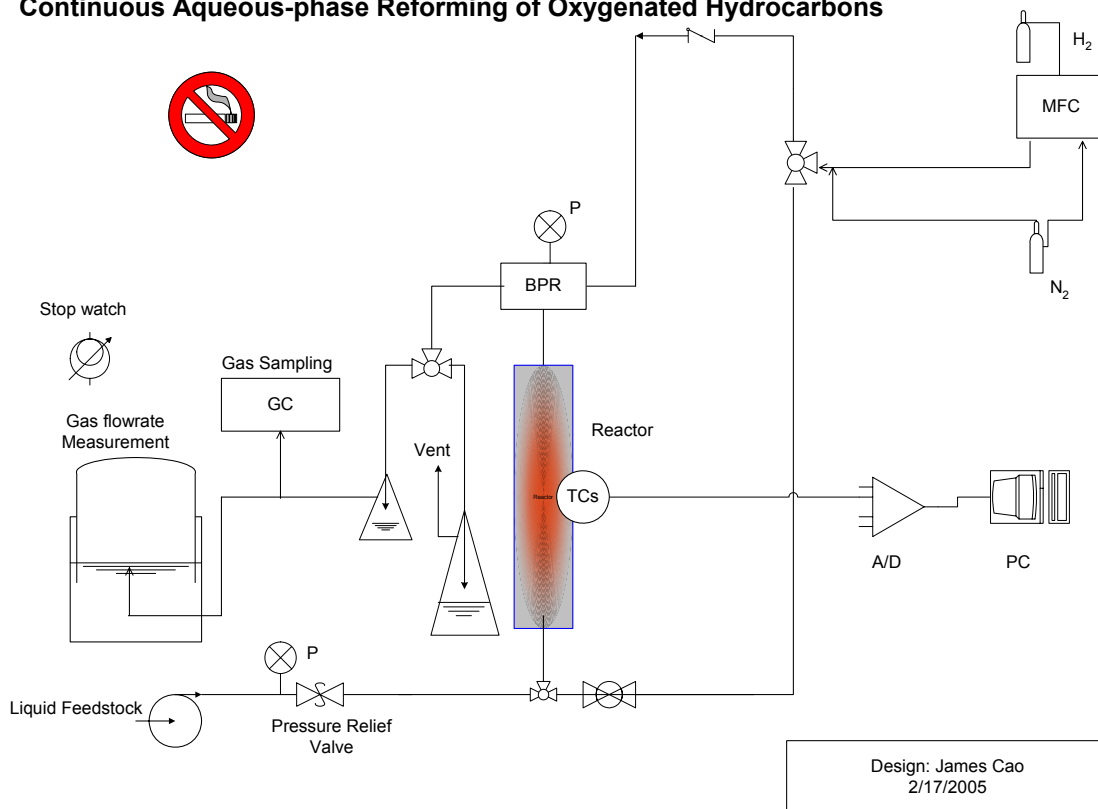
Aqueous Phase Reforming

Approach

- Virent has developed highly active catalysts, which were used to leapfrog the verification of the potential heat transfer issue
- Constructed an isothermal microchannel reactor for catalyst screening and mechanistic studies
- Established a complete product analysis to guide the understanding of reaction mechanisms
- Developed new catalysts based on a hydro thermally stable C support and bimetallic catalysts
- Studied intermediates on a promising catalyst to
 - Develop feedstock structure/reactivity relationships
 - Identify the needs of feed preprocessing, catalyst improvement, reaction condition optimization (e.g., pH or base component)
- Improve bimetallic catalysts
- Reaction engineering innovations

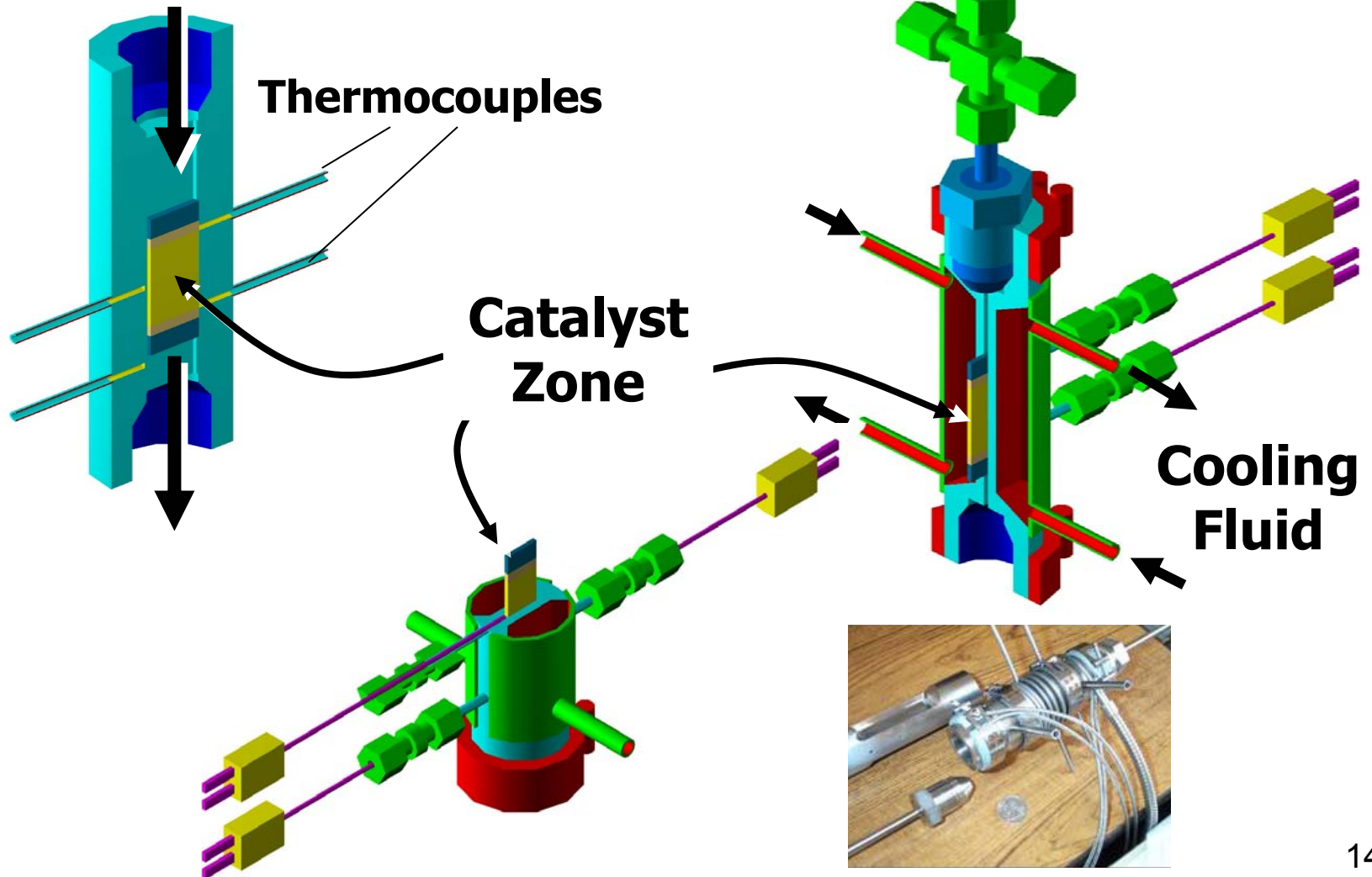
Technical Progress: Continuous Aqueous-phase Reforming Unit

Continuous Aqueous-phase Reforming of Oxygenated Hydrocarbons



Isothermal Reactor Details

Process Flow



Validating Previous APR Results of Sorbitol over Virent Catalyst

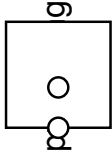

(Runs at different time : 2007 vs 2005)

10% Sorbitol, Virent Catalyst, 225°C, 420~425psi

Run ID	MC-APR-07-06 (new run)	MC-APR-08 (2005)	MC-APR-07-05 (new run)	MC-APR-13 (2005)
Run Temp#(oC)	225	225	225	225
BPR (psi)	425	420	425	420
Feed	10% Sorbitol	10% Sorbitol	10% Sorbitol	10% Sorbitol
Contact Time (min)	7.79	7.68	3.89	3.84
Conversion of substrate	99.88%	100.00%	98.73%	96.76%
% Carbon in gas-phase effluent	88.73%	71.50%	67.80%	56.28%
% Carbon in liquid-phase effluent	9.60%	12.60%	29.47%	48.34%
Sel#%H2	42.58%	37.31%	28.02%	28.33%
Sel#%CHx	38.85%	21.28%	31.18%	15.94%
Carbon Balance	0.98	0.84	0.97	1.04
Hydrogen Productivity (STD L/L-cat/h)	521	460	767	686
Hydrogen	52.82%	54.13%	52.51%	52.22%
CO	0.00%	0.00%	0.29%	0.15%
CO2	34.65%	37.72%	36.48%	41.44%
Methane	5.50%	6.09%	4.45%	4.49%
Ethane	2.31%	2.06%	1.83%	1.70%
C3	3.49%		2.52%	
C4	0.26%		0.17%	
C5	0.03%		0.03%	

- Reproducible results (both conversion and H₂ selectivity) under two different contact times
- More complete gas product analysis with the current setup



Tubular vs. Microchannel Reactor Comparison (Virent Catalyst)

<i>Aqueous phase reforming (continuous PFR)</i>			
			micro-channel
Run ID	AR 56-1	AR 53-1	MC-APR-01
Reactor	1/2" tubular	1/4" tubular	Microchannel 0.06" gap
Liquid feed	10% Sorbitol	10% Sorbitol	10% Sorbitol
P (psig)	420	420	420
T inlet (°C)	225	225	225
T bed (°C)	218.6	223	225
T wall (°C)	228	226	228 (heat transfer fluid)
LHSV	8.96	8.79	7.58
WHSV	1.20	1.20	1.00
Reforming Results			
H ₂ productivity (l/l cat/hr)	266	342	456
Carbon conversion to gas	43%	40%	76%
Sorbitol conversion	100%	99%	99%
H ₂ selectivity	51%	60%	62%
Alkane selectivity	20%	19%	20%
H ₂ /CO ₂	1.1	1.3	1.3
H ₂ /CH ₄	7.5	9.9	9.4

Microchannel reactor operation results in

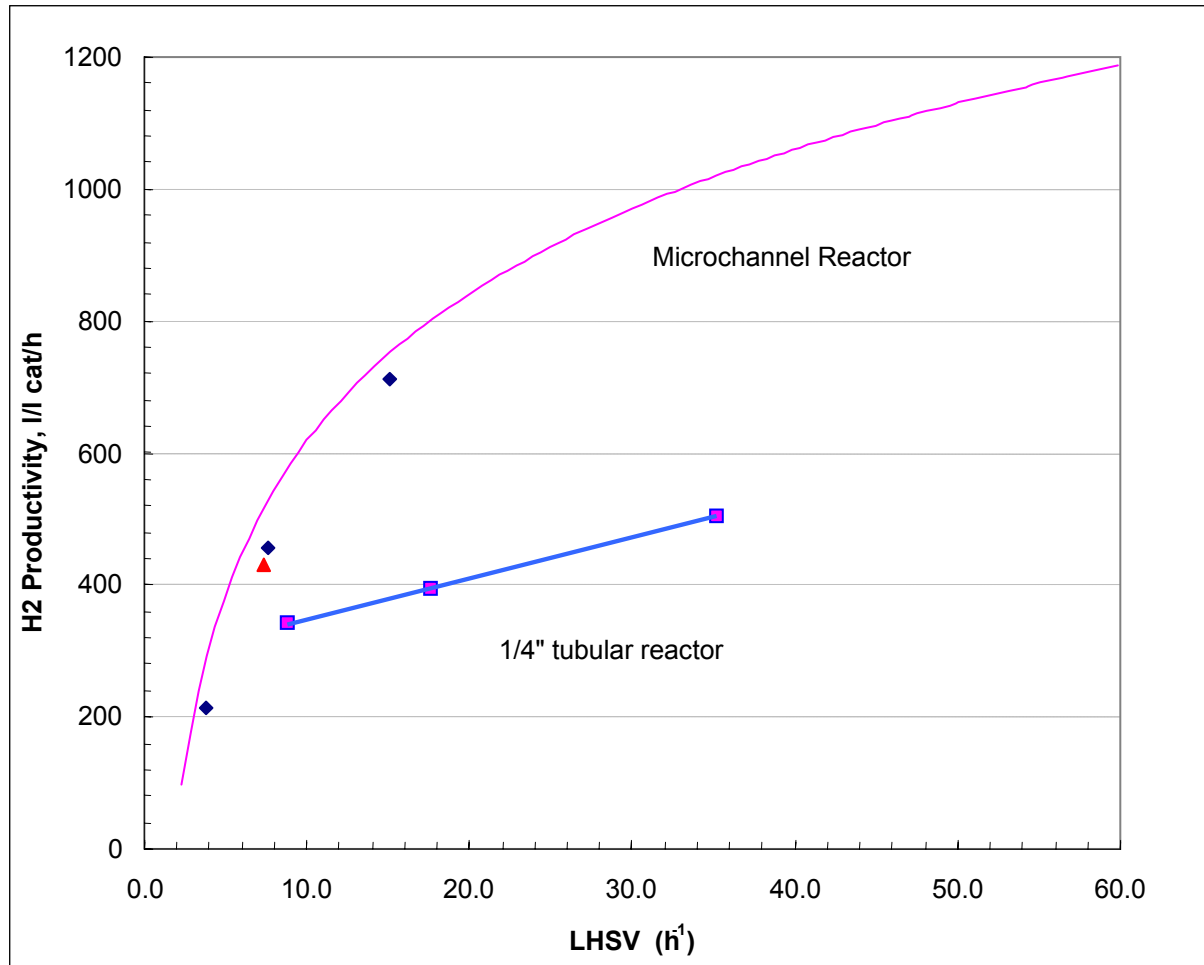
- Minimization of reaction endotherm in catalyst bed
- Greater production of gas phase product at no loss of selectivity
- Greater H₂ productivity

Tubular vs. Microchannel Reactor Comparison (Virent Catalyst)

<i>Aqueous phase reforming (continuous PFR)</i>			
			micro-channel
Run ID	AR 56-1	AR 53-1	MC-APR-01
Reactor	1/2" tubular	1/4" tubular	Microchannel 0.06" gap
Catalyst	Virent T1	Virent T1	Virent T1
Liquid feed	10% Sorbitol	10% Sorbitol	10% Sorbitol
<i>Liquid phase analysis (wt%)</i>	<i>Not analyzed</i>		
Glucose		0.024%	0.033%
Sorbitol (C ₆ H ₁₄ O ₆)		0.189%	0.090%
Arabitol + xylitol		0.093%	-
Erythritol + Threitol (C ₄ H ₁₀ O ₄)		0.137%	-
Glycerol (C ₃ H ₈ O ₃)		0.363%	0.002%
Ethylene Glycol (C ₂ H ₆ O ₂)		0.151%	-
Propylene glycol (C ₃ H ₈ O ₂)		0.797%	-
Methanol		0.597%	0.078%
Ethanol (C ₂ H ₆ O)		0.418%	0.007%
2-Propanol (C ₃ H ₈ O)		0.101%	0.093%
Acetone		0.099%	0.118%
1-Propanol (C ₃ H ₈ O)		0.042%	0.009%

- More complete liquid product conversion in a microchannel reactor
- Concentration of isopropanol and acetone similar in two cases

Hydrogen Productivity Projections Show Advantages of Microchannel Reactor



Effect of Feed Rate on Sorbitol Products (Microchannel Reactor, Virent Catalyst)

Run Temp. °C	225	225	225	225
BPR (psi)	420	420	420	420
Sorbitol Conc. (wt%)	10%	10%	10%	10%
WHSV (g sorbitol/g-cat/h)	1.0346	2.0692	3.1038	4.1384
Contact Time, min	7.68	3.84	2.56	1.92
Sorbitol Conversion	100.0%	96.8%	88.3%	78.7%
% Carbon in gas-phase effluent	71.55%	56.28%	36.30%	22.57%
Hydrogen	54.13%	52.22%	49.15%	47.23%
CO ₂	37.72%	41.44%	44.77%	46.64%
Ethane+ethylene	2.06%	1.70%	1.58%	1.48%
Methane	6.09%	4.49%	4.29%	4.43%
CO	0.00%	0.15%	0.21%	0.23%
H ₂ /CH ₄	8.90	11.63	11.46	10.67
H ₂ /C ₂	26.30	30.73	31.08	31.99

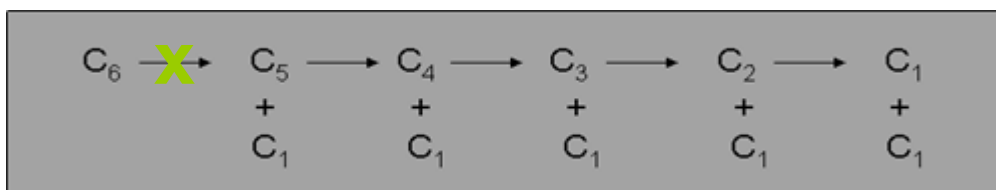
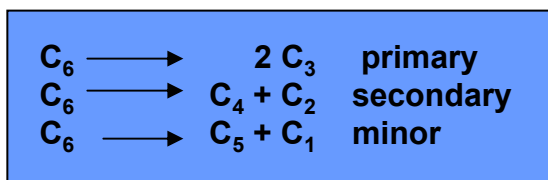
- A microchannel reactor allows mechanistic studies at incomplete conversions under isothermal conditions
- Liquid products at incomplete conversion of sorbitol may provide information on reaction pathways and intermediates
- Higher space velocities result in greater production of liquid products with only modest changes in gas phase product composition

Effect of Feed Rate on Sorbitol Products (Microchannel Reactor, Virent Catalyst)

WHSV g sorbitol/g catalyst-h) 1.0 2.1 3.1 4.1

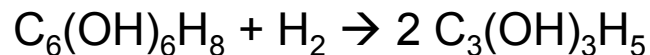
<u>Liquid phase composition (wt%)</u>				
Glucose (C6H12O6)	0.036	0.029	0.037	0.05
Sorbitol (C6H14O6)	0.002	0.33	1.23	2.172
Glycerate (C3H5O4)		0.153	0.307	0.347
Xylitol (C5H12O5)	0.004	0.107	0.236	0.29
Erythritol + threitol (C4H10O4)		0.191	0.316	0.342
Glycerol(C3H8O3)	0.004	0.504	0.822	1.018
1,2,4-Butanetriol (C4H10O3)		0.09	0.132	0.144
Acetic acid (C2H4O2)	0.075	0.1	0.098	0.085
Ethylene Glycol (C2H6O2)		0.275	0.39	0.428
Propylene glycol (C3H8O2)		0.796	0.897	0.941
1,3-Propanediol (C3H8O2)	0.001	0.168	0.161	0.219
Methanol (CH3OH)		0.171	0.199	0.154
1,2-Butanediol(C4H10O2)		0.148	0.166	0.162
Ethanol(C2H6O)	0.036	0.261	0.235	0.216
2-Propanol(C3H8O)	0.223	0.182	0.128	0.088
1-Propanol(C3H8O)		0.147	0.167	0.12

- **Glycerol and propylene glycol are most predominant products**
- **C₄ and C₂ polyols are in approximate balance**
- **Oxygenated products are more consistent with random C-C cleavage than sequential C₁ cleavage**

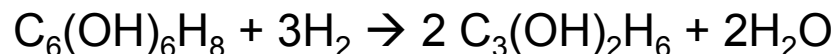


Reaction Pathways

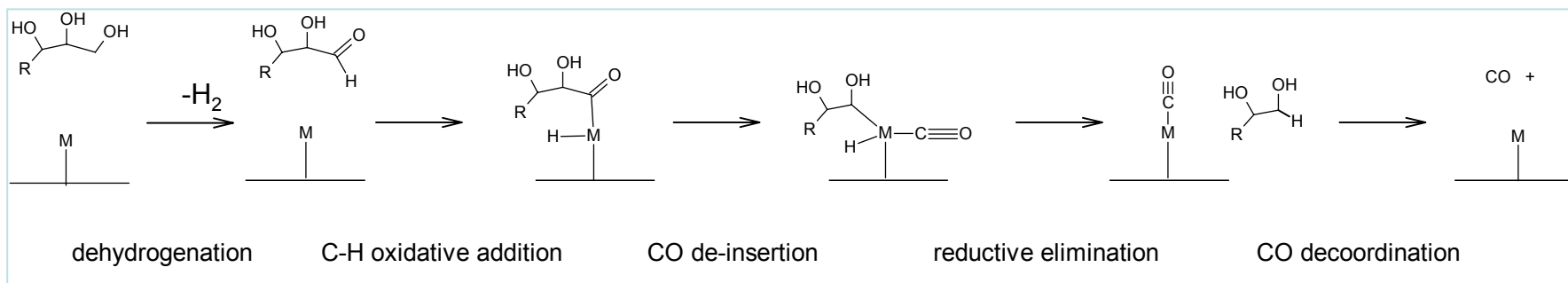
- Random C-C cleavage reduces hydrogen selectivity
 - Production of glycerol from sorbitol requires hydrogenation



- Production of propylene glycol from glycerol requires combination of hydrogenation plus dehydration



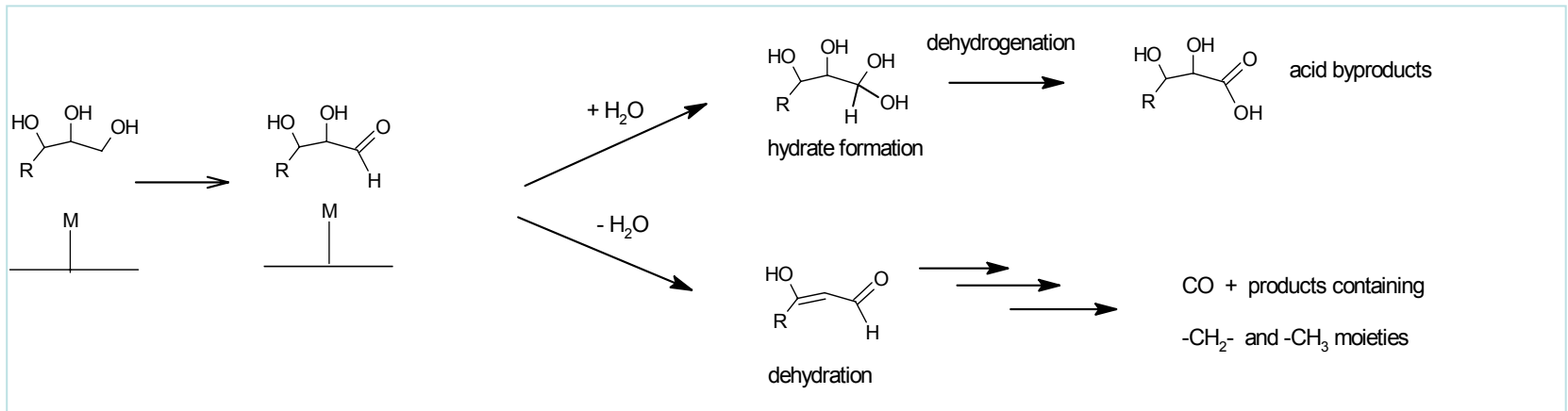
- Catalyzed terminal cleavage, if possible, could lead to improved hydrogen selectivity



First step is dehydrogenation to form the corresponding aldehyde;
 Wilkinson's catalyst (organometallic); heterogeneous examples?

Origins of Reaction By-products

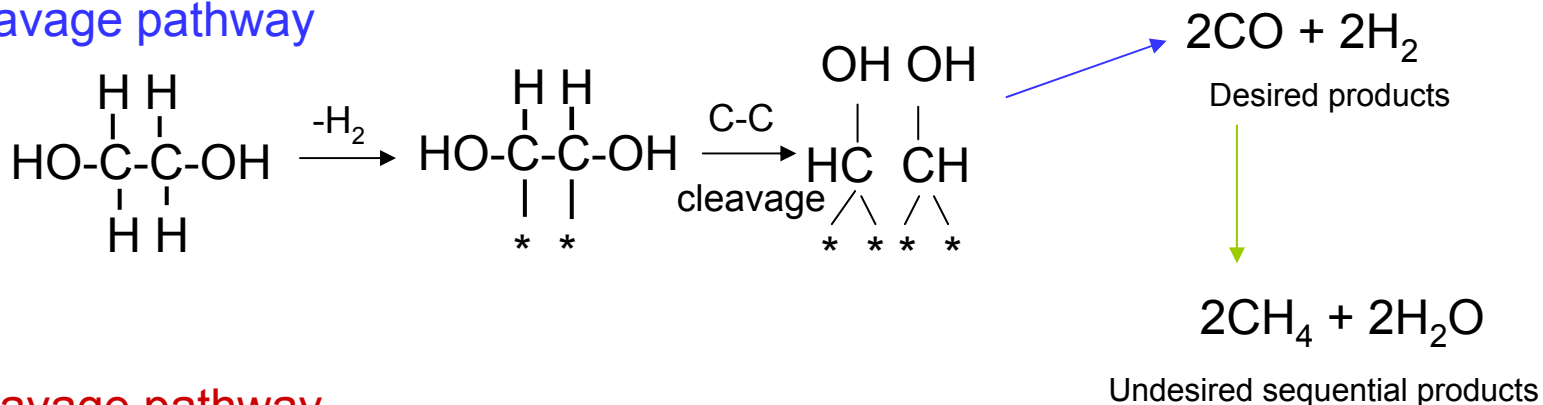
- Hydration followed by dehydrogenation of aldehyde hydrate can lead to acid formation.
- Dehydration (to α , β -unsaturated carbonyls) generates methane and products containing $-\text{CH}_2-$ and $-\text{CH}_3$ moieties
 - Maximizing hydrogen production requires avoiding dehydration of reaction intermediates that subsequently hydrogenate to final alkane products



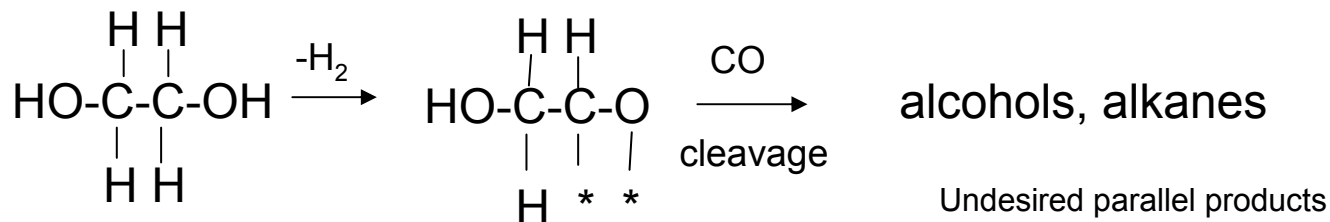
Hydrate formation and dehydration are usually acid- or base-catalyzed reactions and might be promoted by the catalyst support and base in the feed. Understanding support and base effects could be critical to improving selectivity.

Kinetic Control of Reaction Pathways* is Essential For Good Hydrogen Production

C-C cleavage pathway



C-O cleavage pathway

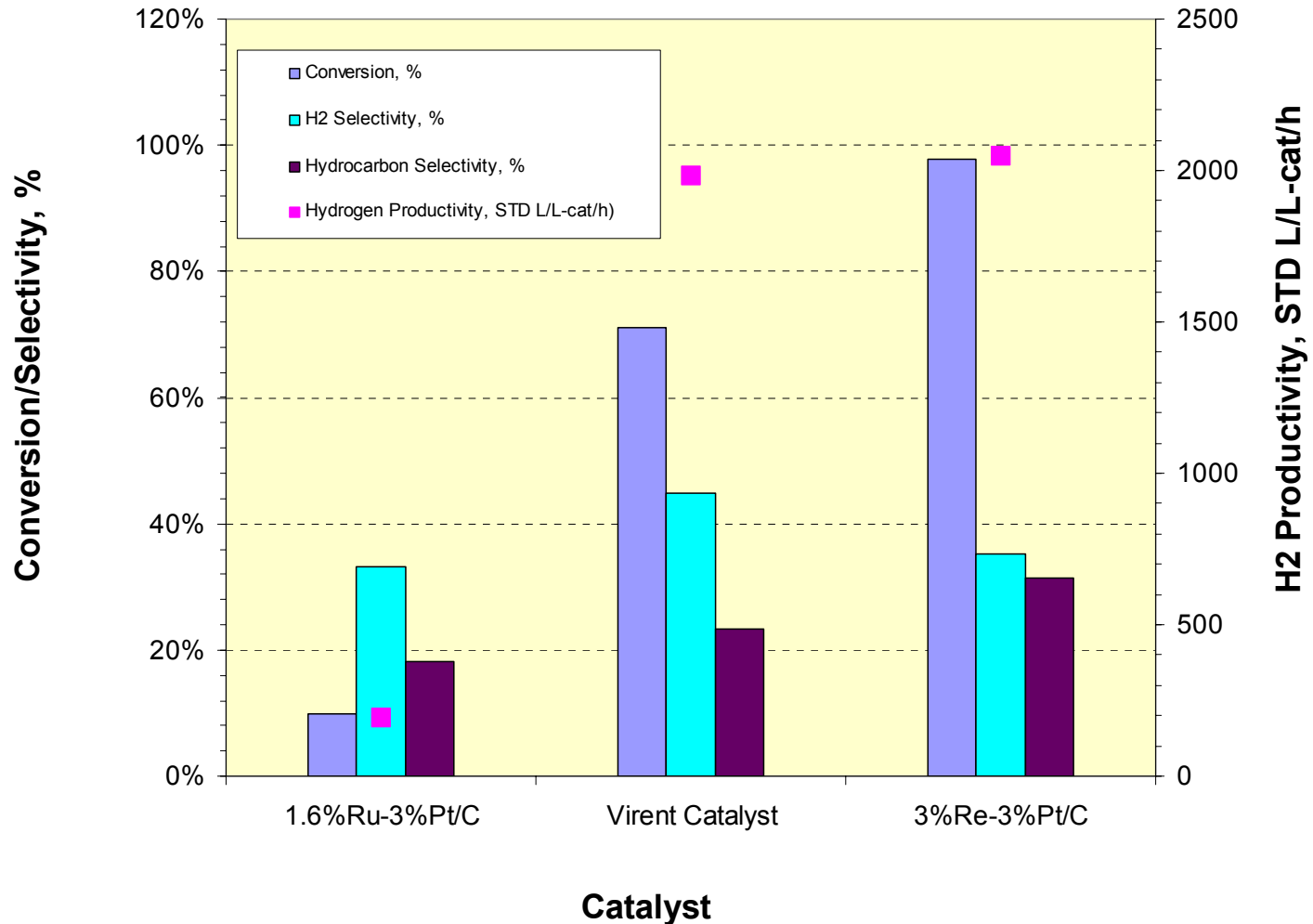


Good catalyst should have good C-C cleavage and water gas shift activity, low C-O bond cleavage and methanation activity

* Adapted from Davda et. al., *Appl. Catal. B*, **56** (2005), 171-186

Catalyst Activity Comparison

10% EG, 225°C, 420psi, CT=1.95~1.97min

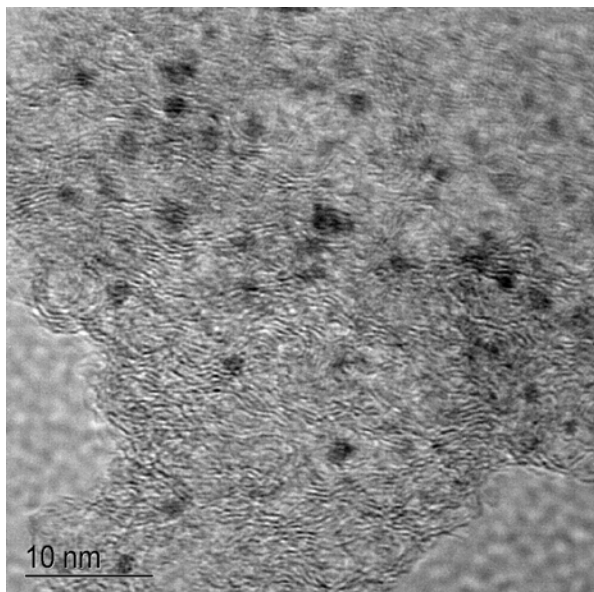


- 1.6%Ru-3%Pt/C was the most active catalyst previously developed at PNNL, but much less active than Virent catalyst.
- Virent catalyst was used to validate the needs in heat transfer improvement
- 3%Pt-3%Re/C catalyst recently developed at PNNL has similar activity and selectivity as that of Virent and can be used for mechanistic studies

Catalyst Characterization Results

Catalyst	Irreversible H uptake ($\mu\text{mol/g}$)	H: (total metal) atomic ratio	BET surface area (m^2/g catalyst)	Pore volume ml/g	Pore size nm
PtRe/C (3wt.% Pt, 3.15wt.% Re)	57.1	0.18	573	0.44	3.0
C support, Engelhard	-		575	0.42	

TEM

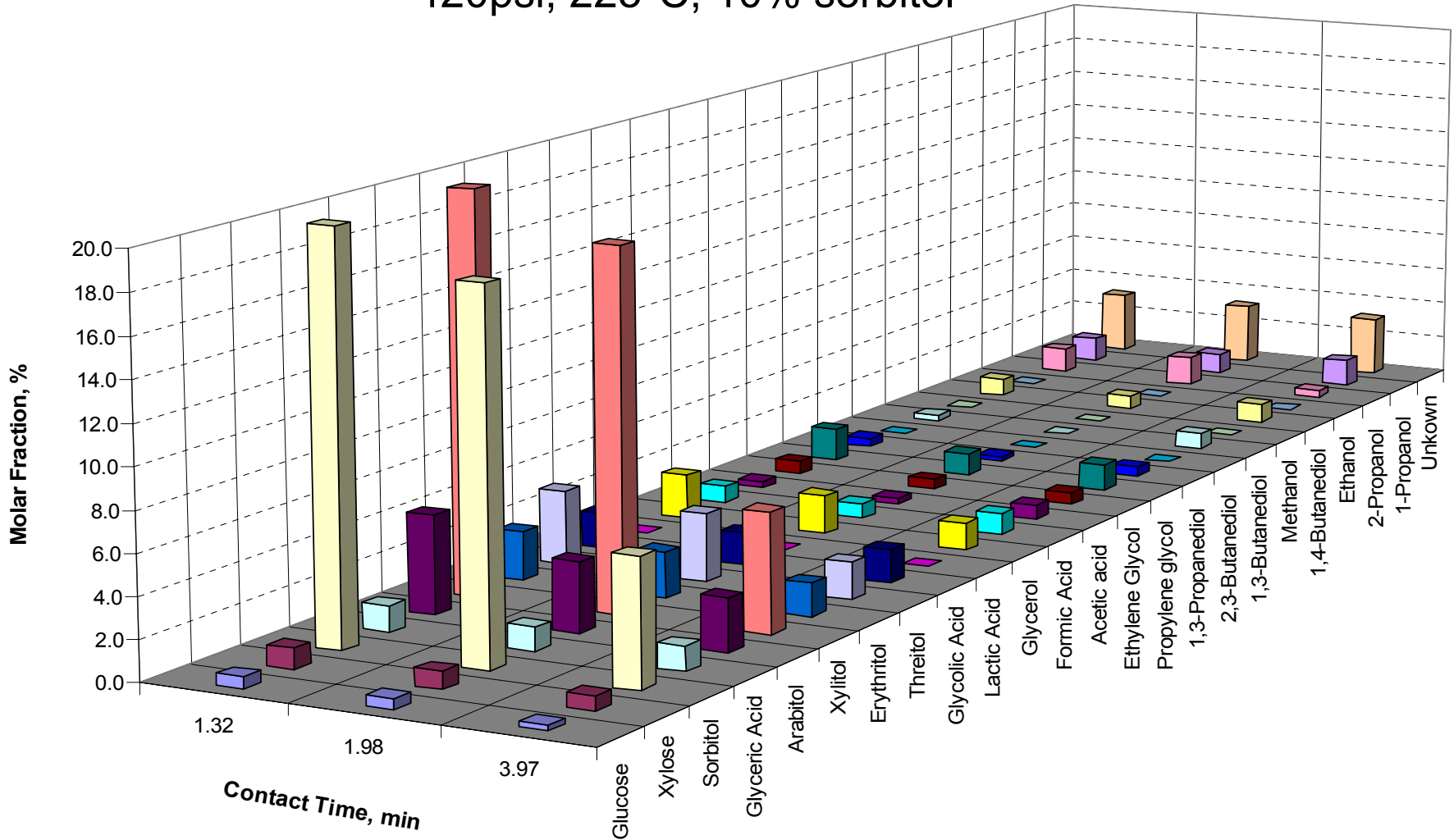


Metal Particle Size Comparison

	PtRe/C
TEM	1-3nm
H/Pt	2-3nm

APR of Sorbitol on 3%Pt3%Re/C

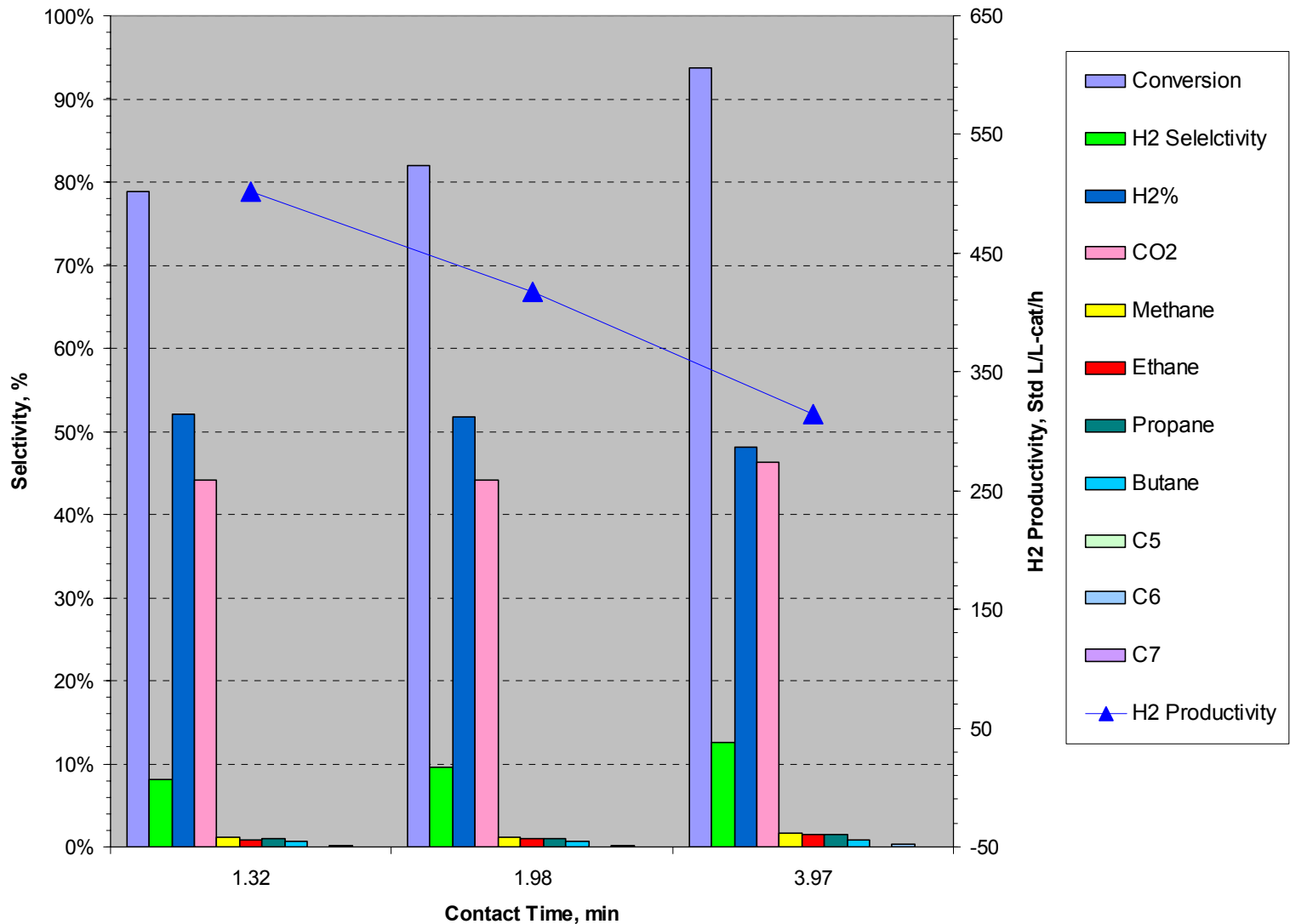
420psi, 225°C, 10% sorbitol



- Liquid products include C₁-C₅ oxygenate intermediates

APR of Sorbitol on 3%Pt3%Re/C

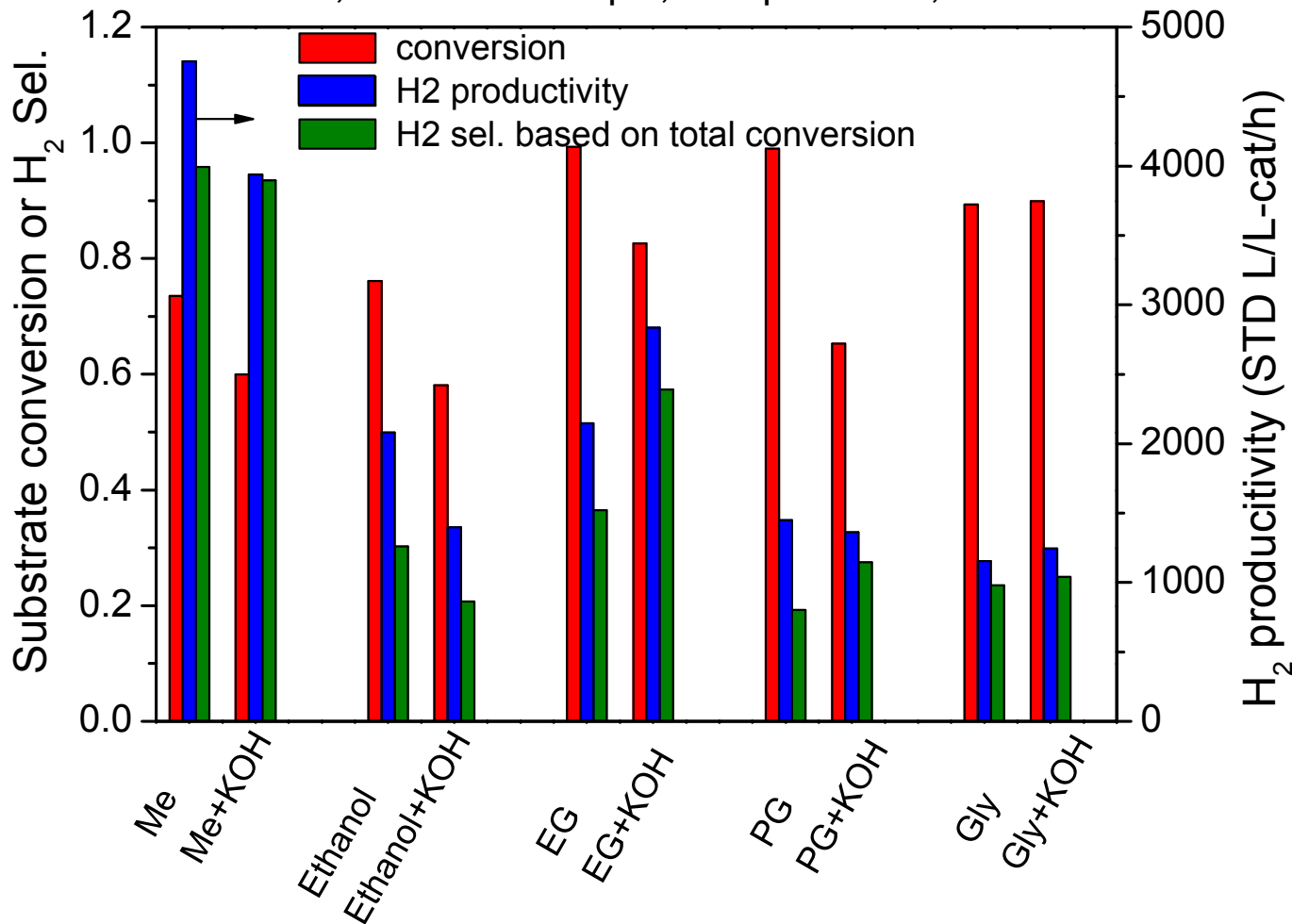
420psi, 225°C, 10% sorbitol



- Gas phase products include C₁-C₆ alkanes which hurt hydrogen selectivity

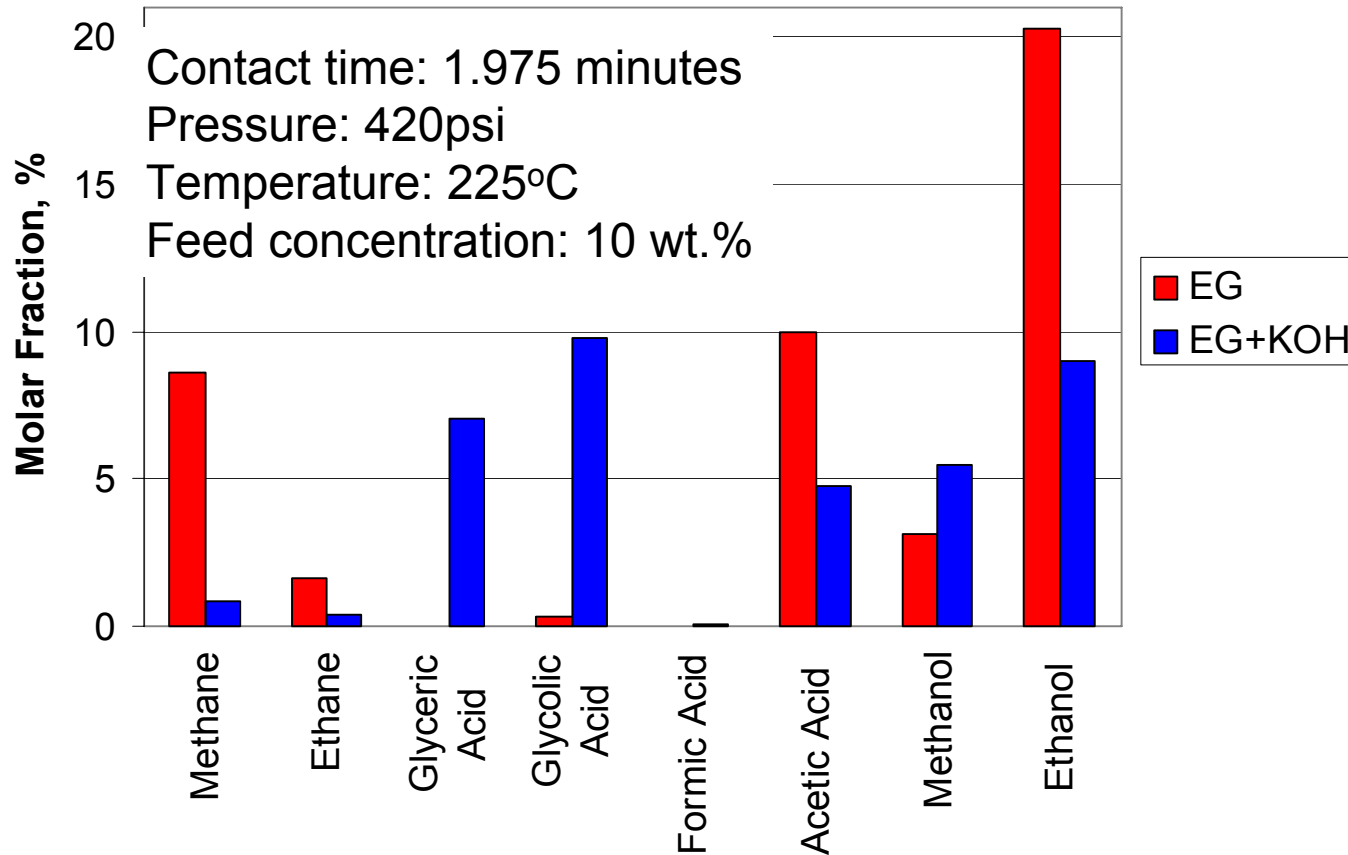
Reactivity of Intermediates and the Effects of KOH Addition

Contact time: 1.975 minutes; Pressure: 420psi; Temp.: 225°C; Feed concentration: 10 wt.%



- H₂ selectivity: EG > ethanol, GLY > PG
- H₂ productivity: methanol > EG > GLY
- EG is a preferred intermediate, addition of KOH significantly increases the H₂ selectivity and productivity from EG.
- Methanol was studied to demonstrate minimal activity in Fisher-Tropsch synthesis, formation of alkanes likely from other pathways.

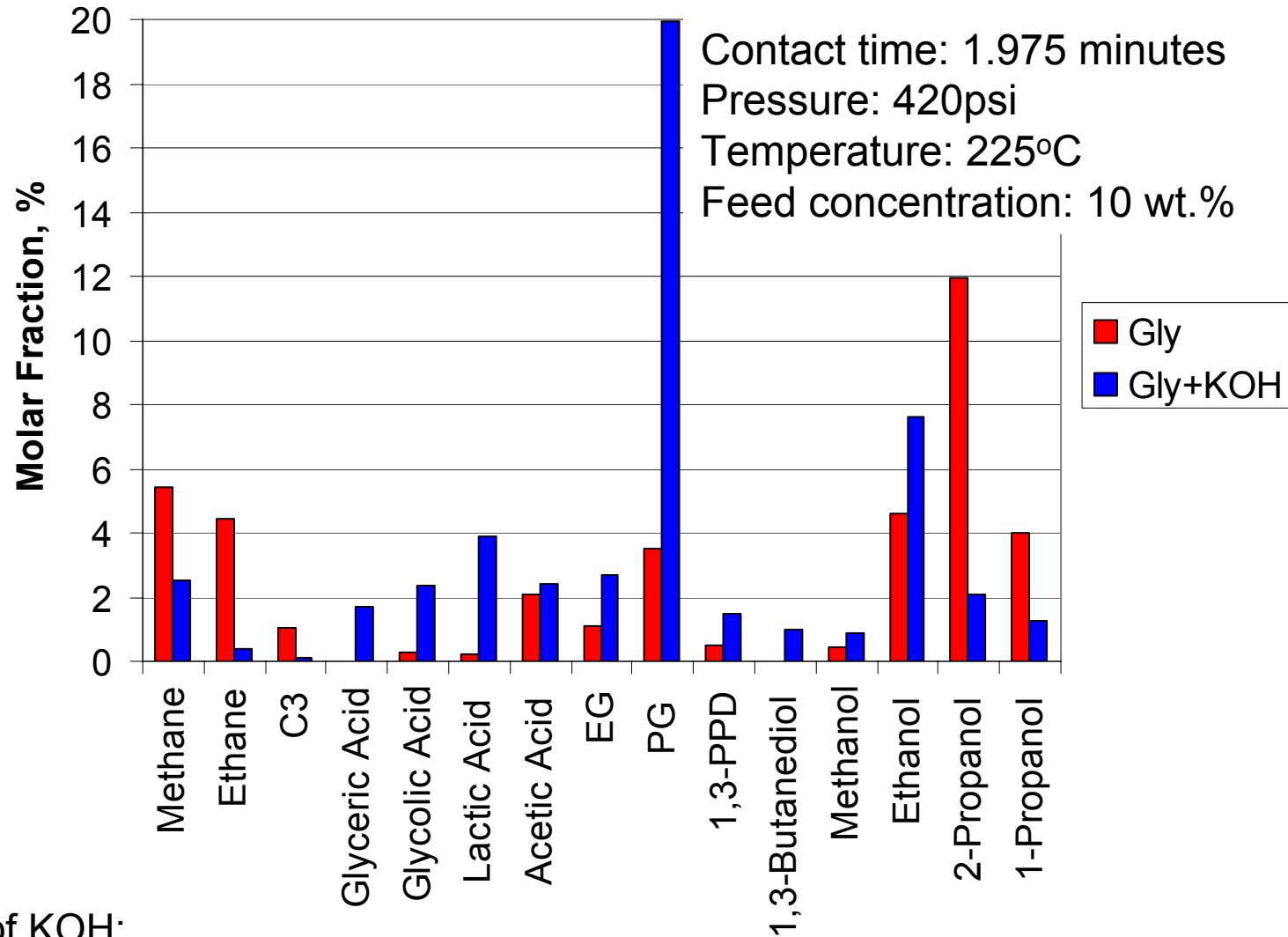
The Effect of KOH on Product Distribution - EG



Addition of KOH:

- Reduces alkane formation - preferred
- Increases acid formation – less preferred

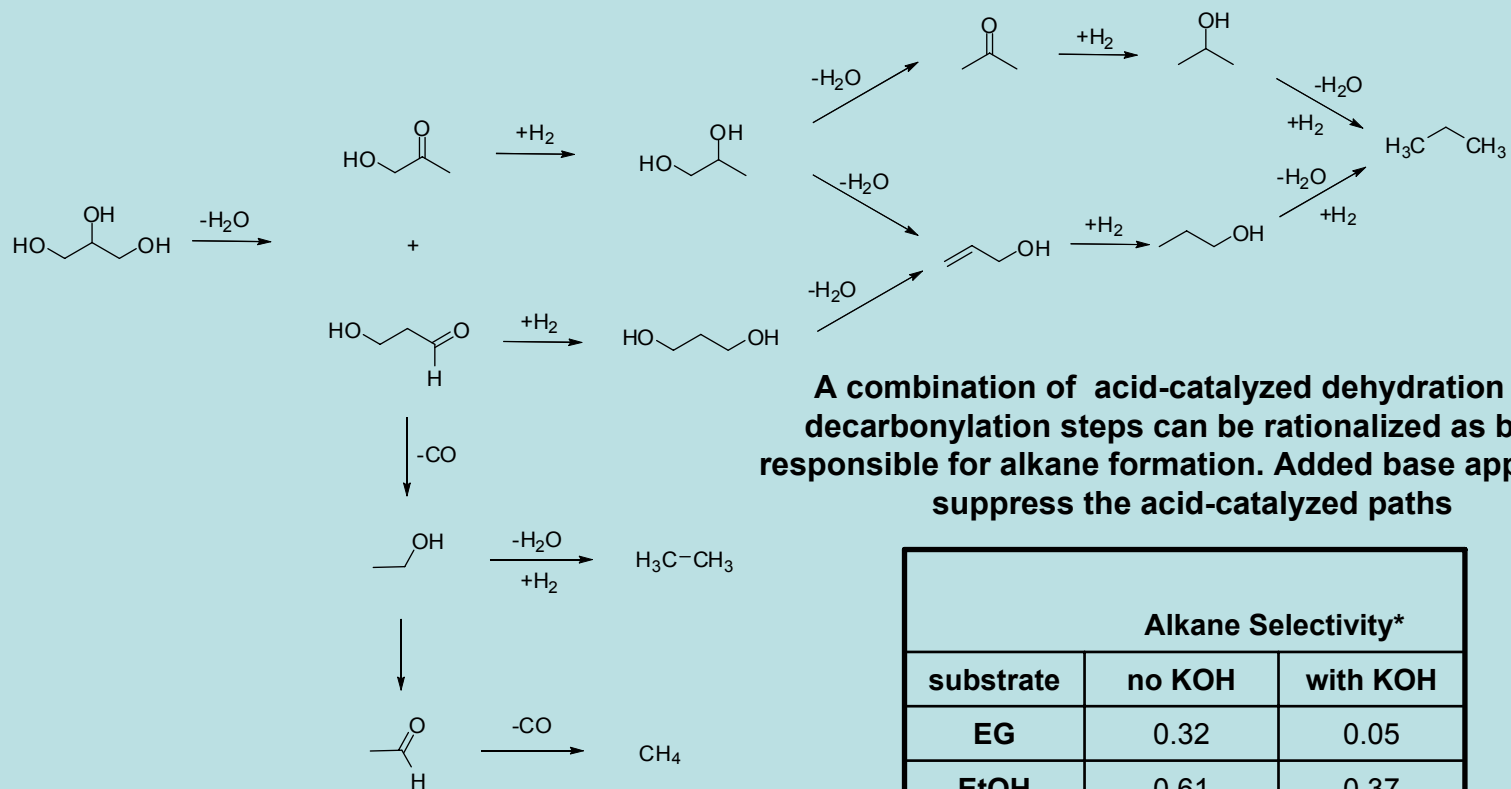
The Effect of KOH on Product Distribution - Glycerol



Addition of KOH:

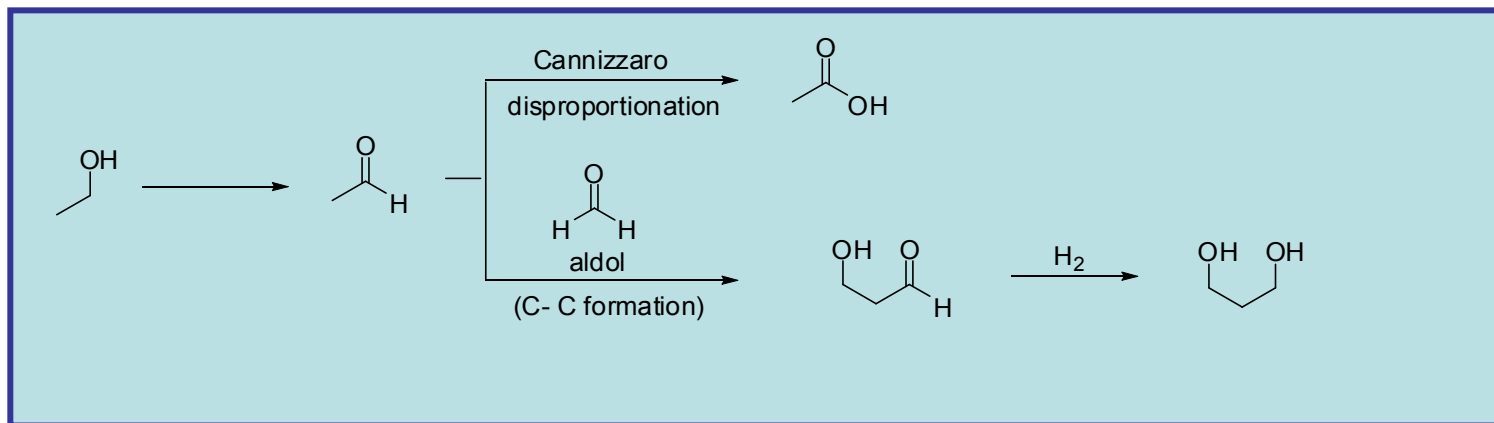
- Reduces alkane formation - preferred
- Increases acid formation – less preferred
- Increases PG formation, forms more complicated products than that from EG

KOH Suppresses the Acid-Catalyzed Pathways to Alkanes



*Alkane selectivity calculated on hydrogen basis at residence time = 3.95 minutes

KOH Catalyzes Pathways to Acids and C_{n+1} Products

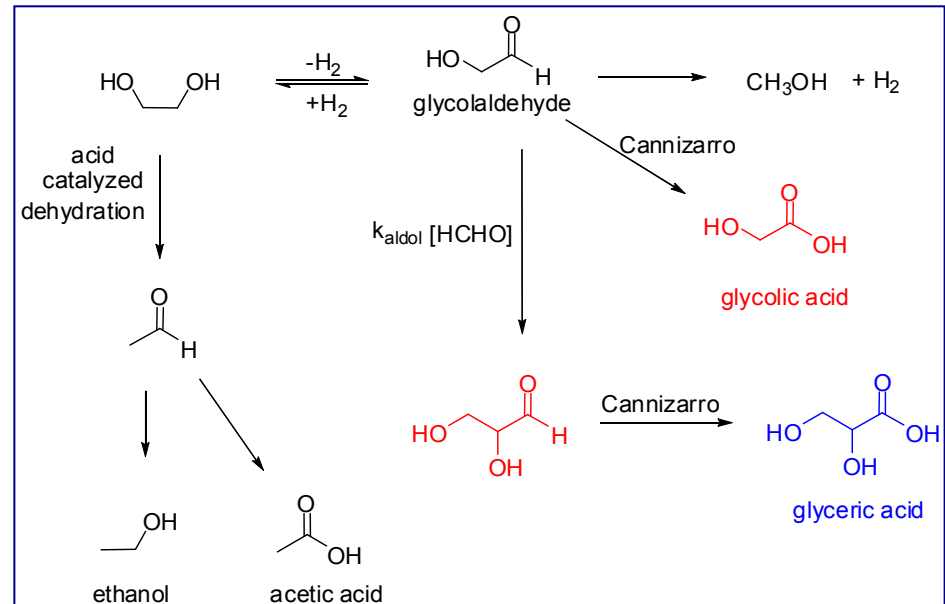
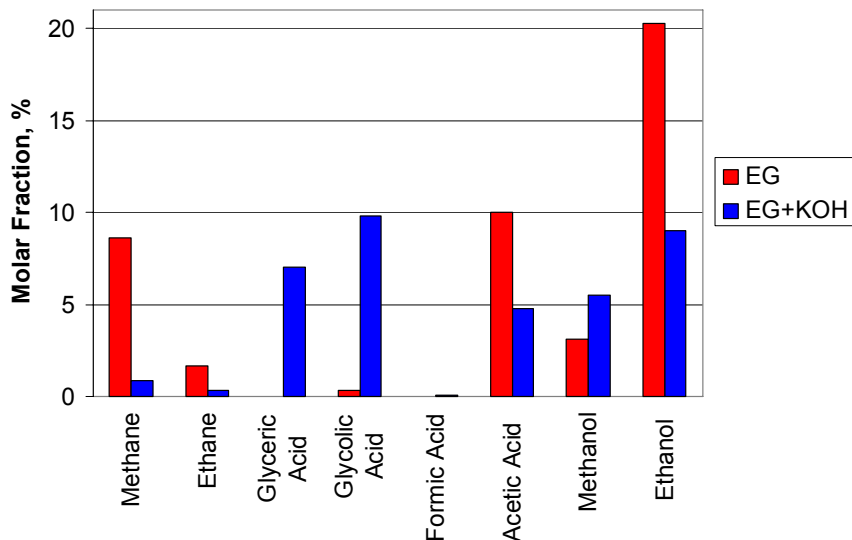


Increased acid formation results from increase in Cannizzaro reaction with all feedstocks when base is used. The Cannizzaro reaction consumes base and is specific to OH^-

Aldol reactions with formaldehyde responsible for C_{n+1} products. More aldol condensation may be occurring between smaller fragments that are not being attributed to aldol chemistry

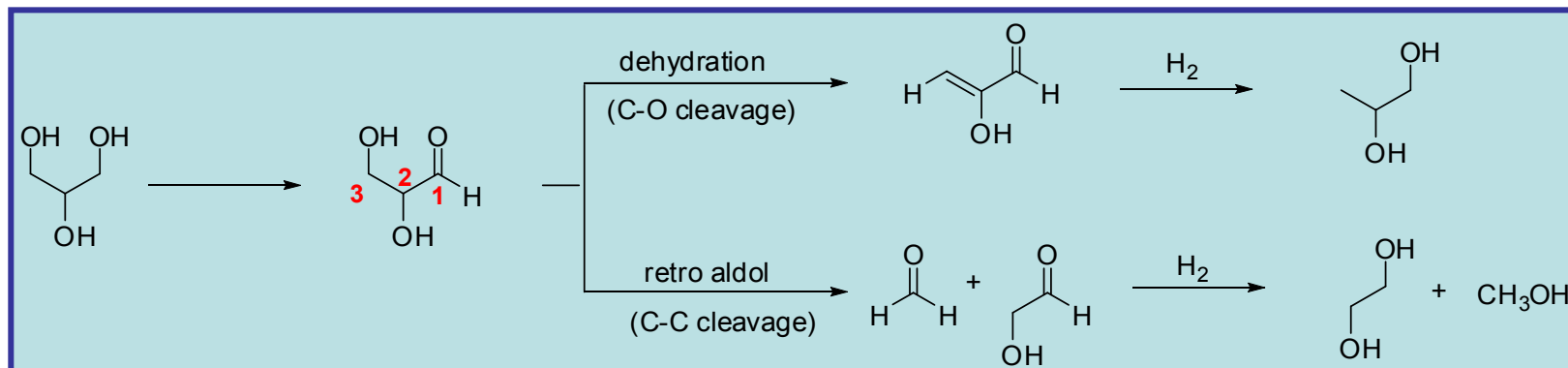
For Ethylene Glycol, KOH Can **Directly** or **Indirectly** Influence the Product Distribution

The addition of base promotes the base-catalyzed aldol reaction with formaldehyde (a C-C forming reaction) and acid formation via the Cannizzaro reaction



- Dehydrogenation of EG yields glycolaldehyde, a key intermediate for hydrogen production.
- The addition of base results in increased acid formation (glycolic and glyceric) through the Cannizzaro and Aldol/Cannizzaro reaction paths stemming from glycolaldehyde.
- The addition of base additionally reduces dehydration chemistry (C-O bond cleavage) leading to reduced ethanol and acetic acid, and increased methanol.

C₃₊ Have Additional Paths Compared to C₁,C₂ and These Affect H₂ Selectivity



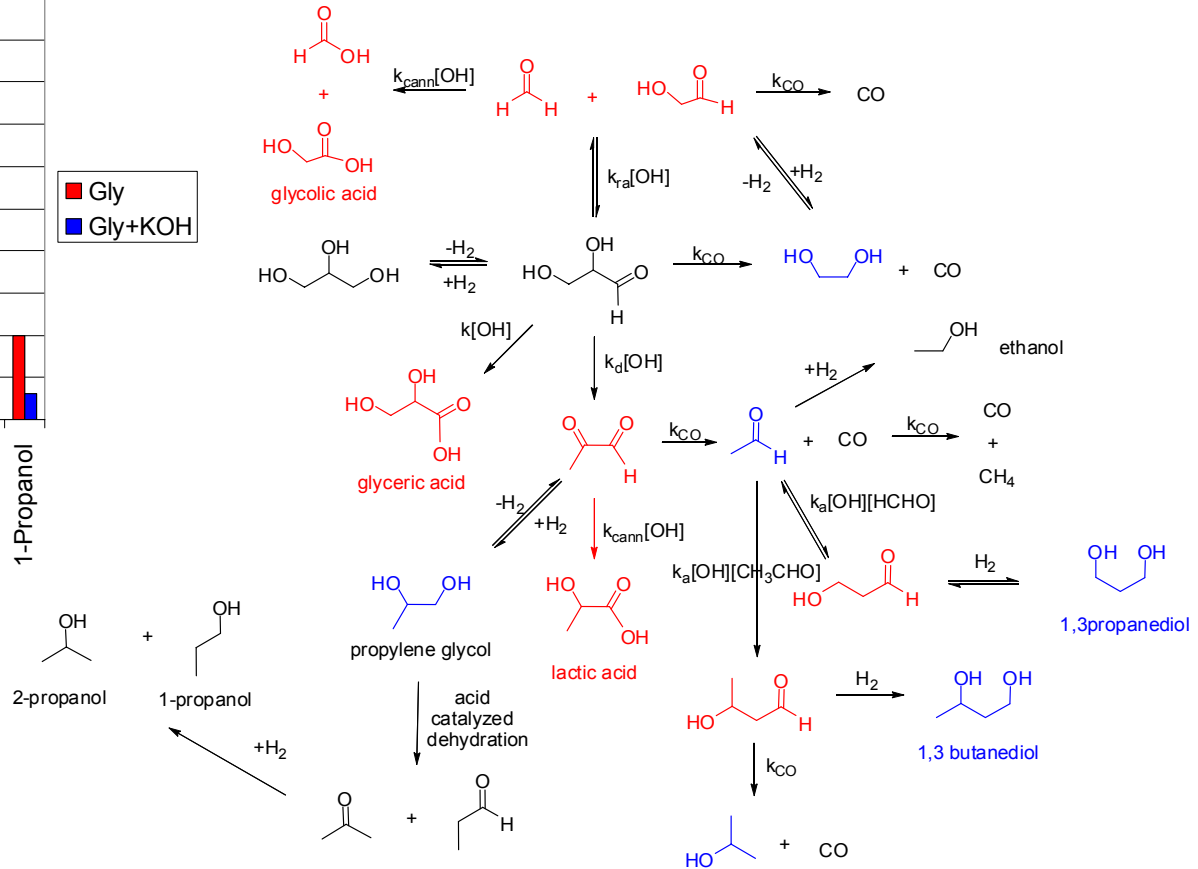
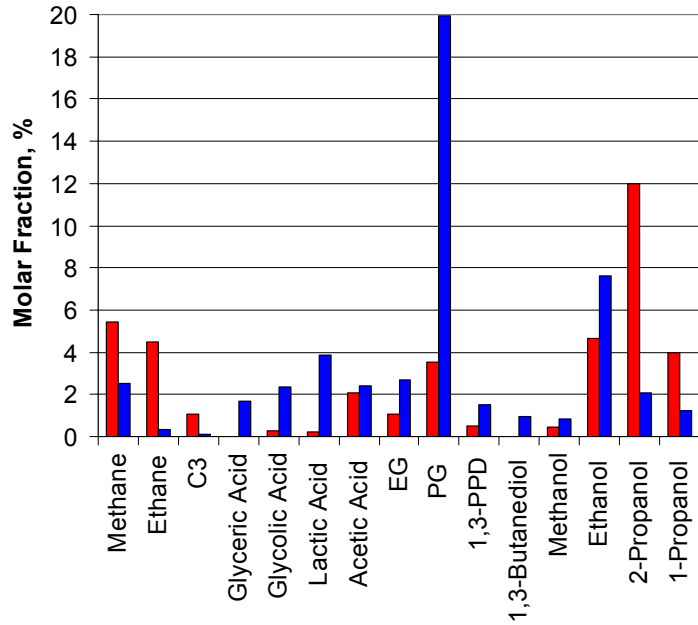
Substrates with 3 or more carbons have reaction pathways not available in C₂ and smaller substrates

Dehydrogenation kinetically activates a C-O bond cleavage manifold (dehydration) at C atoms in a relative 1,3 relationship

Dehydrogenation activates a 2,3 C-C bond cleavage manifold (retro aldol) at hydroxy ketone atoms in a relative 1,3 relationship

Reactivity differences observed between glycerol and other substrates can in part be attributed to the fact that glycerol (and higher carbohydrates) possess base-catalyzed dehydration and retro aldol reaction paths not active in substrates lacking than 1,3-diol units

For Glycerol, KOH Can **Directly** or **Indirectly** Influence the Product Distribution and it is Significantly More Complex



The addition of KOH

- Promotes base-catalyzed formation of glyceric acid, glycolic acid, 1,3-propanediol, and 1,3-butanediol
- Promotes base-catalyzed dehydration of 3-hydroxycarbonyls (glyceraldehyde) to form pyruvaldehyde, leading to an increase in ethanol, lactic acid, and PG.
- Inhibits acid-catalyzed PG dehydration pathways to 1- and 2- propanols.

Substrate Comparison with KOH Addition

	EG	EtOH	PG	GLY
conversion	-	-	-	0
H ₂ selectivity	+	-	+	0
total alkane	-	-	-	-
methane	-	-	0	-
ethane	-	0	-	-
liquid	+	+	+	+
	Acetic Acid	Acetic Acid	Acetic Acid	Acetic Acid
	Methanol		Lactic Acid	Lactic Acid
	Ethanol		Ethanol	Ethanol
				PG
trade off	H ₂ -ALK	H ₂ -LIQ	ALK-LIQ	ALK-LIQ

KOH Effects (Generalized)

- Conversion is reduced
- H₂ selectivity variably affected
- Alkane selectivity reduced
- liquid phase selectivity increased

Tradeoffs

Changes in selectivity toward one component (H₂, alkane, liquid) are usually balanced by a change in only one of the other two components

- Reaction conditions and catalysts should be modified to minimize both alkane and acid formation to enhance H₂ selectivity

Comparison of Ethanol VPR and APR over Pt-Re/C

	ESR	APR
Condition	350°C, ~14.5psi 24.21 wt.% ethanol 6ml/h feed, 25mg catalyst	225°C, ~420psi 10 wt.% ethanol 6ml/h feed, 217.2mg catalyst
H₂ productivity (kg/L-cal/h)	2.43	0.12
H₂ selectivity% (based on complete conversion)	30.8	36.2
Conversion %	98^a	84.7
TOF (min⁻¹) (ethanol molecule/min/Pt site)	130^a	4.86^d
Catalyst deactivation rate (change in conversion percentage/hour)	1.8^b	0.037^c

a) The average from initial 2 hours

b) Based on the data from initial 5 hours

c) Based on the methanol conversion change after the catalyst was tested on 12h/daily base for one month.

d) This TOF is comparable to TOFs reported for other kind of biomass APR. (Nature, vol418, 964)

- High H₂ productivity and TOF indicated the necessity to develop the stable catalyst for ESR process.
- Further H₂ productivity increase in APR process is needed

Future Work

For the rest of FY07

- Identify reaction conditions that minimize acid formation in APR
- Improve APR catalyst selectivity to hydrogen by optimizing Pt/Re ratio
- Develop kinetic models for the design of APR reactor
- Improve the stability and selectivity of ethanol steam reforming catalysts
- Perform preliminary economics

Upcoming key milestones

- Demonstrate improved hydrogen selectivity by modifying catalyst and reaction conditions
- Provide understanding of the reactivity and selectivity of C_2 and C_3 intermediates to improve hydrogen selectivity
- Establish kinetic model on a lead APR catalyst
- Demonstrate 100hr stability of ethanol steam reforming catalyst

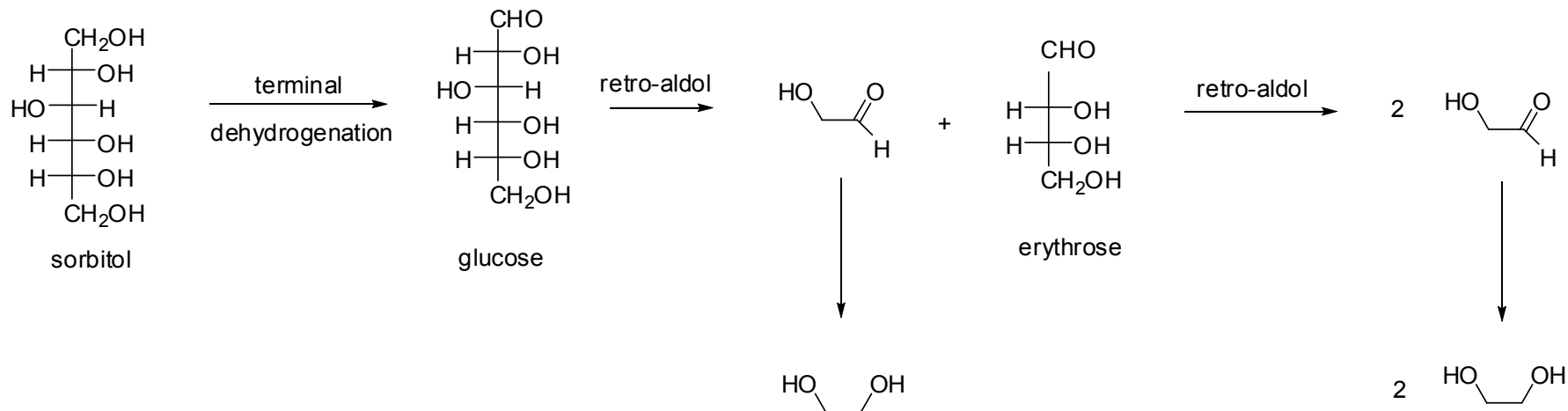
Decision points and any remaining issues

- Start reaction engineering innovation if preliminary economics promising
- Move to reaction engineering innovation and small scale demonstration if stable ethanol SR catalysts can be identified

Future Work for FY08

- Expand the reactivity/structure understanding to C₅ and C₆ polyols, selectively break sorbitol to EG
- Modify catalyst and reaction conditions to improve APR catalyst stability and selectivity
- Establish reactor modeling capabilities for the design and fabrication of a 200W reactor
- Evaluate the effects of feed impurities on catalyst performances
- Compare economics with DOE targets

Strategy for a high selectivity route to ethylene glycol



Because retro-aldol reactions are specific for 2,3 C-C bond cleavage reactions in 1,3-hydroxycarbonyl compounds, selectivity for terminal dehydrogenation in carbohydrate substrates could offer a high selectivity path to ethylene glycol

Summary

- Established an isothermal APR reactor to screen catalysts and understand reaction mechanisms for improved H₂ productivity.
- Intermediates of sorbitol APR have different reactivity and selectivity to H₂ with EG being a preferred intermediate.
- To improve the H₂ productivity and selectivity, catalysts and reaction conditions need to be tailored to minimize alkane and acid formation.
- Active partnership with collaborators in the areas of catalysis, feedstocks, and process economics.
- Apply the knowledge learned to less processed feedstocks.

Additional Slides

Definition of H₂ selectivity used in our work

Definition of H₂ selectivity (Based on complete conversion)

%H₂ sel. =(H₂ molecules produced/H₂ molecules theoretically produced)x100

H₂ theoretically produced = substrate (molecules) x conversion x AA

AA=H₂ numbers/reactant molecules (theoretically)

Substrate	Reaction	AA
Methanol	$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$	3
Ethanol	$\text{C}_2\text{H}_6\text{O} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 6\text{H}_2$	6
EG	$\text{C}_2\text{H}_6\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 5\text{H}_2$	5
(1 or 2)-Propanol	$\text{C}_3\text{H}_8\text{O} + 5\text{H}_2\text{O} \rightarrow 3\text{CO}_2 + 9\text{H}_2$	9
PG or 1,3-PPD	$\text{C}_3\text{H}_8\text{O}_2 + 4\text{H}_2\text{O} \rightarrow 3\text{CO}_2 + 8\text{H}_2$	8
Glycerol	$\text{C}_3\text{H}_8\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 3\text{CO}_2 + 7\text{H}_2$	7
Sorbitol	$\text{C}_6\text{H}_{14}\text{O}_6 + 6\text{H}_2\text{O} \rightarrow 6\text{CO}_2 + 13\text{H}_2$	13

This selectivity is from 0 to 1!

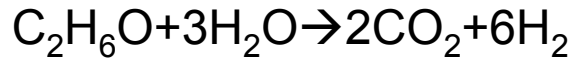
Definition of H₂ selectivity used in literature

Based on gas phase (Dumesic method)

%H₂ sel. = (molecules H₂ produced / C atoms in gas phase) (1/RR) x 100

RR = (theoretical) H₂ molecules / CO₂ molecules

For instance:



$$\text{RR} = 6/2 = 3$$

This selectivity can be from 0 to infinity!