DOE Hydrogen Program

# Bio-Derived Liquids Reforming

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Project ID #: PD4

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# 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

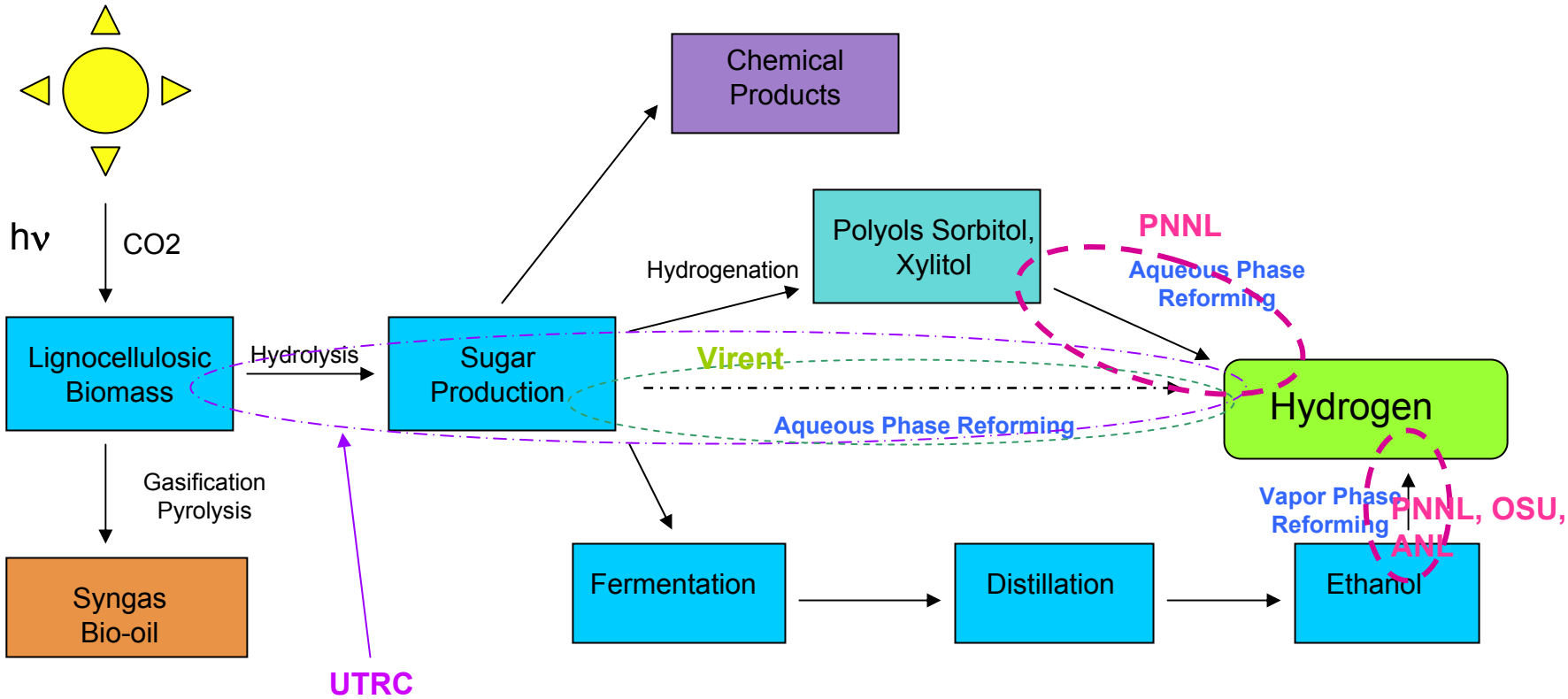
## Partners and Collaborators

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

# Objectives

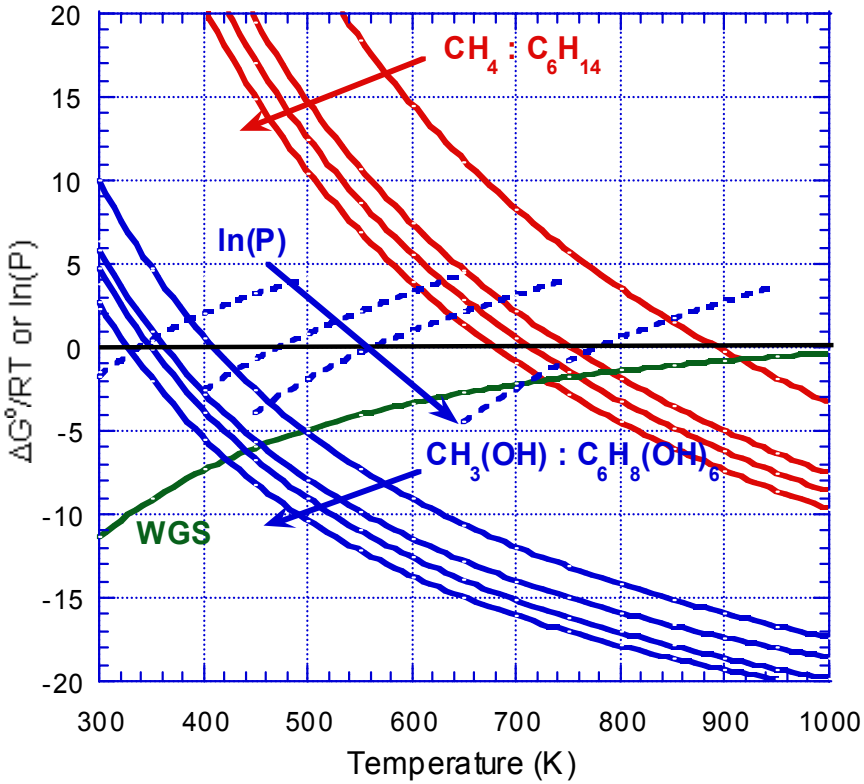
| | |
|---|---|
| Overall | • Assist DOE in evaluating and developing alternatives to gasification and pyrolysis of biomass for hydrogen production that can meet the DOE 2017 cost target of <$3.00 /gge |
| 2007 | • Develop stable and selective catalysts for vapor phase reforming of ethanol to produce hydrogen<br>• Understand the reactivity and selectivity of APR intermediates to enhance the hydrogen productivity |
| 2008 | • Develop catalysts, reaction conditions, and reactors for vapor phase reforming of ethanol to produce hydrogen<br>• 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**

$C_nH_{2n+2} + nH_2O \leftrightarrow nCO + (2n+1)H_2$

**Reforming of Oxygenated Compounds**

$C_nH_{2n+2}O_n + nH_2O \leftrightarrow nCO + (2n+1)H_2$

**Water-Gas Shift**

$CO + H_2O \leftrightarrow CO_2 + H_2$

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

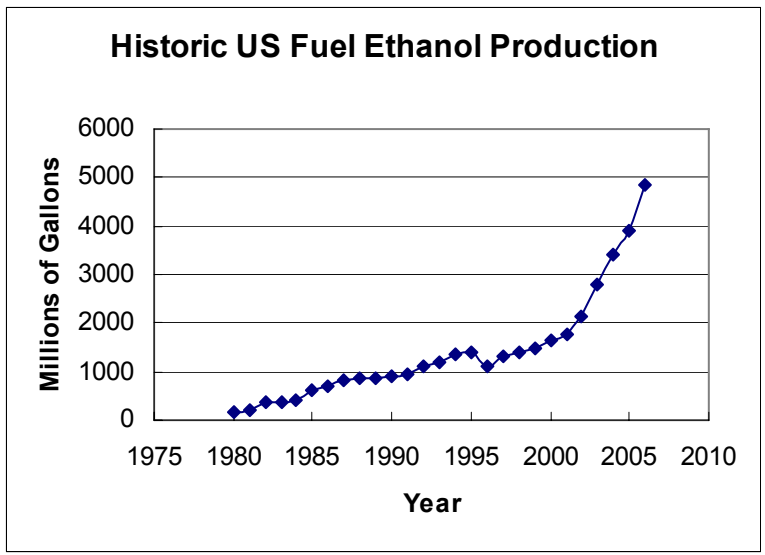


*Courtesy of Virent*

# Biomass Feedstocks

- Biomass can not meet all of the energy needs, but can provide a major contribution.
  - U.S. consumes $7 \times 10^9$ bbl/yr
  - Equivalent to $3.8 \times 10^9$ boe/yr (barrels of oil energy equivalent) biomass could be produced in U.S.($1.3 \times 10^9$ 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 zoetrope 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 $H_2$ purification

# Vapor Phase Ethanol Reforming Options

- Low temperature SR (<500ºC)
  - 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 $H_2$/mole ethanol converted)
- High temperature SR (>500ºC)
  - 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 $O_2$ addition and dilution of $N_2$ in reformat

# A Highly Selective and Active 2wt%Rh on $CeO_2$-$ZrO_2$ Was Previously Developed at PNNL

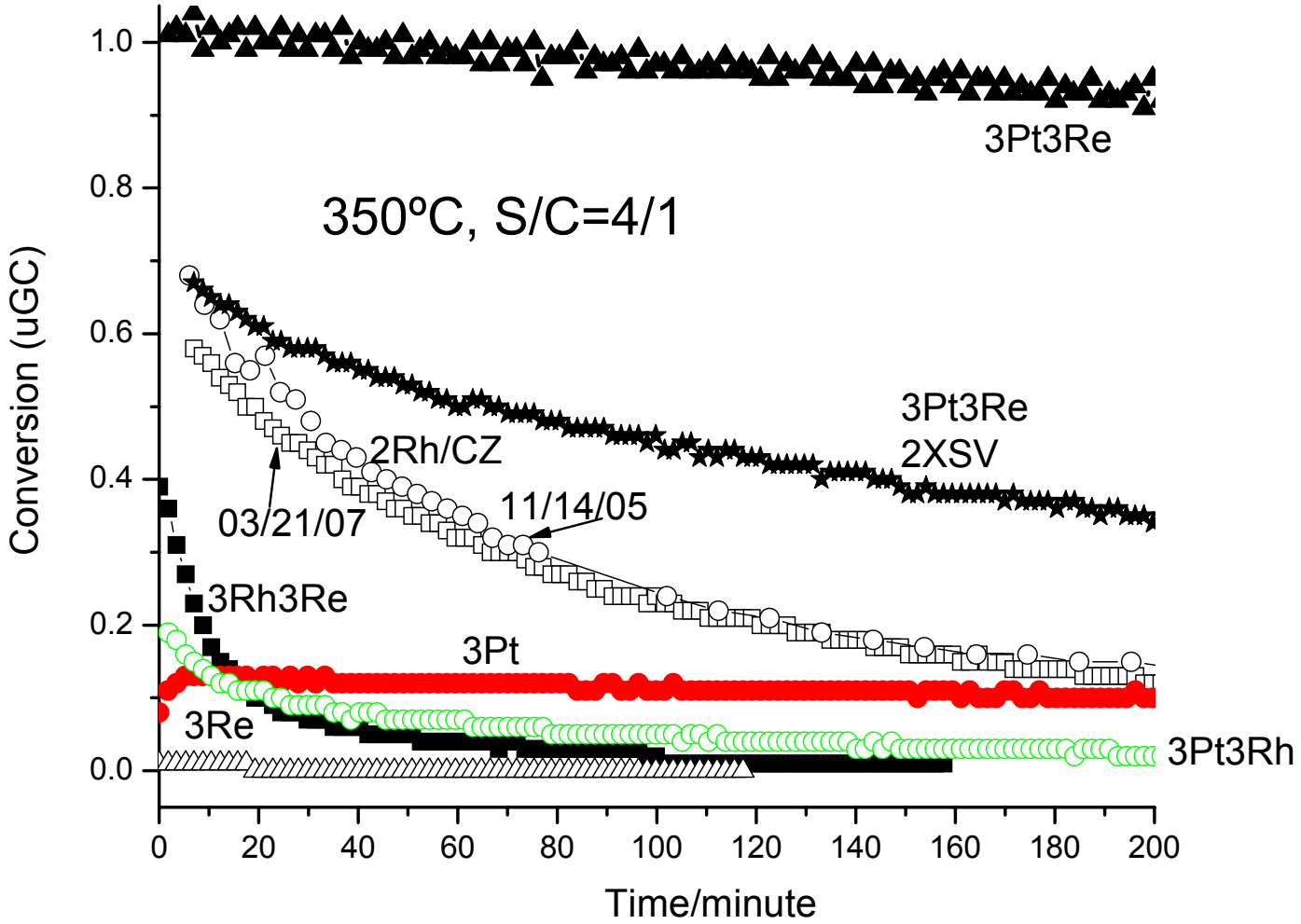
| Catalyst | $X_{EtOH}$ (%) | $H_2$/EtOH (m/m) | $S_{CH4}$ (%) | $S_{CO}$ (%) | $S_{CO2}$ (%) |
|---|---|---|---|---|---|
| 2%Rh/$Ce_{0.8}Zr_{0.2}O_2$ | 100 | 4.3 | 25 | 11 | 64 |
| 2%Rh/$Ce_{0.6}Zr_{0.4}O_2$ | 100 | 4.0 | 26 | 18 | 56 |
| 2%Rh/$Ce_{0.4}Zr_{0.6}O_2$ | 100 | 4.0 | 27 | 20 | 53 |
| 2%Rh/$Ce_{0.2}Zr_{0.8}O_2$ | 95 | 3.6 | 28 | 21 | 50 |
| 2%Rh/$CeO_2$ | 53 | 1.9 | 22 | 32 | 39 |

450ºC, SV: 133,000 ml/g-h; $H_2O$/EtOH/$N_2$ = 8/1/10.6, Data obtained at 10 h TOS



Roh *et al*, *Topics in Catalysis* (in press)

# Improved Catalyst Activity and Stability



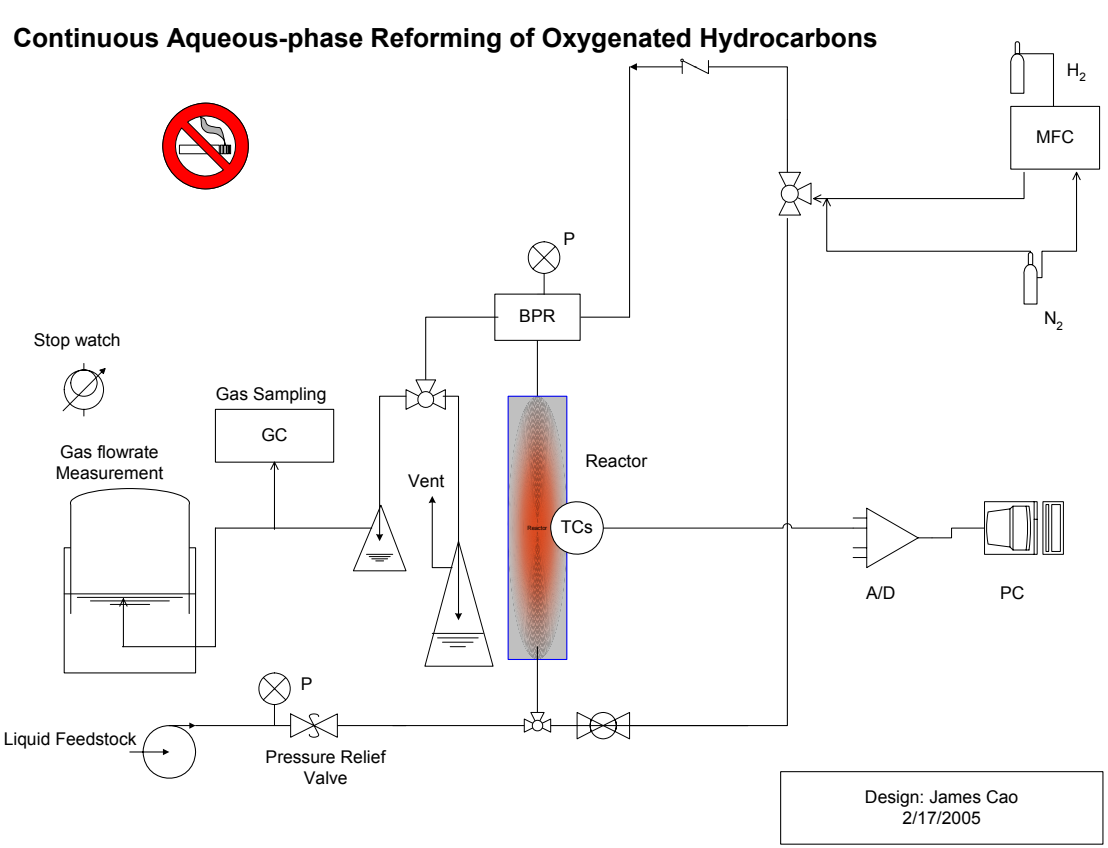

- Rapid catalyst deactivation on 2wt%Rh/$CeO_2$-$ZrO_2$ due to soft carbonaceous deposit
- 3%Pt3%Re/C exhibits improved stability with higher activity

# Aqueous Phase Reforming

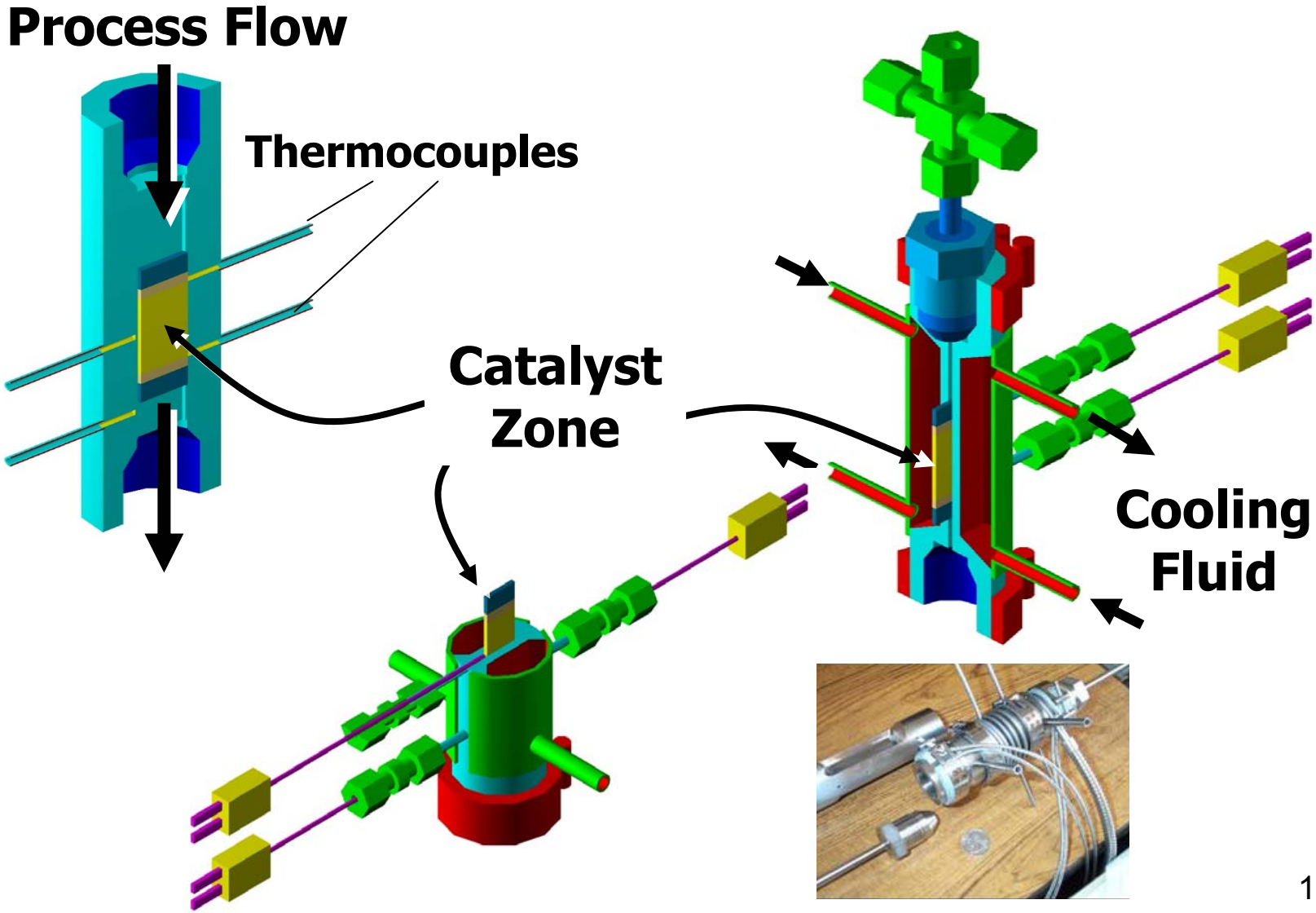
# Approach

- 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



# Isothermal Reactor Details






Cao *et al, Appl.Cat.: General*. 262, 19, **2004**

# Validating Previous APR Results of Sorbitol over Virent Catalyst

(Runs at different time : 2007 vs 2005)

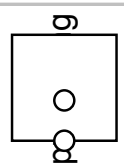
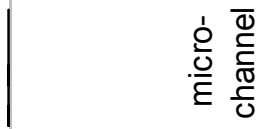
10% Sorbitol, Virent Catalyst, 225°C, 420~425psi

| 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 $H_2$ selectivity) under two different contact times
- More complete gas product analysis with the current setup

# Tubular vs. Microchannel Reactor Comparison

## (Virent Catalyst)

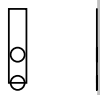
| *Aqueous phase reforming (continuous PFR)* | | | |
|---|---|---|---|
| |  | |   |
| **Run ID** | **AR 56-1** | **AR 53-1** | **MC-APR-01** |
| **Reactor** | **1/2" tubular** | **1/4" tubular** | **Microchannel 0.06" gap** |
| Liquid feed | 10% Sorbitol | 10% Sorbitol | 10% Sorbitol |
| P (psig) | 420 | 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** | | | |
| H2 productivity (l/l cat/hr) | 266 | 342 | 456 |
| Carbon conversion to gas | 43% | 40% | 76% |
| Sorbitol conversion | 100% | 99% | 99% |
| H2 selectivity | 51% | 60% | 62% |
| Alkane selectivity | 20% | 19% | 20% |
| H2/CO2 | 1.1 | 1.3 | 1.3 |
| H2/CH4 | 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 $H_2$ productivity

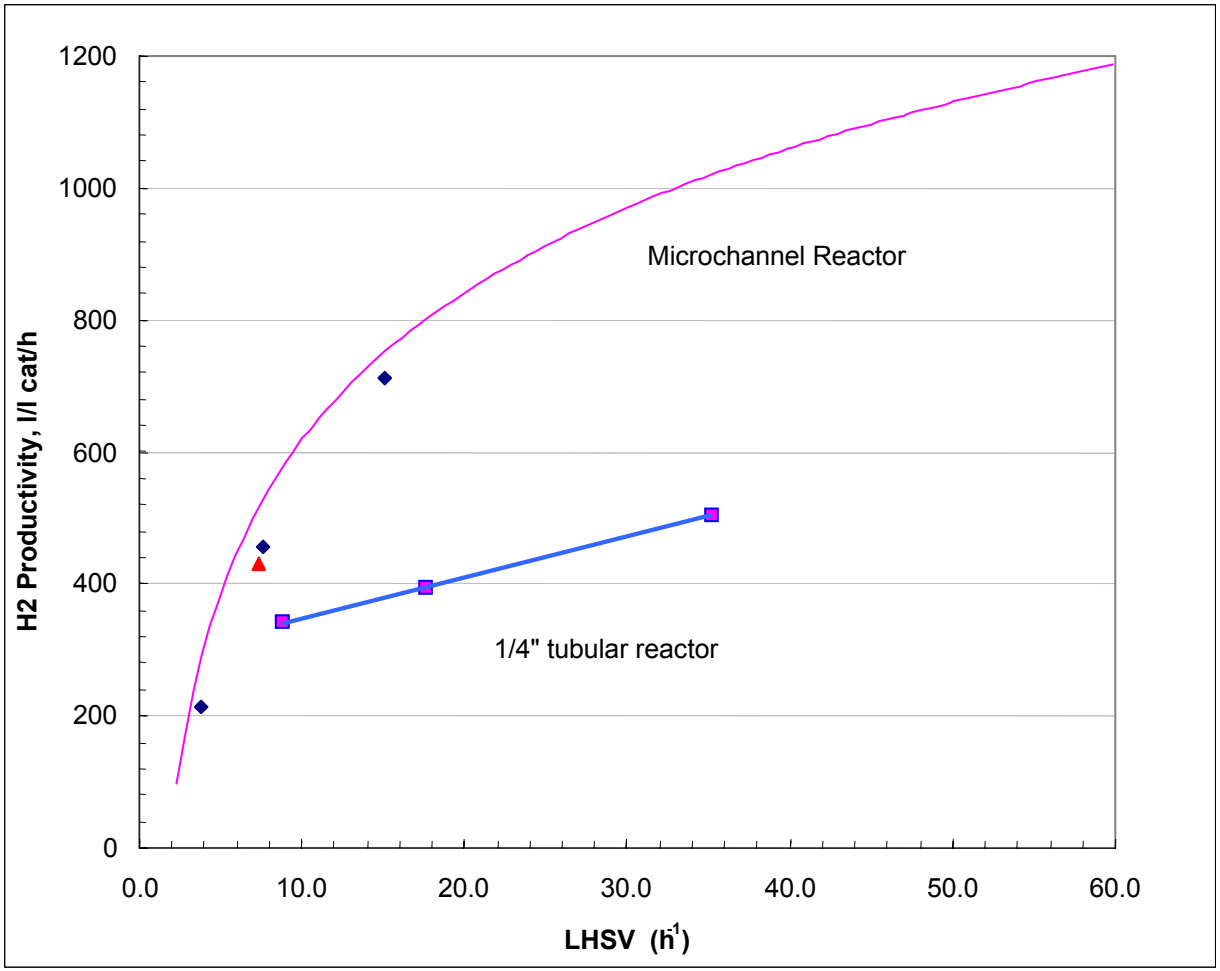
# Tubular vs. Microchannel Reactor Comparison

## (Virent Catalyst)

| *Aqueous phase reforming (continuous PFR)* | | | |
|---|---|---|---|
| | |  | 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 |
| *Liquid phase analysis (wt%)* | *Not analyzed* | | |
| *Glucose* | | *0.024%* | *0.033%* |
| *Sorbitol (C6H14O6)* | | *0.189%* | *0.090%* |
| *Arabitol + xylitol* | | *0.093%* | - |
| *Erythritol + Threitol(C4H10O4)* | | *0.137%* | - |
| *Glycerol(C3H8O3)* | | *0.363%* | *0.002%* |
| *Ethylene Glycol (C2H6O2)* | | *0.151%* | - |
| *Propylene glycol (C3H8O2)* | | *0.797%* | - |
| *Methanol* | | *0.597%* | *0.078%* |
| *Ethanol(C2H6O)* | | *0.418%* | *0.007%* |
| *2-Propanol(C3H8O)* | | *0.101%* | *0.093%* |
| *Acetone* | | *0.099%* | *0.118%* |
| *1-Propanol(C3H8O)* | | *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% |
| CO2 | 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% |
| H2/CH4 | 8.90 | 11.63 | 11.46 | 10.67 |
| H2/C2 | 26.30 | 30.73 | 31.08 | 31.99 |

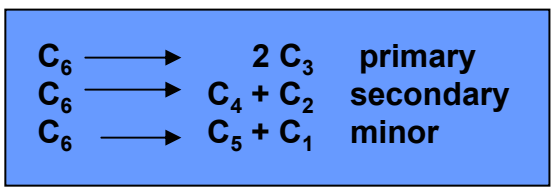
- A microchannel reactor allows mechanistic studies at incomplete conversions under isothermal conditions
- Liquid products at incomplete conversion of sorbitol may provide information on reaction pathways and intermediates
- Higher space velocities result in greater production of liquid products with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

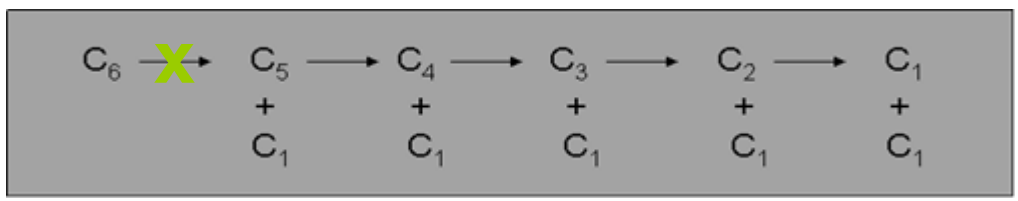
# Effect of Feed Rate on Sorbitol Products

## (Microchannel Reactor, Virent Catalyst)

| WHSV g sorbitol/g catalyst-h) | 1.0 | 2.1 | 3.1 | 4.1 |
|---|---|---|---|---|
| ***Liquid phase composition (wt%)*** | | | | |
| 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**
- **$C_4$ and $C_2$ polyols are in approximate balance**
- **Oxygenated products are more consistent with random C-C cleavage than sequential $C_1$ cleavage**



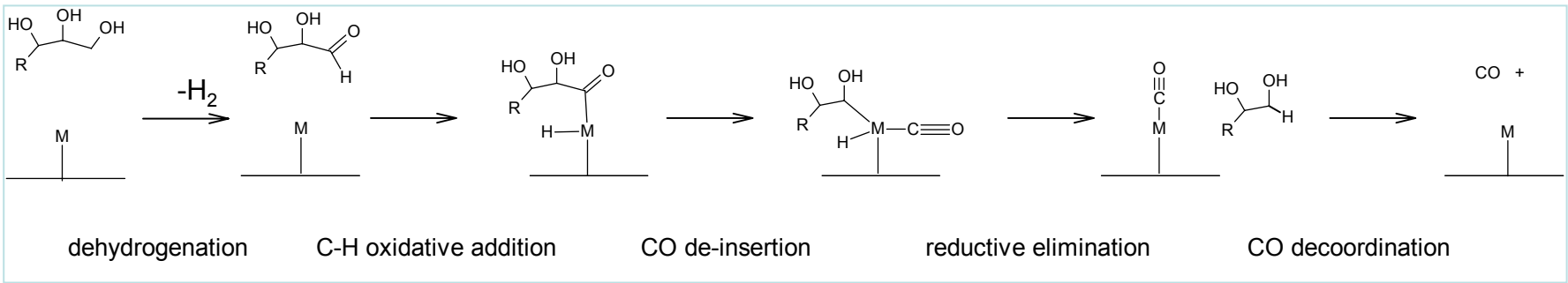



# Reaction Pathways

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

    $C_6(OH)_6H_8 + H_2 \rightarrow 2\ C_3(OH)_3H_5$
  - Production of propylene glycol from glycerol requires combination of hydrogenation plus dehydration

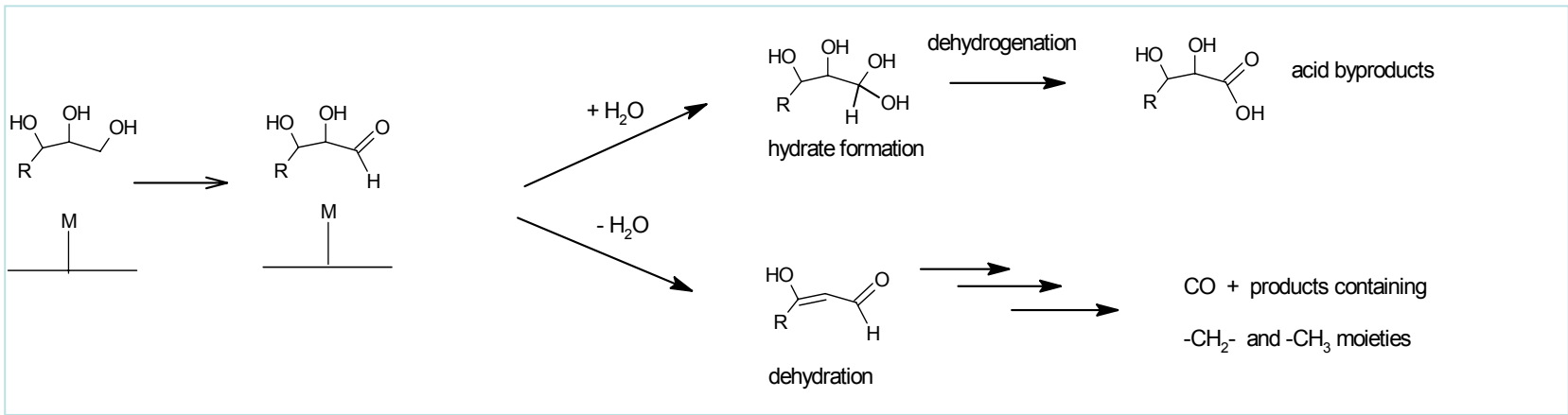
    $C_6(OH)_6H_8 + 3H_2 \rightarrow 2\ C_3(OH)_2H_6 + 2H_2O$
- Catalyzed terminal cleavage, if possible, could lead to improved hydrogen selectivity




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

# Origins of Reaction By-products

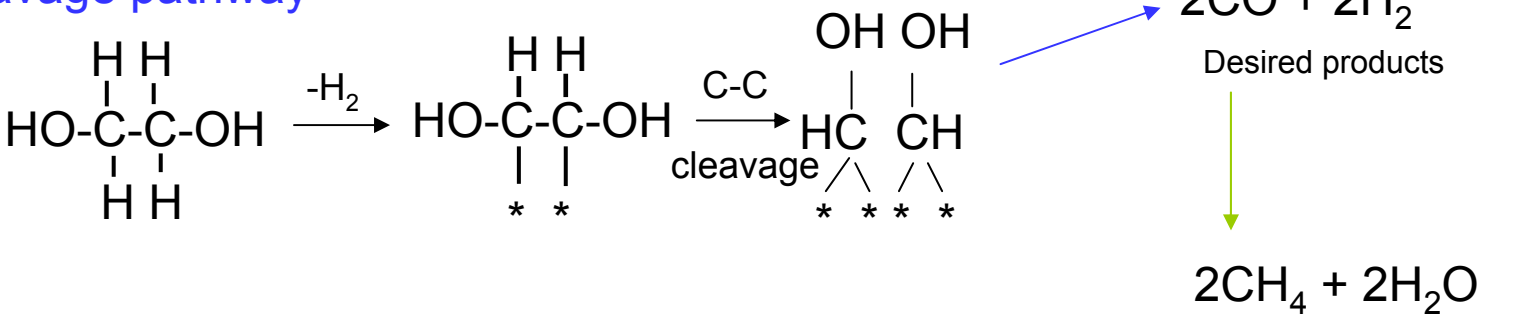
- Hydration followed by dehydrogenation of aldehyde hydrate can lead to acid formation.
- Dehydration (to $\alpha$, $\beta$-unsaturated carbonyls) generates methane and products containing $-CH_2-$ and $-CH_3$ moieties
  - Maximizing hydrogen production requires avoiding dehydration of reaction intermediates that subsequently hydrogenate to final alkane products



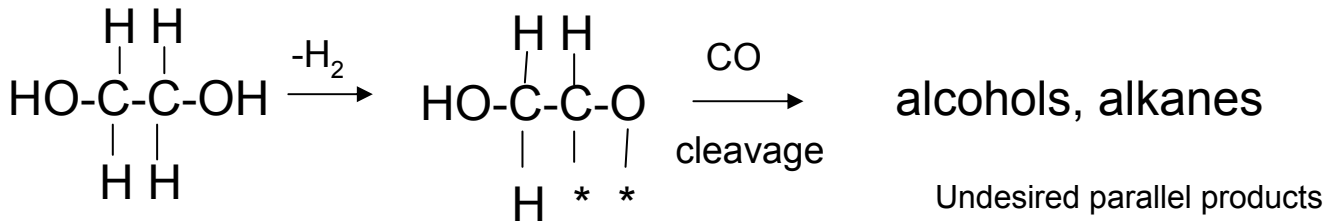

***Hydrate formation and dehydration are usually acid- or base-catalyzed reactions and might be promoted by the catalyst support and base in the feed. Understanding support and base effects could be critical to improving selectivity.***

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

C-C cleavage pathway




C-O cleavage pathway

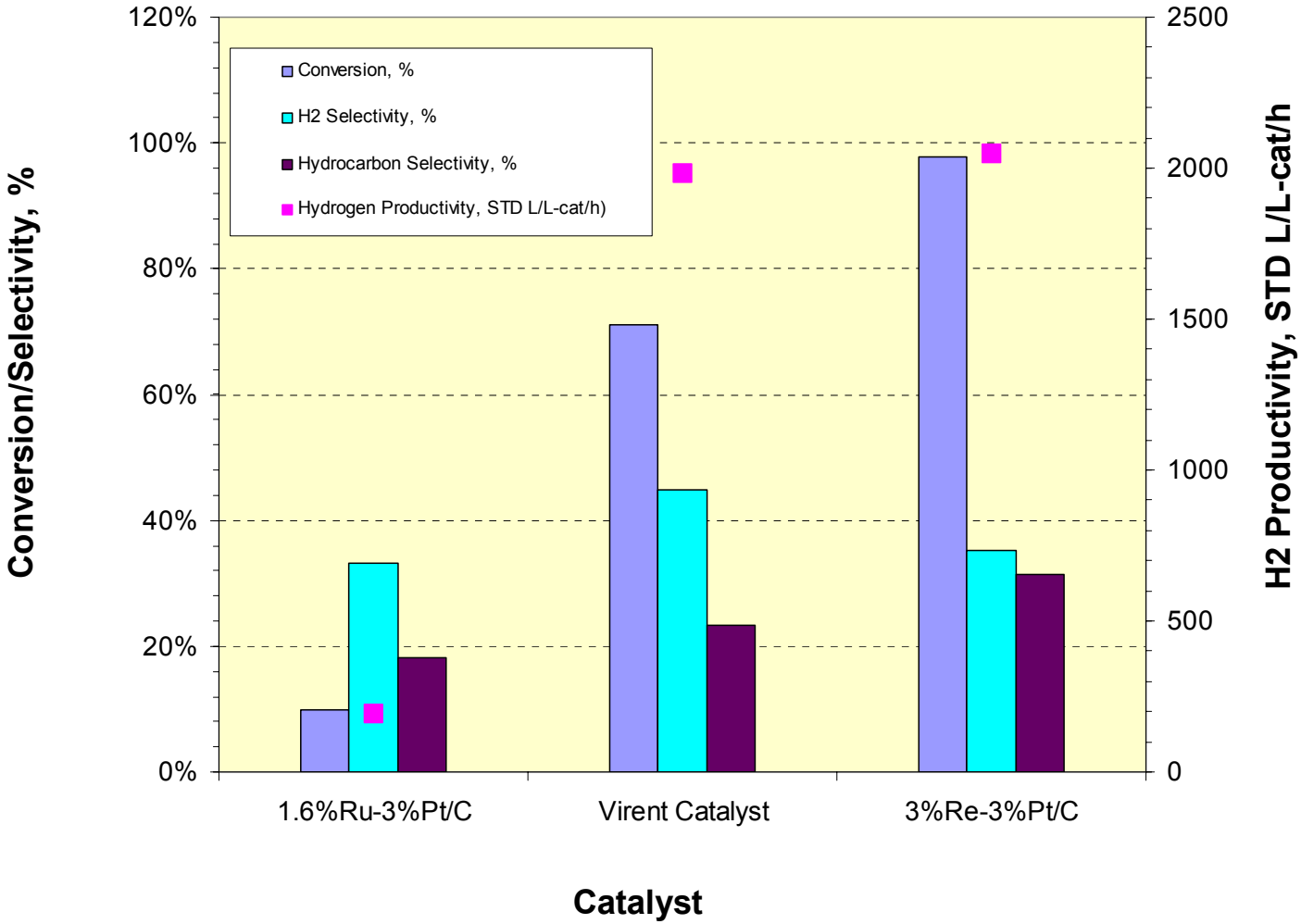



Good catalyst should have good C-C cleavage and water gas shift activity, low C-O bond cleavage and methanation activity

* 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**

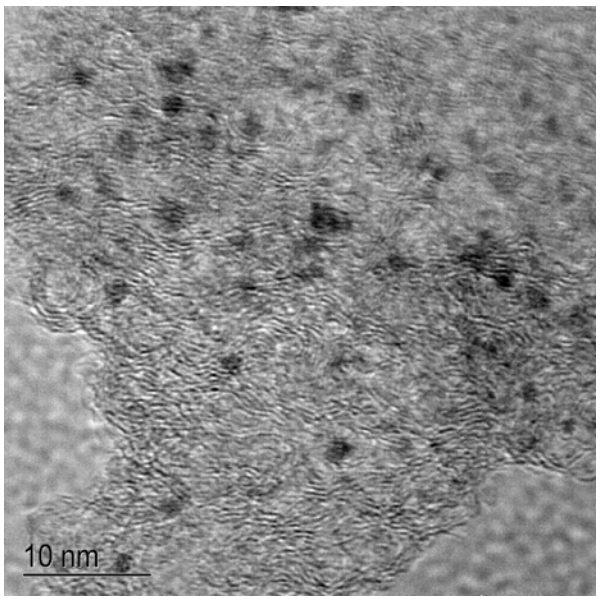



- 1.6%Ru-3%Pt/C was the most active catalyst previously developed at PNNL, but much less active than Virent catalyst.
- Virent catalyst was used to validate the needs in heat transfer improvement
- 3%Pt-3%Re/C catalyst recently developed at PNNL has similar activity and selectivity as that of Virent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

# Catalyst Characterization Results

| Catalyst | Irreversible H uptake (μmol/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

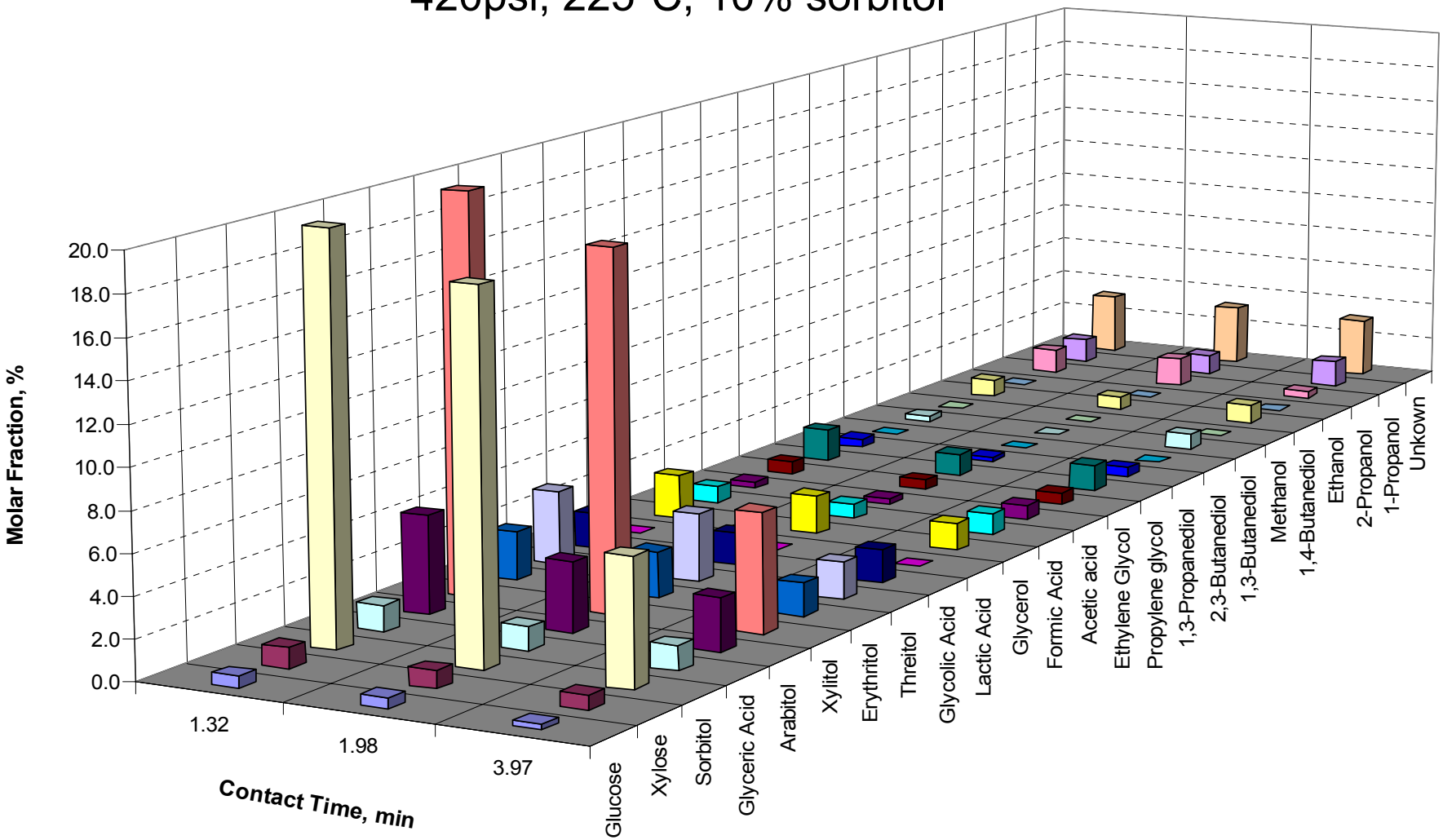



Metal Particle Size Comparison

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

# APR of Sorbitol on 3%Pt3%Re/C

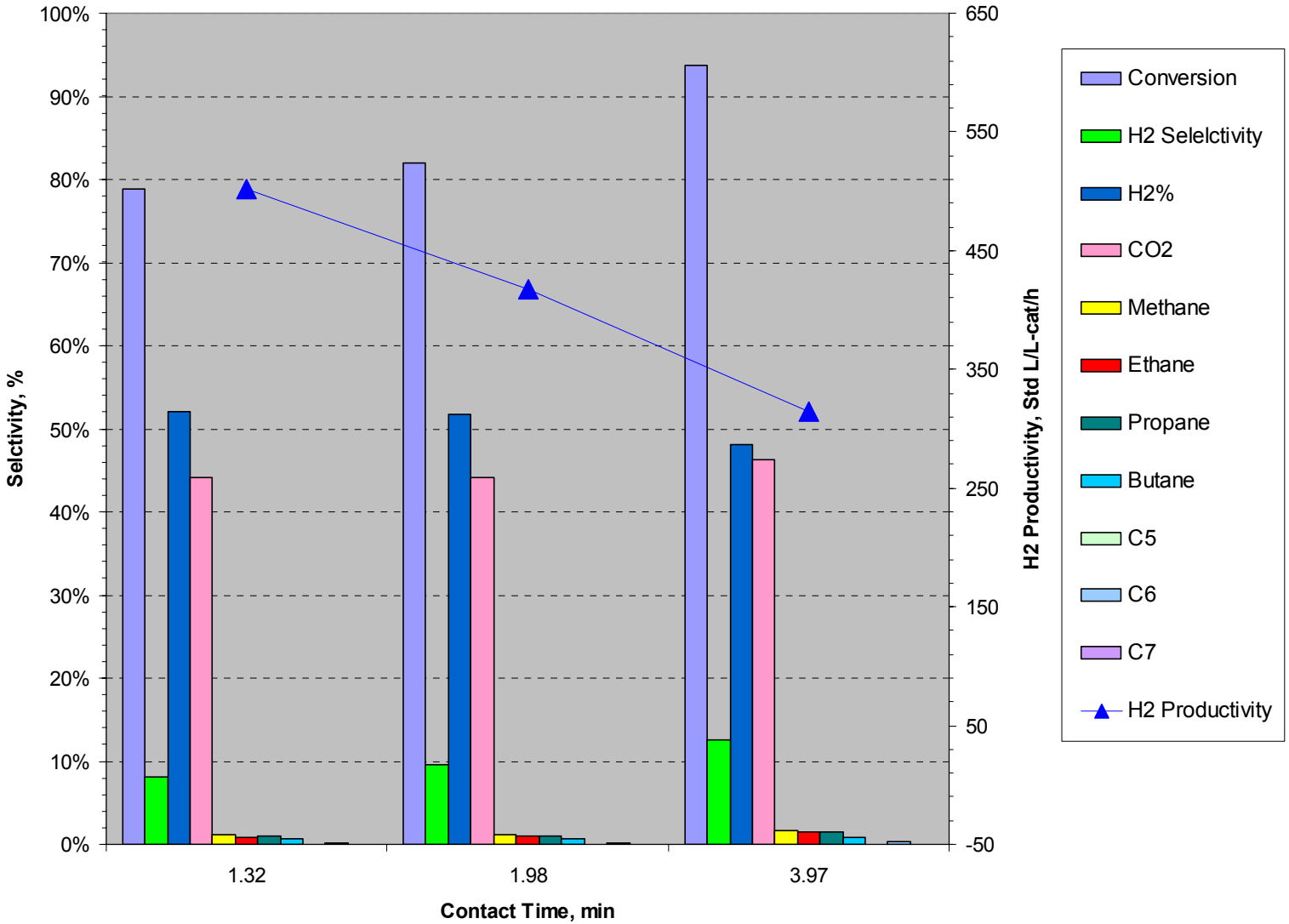
420psi, 225ºC, 10% sorbitol




- Liquid products include $C_1$-$C_5$ oxygenate intermediates

# APR of Sorbitol on 3%Pt3%Re/C

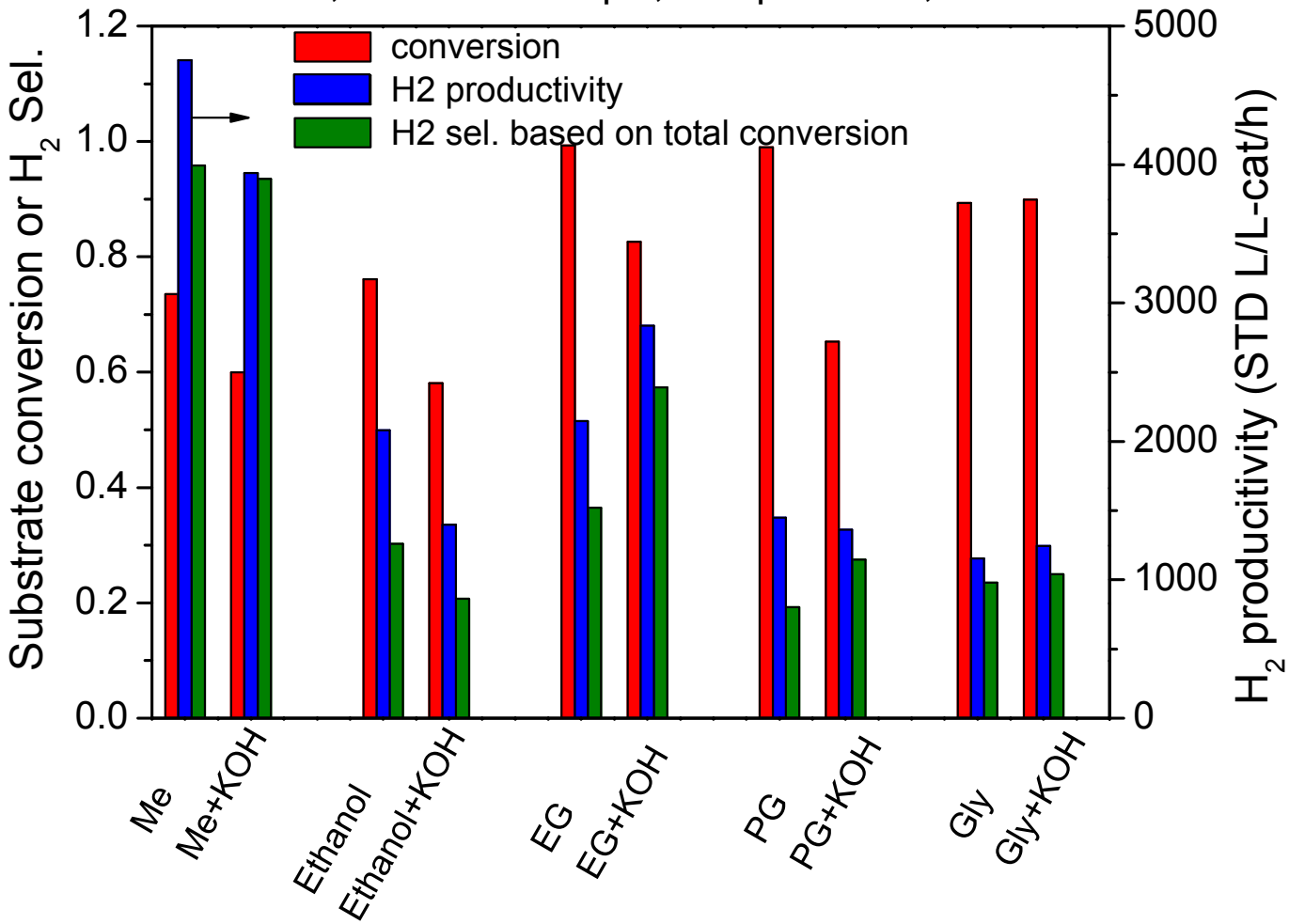
420psi, 225ºC, 10% sorbitol




- Gas phase products include $C_1$-$C_6$ alkanes which hurt hydrogen selectivity

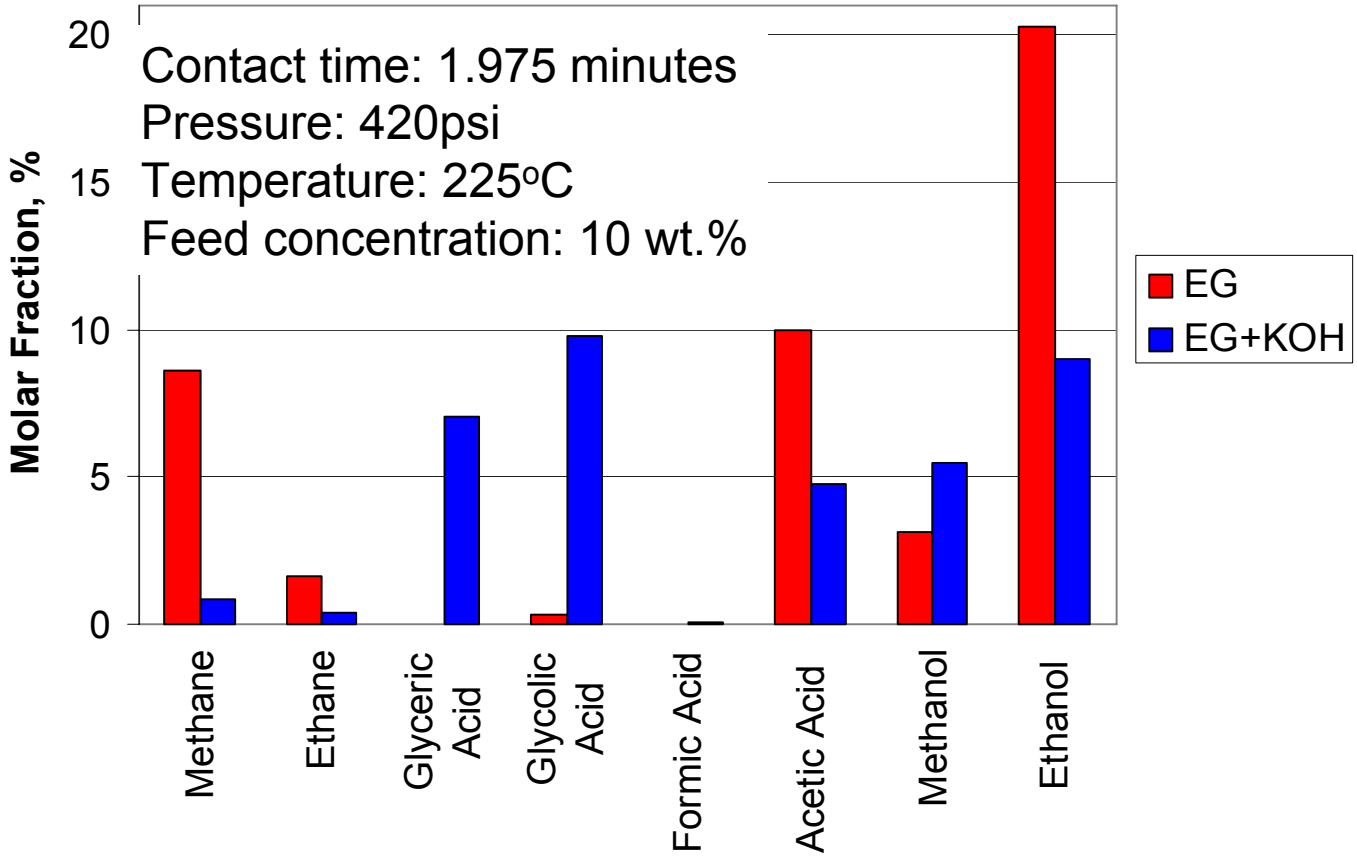
# Reactivity of Intermediates and the Effects of KOH Addition

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




- $H_2$ selectivity: EG>ethanol, GLY>PG
- $H_2$ productivity: methanol>EG>GLY
- EG is a preferred intermediate, addition of KOH significantly increases the $H_2$ selectivity and productivity from EG.
- Methanol was studied to demonstrate minimal activity in Fisher-Tropsch synthesis, formation of alkanes likely from other pathways.

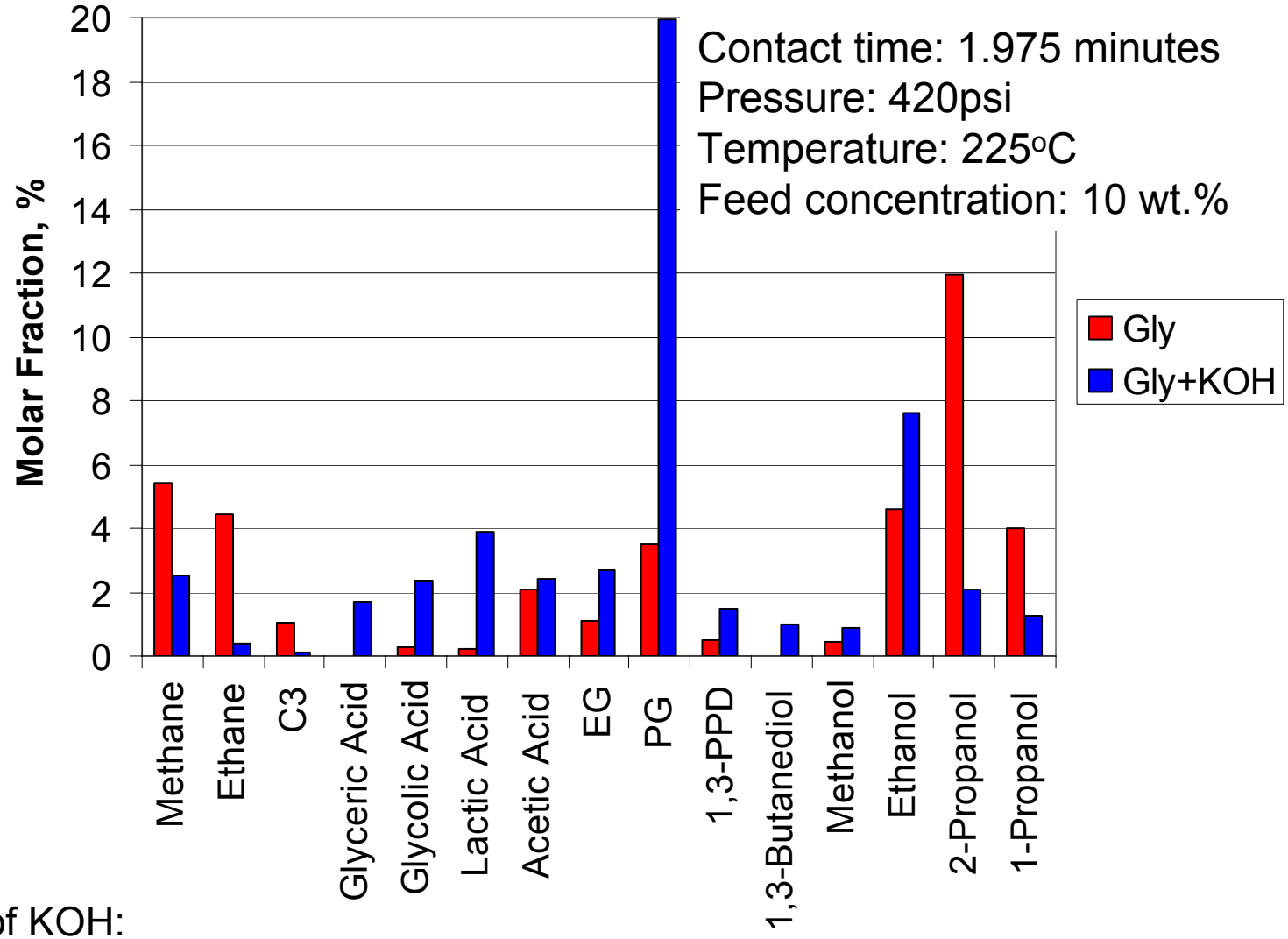
# The Effect of KOH on Product Distribution - EG




Addition of KOH:

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

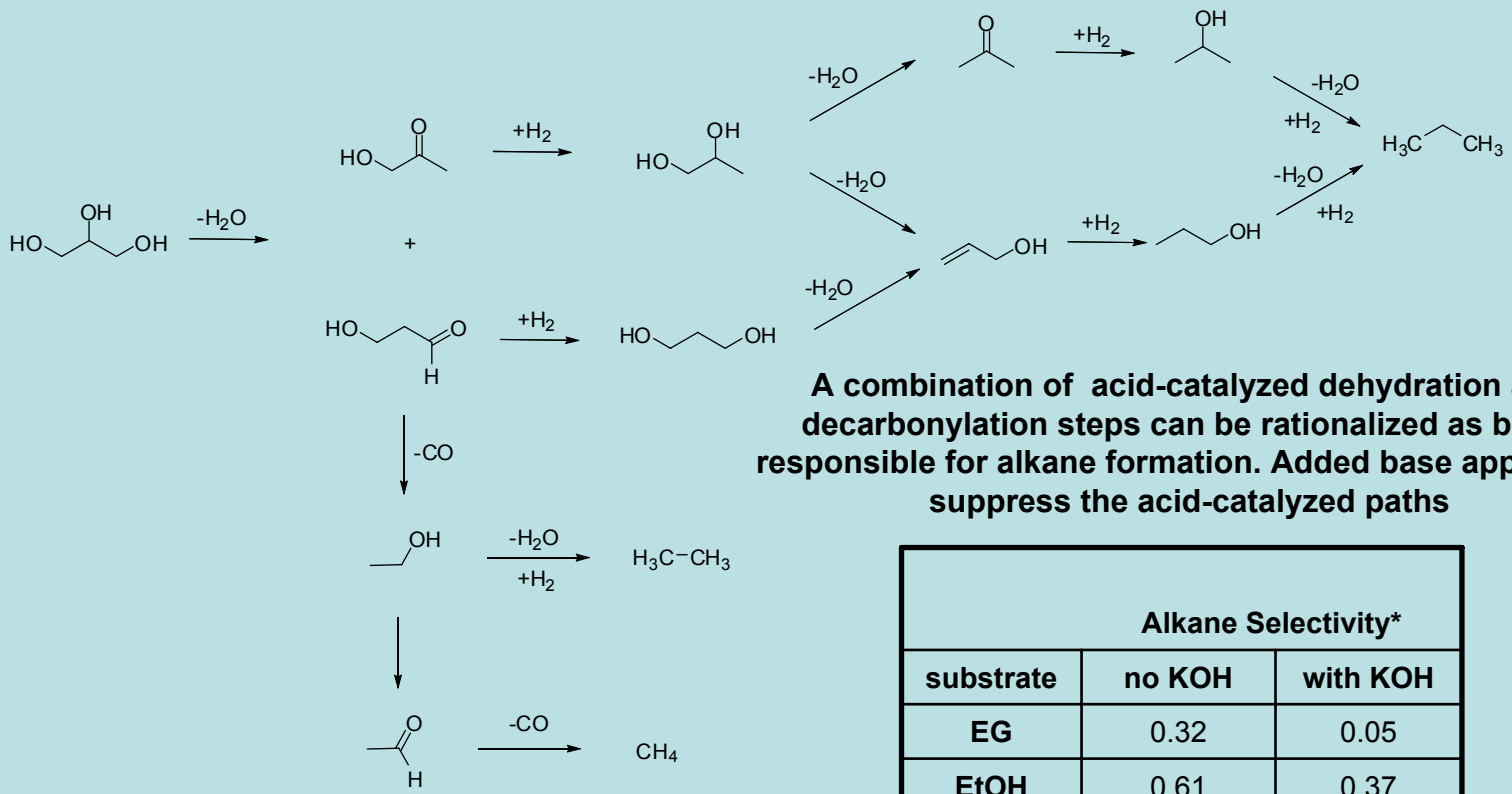
# The Effect of KOH on Product Distribution - Glycerol




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

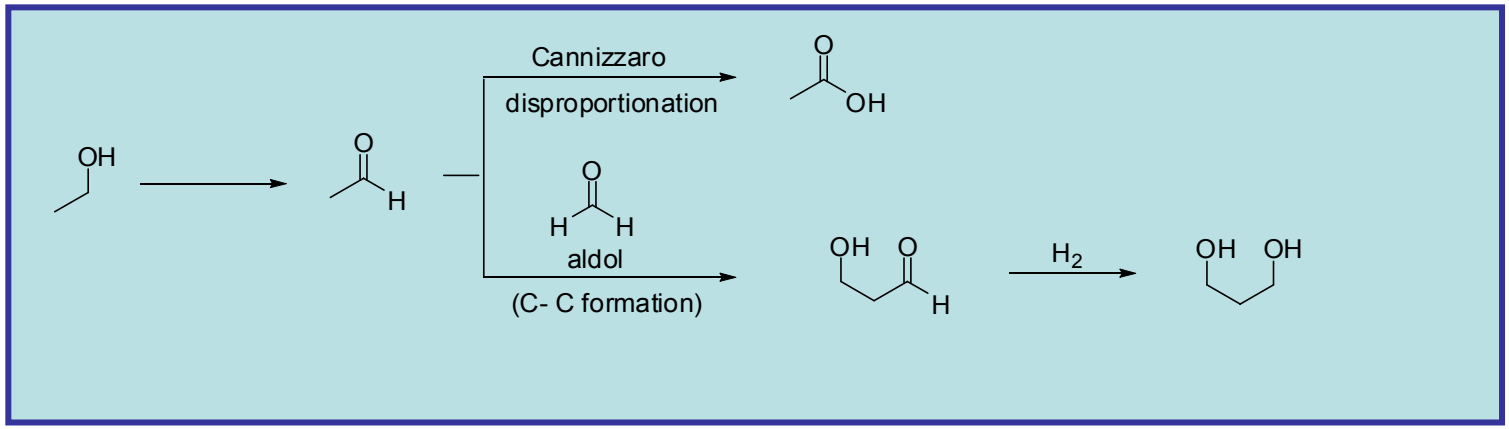



**A combination of acid-catalyzed dehydration and decarbonylation steps can be rationalized as being responsible for alkane formation. Added base appears to suppress the acid-catalyzed paths**

| | Alkane Selectivity* | |
|---|---|---|
| **substrate** | **no KOH** | **with KOH** |
| **EG** | 0.32 | 0.05 |
| **EtOH** | 0.61 | 0.37 |
| **PG** | 0.35 | 0.18 |
| **Glycerol** | 0.26 | 0.06 |

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

# KOH Catalyzes Pathways to Acids and Cn+1 Products

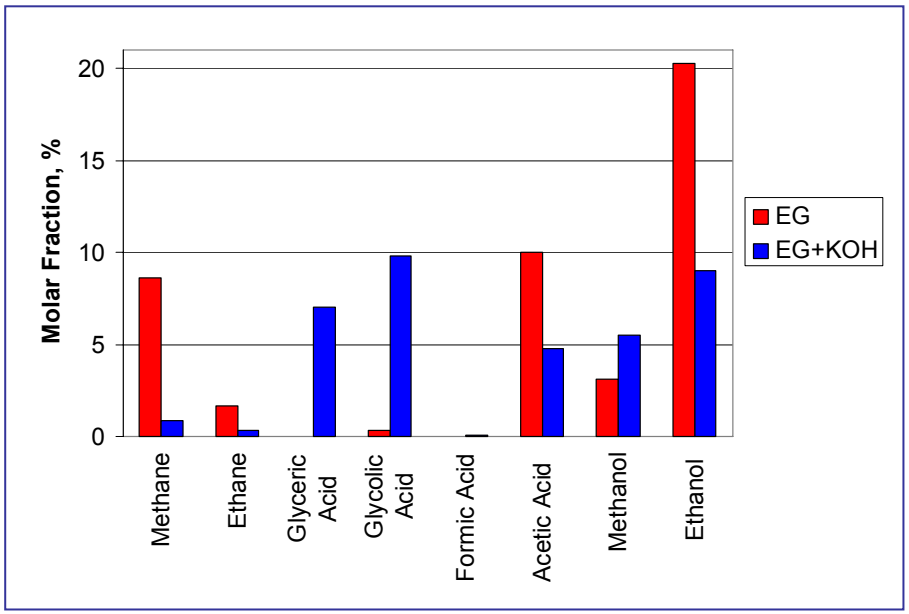


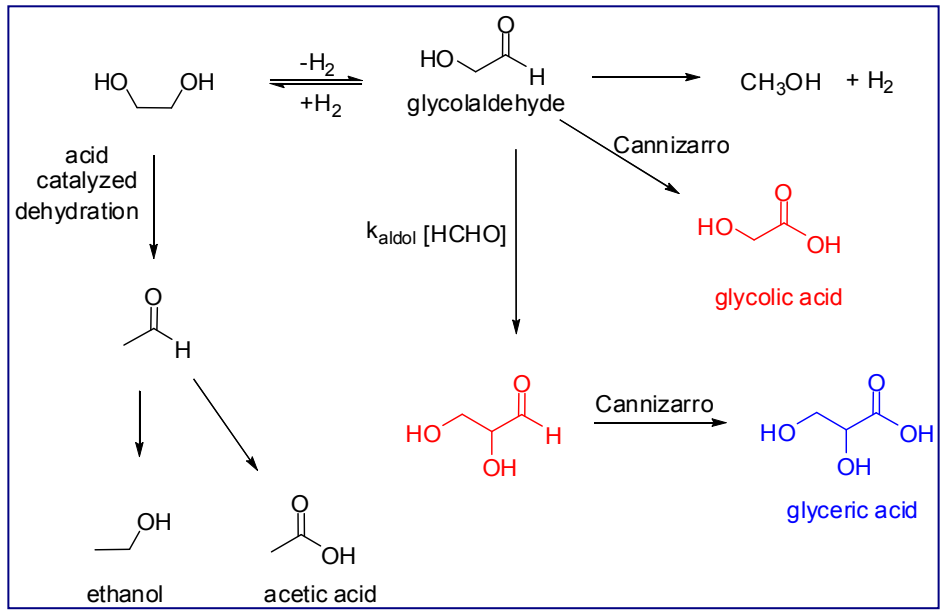

Increased acid formation results from increase in Cannizzaro reaction with all feedstocks when base is used. The Cannizzaro reaction consumes base and is specific to $OH^-$

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

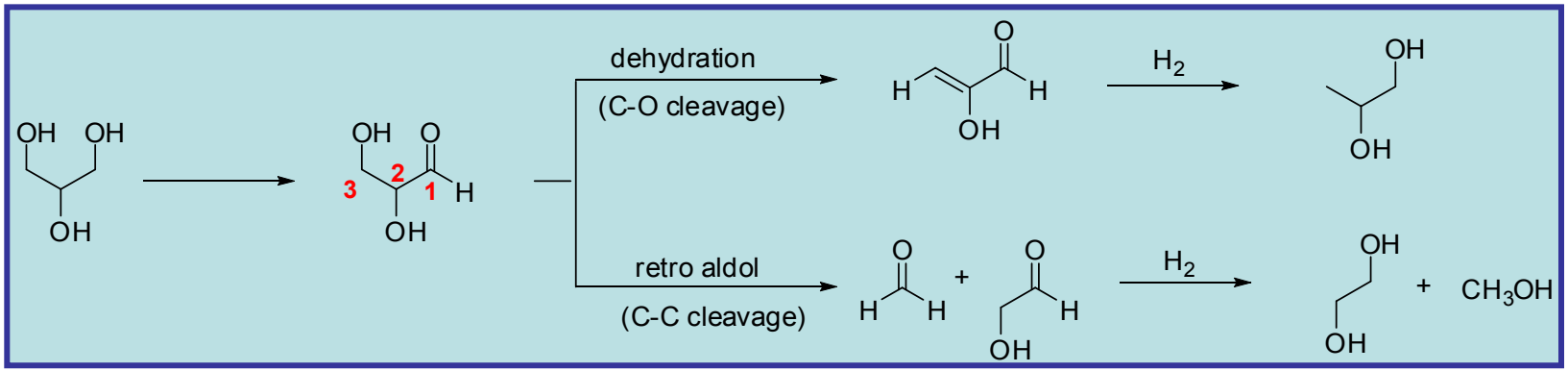
The addition of base promotes the base-catalyzed aldol reaction with formaldehyde (a C-C *forming* reaction) and acid formation via the Cannizzaro reaction




- 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.

# $C_{3+}$ Have Additional Paths Compared to $C_1$,$C_2$ and These Affect $H_2$ Selectivity



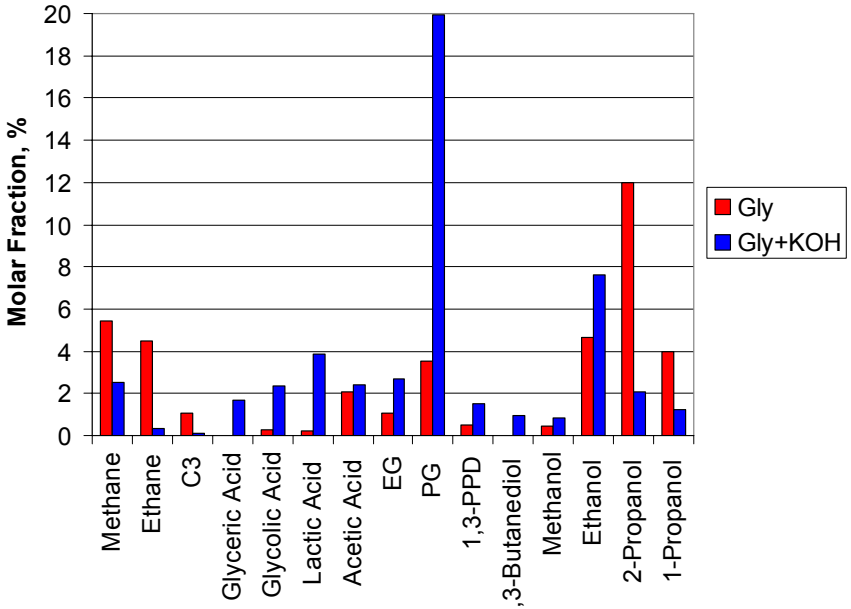

Substrates with 3 or more carbons have reaction pathways not available in $C_2$ and smaller substrates

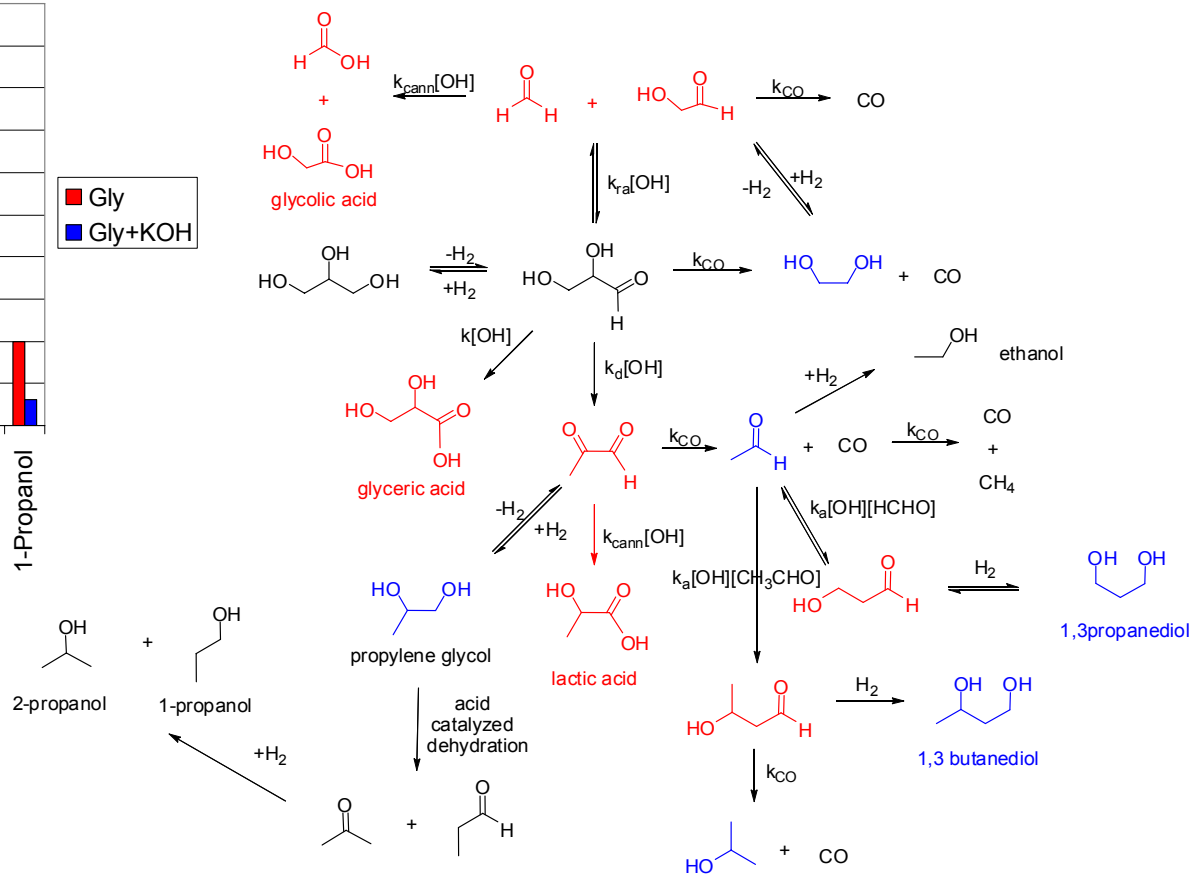
Dehydrogenation kinetically activates a C-O bond cleavage manifold (dehydration) at C atoms in a relative 1,3 relationship

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 |
| **H2 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** | H2-ALK | H2-LIQ | ALK-LIQ | ALK-LIQ |

KOH Effects (Generalized)

- Conversion is reduced
- $H_2$ selectivity variably affected
- Alkane selectivity reduced
- liquid phase selectivity increased

Tradeoffs

Changes in selectivity toward one component ($H_2$, 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 $H_2$ selectivity

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

| | ESR | APR |
|---|---|---|
| **Condition** | **350°C, ~14.5psi<br>24.21 wt.% ethanol<br>6ml/h feed, 25mg catalyst** | **225°C, ~420psi<br>10 wt.% ethanol<br>6ml/h feed, 217.2mg catalyst** |
| **$H_2$ productivity (kg/L-cal/h)** | **2.43** | **0.12** |
| **$H_2$ 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 $H_2$ productivity and TOF indicated the necessity to develop the stable catalyst for ESR process.
- Further $H_2$ 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

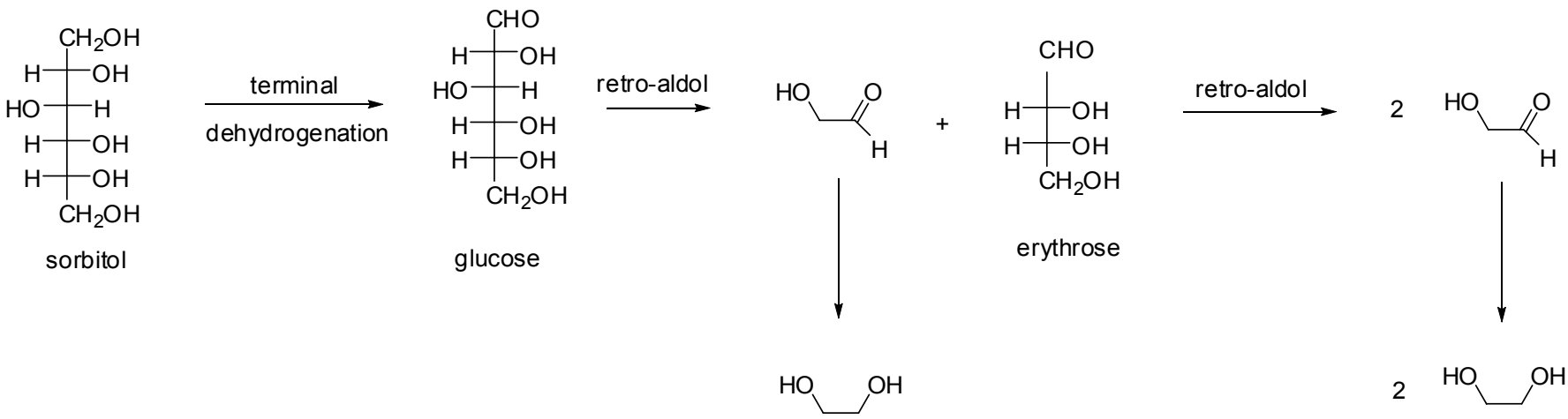
Decision points and any remaining issues

- 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 $C_5$ and $C_6$ 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 $H_2$ productivity.
- Intermediates of sorbitol APR have different reactivity and selectivity to $H_2$ with EG being a preferred intermediate.
- To improve the $H_2$ 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 $H_2$ selectivity used in our work

Definition of $H_2$ selectivity (Based on complete conversion )

%$H_2$ sel. =($H_2$ molecules produced/$H_2$ molecules theoretically produced)x100

$H_2$ theoretically produced = substrate (molecules) x conversion x AA

AA=$H_2$ numbers/reactant molecules (theoretically)

| Substrate | Reaction | AA |
|---|---|---|
| Methanol | $CH_3OH+H_2O \rightarrow CO_2 + 3H_2$ | 3 |
| Ethanol | $C_2H_6O+3H_2O \rightarrow 2CO_2 + 6H_2$ | 6 |
| EG | $C_2H_6O_2+2H_2O \rightarrow 2CO_2 + 5H_2$ | 5 |
| (1 or 2)-Propanol | $C_3H_8O+5H_2O \rightarrow 3CO_2 + 9H_2$ | 9 |
| PG or 1,3-PPD | $C_3H_8O_2+4H_2O \rightarrow 3CO_2 + 8H_2$ | 8 |
| Glycerol | $C_3H_8O_3+3H_2O \rightarrow 3CO_2 + 7H_2$ | 7 |
| Sorbitol | $C_6H_{14}O_6+6H_2O \rightarrow 6CO_2 + 13H_2$ | 13 |

This selectivity is from 0 to 1!

# Definition of $H_2$ selectivity used in literature

Based on gas phase (Dumesic method)

%$H_2$ sel. =(molecules $H_2$ produced/C atoms in gas phase)(1/RR)x100

RR=(theoretical) $H_2$ molecules/$CO_2$ molecules

For instance:

$C_2H_6O+3H_2O \rightarrow 2CO_2+6H_2$

RR = 6/2 = 3

This selectivity can be from 0 to infinity!