# Catalytic Production of Hydrogen, Fuels and Chemicals from Biomass-derived Oxygenated Hydrocarbons

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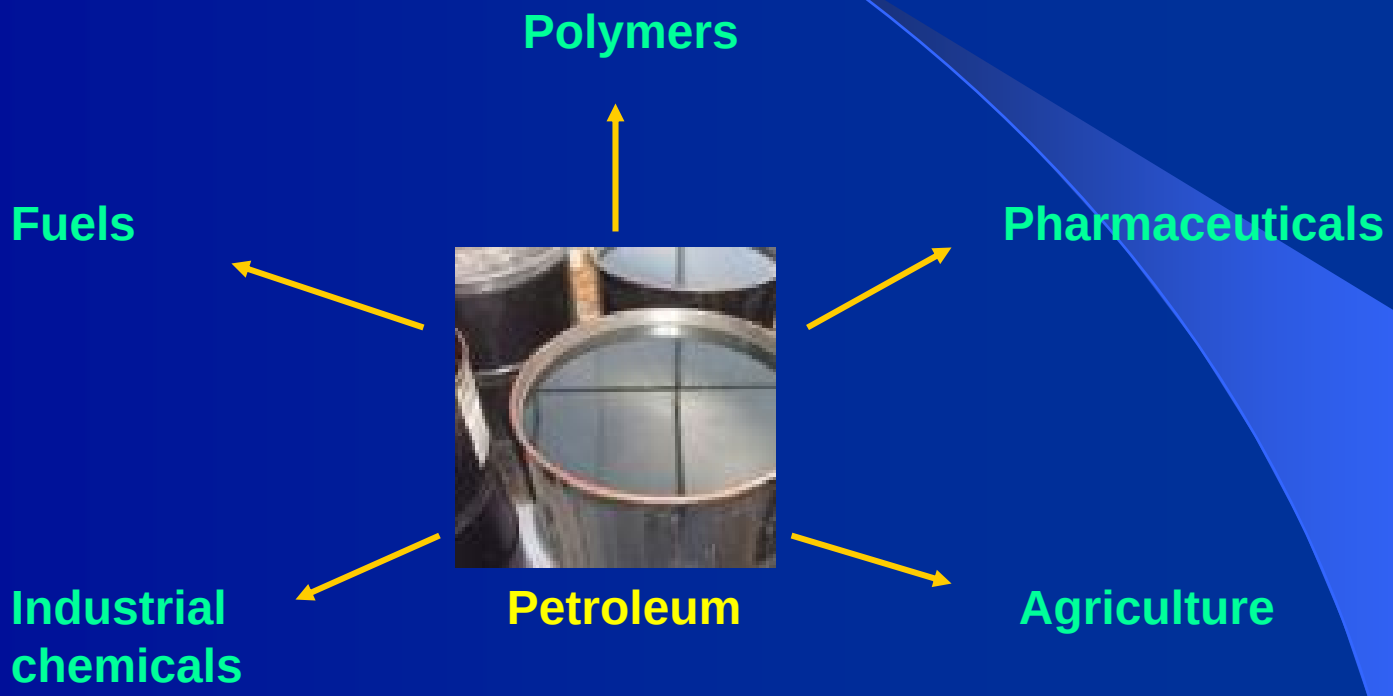
# Motivation: oil in every day life

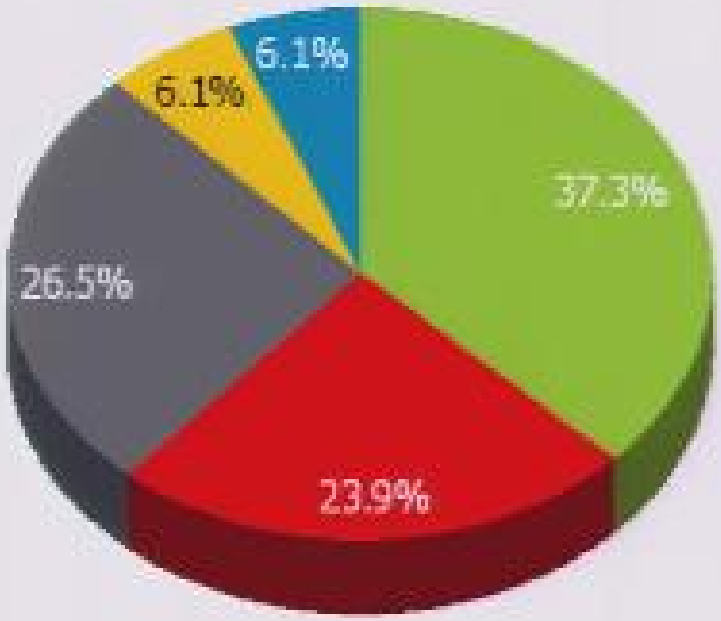
"Oil is the blood of today's society"

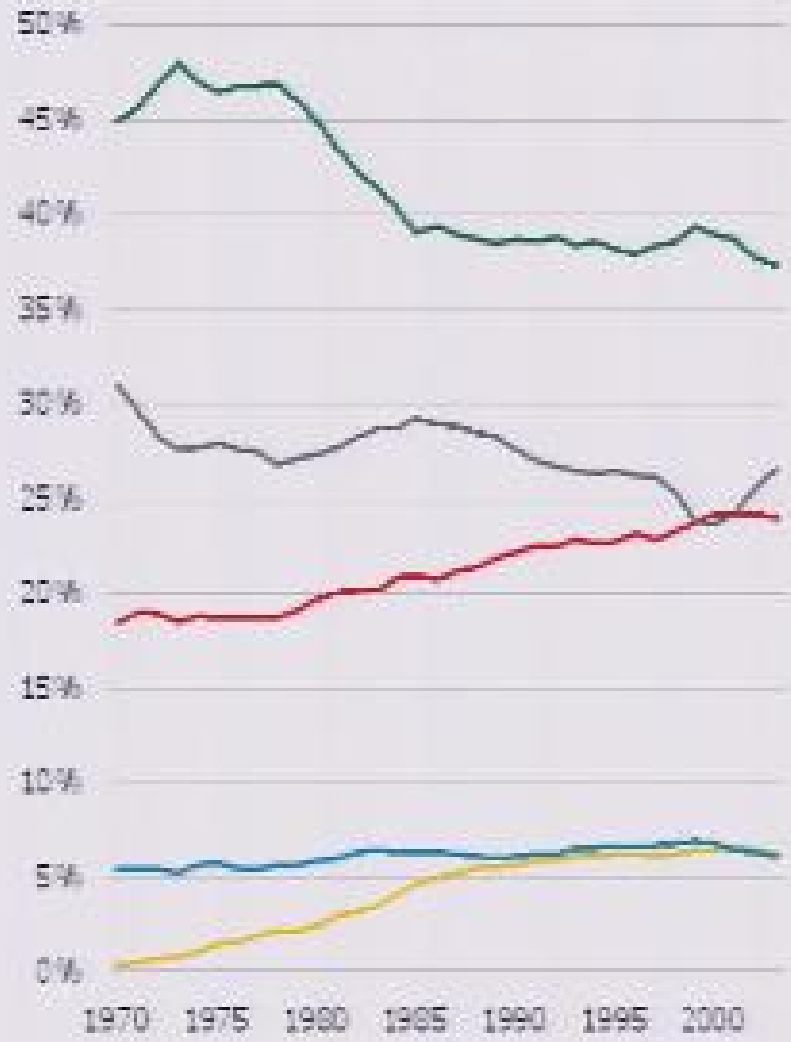



**"Demand for petroleum products in the United States averaged 19.7 million barrels per day in 2004. This represents about 3 gallons of petroleum each day for every person in the country" (DOE annual report 2004)**

# current and historical global energy mix

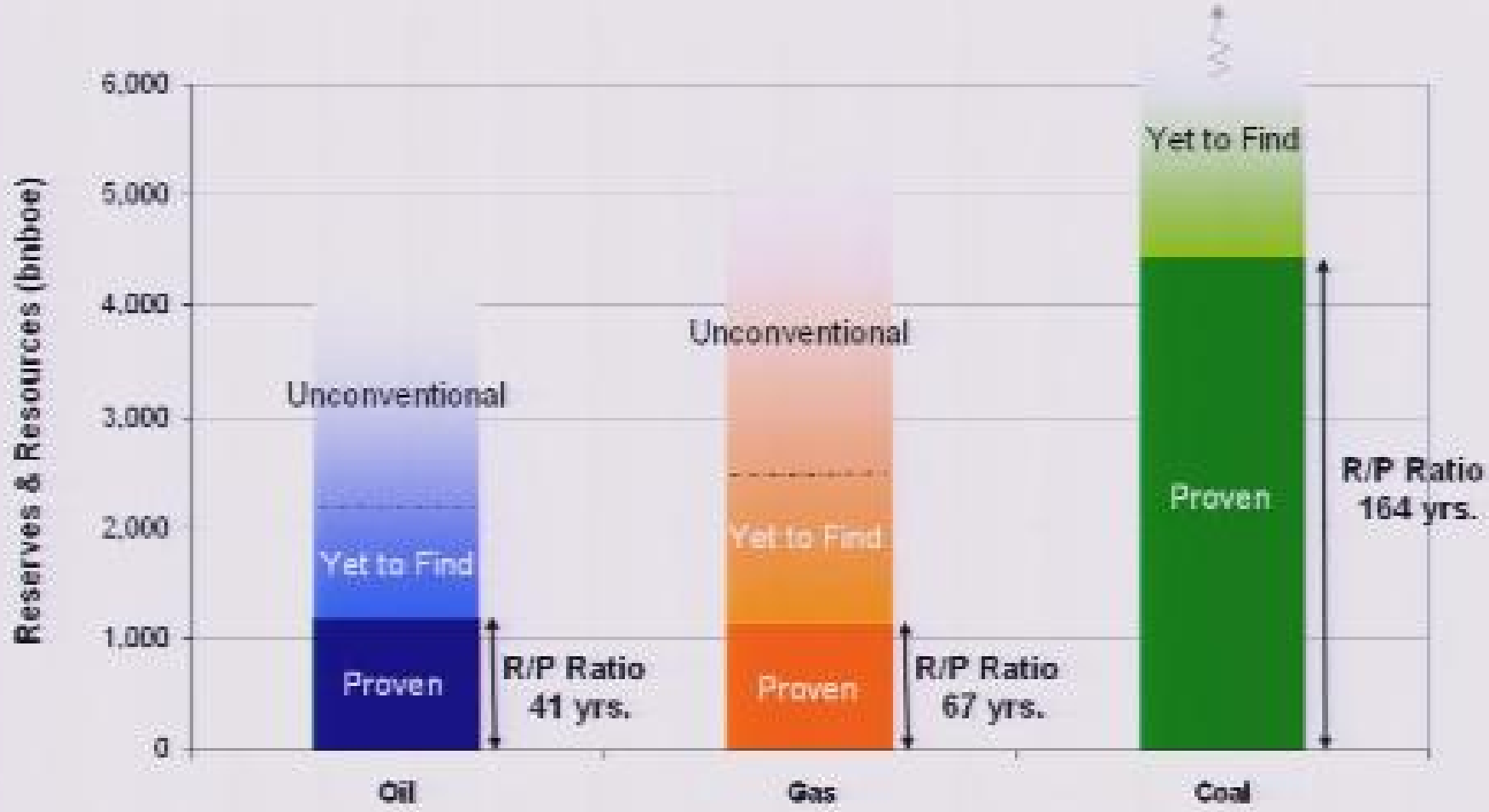
Current global energy supply is dominated by fossil fuels – oil has been the largest component of the energy mix for many decades; gas has grown strongly since the 1970's; coal has been growing in the last four years; hydro is constant and nuclear has plateaued




Source: BP Statistical Review

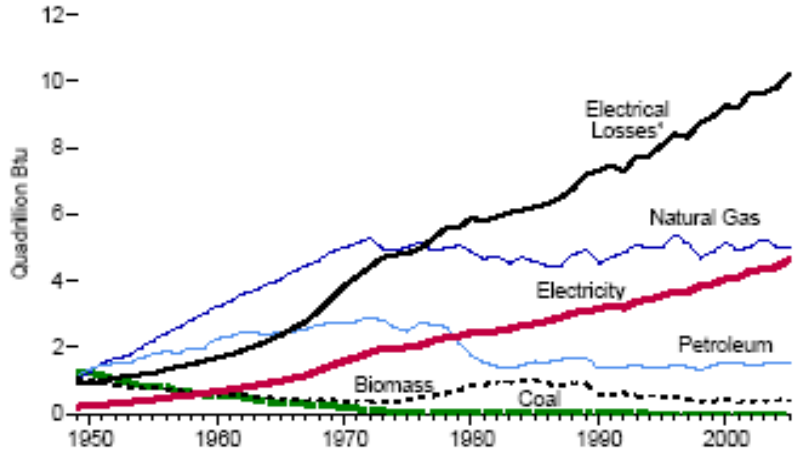
# substantial global fossil resources




Source: World Energy Assessment 2001, HIS, WoodMackenzie, BP Stat Review 2005, BP estimates

# U.S. Energy Consumption: End-Use

**Residential, By Major Source**




* Electrical system energy losses associated with the generation, transmission, and distribution of energy in the form of electricity.

Note: Because vertical scales differ, graphs should not be compared.
Sources: Tables 2.1b–2.1e.

# Biomass Potential

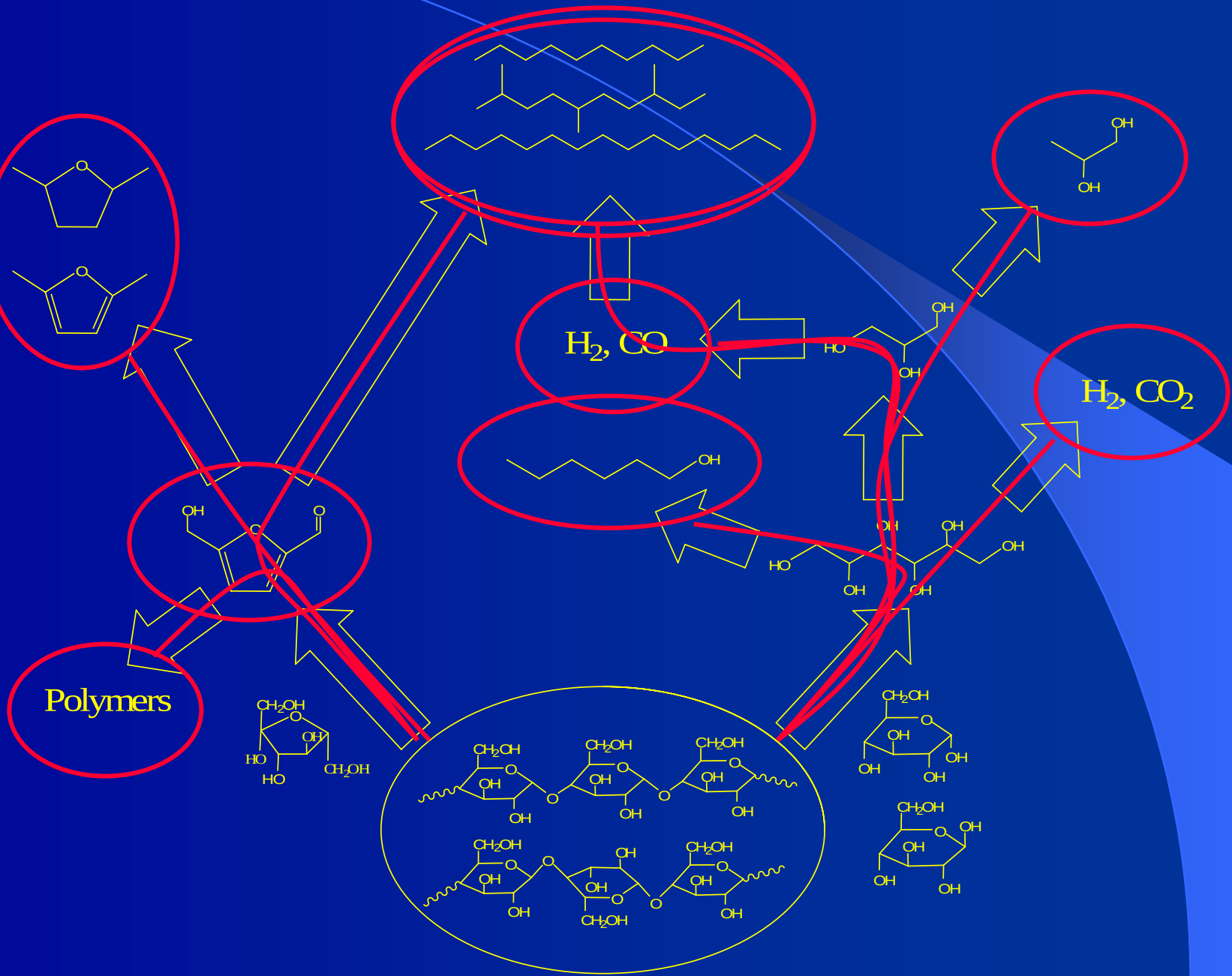
- 1.3 x $10^9$ (billion) dry tons per year (U.S.)
- Equivalent to 3.5 x $10^9$ barrels of oil (boe)
- 1 boe = 5.8 x $10^6$ (million) BTU = 6.1 x $10^9$ J
- Equivalent to 20 x $10^{15}$ (quadrillion) BTU/year
- U.S. energy consumption = 140 x $10^{15}$ BTU/year
- U.S. biomass potential = 15%
- Global Biomass production = 95 x $10^{15}$ BTU/year
- Woody biomass production = 40 x $10^{15}$ BTU/year
- Global energy consumption = 315 x $10^{15}$ BTU/year
- Global biomass potential = 30%

# Biomass – Transportation Sector

- Total energy consumed in U.S. = 140 quads
- Residential = 22 quads (16%)
- Commercial = 18 quads (13%)
- Industrial = 32 quads (23%)
- Transportation = 28 quads (20%)
- Electric Power = 41 quads (29%)
- Biomass = 20 quads
- Biomass potential = 70% of transportation

# Overview of Routes (at UW) for Biomass Conversion to Hydrogen, Fuels and Chemicals

# UW Routes to $H_2$, Fuels & Chemicals

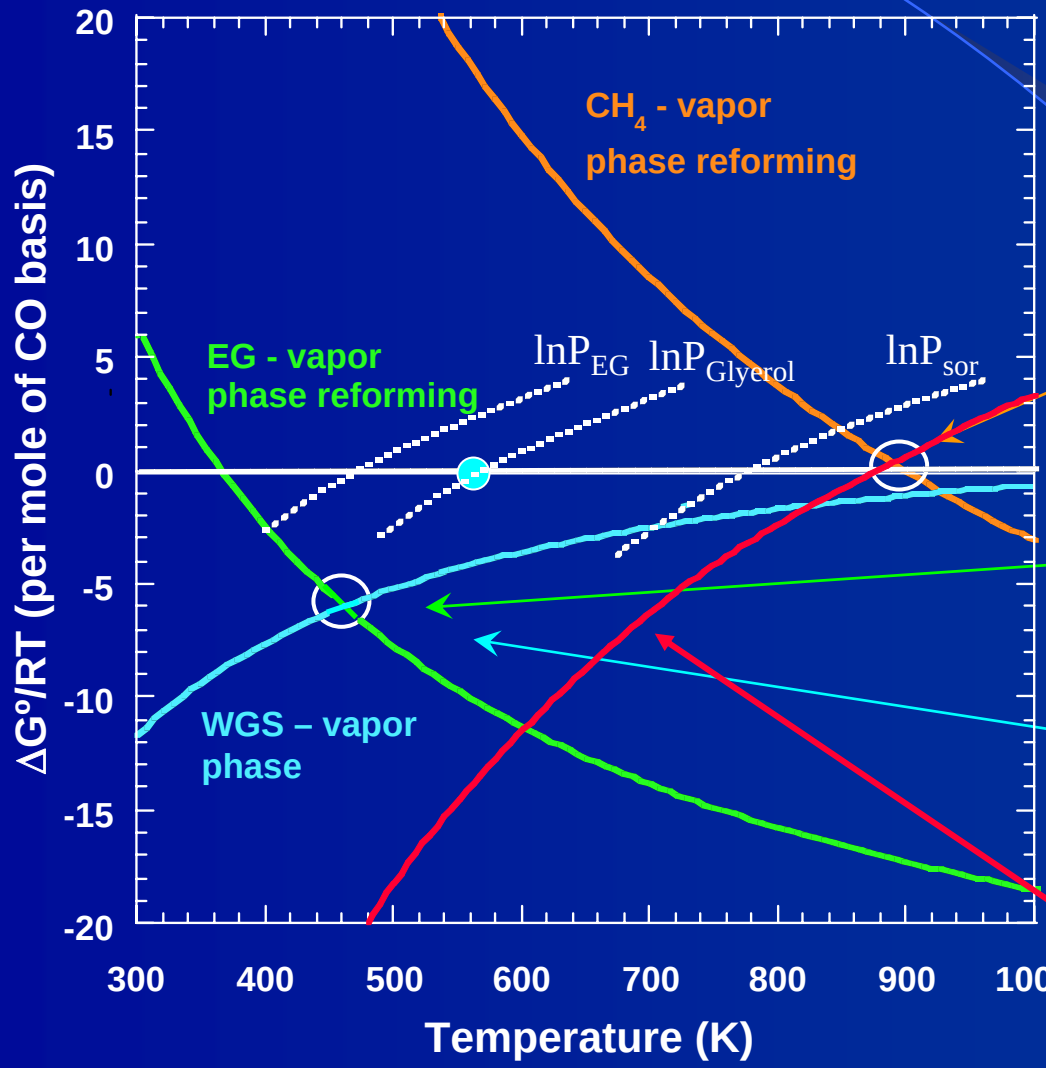


# Production of Hydrogen from Biomass-derived Carbohydrates

# Reforming Thermodynamics

$CH_4 + H_2O \rightarrow CO + 3\,H_2$ reforming

$CO + H_2O \rightarrow CO_2 + H_2$ water-gas shift




**Methane reforming at high temperatures**

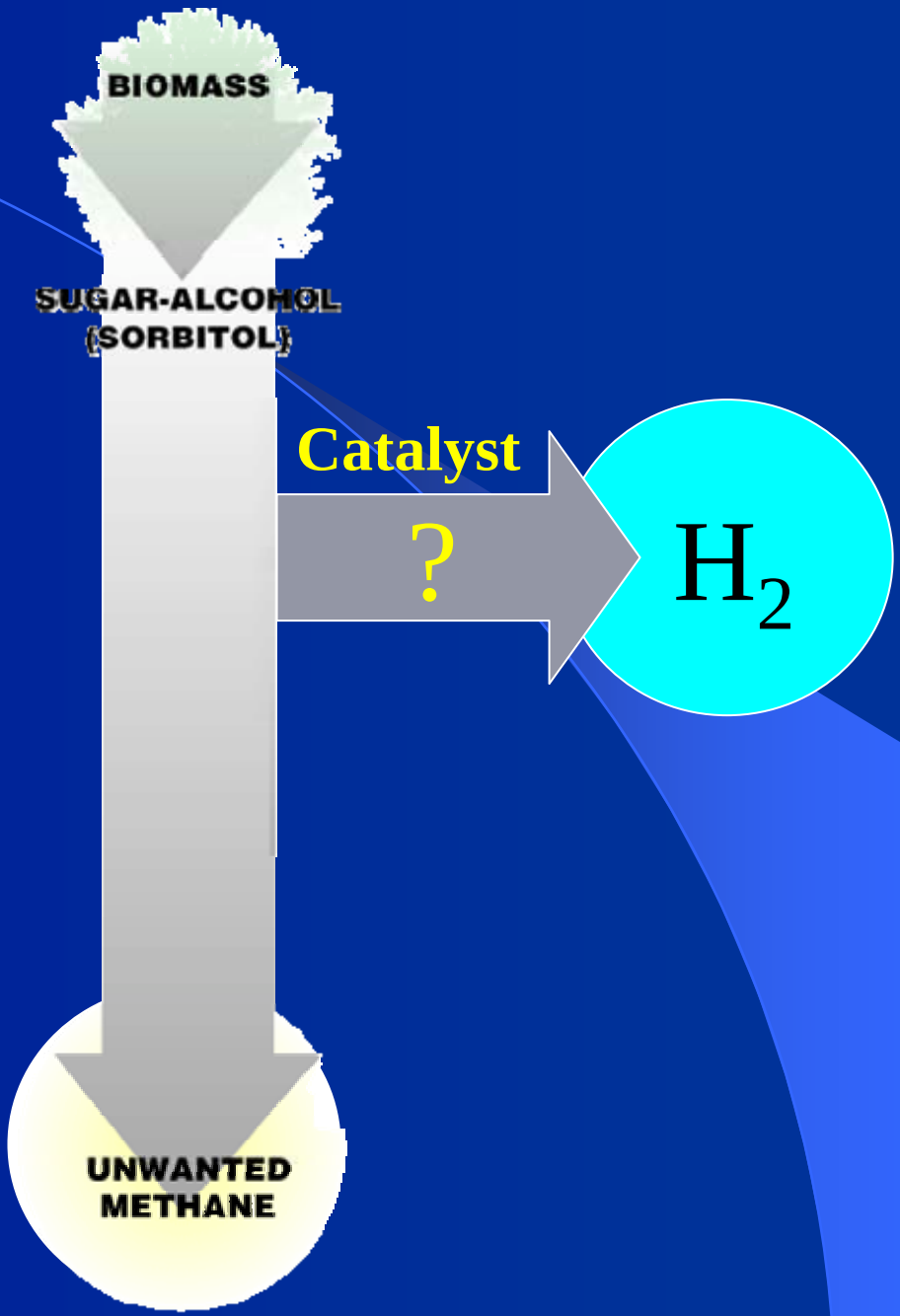
**Oxygenate reforming at low temperatures**

**Favorable Water-gas shift**

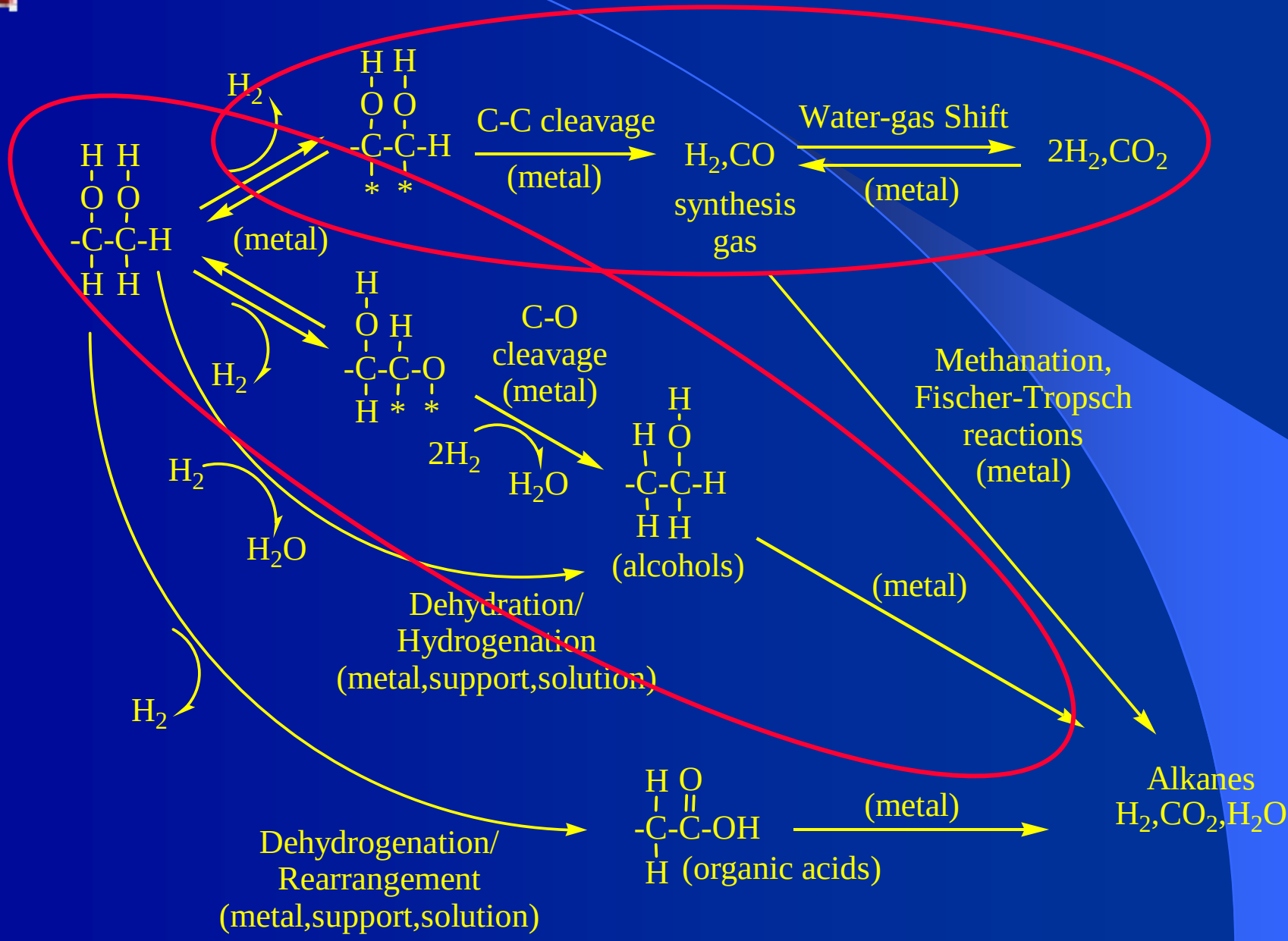
**Methanation favorable at low temperatures**

# The Challenge:

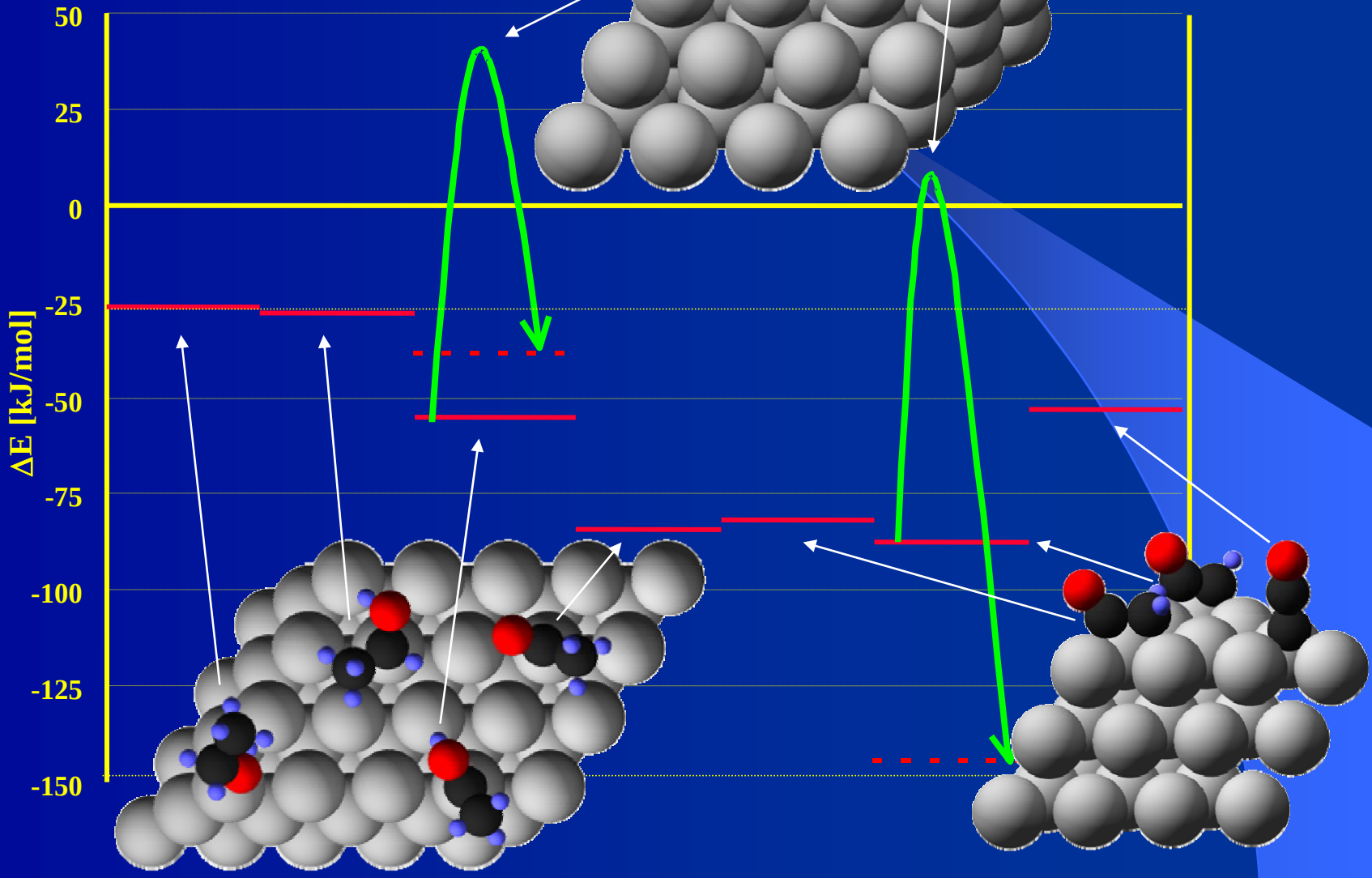
Can we find catalysts that produce $H_2$ versus $CH_4$?



# Selectivity Challenges



# Potential Energy Diagram: Ethanol/Pt(111)




Alcala, Mavrikakis, Dumesic, ***J. Catal***. **218**, 178 (2003)

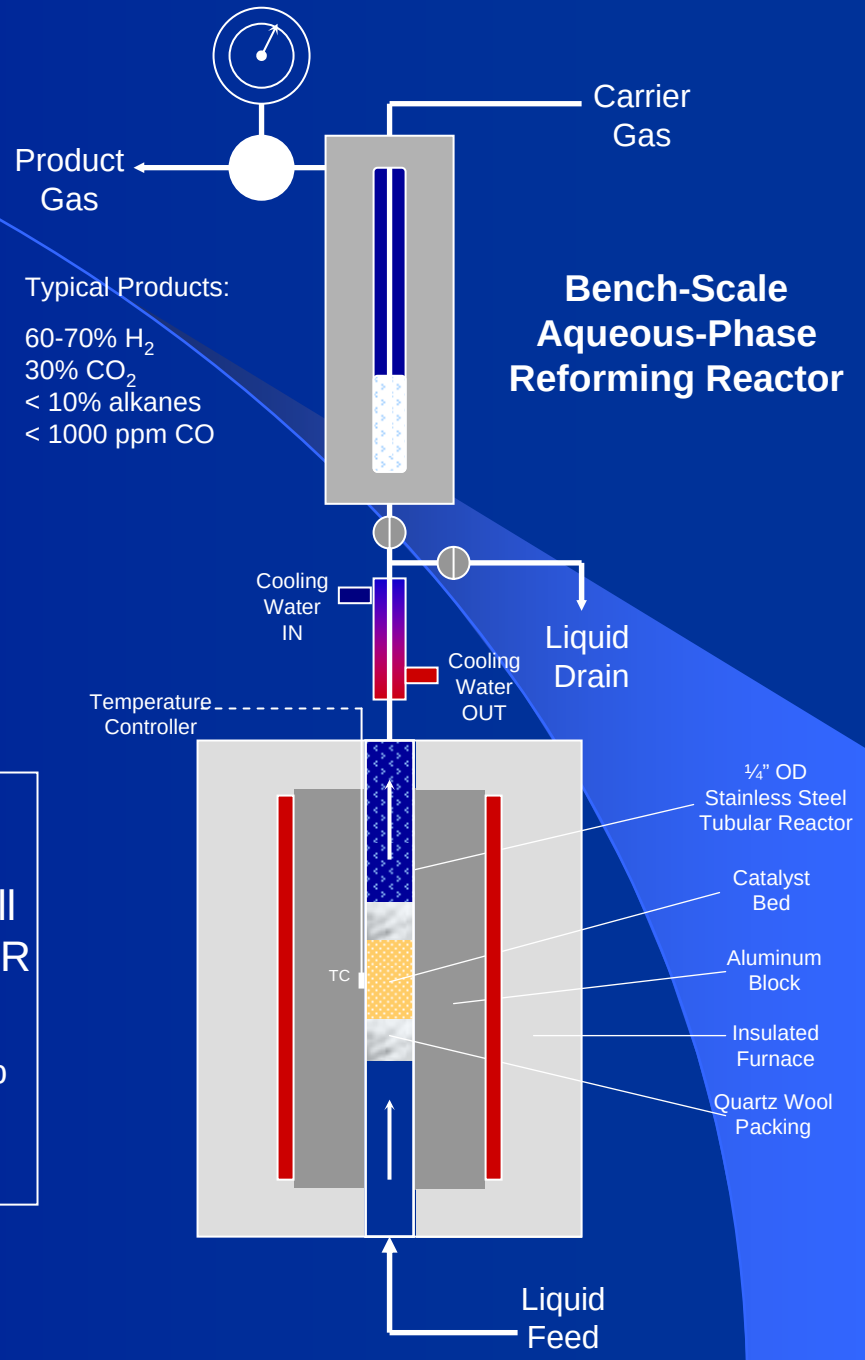
# Reforming of Oxygenates over Supported Metal Catalysts

# Liquid Phase Kinetics

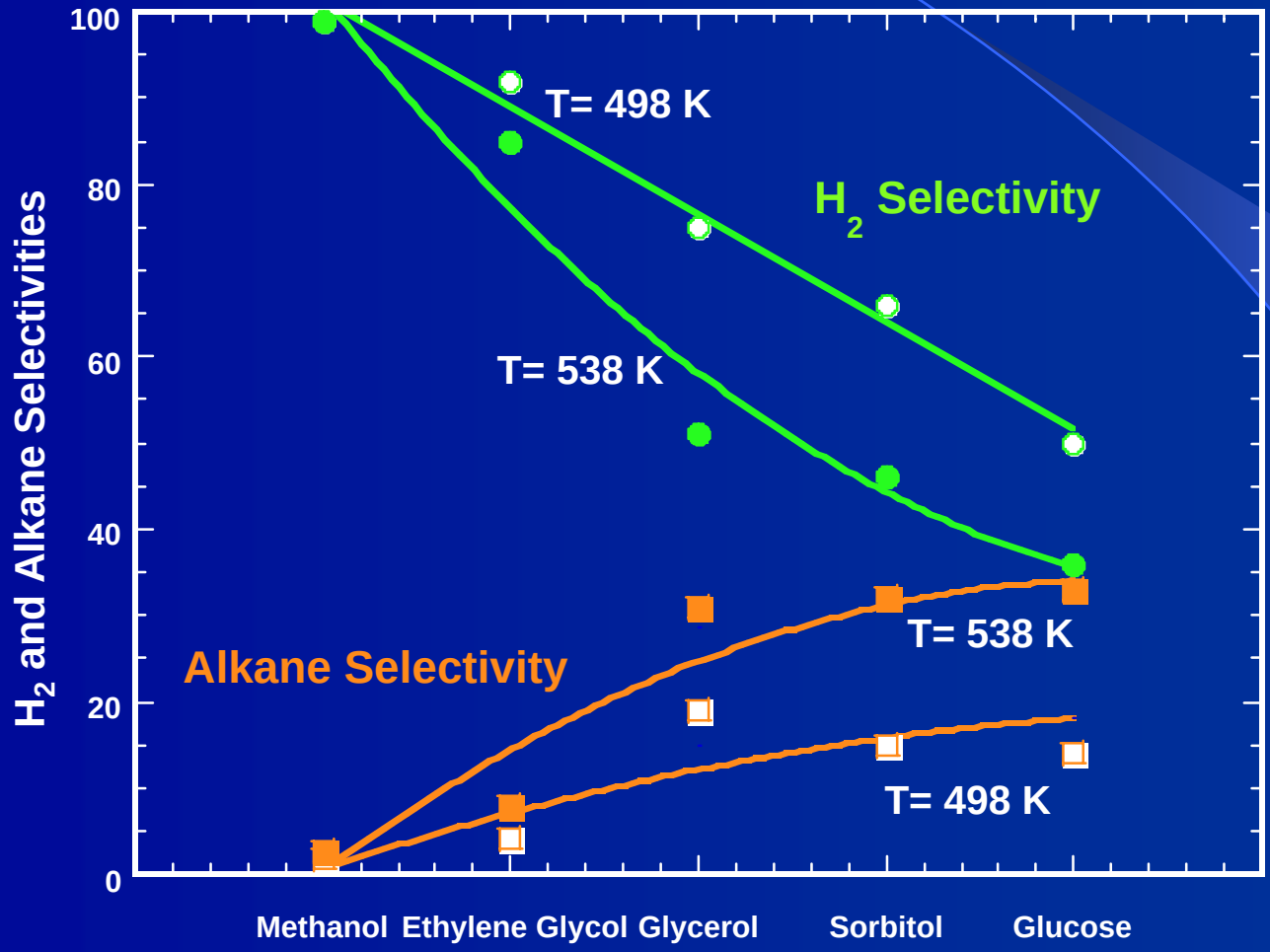
- Pressure maintained above bubblepoint pressure of feed at reaction temperature
- Differential reactor (verified kinetic control) or high-conversion operation
- Product analysis via GC, HPLC, TOC

**$H_2$ Selectivity** = $\dfrac{H_2 \text{ Produced} \times 100\%}{H_2 \text{ that would be produced if all carbon products were from APR}}$

**Alkane Selectivity** = $\dfrac{\text{Carbon as alkanes} \times 100\%}{\text{Total carbon in products}}$



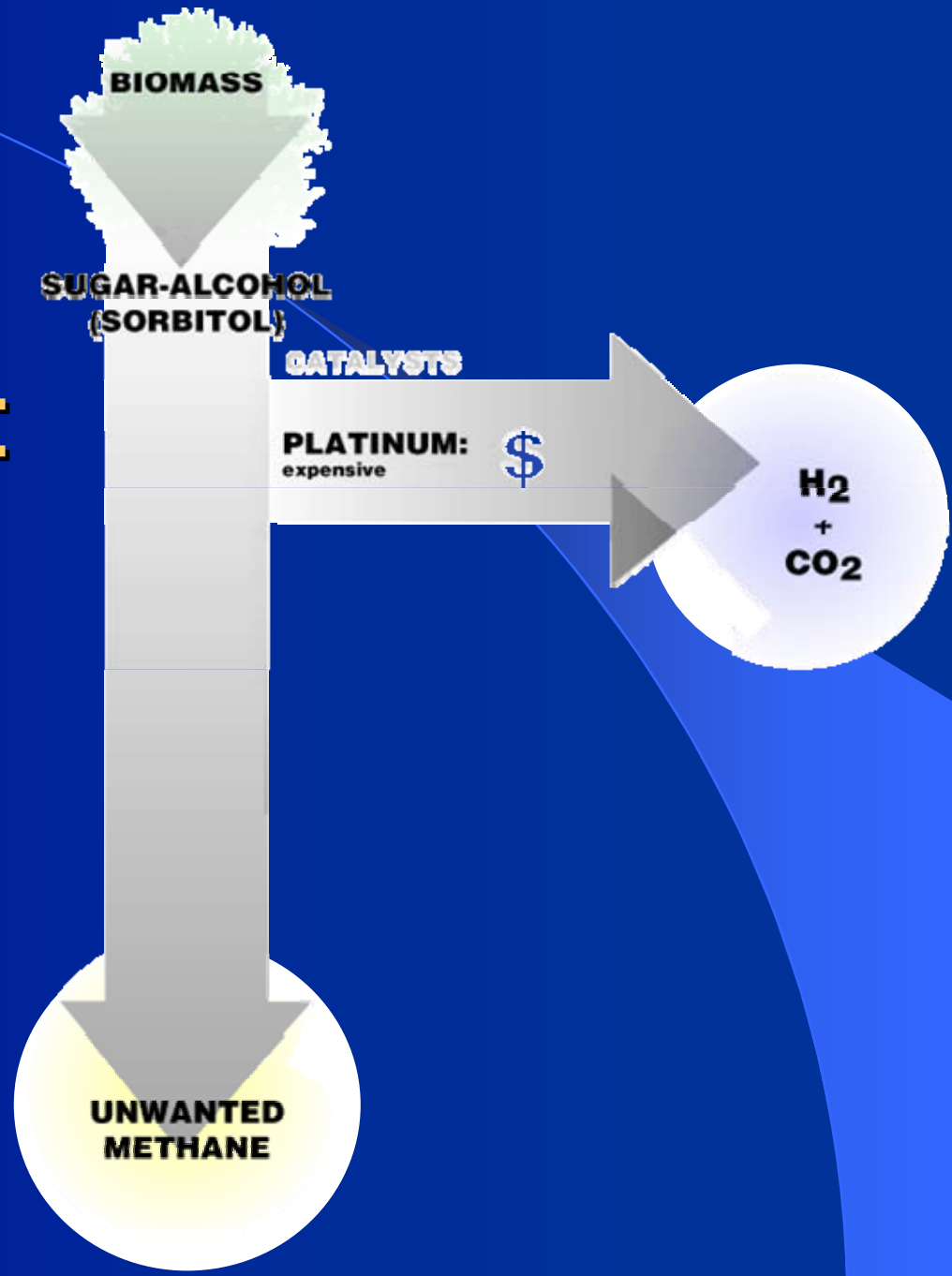
# Aqueous-phase Reforming of Oxygenates over $Pt/Al_2O_3$




- 1 wt% feed
- High Conversions
- Clean reaction – gas phase products
- Complete Carbon Balance

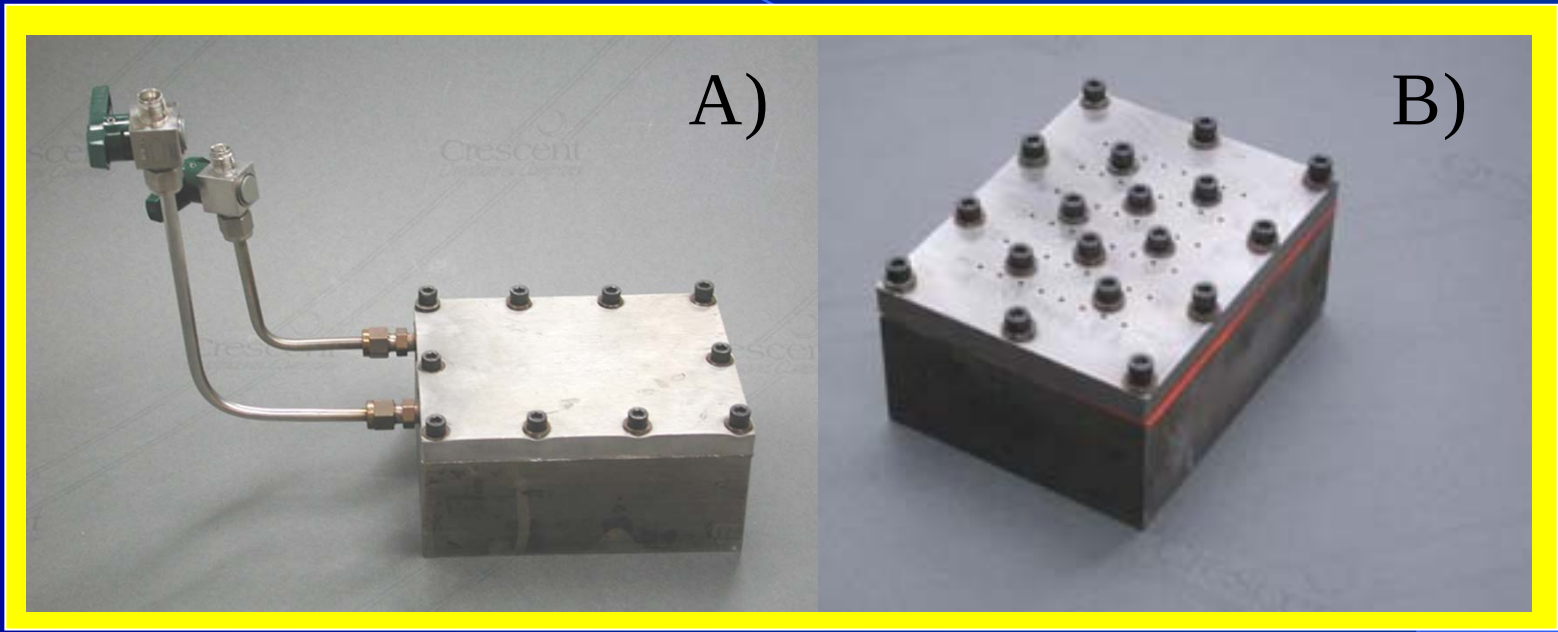
Cortright, Davda, Dumesic, ***Nature*** **418**, 964 (2002)

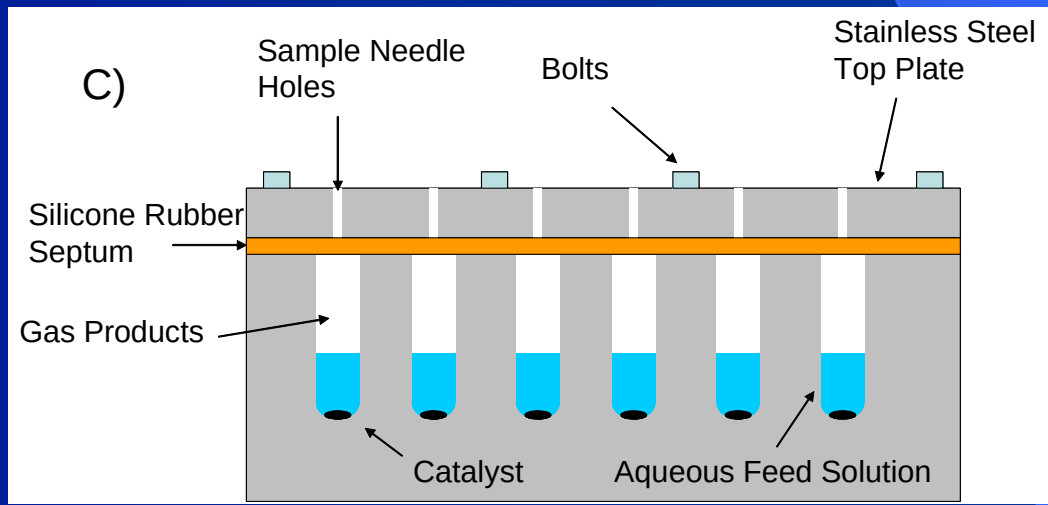
# Demonstration: Biomass to $H_2$ over Pt



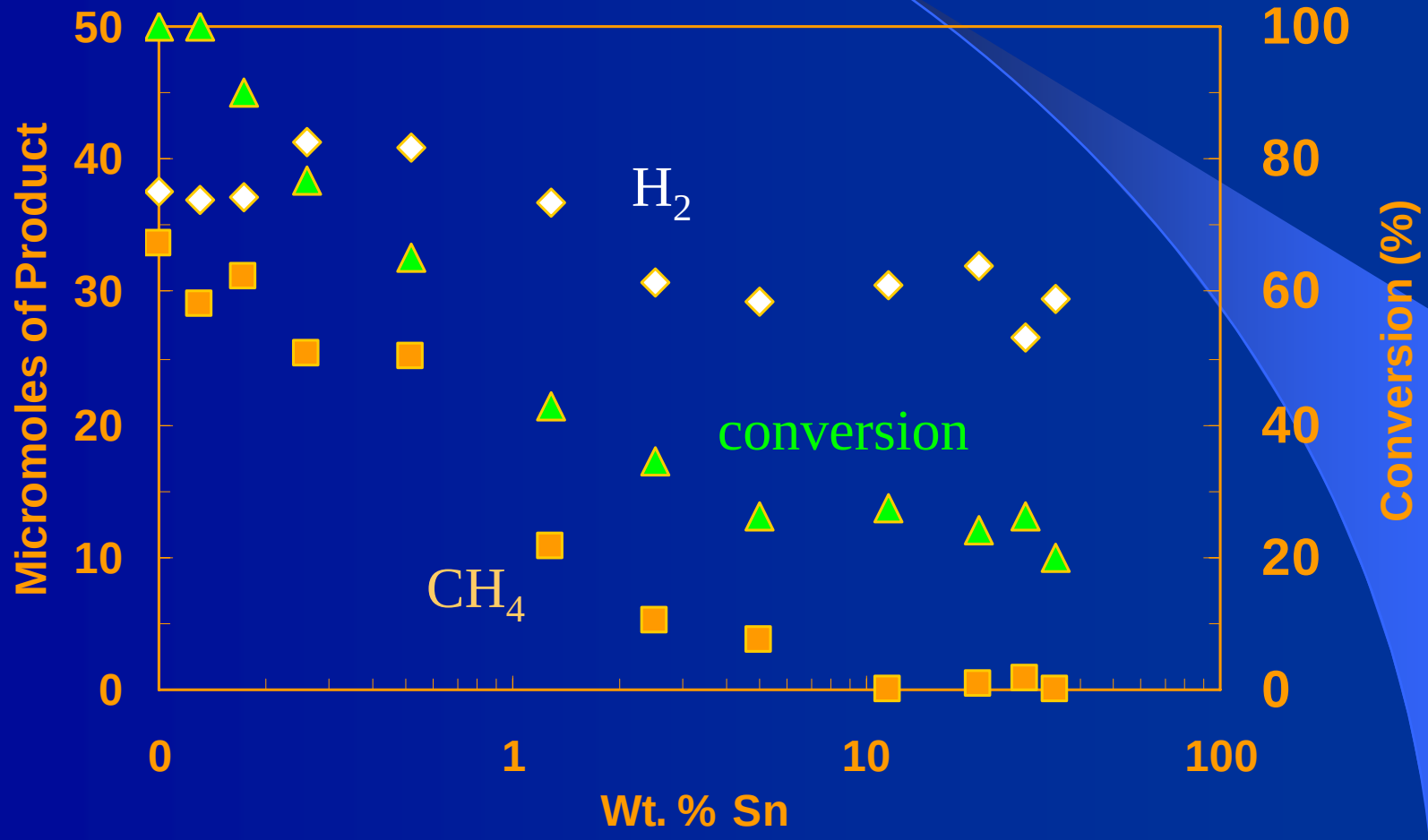
# Non-precious Metal Catalysts

# High-Throughput Reactor





# High-Throughput Studies of Raney-NiSn




Huber, G.W.; Shabaker, J.W.; and Dumesic. J.A.; "Raney Ni-Sn Catalyst for H2 from Biomass-Derived Hydrocarbons", *Science*, **300**, 2075-2077 (2003)

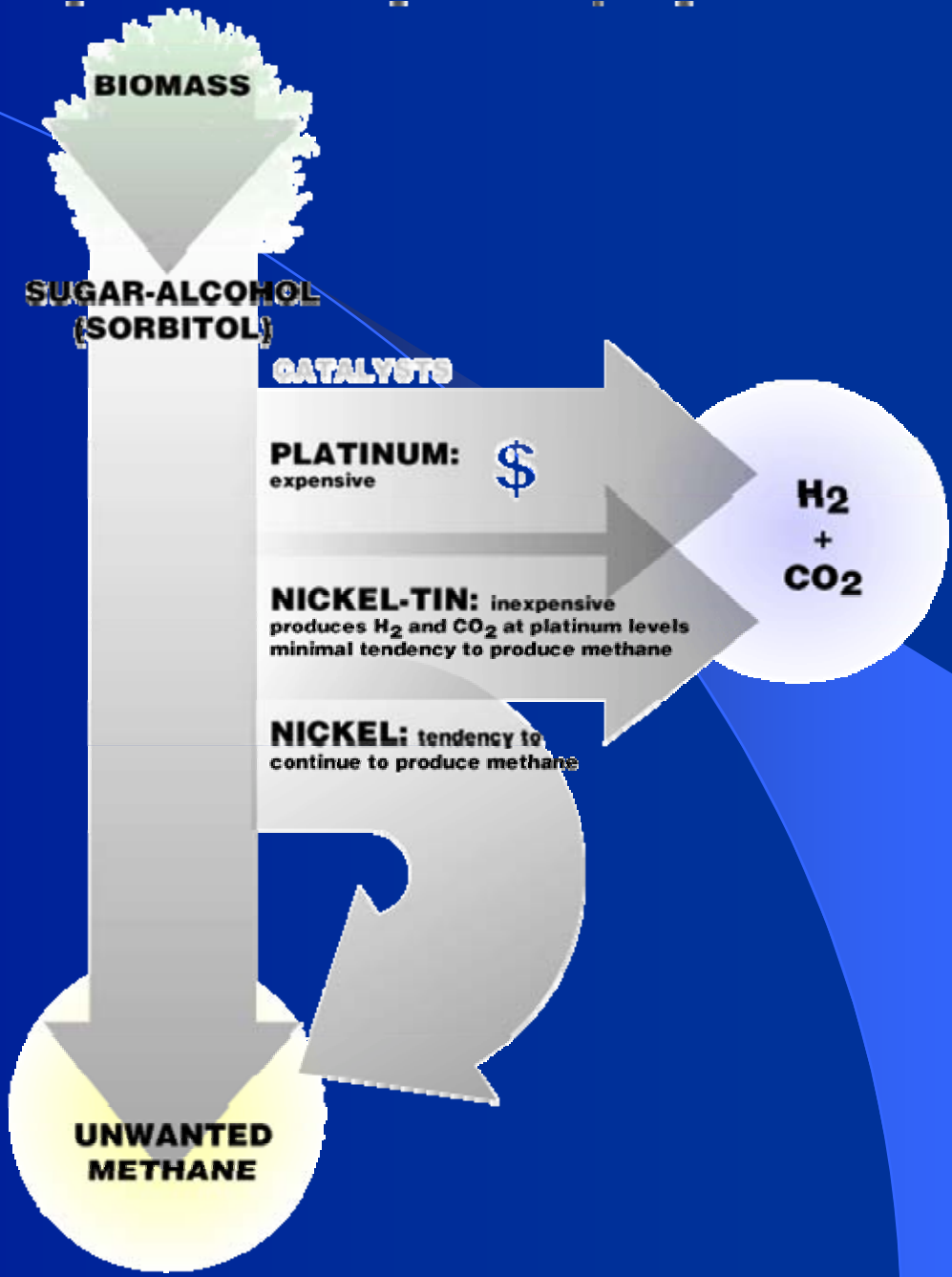
# EG-Reforming on Raney-NiSn: Packed-bed APR Reactor

| Catalyst | $H_2$ Selectivity % | Alkane Selectivity % | $H_2$ TOF $min^{-1}$ | $CH_4$ TOF $min^{-1}$ | $H_2$ Rate $\mu mol\ cm^{-3}\ min^{-1}$ |
|---|---|---|---|---|---|
| Raney Ni | 47 | 33 | 1.1 | 0.28 | 360 |
| Raney $Ni_{270}Sn$ | 57 | 27 | 1.4 | 0.23 | 430 |
| Raney $Ni_{14}Sn$ | 93 | 5 | 1.4 | 0.031 | 360 |
| $Pt/Al_2O_3$ | 98 | 0 | 5.3 | 0 | 450 |

**Addition of Sn:** **Improves $H_2$ selectivity** **Decreases $CH_4$ selectivity**

**$Ni_{14}Sn \sim Pt/Al_2O_3$**

# Catalysts for Biomass Conversion



# Virent Energy Systems

## 10kWe APR/HICE Genset Specifications

(Preliminary)

### SuperNatural™ Gas Properties

Composition (by volume)

| | |
|---|---|
| Hydrogen: | ~30% |
| Methane: | ~10% |
| Ethane: | ~10% |
| Propane: | ~10% |
| $CO_2$: | ~40% |

| | |
|---|---|
| Heating Value: | 600 BTU/ft³ |
| Pressure (exit of APR): | 400-500 psig |

### Feedstocks

- Glycerol (50% concentration)
- Sorbitol (future: late 2006)
- Glucose (future: late 2006)

### Integration

- Ford 1.6 liter, 4-Cylinder HCNG ICE/11.5 kW Genset
- Catalytic Burner can supply process heat
- ICE Exhaust heat integration
- Combined Heat and Power Mode (CHP)
- Optional PSA or Pd Membrane for pure hydrogen

### APR Weight & Dimensions

- 2 m Wide x 1 m Deep x 1.5 m High
- 725 Kg (without fuel)

### APR/HICE Performance at 10kWe output

| | |
|---|---|
| APR Efficiency: (LHV inputs/LHV outputs) | 90% |
| Feedstock Consumption: (Glycerol) | ~2.2 gal/hr |
| Gas flow rate into ICE: | 90 liters/min |
| HICE Genset Efficiency: | 32% |

**APR/HICE System: Distributed Renewable Energy Generation.**

- **No Fossil Fuels Required.** Generate carbon neutral, high energy fuels from renewable widely available biomass-derived feedstocks
- **Unteathered Operation.** The APR/HICE system can operate independently from the electrical grid or natural gas supplies.
- **Localized Production.** On-demand hydrogen and alkanes with low capital investment
- **Friendly Operating Conditions.** Significantly lower operating temperatures (240°C v. 800°C) allows for feedstock reformation and water-gas shift reaction to take place in one processing step.
- **Simple Purification.** Output pressures of APR hydrogen rich effluent (typically 10 to 50 bar) can be effectively purified, if desired, using either a pressure swing adsorption or palladium membrane technologies
- **Flexible.** Can produce multiple fuels and fuel blends tailored to the needs of the power conversion device.

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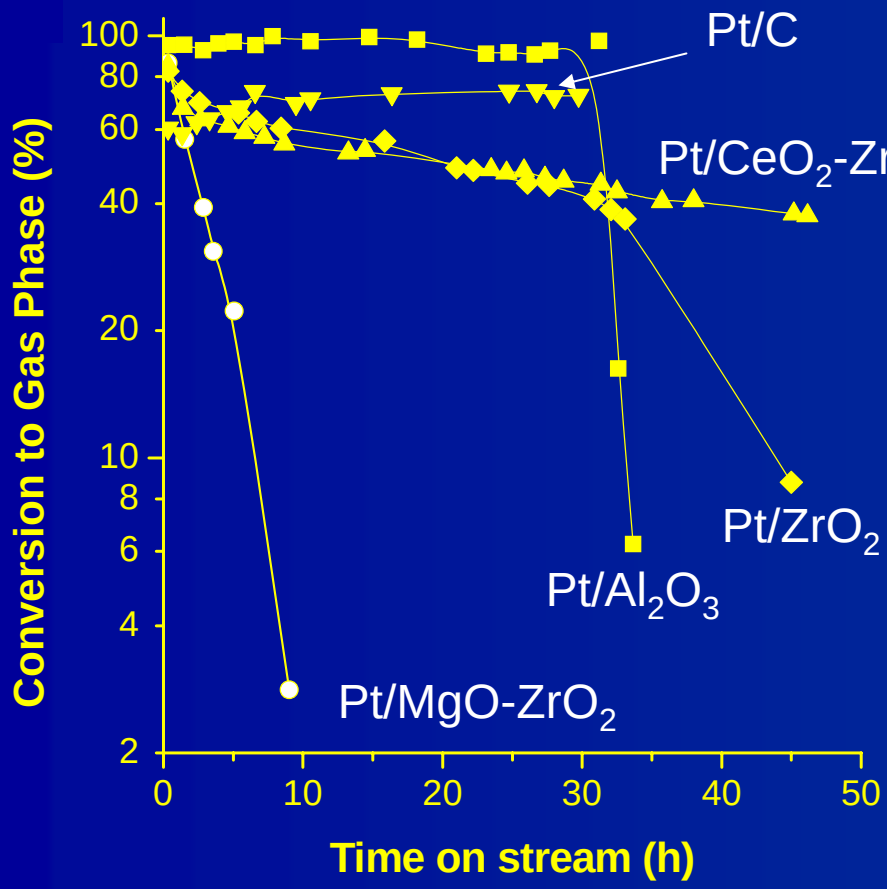
# Vapor-phase Conversion of Glycerol to CO:$H_2$ Mixtures

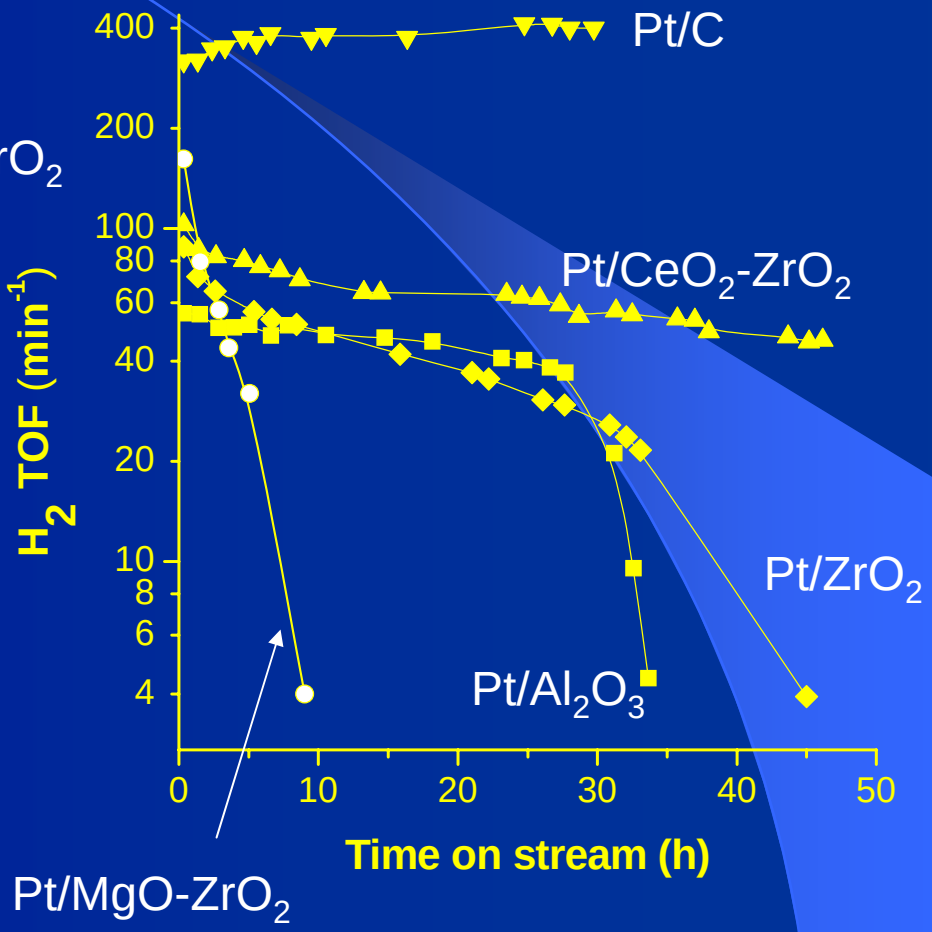
# Sources of Glycerol

- By-product waste-stream from biodiesel production, i.e., trans-esterification of tri-glycerides, leading to ~80 wt% glycerol in water
- Glucose fermentation, leading to 25 wt% glycerol in water (compared to 5% for ethanol)
- Catalytic hydrogenolysis of xylitol and sorbitol ($C_5$ and $C_6$ sugar-alcohols)

# Glycerol Conversion to Synthesis Gas at 350$^{o}$C

# Glycerol Reactivity (350°C)



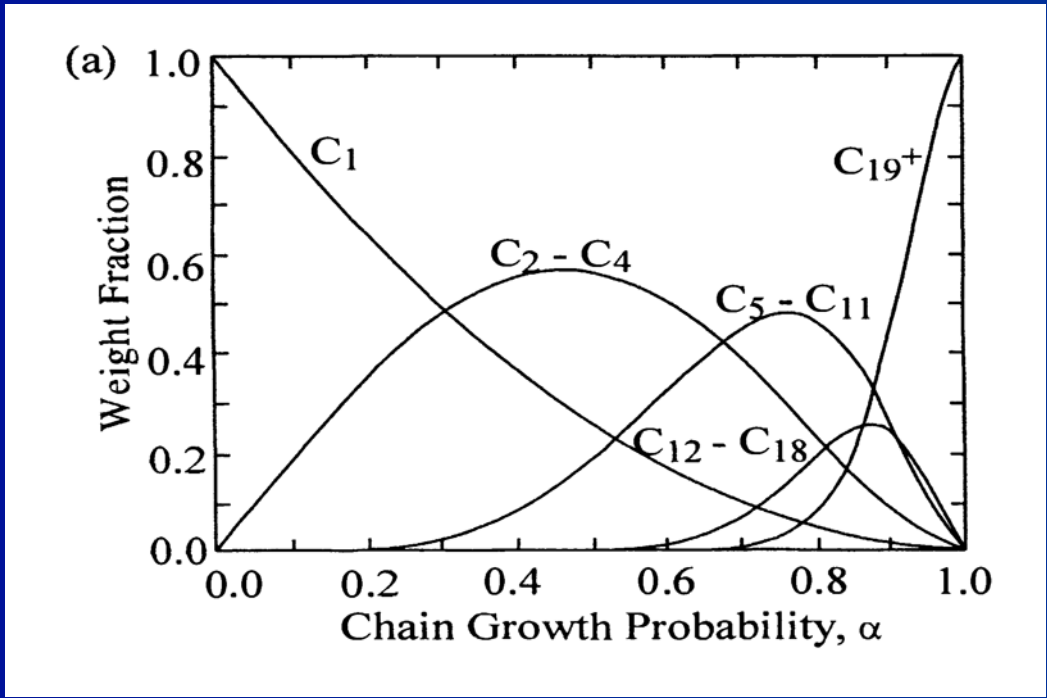
# Coupling of Glycerol Conversion with Fischer-Tropsch Synthesis

# Fischer-Tropsch Synthesis

Higher hydrocarbons from synthesis gas ($H_2$:CO)

$$n\ CO + (2n+1)\ H_2 \rightarrow C_nH_{2n+2} + n\ H_2O$$

Typical catalysts include: Fe, Co, and Ru



# Coupling Gasification & FT Synthesis

$$C_3O_3H_8 \xrightarrow{1} 3CO + 4H_2$$ 83 kcal/mol

$$2.24(CO + 2H_2 \xrightarrow{2} \frac{1}{8}C_8H_{16} + H_2O)$$ -81 kcal/mol

$$0.28(C_8H_{16} + H_2 \xrightarrow{3} C_8H_{18})$$ -10 kcal/mol

$$0.76(CO + H_2O \xrightarrow{4} CO_2 + H_2)$$ -7 kcal/mol

-98

$$C_3O_3H_8 \xrightarrow{5} 0.28C_8H_{18} + 0.76CO_2 + 1.48H_2O$$ -15 kcal/mol

$$C_3O_3H_8 + 3.5O_2 \longrightarrow 3CO_2 + 4H_2O$$ -354 kcal/mol

$$\frac{\Delta H_1}{\Delta H_c(Gly)} = 24\%$$

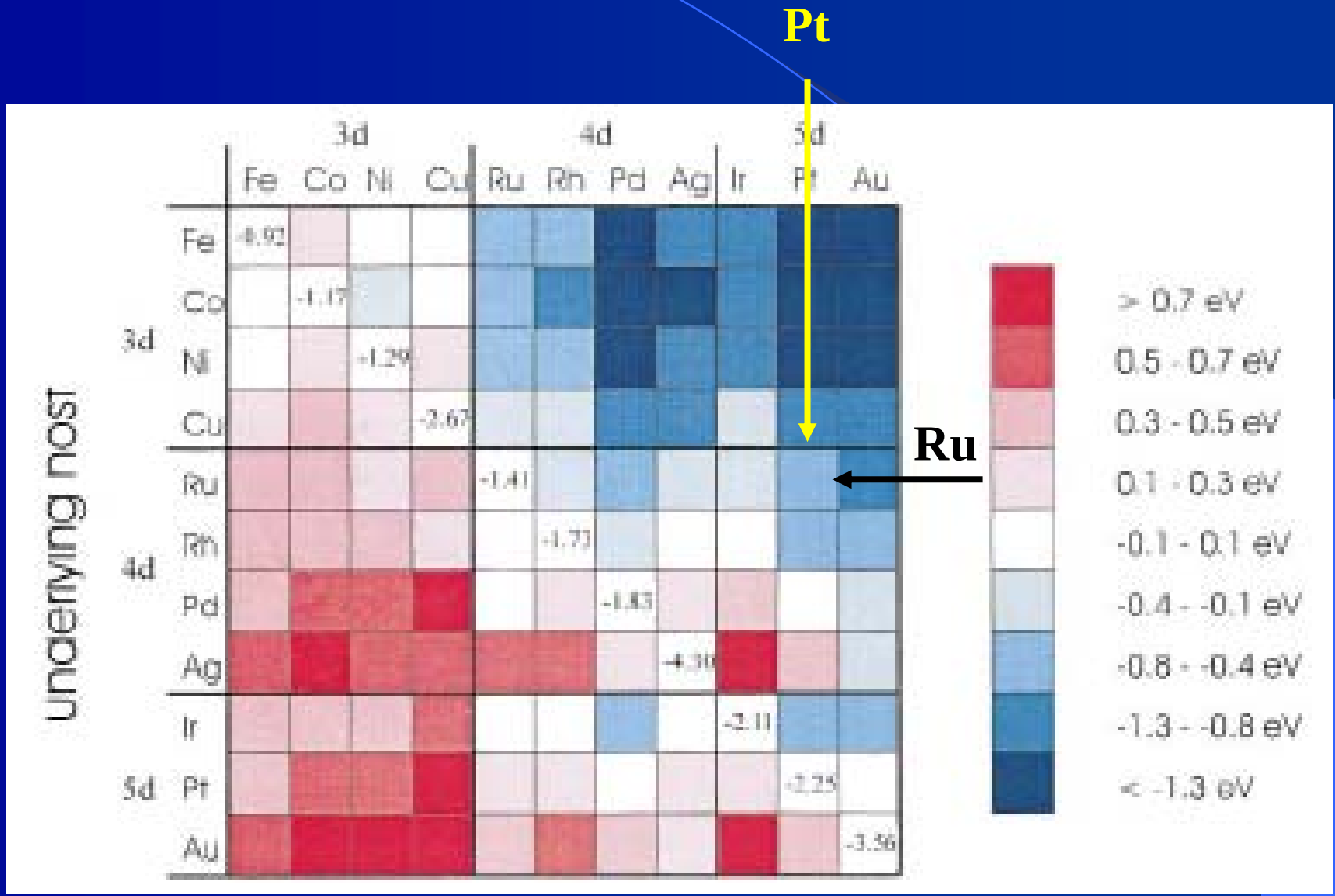
$$\frac{\Delta H_5}{\Delta H_c(Gly)} = -4\%$$

# Reforming Catalysts

- Fischer-Tropsch synthesis typically carried out at 500 – 550 K (and 10 – 50 bar)
- Heat must flow from FT to reforming catalyst (Temperature for FT > T for reforming)
- Pt/C not active below ~573 K
  - $\Theta_{CO}$ increases as T decreases
  - Additives needed to lower adsorption energy of CO on Pt
- Surface alloys may be useful!!

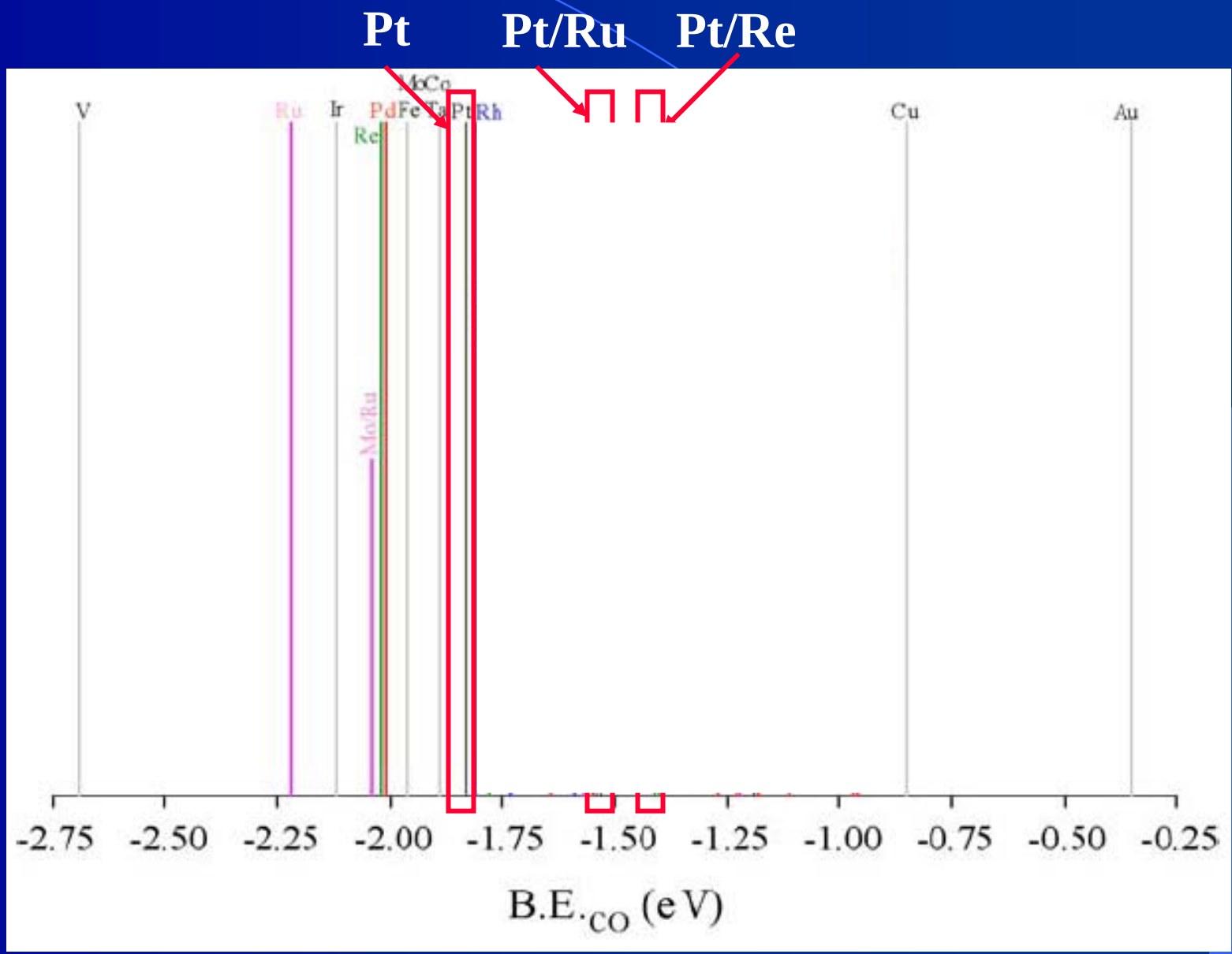
# d-band shift

## Nørskov et al., J. Catal. **199**, 123 (2001)

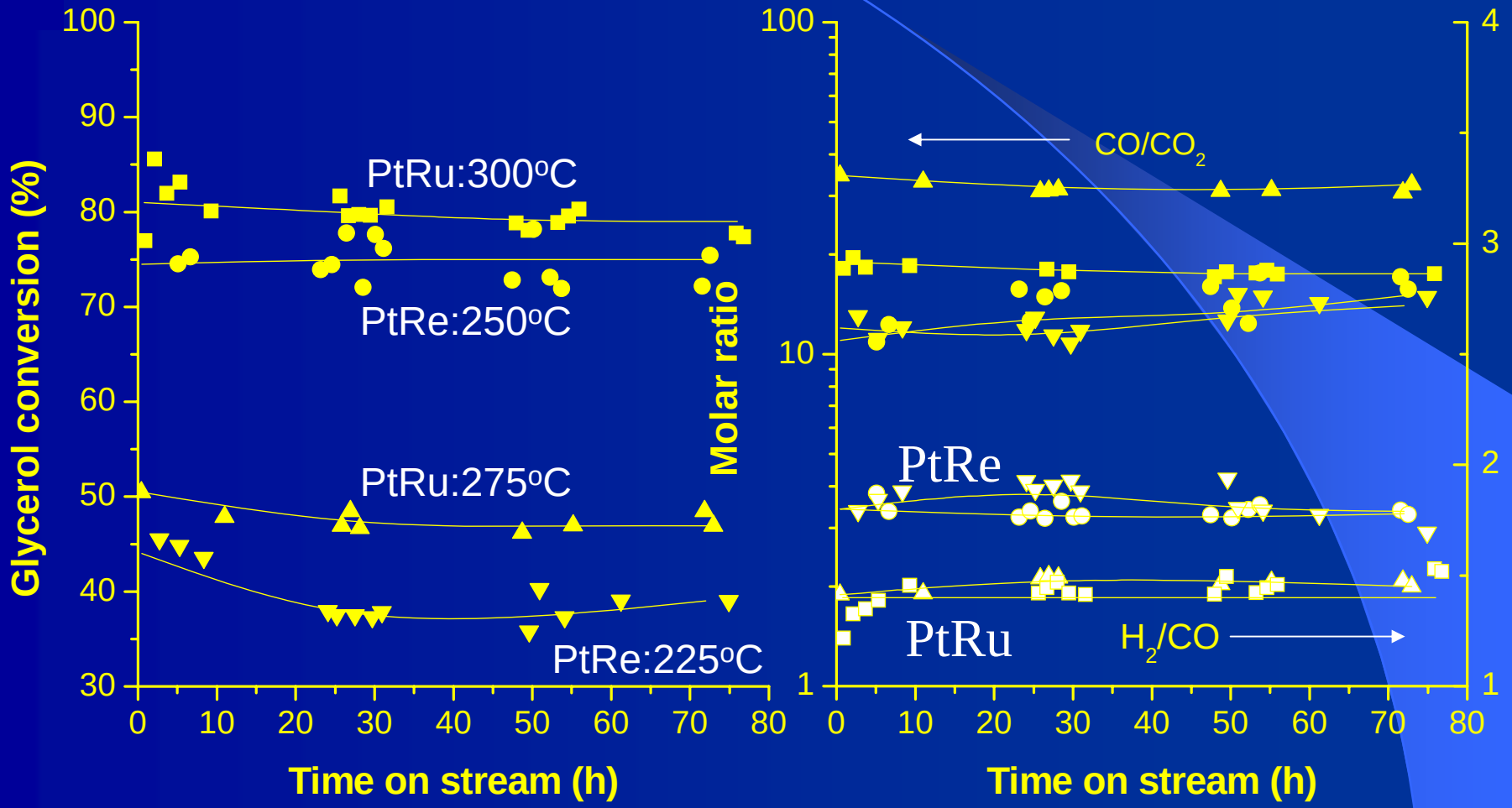


# CO Adsorption on Near Surface Alloys

Greeley & Mavrikakis, Catal. Today **111**, 52 (2006)

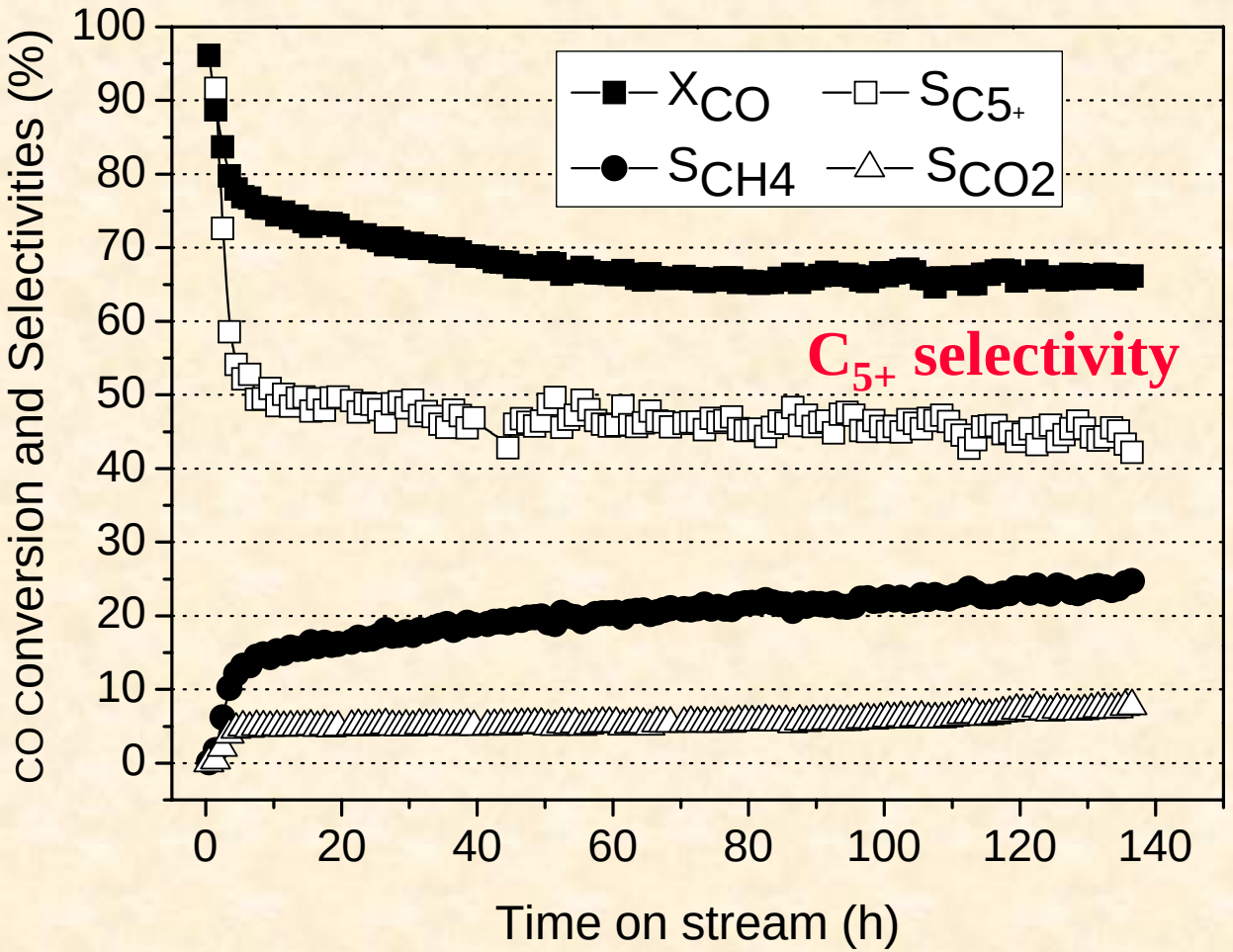


# Glycerol Conversion: Pt-Ru & Pt-Re

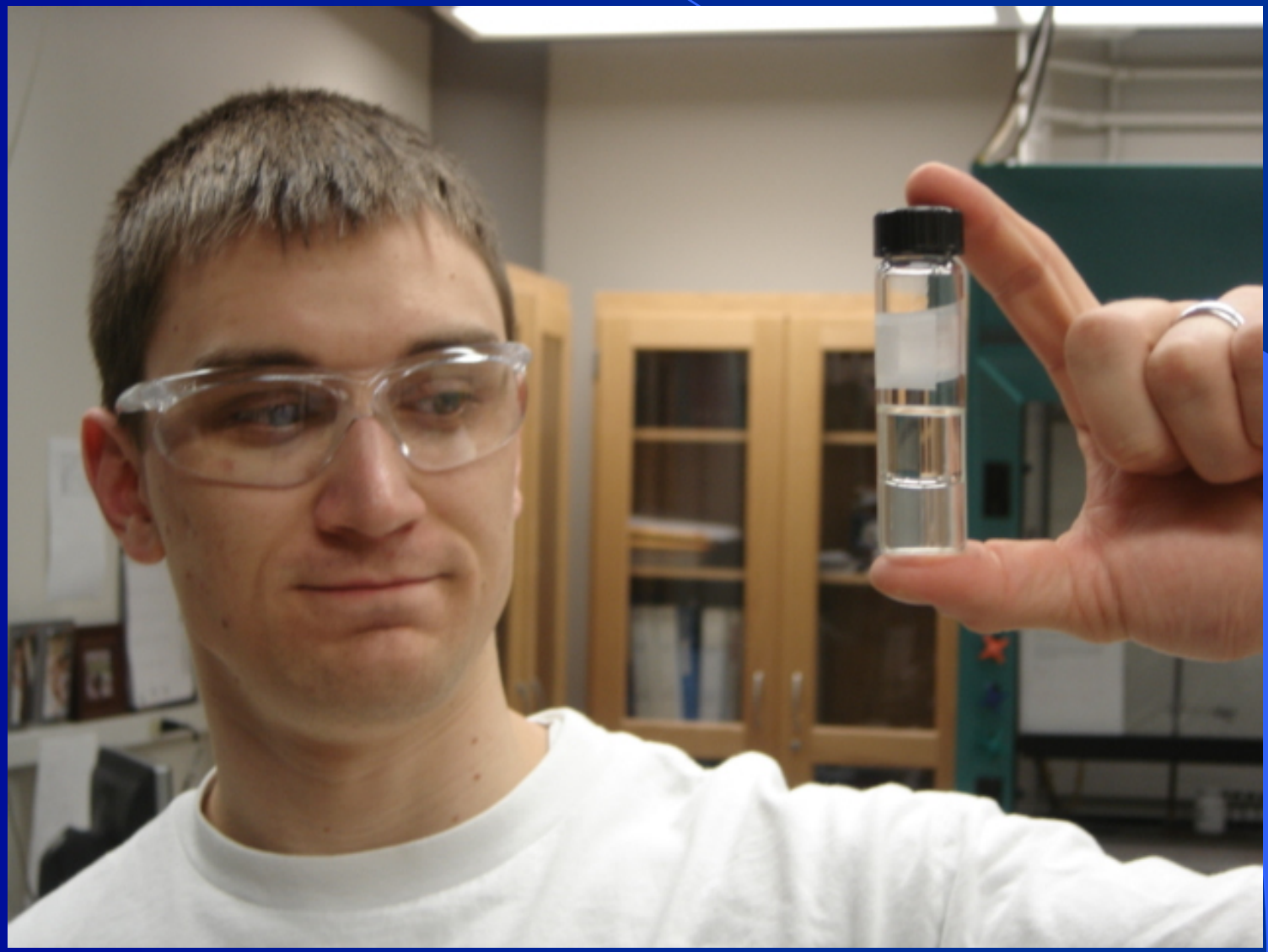



Soares, Simonetti, Dumesic, *Angewandte Chemie* **45**, 3982 (2006).

# FT Data at 275°C & 10 bar

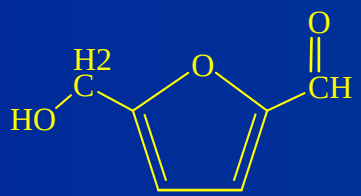


# Dante and the FT product



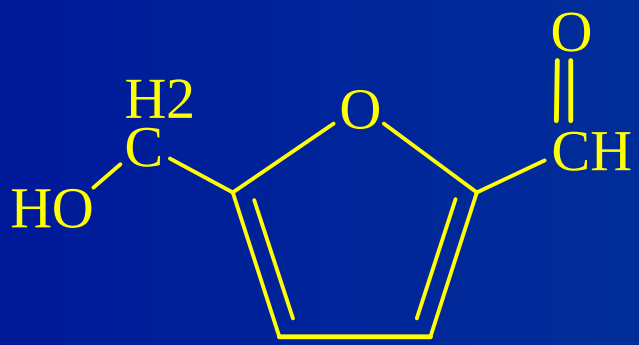
# Production of Value-added Chemicals from Carbohydrates: HMF* from Hexoses

* Hydroxymethylfurfural



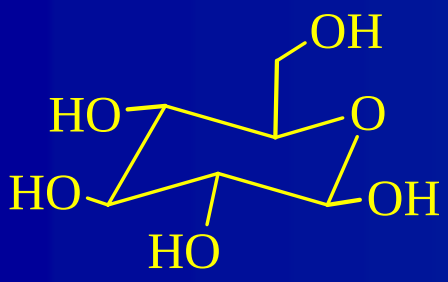
# Sleeping Giant*

"HMF and its oxidation product 2,5-furandicarboxylic acid are so called 'sleeping giants' in the field of intermediate chemicals from regrowing resources."

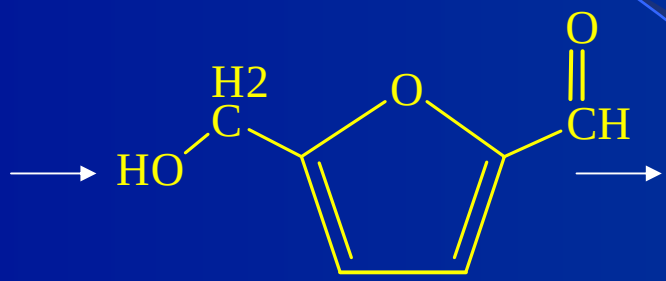



* M. Bicker, J. Hirth and H. Vogel, Green Chemistry, 2003.

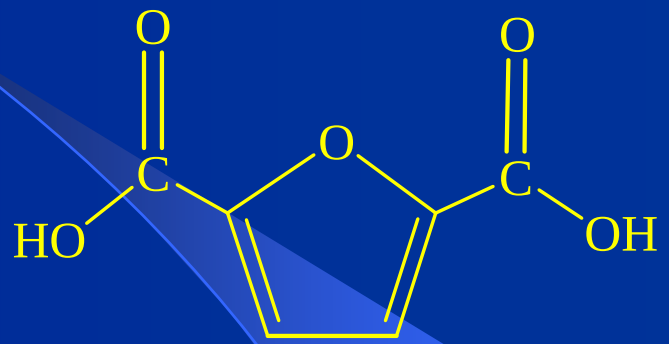
# Chemicals from HMF



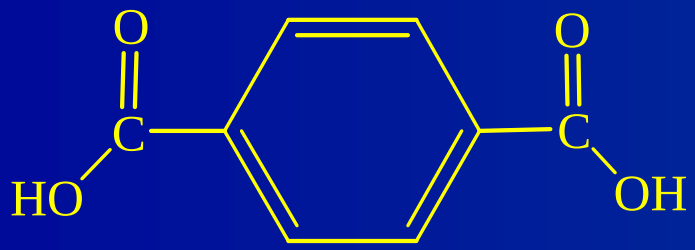

$C_6$-sugar



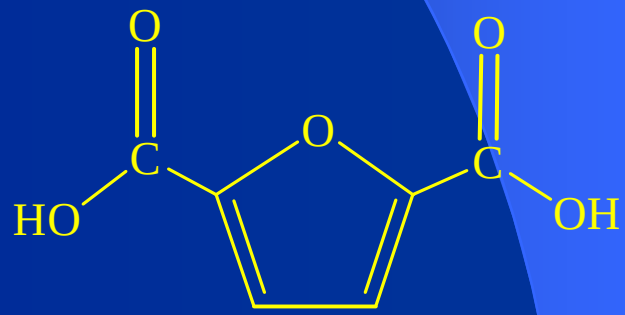

HMF




Furan dicarboxylic acid (FDCA)

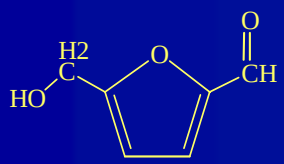



Terephthalic acid

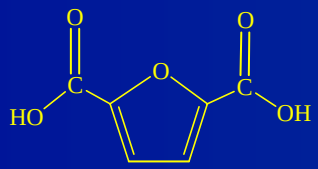



FDCA

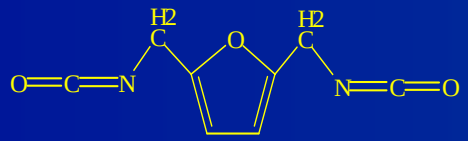
# HMF-derived Polymers

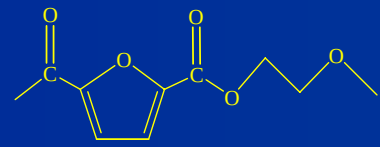



HMF

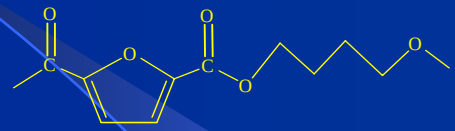



**Furan dicarboxylic acid (FDCA)**

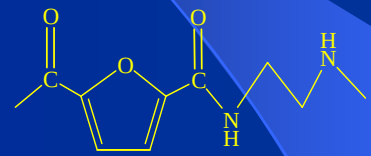


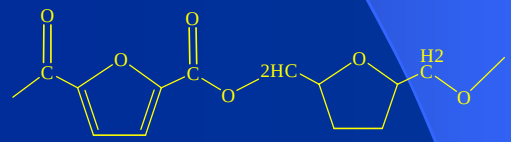

**Polyethylene terephthalate (PET)**



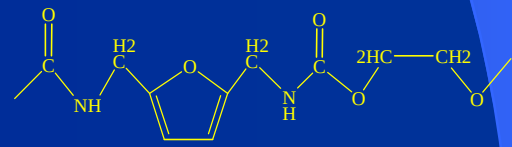

**Polybutylene terephthalate (PBT)**




**A polyamide (Nylon)**

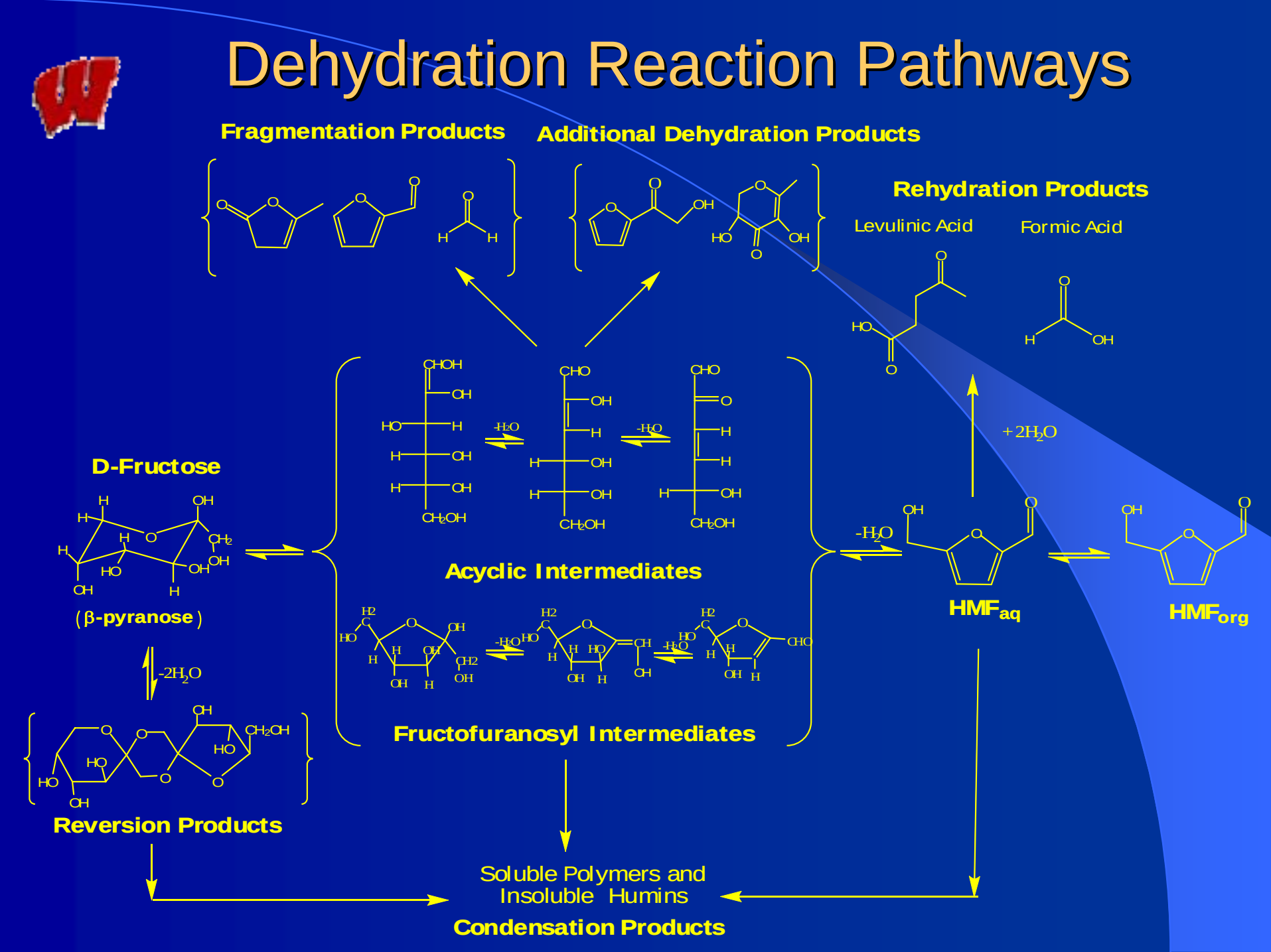



**A 100 % renewable polyester**




**A polyurethane**

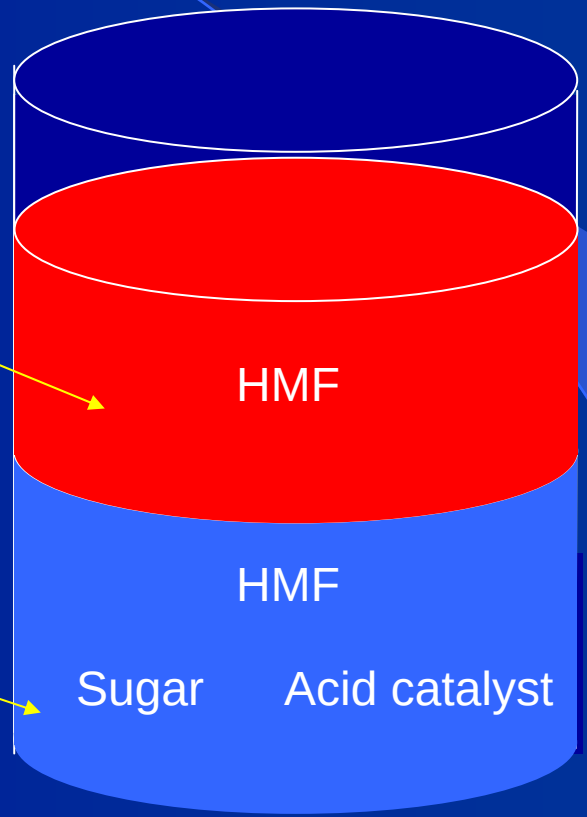
# Dehydration Reaction Pathways



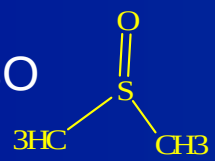
# Approach to Achieve High Selectivity for HMF

Extracting solvent, e.g., MIBK, butanol

Aqueous layer containing promoters (e,g, DMSO, NMP)

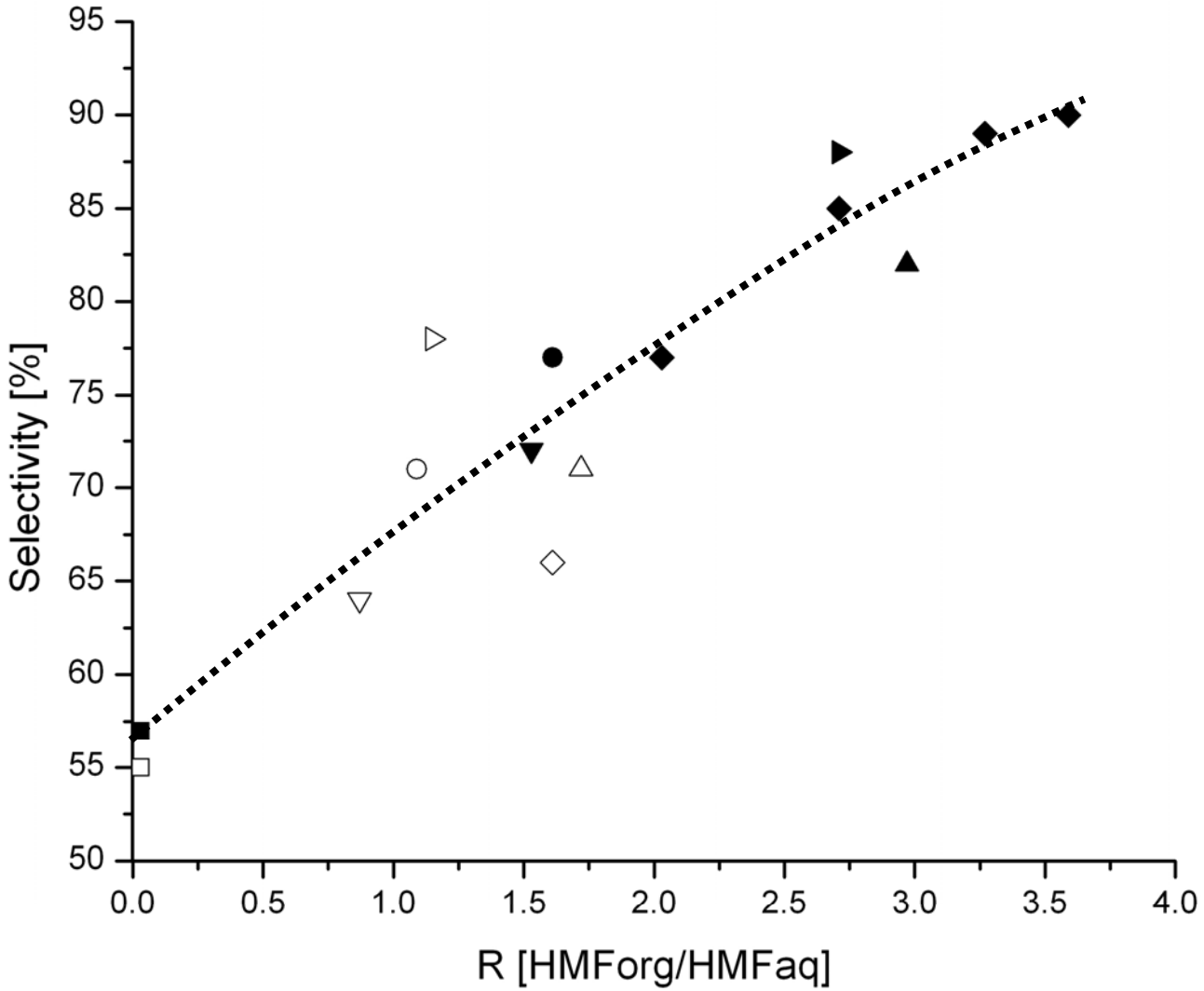
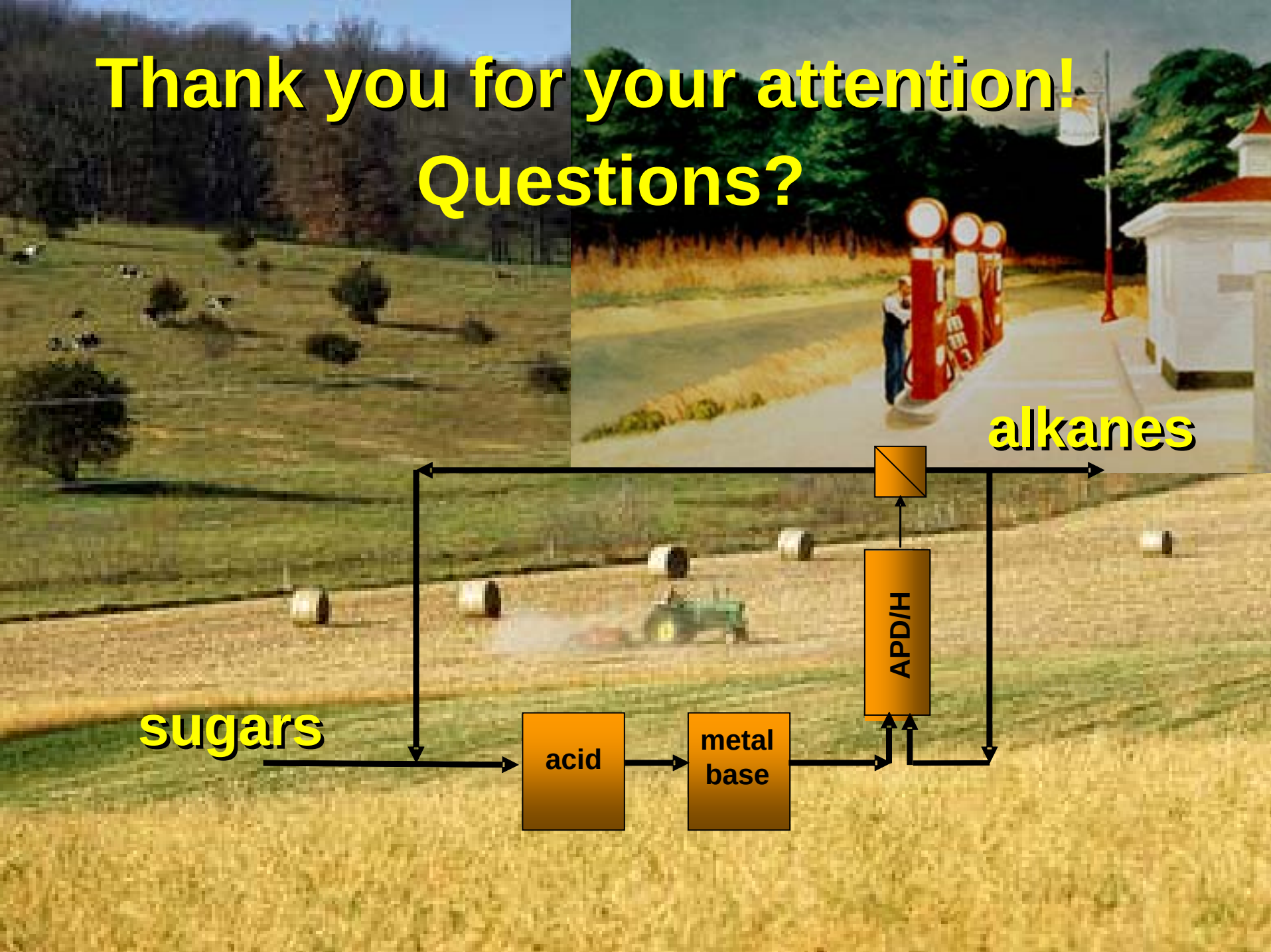



Dimethylsulfoxide, DMSO




N-methylpyrrolidinone,NMP

# HMF selectivity vs Extraction Ratio



# Thank you for your attention!
# Questions?