1st Brazil-U.S. Biofuels Short Course: Providing Interdisciplinary Education in Biofuels Technology

July 27 - August 7, 2009

University of Sao Paulo, Sao Paulo, Brazil

Conversion Technologies – Chemical and Catalytical Processing: Gas phase route

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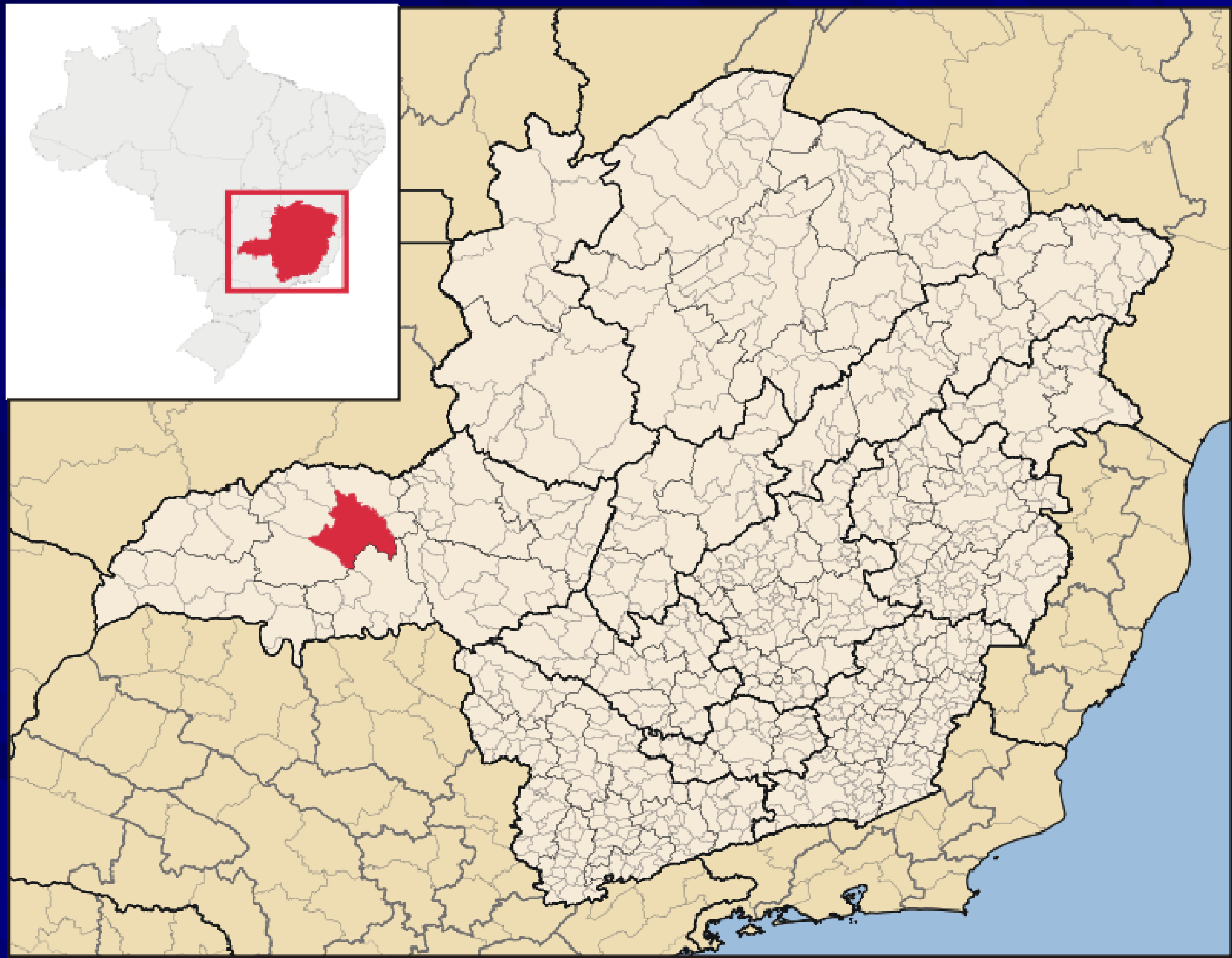
Uberlandia?! Where is it?



Outline

- Objectives – General Background
- Glycerol as a block molecule
  - Synthesis gas by low gas-phase glycerol aqueous solution reforming at low temperature
  - Coupling the reforming and WGS for H_2 production
  - Coupling the reforming and FTS for liquid fuel production
  - Partial Conclusions
- Direct Sugar/Polyol Conversion – New Biorefinery approach
  - Integration of Reforming and Deoxygenation reactions
  - C-C coupling reactions
  - Partial Conclusions
- Conclusions
- Acknowledgements

Main Objective

Chemical and Catalytical processing Platform

Prof. Ulf Lecture

Cellulosic derivatives Sugars

This Lecture: **Gas phase route**

Dr. Yuryi Lecture: HMF-based route

Biomass

Platform 1: Ethanol

Platform 2: Thermochemical

- ✓Fuels
- ✓Chemicals/Commodities
- ✓Energy
- ✓Plastics and Polymers

Dr. Lawrence Russo (U.S. Department of Energy) Seminar (Monday/27-July)

Heuristics for Chemical and Catalytical Processing Biomass

- Limit the number of processing steps
  - Less operations = lower cost
- Use renewable reagents/solvents
- Minimize solvent use
  - Use concentrated feeds
- Efficient product separation
  - Spontaneous separation of hydrophobic products
- Cascades of flow reactors
  - Facilitate transport between processing steps
- ***Integrated Processes – Energy Balance & Thermodynamics***
  - Find good catalyst(s)

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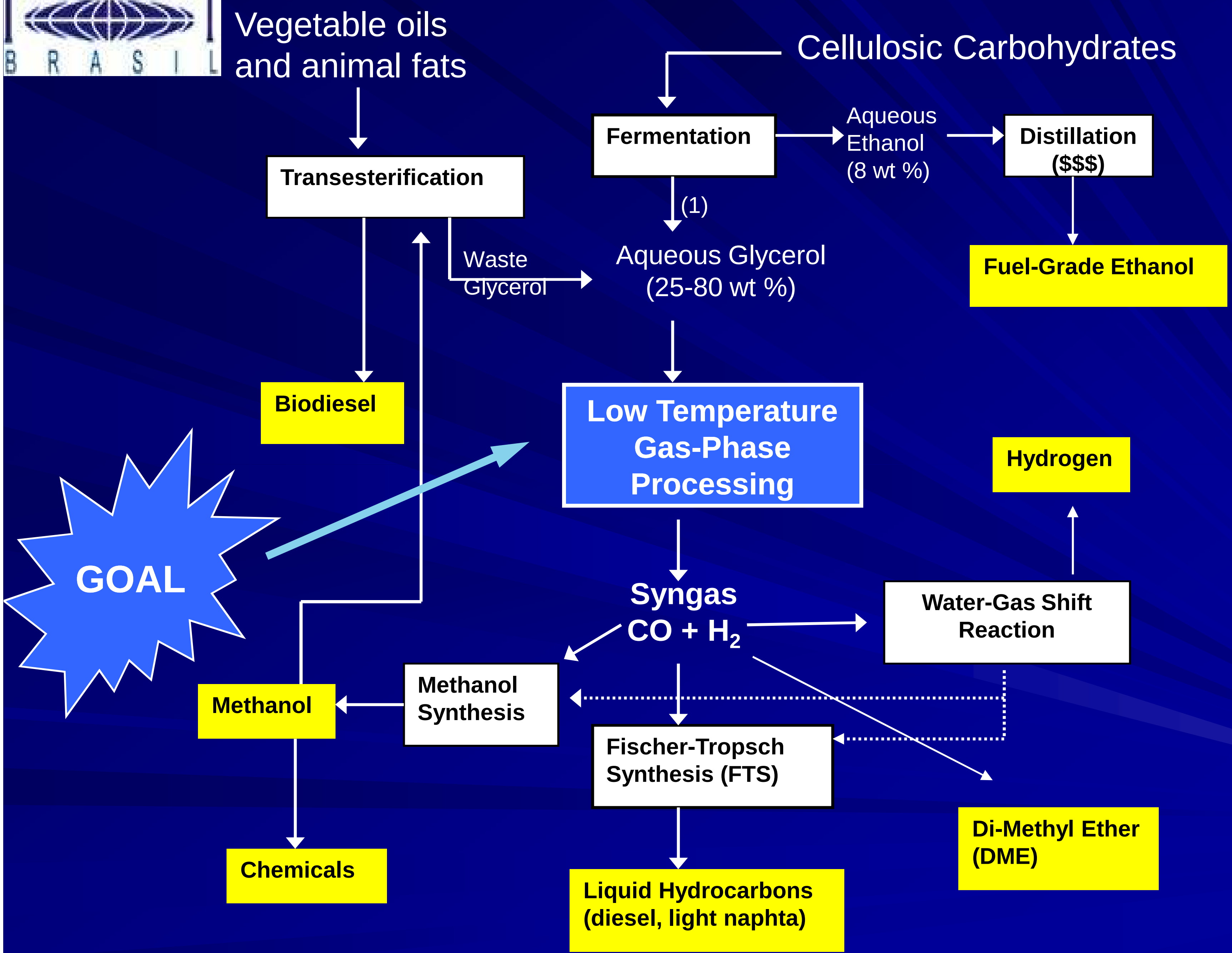
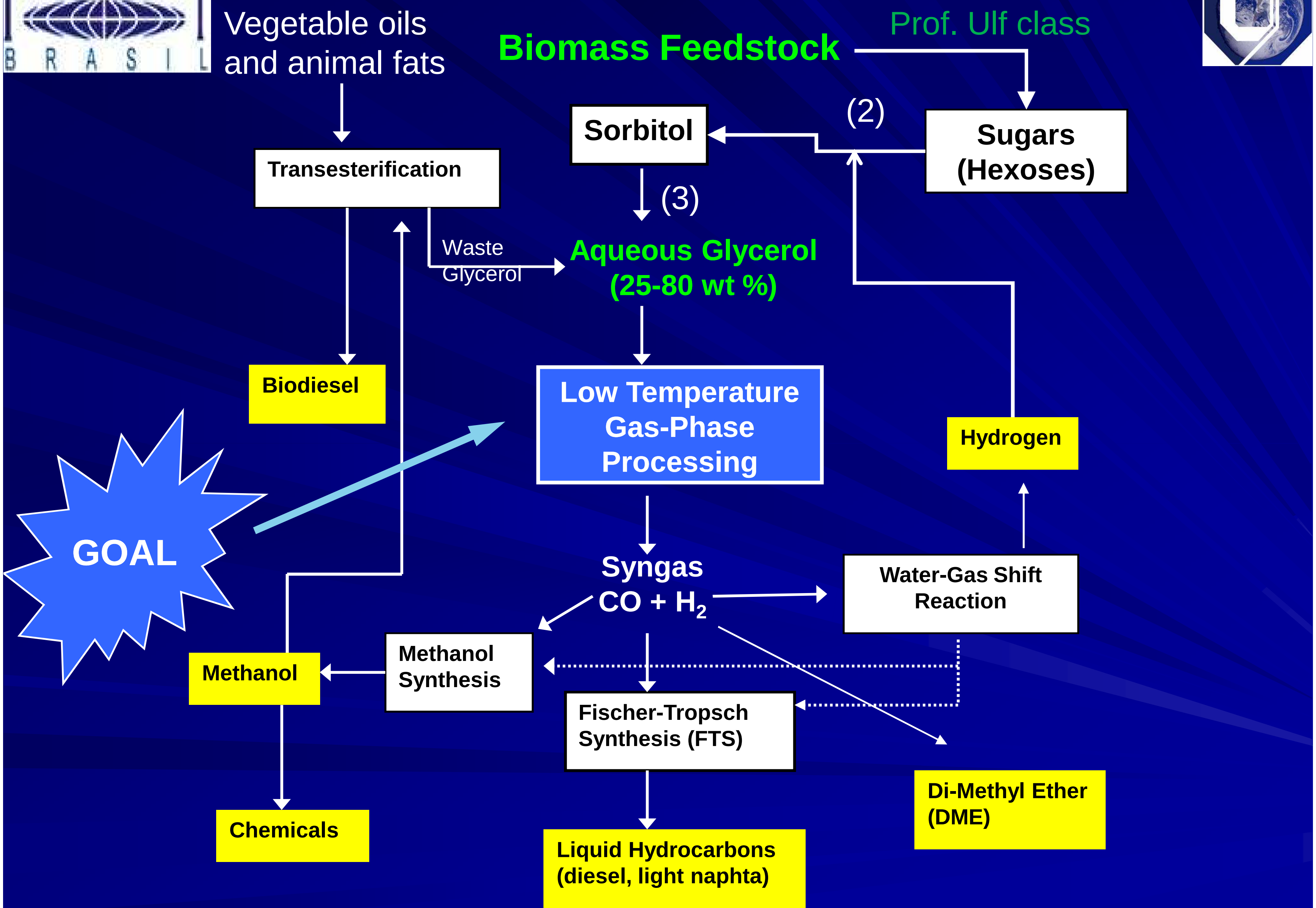
Current proven processes using biomass feedstock

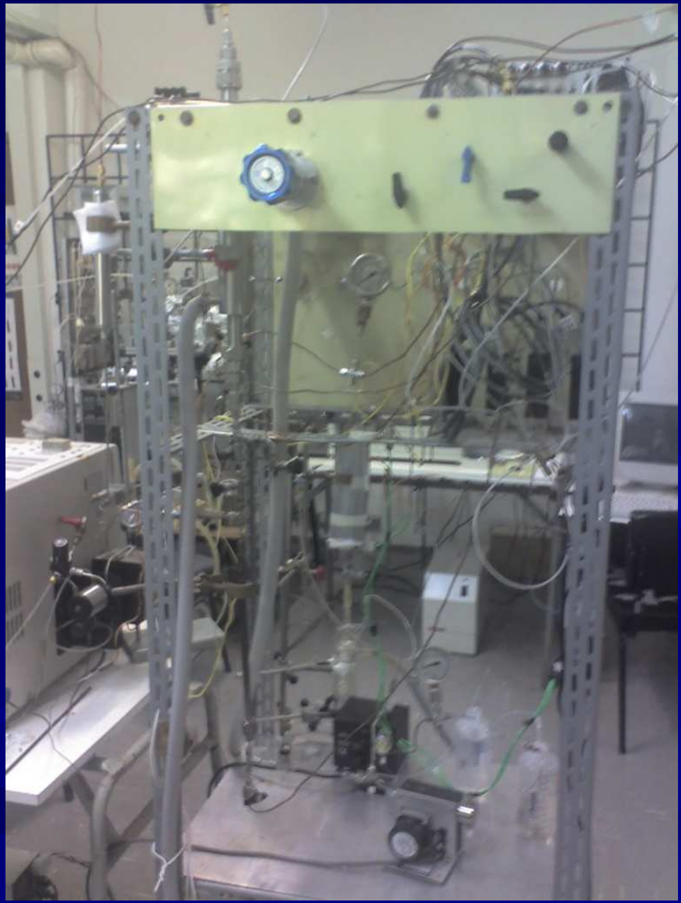


(1) C. S. Gong, J. X. Du, N. J. Cao, G. T. Tsao, *Appl. Biochem. Biotech.* **2000**, *84-86*, 543-559



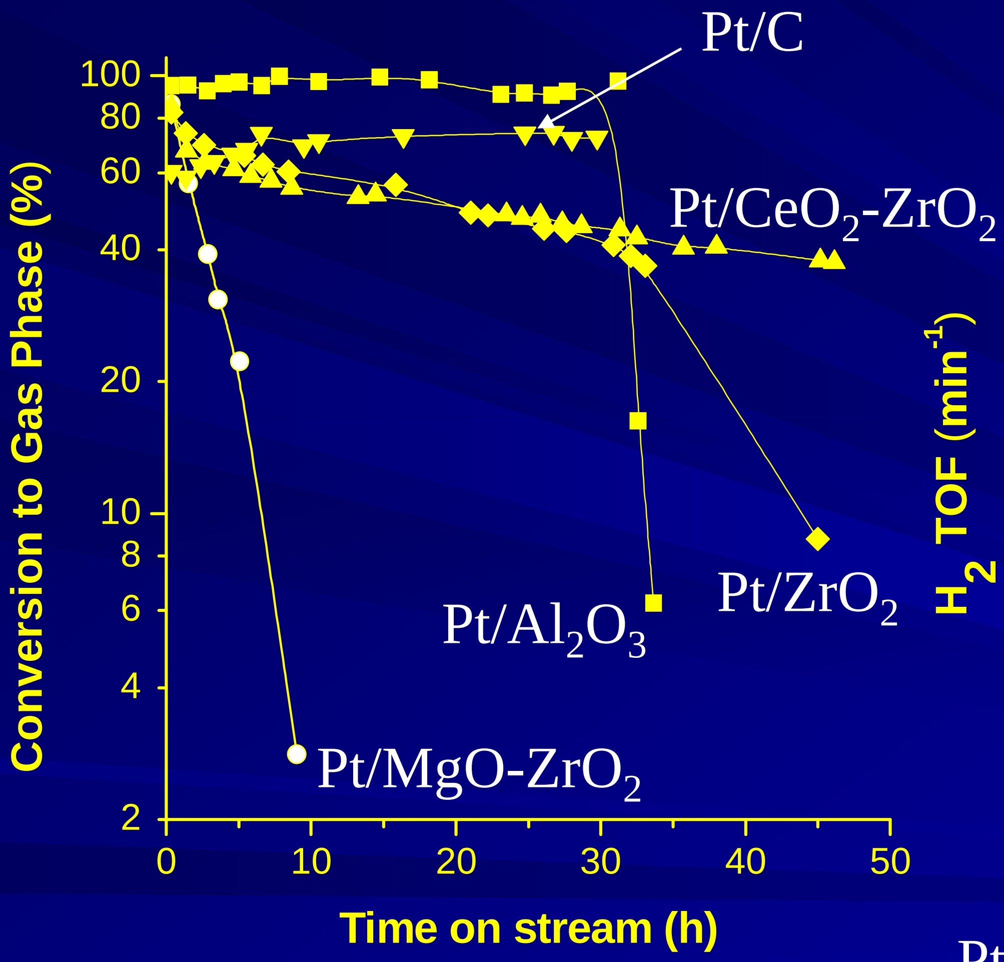
(2) Gallezot et al., Appl. Catal., A: General, v 331, p. 100-104, 2007 (3) E. Tronconi et al.; Chem. Eng. Sci., 47(9-11), 2451-2456,1992

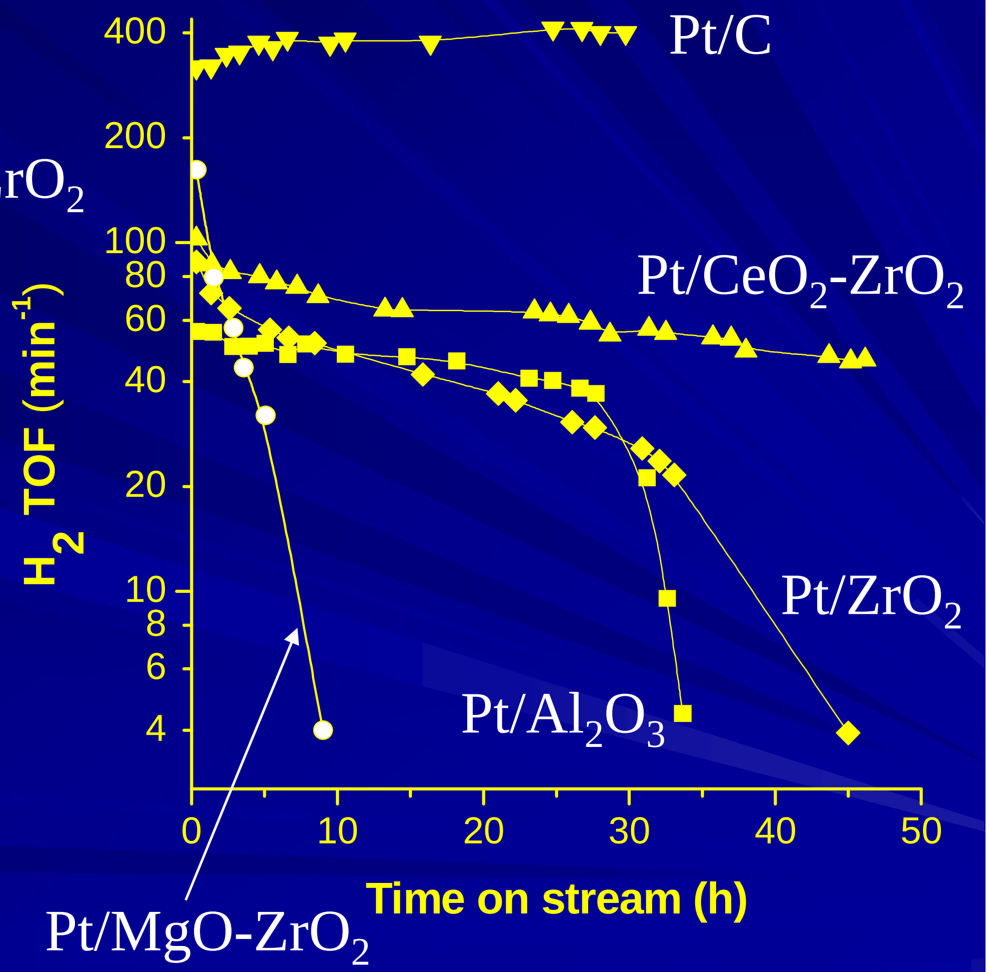
Catalytic testing units - UFU



Catalyst Screening

(T = 623 K , P = 1 bar, and 30 wt% Glycerol)





From R. R. Soares, D. A. Simonetti, J. A. Dumesic, *Angewandte Chemie-International Edition*, **2006**, *45*, 3982-3985.

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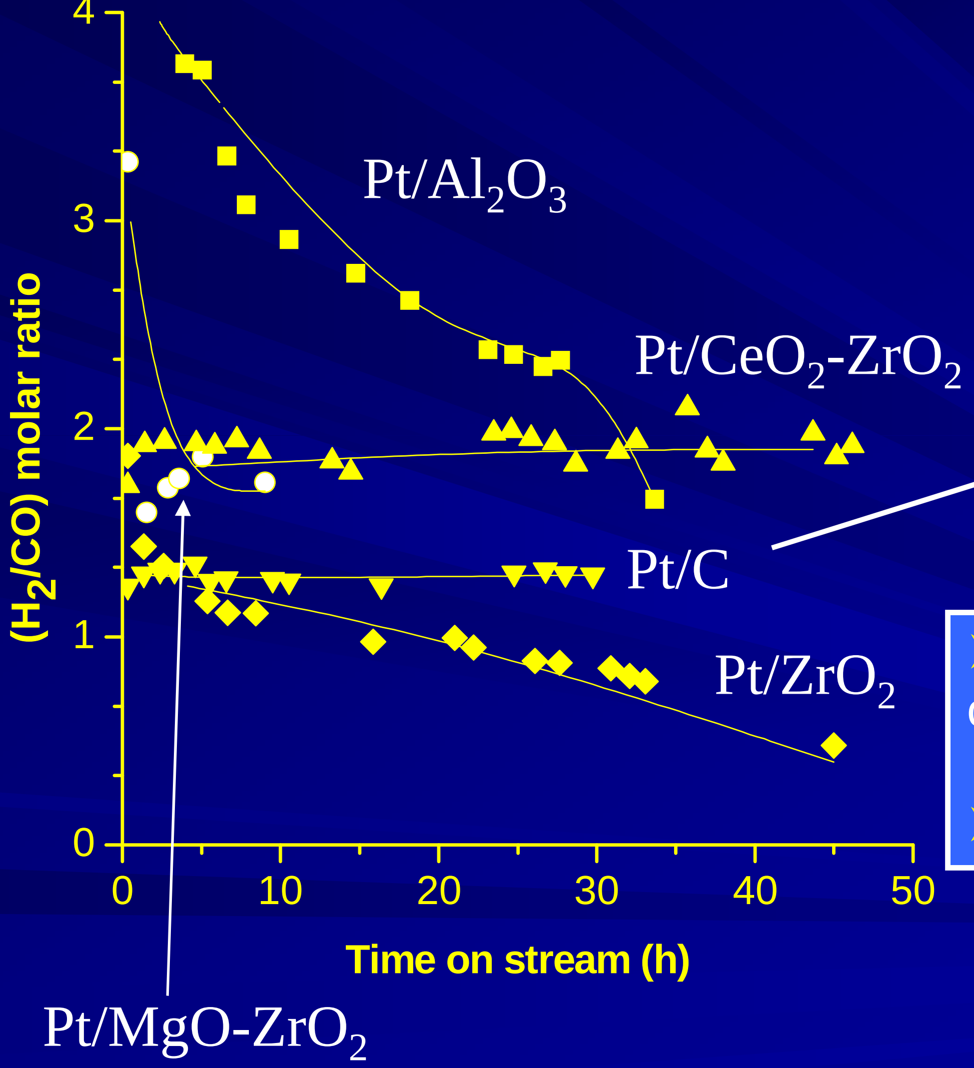

$C_3H_8O_3 \rightarrow 3CO + 4H_2$

$[H_2/CO] = 1.33$

Only Glycerol decomposition takes place

- WGS takes place on the oxide-supported catalysts.
- The WGS sites are blocked.

From R. R. Soares, D. A. Simonetti, J. A. Dumesic, *Angewandte Chemie-International Edition*, **2006**, *45*, 3982-3985.

Catalyst Screening

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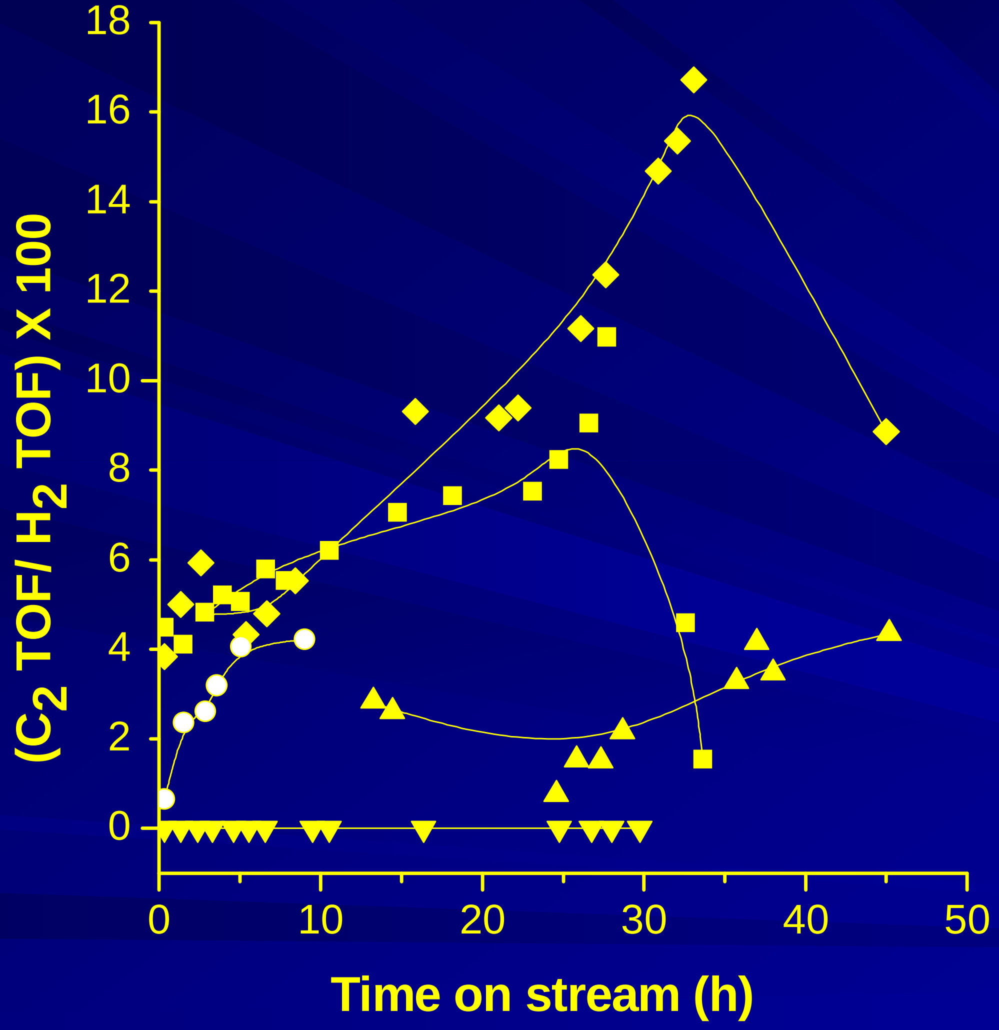
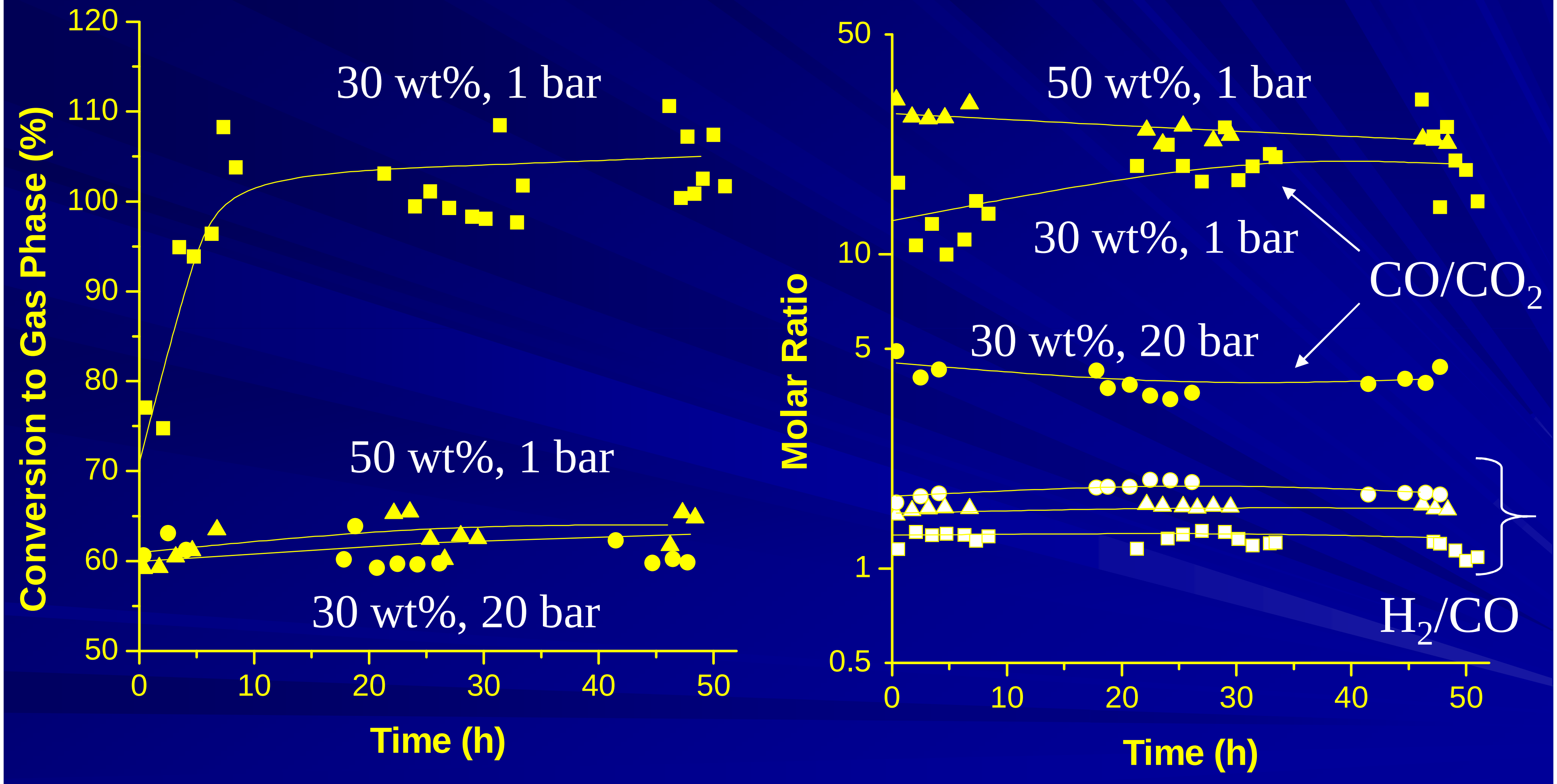


It suggests that one of the modes of catalyst deactivation is the coke formation by dehydration reactions.

From R. R. Soares, D. A. Simonetti, J. A. Dumesic, *Angewandte Chemie-International Edition*, **2006**, *45*, 3982-3985.

Pt/C stability at different reaction conditions



From R. R. Soares, D. A. Simonetti, J. A. Dumesic, *Angewandte Chemie-International Edition*, **2006**, *45*, 3982-3985.

Results from Initial Kinetics Measurements

- **Pt/C (inert support) showed**
  - The best stability
  - High activity and selectivity

- Support plays important role:
  - Water-gas shift
  - Deactivation

However, for fuel and chemicals production:

Can we carry out two reactions at same conditions (T,P) over either consecutive beds or in separate reactors?

What do we need to do?

- **Find a catalyst that works in the T and P range of FT**

What is the problem ?

- Pt/C shows low activity below 573 K and under pressure
  - Θ_{CO} increases as T decreases (and P increases)

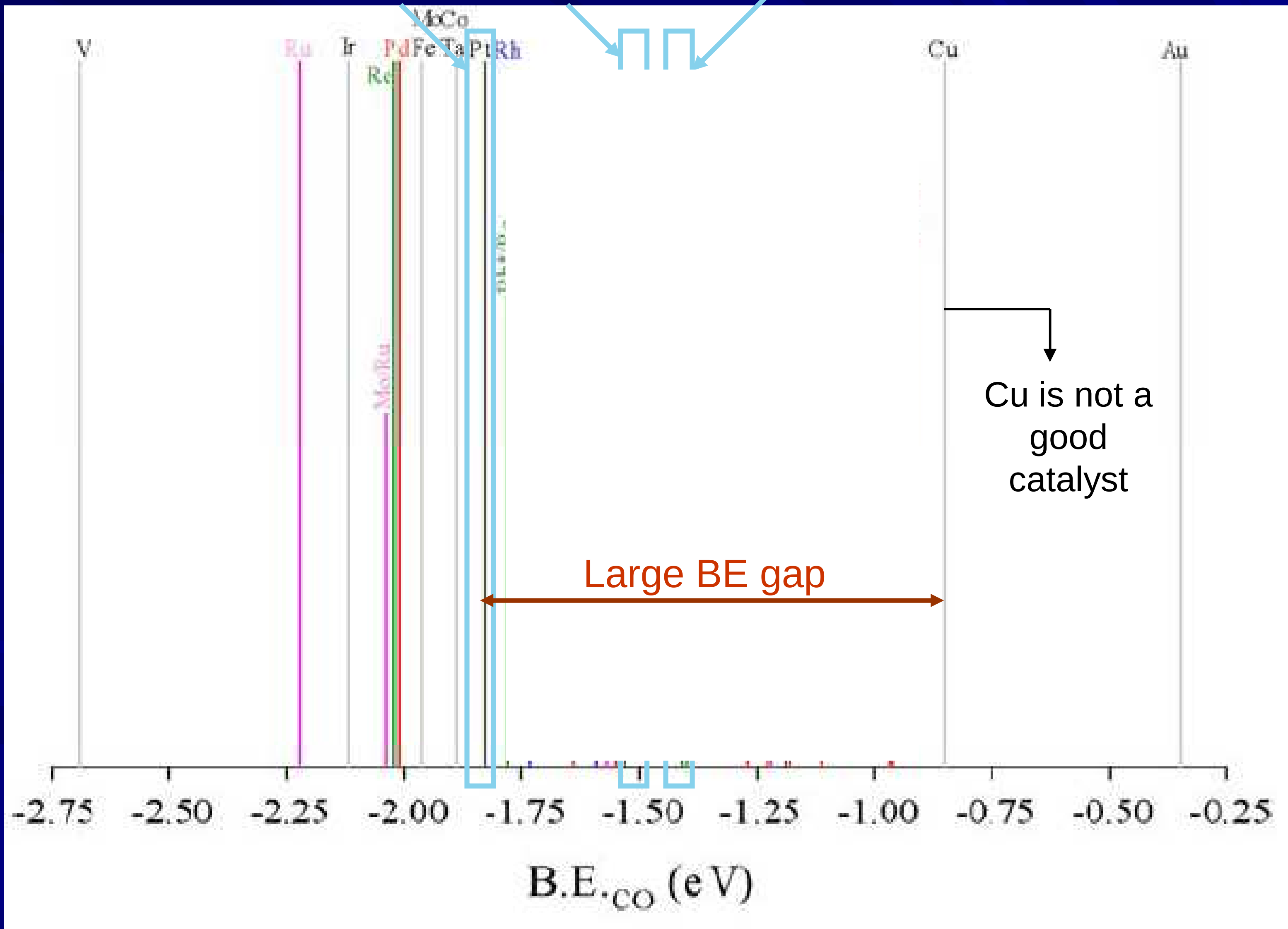
What is a potential solution ?

- Additive to weaken adsorption of CO on Pt

DFT : CO Adsorption on Near Surface Alloys

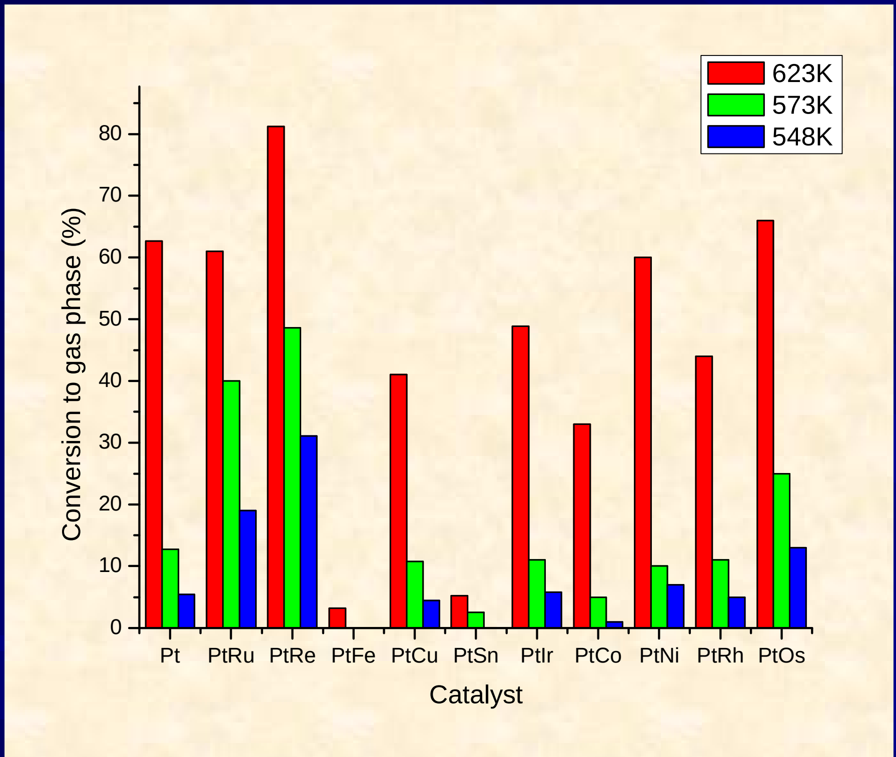
Greeley & Mavrikakis, Catal. Today **111**, 52 (2006)

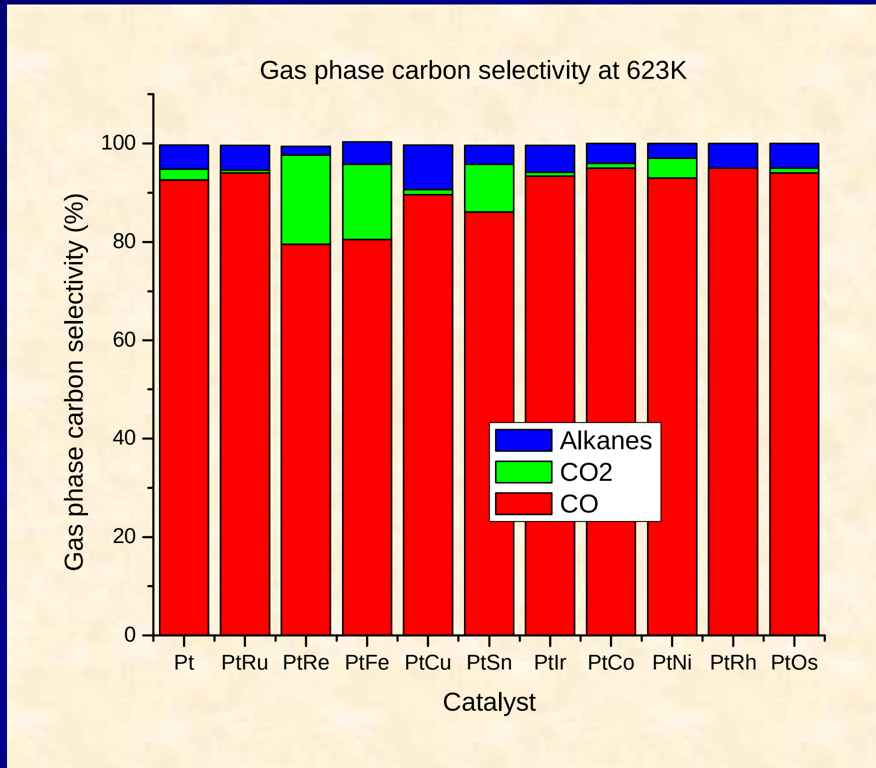
Pt {**Pt/Ru** **Pt/Re**} → **Good candidates !**



Bimetallic catalyst screening
(P = 1 bar and 30 wt% Glycerol)

Glycerol Reactivity and Selectivity over Pt-Me/C bimetallic catalysts

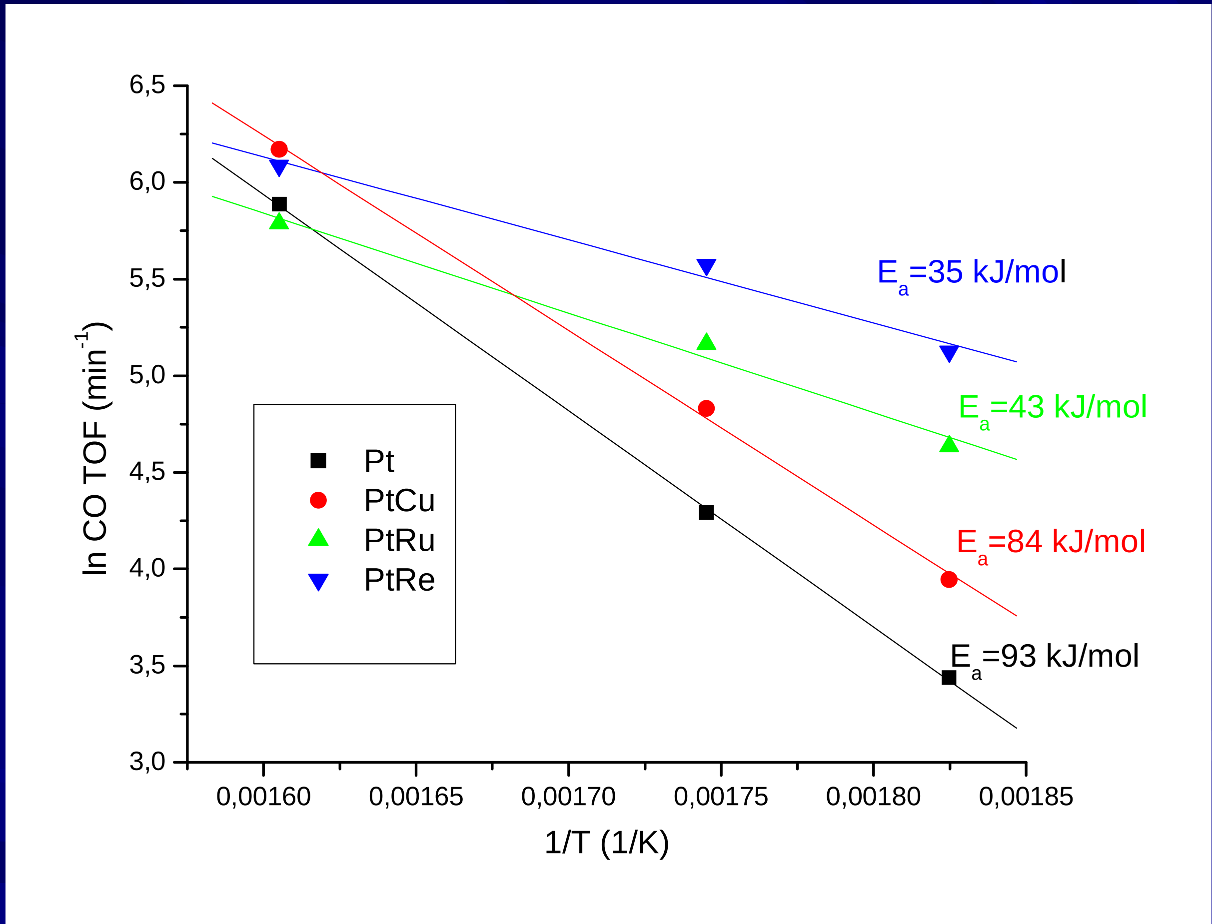




From E. L. Kunkes, R. R. Soares, D. A. Simonetti, and J. A. Dumesic,; *Applied Catalysis B, 90 (2009) 693-698.*

Bimetallic catalyst screening
(P = 1 bar and 30 wt% Glycerol)

Apparent Activation Energies measurements from Pt-Me/C bimetallic catalysts

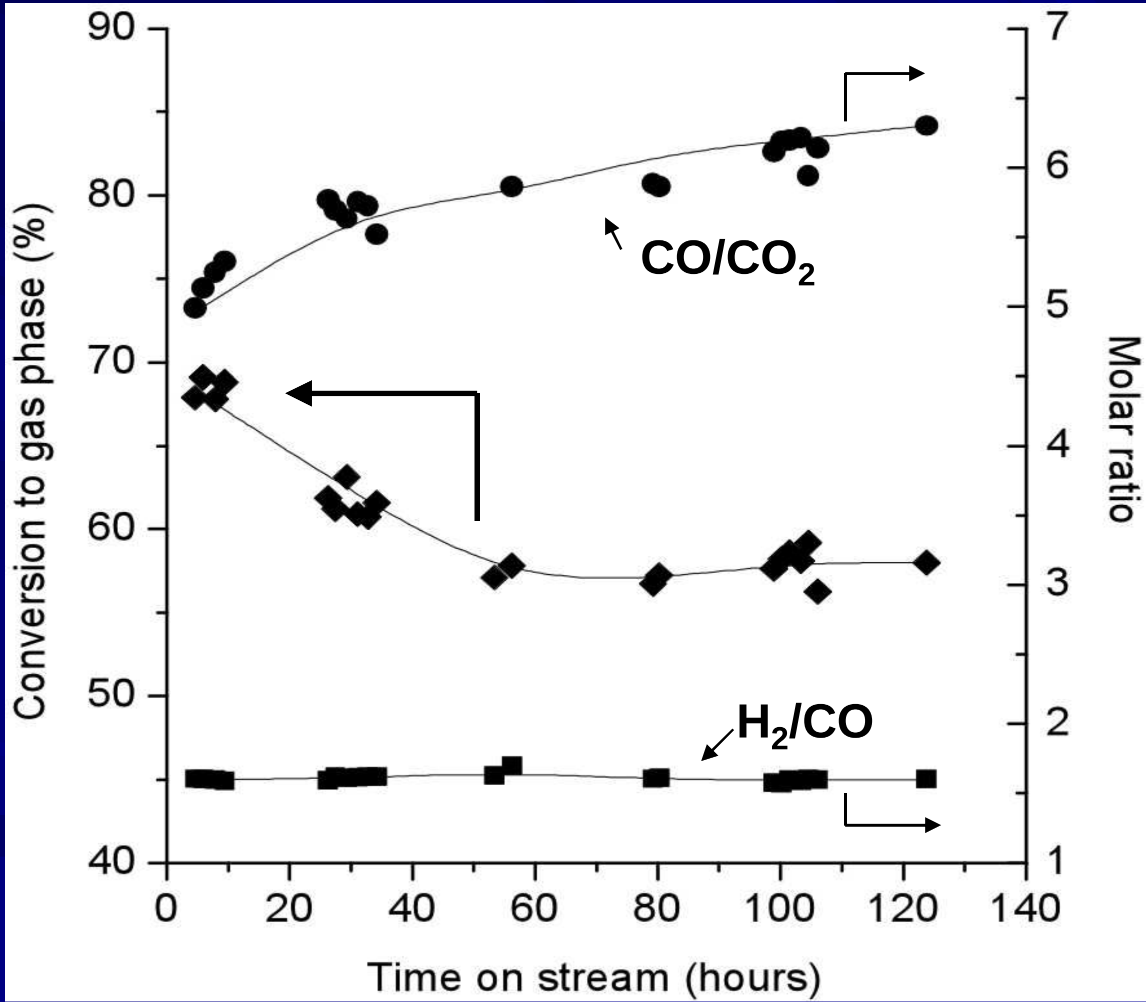


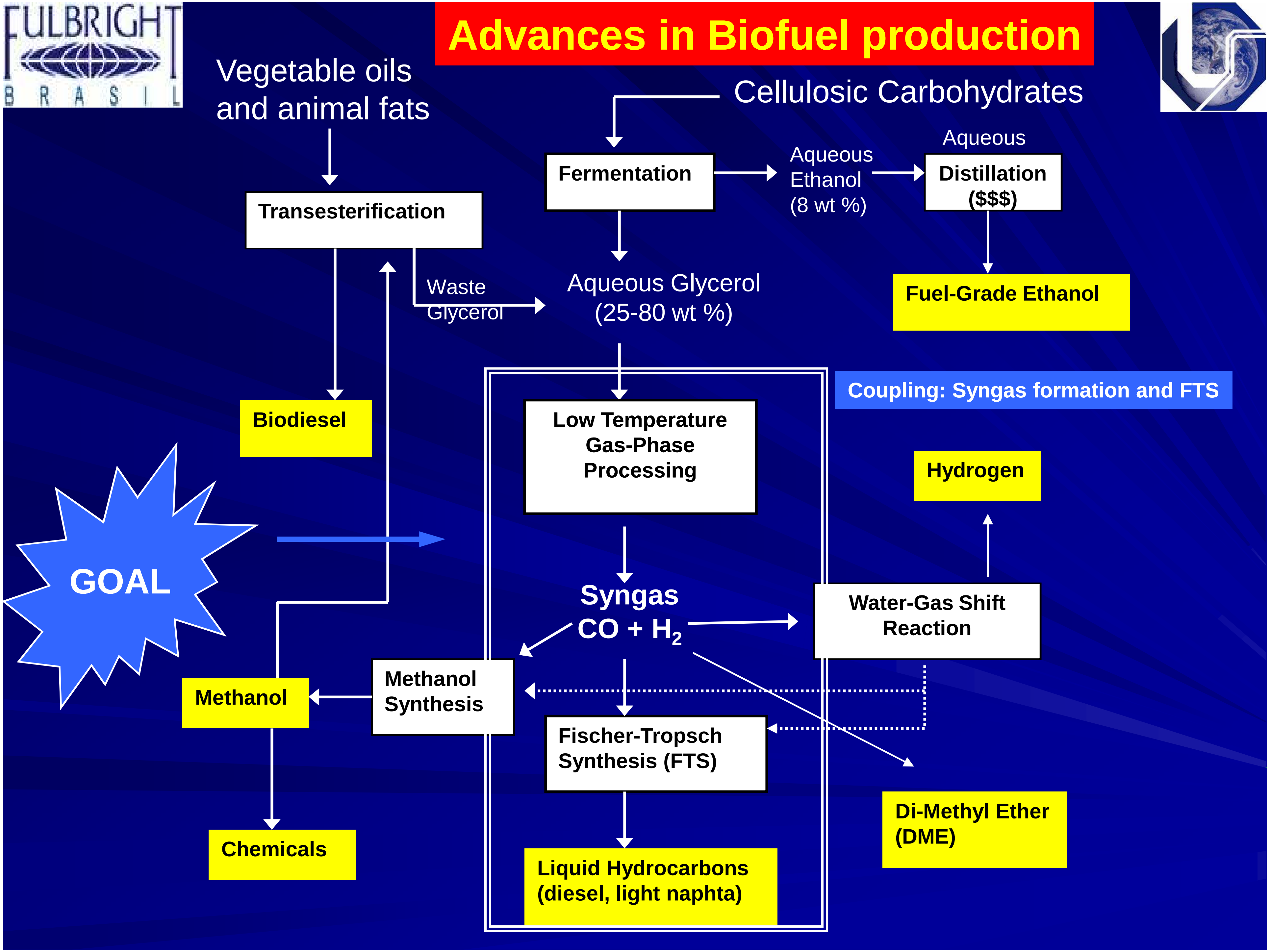
✓ **Reaction mechanism may proceed differently on the Ru and Re promoted catalyst**

From E. L. Kunkes, R. R. Soares, D. A. Simonetti, and J. A. Dumesic,; *Applied Catalysis B, 90 (2009) 693-698.*

Glycerol Conversion to Synthesis Gas

(Pt-Re/C with 30% Glycerol at 548 K and 8.3 bar)





FULBRIGHT
BRASIL
Advances in Biofuel production
Vegetable oils and animal fats
Cellulosic Carbohydrates
Transesterification
Fermentation
Aqueous Ethanol (8 wt %)
Aqueous
Distillation ($$$)
Waste Glycerol
Aqueous Glycerol (25-80 wt %)
Fuel-Grade Ethanol
Biodiesel
Coupling: Syngas formation and FTS
Low Temperature Gas-Phase Processing
Hydrogen
GOAL
Syngas
$CO + H_2$
Water-Gas Shift Reaction
Methanol Synthesis
Methanol
Fischer-Tropsch Synthesis (FTS)
Di-Methyl Ether (DME)
Chemicals
Liquid Hydrocarbons (diesel, light naphta)

Advances in Biofuel production

Coupling Gasification & FT Synthesis

Advantage: Heat integration

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

$$2.24CO + 4.48H_2 \xrightarrow{2} 0.28C_8H_{16} + 2.24H_2O$$ -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

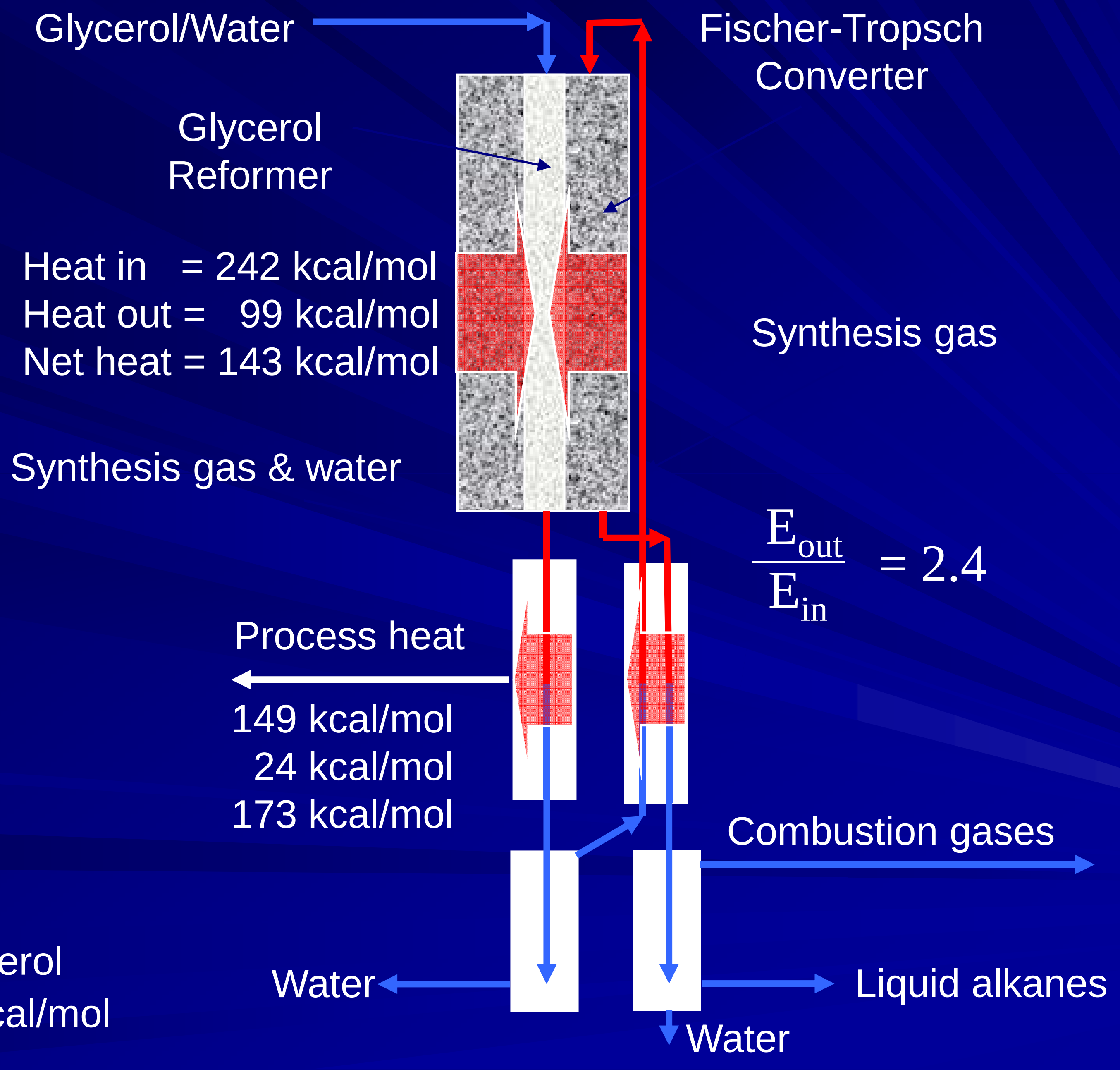
(Sum of steps 2–4: -98)

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

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

From R. R. Soares, D. A. Simonetti, J. A. Dumesic, *Angewandte Chemie-International Edition*, **2006**, *45*, 3982-3985.

Heat Integration



T = 275°C
P = 10 bar
30 wt% Glycerol
ΔH_c = 354 kcal/mol

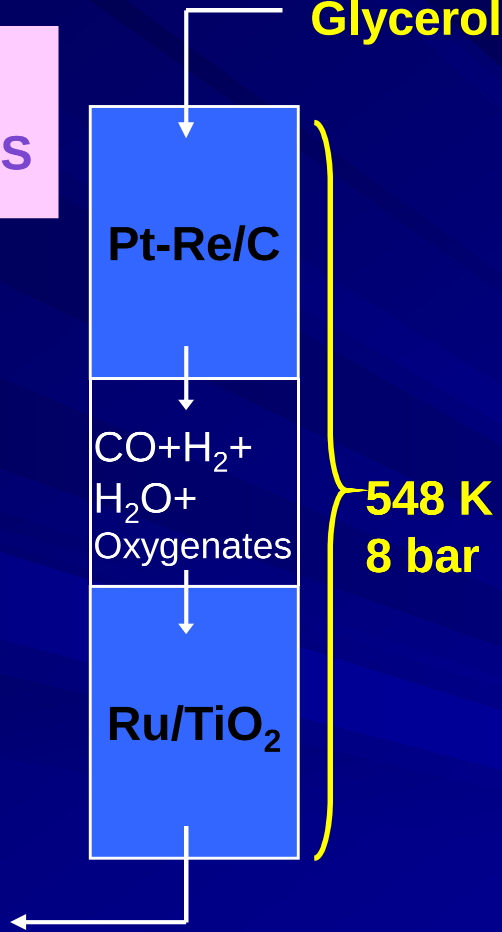
Advances in Biofuel production

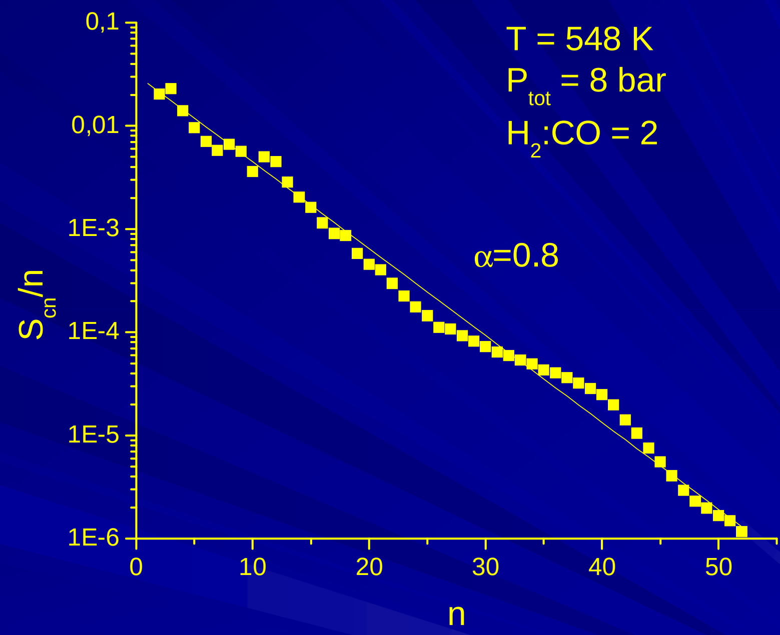
Two-bed system :

Syngas formation & FTS

X_{CO} = 30%

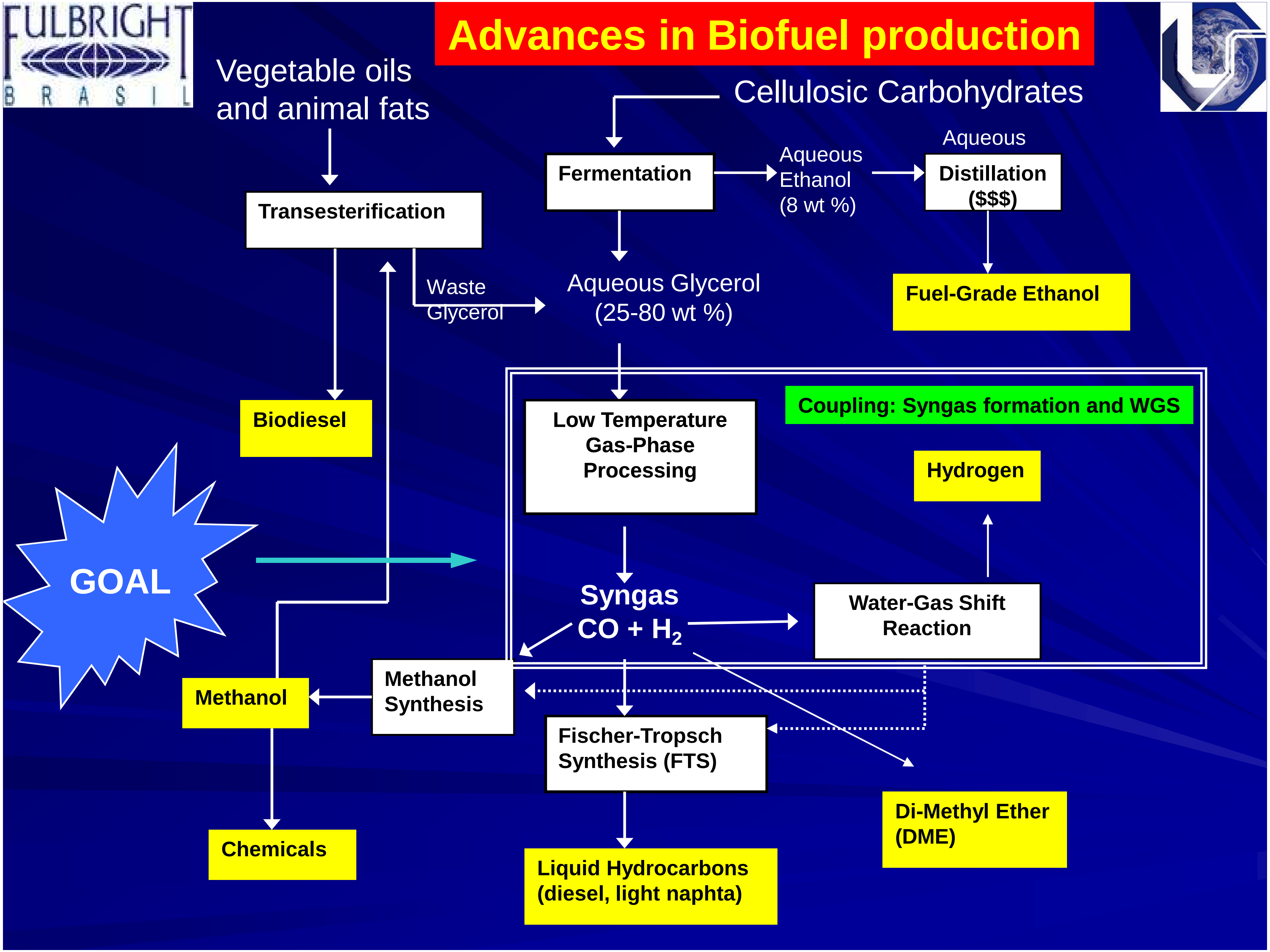
S_{C5+} = 38%
S_{CH4} = 15%
S_{CO2} = 4.5%





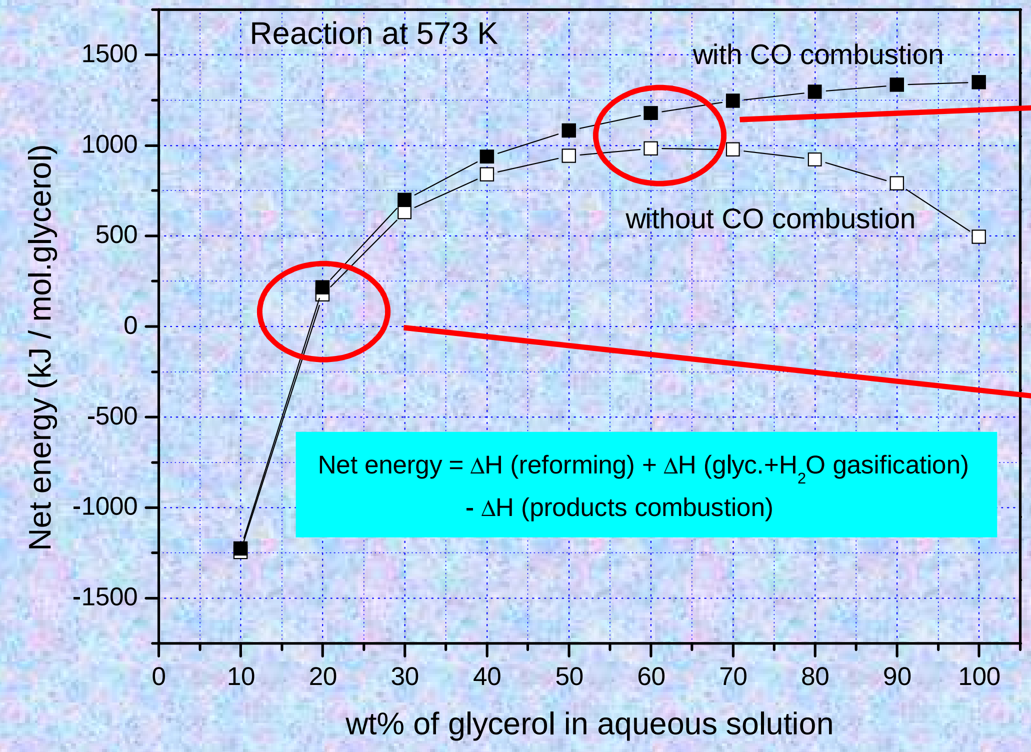
➢ **This method may allow for economic operation of a small-scale FT reactor by having a heat-integrated catalytic process.**

From D. A. Simonetti, J Rass-Hansen, E. L. Kunkes, R. R. Soares, and J. A. Dumesic, *Green Chemistry,9, 2007, 1073-1083*



Advances in Biofuel production
Vegetable oils and animal fats
Cellulosic Carbohydrates
Transesterification
Fermentation
Aqueous Ethanol (8 wt %)
Aqueous
Distillation ($$$)
Waste Glycerol
Aqueous Glycerol (25-80 wt %)
Fuel-Grade Ethanol
Biodiesel
Coupling: Syngas formation and WGS
Low Temperature Gas-Phase Processing
Hydrogen
GOAL
Syngas
CO + H2
Water-Gas Shift Reaction
Methanol Synthesis
Methanol
Fischer-Tropsch Synthesis (FTS)
Chemicals
Liquid Hydrocarbons (diesel, light naphta)
Di-Methyl Ether (DME)

Advantages:
Heat Integration



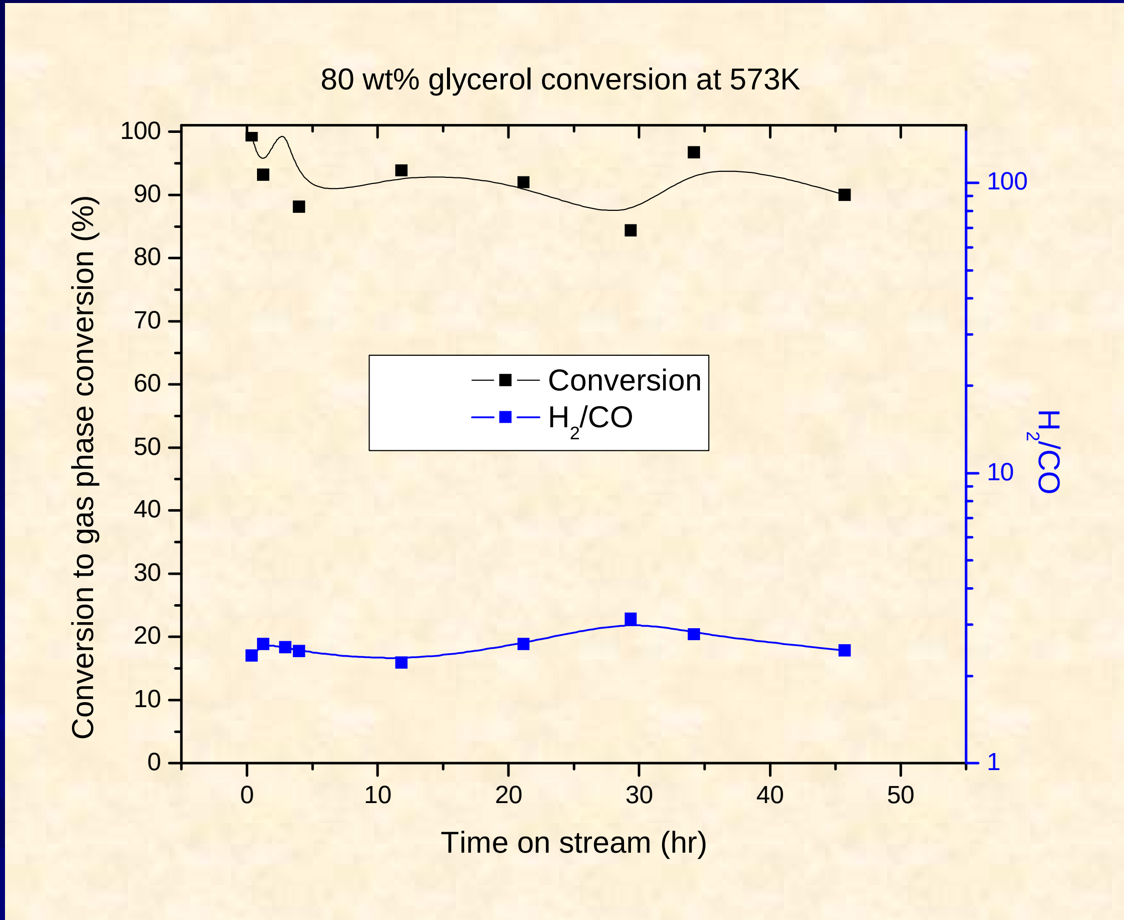
A maximum energy balance at 60 wt% glycerol

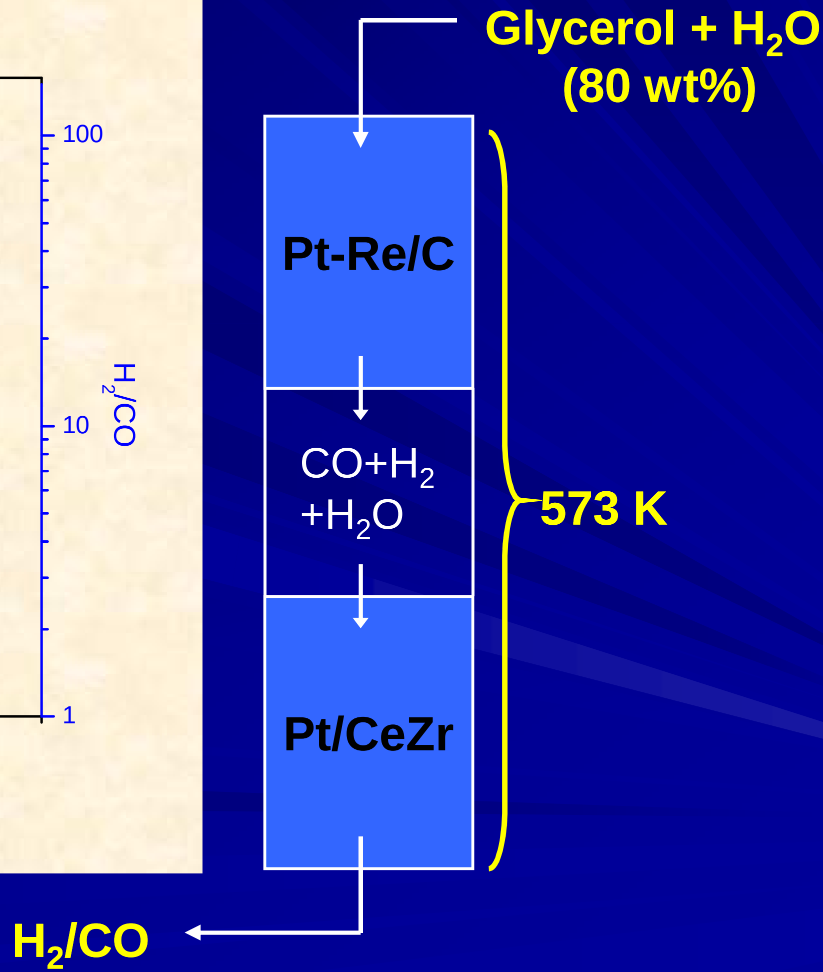
A positive energy balance for glycerol concentration higher than 18 wt%

From E. L. Kunkes, R. R. Soares, D. A. Simonetti, and J. A. Dumesic,; *Applied Catalysis B, 90 (2009) 693-698.*

Results

Two-beds system : Syngas formation & WGS





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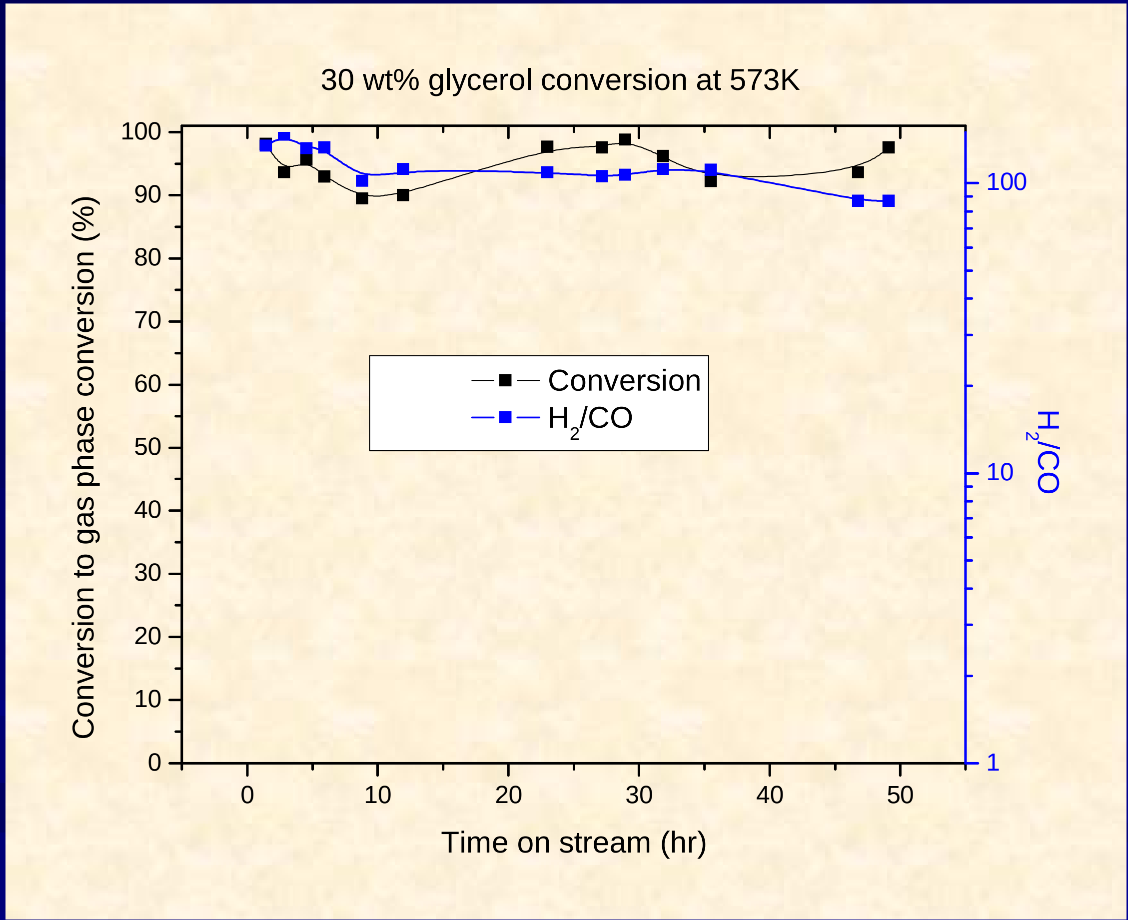

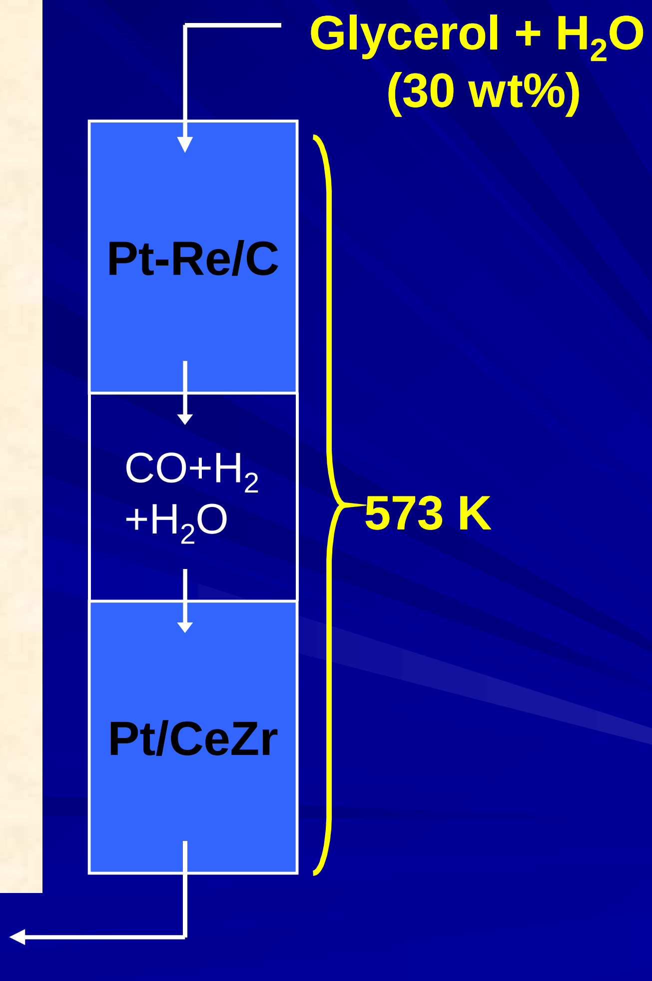

From E. L. Kunkes, R. R. Soares, D. A. Simonetti, and J. A. Dumesic,; *Applied Catalysis B, 90 (2009) 693-698.*

Results

Summary of the results of the coupled reactions

	Glycerol (wt %)		
	30	**50**	**80**
Carbon Conversion (%)	95	100	94
Alkane Selectivity (%)	4	5	8
H_2/CO ratio	97	27	2.6
H_2 Yield (%)	80	78	78

Partial Conclusions

- We showed that liquid fuels and chemicals can be produced from glycerol via a two-step gas-phase process that involves the catalytic conversion of glycerol to H_2 and CO combined with subsequent water-gas shift and Fischer-Tropsch synthesis.

- The experimental results validated the “Rational Design” approach of the catalyst selection by using DFT simulations.

- This two-step process serves as an energy-efficient alternative to current biomass-based processes to produce fuels and chemicals.

- We showed that valuable chemicals can be produced from glycerol via one-step aqueous-phase reforming.

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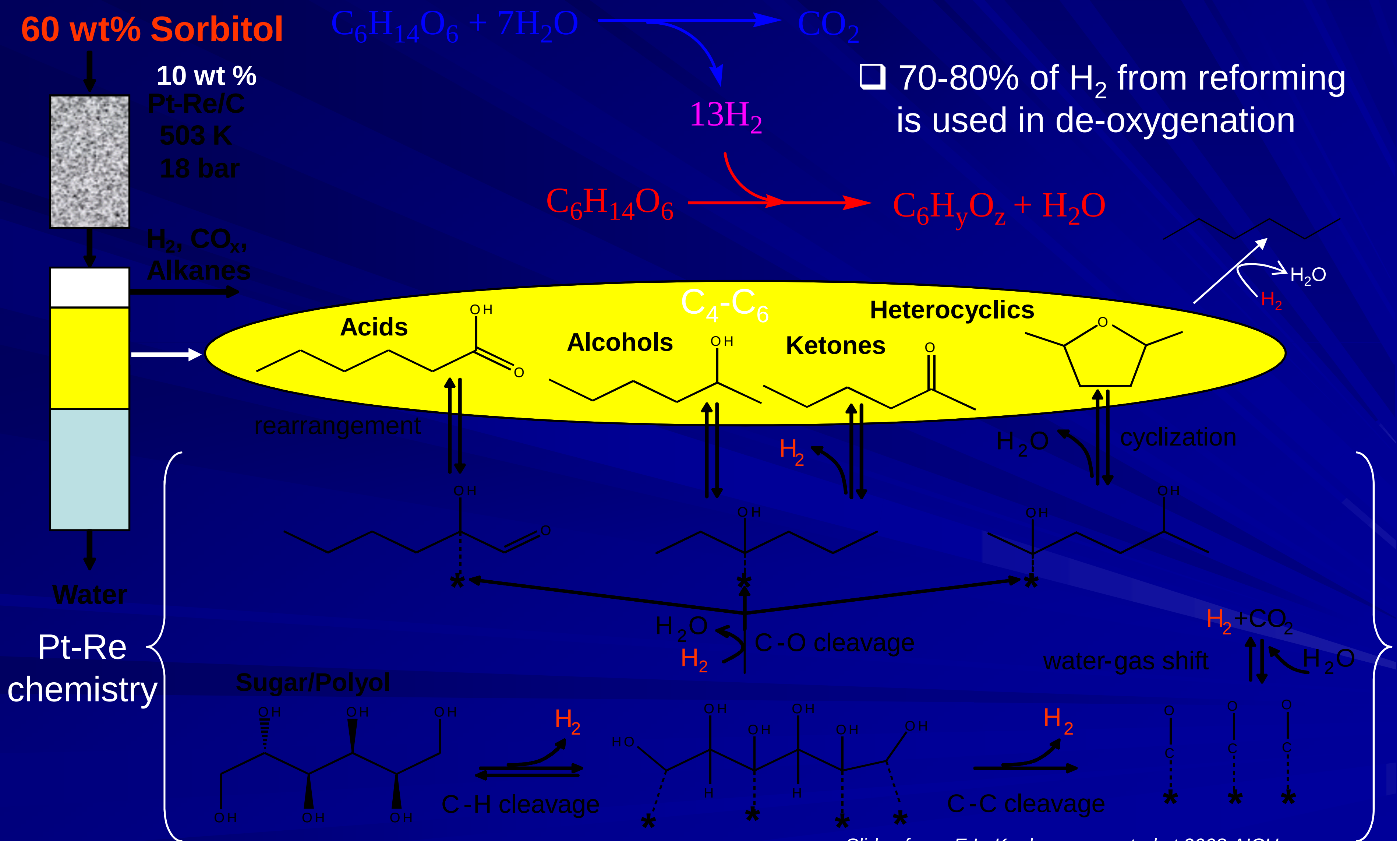
E. L. Kunkes et al.; SCIENCE, 2008

Slides from E.L. Kunkes presented at 2008 AIChe

Integration of reforming and deoxygenation

- 70-80% of H_2 from reforming is used in de-oxygenation



E.L. Kunkes et al. ***Science*** *(2008) 322 417-421*

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Some facts

- **Intermediate pressures and temperatures**
  - Provide the greatest yields of monofunctional products
- **60 wt% sorbitol conversion at 503K and 18 bar**
  - 1 kg of organic phase (sorb_503_18) for every 3.5 kg of sorbitol
  - 70 % of maximum possible efficiency (complete balance between reforming and deoxygantion)
  - Sorb_503_18 retains 65% of the energy in sorbitol feed
- **Monofucntional hydrocarbons can be used directly**
  - Solvents, chemical intermediates, fuels and fuel additives
- **C_6 is the limit ? (C-C coupling processes)**
  - Gasoline additives (aromatics)
  - Diesel and Jet fuels C_8-C_{12}

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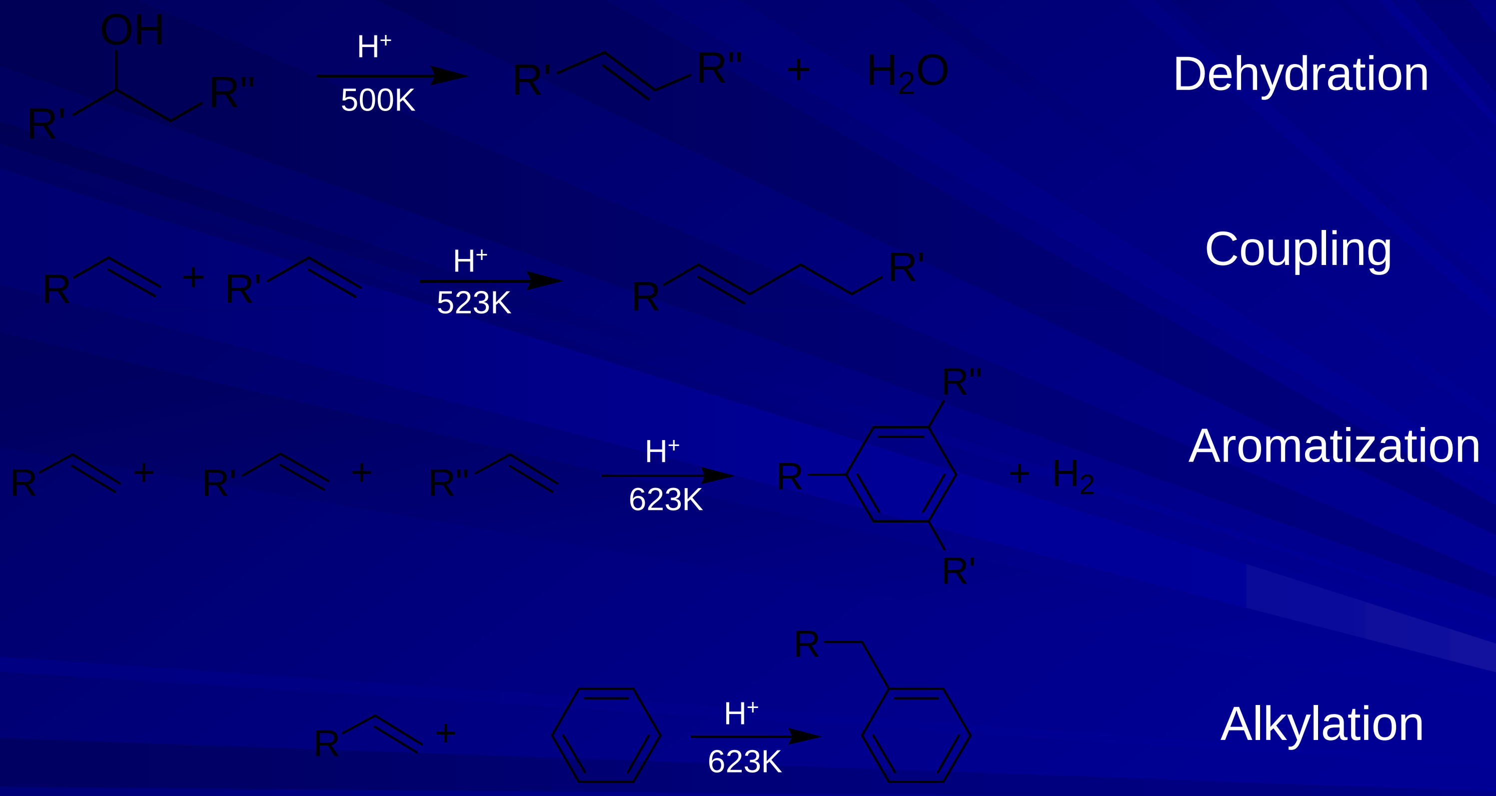
C-C coupling Reactions

- **Coupling of alkenes**



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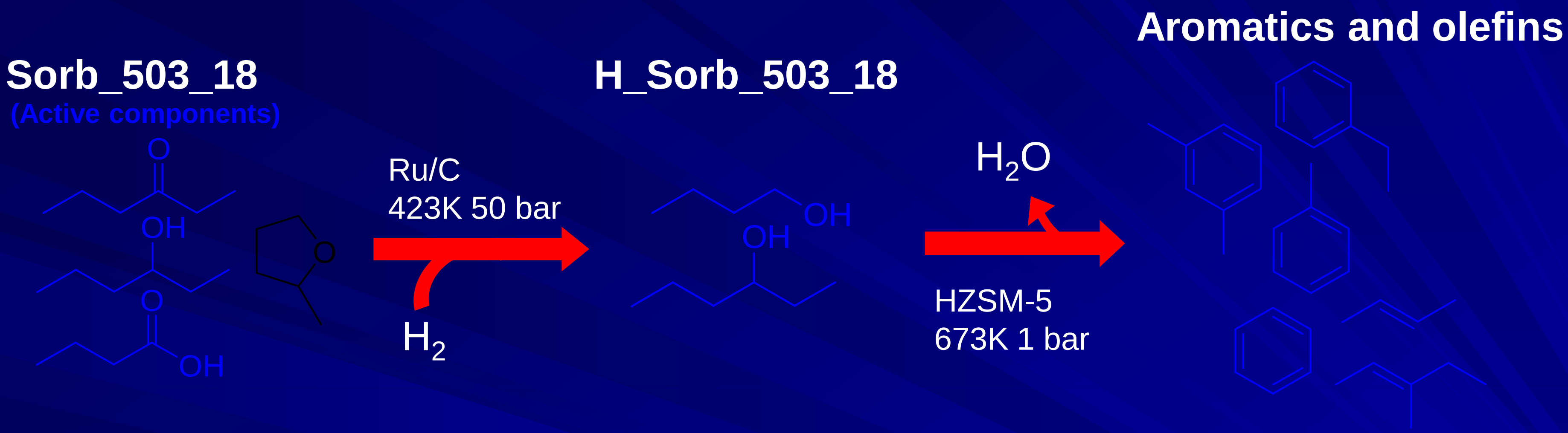
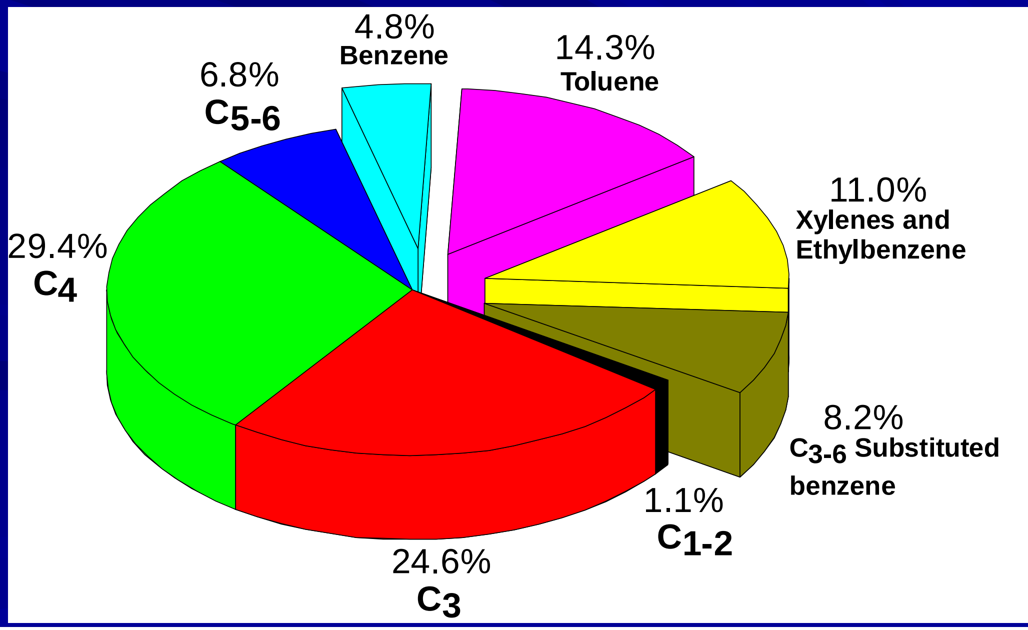
Hydrogenation-Aromatization



❑ 40 % conversion of Sorb_503_18 into fuel grade aromatics



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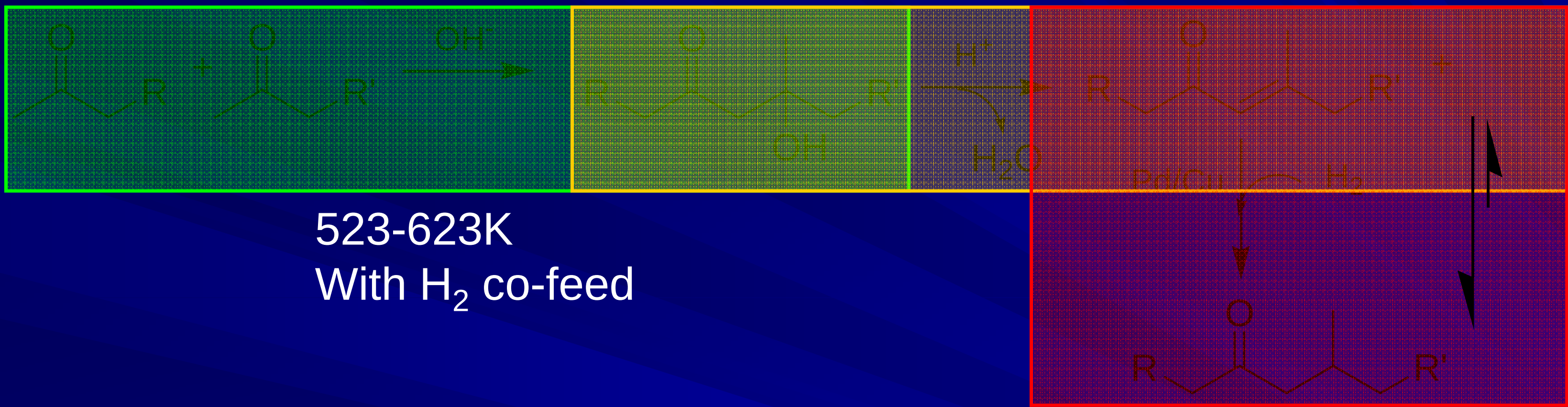
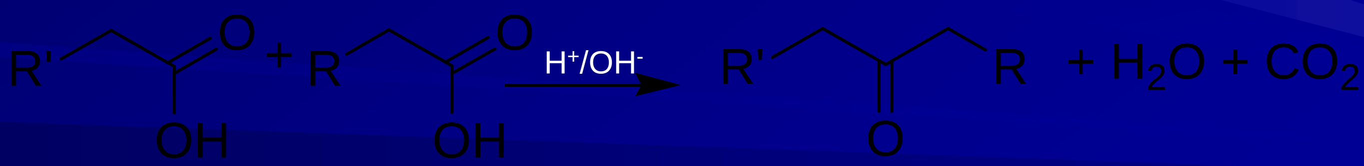
C-C coupling Reactions (contd.)

- **Aldol condensation-dehydration-hydrogenation**



523-623K
With H_2 co-feed

- **Ketonization of carboxylic acids**



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Vapor phase aldol condensation

Sorb_503_18

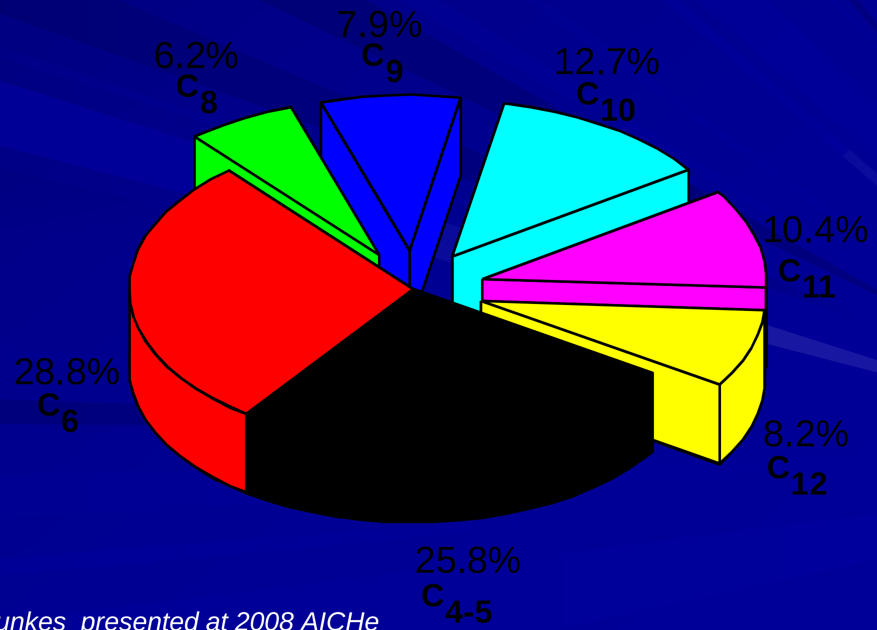
(Active components)

Condensation products

Singly-branched C_8-C_{12} alkanes

Acid Neutralization Required

- acids deactivate basic catalyst !
- ~40% conversion to C_8-C_{12}
- ~85% conversion of 2-ketones



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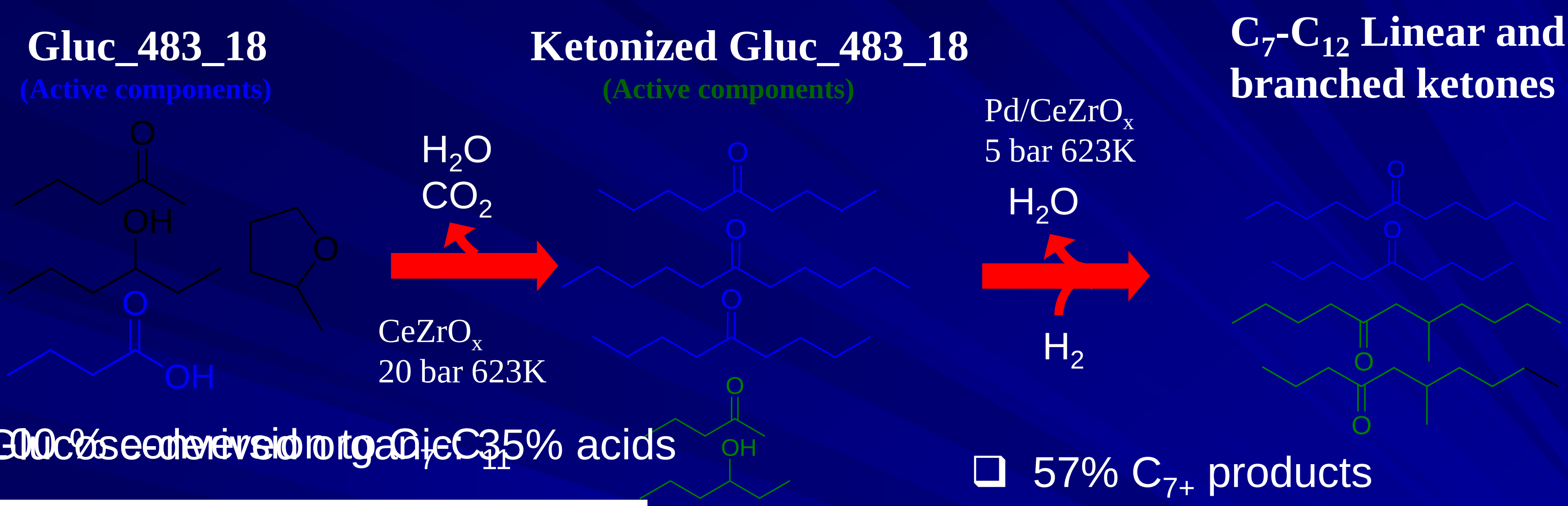
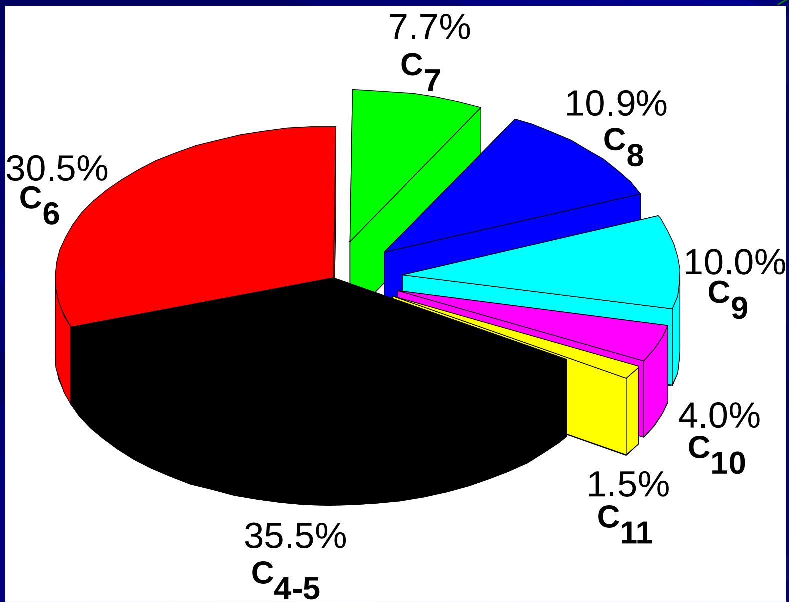
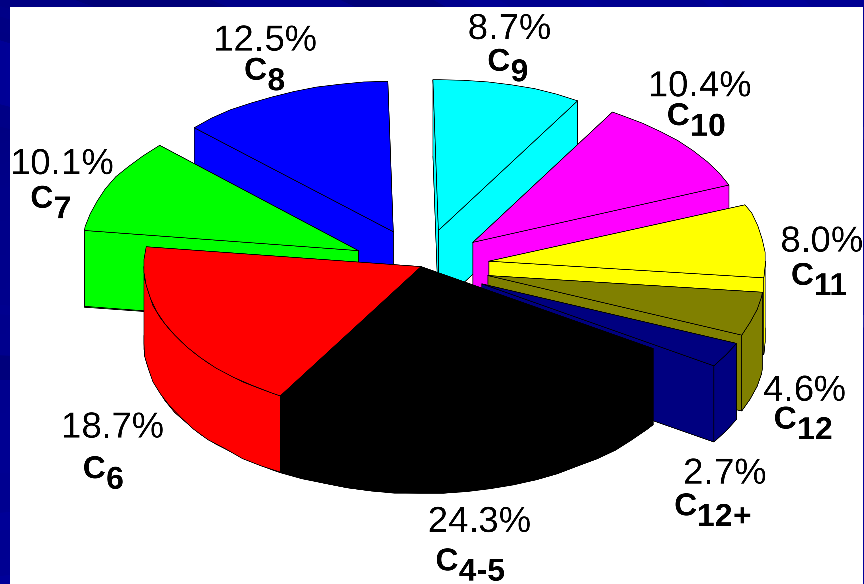
Ketonization and Condensation



- Glucose derived organic acids
- 100% conversion to C_7-C_{11} 35%

- 57% C_{7+} products





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Partial Conclusions

- Strategy: Remove oxygen but retain some functionality
- Sugar/polyol conversion involves a balance between C-C and C-O cleavage reactions
  - Endothermic C-C cleavage (reforming) provides H_2
  - Exothermic C-O cleavage (deoxygenation) consumes H_2
  - PtRe/C catalyzes both reactions (heat and H_2 integration in single reactor)
- Intermediate temperatures and pressures achieve maximum yield of mono-functional products
  - High temperatures and pressures → alkanes (non-functional)
  - Low temperatures/pressures → oxygenated aq. products
- Targeted C-C coupling reactions yield fuel grade products

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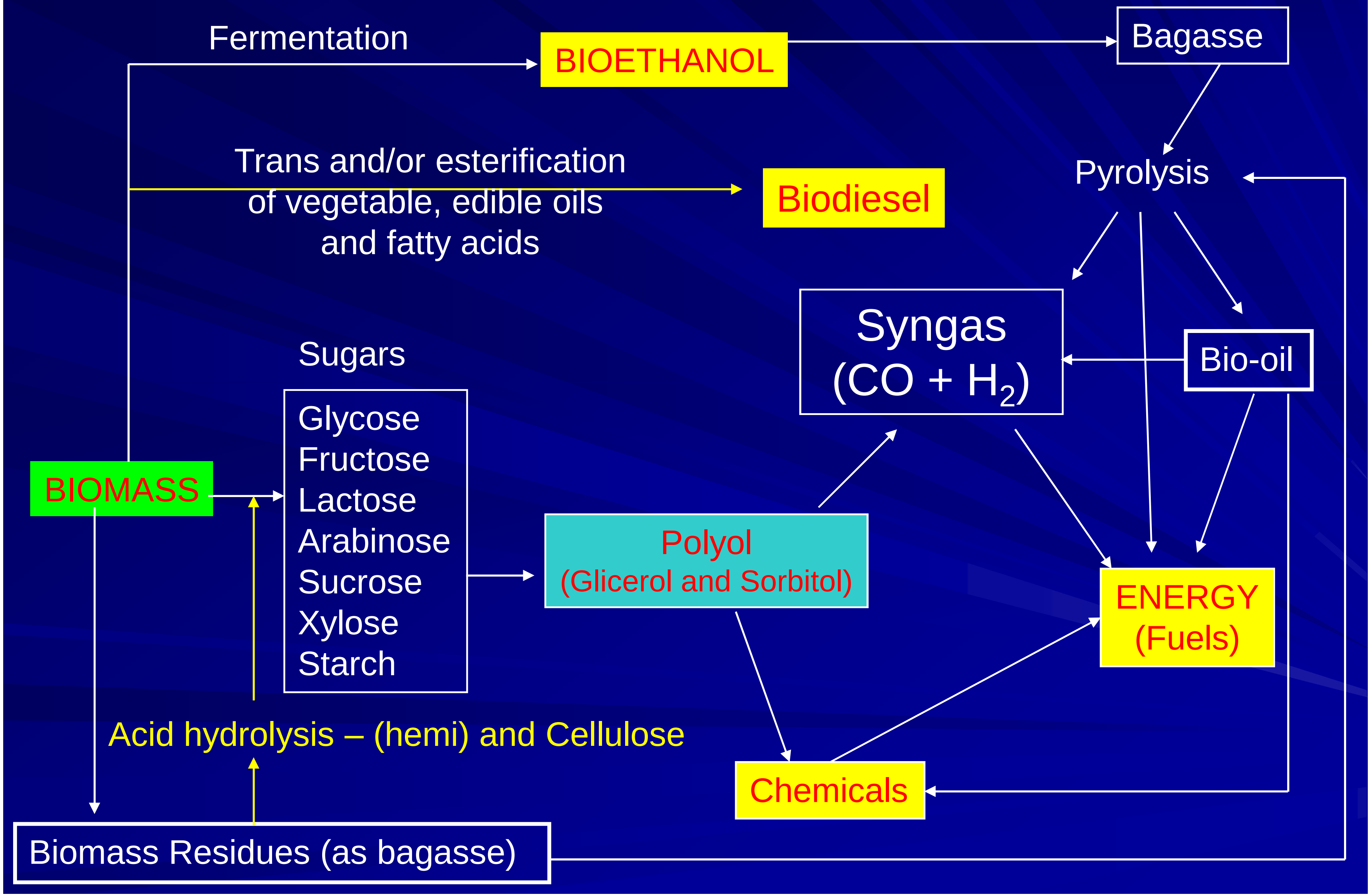
Conclusion : Chemical and Catalytic Platform will be an alternative for future biorefineries



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- U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Chemical Sciences Division
- CAPES and UW for post-doctoral grants
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- FAPEMIG and PETROBRAS for UFU Biofuel Research
- FULBRIGHT (THAIS COSER et al.)

Catalytic Bio-Reforming Team

Dante A Simonetti

Prof. James A Dumesic

Edward L Kunkes

Thank you !

Questions ?

rrsoares@ufu.br

The Reaction Network