

# Homogeneous catalysts for selective deoxygenations of sugar polyols to polymer precursors and fine chemicals – motivation, strategies, challenges and catalyst design

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**Marcel Schlaf**

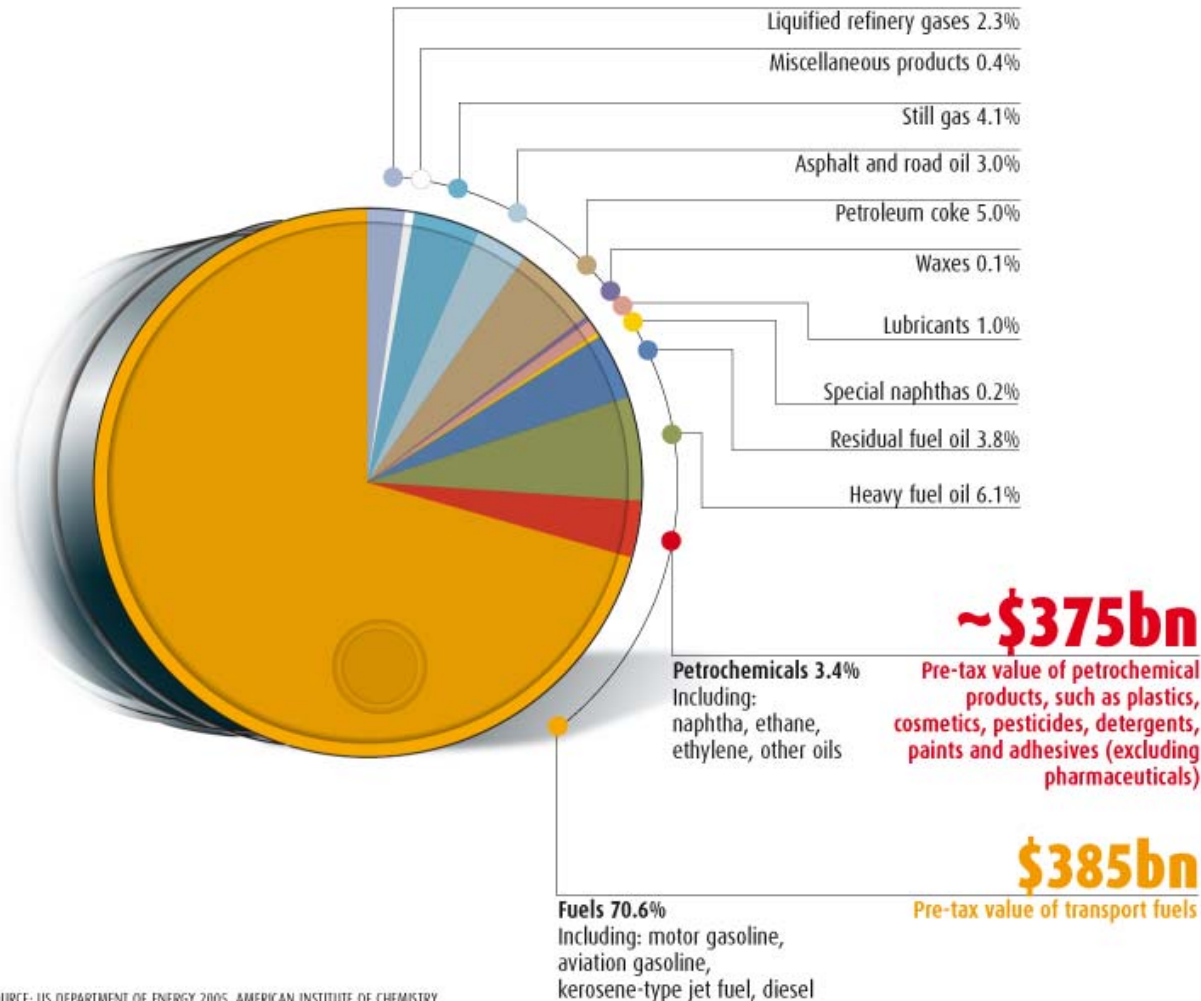
Department of Chemistry, University of Guelph

Guelph-Waterloo Centre for Graduate Work in Chemistry (GWC)<sup>2</sup>

# The Value of Petrochemicals (US Numbers)

## OIL BARREL BREAKDOWN

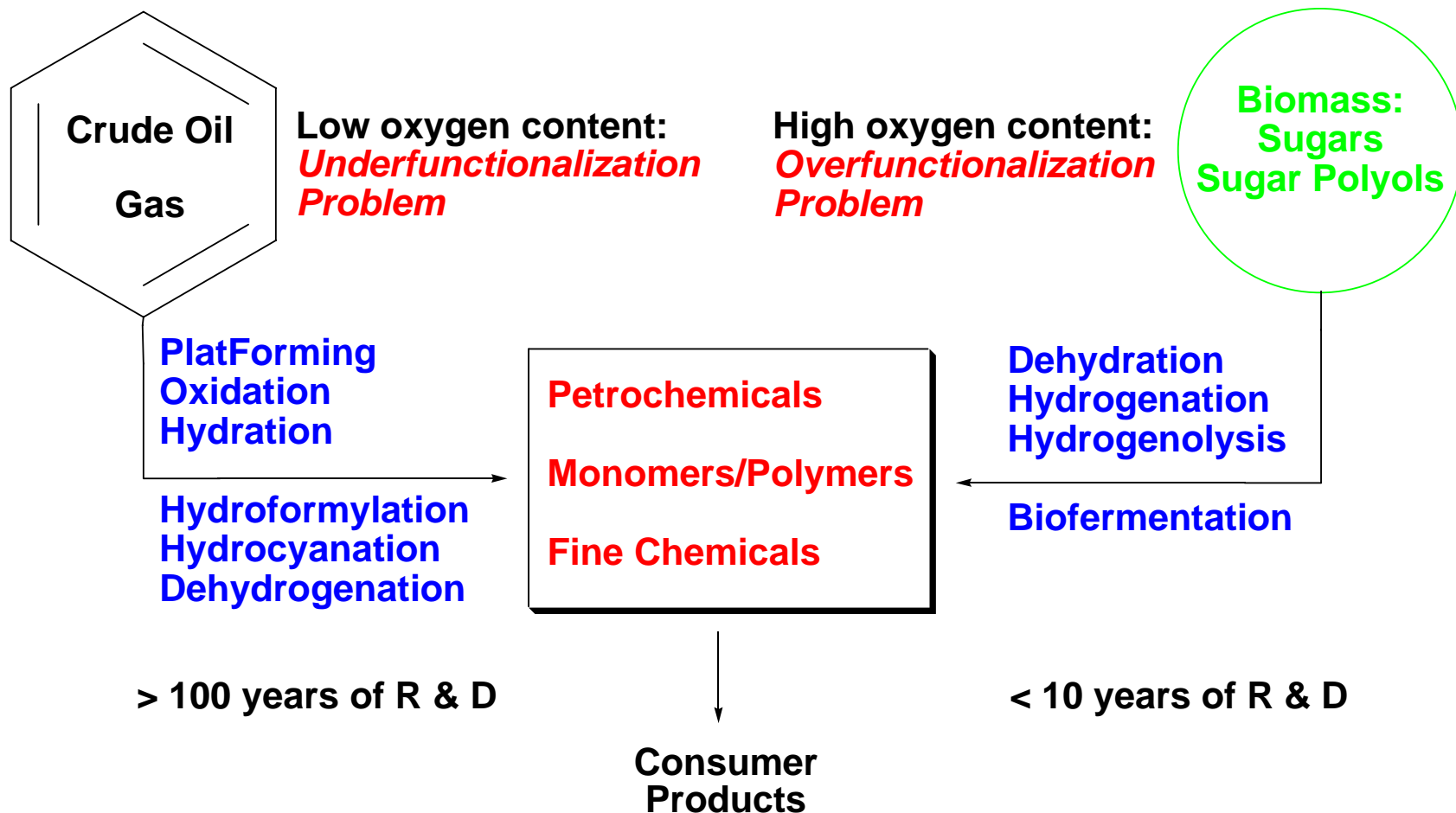
Despite consuming a small fraction of US oil compared with fuel, petrochemical products are worth more



SOURCE: US DEPARTMENT OF ENERGY 2005, AMERICAN INSTITUTE OF CHEMISTRY

- Only ~ 3.5 % of all crude oil processed ends up in petrochemicals – over 70 % is used as fuel.
- In spite of this, these chemicals are worth as much as the fuel !

# The Deoxygenation Challenge



Schlaf, M., *Dalton Trans.*, 2006, 4645-4653.

# Sugar Polyols - A Renewable Resource

## Est. Production 2007 [t/a]:

> 1 × 10<sup>6</sup> (and growing →  
Bio-Diesel glycerol glut ...)

? – produced by Cargill as  
a non-caloric sweetener

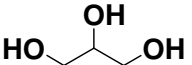
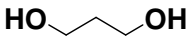
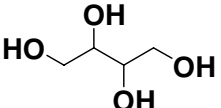

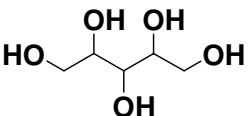
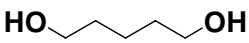
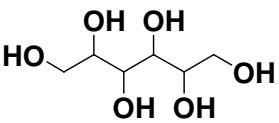
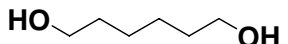
25,000 (Xylose)

30,000 (Xylitol)

5,000,000 (glucose)

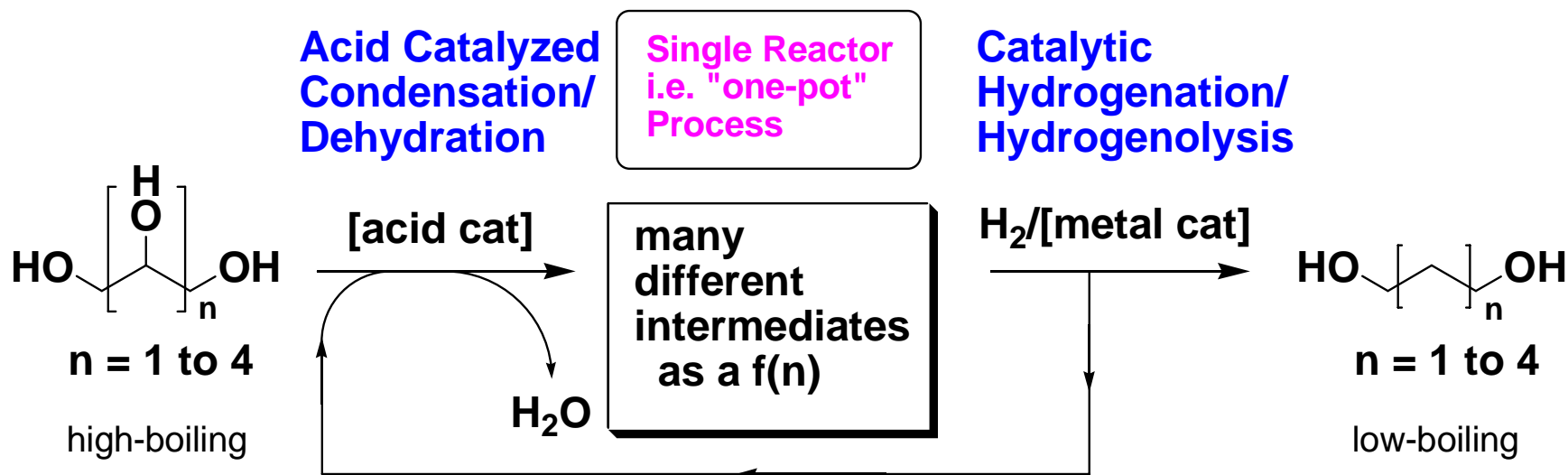
600,000 (sorbitol)

130,000,000 (sucrose)

Biomass	$\alpha,\omega$ -diol	Application
 <p>n=3: Glycerol (Waste By-product of Bio-Diesel production)</p>	 <p>1,3-propanediol</p>	<p>Sorona™ (DuPont)/ Corterra™ (Shell)</p>
 <p>n=4: Erythritol (Biofermentation of Corn sugar/starch)</p>	 <p>THF</p>	<p>Lycra™ / Industrial Solvent</p>
 <p>n=5: Xylitol (Acid digestion/pyrolysis of hemi-cellulose, e.g. corn cobs)</p>	 <p>1,5-pentanediol</p>	<p>Thermoplastic Polyurethanes Polyesters</p>
 <p>n=6: Glucitol (Sorbitol) (Hydrogenation of glucose from corn/beet/cane sugar)</p>	 <p>1,6-hexanediol</p>	<p>Polyurethanes Polyesters Potential Nylon-6,6 precursor</p>

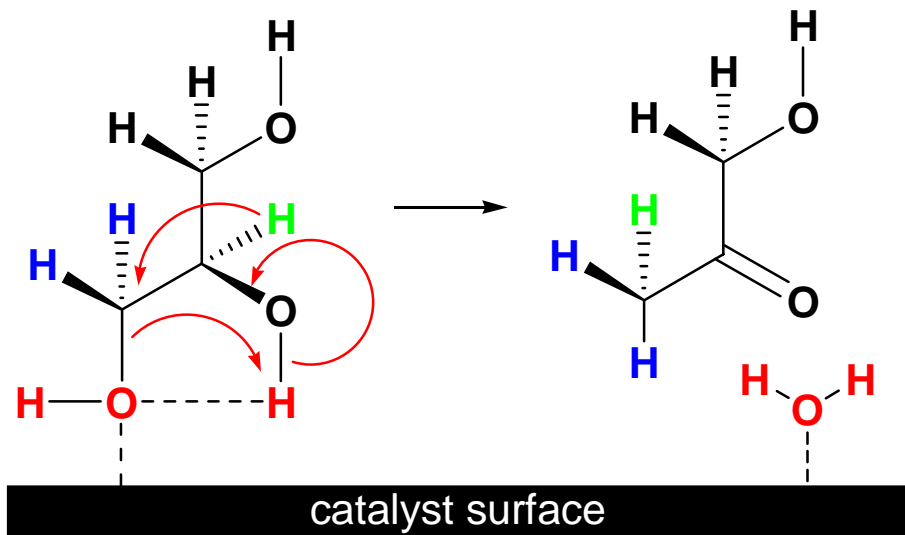
a) M. McCoy, *C & EN News*, **2005**, 83(8), 19-20. b) F.W. Lichtenthaler, *Acc. Chem. Res.*, **2002**, 35, 728-737.

# How to Reduce the Oxygen Content ?



- Controlled Acid (Brønstedt or Lewis) Catalyzed Dehydration. (*carbocations*  $\rightarrow$  *thermodynamic bias for loss of secondary OH*)
- Hydrogenation and/or Hydrogenolysis of C=O, C=C, C-O.
- Iterative Repetition in Single Reactor if Required.

# Glycerol Deoxygenation – Selectivity with Heterogeneous Catalysts



[Cat.]/ [Acid]	T [°C]	Conv. [%]	1,2-diol [%]	1,3-diol [%]
Raney-Ni/ none <sup>a</sup>	190	97	69	0 (?)
CuCrO <sub>4</sub> / none <sup>b</sup>	200	65	59	0 (?)
Ru-C/ Amberlyst <sup>c</sup>	140	41	18	<1
Ru-C/ Amberlyst <sup>d</sup>	120	79	75	0

a) A. Perosa *et al.*, *Ind. Eng. Chem. Res.*, 44, **2005**, 8535-8537.

b) G.J. Suppes *et al.*, *Appl. Cat. A*, 281, **2005**, 225-231.

c) K. Tomishige *et al.*, *Catal. Commun.*, 6, **2005**, 645-649.

d) K. Tomishige *et al.*, *Appl. Cat. A*, 318, **2007**, 244-251.

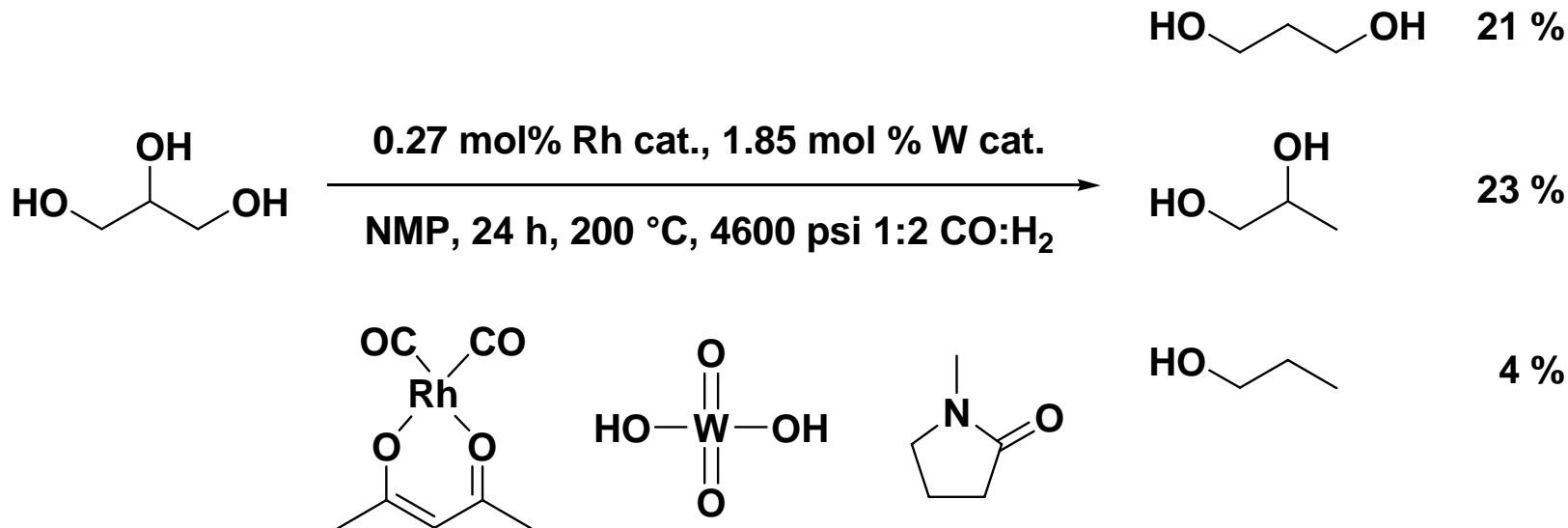
On heterogeneous acid catalysts steric, i.e., kinetic factors favour the dehydration of a terminal OH on the catalyst surface:

**glycerol → acetol → 1,2-propanediol**

*Reactive distillation* of glycerol over solid acid catalysts (CuCrO<sub>4</sub>) gives acetol.<sup>e</sup>

e) G.J. Suppes, W.R. Sutterlin *et al.*, *AIChE*, **2006**, 52, 3543-3548.

# Glycerol to 1,3-Diol: Known Catalysts



T.M. Che, Celanese Corporation, US Patent 4,642,394, 1987

**Working Hypothesis:** With homogeneous acids dehydration can in solution occur under thermodynamic control through protonation of a secondary hydroxyl function and formation of 3-hydroxy-propanal via the more stable carbo-cation intermediate.

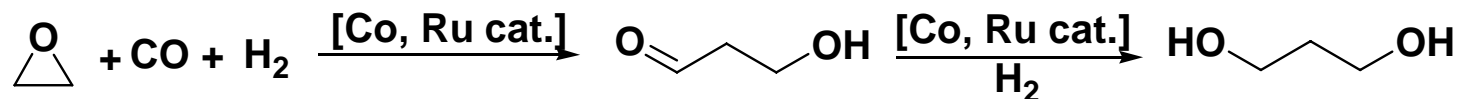
**glycerol → 3-hydroxy-propanal → 1,3-propanediol**

# 1,3-Diol Production: The State of the Art

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## Petrochemical route: SHELL:

- “One-pot” homogeneous hydroformylation/hydrogenation.

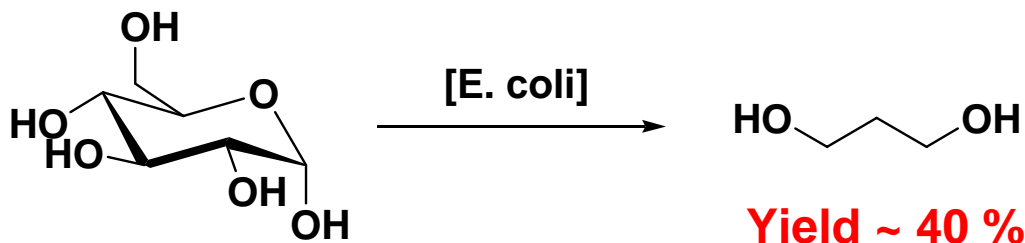


Paul Weider *et. al.*, US patent 6.903,044, 2005 + 16 previous patents

**Yield > 80 %**

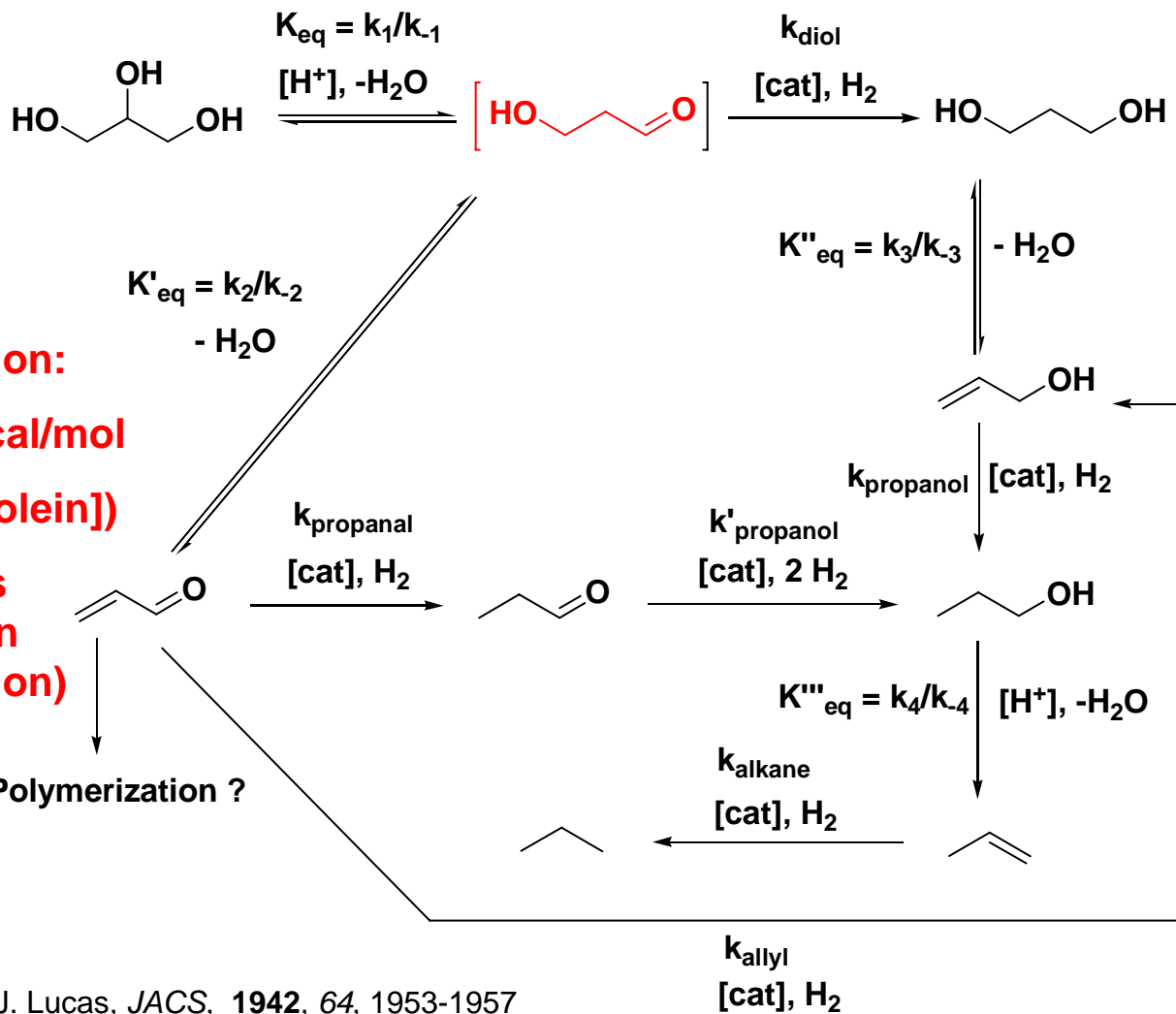
## Biotech route: DuPont with Tate & Lyle

~ 100,000 ton/a name plate capacity facility on stream in Loudon, TN, USA



S. Vollenweider, C. Lacroix, *Appl. Microbiol. Biotechnol.*, 2004, 64, 16-27 and references therein.

# Glycerol to 1,3-Propanediol



aqueous solution:

$\Delta H(K'_{eq}) \approx 6 \text{ kcal/mol}$

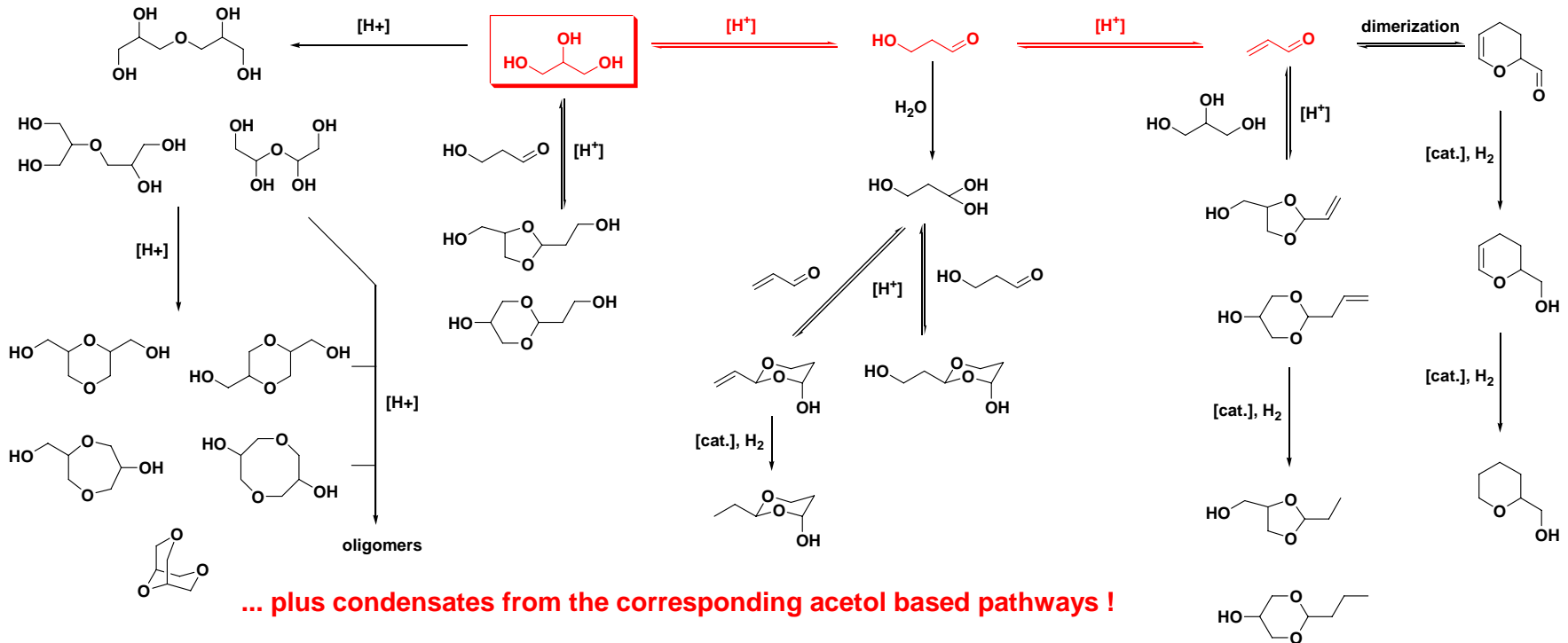
$K'_{eq} = f(T, [\text{acrolein}])$

(dehydration is unfavourable in aqueous solution)

a) D. Pressman, H.J. Lucas, *JACS*, **1942**, *64*, 1953-1957

b) R.H. Hall, E.S. Stern, *J. Chem. Soc.*, **1950**, 490-498

# Welcome to the Wonderful World of Glycerol Chemistry

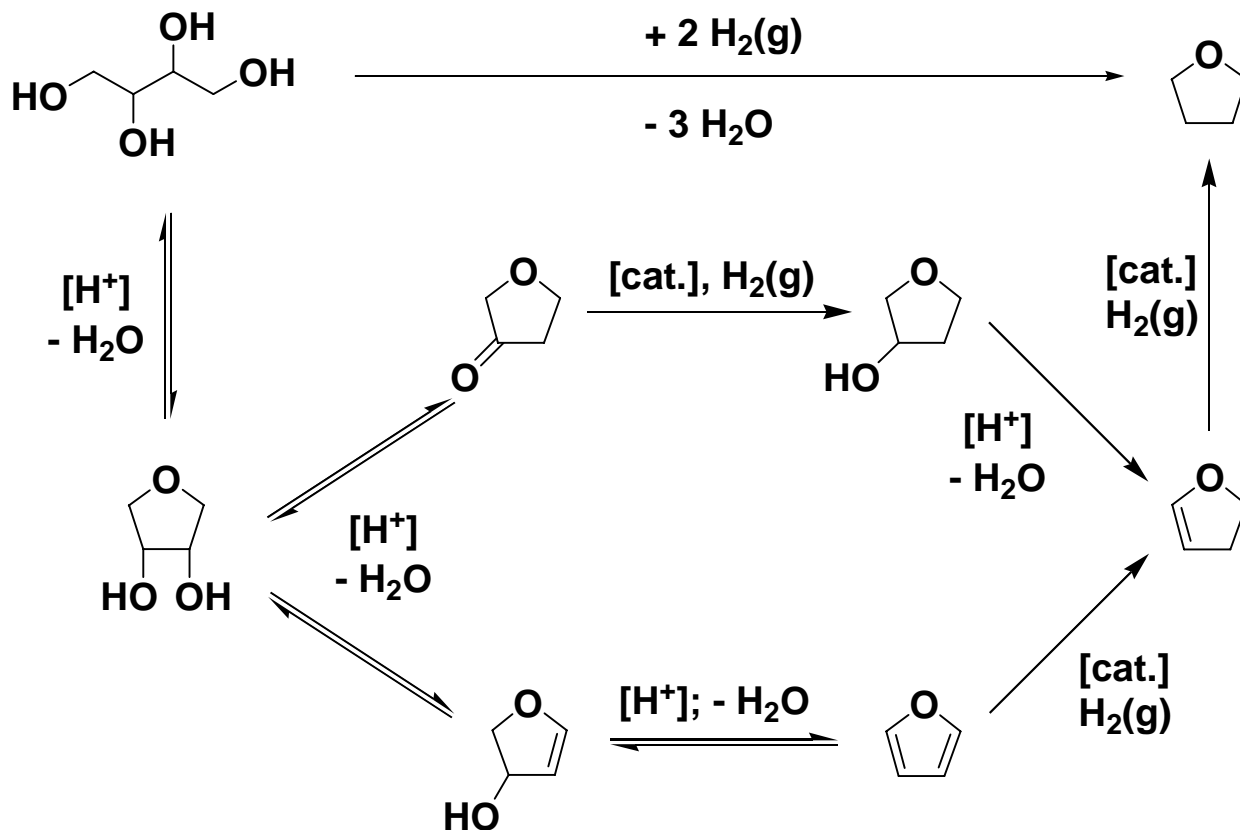


- S. Vollenweider, C. Lacroix, *Appl. Microbiol. Biotechnol.*, **2004**, 64, 16-27.
- S. Cassel et al., *Eur. J. Org. Chem.* **2001**, 875-896.

**At least 10 parameters influence these condensation reactions:**

**Type of and [acid], [H<sub>2</sub>O], T, solvent, [glycerol], time, type of and [cat.], [H<sub>2</sub>]**

# C-4: Erythritol to THF



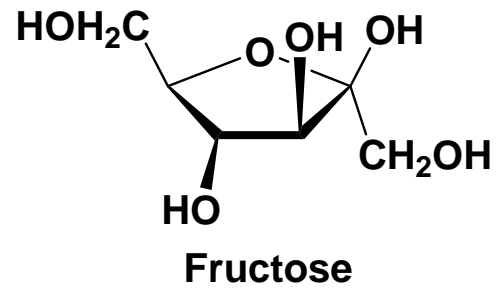
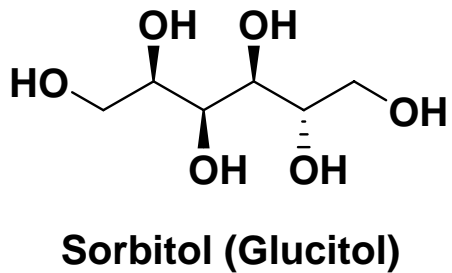
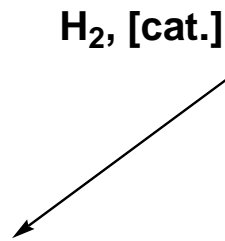
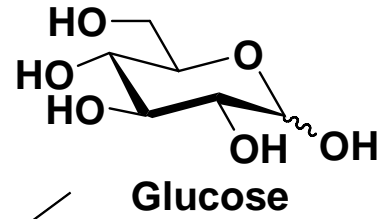
- Much simpler due to ring formation.
- Realized with heterogeneous Re/Ni/C in dioxane solvent at 200 °C and 500 psi hydrogen pressure: up to 95 % conversion with up to 55 % selectivity to the desired THF – not commercialized yet (?).

L.E. Manzer, DuPont, US Patent 6,593,481, 2003.

# C-6: Glucose/Fructose



Corn Starch

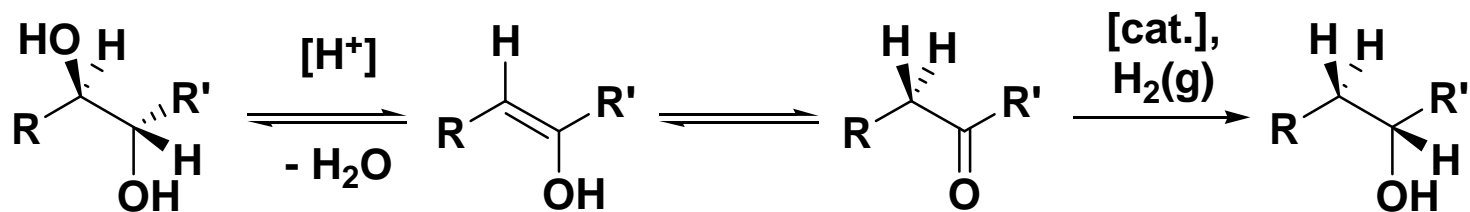




# Basic Reactions 1 & 2: Hydrogenation

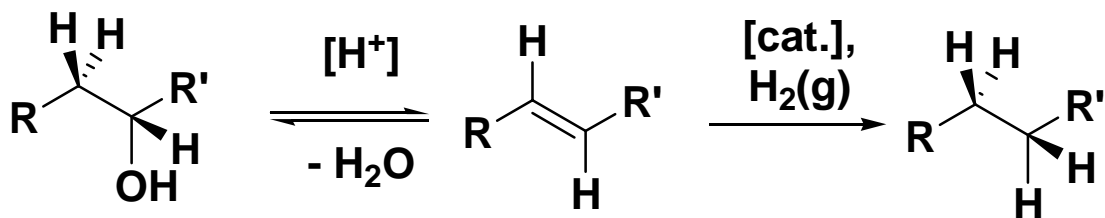
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1) Dehydration of *vic*-diols and hydrogenation of the resulting C=O double bond:



R = alkyl, hydroxy alkyl; R' = H, alkyl, hydroxy alkyl

2) Dehydration of alcohols and hydrogenation of the resulting C=C double bond:

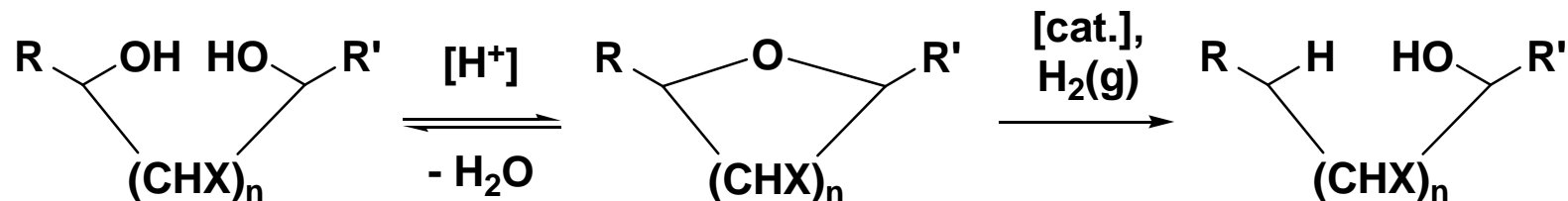


... not necessarily trivial under aqueous acidic conditions !

# Basic Reactions 3: Hydrogenolysis

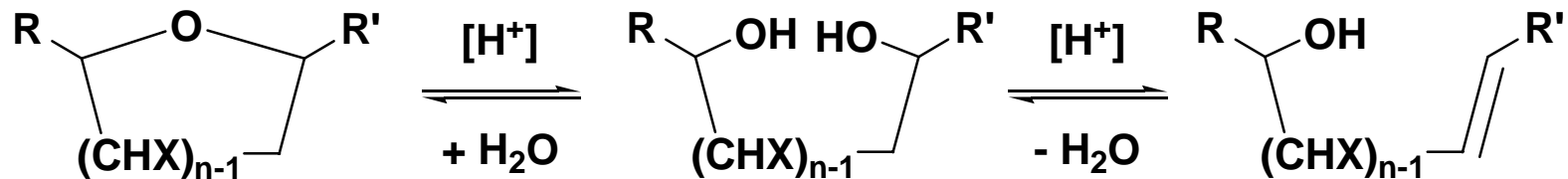
## 3) Condensation of alcohols to oxacycles and hydrogenolysis of the resulting ether:

### a) Direct Hydrogenolysis



X = H, OH, alkyl, aryl; n = 2,3,4

### b) Rehydration, Loss of Water, Hydrogenation $\rightleftharpoons$ Reactions 1 or 2

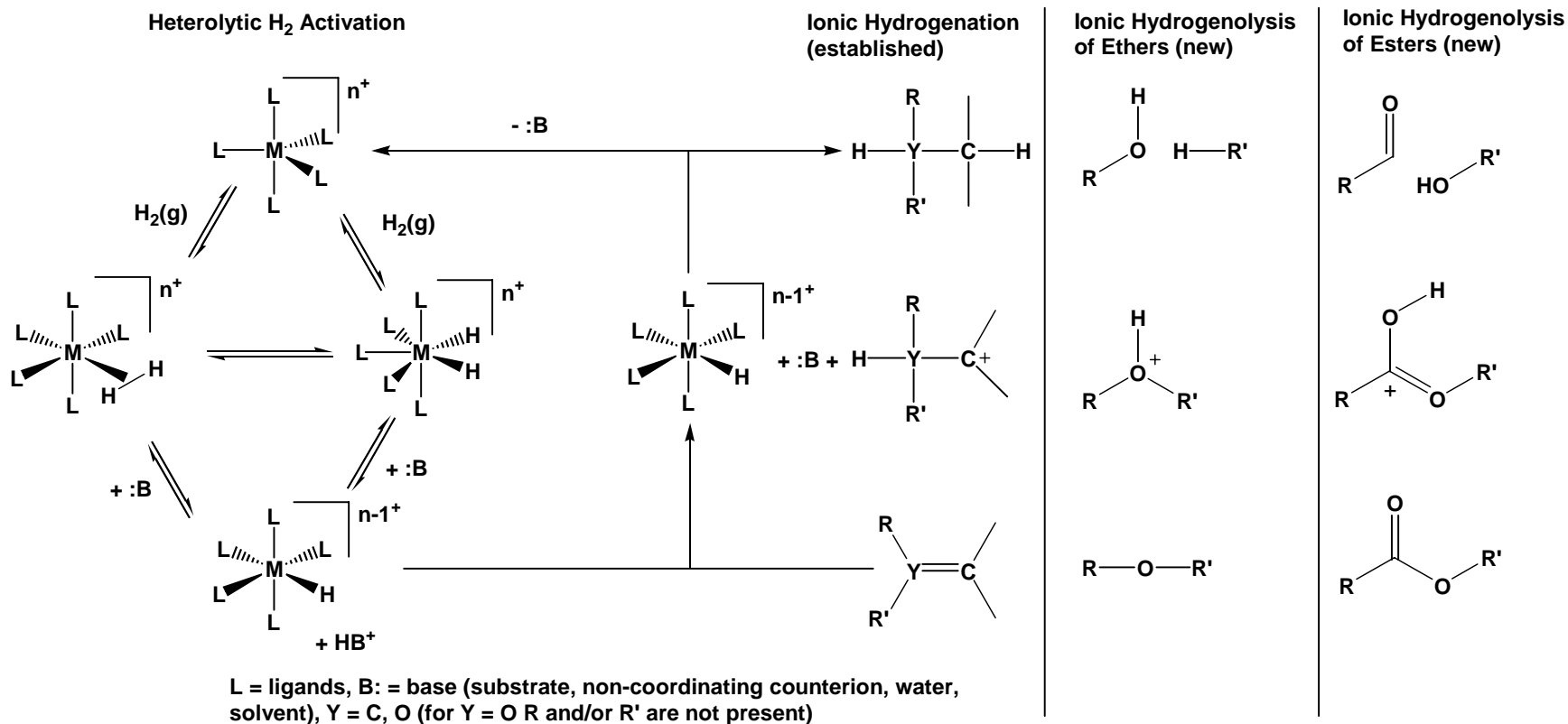


# Working Hypothesis and Catalyst Design Criteria

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- **Working hypothesis 1:**  
For the targeted deoxygenation reactions homogeneous are better than heterogeneous catalysts – why ?
- **Catalyst Design Criteria:**
  1. “Single Reactor” for dehydration and hydrogenation/hydrogenolysis:  
*Catalyst must tolerate aqueous acidic conditions and be thermally stable – the higher the better, ideally to > 200 °C.*
  2. Metal must have low oxophilicity to avoid catalyst poisoning by water or alcohol substrate:  
*Limited to late transition metals (Ru, Rh, Pd, Pt).*
  3. Acid and solvent must be non-coordinating:  
*Acid: HOTf or other non-oxidizing acid.*  
*Solvent: Sulfolane (b.p. 283 °C) or NMP (b.p. 202 °C).*
- **Working hypothesis 2:**  
Electron poor cationic complexes of ruthenium or rhodium that can activate hydrogen gas in a heterolytic fashion will be good catalysts and fulfill all design criteria.

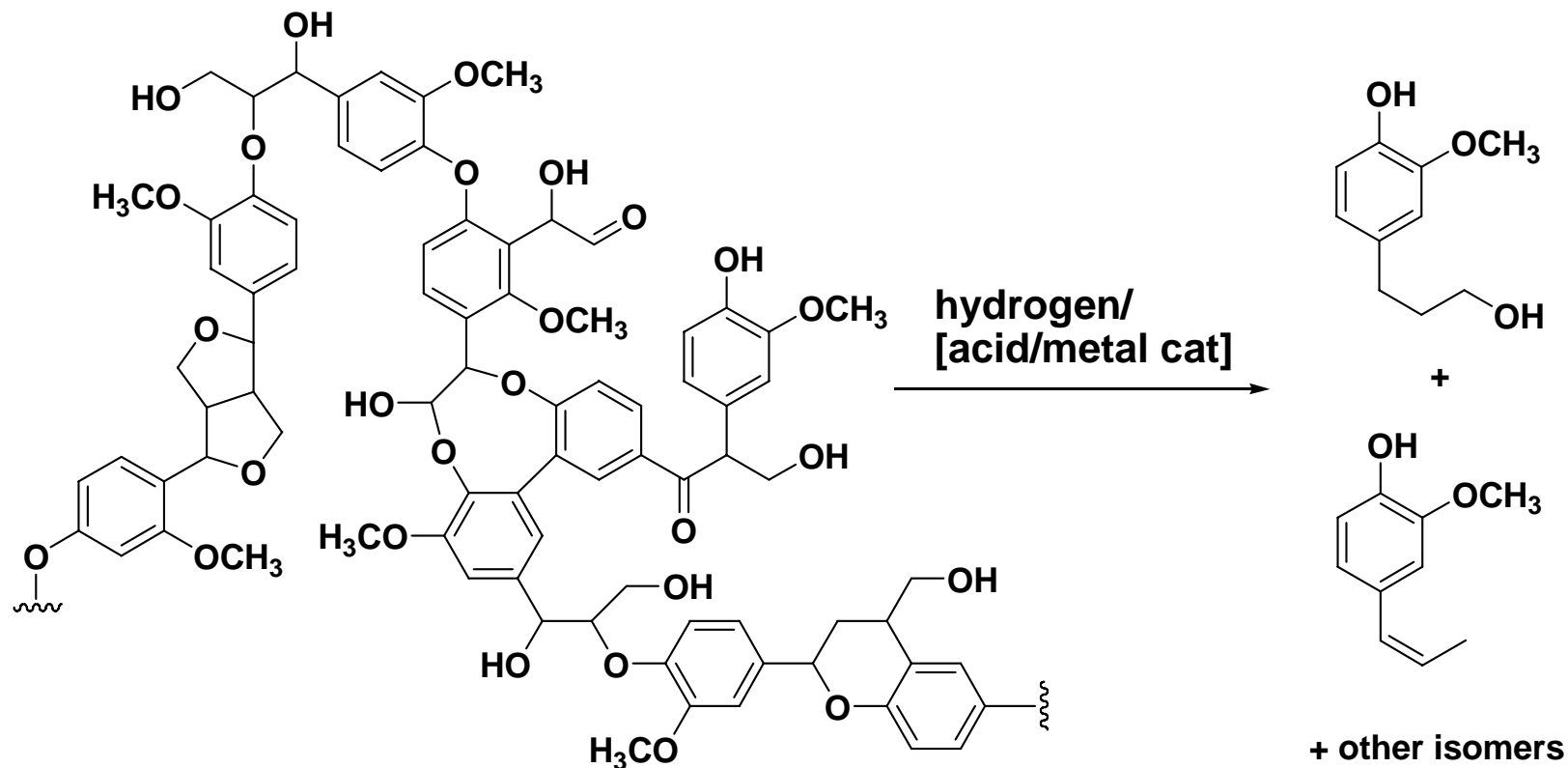
# Ionic Hydrogenation & Hydrogenolysis



**Heterolytic hydrogen activation allows activation of double bonds - and maybe ethers and esters too ...**

Review on ionic hydrogenations: R. M. Bullock, *Chem. Eur. J.*, **2004**, *10*, 2366-2374.

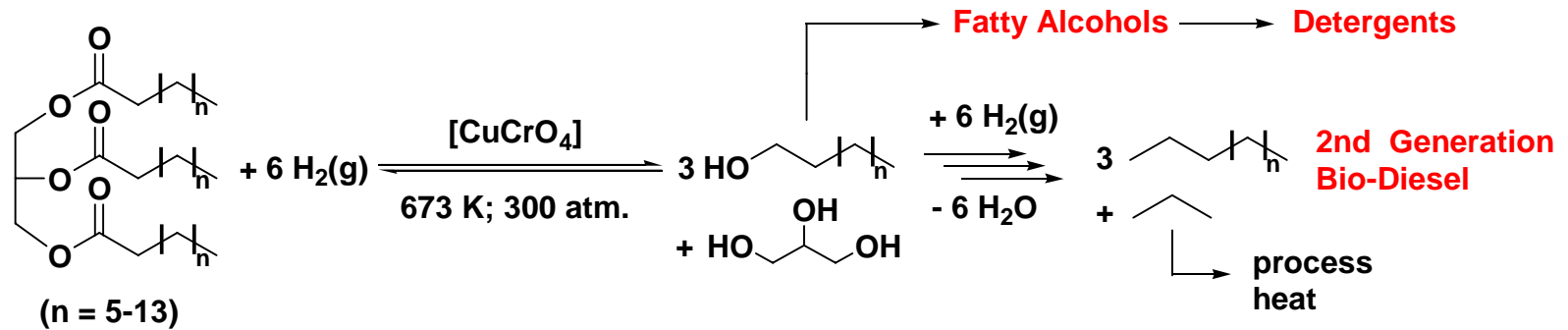
# Ether Hydrogenolysis: Phenolics from Lignin ?



Typical composition of lignin  
(non-sulfonated form)  
(Source: Lignin Institute)

- Propyl catechols could serve as platform for epoxy and other resins.
- **Coking** would not be a problem with homogeneous systems.

# Esters: Total Hydrogenolysis of Triglycerides ?



- Circumvents trans-esterification – no glycerol !
- Challenge:

**Crossover T**  
 $\Delta H/\Delta S$   
**200-400 K**

**Kinetics**

High  $E_{\text{act.}}$

High T



**Thermodynamics**  
 (numbers for FAME)

$$K_p^{300 \text{ K}} = 10^3 \text{ atm}^{-1}$$

$$K_p^{600} = 10^{-1} \text{ atm}^{-1}$$

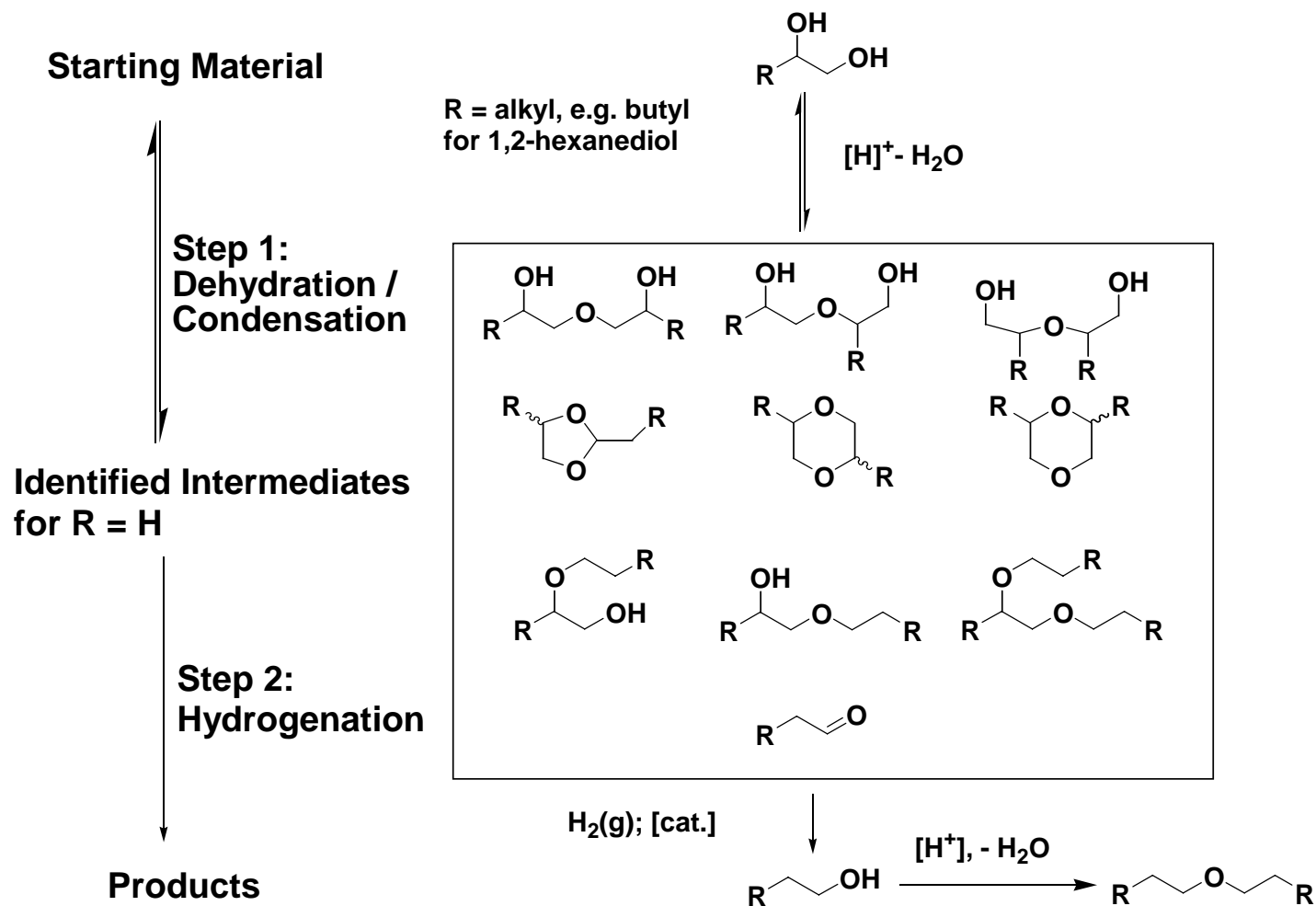
- High  $E_{\text{act.}}$  Requires high T.
- High T requires high p for good conversion.
- Energy/infrastructure intensive and expensive.
- **Can homogeneous catalysts lower the  $E_{\text{act.}}$  ?**

a) T. Turek & D.L. Trimm, *Catal. Rev. – Sci. Eng.* **1994**, 36, 645-683.

b) U.R. Kreutzer, *J. Am Oil. Chem. Soc.*, **1984**, 61, 343-348.

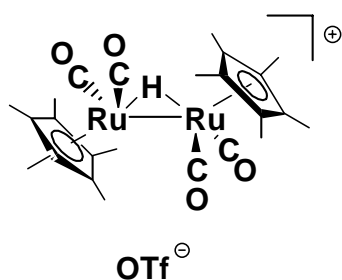
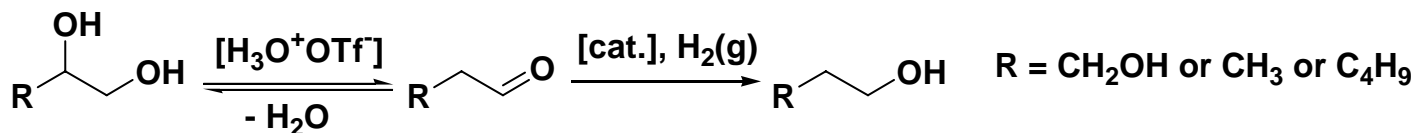


# 1,2-Diols as Models for Polyol Deoxygenations



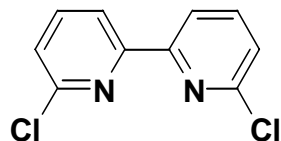
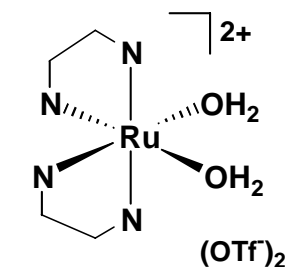
Schlaf, M.; Ghosh, P.; Fagan, P. J.; Hauptman, E.; Bullock, R. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 3887-3890.

# Catalysts Investigated to Date:

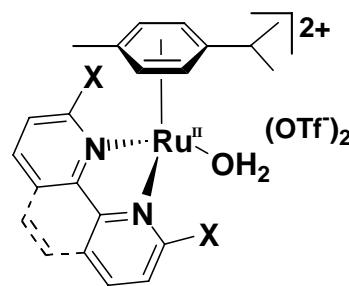


BNL/DuPont Catalyst - deactivated by water.

1



2



X = H, NH<sub>2</sub>

3

coming to a  
patent server  
near you ...  
(hopefully)

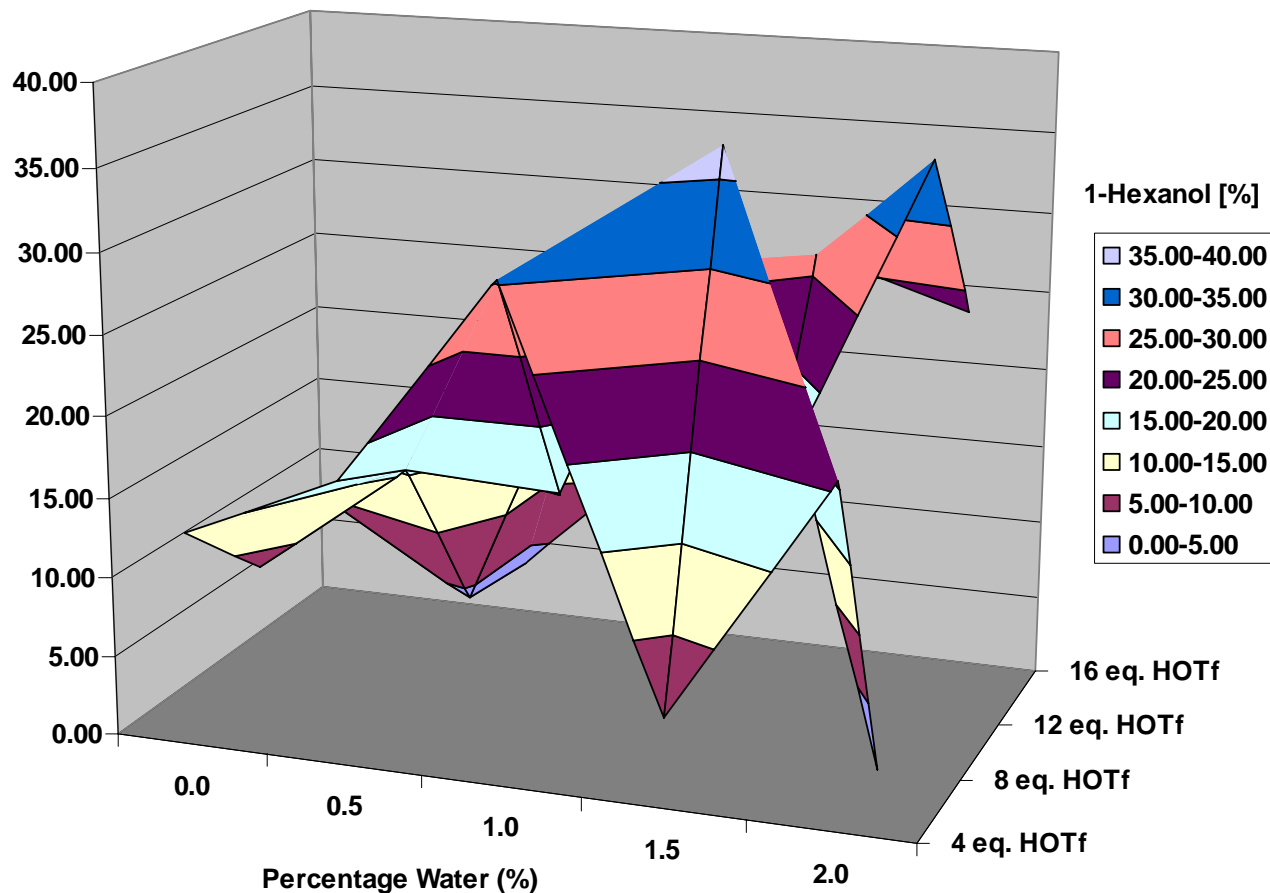
4

Catalyst	1	2	3	4
Temp. Limit [°C]	< 150	< 150	< 125	> 200
Diol ?	Yes	Yes	Yes	Yes
Glycerol ?	< 1%	No	No	Maybe

1) US 6,555,717 & US 6,462,206. 2) Xie, Z.; Schlaf, M. *J. Mol. Catal. A: Chem.* **2005**, 229, 151-158. 3) Dykeman, R. R.; Luska, K. L.; Thibault, M. E.; Jones, M. D.; Schlaf, M.; Khanfar, M.; Taylor, N. J.; Britten, J. F.; Harrington, L. *J. Mol. Catal. A: Chem.* **2007**, *In Press*. 4) Provisional patent in the works ...

# The Influence of [HOTf] and [H<sub>2</sub>O]: Parallel Reactor Runs

1,2-Hexanediol Deoxygenation with [Ru(p-cymene)(Phen)(H<sub>2</sub>O)](OTf)<sub>2</sub>



24 well parallel reactor from HEL Group (UK)

Yield of 1-hexanol from 1,2-hexanediol with Ru-catalyst **3** as a function of acid and water concentration

# Acknowledgements

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Dr. Laura Harrington (X-ray, McMaster)  
Nick Taylor † (X-ray, Waterloo)



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