

CATALYTIC CONVERSION OF CARBOHYDRATES TO (OXYGENATES) HYDROCARBONS

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CHALLENGES FOR SUSTAINABLE DEVELOPMENT

Replacement of fossil fuels for energy

Hydrogen economy (?)

Production of chemicals from renewable resources

Cheap H₂

Carbon dioxide (CO₂)

Carbohydrates (C₆H₁₂O₆)

Using nature for
CO₂ conversion

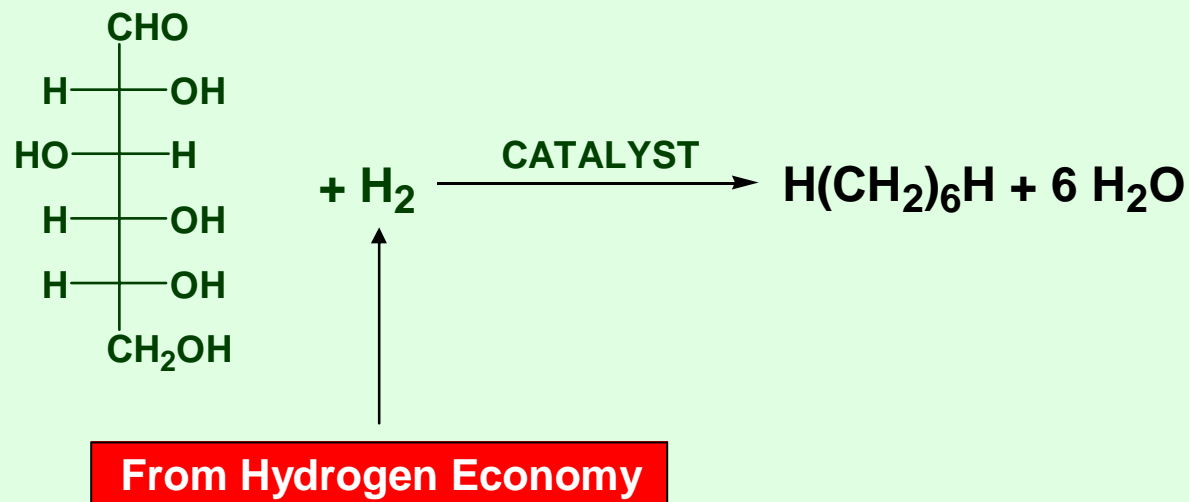
Molecular level understanding of pollution prevention

Green chemistry



GREENOMICS

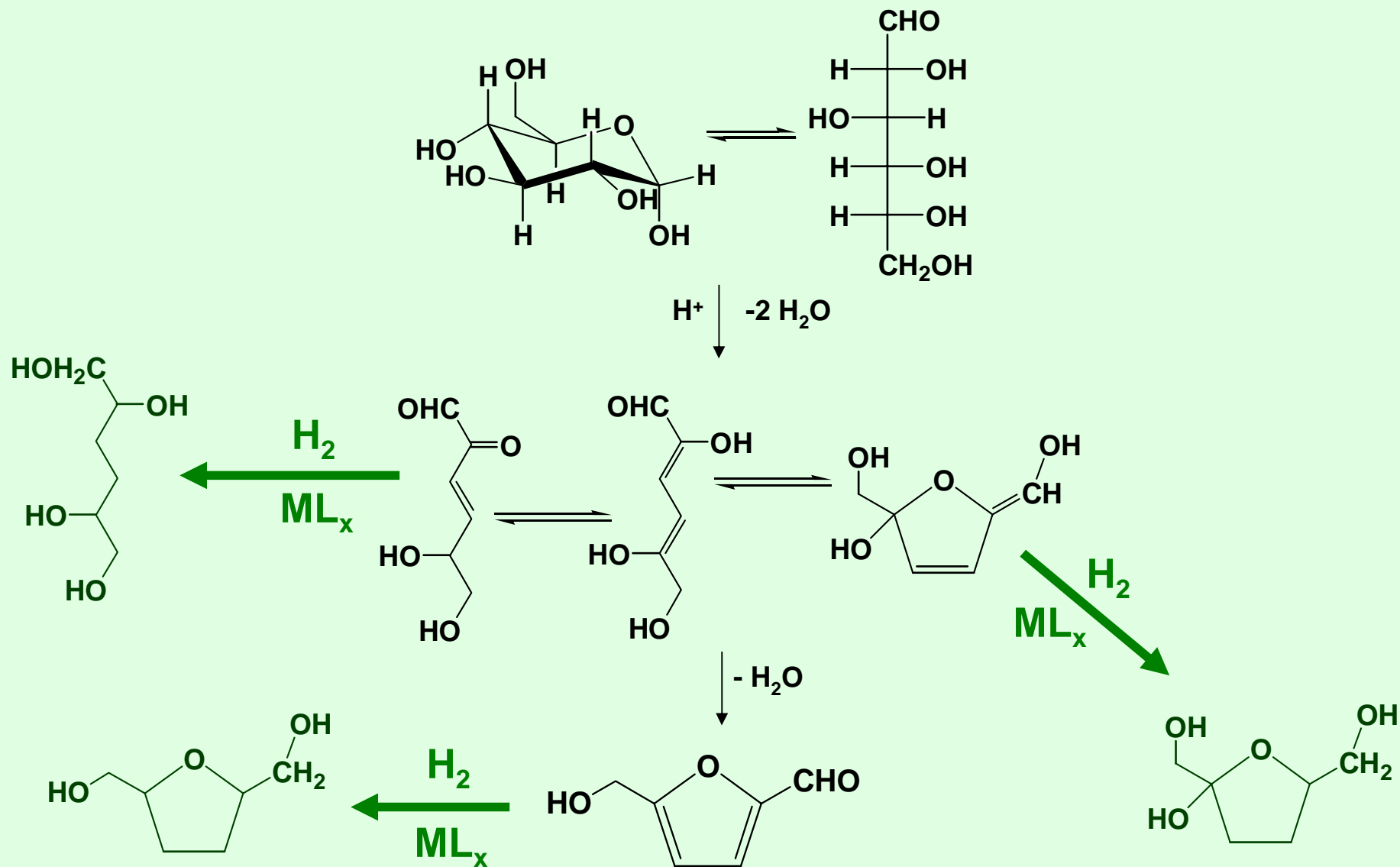
CATALYTIC CONVERSION OF CARBOHYDRATES



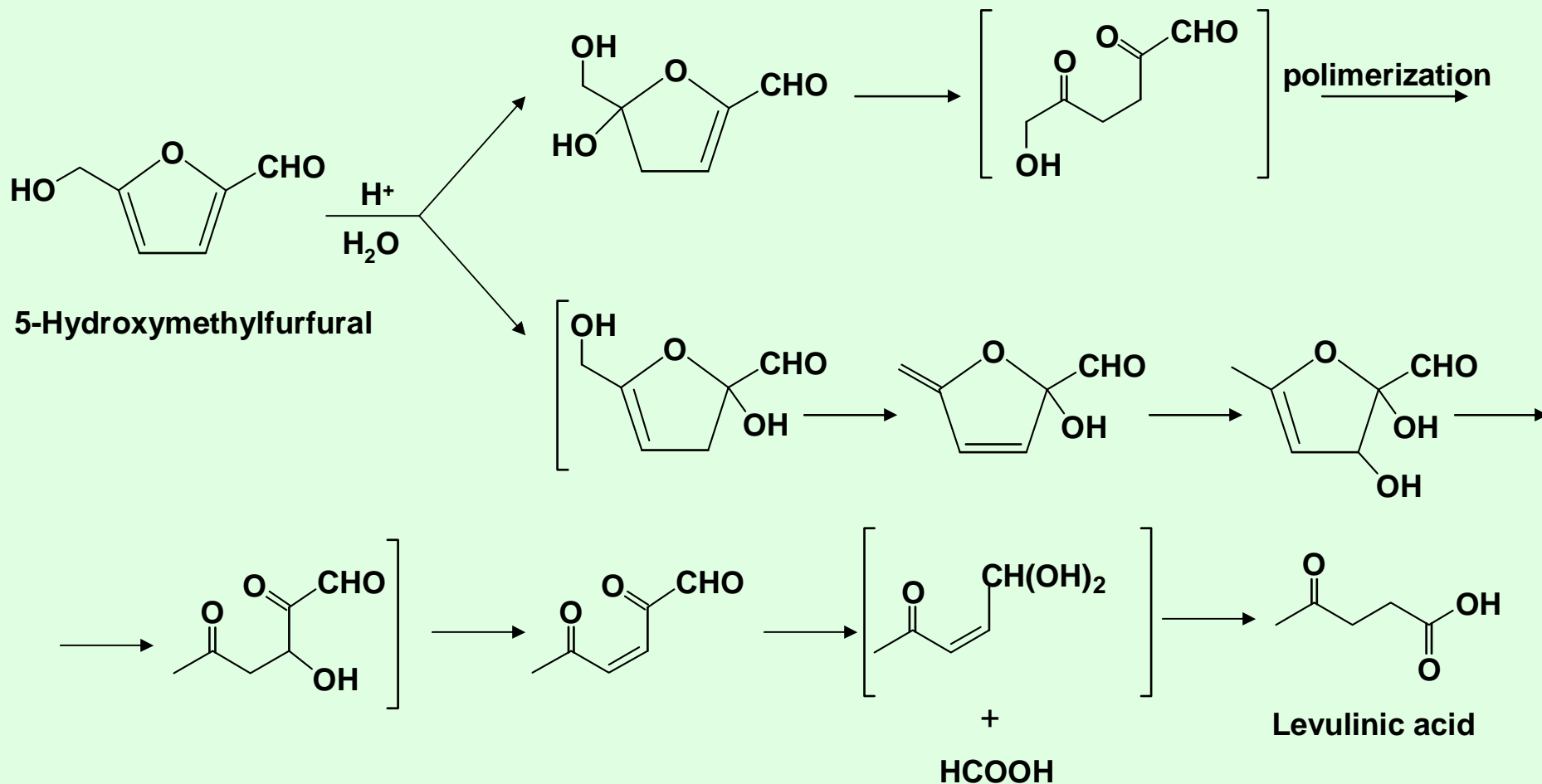
Catalytic dehydration combined with catalytic hydrogenation and hydrogenolysis could provide a renewable feedstock for the petrochemical industry.

FORMATION OF 5-HYDROXYMETHYLFURFURAL FROM GLUCOSE

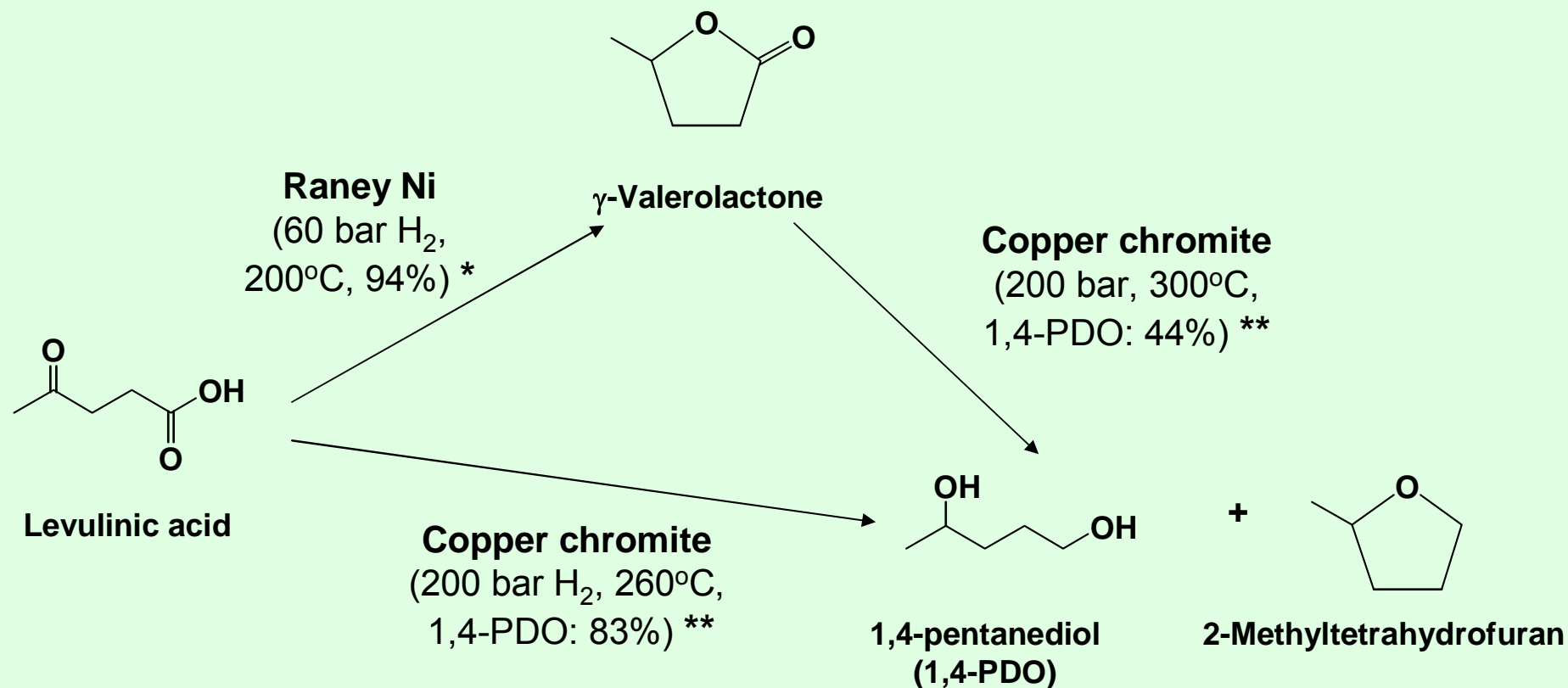
HYDROGENATION OF THE IN SITU FORMED C,C- AND C,O-DOUBLE BONDS ????



FORMATION OF LEVULINIC ACID FROM 5-HYDROXYMETHYLFURFURAL



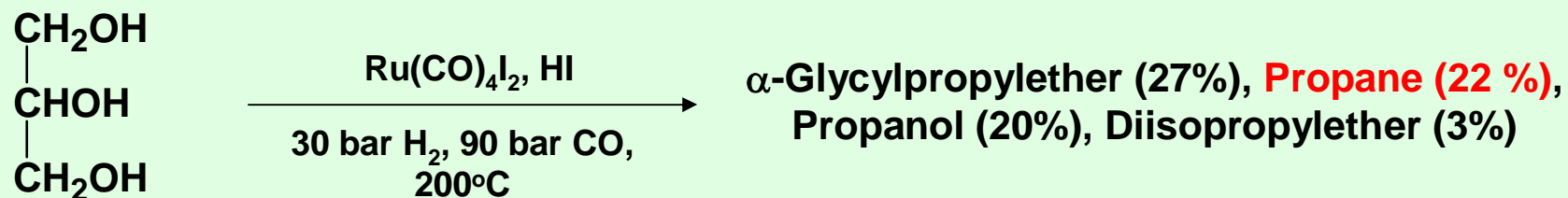
HYDROGENATION OF LEVULINIC ACID



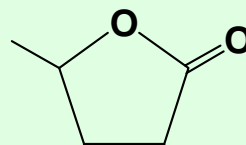
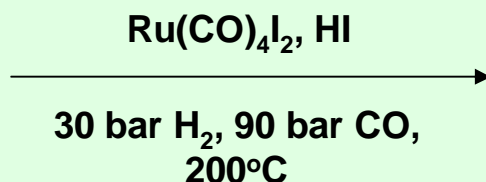
*Leonard, R. H. *Ind. Eng. Chem.*, **1956**, 48, 1331.

Christian, R. V.; Brown, H.D.; Hixon, R.M. *J. Am. Chem. Soc.*, **1947, 69, 1961.

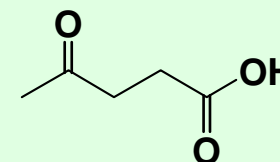
COULD WE CONVERT CARBOHYDRATES TO OXYGENATES ? OR HYDROCARBONS?



Glucose
or
Fructose

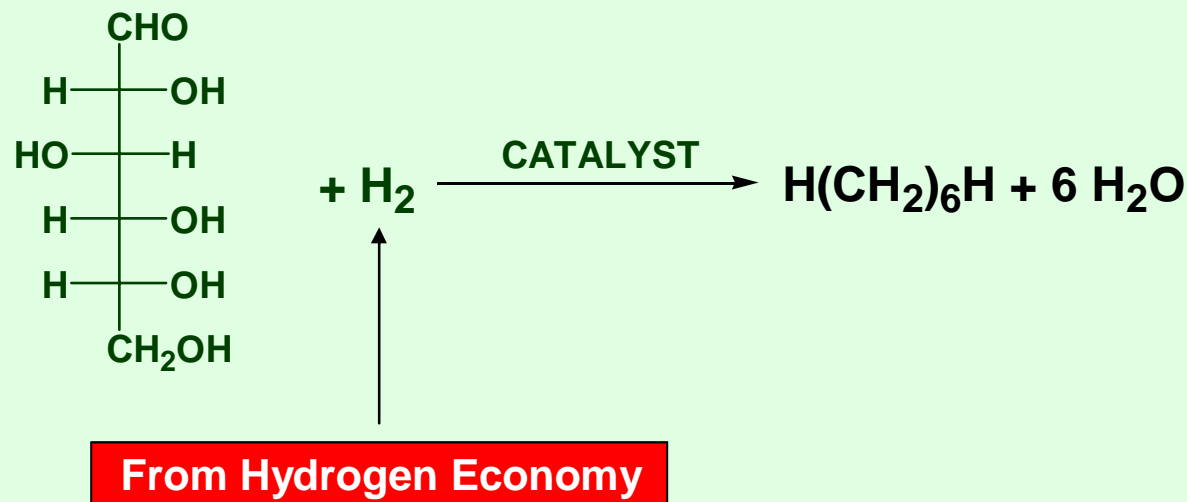


γ -Valerolactone
(20-40 %)



Levulinic acid
(0-5 %)

CATALYTIC CONVERSION OF CARBOHYDRATES



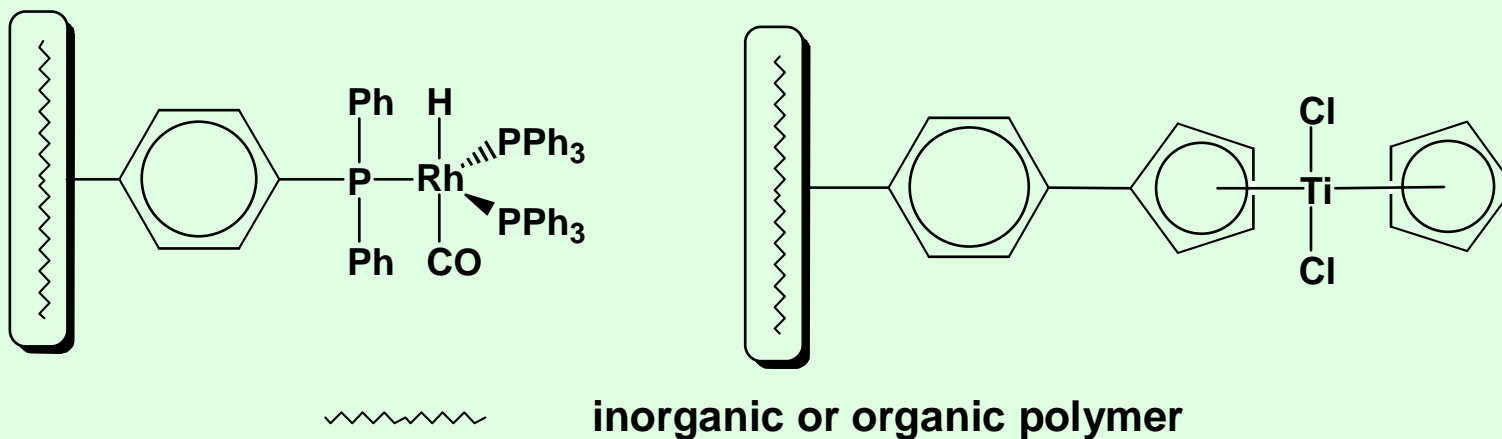
Catalytic dehydration combined with catalytic hydrogenation and hydrogenolysis could provide a renewable feedstock for the petrochemical industry.

Carbohydrates are water soluble.
The products have limited solubility in water.
Water is a side product.

→ **Aqueous biphasic
catalysis**

HETEROGENIZATION OF HOMOGENEOUS CATALYSTS

Polymers have been used as heterogenizing agent, which chemically binds ligands.



Ship-in-the-bottle catalysts using zeolites or carbon nanotubes as the bottle.

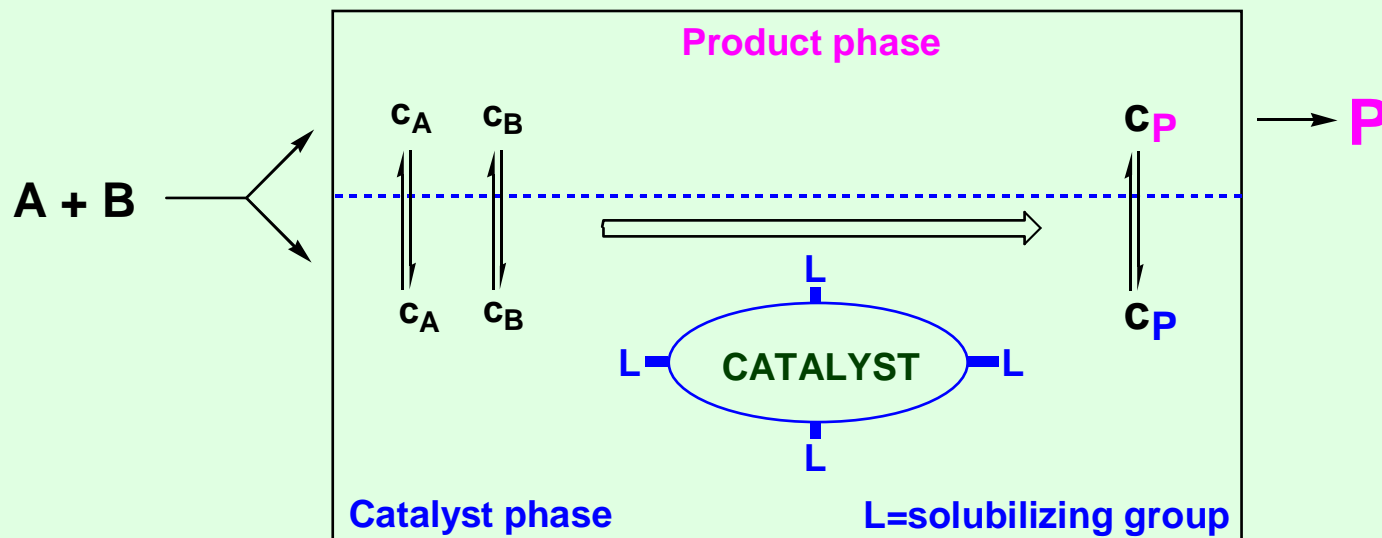
Membrane separation of supramolecular homogeneous catalysts.

Two phase catalysis (liquid-liquid or solid-liquid).

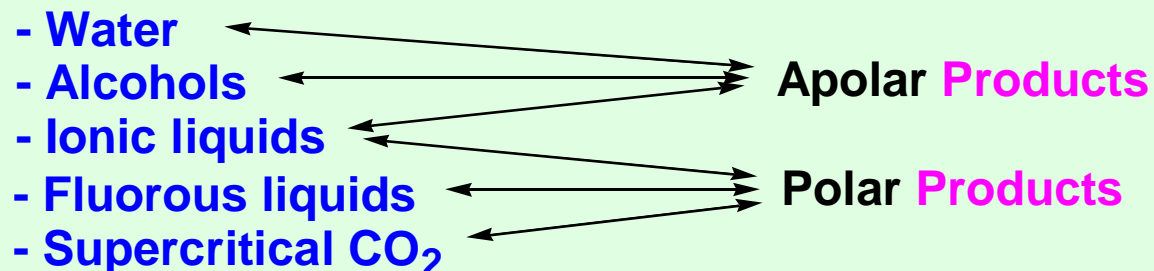
Catalyst leaching is a major challenge, as a heterogenized catalyst could undergo reversible or irreversible reactions to form species soluble in the reaction media, which could dramatically change as the reactants are consumed and the products and/or side products are formed.

LIQUID-LIQUID BIPHASE CATALYSIS

Allows the use of highly selective solution chemistry with the added benefit of easy separation of the product from the catalyst.

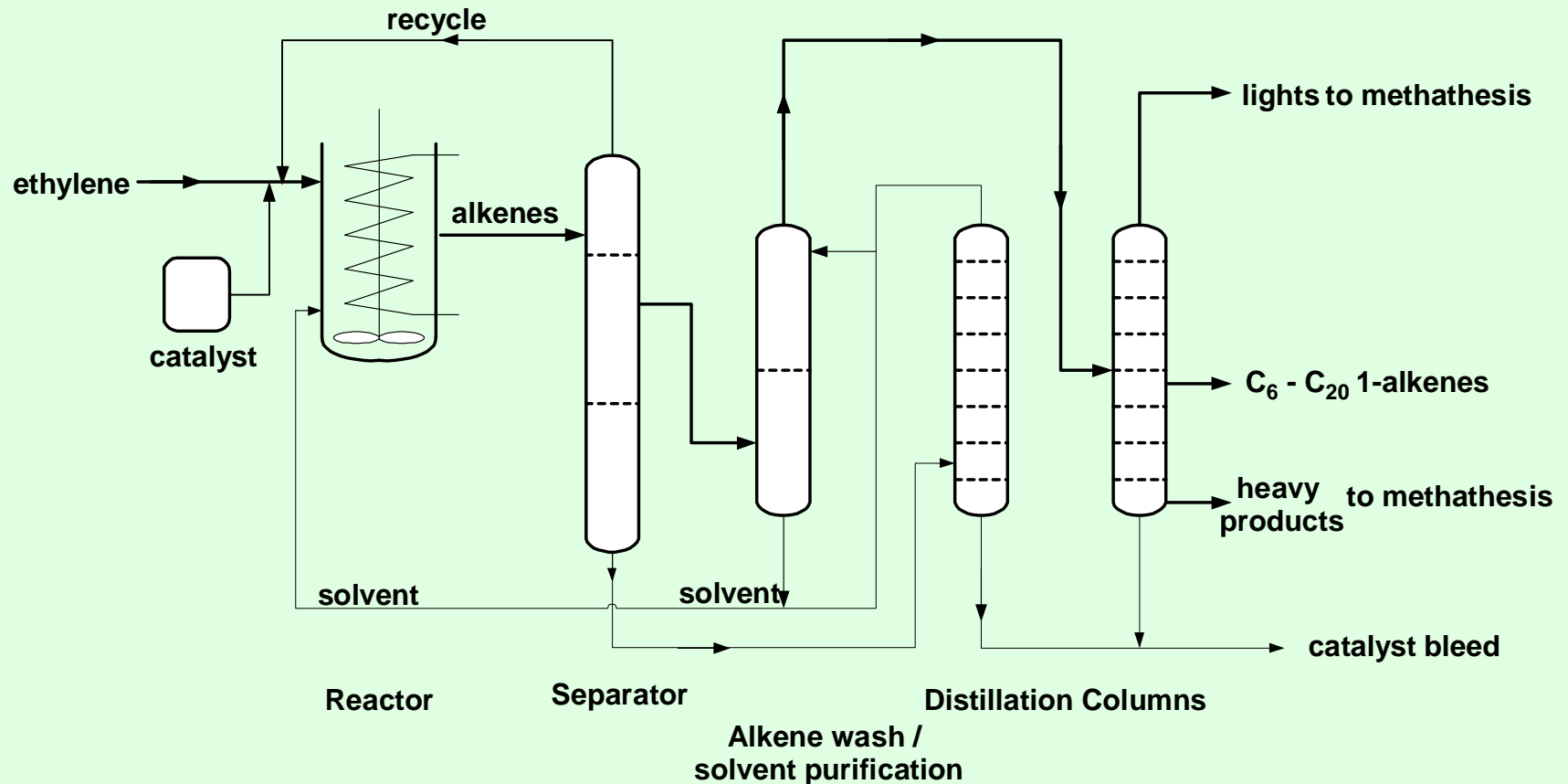


The solvent properties of the **products** govern the selection of the catalyst phase.



SHELL HIGHER OLEFIN PROCESS (SHOP)

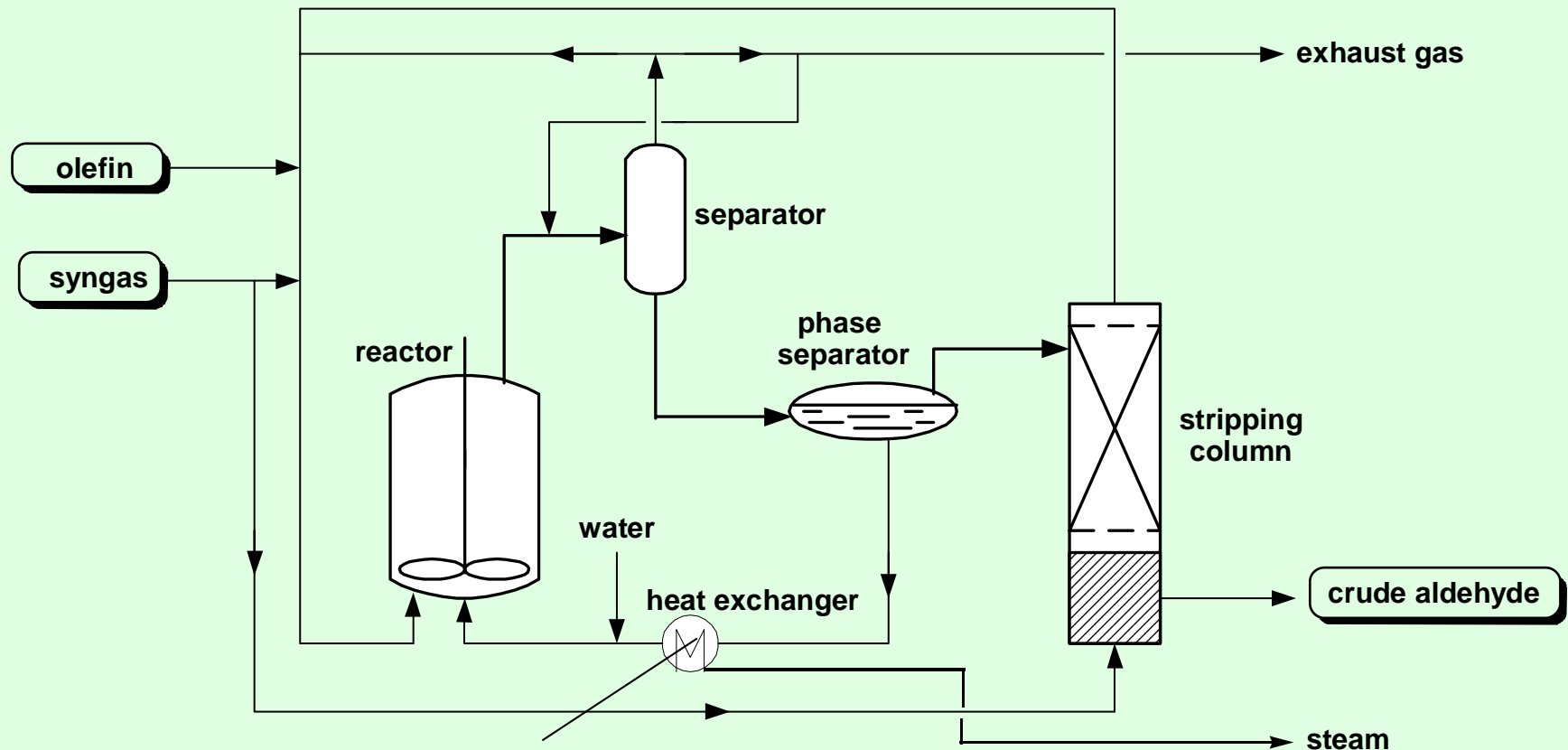
$\text{Ni}(\text{R}_2\text{PCH}_2\text{COOH})\text{L}_x$ in 1,4-butanediol, 80-120°C, 1500 psi ethylene



- SHOP was developed by W. Keim, uses butanediol as the catalyst phase and a nickel catalyst modified with a diol soluble phosphine $\text{R}_2\text{PCH}_2\text{COOH}$.
- While ethylene is highly soluble in butanediol, the higher olefins phase separate from the catalyst phase.
- The typical size of a SHOP plant is 250,00 tons per year.

RUHRCHEMIE/RHONE-POULENC OXO PROCESS

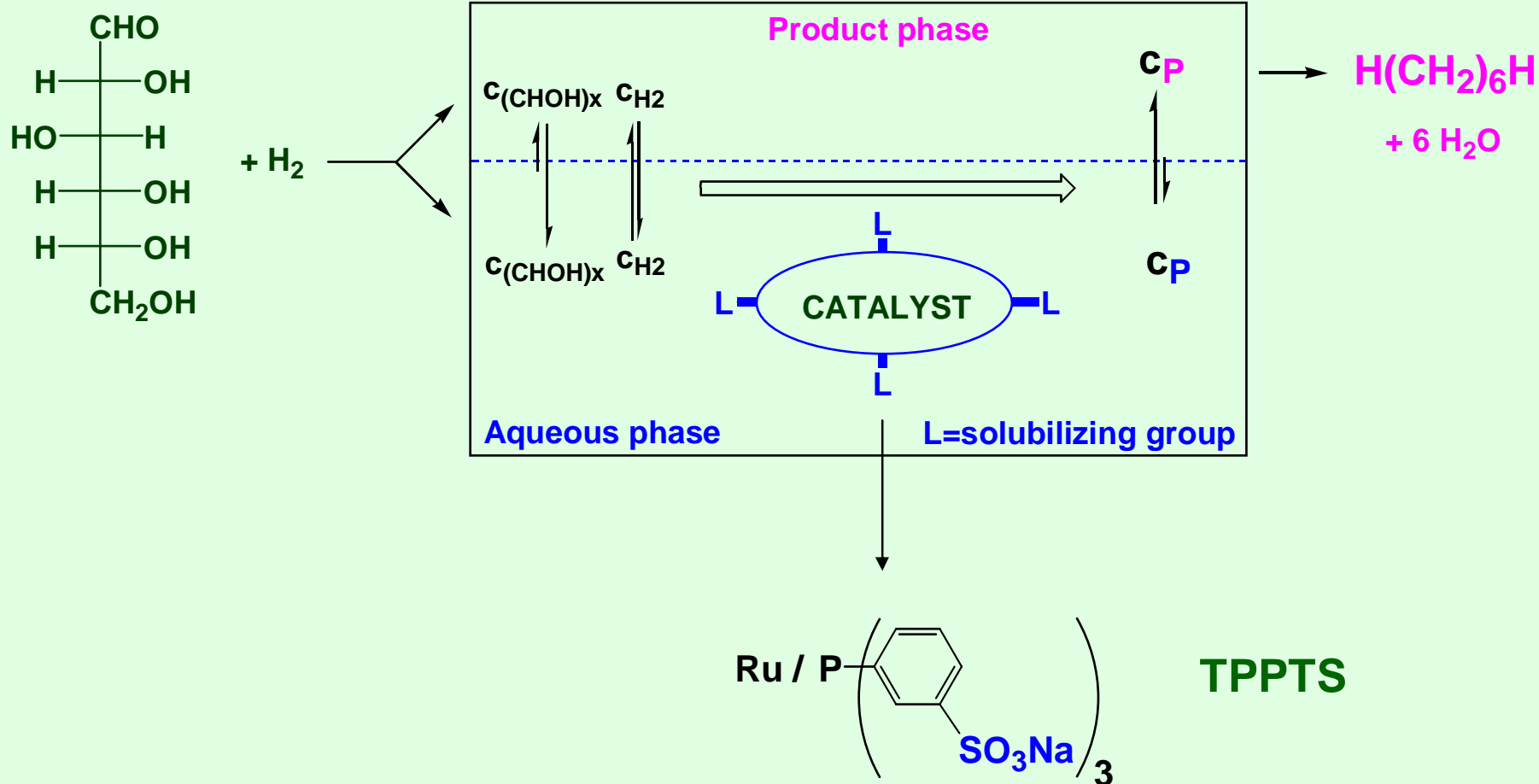
$\text{HRh}(\text{CO})[\text{P}(\text{C}_6\text{H}_4\text{SO}_3\text{Na})_3]_3$ in water, 110-130°C, 40-60 bar CO/H_2 (1:1)



Angev. Chem. Int. Ed. Eng. 1993. 32. 1524-1544

- Ruhrchemie/Rhone-Poluenc oxo process, developed by E. Kuntz and commercialized by B. Cornils, uses water as the catalyst phase and a rhodium catalyst modified with the water soluble $\text{P}(\text{m-C}_6\text{H}_4\text{SO}_3\text{Na})_3$
- While propylene is highly soluble in water, the butanals phase separate from the catalyst phase
- The typical size of a Ruhrchemie/Rhone-Poluenc oxo plant is 150,00 tons per year

CARBOHYDRATES CONVERSION WITH WATER SOLUBLE CATALYST



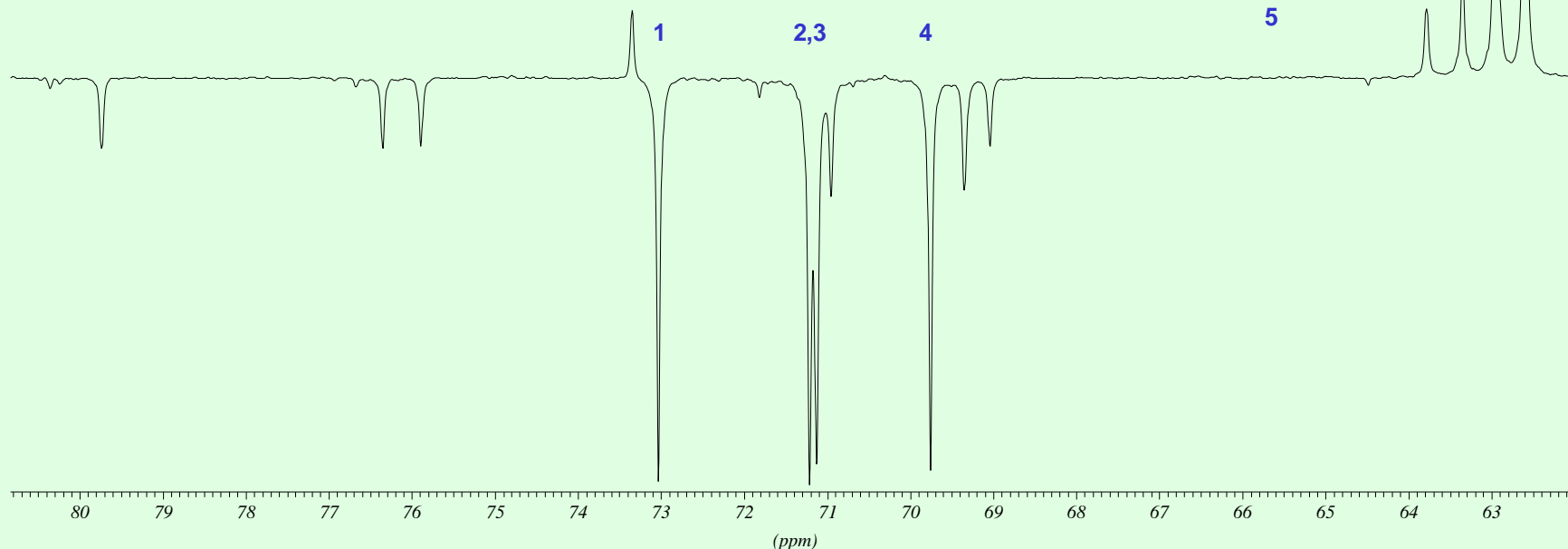
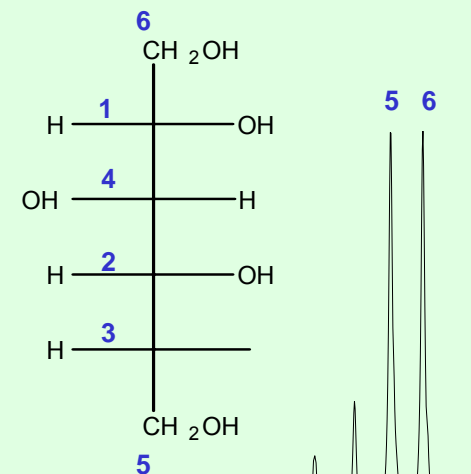
CATALYTIC HYDROGENATION OF SUCROSE

$C_{12}H_{22}O_{11} = 0.66M$; $H_2SO_4 = 0.5M$; $RuCl_3 = 0.013mM$; TPPTS = 0.066mM; NaI = 0.026mM

100 bar H_2 , 8h, samples at 4h, 8h at 100°C

Ratio sucrose : Ru : TPPTS : NaI = 50 : 1 : 5 : 2

At low acid concentration the main product is D-sorbitol.



Hydrogenation of D-fructose with water soluble phosphine modified ruthenium catalysts

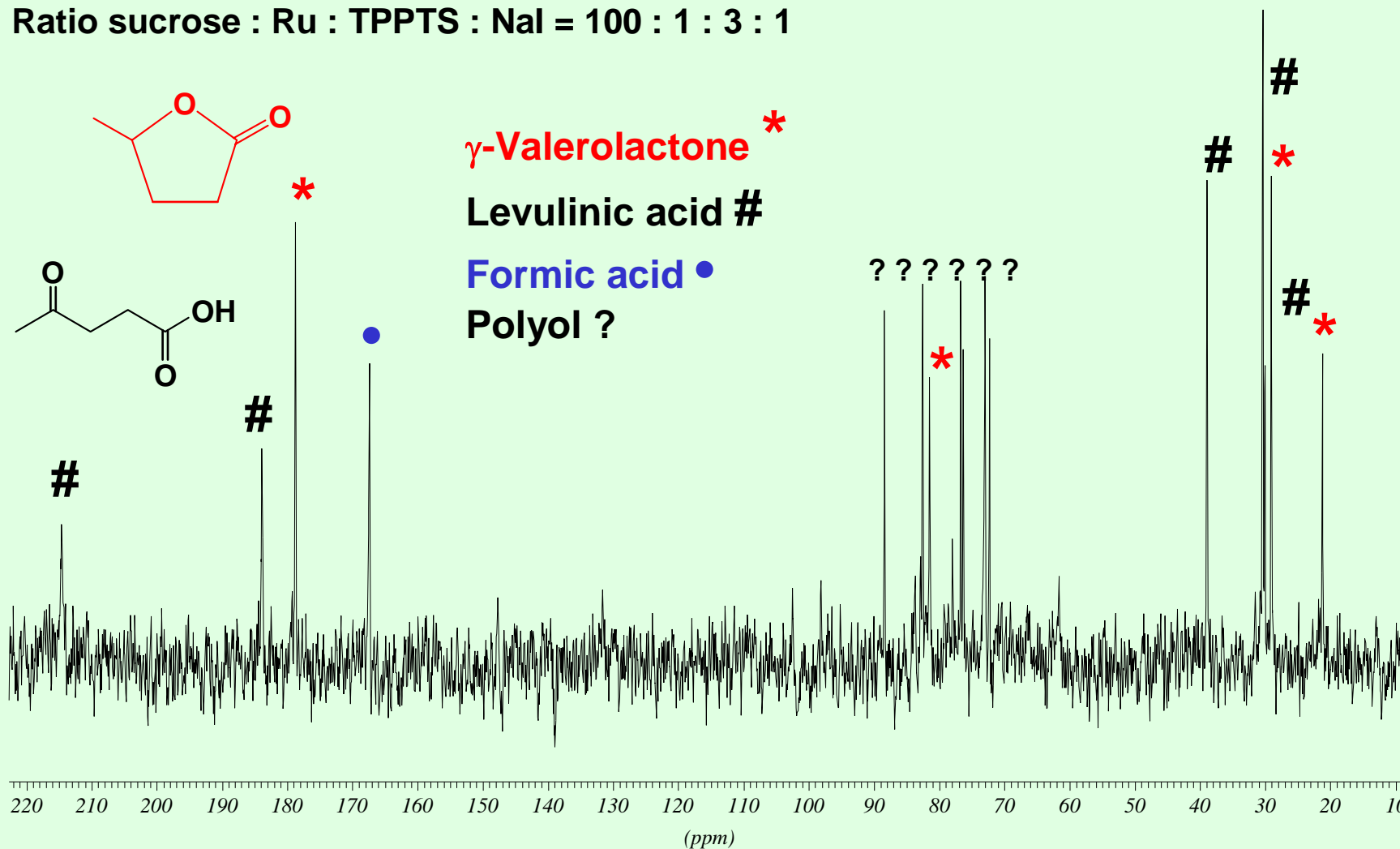
Joo, F et al. *Inorg. Chim. Acta* **1977**, 25, L61 and Heinen, A. W. et al. *J. Mol. Cat. A Chemical* **1999**, 142, 17.

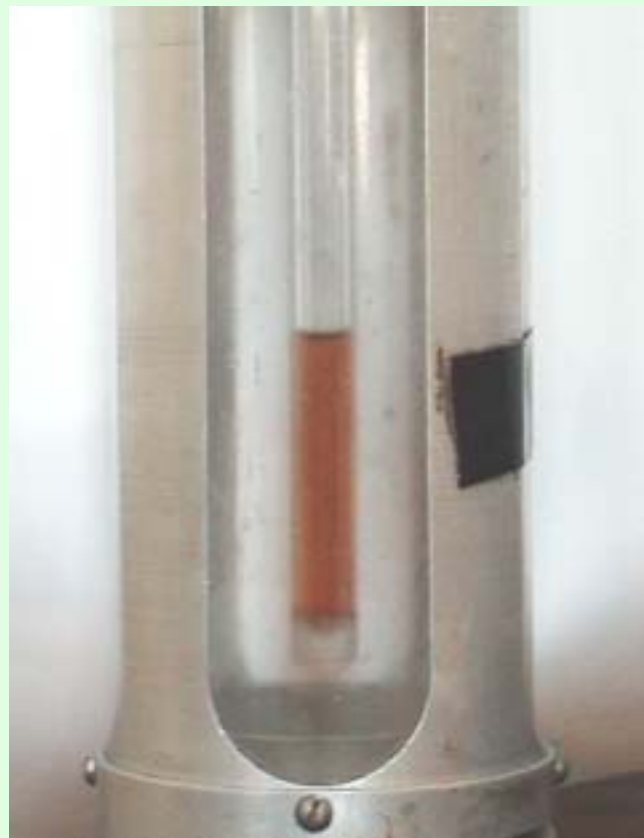
CATALYTIC CONVERSION OF SUCROSE

$C_{12}H_{22}O_{11} = 0.6M$; $H_2SO_4 = 1.8M$; $RuCl_3 = 0.006mM$; TPPTS = 0.02mM; NaI = 0.008mM

85 bar H_2 , 4h at 140°C.

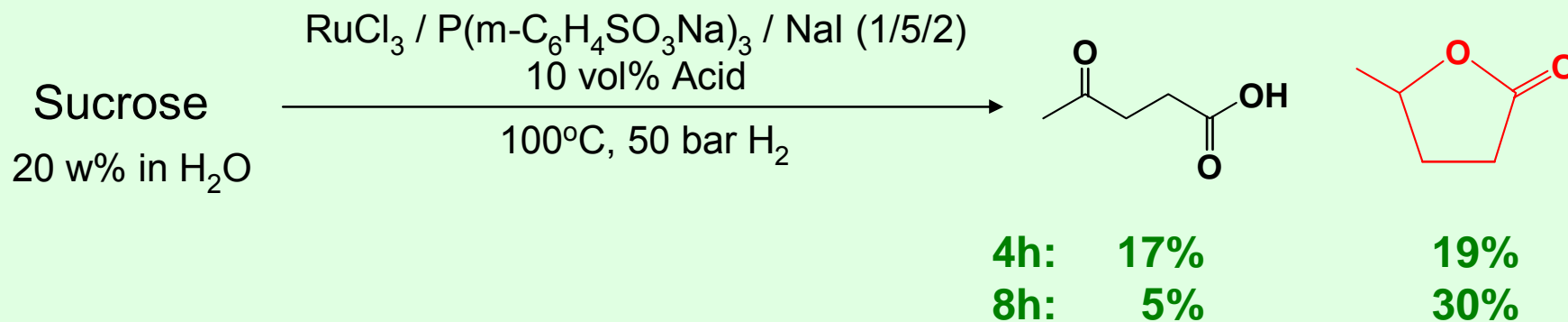
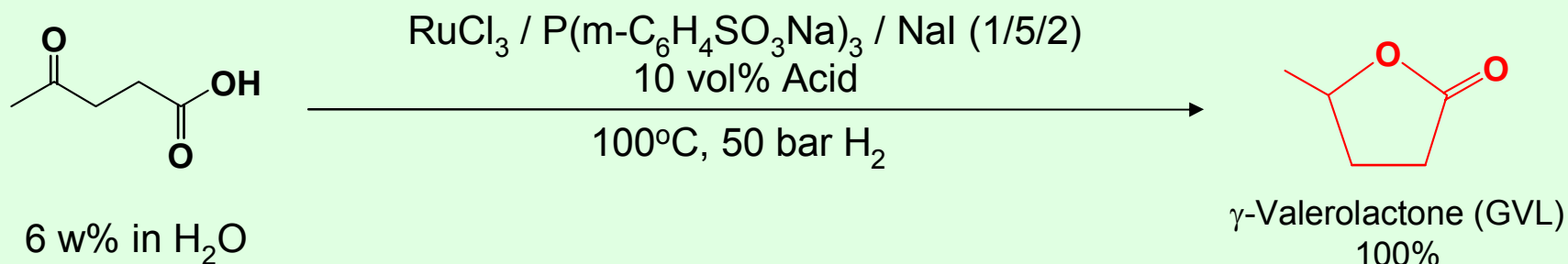
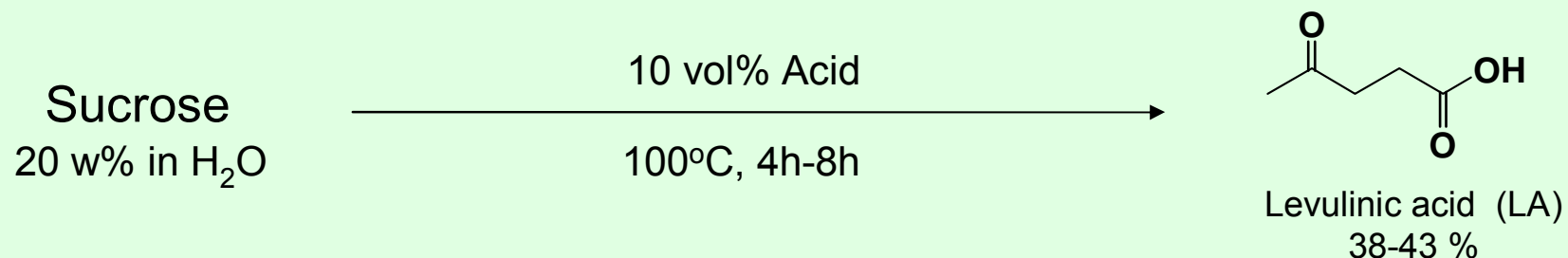
Ratio sucrose : Ru : TPPTS : NaI = 100 : 1 : 3 : 1



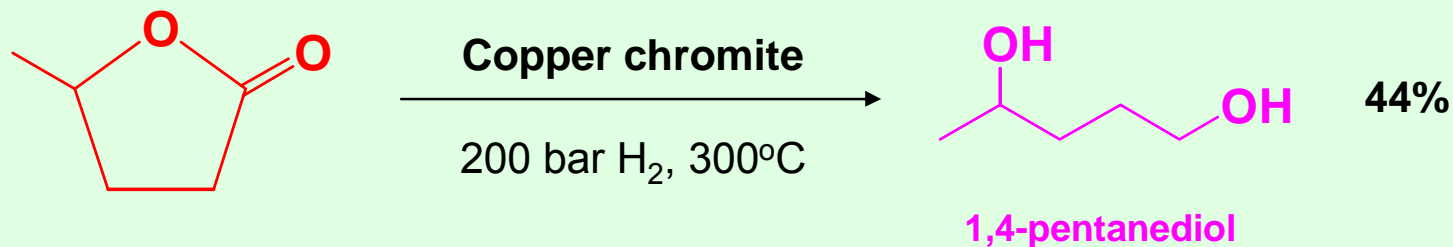


Sucrose 20 w% in H_2O 10 vol% Acid
 RuCl_3 / $\text{P(m-C}_6\text{H}_4\text{SO}_3\text{Na)}_3$ / NaI (1/5/2) 50 bar H_2

ACID (HCl, H₂SO₄) CATALYSTS COMBINED WITH WATER SOLUBLE RUTHENIUM CATALYST



HYDROGENATION OF γ -VALEROLACTONE



Christian, R. V.; Brown, H.D.; Hixon, R.M. *J. Am. Chem. Soc.*, **1947**, 69, 1961.

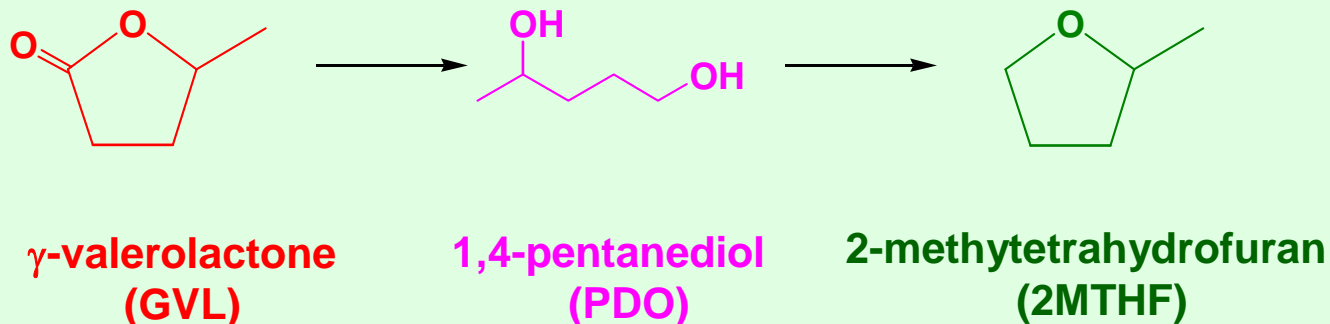
HYDROGENATION OF LACTONES

0.05 mmol Ru(acac)₃, 0.5 mmol P(Octyl)₃, 0.25 mmol NH₄PF₆, 16 mL tetraglyme
50 bar H₂ at room temperature, then heated to 200 °C for 3 h.

	Conversion	Diol
γ -Butyrolactone (78 mmol)	99%	99%
δ -Valerolactone (65 mmol)	26%	94%
ϵ -Caprolactone (65 mmol)	20%	92%

Hara, Y.; Inagaki, H.; Nishimura, S.; Wada, K. *Chem. Lett.*, **1992**, 1983.

Reduction of γ -valerolactone to 1,4-pentanediol and to 2-methyltetrahydrofuran



Reaction conditions

NO SOLVENT

$\text{Ru}(\text{acac})_3$	12.1mg (30 μmol)
NH_4PF_6	85.9mg (527 μmol)
PBU_3	270 μl (1 mmol)
γ -valerolactone	1.261g (12.6 mmol)

Pressure: H_2 70 bar (at room temperature)

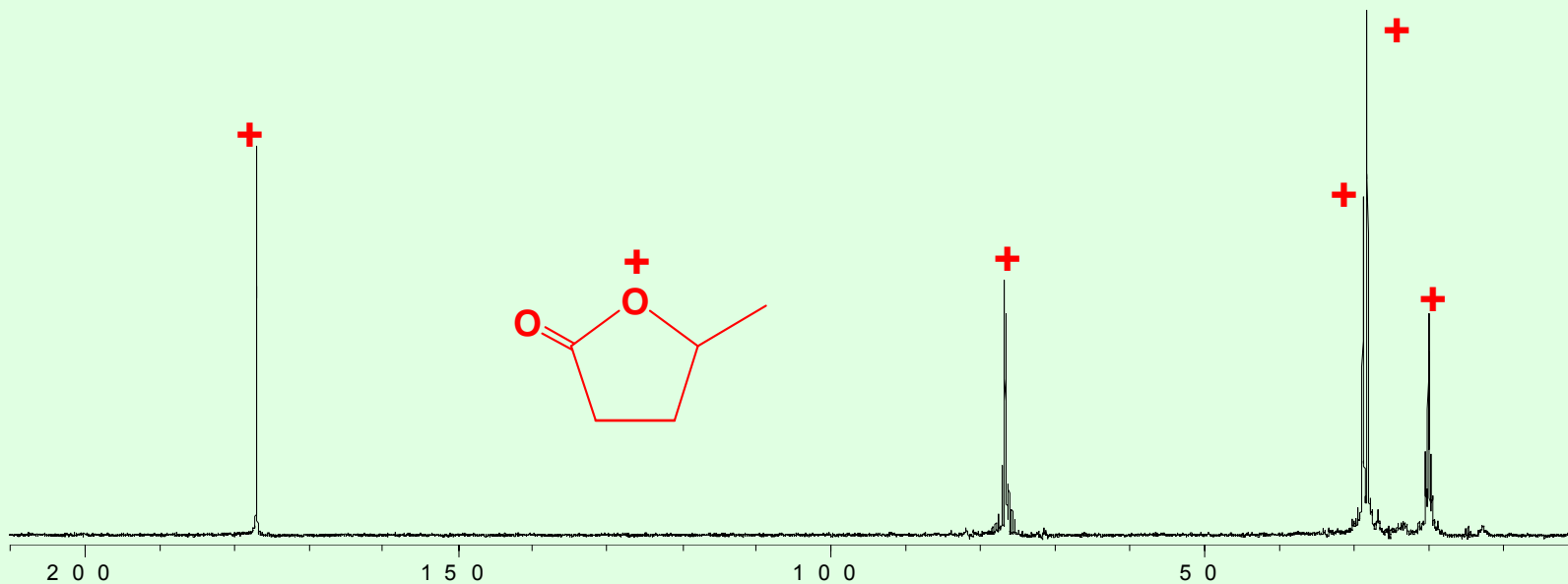
Heating: 200°C, 60h

Yield 72%

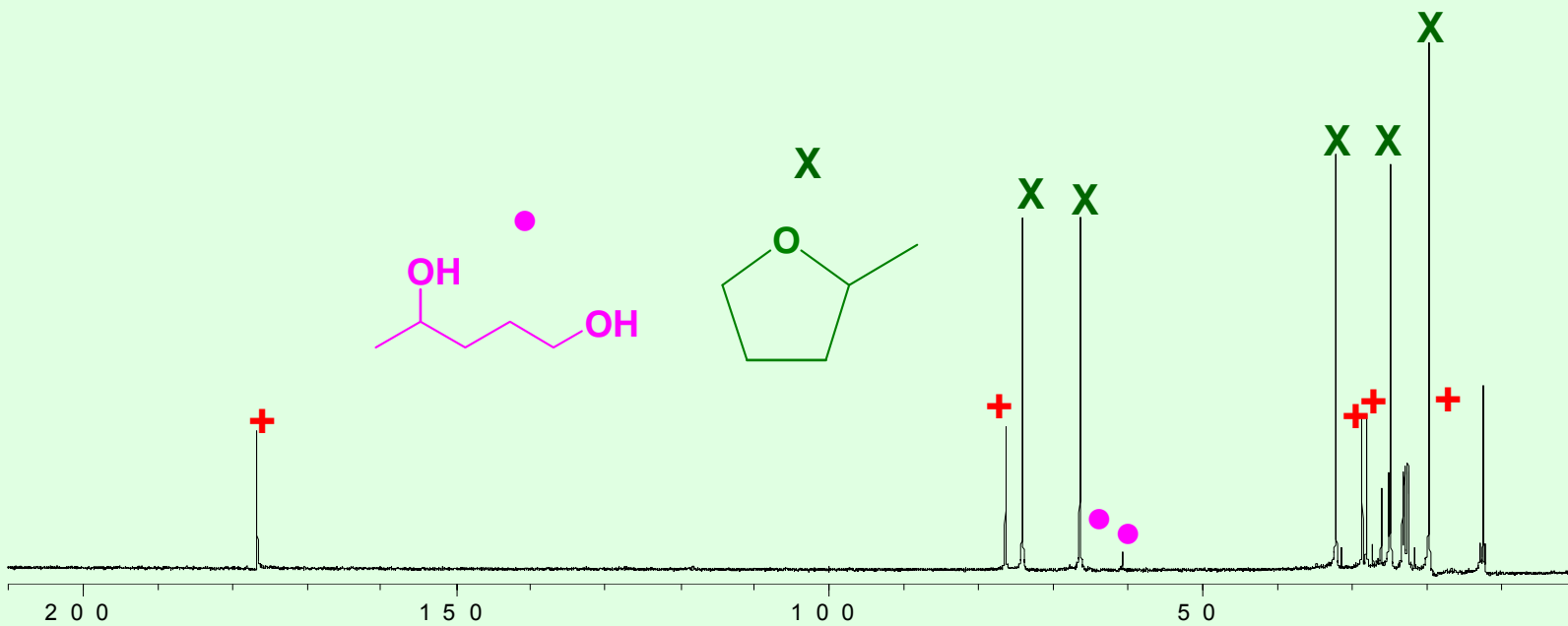


HP-NMR investigation of the reduction of γ -valerolactone

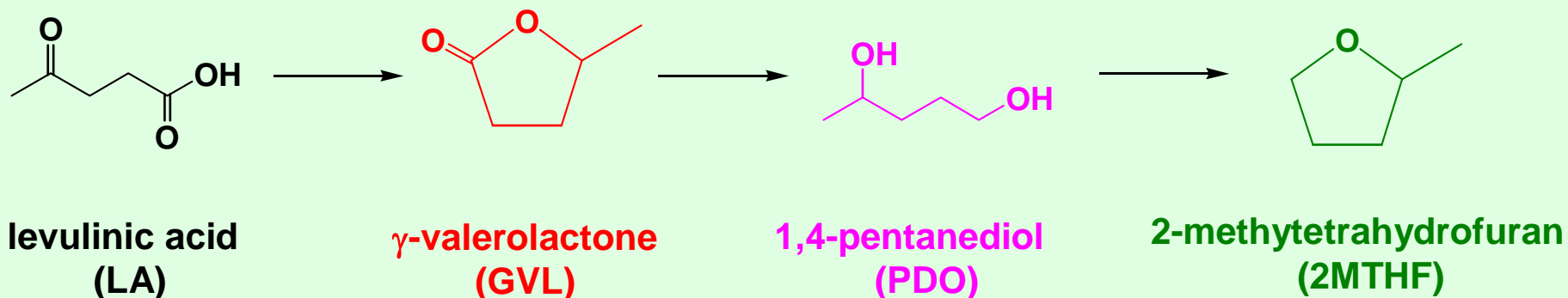
Start



60h



REDUCTION OF LEVULINIC ACID TO 2-METHYLTETRAHYDROFURANE



Reaction conditions

NO SOLVENT

Ru(acac) ₃	9.6mg (24 μ mol)
NH ₄ PF ₆	68.2mg (418 μ mol)
PBu ₃	210 μ l (855 μ mol)
Levulinic acid	1.121g (9.65 mmol)

Pressure: H₂ 80 bar (at room temperature)

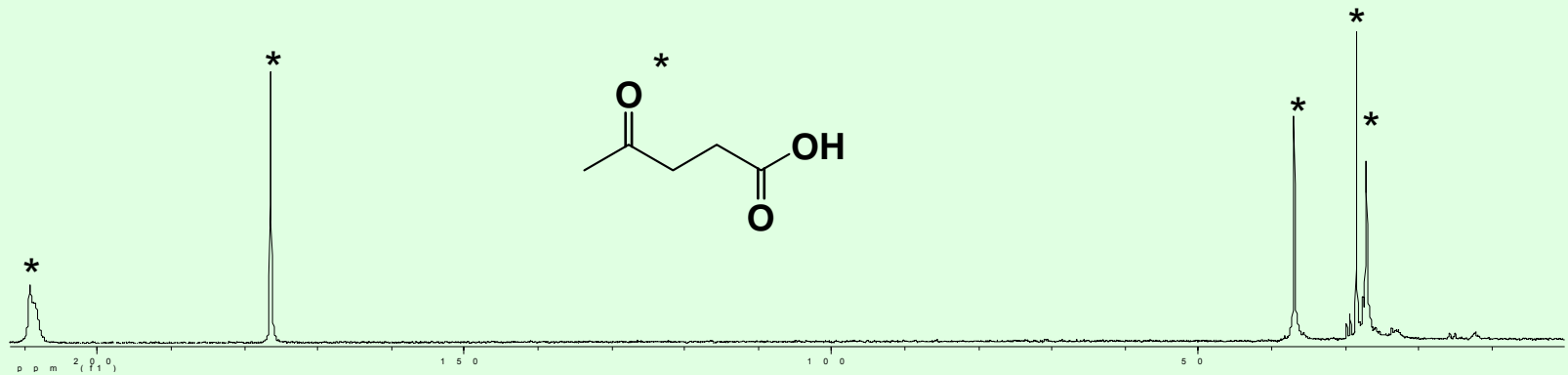
Heating: 4h + 7x6h at 200°C

The high pressure NMR tube was repressurized with H₂ to 80 bar at room temperature after the first 4 hours and after every six hours.

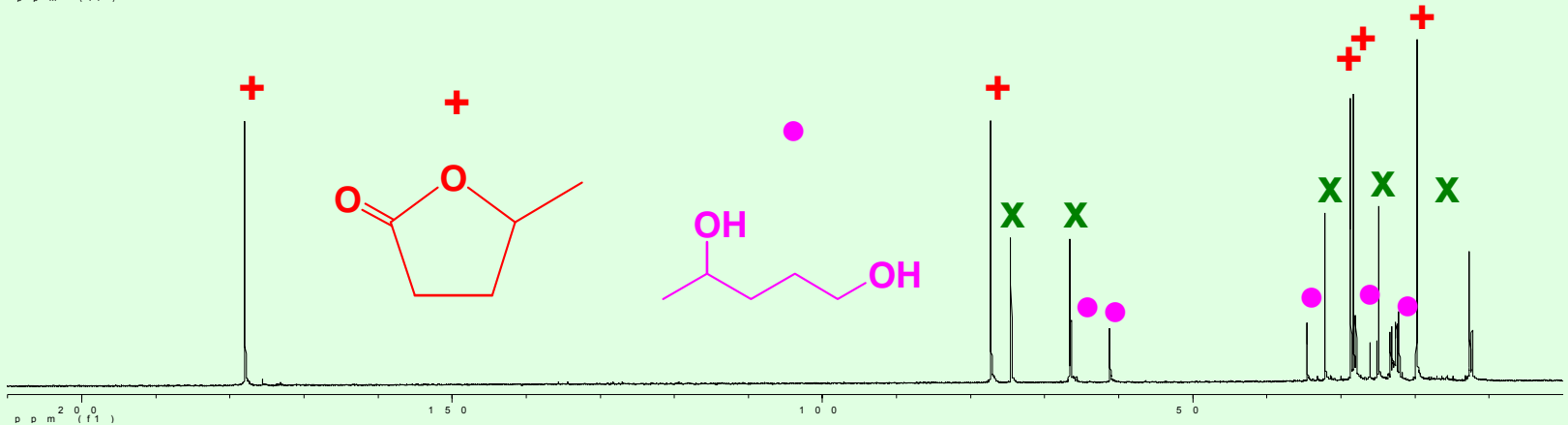
Yield is almost quantitative.

REDUCTION OF LEVULINIC ACID TO 2-METHYLTETRAHYDROFURANE

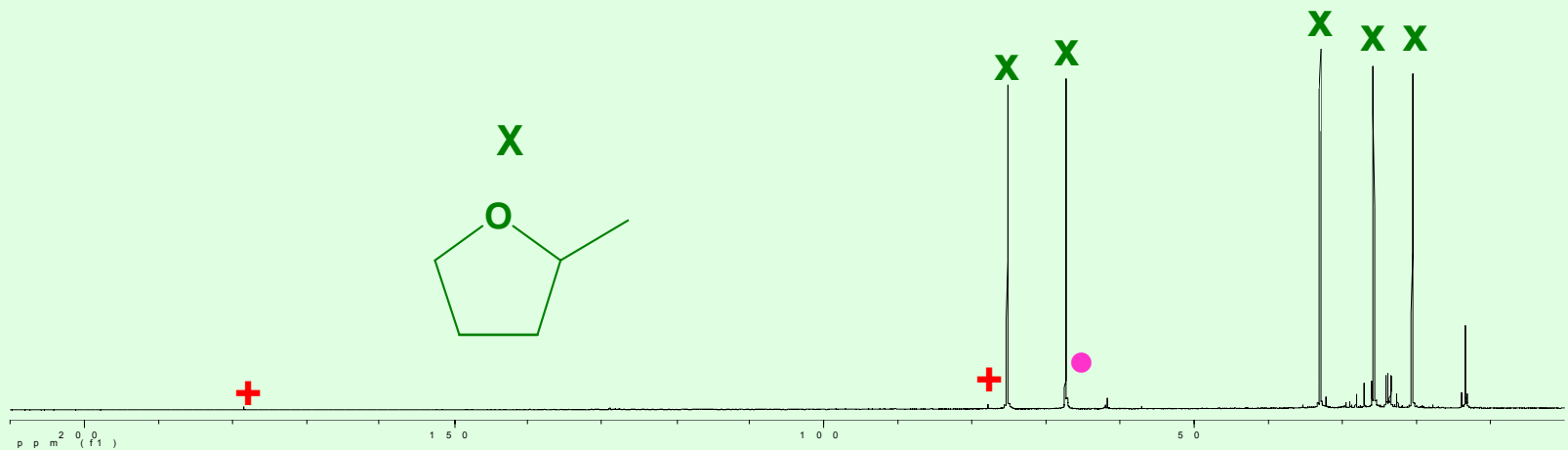
Start



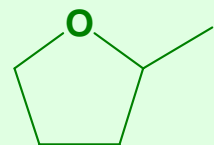
22h



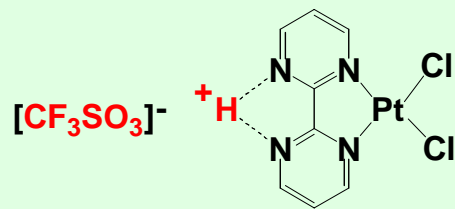
46h



REDUCTIVE CONVERSION OF 2-METHYLTETRAHYDROFURAN



2MTHF



$\text{CF}_3\text{SO}_3\text{H}$
70 bar H_2 at 100°C for 15hrs

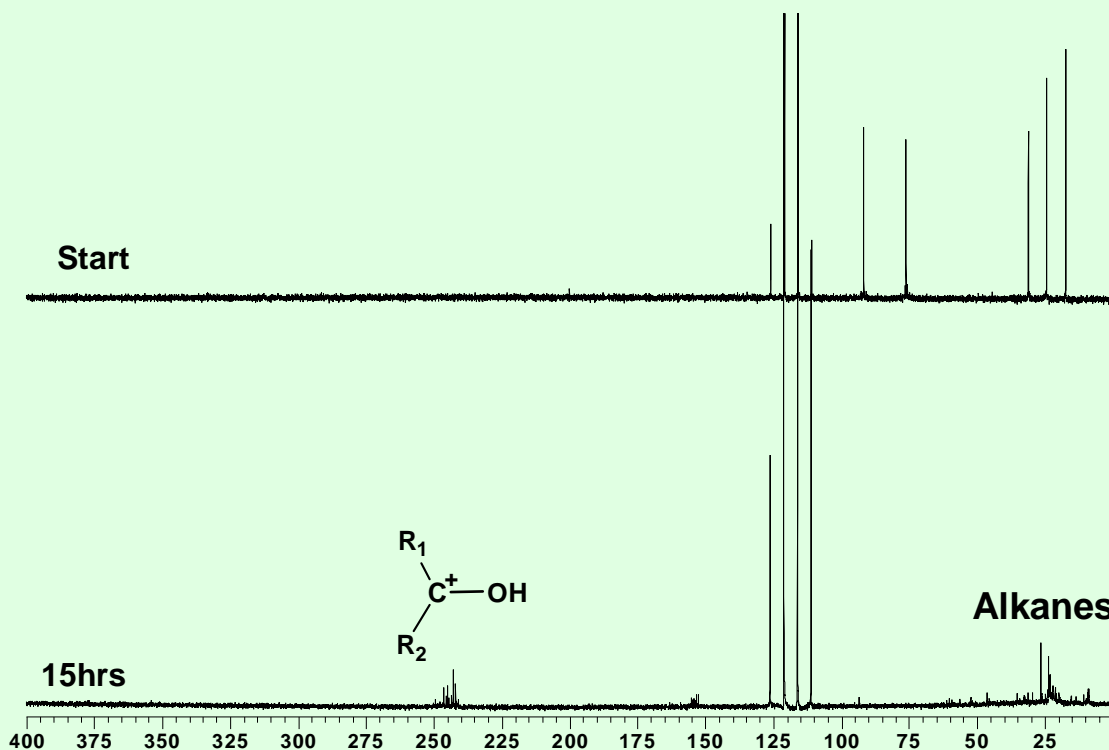


Pentanes*
(and lower alkanes)

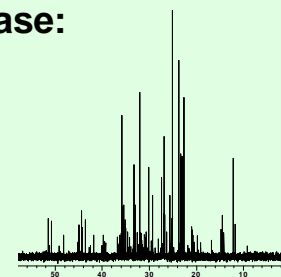
*GC-MS measurements showed the formation of a mixture of pentanes (and some C_3 -alkanes)

Protonated 2-MTHF was converted to hydroxy-carbocations (250 ppm) and to alkanes, mostly to pentanes.

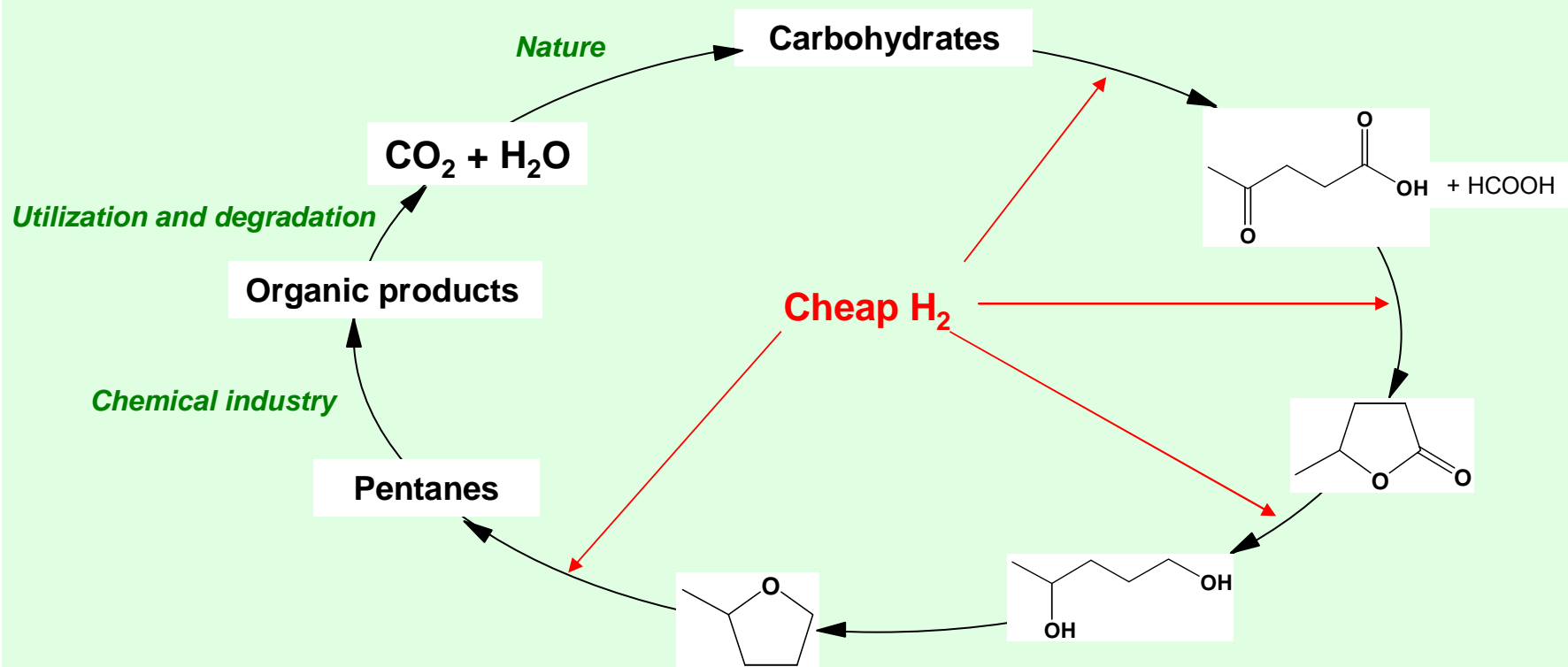
The alkanes have formed an organic renewable oil phase:



Alkanes



THE ELEMENTARY STEPS OF A SUSTAINABLE SYNTHESIS OF RENEWABLE HYDROCARBONS HAS BEEN DEMONSTRATED



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HIT-team in 2003 (www.hit-team.net)