SLOVAK RESEARCH AND DEVELOPMENT AGENCY

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CATALYTIC CONVERSION OF BIOMASS INTO VALUABLE CHEMICALS

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STU FCHPT

BIOMASS CONVERSION

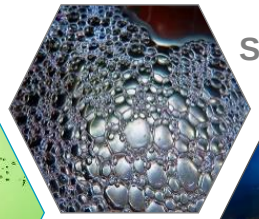
WHY BIOMASS CONVERSION?

HEMICELLULOSES
CELLULOSE

DESIRED PRODUCTS

Bulk chemicals

Green solvents



Surfactants

Plastics

Jet fuels

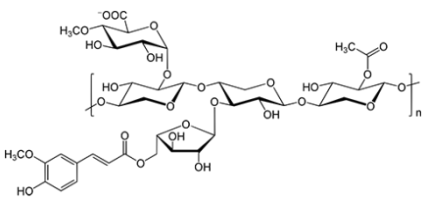
Material

Drugs

Replacement

PETROLEUM

BIOMASS CONVERSION



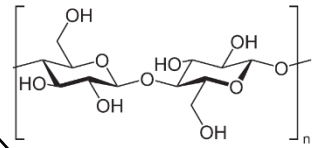
LIGNOCELLULOSE

Fractionation

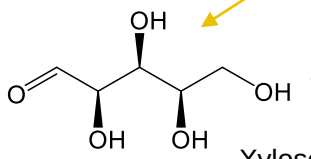
HEMICELLULOSES

LIGNIN

CELLULOSE

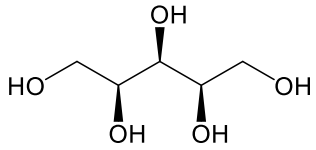


$H^{\oplus}/H_2O$

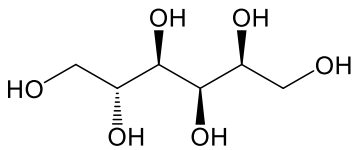


Xylose

H_2



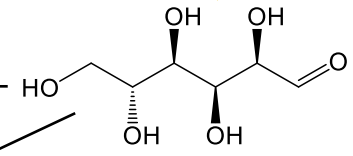
Xylitol



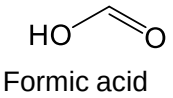
Sorbitol

H_2

$H^{\oplus}/H_2O$



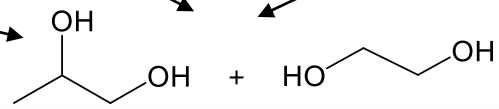
Glucose



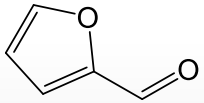
Formic acid

H_2

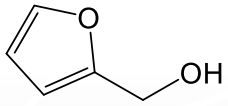
Hydrogen



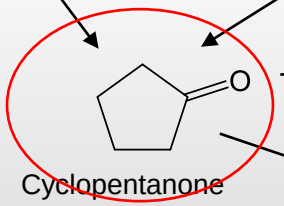
Propylene glycol **(PG)** Ethylene glycol **(EG)**



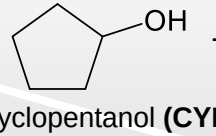
Furfural **(FUR)**



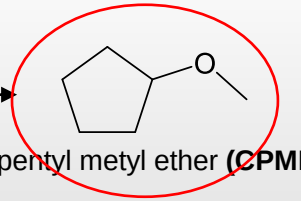
Furfurylalcohol **(FAL)**



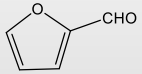
Cyclopentanone **(CYPon)**

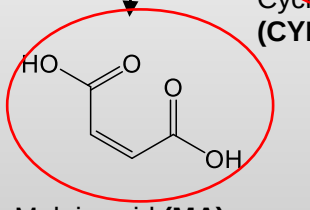


Cyclopentanol **(CYPol)**

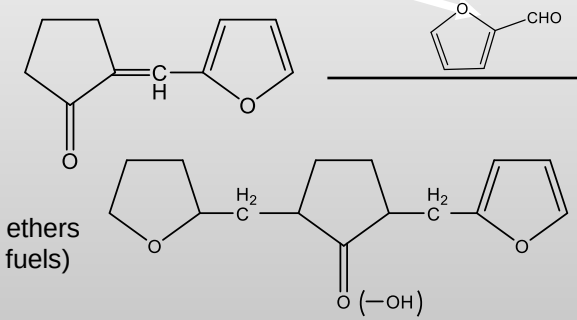


Cyclopentyl metyl ether **(CPME)**

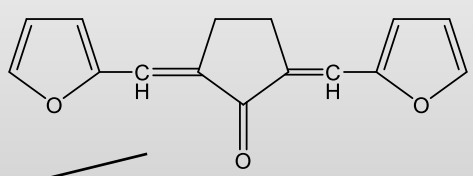




Maleic acid **(MA)**



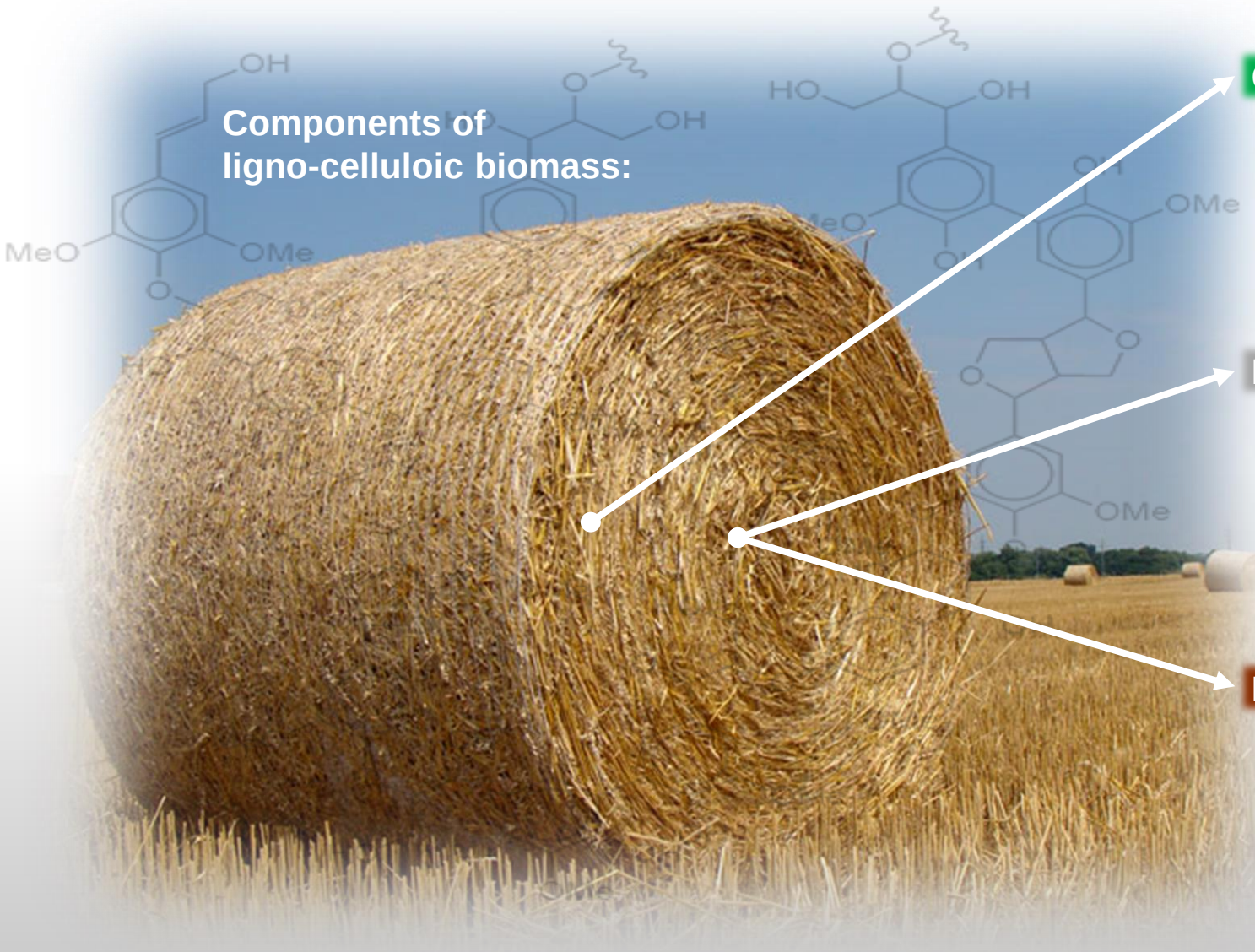
Cyclic ethers
(C_{15} – fuels)



2,5-bis(2-furylmethylidene)cyclopentane-1-one
(F_2C)

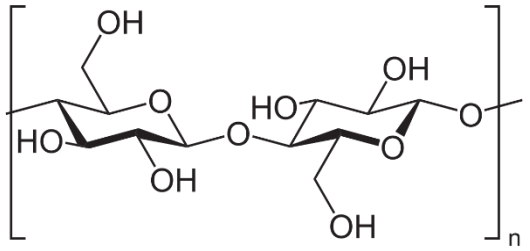
Product separation !

BIOMASS CONVERSION

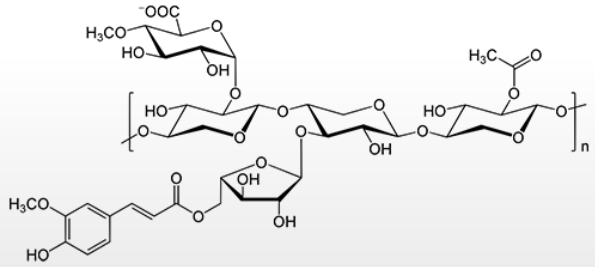


Components of
ligno-celluloic biomass:

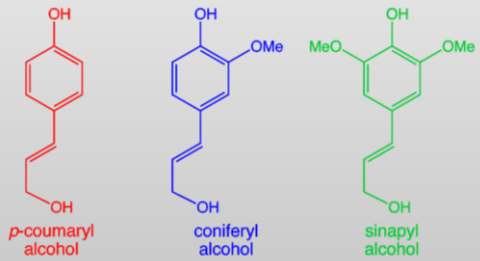
CELLULOSE



HEMICELLULOSES (xylan)



LIGNIN (phenolics)



LIGNIN CONVERSION

LIGNIN

Thermochemical processes

LIGNIN
15 – 30 wt.%
depends on type of biomass

BIO-OIL
aromatic aldehydes (e.g. VANILLIN)
other aromatic alcohols, ketones, esters, phenols, oligomers

pharmaceutical, food and fragrance industry

Bio fuels

WHY NOT LIGNIN?

Catalytic processes

Products (identification; isolation)

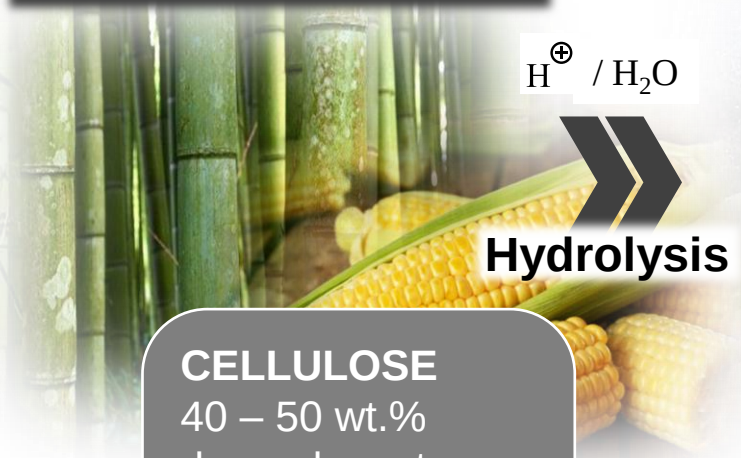
Products in low yields

Polymerization

Catalyst deactivation

CELLULOSE CONVERSION

CELLULOSE



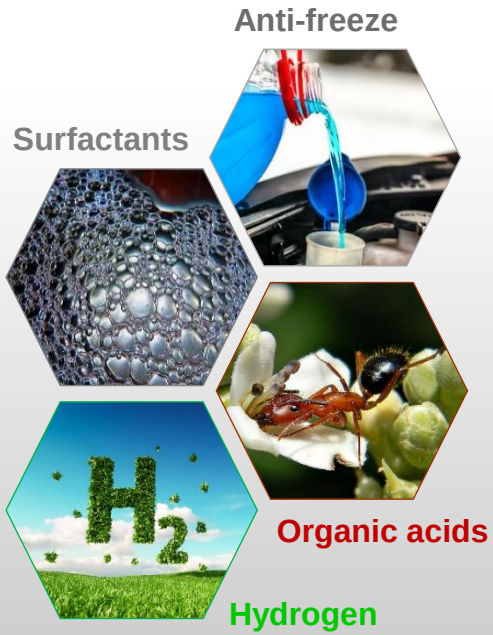
$H^{\oplus}$ / H_2O

Hydrolysis

CELLULOSE
40 – 50 wt.%
depends on type of biomass
(90% in cotton fiber)

SUGARS
Glucose
Mannose
Sorbitol
Mannitol

DIFFERENT PRODUCTS

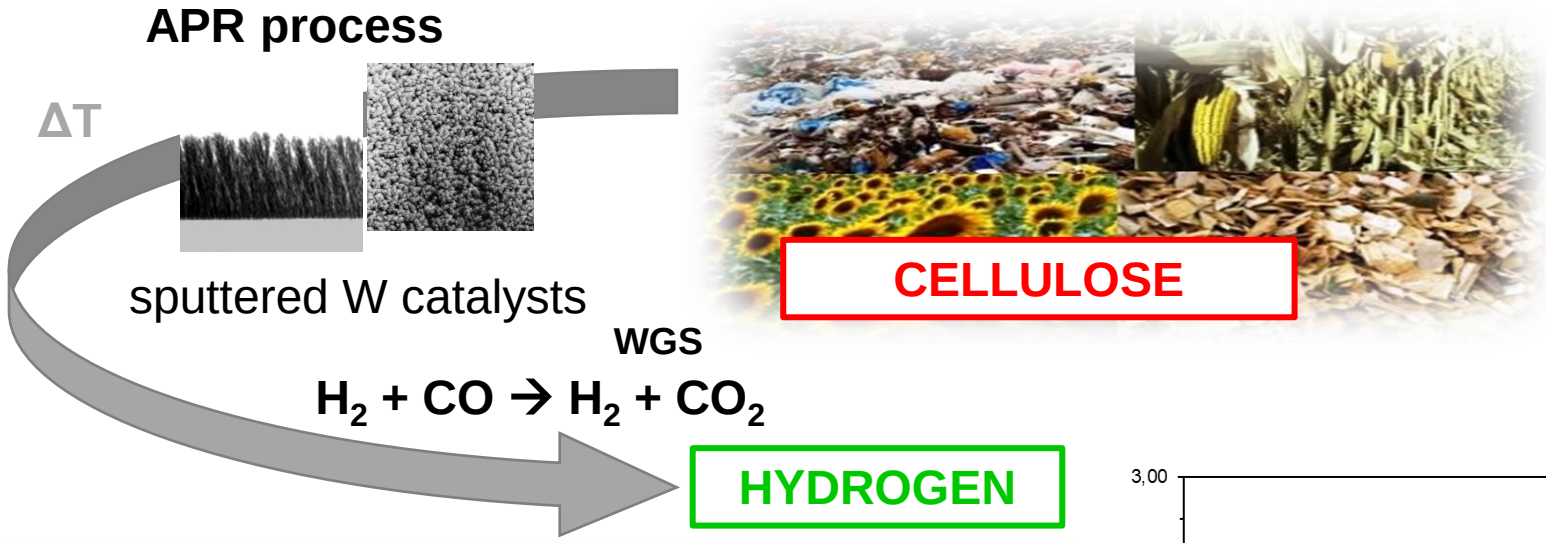


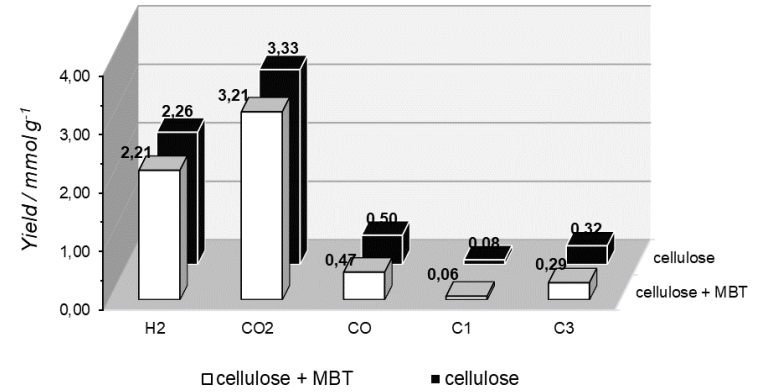
OUR FOCUS:

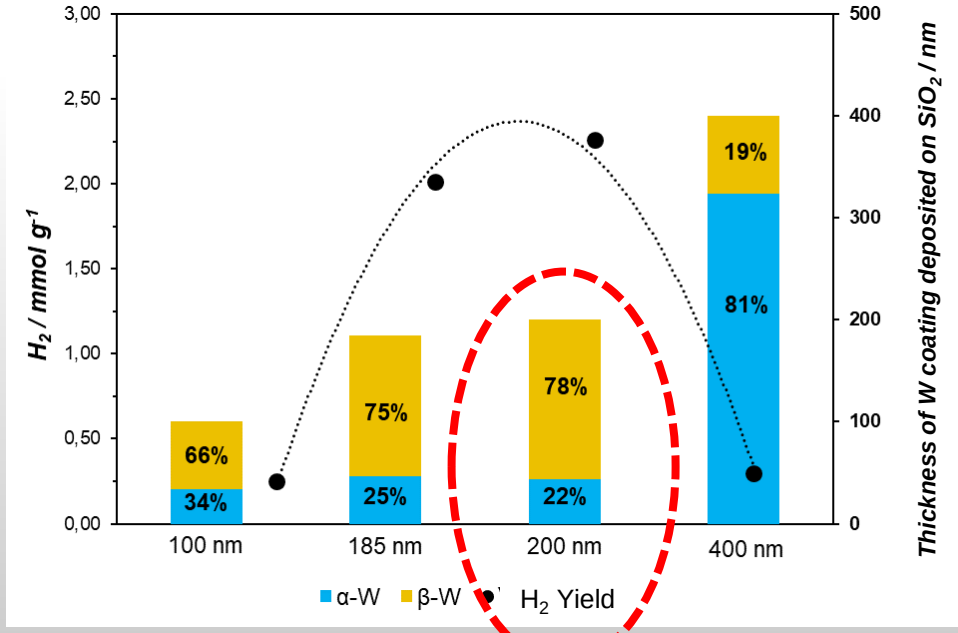
H_2 formation

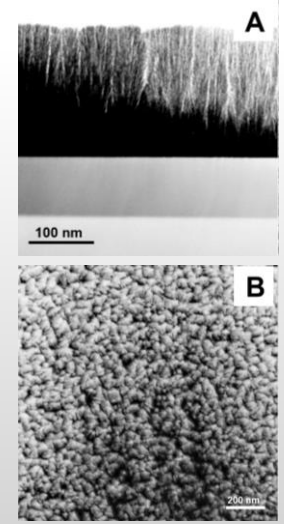
Formic acid preparation

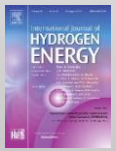
CELLULOSE CONVERSION









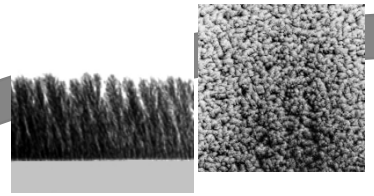


Soták T., Hronec M., Vávra I., Dobročka E.: *Int. J. Hydrogen Energ.* **2016**, 41(47), 21936 - 21944.

CELLULOSE CONVERSION

APR process

ΔT

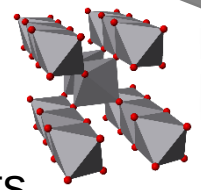


sputtered W catalysts

CELLULOSE

Oxidation

$\Delta T, pO_2$



Mo-V catalysts

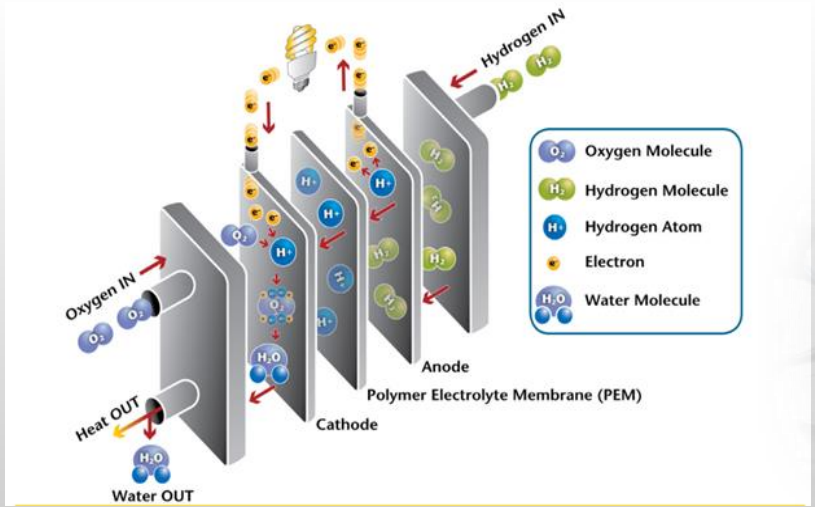
WGS

$H_2 + CO \rightarrow H_2 + CO_2$

65% yield FAc

HYDROGEN

FORMIC ACID

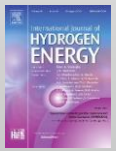


Hydrogen storage

Leather

Textile treatment

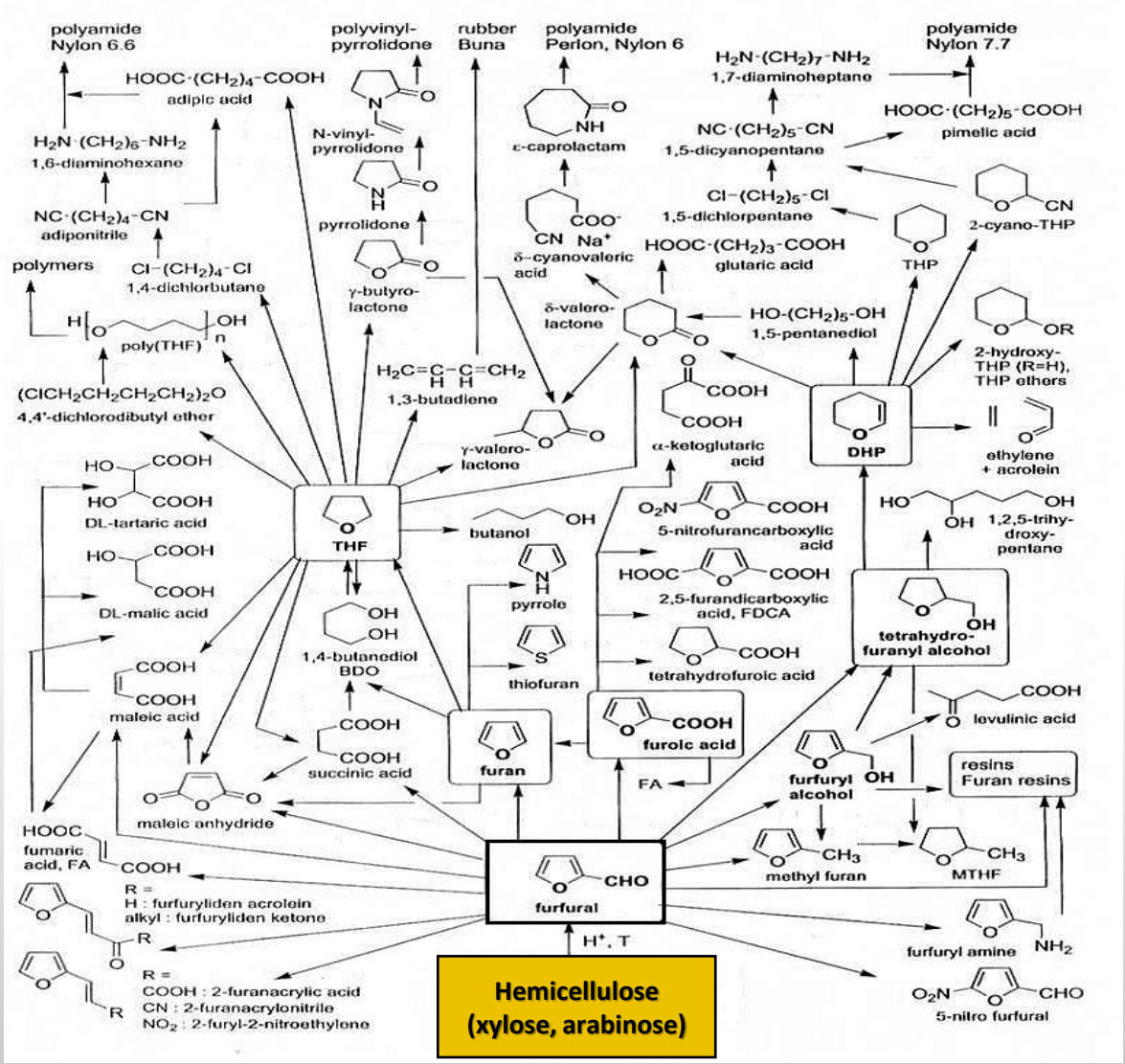
Rubber

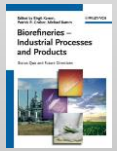


Soták T., Hronec M., Vávra I., Dobročka E.: *Int. J. Hydrogen Energ.* **2016**, 41(47), 21936 - 21944.

HEMICELLULOSE CONVERSION

- esterification
- hydrogenation
- decarbonylation
- ring-opening reactions





B. Kamm et al.: *Biorefineries – Industrial processes and products. Status quo and future directions*, WILEY-VCH,**2006**, vol.2

HEMICELLULOSE CONVERSION

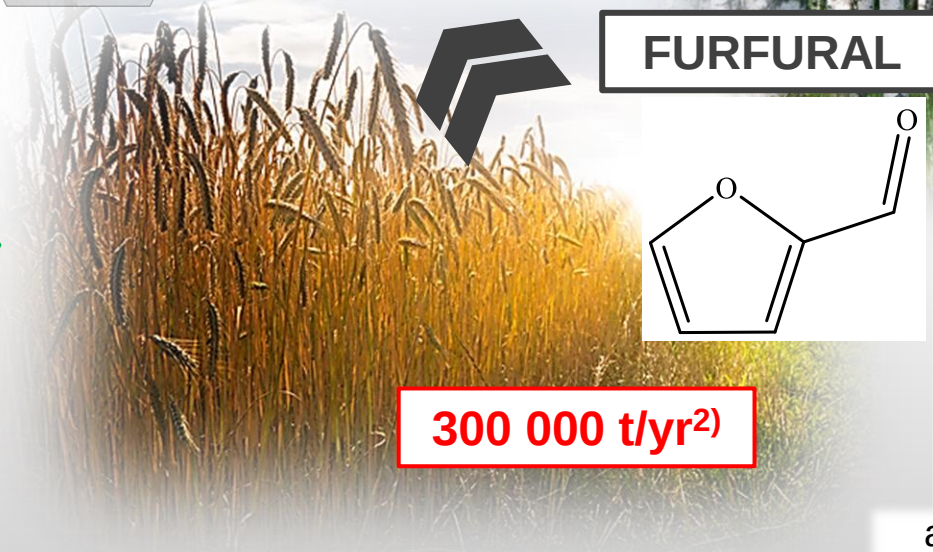
HEMICELLULOSES

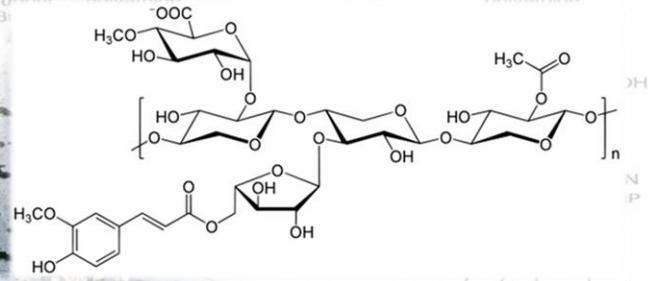

Resins


Organic solvents


Adhesives


Bio-fuels





Xylan (from birchwood)

$H^{\oplus}$

H_2O

FURFURAL

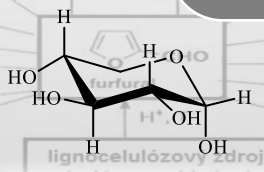
300 000 t/yr[2)]

Dehydratation

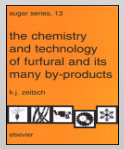
$H^{\oplus}$

acid catalyst
160-180 °C[1)]

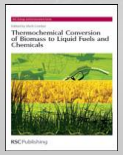
SUGARS
Xylose
Arabinose
Xylitol
Arabitol



Xylose (pentose)

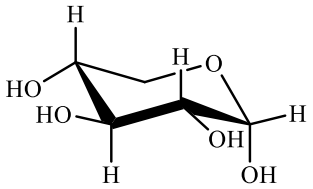


[1]K.J. Zeitsch: *The Chemistry and Technology of Furfural and its Many By-Products. Elsevier*, **2000.**



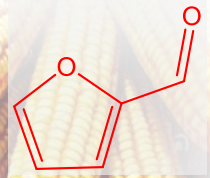
[2]G. Akien et al.: *Conversion of Carbohydrates to Liquid Fuels.* RSC Publishing, **2010.**

HEMICELLULOSE CONVERSION



Xylose (pentose)

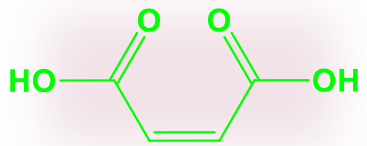
acid catalyst
160-180 °C



Furfural

$\Delta T, O_2$

catalyst

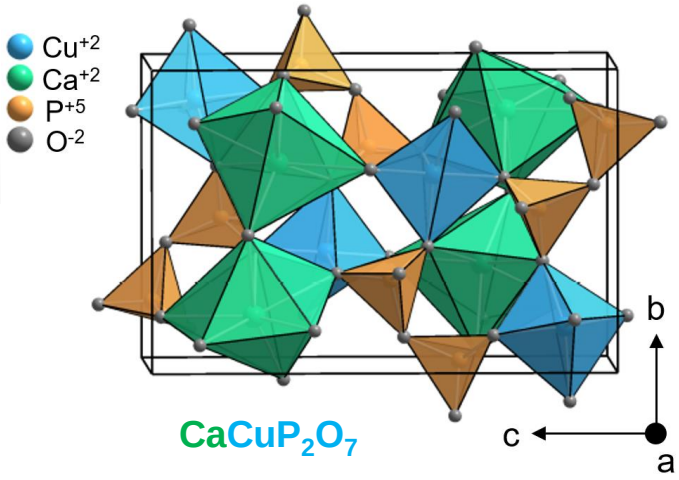


Maleic acid

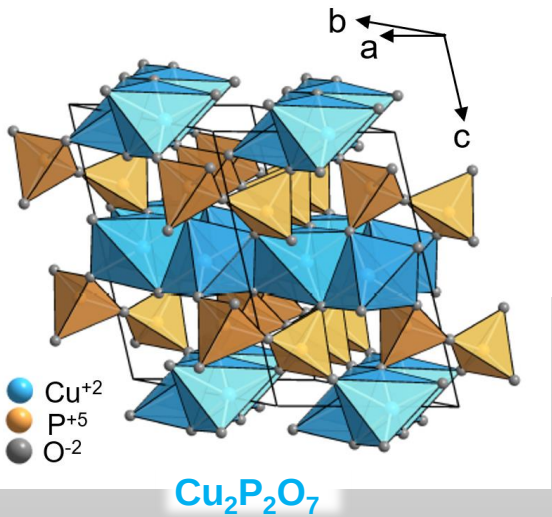
Reaction conditions:
t = 115 °C
$p(O_2)$ = 0,8 MPa
time = 18 h

- $Cu_2P_2O_7$
- $MCuP_2O_7$

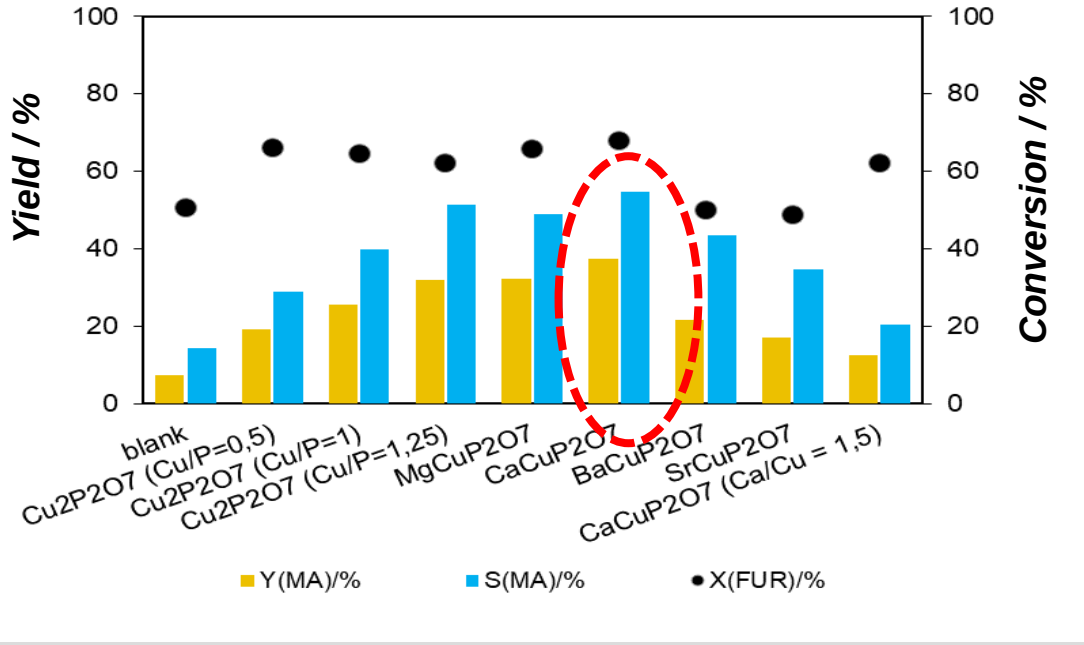
M = Mg, Ca, Ba, Sr



$CaCuP_2O_7$



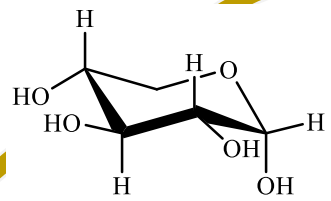
$Cu_2P_2O_7$



Soták T., Hronec M., Gál M., Dobročka E., Škriniarová J.: *Catal. Lett.* **2017**, 147, 2714 - 2723.

Bodišová J., Soták T., Naumowicz M., Sokolová R., Hronec M., Híveš J., Gál M.: *J. Electroanal. Chem.* **2018**, 821, 126 - 130.

HEMICELLULOSE CONVERSION

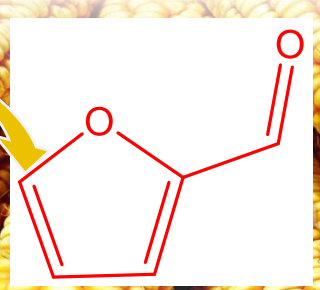


Xylose (pentose)

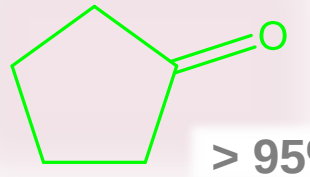
$H^{\oplus}$

acid catalyst
160-180 °C

Furfural



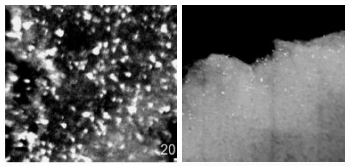
Cyclopentanone



Reaction conditions:
t = 160 °C
$p(H_2)$ = 3,0 MPa
time = 1 h

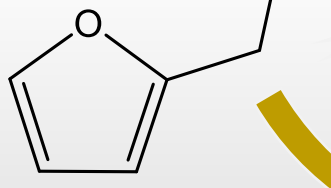
> 95% selectivity

Pd-Cu catalysts



Ni catalysts

Furfuryl alcohol



Drugs (cyclopentobarbital)

Fragrances (jasmine)

Pesticides

Fuels

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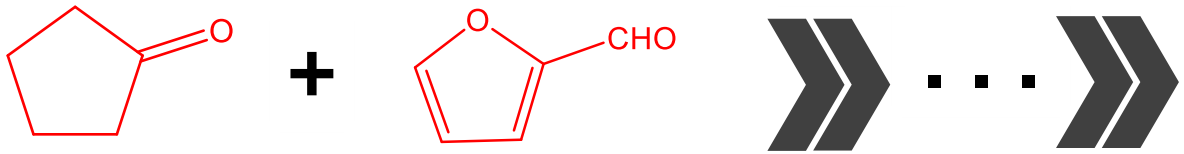
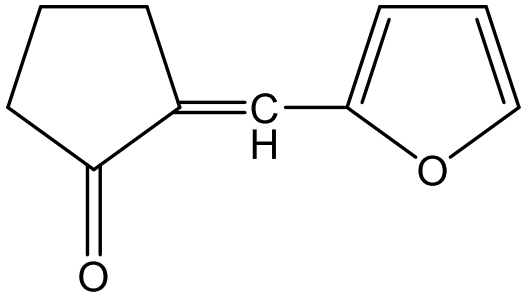
HEMICELLULOSE CONVERSION

Cyclopentanone + **Furfural**

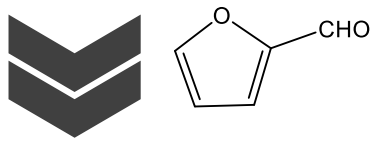


base

aqueous-phase aldol condensation

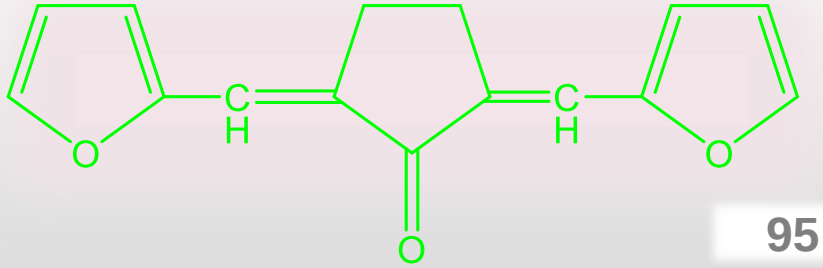


FC dimer



Jet fuel

Diesel fuel



F_2C trimer

95 mol% yield

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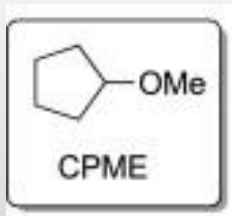
UNSYMMETRIC ETHERS PREPARATION

Cyclopentanol + **Methanol** → (ΔT, catalyst) → **CPME** Cyclopentyl methyl ether → **„green" solvent**

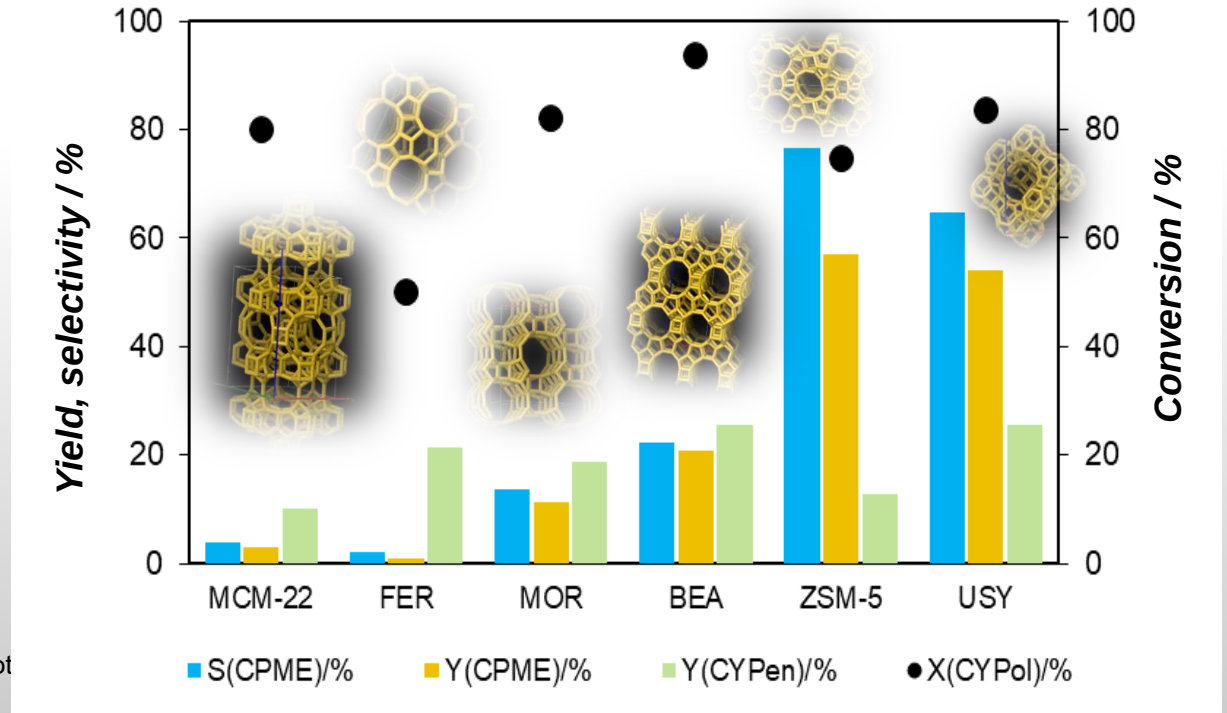
Solvent in organic synthesis

- high boiling point
- low solubility in water
- stability



bp: 106 °C
mp: <–140 °C
vaporization energy (bp): 69.2 kcal/kg
solubility in water: 1.1 g/100 g (23 °C)
flash point: –1 °C
ignition point: 180 °C
explosion range: 1.1–9.9 vol%

Reaction conditions:
t = 100 °C
WSHV = 0,25 g_{CYP} g_{cat}^{-1} h^{-1}
time = 6 h



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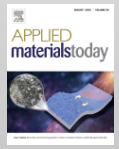

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PRODUCTS SEPARATION

- *Collaboration with:*

Chulalongkorn University

Silpakorn University

Wongsawa T., Hronec M., Soták T., Leepipatpiboon N., Pancharoen U., Phatanasri, S.: *Fluid Phase Equilib*. **2014**, 365, 88–96.

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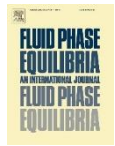

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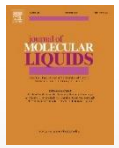

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CEITEC Brno, Czech Republic

- Catalysts characterization and evaluation

SLOVAK RESEARCH AND DEVELOPMENT AGENCY

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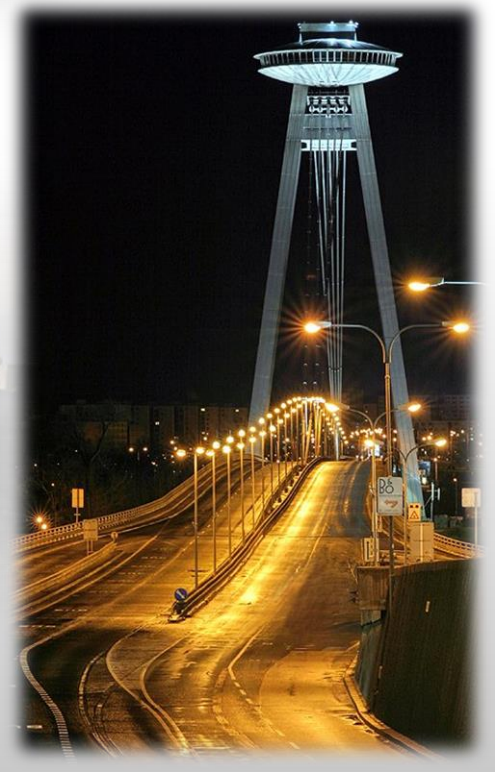

THANK YOU FOR YOUR KIND ATTENTION