



ENFiber

European Network for Valorising Food
Processing Waste into Sustainable Fibers

Cellulose and hemicellulose chemistry **Polysaccharide chemistry**

Brigita Hočevar
National Institute of Chemistry



Funded by
the European Union

Outline

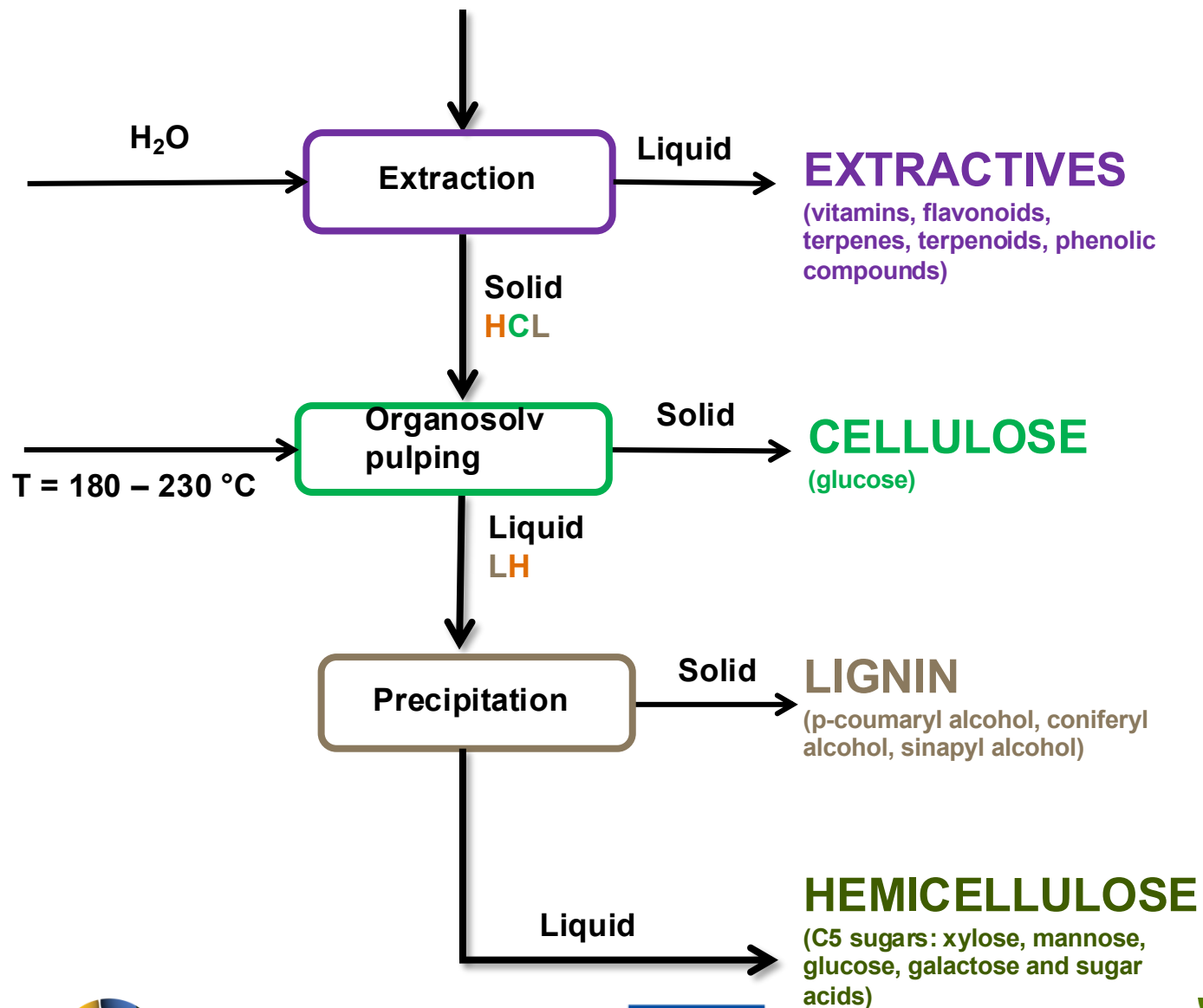
- Lignocellulosic biomass depolymerization
- Cellulose and hemicellulose

Case study: From glucose to adipic acid

- Polysaccharides

N-containing compounds from polysaccharides

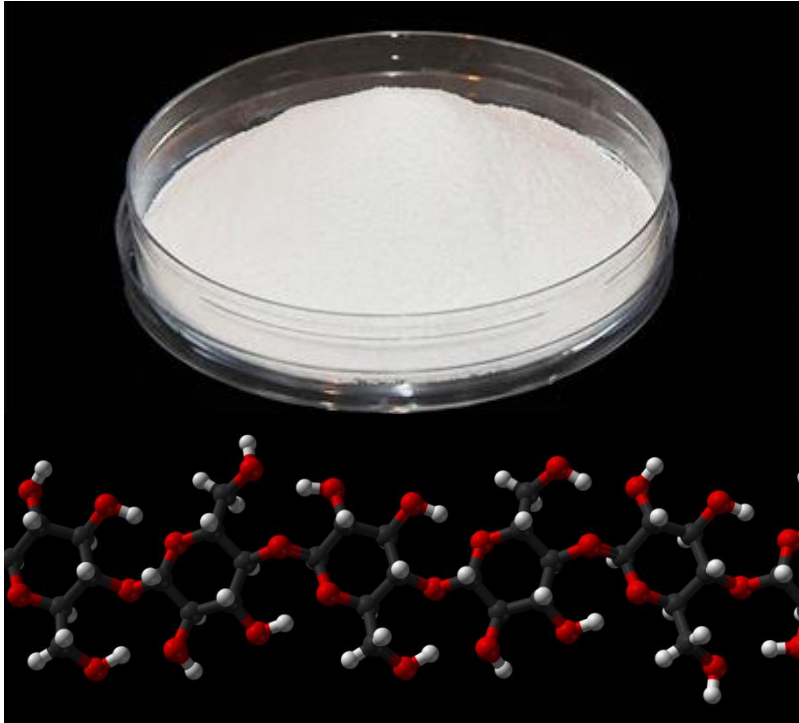
LIGNO(HEMI)CELLULOSIC BIOMASS



EXTRACTIVES



What is cellulose?



Appearance: White fibrous solid/powder

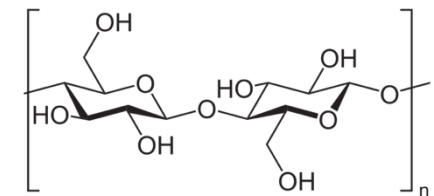
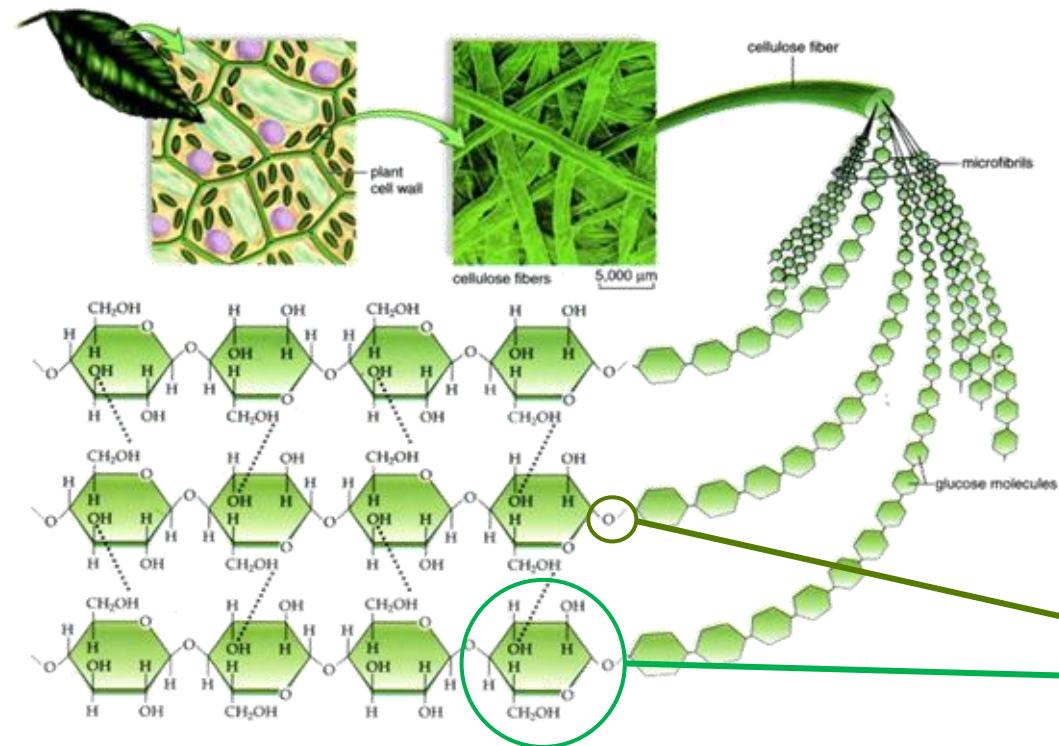
Chemical formula: $(C_6H_{10}O_5)_n$

Cellulose from wood: 300 – 1700 units

Cotton fibers: 800 – 10 000



Cotton fibers →
90 % of cellulose



Linear polymer of
β(1→4) linked
D-glucose units

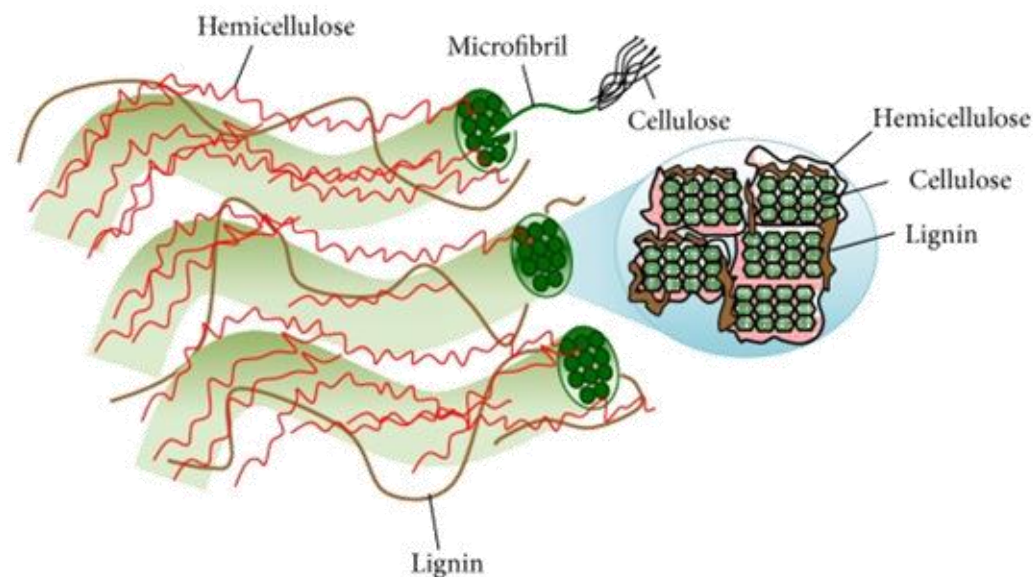
Cellulose consists of **crystalline** and **amorphous** regions.

Different **crystalline structures** of cellulose are known → corresponding to the location of **hydrogen bonds** between and within strands.

Treating with strong acid → amorphous regions break up → producing **nanocrystalline cellulose**

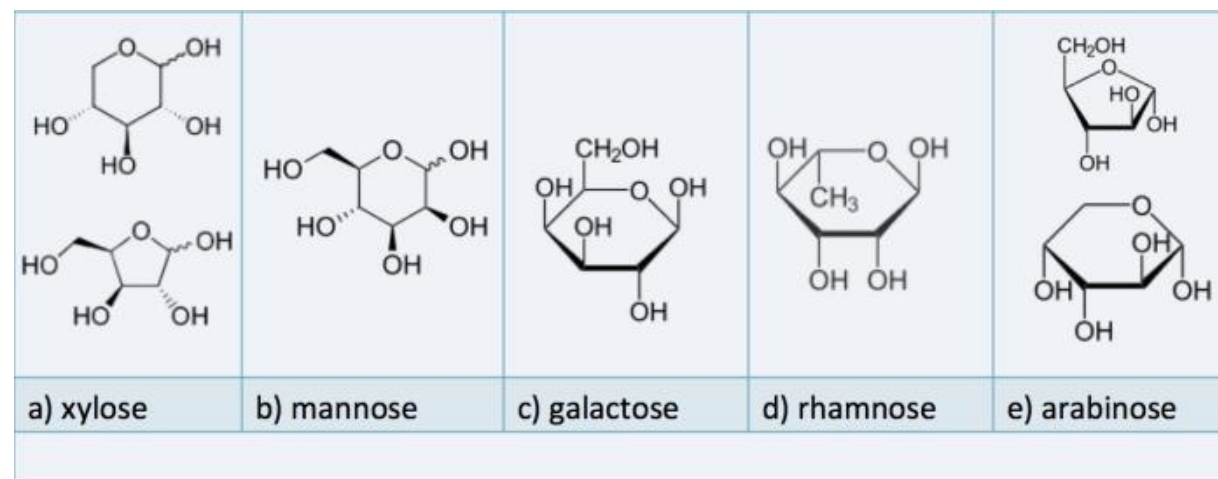


What is hemicellulose?



Appearance: White to brownish crystalline powder
Chemical formula: Pentose/hexose mixture

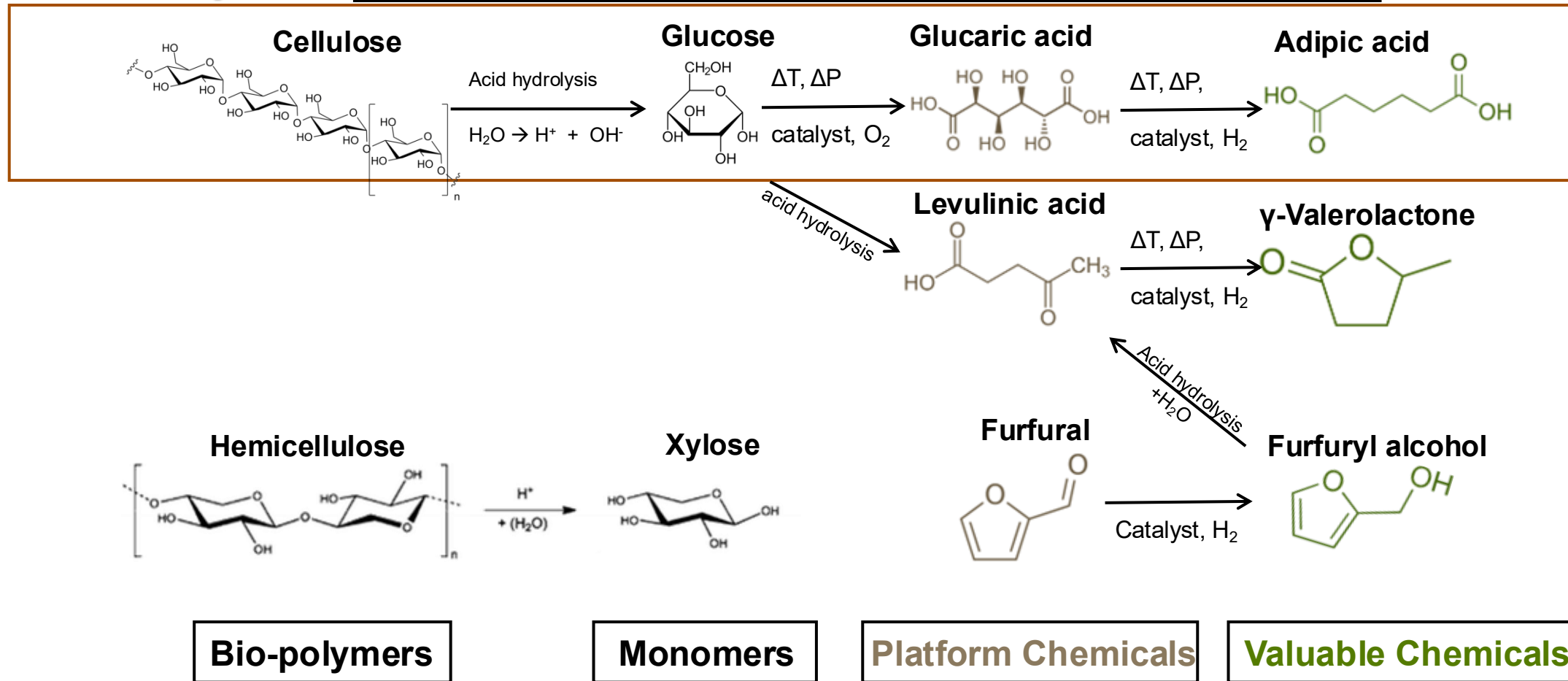
- Polysaccharide mixture:** Built from a random, amorphous structure of 100 to 200 (or up to several hundred) sugar units.
- Pentose sugars:** Primarily **xylose** and **arabinose**.
- Hexose sugars:** Includes **glucose**, **mannose**, and **galactose**.



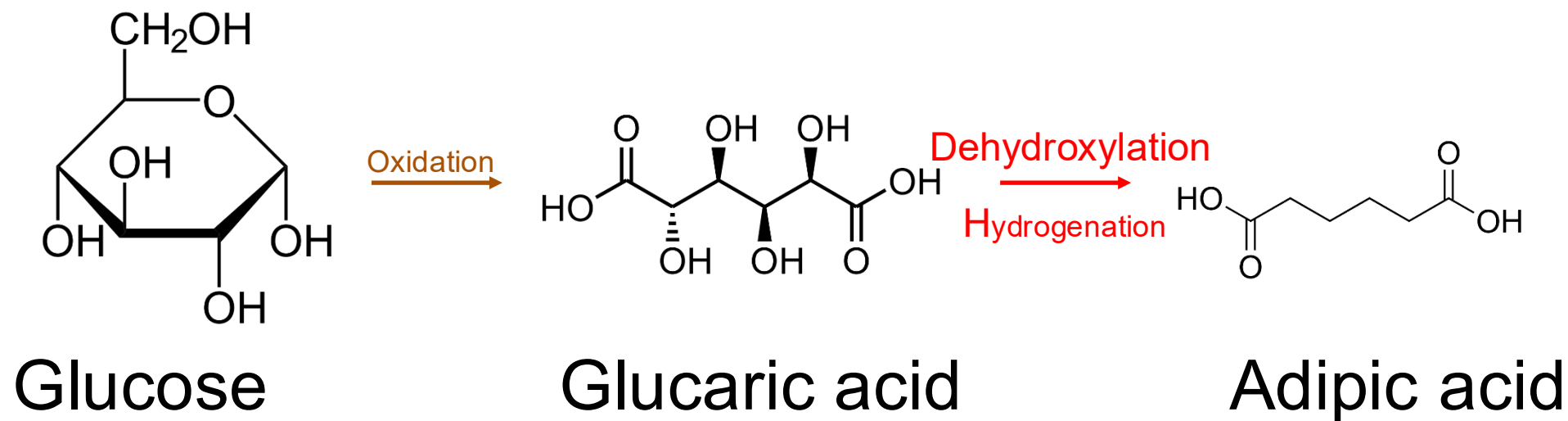
CELLULOSE AND HEMICELLULOSE VALORISATION:

Case study

TOP – DOWN CHEMO-CATALYTIC APPROACH

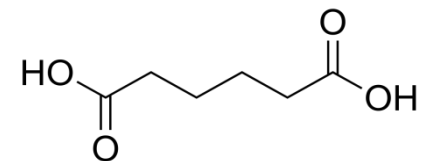


Case study: FROM GLUCOSE TO ADIPIC ACID

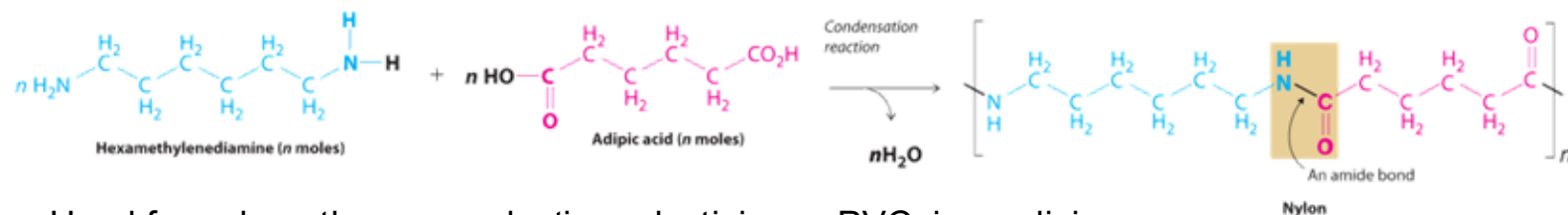




Adipic acid



- 3.7 billion kg produced annually
- 7 billion USD/year
- 75 % of the total output is used as a monomer for **nylon 66 production** (polycondensation reaction with hexamethylene diamine)



- Used for polyurethanes production, plasticizers, PVC, in medicine,...

Appearance:	White crystalline powder
Chemical formula:	$C_6H_{10}O_4$
Molar mass:	146.14 g mol ⁻¹
Melting point:	T = 152.1°C
Solubility:	soluble in MeOH, EtOH, acetone, H ₂ O



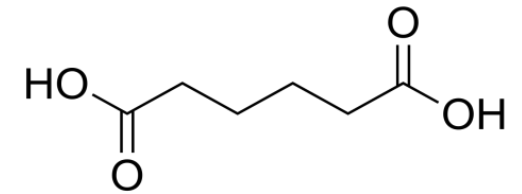
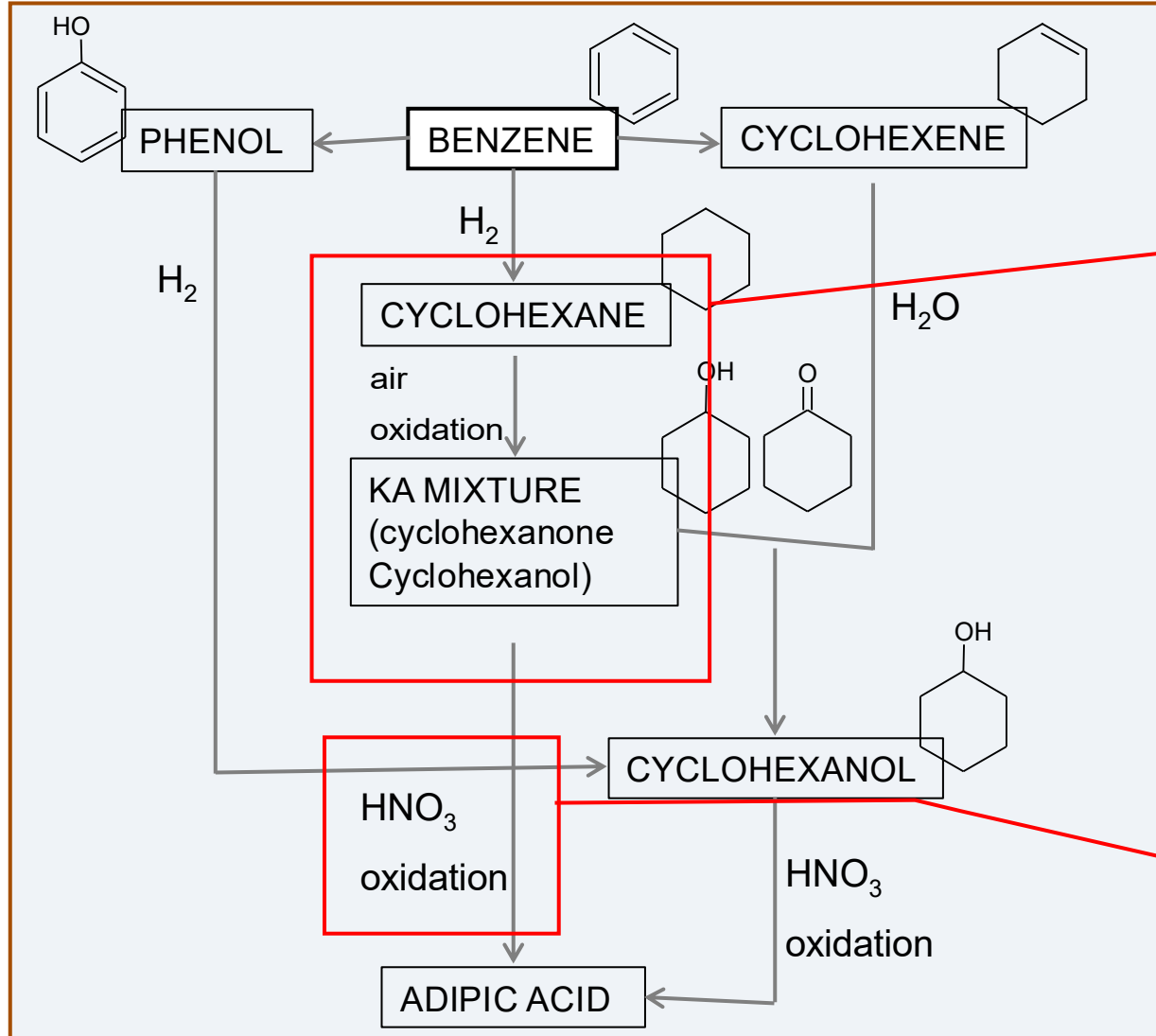
Funded by
the European Union



WHY WE ARE LOOKING FOR SUSTAINABLE ALTERNATIVES?

Conventional petrochemical process for the production of ADIPIC ACID

- crude oil as a feedstock
- benzene as a reactant
- low yields
- runaway exothermic reactions
→ explosion risk
- high cost of corrosion resistant equipment

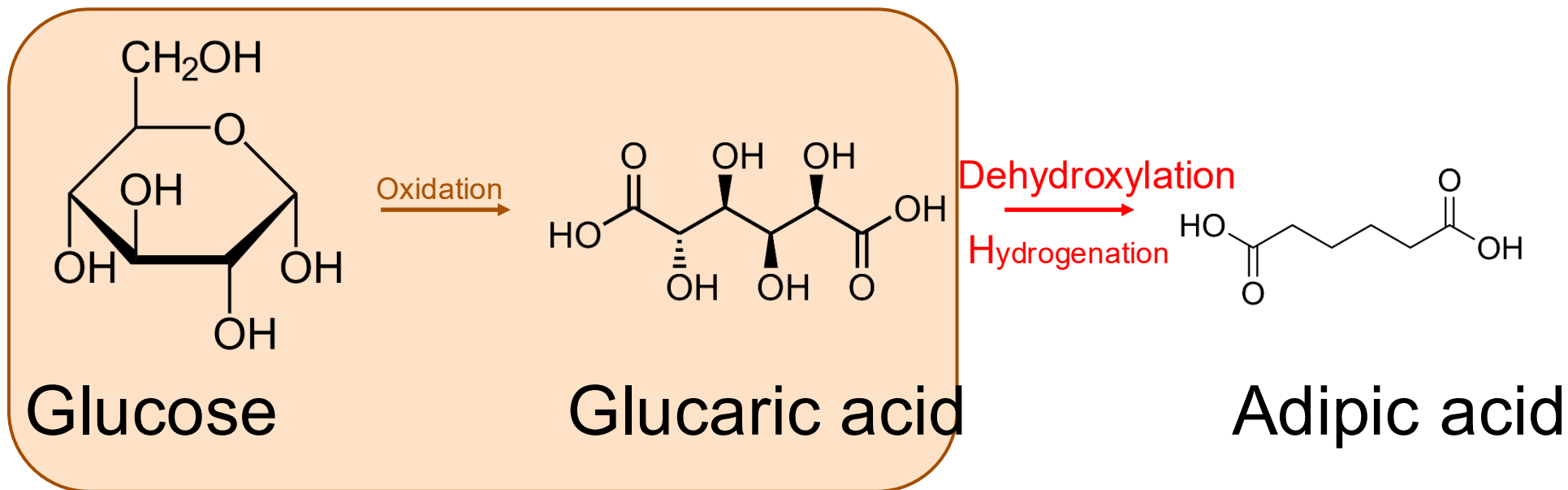


Low conversion of the oxidation step (4-11 %)



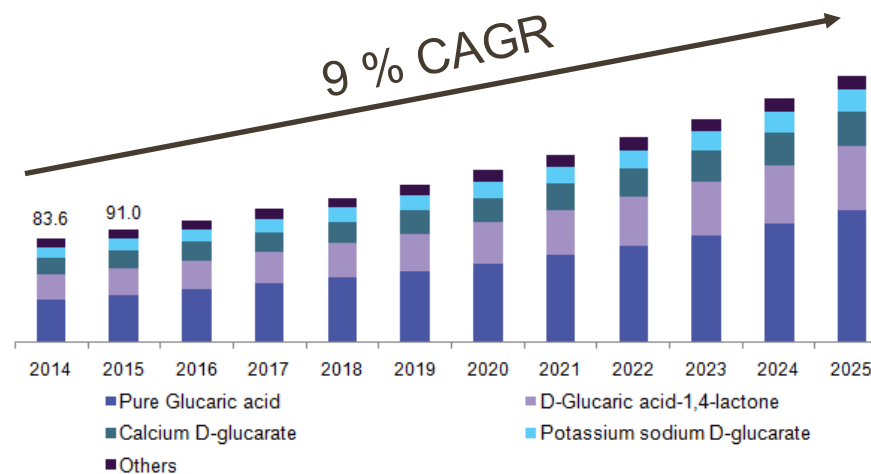
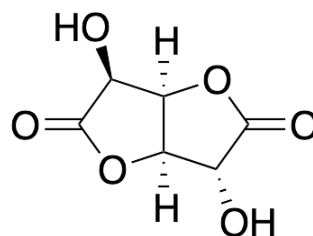
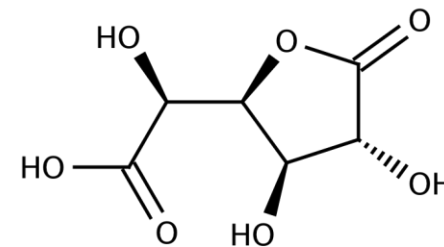
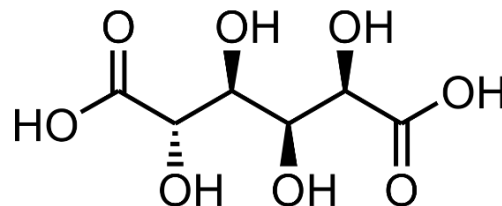
N₂O & NO_x formation
Exothermic reaction

Case study: FROM GLUCOSE TO ADIPIC ACID



Glucose Oxidation → Glucaric acid

- In 2004 → US DOE classifies it as “building block” chemical with many potentials
- **Glucaric acid uses:**
 - Retardant in textile dying
 - Detergents and surfactants
 - Precursor for **Bio-based adipic acid**
 - Current industrial practice nitric acid oxidation
 - NO_x emissions & nitric acid discharge
 - Low reaction T → exothermic reaction → low yields



Our investigation

Glucose $\xrightarrow[\text{AuPt/ZrO}_2]{\text{Oxidation}}$ Glucaric acid

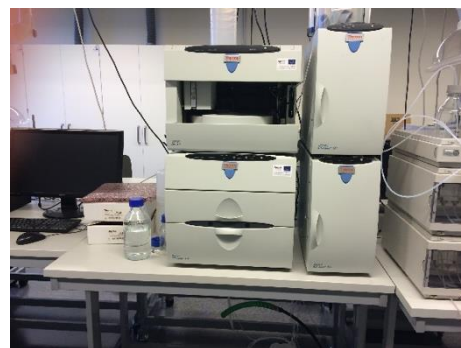
AuPt/ZrO₂

- Study the difference between Au, AuPt and AuCu (50:50 mol.%) catalysts supported on ZrO₂ (base free aqueous reactions with O₂)
- Catalyst synthesis
- Characterization: XRD, TEM, oxygen chemisorption and XPS
- Microkinetic and DFT study

Experiments and analysis Parr 5000

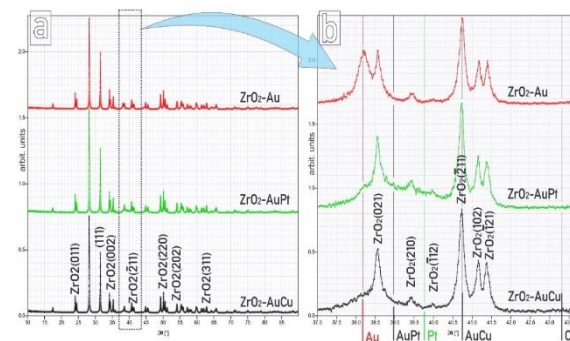


Ion chromatography

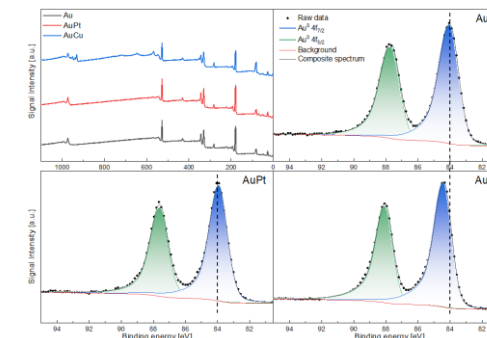


Catalyst characterization

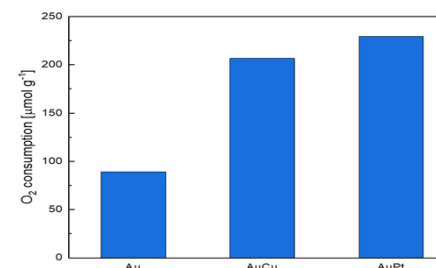
XRD



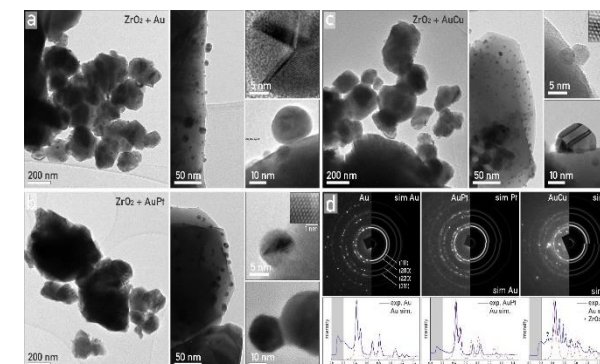
XPS



Oxygen chemisorption



TEM



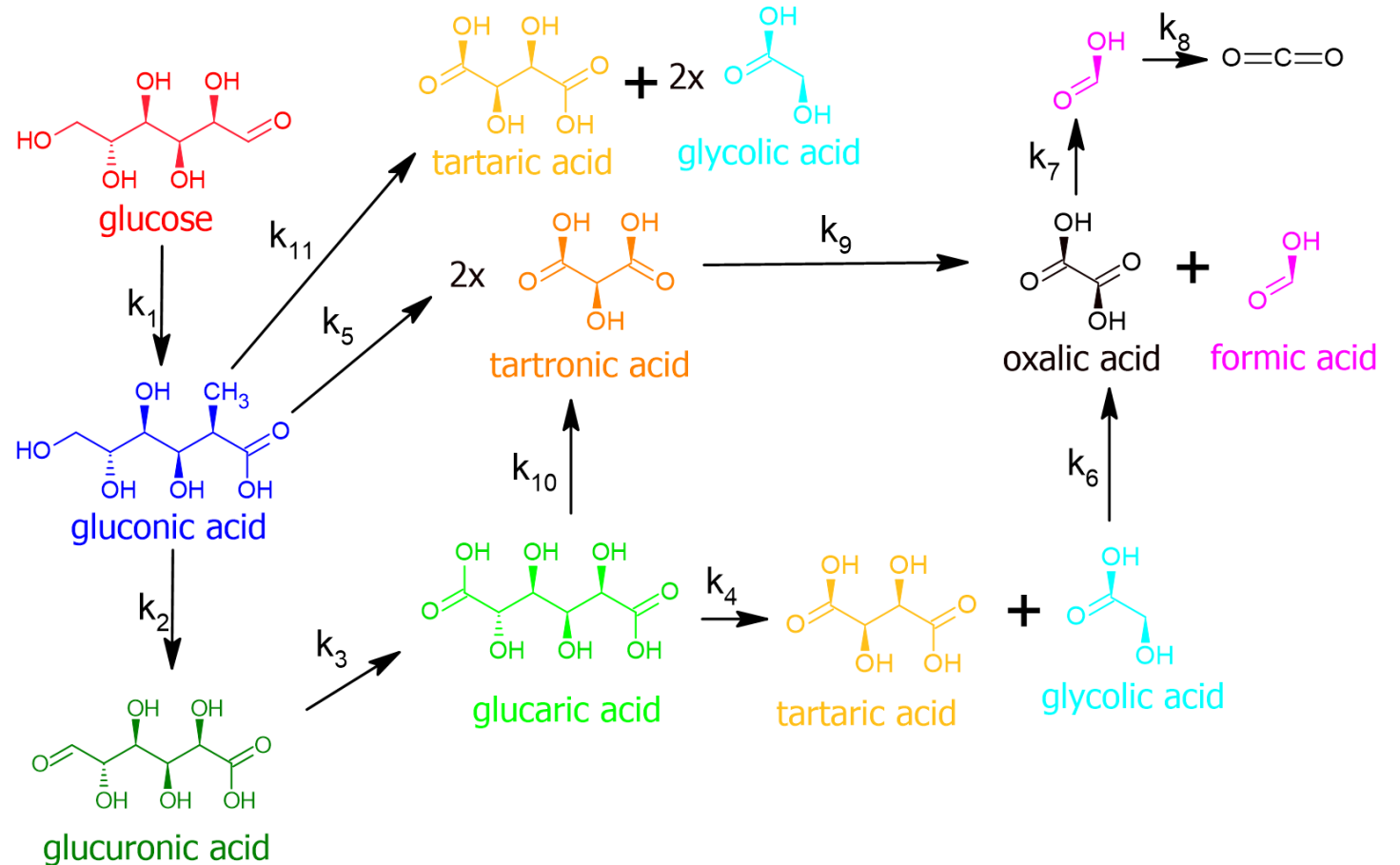
Key findings:

- AuPt/ZrO₂ & AuCu/ZrO₂ → alloy (XRD)

- AuCu/ZrO₂ particle size distribution less homogeneous than AuPt/ZrO₂
- AuPt/ZrO₂ → best O₂ activation

Microkinetic model development

- Number of experiments: **37**
- Experimentally determined points: **259**
- Temperatures: **60, 80 100 and 120 °C**
- Pressures: **16 and 30 bar_a**
- Kinetic model encompasses all the data points → **output: reaction rate constants and corresponding activation energies**



Microkinetic model development

Descriptive model → determine k_i and E_{a_i}

fminsearch (Nelder-Mead) → main regression
lsqnonlin (Levenberg-Marquardt) → confidence interval

ODE15s

Adsorption/desorption

$$r_j^{\text{ads}} = k_j^{\text{ads}} \cdot C_j^L \cdot \theta_{\text{vs}} \quad (1)$$

$$r_j^{\text{des}} = k_j^{\text{des}} \cdot \theta_j \cdot n_{\text{TS}} \quad (2)$$

Surface reaction rate

$$r_j^{\text{surf}} = k_j^{\text{surf}} \cdot \theta_j \cdot \theta_{\text{O}_2} \cdot n_{\text{TS}} \quad (3)$$

Arrhenius in logarithmic form

$$k_j^{\text{surf}}(T_2) = k_j^{\text{surf}}(T_1) \cdot \exp\left(\frac{E_{a_j}}{R} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right) \quad (4)$$

Vacant sites balance equations

$$\frac{d\theta_{\text{vs}}}{dt} = (-V_L \cdot \sum_j^n r_j^{\text{ads}} + \sum_j^n r_j^{\text{des}} + \sum_j^n \pm r_j^{\text{surf}}) \cdot \frac{1}{n_{\text{TS}}} \quad (9)$$

Oxygen transfer G-L

$$\frac{dn_{\text{O}_2}^G}{dt} = -k_{\text{GL}} \cdot A \cdot \left(\frac{p_{\text{O}_2}}{P_{\text{He}}} - C_{\text{O}_2}^L\right) \quad (5)$$

Liquid phase balance equation

$$\frac{dC_j^L}{dt} = -r_j^{\text{ads}} + \frac{r_j^{\text{des}}}{V_L} \quad (6)$$

Liquid phase balance equation for O_2

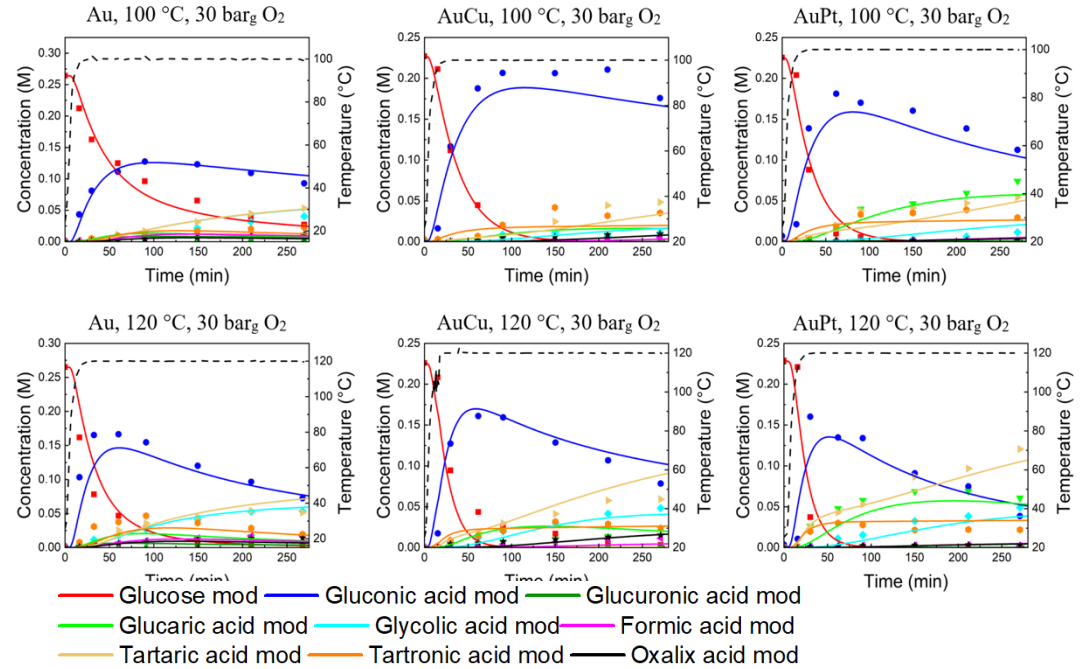
$$\frac{dC_{\text{O}_2}^L}{dt} = k_{\text{GL}} \cdot a \cdot \left(\frac{p_{\text{O}_2}}{P_{\text{He}}} - C_{\text{O}_2}^L\right) \cdot \frac{1}{V_L} - r_j^{\text{ads}} + \frac{r_j^{\text{des}}}{V_L} \quad (7)$$

Surface coverage

$$\frac{d\theta_j}{dt} = (r_j^{\text{ads}} \cdot V_L - r_j^{\text{des}} + \sum_j^n \pm r_j^{\text{surf}}) \cdot \frac{1}{n_{\text{TS}}} \quad (8)$$

Solving differential Eq.

$$R^2 = \sum (C_{\text{exp}} - C_{\text{mod}})^2$$



Predictive model → determine t_{react} and T_{react}

Iterative loop with fixed parameters k_i and E_{a_i}

ODE15s

Adsorption/desorption

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Surface reaction rate

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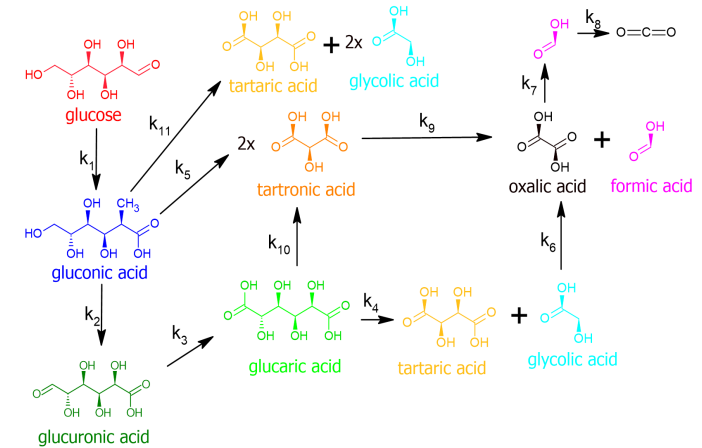
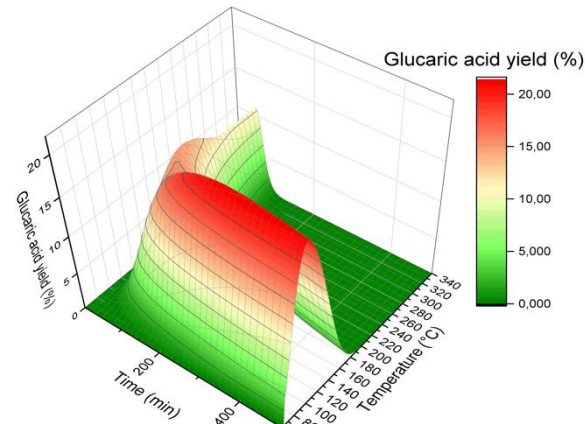
Liquid phase balance equation for O_2

$$\frac{dC_{\text{O}_2}^L}{dt} = k_{\text{GL}} \cdot a \cdot \left(\frac{p_{\text{O}_2}}{P_{\text{He}}} - C_{\text{O}_2}^L\right) \cdot \frac{1}{V_L} - r_j^{\text{ads}} + \frac{r_j^{\text{des}}}{V_L} \quad (7)$$

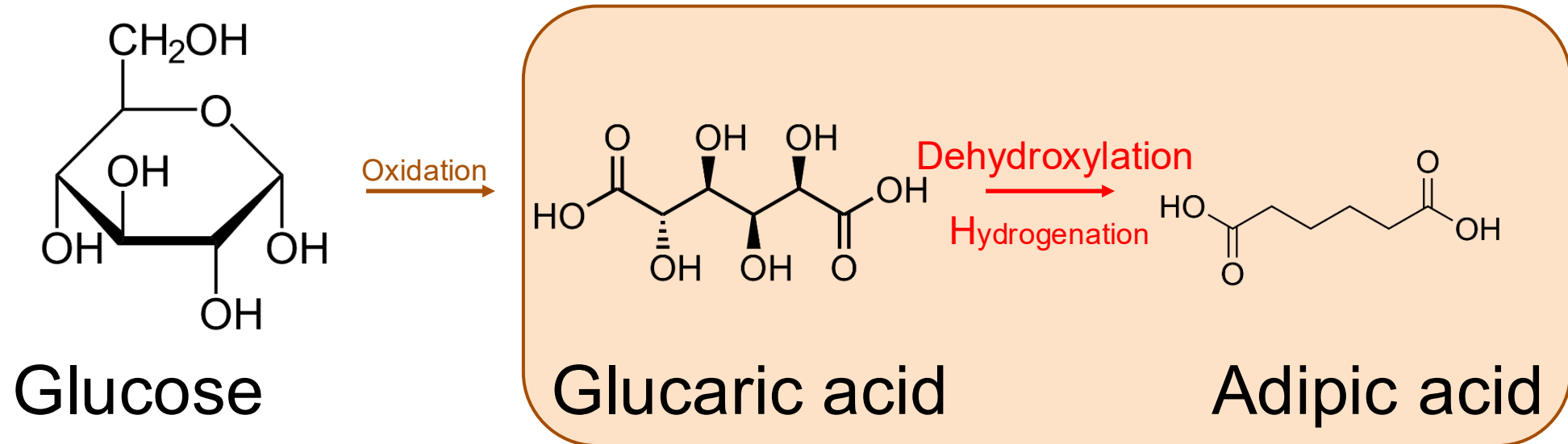
Surface coverage

$$\frac{d\theta_j}{dt} = (r_j^{\text{ads}} \cdot V_L - r_j^{\text{des}} + \sum_j^n \pm r_j^{\text{surf}}) \cdot \frac{1}{n_{\text{TS}}} \quad (8)$$

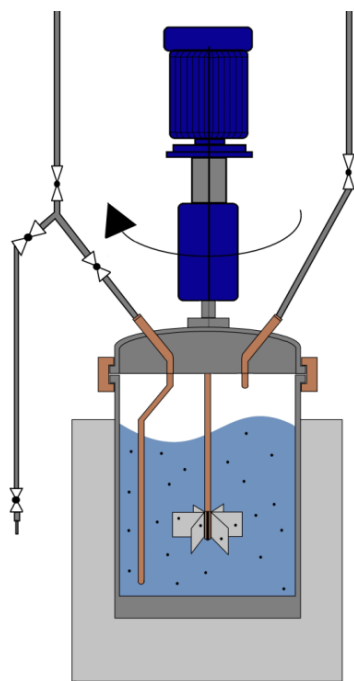
Solving differential Eq.



Case study: FROM GLUCOSE TO ADIPIC ACID

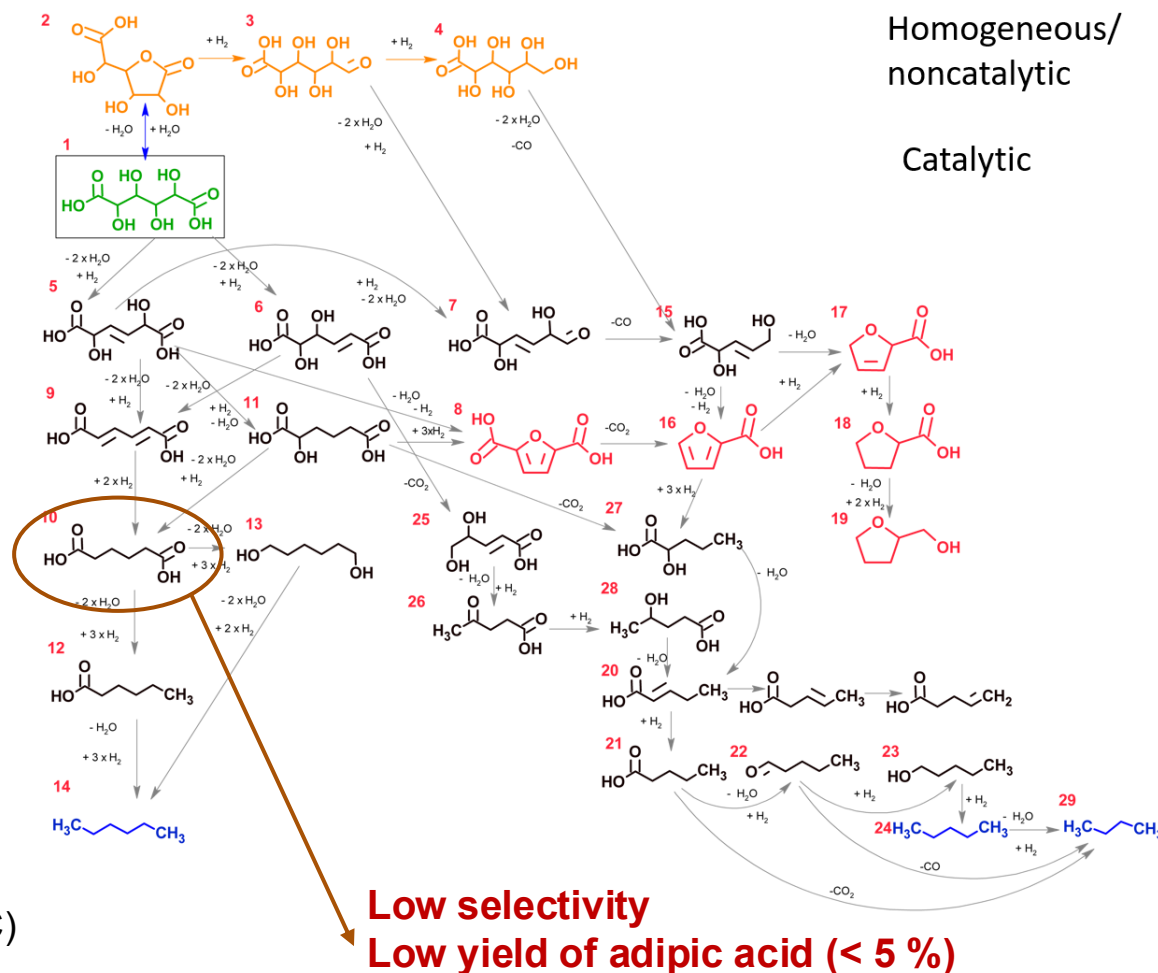


Deoxydehydration (DODH) of **biobased ALDARIC ACID** in aqueous phase



Reaction conditions:

- **Green solvent : H₂O**
- Heterogeneous metal catalysts
NiMo/γ-Al₂O₃, Pt/γ-Al₂O₃,
Ru/SiO₂, Rh/SiO₂, Ni/SiO₂,
Pt/SiO₂ Ru/C, Rh/C, Ni/C, Pt/C
- Moderate temperatures (125-200°C)
- High H₂ pressure (initial 5 MPa)



Article

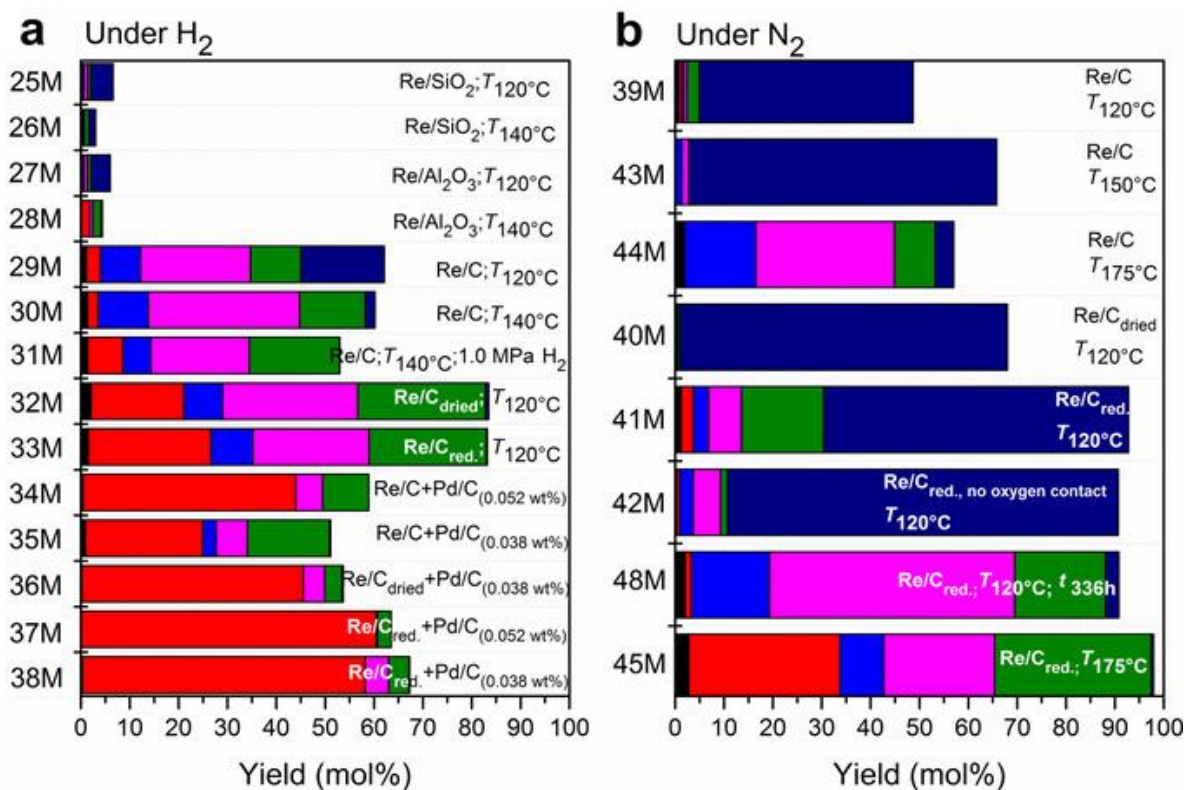
Aqueous Dehydration, Hydrogenation, and Hydrodeoxygenation Reactions of Bio-Based Mucic Acid over Ni, NiMo, Pt, Rh, and Ru on Neutral or Acidic Catalyst Supports

Brigita Hočevar, Miha Grlic and Blaž Likozar

Department of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia; brigita.hocevar@ki.si (B.H.); blaz.likozar@ki.si (B.L.)

* Correspondence: miha.grlic@ki.si; Tel.: +386-1-4760540

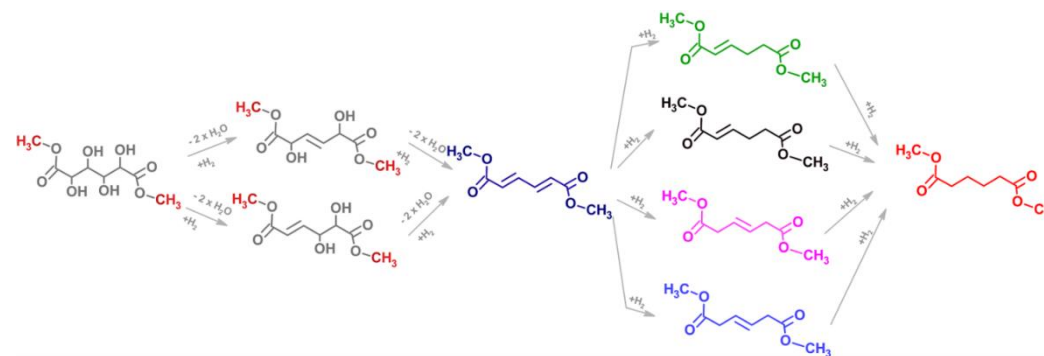
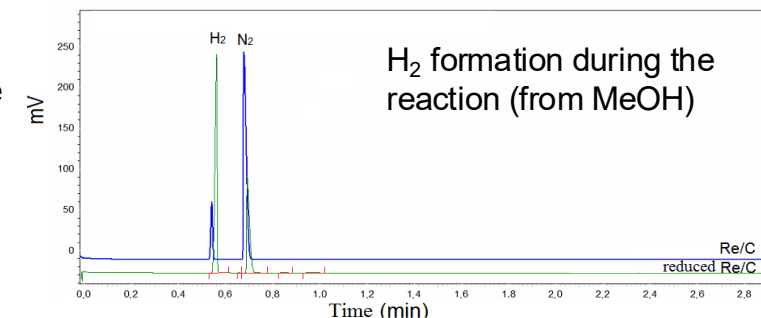
Heterogeneous DODH of **biobased ALDARIC ACID** in methanol with rhenium catalysts



- Product selectivity can be controlled
- Using MeOH as reducing agent and only Re/C, unsaturated products are formed

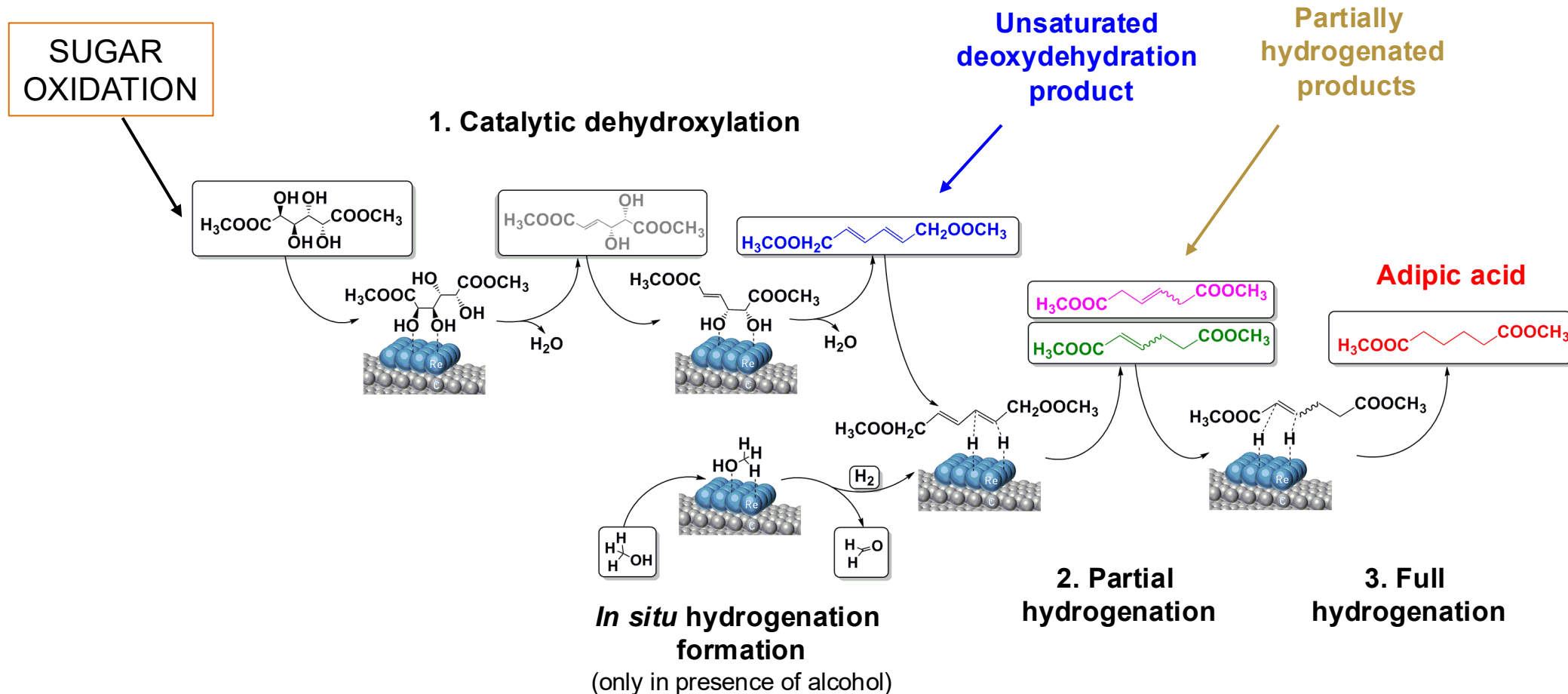
Yield of saturated methyl adipate is maximized by

- Extended reaction time
- Reducing (H₂) atmosphere
- Use of Pd cocatalyst



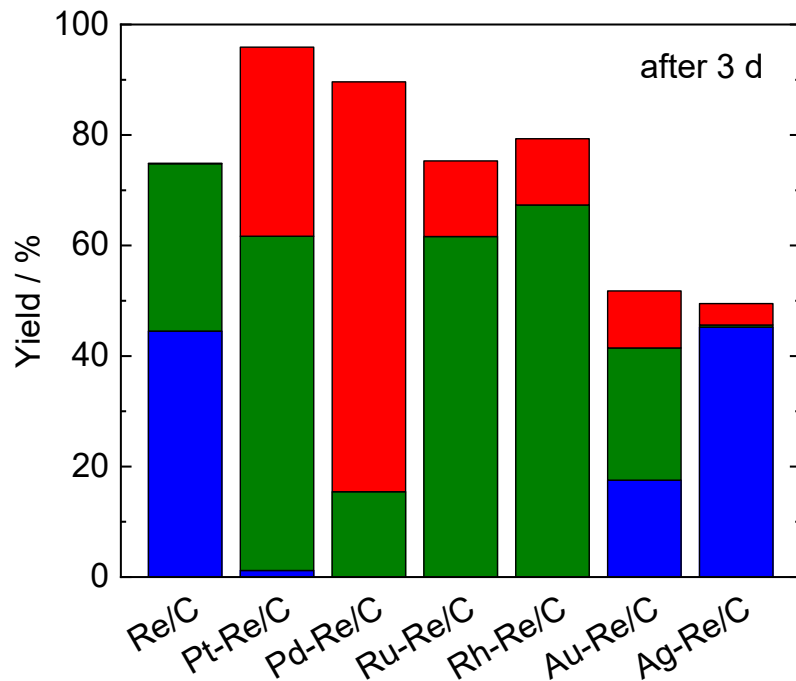
Renewable adipic acid from biomass: Dehydroxylation of aldaric acids

Multi-step one-pot reaction



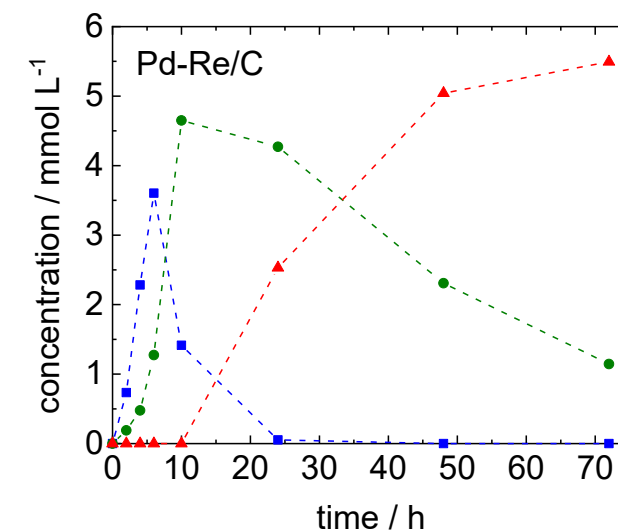
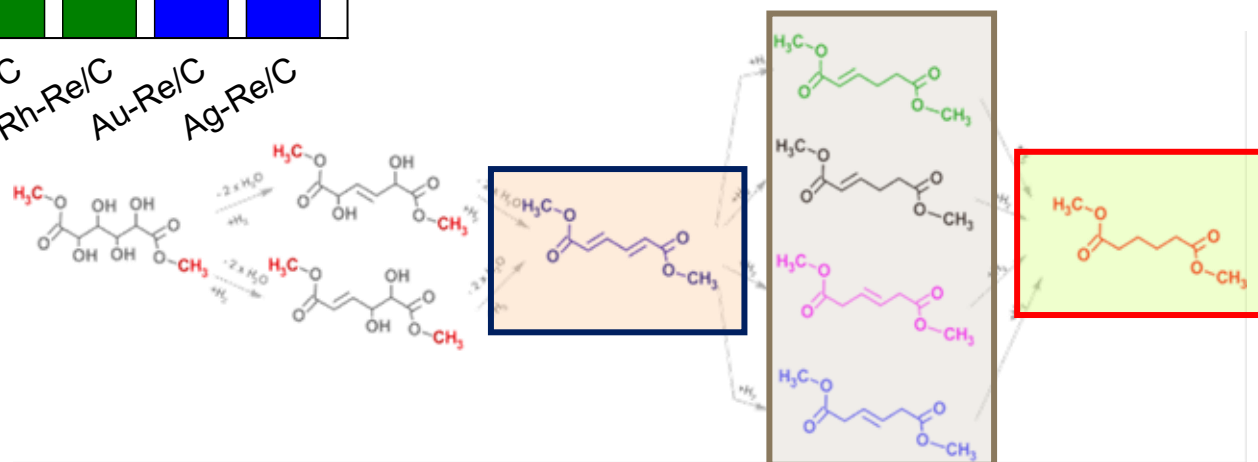
➡ **Patent (EP3782976) and publication in *Angew. Chem. Int. Ed.***

Heterogeneous DODH of **biobased ALDARIC ACID** in methanol with bimetallic catalysts

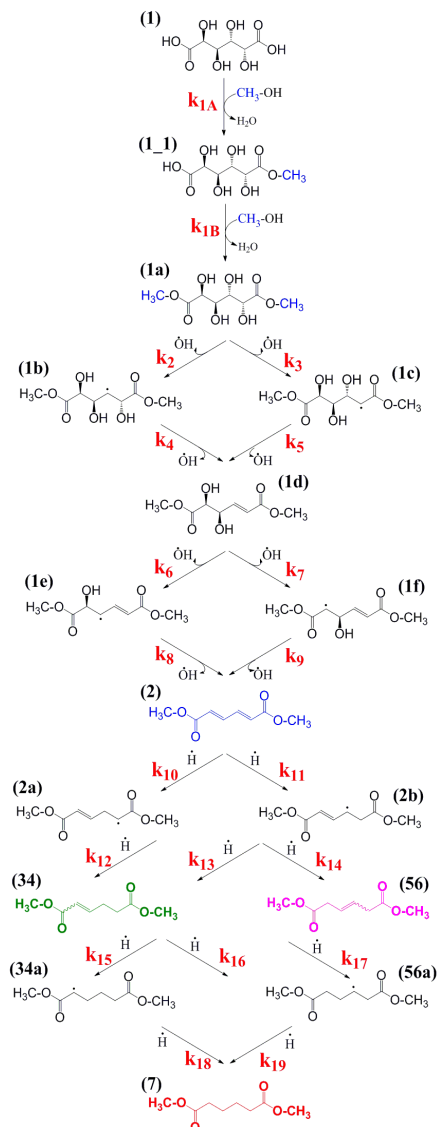


End of the reaction

- Most bimetallic catalysts facilitate the hydrogenation reaction
- Large amounts of adipate can be obtained
- Pd and Pt are best-suited to steer the reaction towards adipates



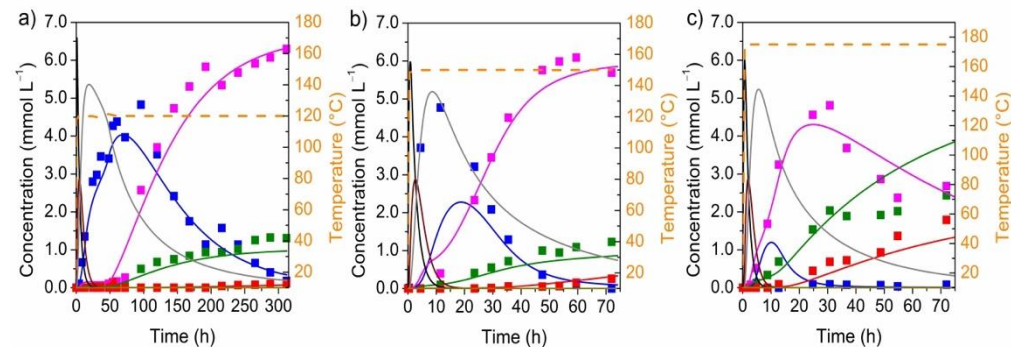
Multiscale kinetic modelling



i	r_i	$k_i^{\text{cat}} (T=120^\circ\text{C})$ (mol L ⁻¹ s ⁻¹)	$E a_{i,\text{DFT}}$ (kJ mol ⁻¹)
1A_hom	$k_i^{\text{hom}} Q_{\text{CH}_3\text{OH}}^L Q_{11}^L$	10 ⁻² (a)	30
1B_hom	$k_i^{\text{hom}} Q_{\text{CH}_3\text{OH}}^L Q_{11}^L$	10 ⁻² (b)	30
1A	$k_i^{\text{cat}} Q_{\text{CH}_3\text{OH}}^{\text{ads}} Q_{11} n_{\text{TS}}$	1	50
1B	$k_i^{\text{cat}} Q_{\text{CH}_3\text{OH}}^{\text{ads}} Q_{11} n_{\text{TS}}$	1	50
2	$k_i^{\text{cat}} Q_{1a}^{\text{ads}} Q_T n_{\text{TS}}$	10	78
3	$k_i^{\text{cat}} Q_{1a}^{\text{ads}} Q_T n_{\text{TS}}$	10	39
4	$k_i^{\text{cat}} Q_{1b}^{\text{ads}} Q_T n_{\text{TS}}$	> 10 ⁴	40
5	$k_i^{\text{cat}} Q_{1c}^{\text{ads}} Q_T n_{\text{TS}}$	> 10 ⁴	45
6	$k_i^{\text{cat}} Q_{1d}^{\text{ads}} Q_T n_{\text{TS}}$	8.79 · 10 ⁴	38
7	$k_i^{\text{cat}} Q_{1d}^{\text{ads}} Q_T n_{\text{TS}}$	3.26 · 10 ⁴	71
8	$k_i^{\text{cat}} Q_{1e}^{\text{ads}} Q_T n_{\text{TS}}$	> 10 ⁵	74
9	$k_i^{\text{cat}} Q_{1f}^{\text{ads}} Q_T n_{\text{TS}}$	> 10 ⁵	44
10	$k_i^{\text{cat}} Q_2^{\text{ads}} Q_H^{\text{ads}} n_{\text{TS}}$	5.34	127
11	$k_i^{\text{cat}} Q_{1a}^{\text{ads}} Q_H^{\text{ads}} n_{\text{TS}}$	35.21	96
12	$k_i^{\text{cat}} Q_{2a}^{\text{ads}} Q_H^{\text{ads}} n_{\text{TS}}$	5.0 · 10 ⁴	72
13	$k_i^{\text{cat}} Q_{2b}^{\text{ads}} Q_H^{\text{ads}} n_{\text{TS}}$	1	93
14	$k_i^{\text{cat}} Q_{2b}^{\text{ads}} Q_H^{\text{ads}} n_{\text{TS}}$	1 · 10 ⁴	124
15	$k_i^{\text{cat}} Q_{34}^{\text{ads}} Q_H^{\text{ads}} n_{\text{TS}}$	5.4 · 10 ⁻³	133
16	$k_i^{\text{cat}} Q_{34}^{\text{ads}} Q_H^{\text{ads}} n_{\text{TS}}$	1.28 · 10 ⁻⁵	116
17	$k_i^{\text{cat}} Q_{56}^{\text{ads}} Q_H^{\text{ads}} n_{\text{TS}}$	0.32	117
18	$k_i^{\text{cat}} Q_{3a}^{\text{ads}} Q_H^{\text{ads}} n_{\text{TS}}$	> 10 ⁴	110
19	$k_i^{\text{cat}} Q_{3b}^{\text{ads}} Q_H^{\text{ads}} n_{\text{TS}}$	> 10 ⁴	119

(a) homogeneous esterification in liquid phase – monoester

(b) homogeneous esterification in liquid phase – diester



The dehydroxylation over Re/C (5% Re) catalyst in methanol under initial inert (N₂) gaseous atmosphere at a) 120 °C, b) 150 °C and c) 175 °C plateau reaction temperature



Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec



Full Length Article

Multiscale kinetic modelling of de-hydroxylation of mucic- to adipic acid esters over Re/C

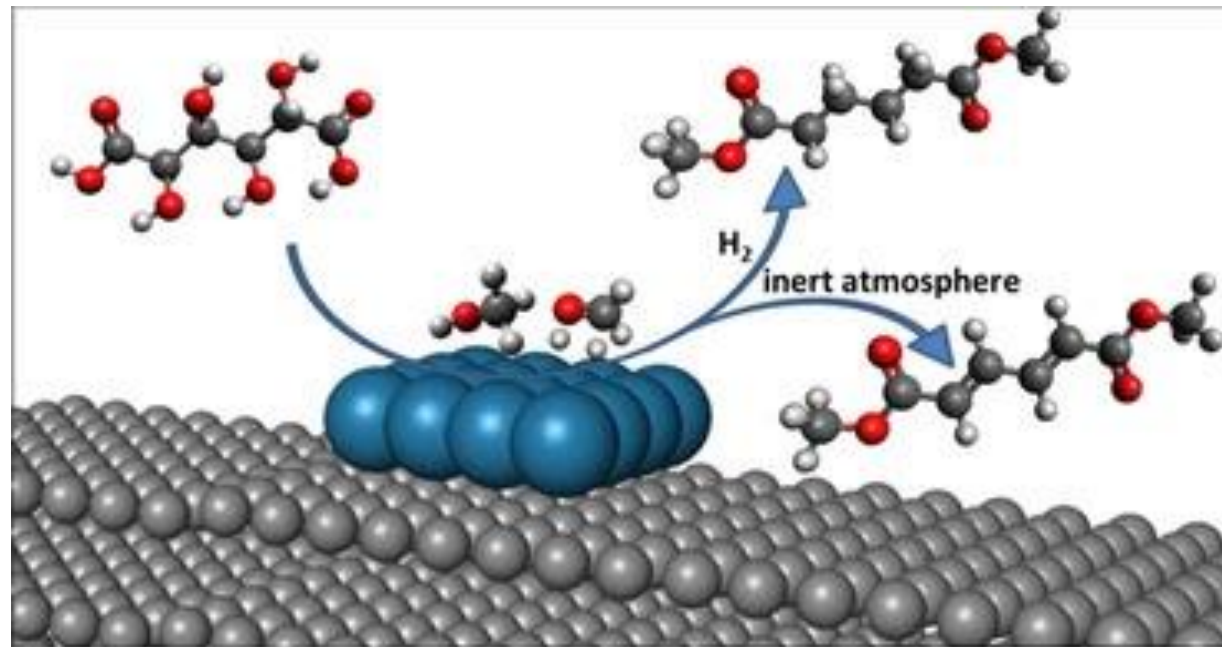
Brigita Hočevar^a, Anže Prašnikar^a, Sašo Gyergyek^b, Matej Huš^{a,c,d}, Miha Grilc^a, Blaž Likozar^{a,*}

Biobased ADIPIC ACID: take home message

Benefits of the developed sustainable process:

- High yields (> 90 mol%)
- No harmful gas emissions
- No harmful side products
- Heterogeneous catalysis (**solid Re/C**)

- Easy separation of catalyst (filtration)
- Reuse of catalyst (filtration-reduction)
- Reuse of solvent (distillation)
- Easy transition to continuous process
(fixed bed reactor)



Patented process: EP3782976

**Sustainable process for producing muconic, hexenedioic and adipic acid
(and their esters) from aldaric acids by heterogeneous catalysis**

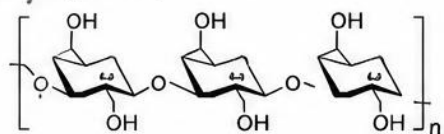
WHAT ARE POLYSACCHARIDES?

HOMOPOLYSACCHARIDES

Built from one type of monosaccharide

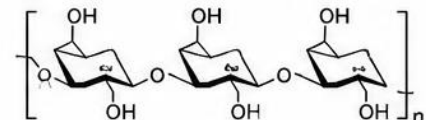
- Cellulose**

(β -1 $\rightarrow$ 4 D-glucose)



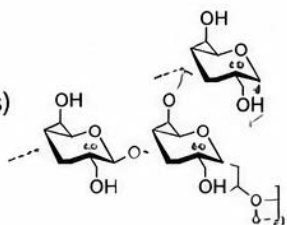
- Starch**

(α -1 $\rightarrow$ 4 D-glucose)



- Dextran**

(α -1 $\rightarrow$ 6 D-glucose, with α -1 $\rightarrow$ 3 branches)

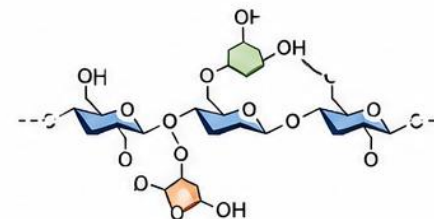


HETEROPOLYSACCHARIDES

Built from two or more types of monosaccharides

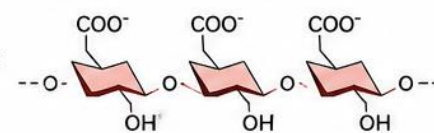
- Hemicellulose**

(e.g., xylan: xylose backbone with side groups)



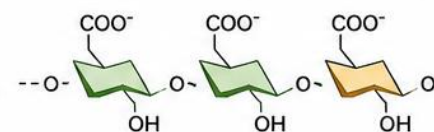
- Pectin**

(rich in galacturonic acid)



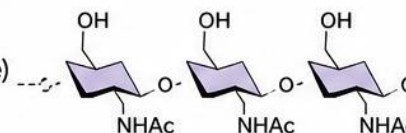
- Alginate**

(mannuronic acid and guluronic acid)



- Chitin**

(N-acetyl-D-glucosamine)

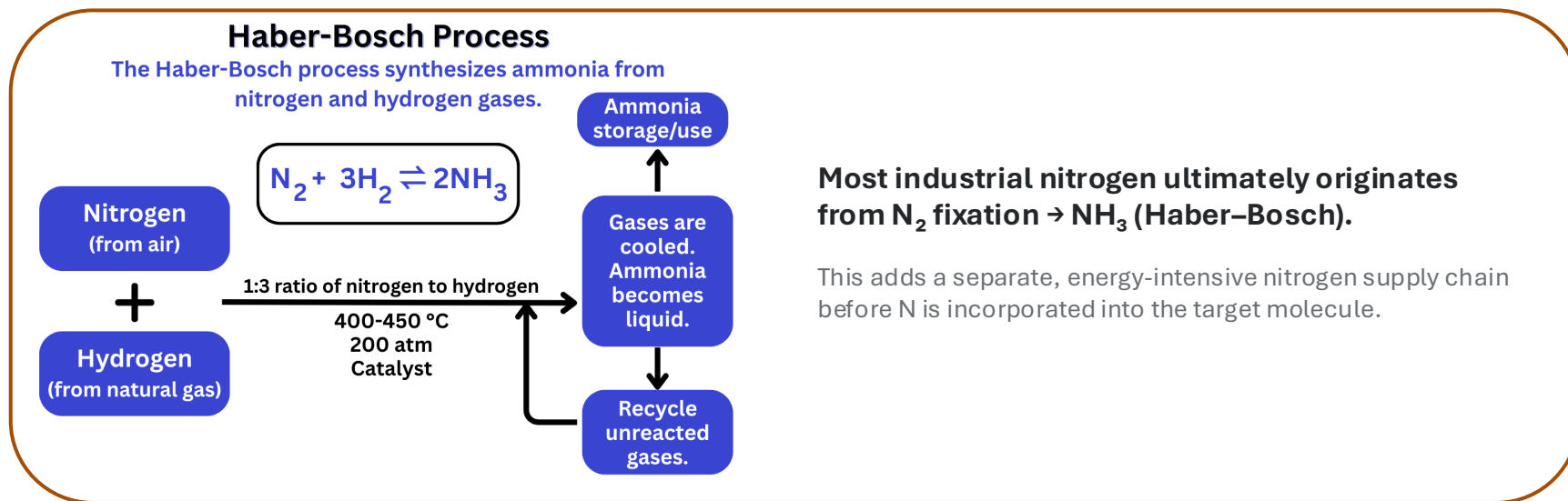
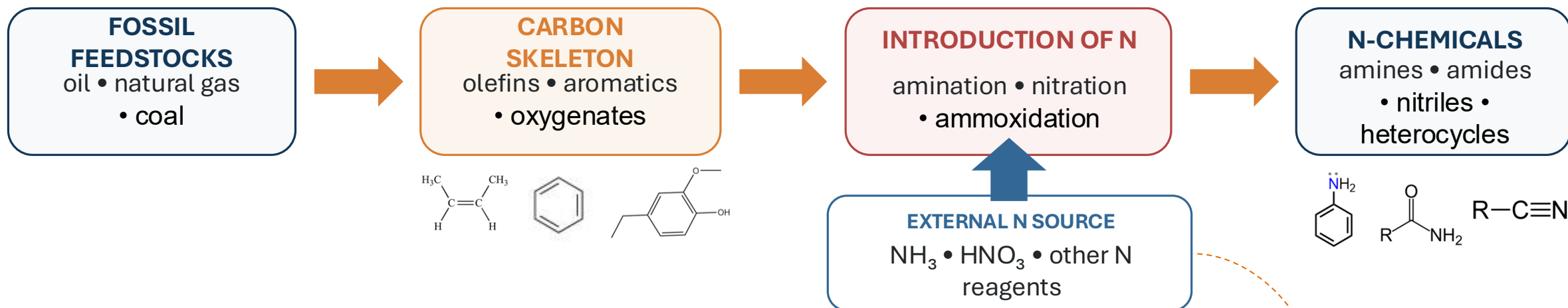


Chemical functional groups in polysaccharides

FUNCTIONAL GROUP	TYPICAL POLYSACCHARIDES	CHEMICAL FEATURE	EFFECT ON PROPERTIES
Hydroxyl -OH	Cellulose, starch, hemicellulose, dextran	H-bond donor & acceptor	Hydrophilicity • H-bonding • crystallinity • chemical reactivity
Carboxyl -COOH / -COO ⁻	Pectin, alginate, oxidised cellulose	pH-dependent negative charge	Water affinity • solubility • ion binding • swelling • gelation
Acetyl -COCH ₃	Hemicelluloses	Reduces available -OH	↓ hydrophilicity • altered solubility • H-bonding • accessibility
Amino -NH ₂ / -NH ₃ ⁺ Acetamido -NHCOCH ₃	Chitosan , chitin	pH-dependent positive charge	Solubility at acidic pH • ionic interactions • adsorption • reactivity

Conventional production of N-containing compounds

Nitrogen is commonly introduced into fossil-derived carbon skeletons in additional chemical steps



Conventional production of N-containing compounds

Key drawbacks

Fossil carbon dependence

Non-renewable feedstocks and associated greenhouse-gas emissions.

Extra synthetic steps

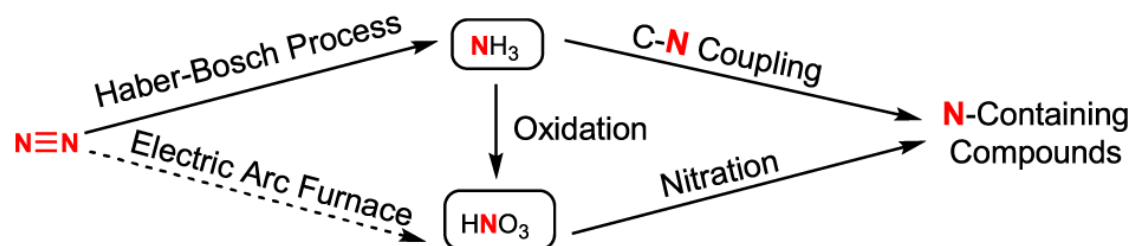
Nitrogen must be introduced after the carbon skeleton has been produced.

Harsh reagents & conditions

Processes may require NH_3 , HNO_3 , H_2 , high temperature/pressure or strong catalysts.

Waste & selectivity

Multi-step functionalisation can generate salts/by-products and require extensive purification.



Opportunity: use N-containing biomass such as CHITIN → carbon and nitrogen are already present in the same renewable feedstock.

Crab shells



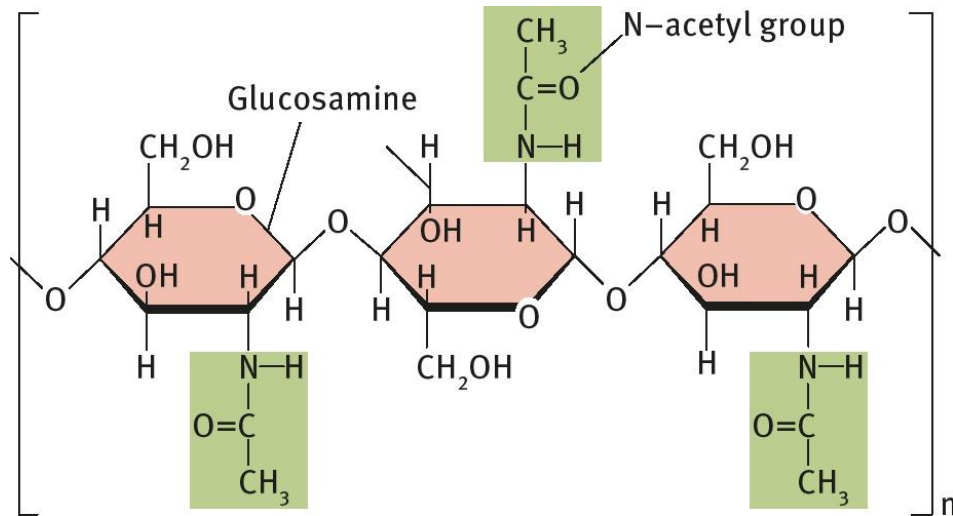
Crab shells* are primarily composed of :

- **calcium carbonate** (40–60%) - Forms the hard, mineralized matrix that gives the shell its rigidity, structural strength, and resistance to external stress
- **chitin** (15–30%) - A tough, fibrous natural biopolymer made of modified glucose units that provides flexible structural integrity and acts as the scaffolding framework
- **proteins** (15–40%) – Organic molecules interwoven tightly with the chitin fibers to form a complex, resilient matrix
- **Minor Components:**
 - **Carotenoids:** Pigments like astaxanthin that give the outer shell its characteristic color
 - **Trace Minerals:** Small quantities of elements such as magnesium, phosphorus, sodium, and iron

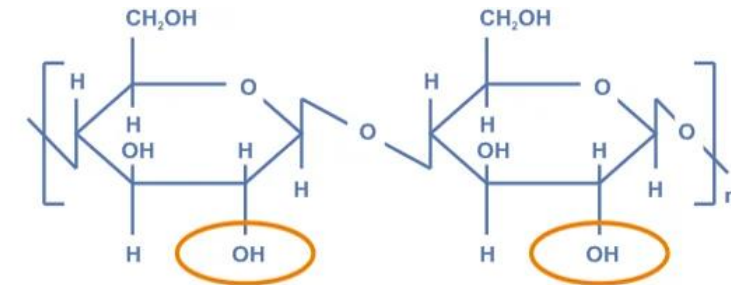
*shell composition depends on species/source

Chitin

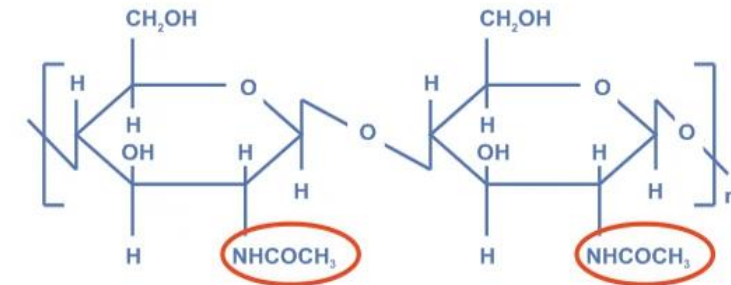
Chitin is a long, unbranched linear polysaccharide made of repeating units of *N*-acetyl-D-glucosamine linked together by **β - (1 $\rightarrow$ 4) glycosidic bonds**



Difference from Cellulose: It is very similar to cellulose, but instead of a hydroxyl (-OH) group on carbon-2 of each sugar ring, chitin has an **acetamido group**



Cellulose



Chitin

Nawrotek, K., Zarzycki, R., & Modrzejewska, Z. (2010). How to change a shrimp into an intelligent drug carrier? *Copernican Letters*, 1, 18–25.
DOI: 10.12775/CL.2010.003

From shell to chitin and to chitosan

Deproteinization – removal of proteins

- Chemical: typically 1–5 M NaOH
- Temperature: ~60–100 °C
- Time: ~1–6 h

Demineralization – removal of CaCO_3 and other minerals

- Chemical: typically 0.5–2 M HCl
- Temperature: room temperature (~20–30 °C)
- Time: ~0.5–3 h
- HCl dissolves CaCO_3 , producing soluble CaCl_2 and releasing CO_2

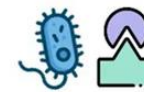
Deacetylation – chitin → chitosan

- Chemical: concentrated NaOH, typically 40–50 wt%
- Temperature: ~80–120 °C
- Time: ~1–5 h
- Removes acetyl groups ($-\text{NHCOCH}_3$), generating free amino groups ($-\text{NH}_2$).
- Chitosan is generally obtained when the degree of deacetylation is >50%, although commercial materials often have substantially higher values

Chemical extraction



Biological extraction



Source

Alkaline treatment
NaOH

Deproteinization

Proteases

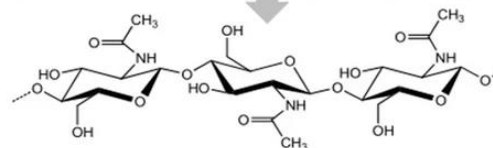
usually under much milder conditions:
(T ~30–60 °C, several hours)

Acid treatment
HCl

Demineralization

Lactic acid-producing
bacteria

fermentation with lactic-acid-producing
bacteria:
typically 1–3 days at ~30–40 °C



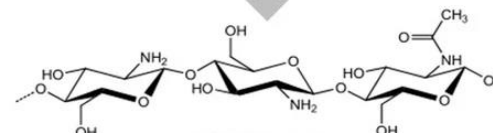
Chitin

Alkaline treatment
NaOH

Deacetylation

Deacetylases

chitin deacetylases under considerably
milder conditions



Chitosan

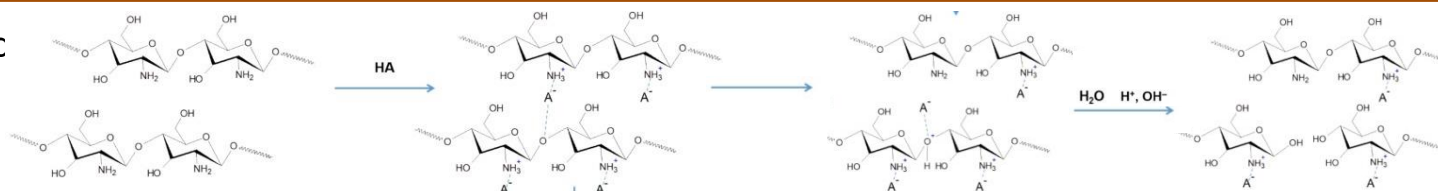
Yabushita et al., 2015, ChemSusChem, 8, 3760–3763. DOI: 10.1002/cssc.201501224
Verardi et al., 2023, Clean Technologies and Recycling, 3, 4–43. DOI: 10.3934/ctr.2023002
El-Araby et al., 2023, Frontiers in Chemistry, 11, 1327426. DOI: 10.3389/fchem.2023.1327426

Chitin and chitosan depolymerization

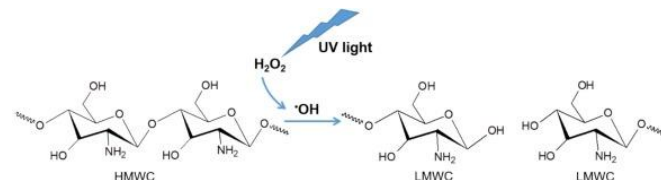
Depolymerization of chitin and chitosan breaks their long polymer chains into smaller fragments, such as chitooligosaccharides (COS) or monosaccharides, to improve solubility and facilitate further chemocatalytic conversion into added value N-containing chemicals.

Depolymerization Methods

Acid Hydrolysis: Uses strong acids like hydrochloric acid (HCl) or acetic acid to protonate glycosidic bonds, causing water molecules to cleave the polymer chain

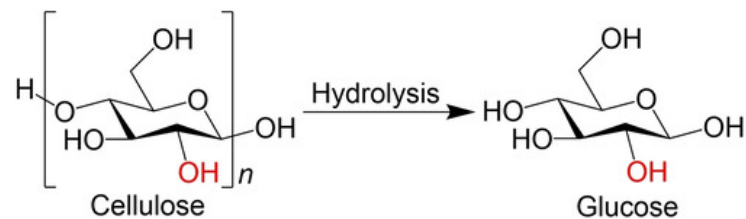


Oxidative Degradation: Employs oxidizing agents like hydrogen peroxide (H_2O_2), often paired with gamma or microwave irradiation, to split bonds efficiently via free radicals

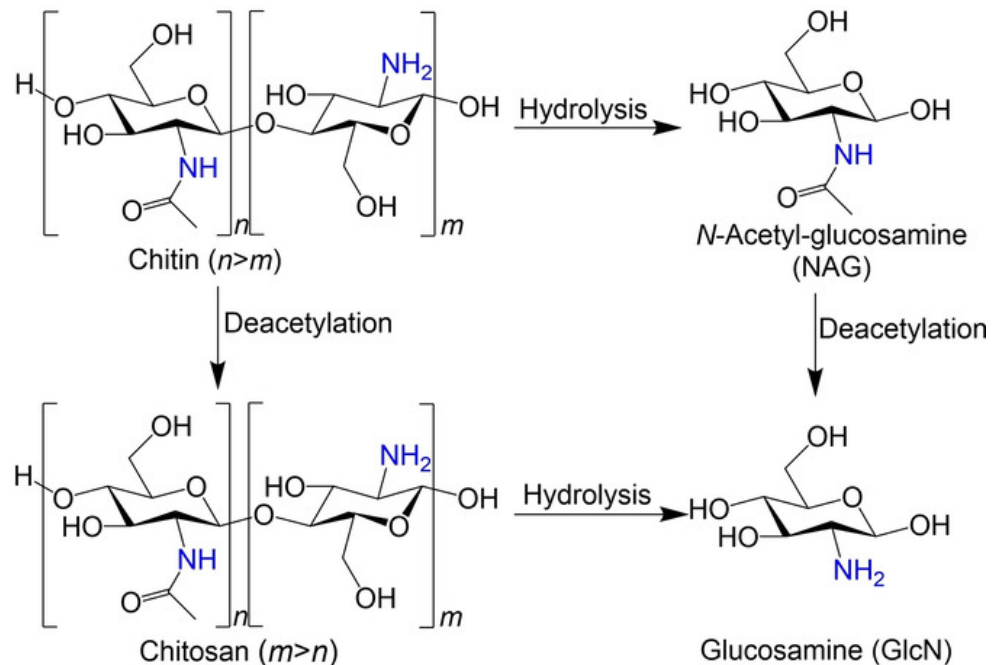


Enzymatic Cleavage: Uses specific enzymes like chitosanases, chitinases, or non-specific cellulases to target and break glycosidic links under mild, eco-friendly conditions

Chitin and chitosan depolymerization

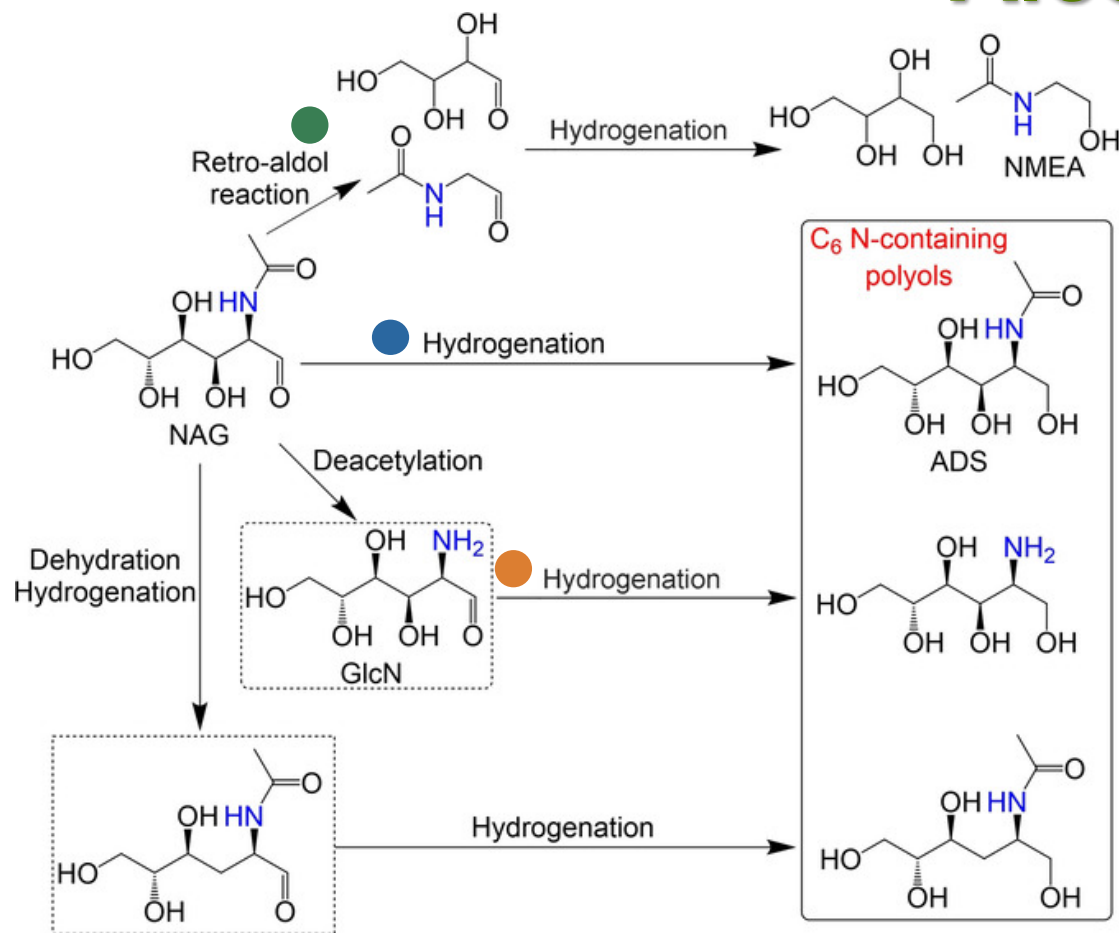


Both chitin and chitosan are typical N-containing biopolymers, and the structures of them are similar to that of cellulose.



N-Acetyl-glucosamine (NAG) and **glucosamine (GlcN)** are the main monomers of chitin and chitosan

Chemocatalytic Conversion of Chitin to Amino Alcohols



● Retro-aldol + hydrogenation

C–C cleavage generates shorter-chain N-containing products, including NMEA (N-acetylmonoethanolamine).

● Direct hydrogenation

Reduction of the aldehyde group gives C₆ N-containing polyols.

● Deacetylation + hydrogenation

Removal of the acetyl group forms glucosamine-derived amino polyols.

Reaction conditions

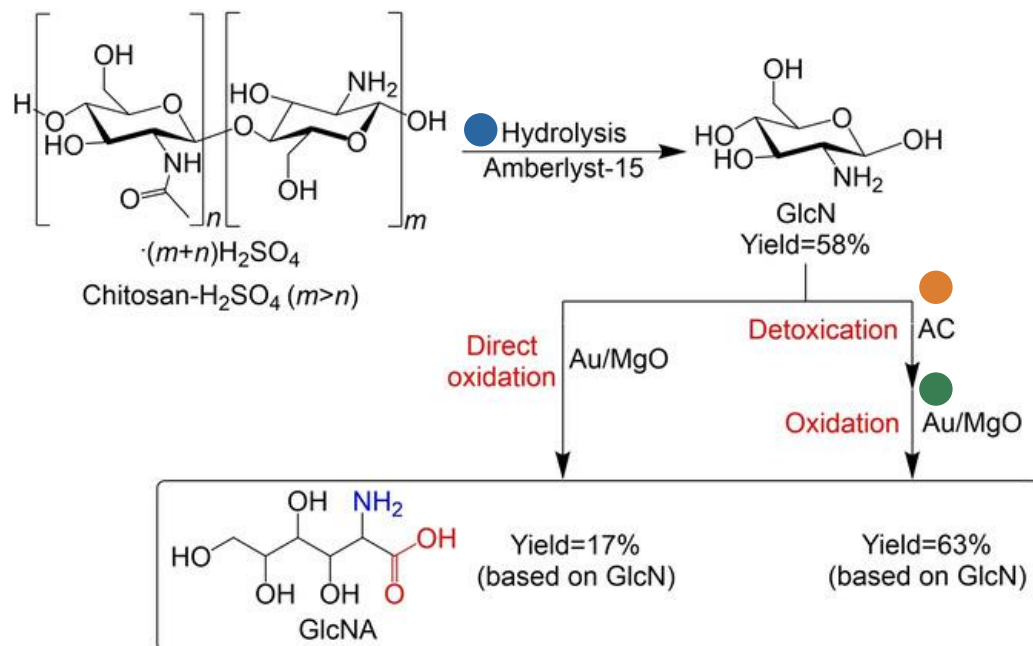
Ru/C
H₂ (40 bar)
aqueous phase
elevated temperature (180 °C)
C₆ N-containing polyols,
reaching about **72% yield**

Key advantage: the nitrogen already present in chitin is retained in valuable products.

USAGE: Pharmaceutical intermediates, functional polymers, surfactants, N-containing fine chemicals

DOI: 10.1039/c4gc01631a

Chemocatalytic Conversion of Chitin to Amino Acids



renewable production of a functional amino acid without introducing N into a fossil carbon skeleton.

1 Hydrolysis

Chitosan is hydrolysed over the solid acid catalyst Amberlyst-15 to glucosamine (GlcN).

2 Detoxification

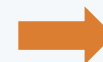
Activated carbon removes hydrolysis-derived impurities (humin-like by-products) that inhibit the oxidation catalyst (Au/MgO).

3 Selective oxidation

GlcN is oxidised over Au/MgO to D-glucosaminic acid (GlcNA), retaining the amino functionality.

Effect of detoxification

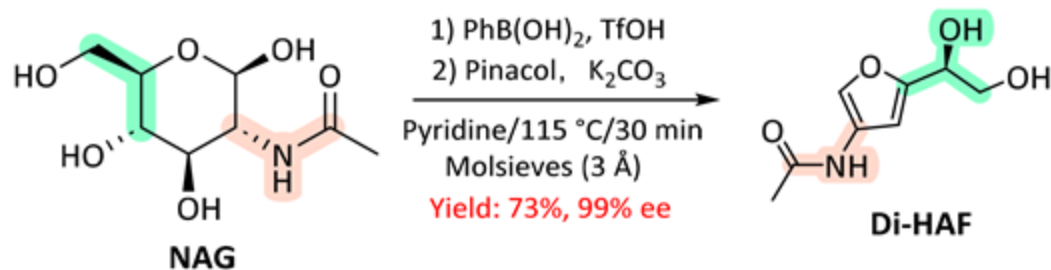
17%
direct oxidation



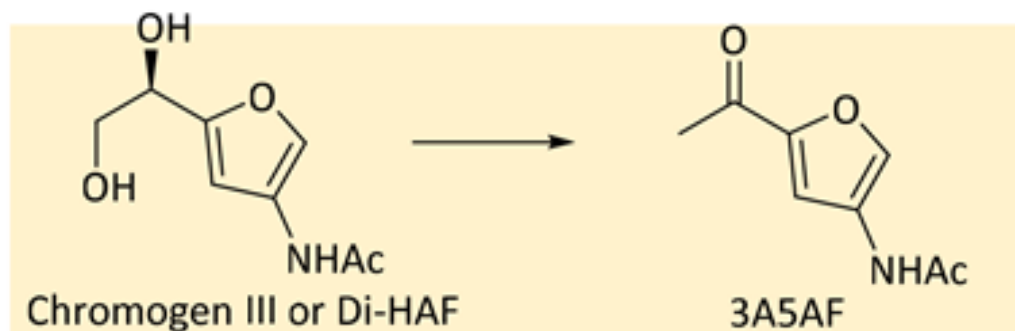
63%
after detoxification

USAGE: chiral building block, pharmaceuticals & fine chemicals, glycosidase inhibitors / amino-acid synthesis, metal-chelating ligands, functional materials

Chemocatalytic Conversion of Chitin to N-containing furans



Acid-catalysed **dehydration and cyclisation** of N-acetyl-D-glucosamine (NAG) to the chiral N-containing furan **Di-HAF** (dihydroxyethyl acetamidofuran)



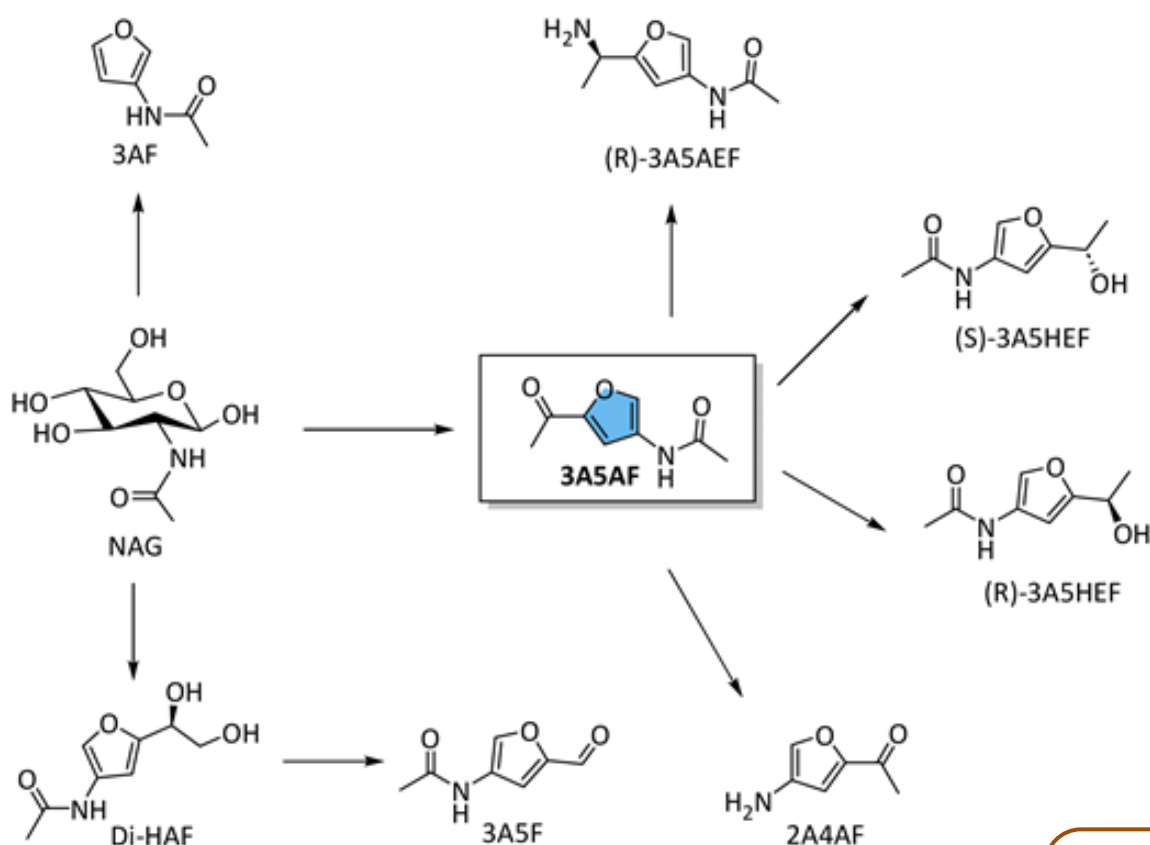
Acid-catalysed **dehydration** of Di-HAF into 3-acetamido-5-acetylfuran (3A5AF), where the **1,2-dihydroxyethyl side chain of Di-HAF is converted into an acetyl group**, and **acetamido functionality is retained**.



Funded by
the European Union



Chemocatalytic Conversion of Chitin to N-containing furans



Once 3A5AF is obtained, its two functional groups—the **acetamido group** and **acetyl side chain**—allow several selective catalytic transformations. These include **hydrogenation/reduction**, **reductive amination**, **deacetylation**, and further **oxidation** or **dehydration** reactions

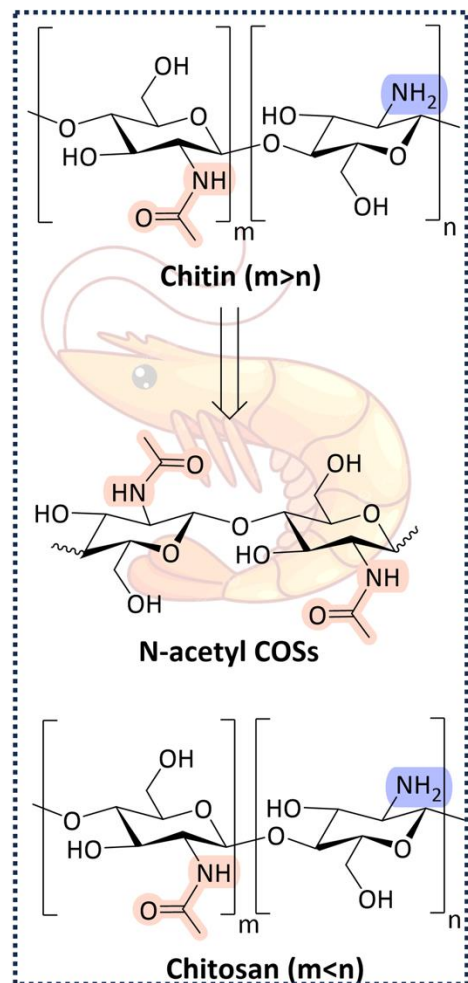
Catalytic transformations:

- **Dehydration / cyclisation** → N-containing furans
- **Hydrogenation / reduction** → chiral furan alcohols
- **Reductive amination** → N-rich furan derivatives
- **Deacetylation** → free amino functionality
- **Oxidation** → functionalized furan intermediates
- **Diels–Alder + aromatization** → N-containing aromatics

Potential applications

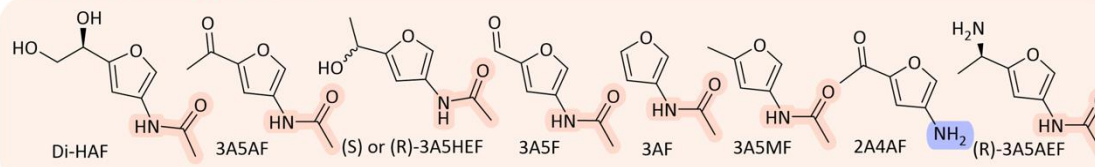
Pharmaceutical precursors, fine chemicals, N-heterocycles, chiral building blocks, N-containing aromatics, polymer/material precursors

Chemocatalytic Conversion of Chitin and Chitosan

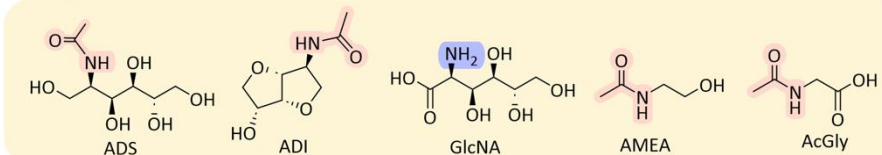


Wang et al., 2025, Green Chem., 27, 3601–3626.
DOI: 10.1039/D4GC05368K

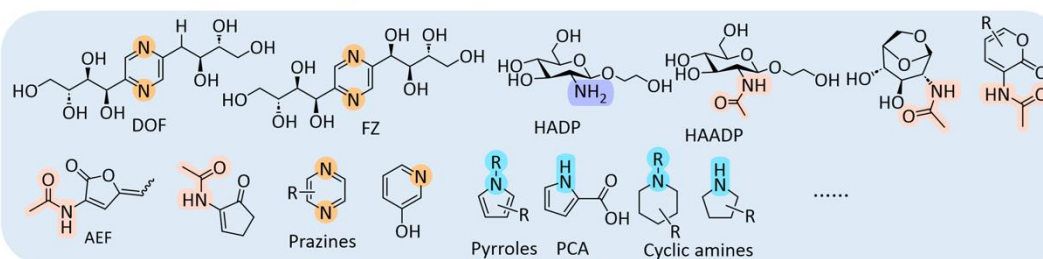
N-containing furans



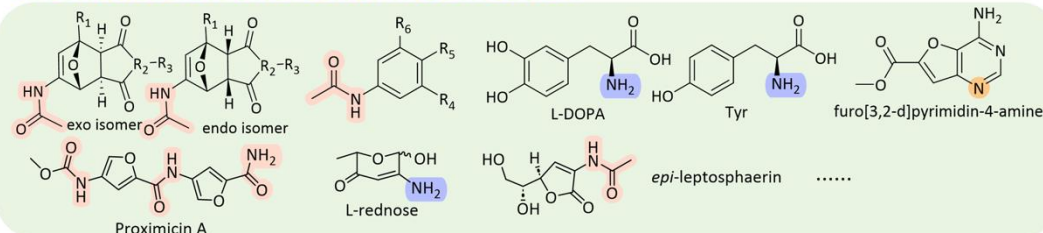
Polyols and amino acids



N-containing heterocyclic compounds



Aromatization and other modification



Conclusions

- **Polysaccharides are more than structural biopolymers – they are renewable feedstock for the sustainable chemicals**
- **Chemical functionality defines valorisation pathways**
–OH, –COOH, –NH₂ and –NHAc groups determine **reactivity, selectivity and accessible products**
- **Cellulose & hemicellulose provide renewable carbon platforms**
Depolymerisation to sugars followed by **oxidation, hydrogenation and deoxydehydration** enables access to platform chemicals and monomers, including **bio-based adipic acid**.
- **Chitin & chitosan offer an additional advantage: naturally incorporated nitrogen**
Their monomers, **NAG and GlcN**, contain both carbon and nitrogen, avoiding the need to introduce N into an already prepared carbon skeleton.
- **Chemocatalysis opens multiple N-retaining pathways**
Hydrogenation → N-containing polyols
Oxidation → amino acids
Dehydration/cyclisation → N-containing furans

Understanding polysaccharide chemistry allows us to use the functionality already provided by nature to design selective catalytic routes toward renewable chemicals, monomers and materials.

Acknowledgement



COST (European Cooperation in Science and Technology) is a funding agency for research and innovation networks. Our Actions help connect research initiatives across Europe and enable scientists to grow their ideas by sharing them with their peers. This boosts their research, career and innovation.

THANK YOU FOR YOUR ATTENTION