SRIP CIRCULAR ECONOMY

REPUBLIC OF SLOVENIA
MINISTRY OF ECONOMIC DEVELOPMENT AND TECHNOLOGY

EUROPEAN UNION
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Strategic research and innovation partnership (SRIP) –
Networks for the transition to circular economy

Sustainable Business Models in Circular Bioeconomy

Local2Local: A Potential for Bio-refining in Eastern Europe?

KEMIJSKI INŠTITUT

Blaž Likozar, National Institute of Chemistry
23 September 2019 | Brussels

Investment is co-financed by the Republic Slovenia and the EU under the European Regional Development Fund.

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Context

- In Slovenia, the „Technologies for sustainable biomass transformation and new bio-based materials“ are a part of the „Networks for the transition to circular economy“
- „Networks for the transition to circular economy “ are 1 of 9 S4 (Slovenia's Smart Specialisation Strategy) Priority Areas
- The Priority Area is coordinated by a national cluster-like entity, Strategic Research and Innovation Partnership (SRIP) Networks for the transition into circular economy

SMART SPECIALISATION PLATFORM

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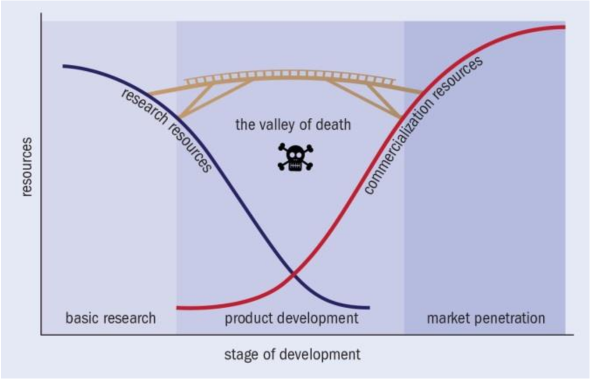
Why even interesting?

- In terms of relative forest coverage, Slovenia is the third in the European Union after Finland & Sweden (http://www.slovenia.si/slovenia/country/geography/slovenia-a-land-of-forests/).
- Existing chemical industry is strong (at least 25% among 1st 20 companies considering revenue or employees).
- There´s an interest to increase bio-based product share (European Bioeconomy in Figures 2008 – 2015, BIC, 2012, BIC, 2018).

(Source: http://www.slovenia.si)

But…

- European „Valley of death“: model of risk profile for companies of innovation processes.
- Slovenian (additional) „Valley of death“: lacking basic/commodity chemicals.
- Large-scale biomass bio-refinery optimal for Slovenia?



(Source: James Dacey, Navigating the valley of death, 2014)

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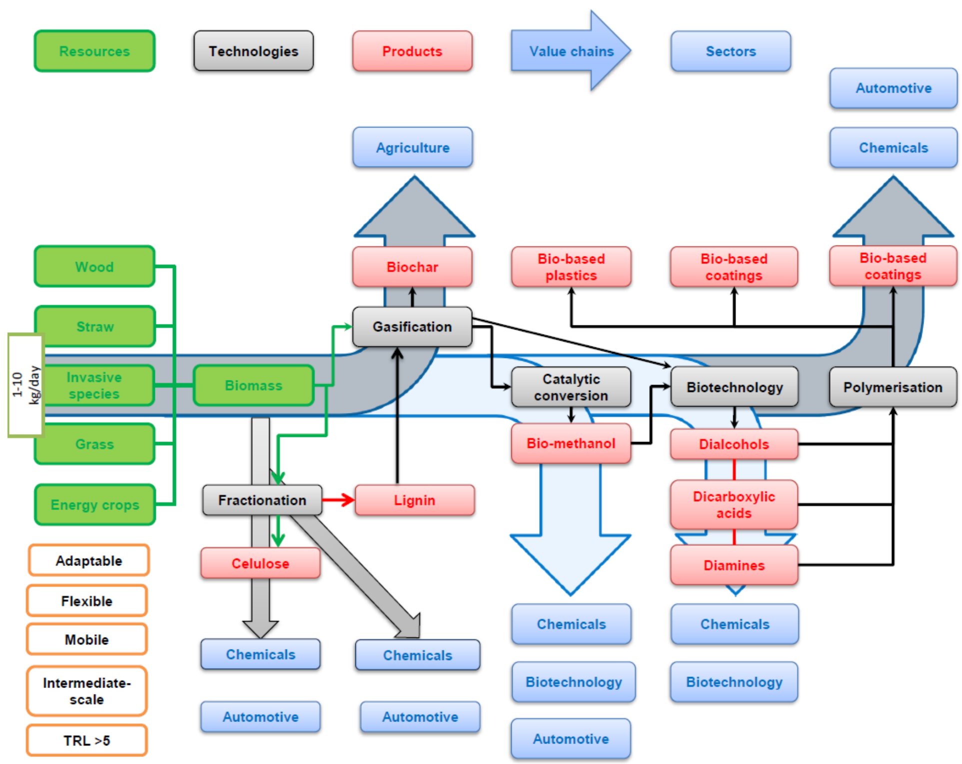
Local (hence smaller) bio-refinery concept (Slovenia)



Local (hence smaller) bio-refinery concept (Slovenia) (ctd.)

- Strength: abundant biomass resources / willing industrial partners.
- Weakness: middle of bio-chemicals/materials value chain missing / very high-CAPEX technologies.
- Threat: loss of competitive market advantage / not developing own bio-based processes (buying them).
- Opportunity: companies with strong bio-based interests / state-of-the-art chemicals or plastic production.

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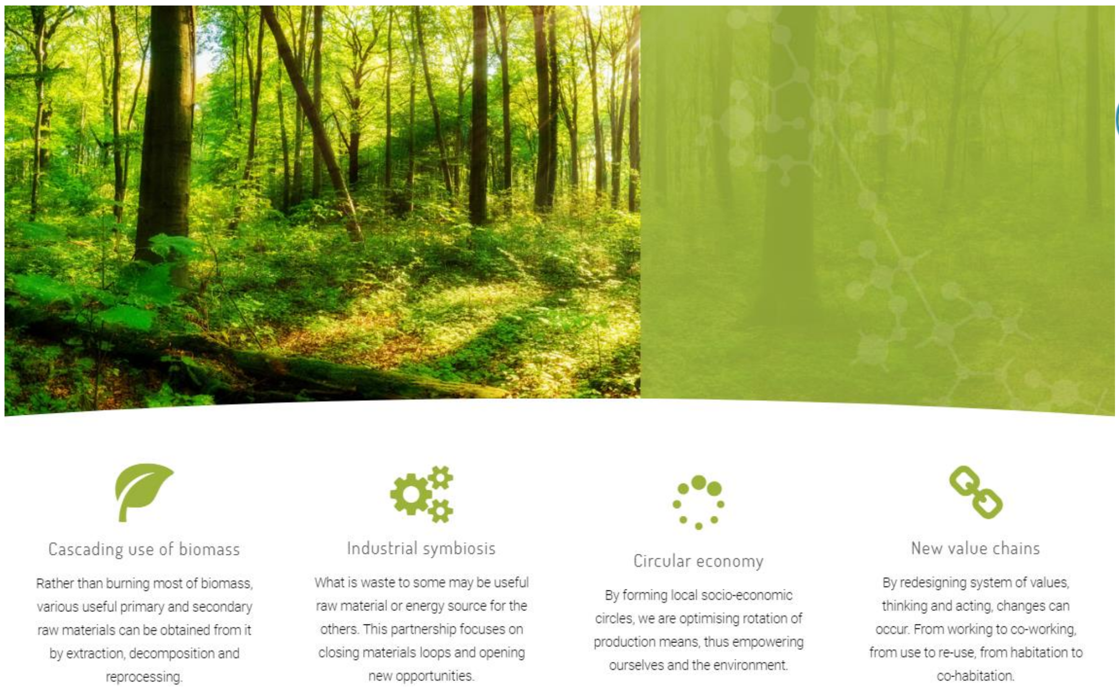
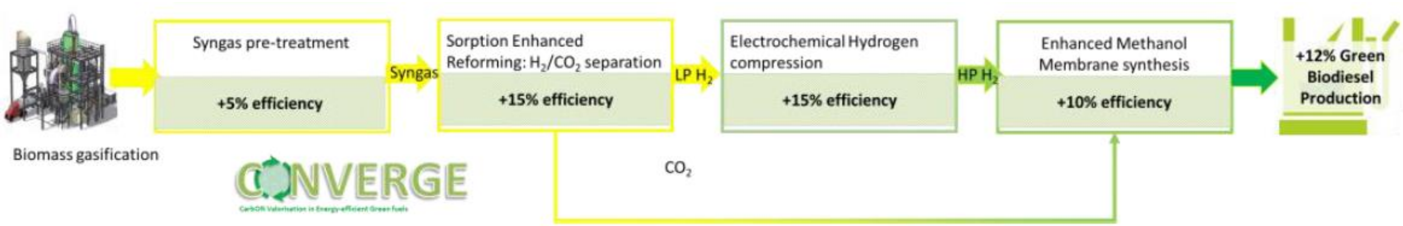
Related showcase projects:
CEL.CYCLE / CONVERGE



CELCYCLE
Discarded potentials of biomass

(CEL.CYCLE, 2019)



(CONVERGE, 2019)

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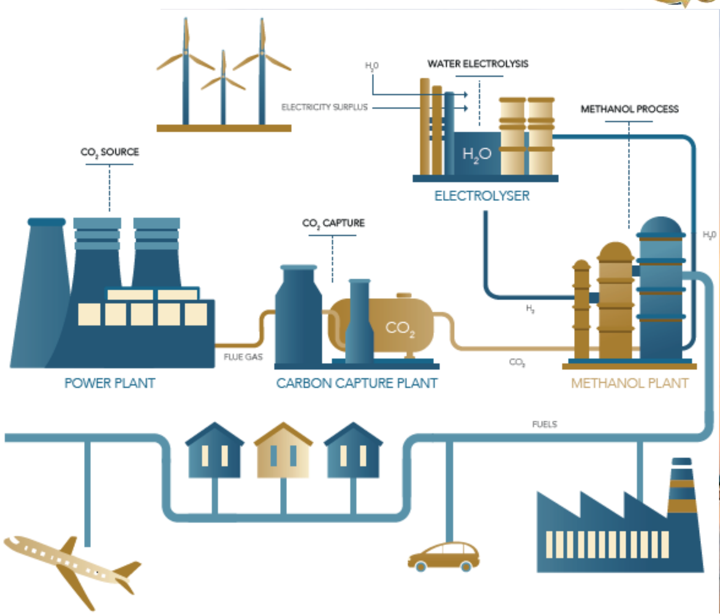
Related CCU showcase projects:
MefCO2 / FReSMe



(MefCO2, 2019)

(FReSMe, 2019)

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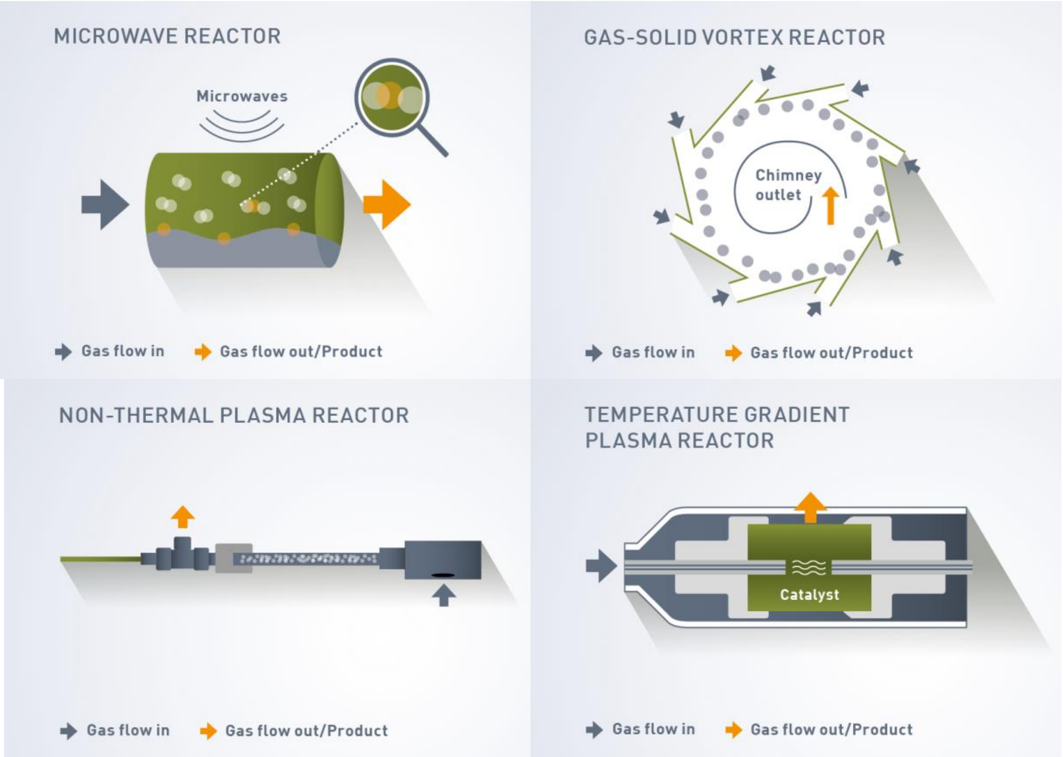
Related showcase projects: OPERH_2 / ADREM

(SRIP, 2019)



(ADREM, 2019)

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Bio-based company examples: **Helios**
Resource: oleo-chemicals
Product (*i.a.*): coatings

(Helios, 2019)

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Bio-based company examples: **Melamin**
Resource: bio-methanol
Product (*i.a.*): resins

(Melamin, 2019)

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Bio-based company examples: **Tanin**
Resource: wood
Product (*i.a.*): furfural

(Tanin, 2019)

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Bio-based company examples: **Acies Bio**
Resource: whey
Product (*i.a.*): chemicals

(Acies Bio, 2019)

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Thank you for your attention!

Contact:

Blaž Likozar
blaz.likozar@ki.si
T: 00386 1 4760 281

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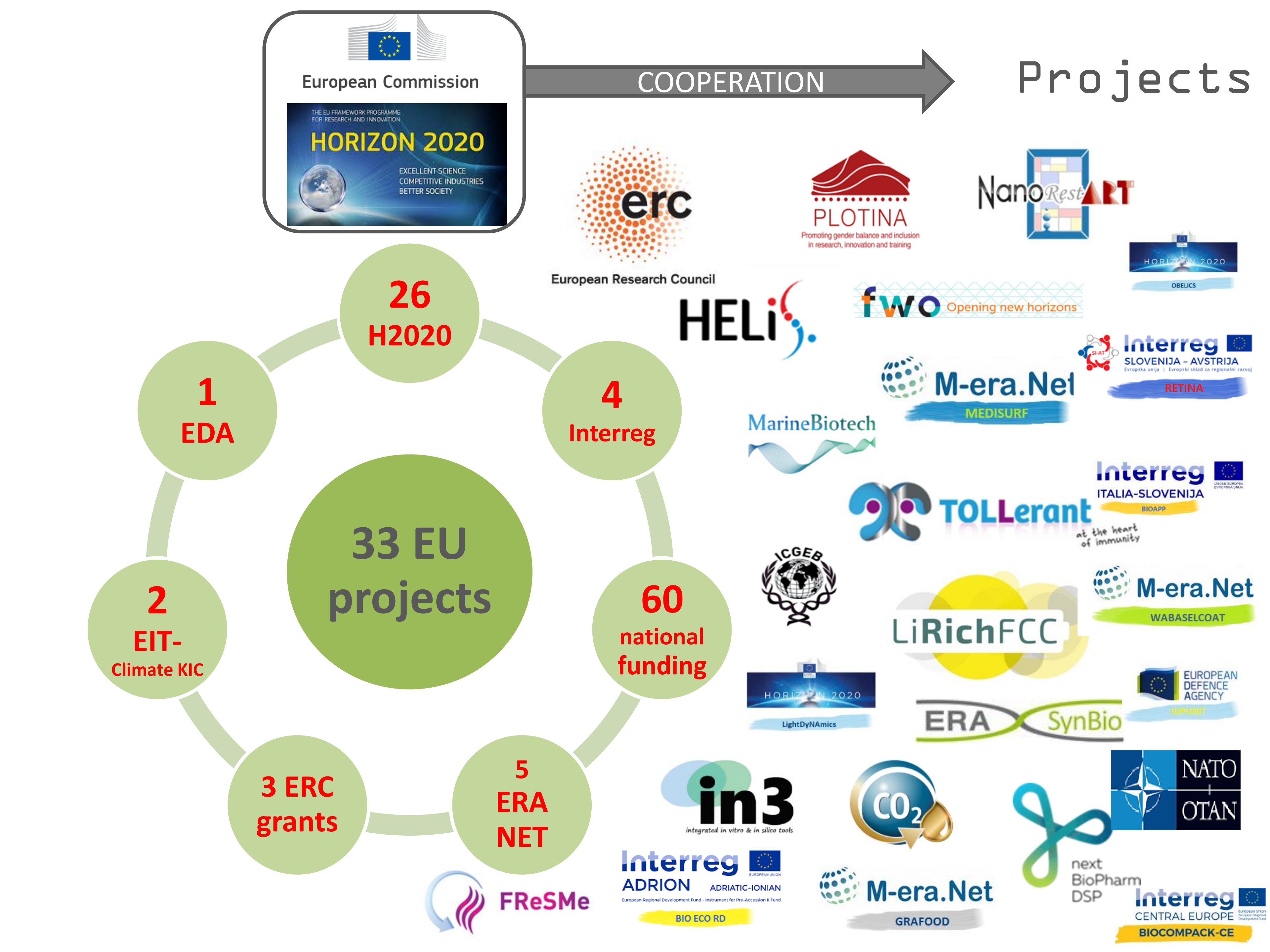
Investment is co-financed by the Republic Slovenia and the EU under the European Regional Development Fund



European Commission
THE EU FRAMEWORK PROGRAMME FOR RESEARCH AND INNOVATION
HORIZON 2020
EXCELLENT SCIENCE
COMPETITIVE INDUSTRIES
BETTER SOCIETY
COOPERATION
Projects
33 EU projects
26 H2020
4 Interreg
60 national funding
5 ERA NET
3 ERC grants
2 EIT-Climate KIC
1 EDA
erc
European Research Council
PLOTINA
Promoting gender balance and inclusion in research, innovation and training
NanoRestART
HORIZON 2020
OBELICS
HELiS
fwo Opening new horizons
Interreg
SLOVENIJA - AVSTRIJA
RETINA
M-era.Net
MEDISURF
MarineBiotech
Interreg
ITALIA-SLOVENIJA
BIOAPP
TOLLerant
at the heart of immunity
ICGEB
LiRichFCC
M-era.Net
WABASELCOAT
HORIZON 2020
LightDyNAmics
EUROPEAN DEFENCE AGENCY
ERA SynBio
NATO OTAN
in3
integrated in vitro & in silico tools
CO_2
next BioPharm DSP
FReSMe
Interreg
ADRION
ADRIATIC-IONIAN
BIO ECO RD
M-era.Net
GRAFOOD
Interreg
CENTRAL EUROPE
BIOCOMPACK-CE

National Institute of Chemistry, Slovenia
Department of Catalysis and Chemical Reaction Engineering

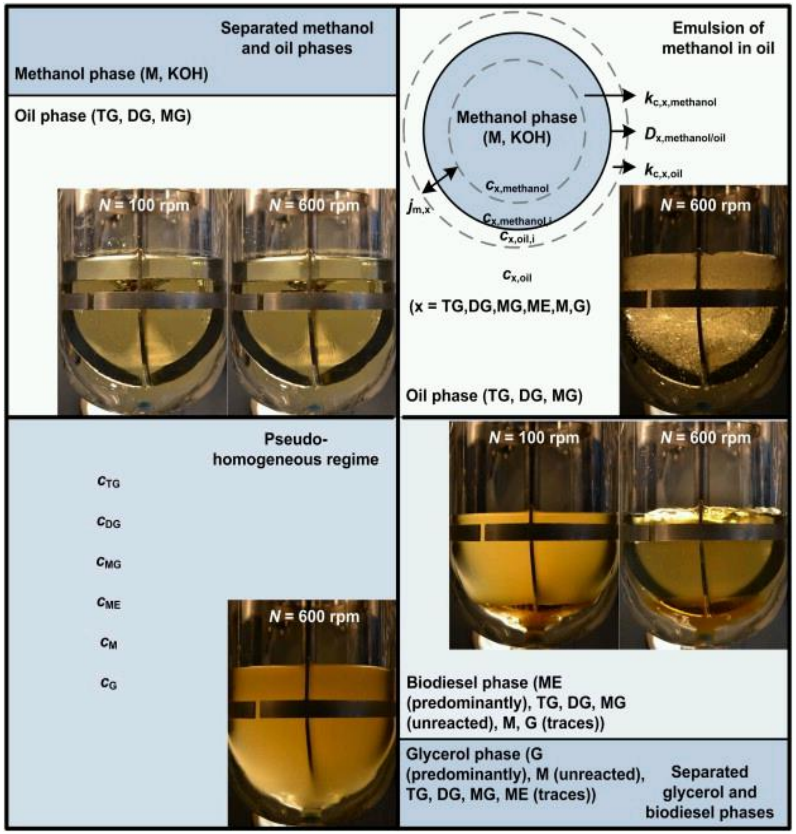
Research topics

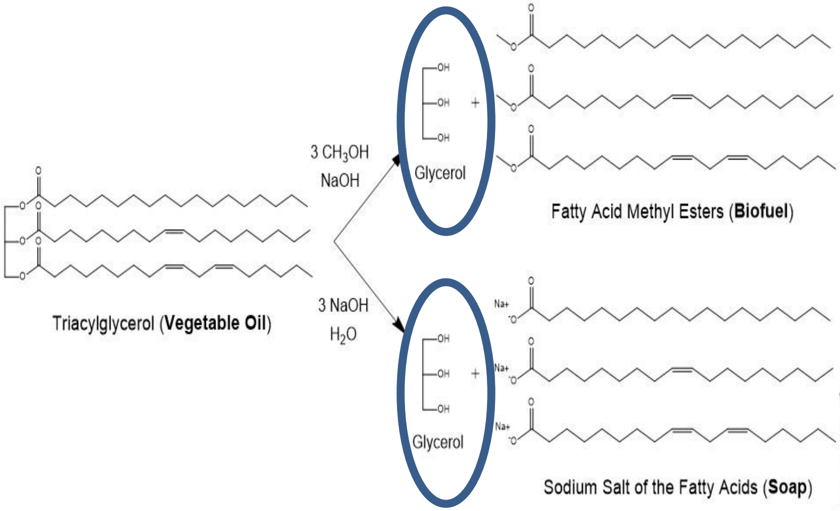
- Research subfield: Carbon dioxide activation
- Research subfield: Methane activation & conversion
- Research subfield: Hydrogen & fuel cells & electrocatal.
- Research subfield: Pharmaceutical process engineering
- Research subfield: **Biomass-derived building blocks**

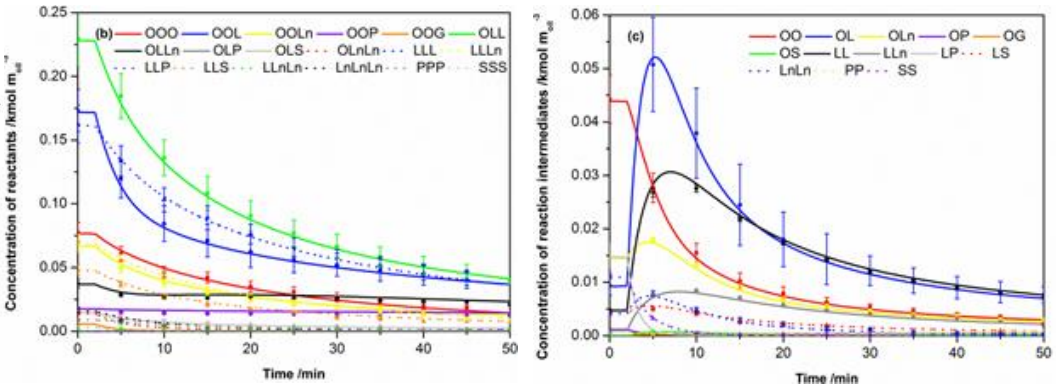
CONCEPT: BIOREFINERY

PAST WORK: 1ST GENERATION BIOFUELS

- Transesterification of vegetable oils
- Novel kinetic model based on different glyceride and fatty acid ester composition
- Integration of thermodynamics, fluid mechanics, transport phenomena and chemical kinetics
- Batch, continuous and membrane reactor operation using homogeneous, heterogeneous inorganic and enzymatic catalysis

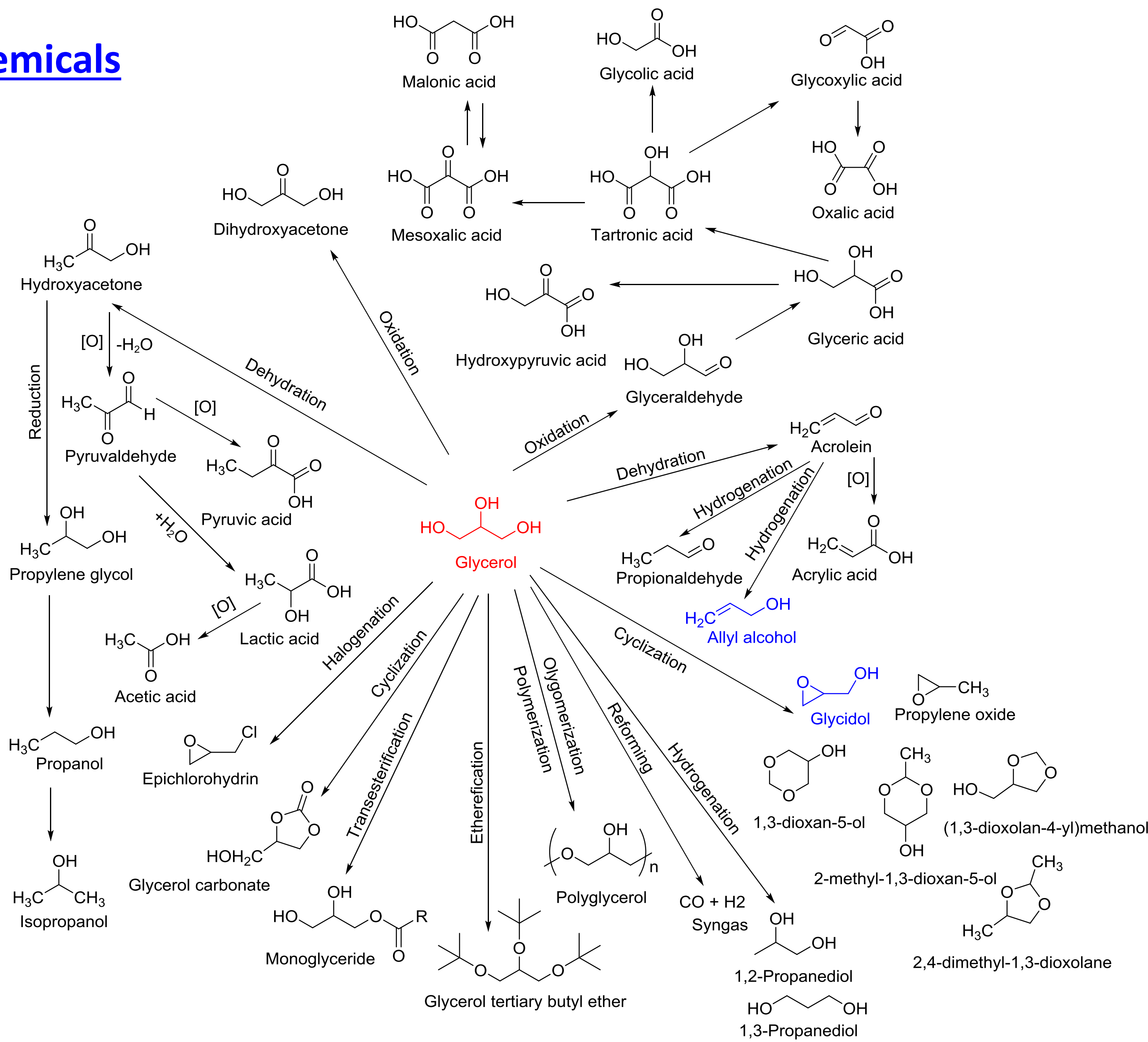




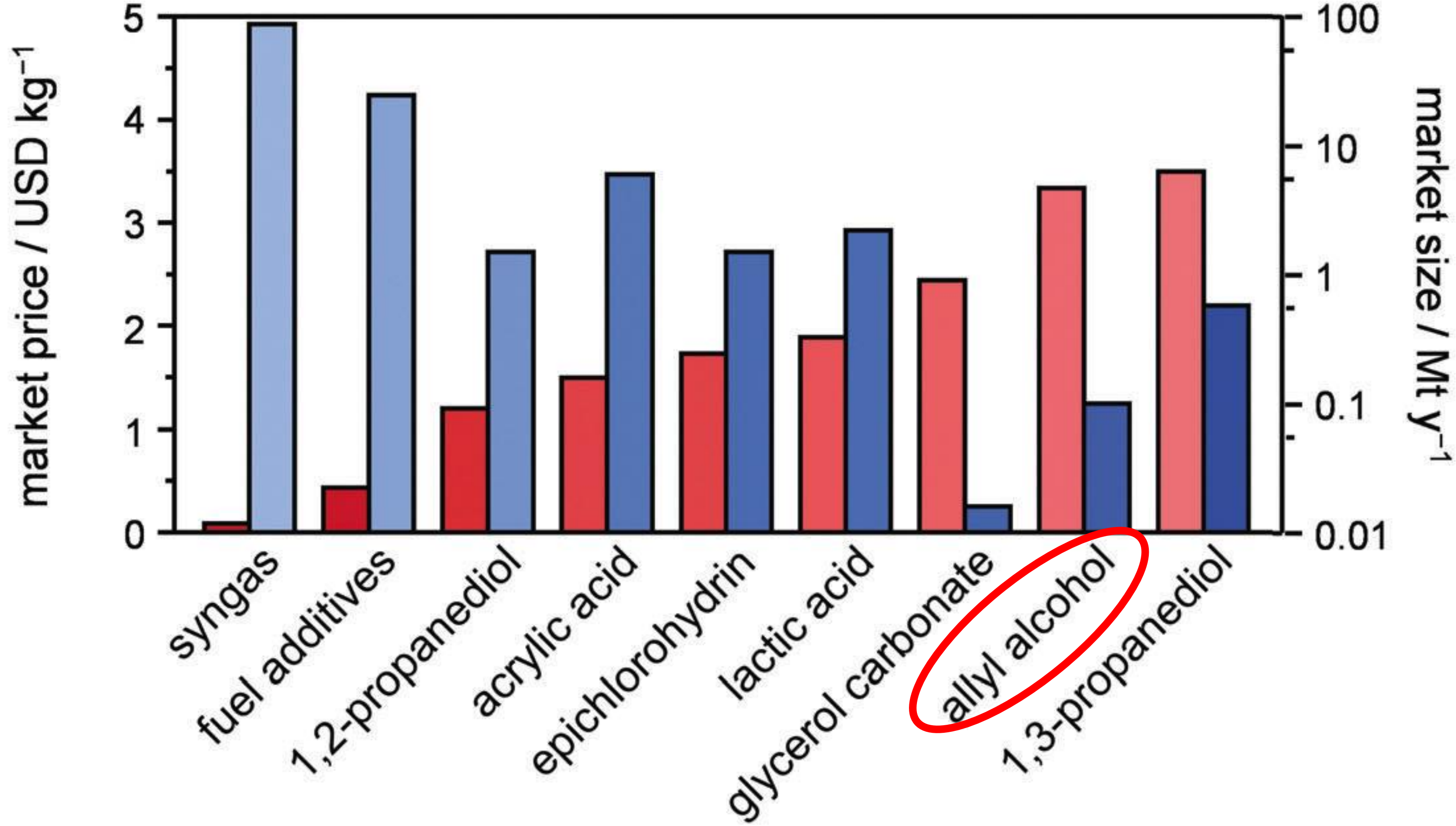


1. Blaž Likozar *et al.*, *Fuel Process Technol.*, **2016**, *142*, 326.
2. Blaž Likozar and Janez Levec, *Appl. Energ.*, **2014**, *123*, 108.
3. Blaž Likozar and Janez Levec, *Fuel Process Technol.*, **2014**, *122*, 30.

Commodity Chemicals from Glycerol



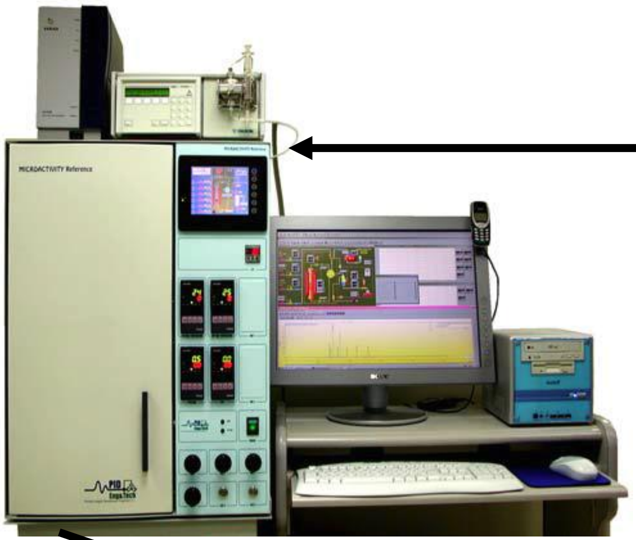
Market size and price of glycerol derivatives



G.M. Lari, G. Pastore, M. Haus, Y. Ding, S. Papadokonstantakis, C. Mondelli, **J. Perez-Ramirez**, Environmental and economical perspectives of a glycerol biorefinery, **Energy Environ. Sci. (2018).**

Catalyst Testing

Process Integral Development



Microactivity Reference (PID Eng&Tech):

(i) mass flow controllers for feeding N_2 (Messer, 99.999%);
(ii) a high-performance liquid chromatography (HPLC) pump for the feeding of the glycerol solution;
(iii) a tubular stainless steel microreactor (i.d.=6 mm) heated in an oven, and
(iv) a liquid–gas separator located downstream of the reactor and kept at 273 K.

Reactor Characteristics:

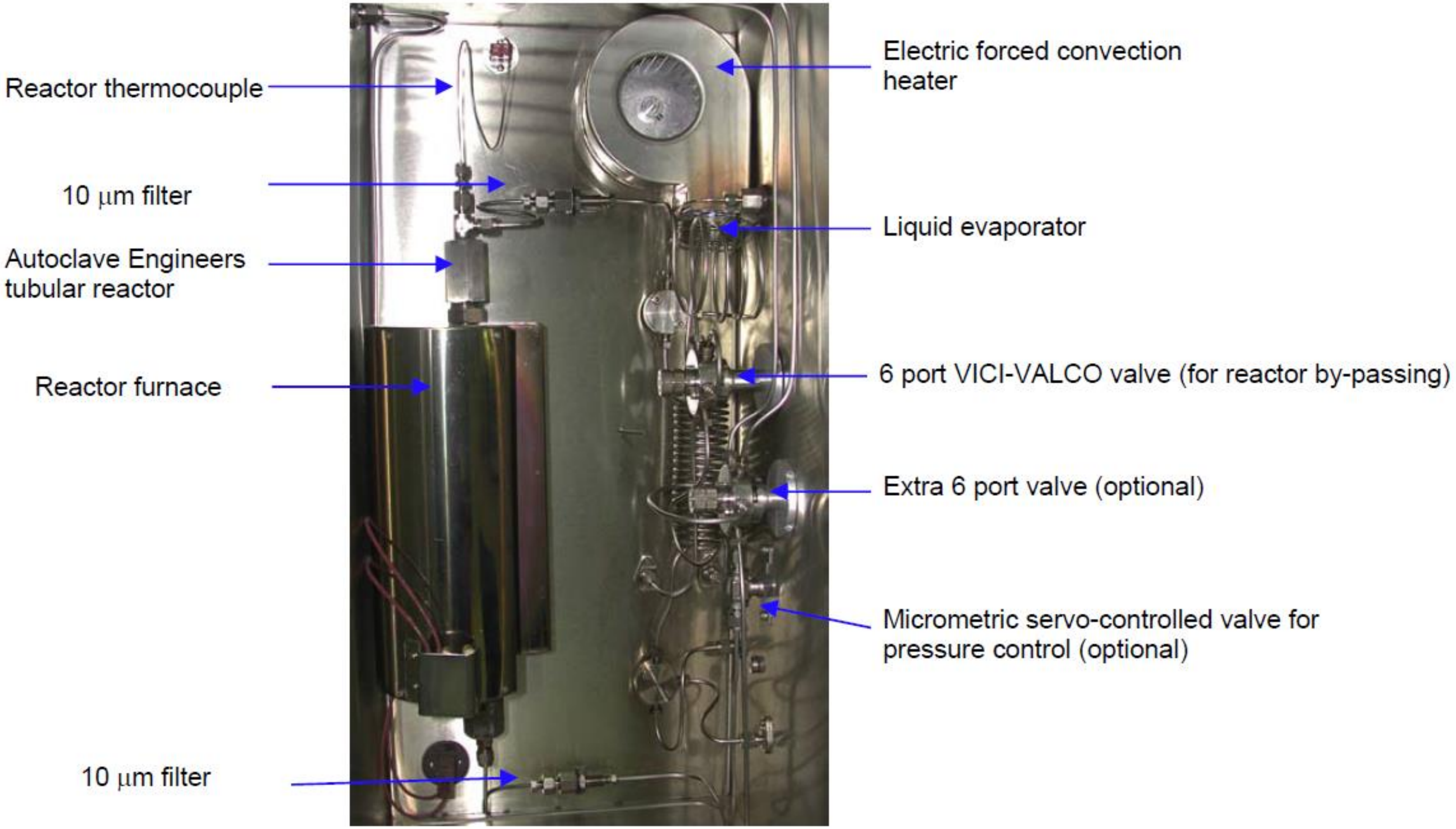
- Maximum working pressure up to 100 ± 0.1 bar.
- Maximum working temperature up to 700ºC ± 1ºC.
- 3x high precision mass flow controllers with digital communications.
- It operates with flows that range from tens of ml/min to even liters/min.
- Thermocouple placed directly in catalyst bed.

GC-MS Agilent 7890A with Agilent 5975C mass detector

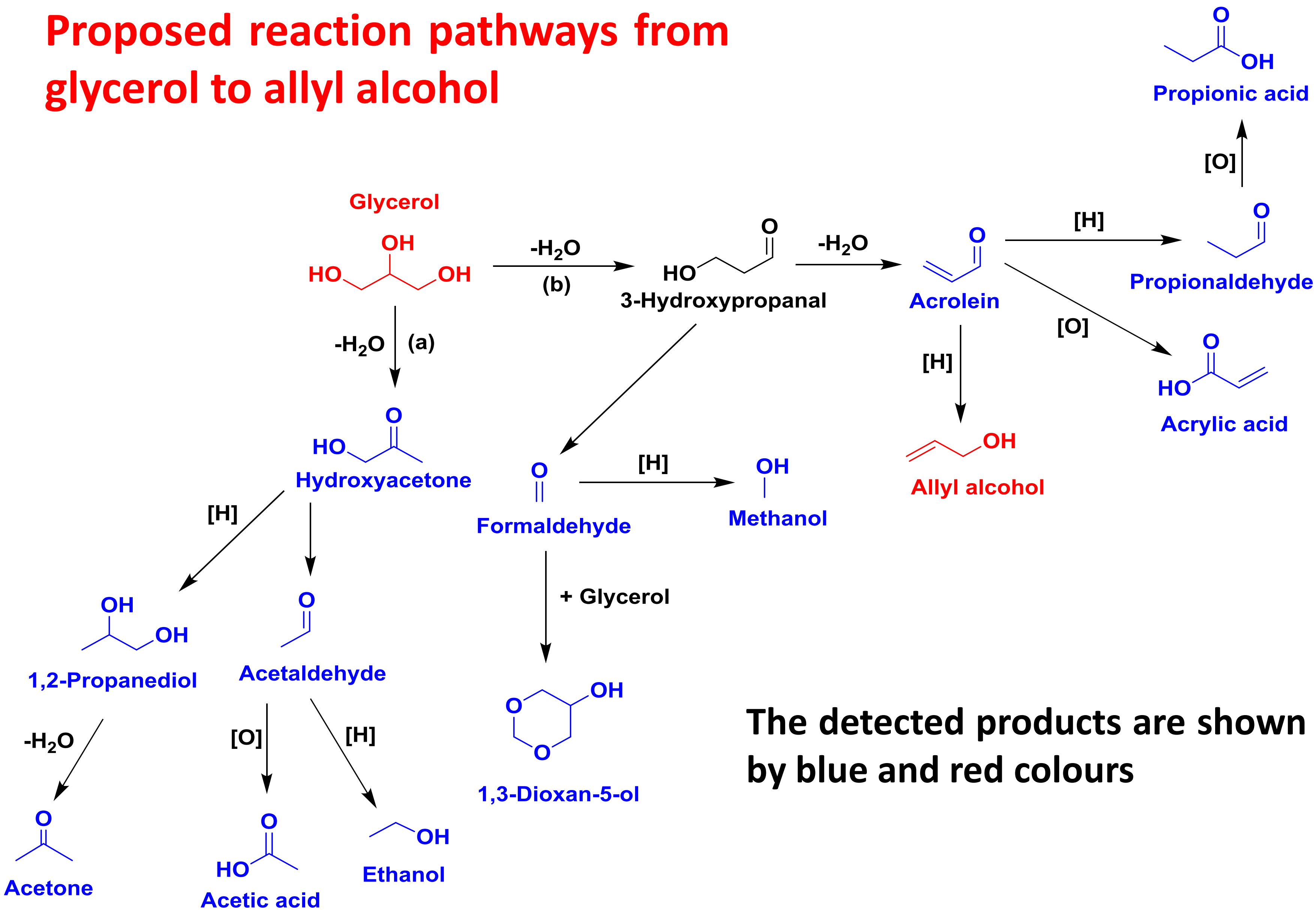
DB-WAX Ultra Inert
30m, 0.25mm, 0.25μm GC column

Catalyst Testing

Setup is used for the Continuous Gas-Phase Conversion of Glycerol

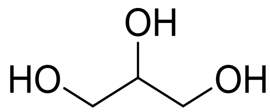
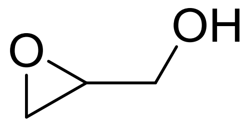


Proposed reaction pathways from glycerol to allyl alcohol



The detected products are shown by blue and red colours

Comparison of glycerol and glycidol compounds

Name	Chemical Formula	Chemical Structure	Price $/kg	Application
Glycerol	$C_3H_8O_3$		**0.1-0.6**	Cosmetics, soaps, pharmaceuticals and personal care products, food and tobacco industries.
Glycidol	$C_3H_6O_2$		**546-24200**	Chemical intermediate in organic synthesis, precursor of pharmaceuticals, perfumes and cosmetics, detergents, paints, demulsifiers, dye levelling agent, synthesis of antiviral and analgesic drugs. Especially an important group of antiviral drugs constitute active compounds fighting HIV.

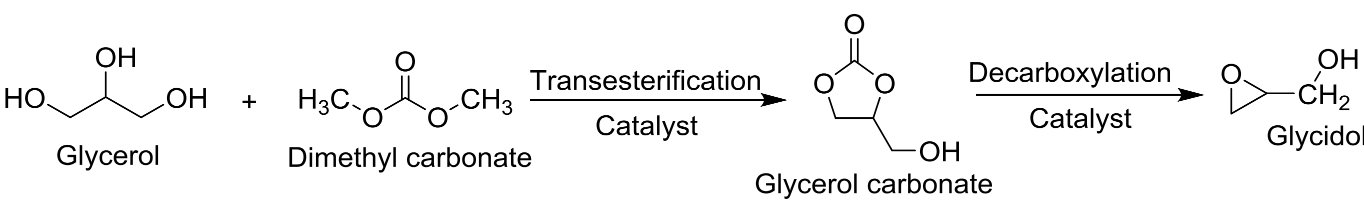
Green glycidol pilot plant in the UK

- Green Lizard Technologies (GLT)
- Queen's University Belfast
- Dixie Chemicals and Felda Global Ventures

If the pilot plant is successful, GLT and its development partners will invest around £17m (US$ 25m) for a full-scale production plant, which could open as early as 2021.

https://www.thechemicalengineer.com/news/green-glycidol-pilot-plant-in-the-uk/

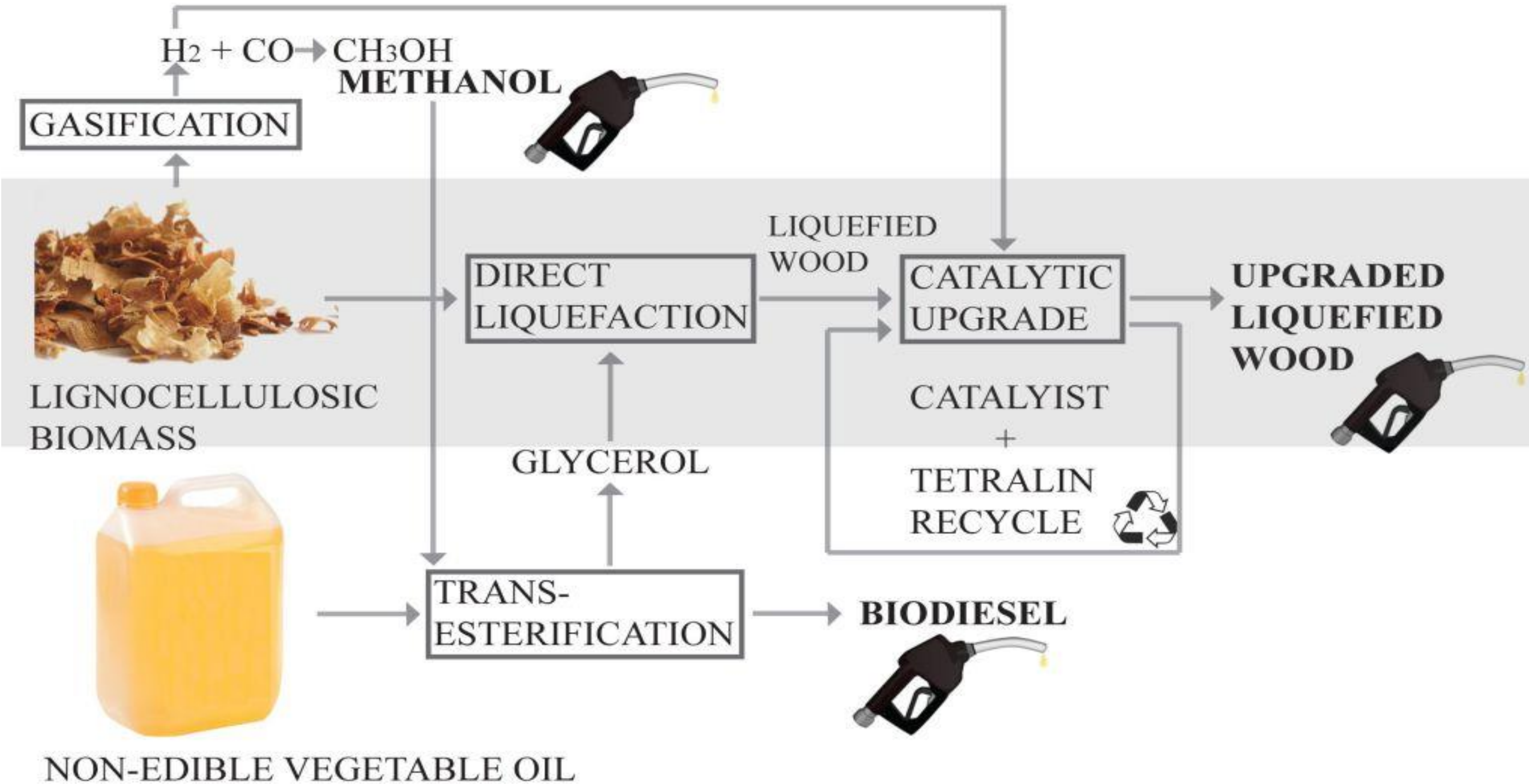
Transesterification of glycerol



Conclusion

Allyl alcohol and **glycdiol** are perspective products as the chemicals targets in the glycerol biorefinery.

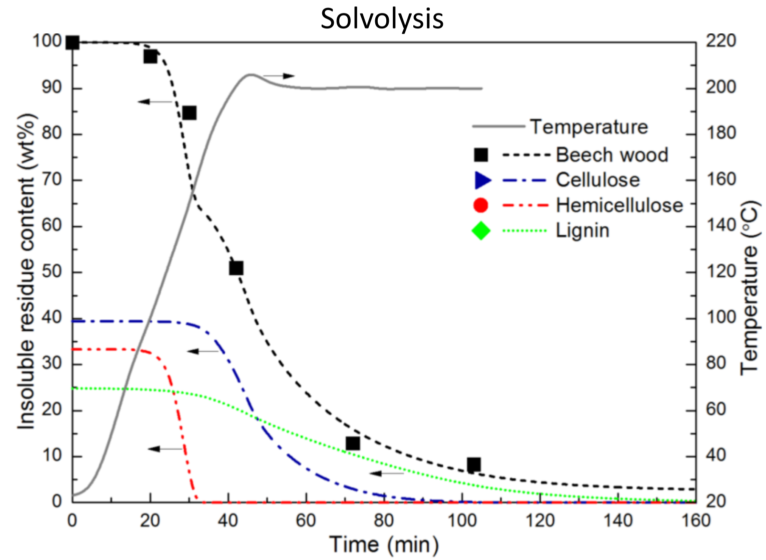
PAST WORK: 1ST TO 2ND GENERATION BIOFUELS



PAST WORK: 2ND GENERATION BIOFUELS

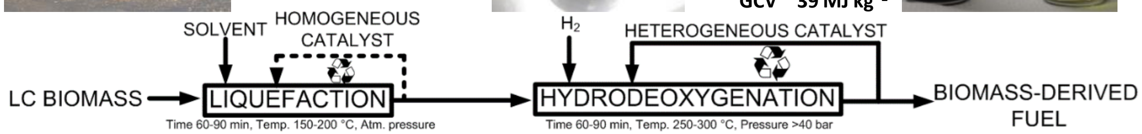
SOLVOLYSIS AND HYDRODEOXYGENATION OF LC BIOMASS

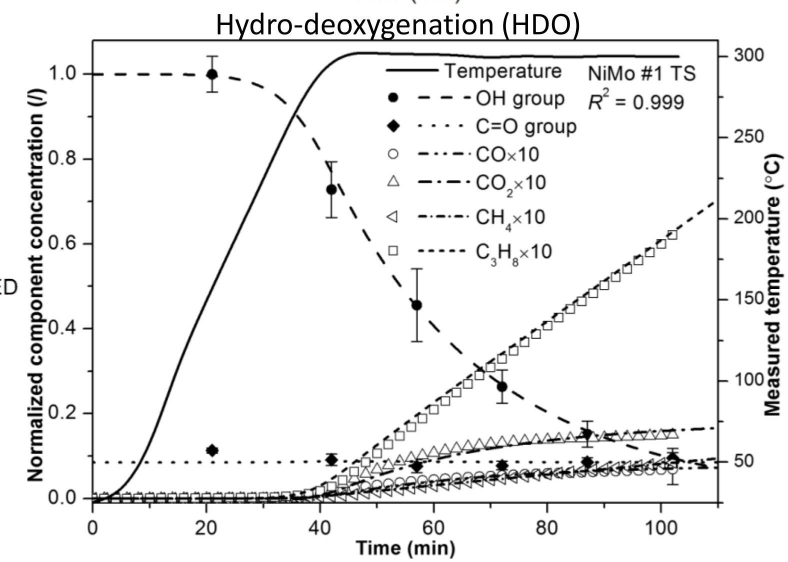
- Depolymerization and solubilization of lignocellulosic biomass
- Catalytic conversion of liquefied biomass to fuel
- Lumped kinetic models developed for solvolysis and HDO
- Screening of 30 synthetized and commercial HDO catalysts

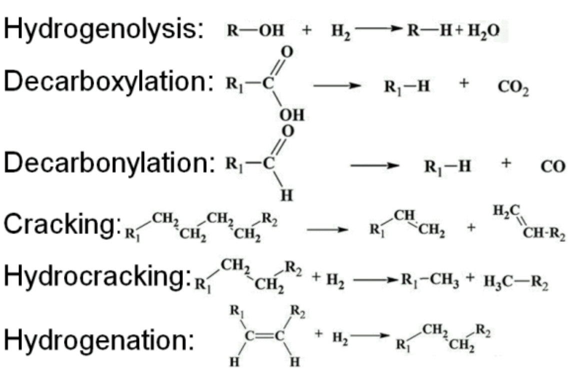


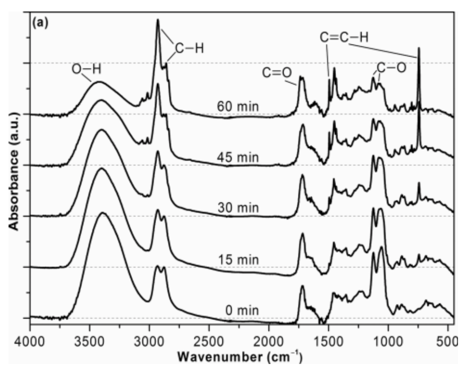
Liquefied biomass
Polar
Density ~ 1.2 kg L^{-1}
GCV ~ 22 MJ kg^{-1}

Non-polar (oil) phase
Non-polar
Alkanes, Alkenes
Density ~ 0.85 kg L^{-1}
GCV ~ 39 MJ kg^{-1}



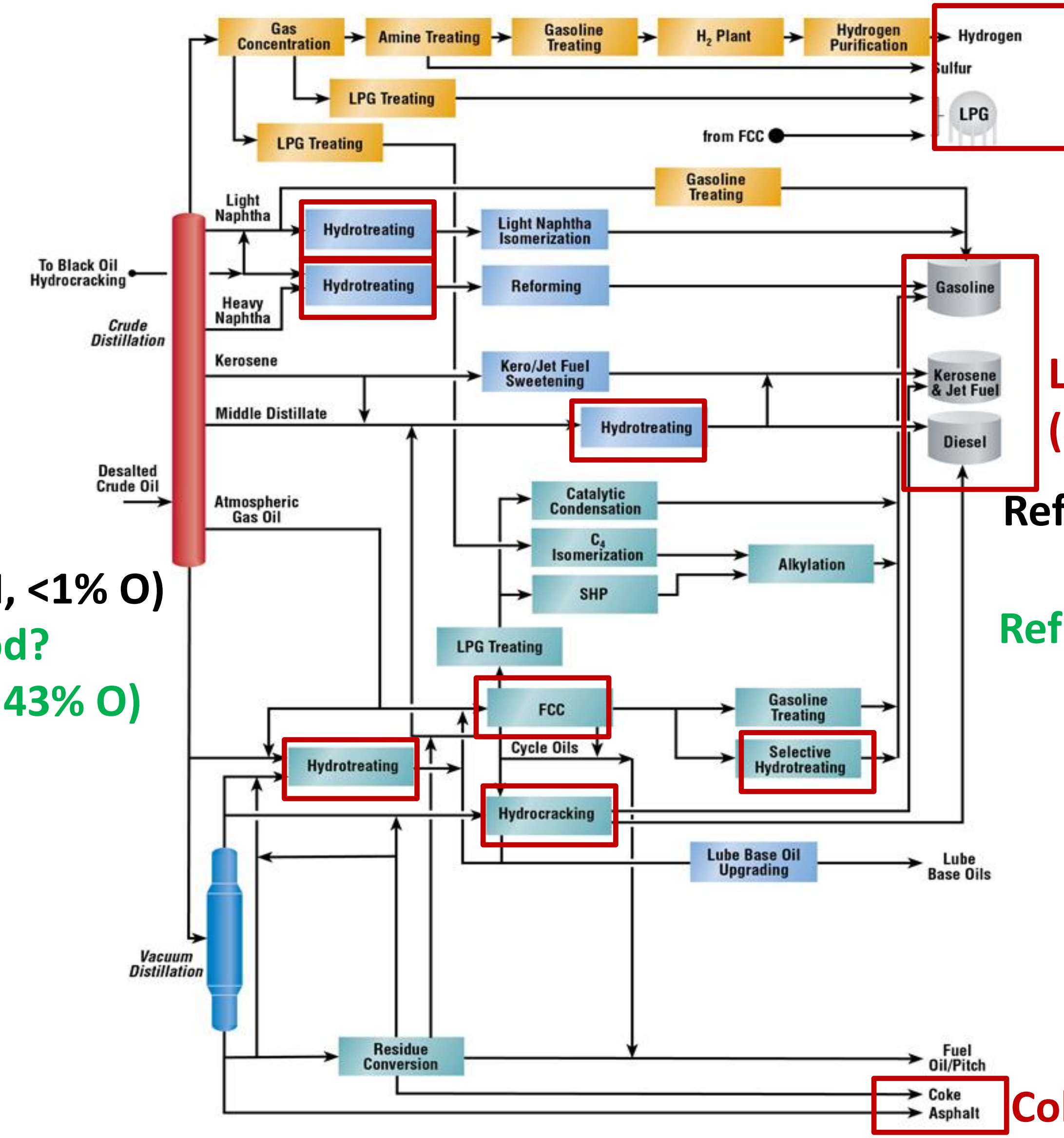






1. Miha Grilc *et al.*, *Biomass Bioenerg.*, **2014**, *63*, 300. Highly Cited Paper
2. Miha Grilc *et al.*, *Appl. Catal. B.*, **2014**, *150*, 275. Highly Cited Paper
3. Miha Grilc, et al., *Appl. Catal. B.*, **2015**, *163*, 467. Highly Cited Paper
4. Miha Grilc *et al.*, *Catal. Today.*, **2015**, *256*, 302.
5. Miha Grilc *et al.*, *ChemCatChem.*, **2016**, *8*, 180.
6. Miha Grilc *et al.*, *PCT Patent*, **2016**, PCT/IT2016/000140

BIOMASS TO FUELS: OIL REFINERY ANALOGY



Gas

Liquid fuel
(85% C, 15% H, 0% O)

Coke and asphalt

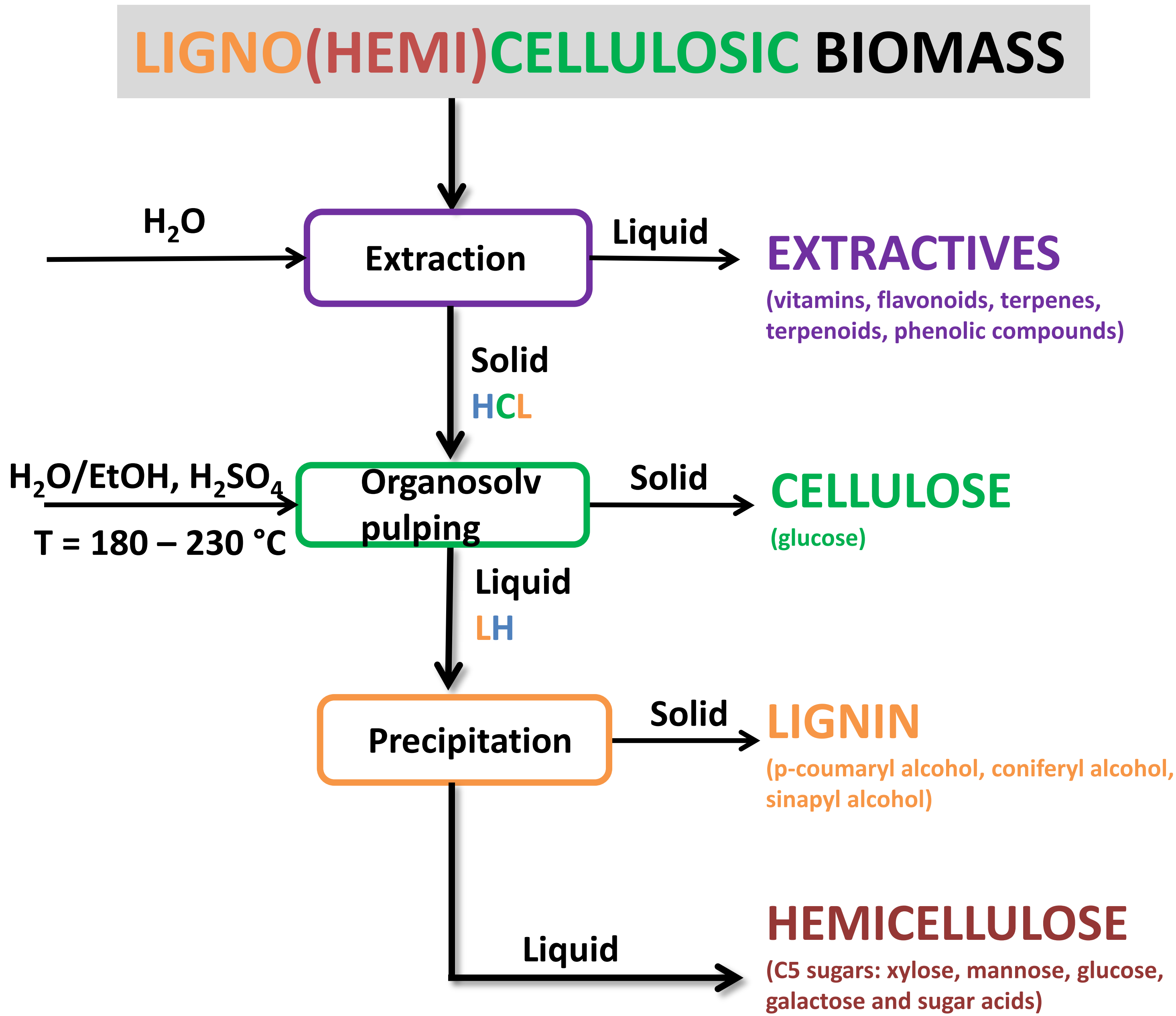
Feedstock:

Crude oil?
(85% C, 12% H, <1% O)

Liquefied wood?
(48% C, 9% H, 43% O)

Refining costs (crude oil):
80 €/ton

Refining costs (liq. wood):
600 €/ton


LIGNO(HEMI)CELLULOSIC BIOMASS
H2O
Extraction
Liquid
EXTRACTIVES
(vitamins, flavonoids, terpenes, terpenoids, phenolic compounds)
Solid
HCL
H2O/EtOH, H2SO4
T = 180 – 230 °C
Organosolv pulping
Solid
CELLULOSE
(glucose)
Liquid
LH
Precipitation
Solid
LIGNIN
(p-coumaryl alcohol, coniferyl alcohol, sinapyl alcohol)
Liquid
HEMICELLULOSE
(C5 sugars: xylose, mannose, glucose, galactose and sugar acids)

EXTRACTIVES

- Bark extracts – soluble in water and organic solvents
- Use as a nutritional supplement
- Antioxidant activity
- Estimated value on the market: 2000 €/kg

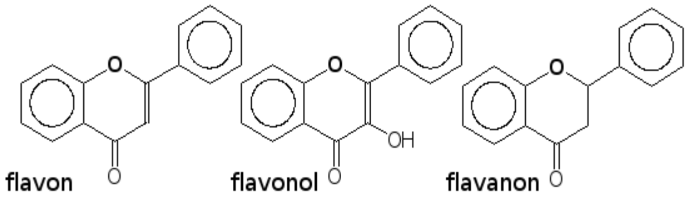
AIM

- The development of:
  - separation,
  - isolation,
  - purification methods.

Value-added components:

- Flavonoids
- Polyphenols

NARAVNI POLIFENOLI ABIGENOL® IZ KOČEVSKEGA GOZDA



EXTRACTION METHODOLOGY

PRE-TREATMENT → ISOLATION → PURIFICATION

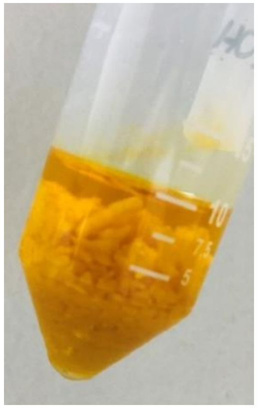
Pre-treatment:

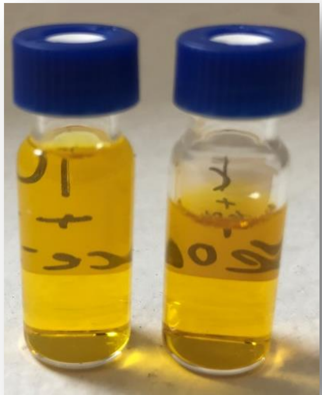
- Cutting
- Milling
- Vacuum drying
- Lyophilisation
- Steam/CO_2 explosion

PRE-TREATMENT IMPORTANCY OFTEN NEGLECTED ON THE BENCH SCALE

- Significantly affects the isolation step (scale-up)
- Aim: Increase of the surface area and target accessibility
- Hazard: Degradation of target components
- Hazard: Can significantly contribute to the investment/operation costs

PRE-TREATMENT → **ISOLATION** → PURIFICATION





Classic extraction methods:
- Water extraction
- Organic solvent extraction
- Acid treatment

Green extraction:
- Supercritical extraction
- DES extraction

Physical-mechanical assistance:
- Ultrasound
- Microwave
- Electroporation

SOLID-LIQUID EXTRACTION
- Solvent extraction (water, ethanol, acetone, EA, DES)
- High pressure and supercritical extraction
- Assisted by: ultrasound, microwave, electroporation
- Parameters: *t*, *T*, S:L ratio, solvent type

Available analytics

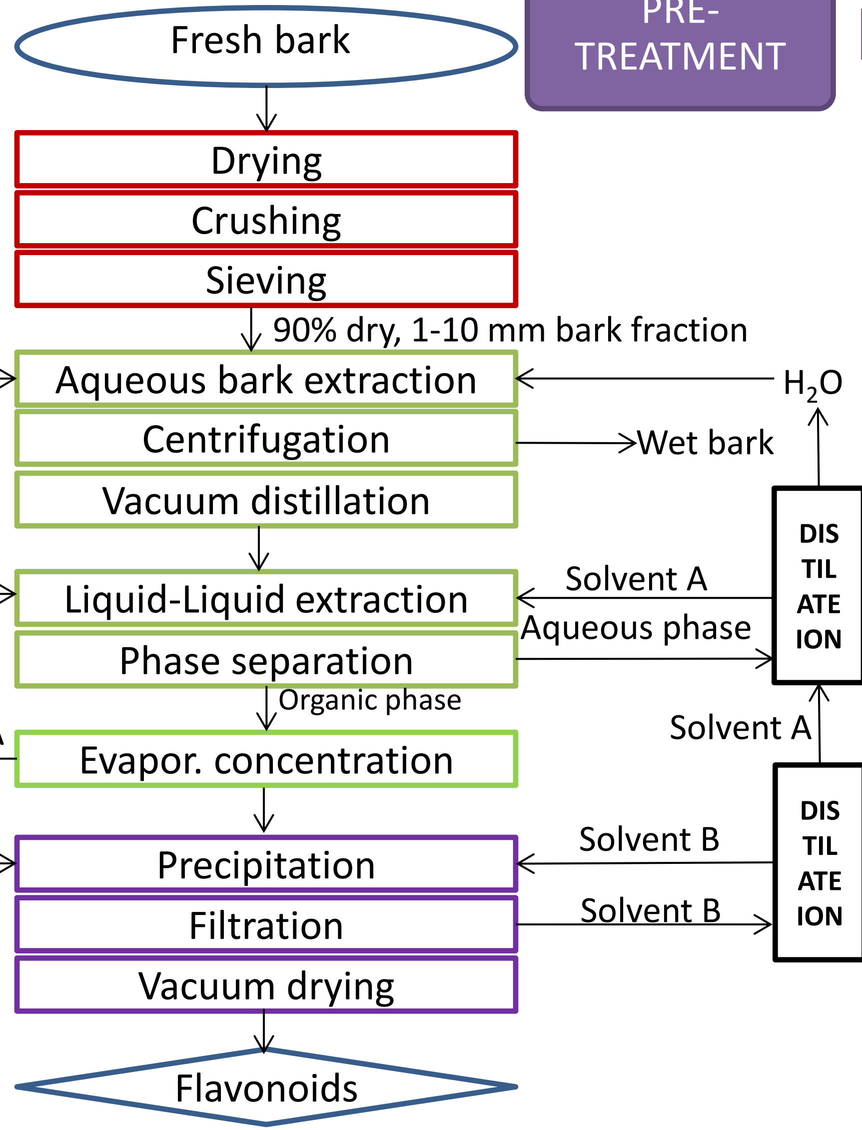
- GCMS
- UHPLC
- UV-VIS (online)
- NMR (online)
- FTIR (online)
- FBRM (online)

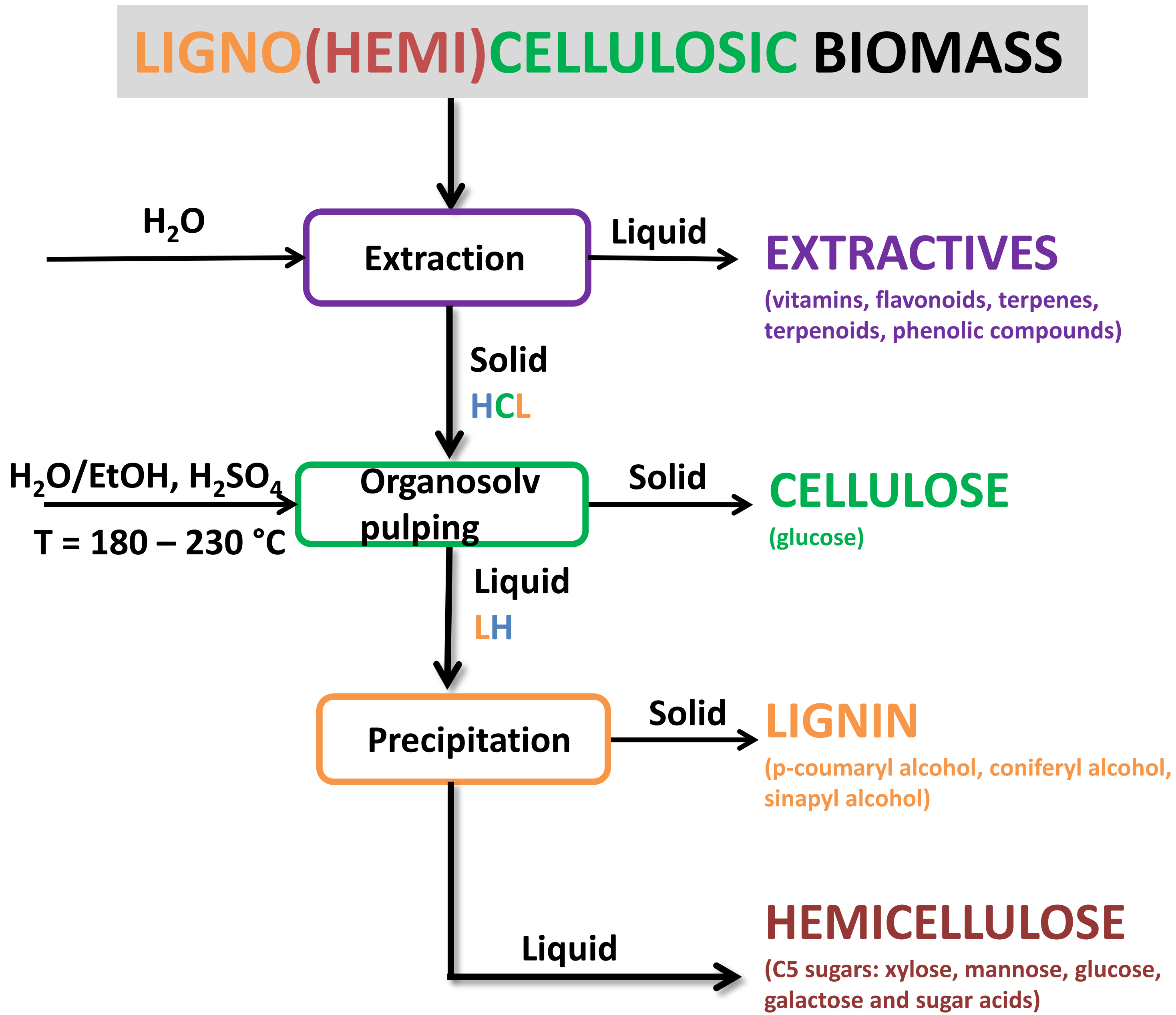
PRE-TREATMENT → ISOLATION → PURIFICATION

Purification methods:

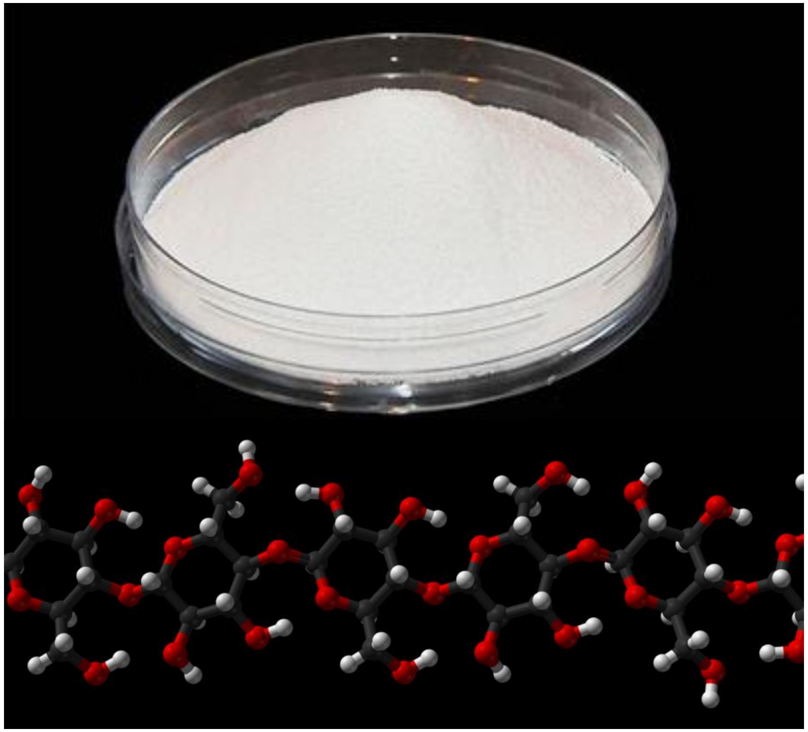
- Antisolvent precipitation
- Re-extraction
- Chromatography
- Filtration
- Centrifugation
- Distillation

Benchmark: Flavonoids extraction from bark

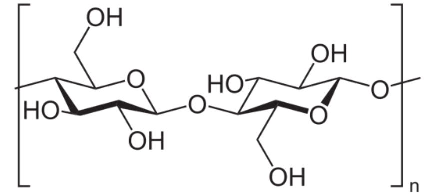


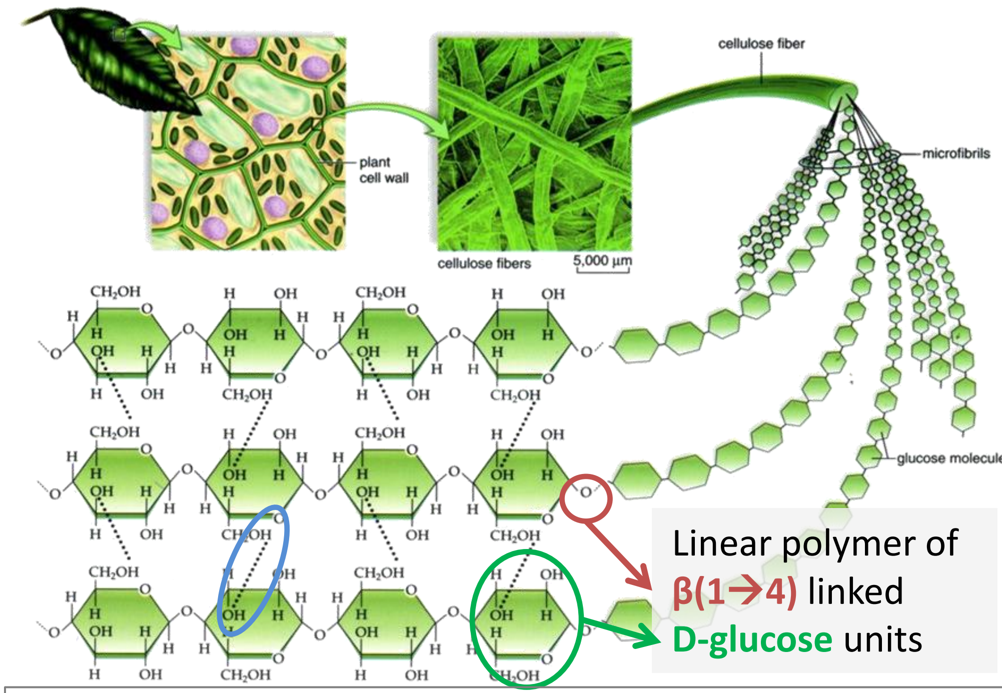


LIGNO(HEMI)CELLULOSIC BIOMASS
H_2O
Extraction
Liquid
EXTRACTIVES
(vitamins, flavonoids, terpenes, terpenoids, phenolic compounds)
Solid
HCL
H_2O/EtOH, H_2SO_4
T = 180 – 230 °C
Organosolv pulping
Solid
CELLULOSE
(glucose)
Liquid
LH
Precipitation
Solid
LIGNIN
(p-coumaryl alcohol, coniferyl alcohol, sinapyl alcohol)
Liquid
HEMICELLULOSE
(C5 sugars: xylose, mannose, glucose, galactose and sugar acids)



Cellulose



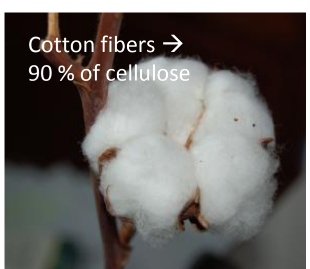


Linear polymer of $\beta(1 \rightarrow 4)$ linked **D-glucose** units

Appearance:	White crystalline powder
Chemical formula:	$(C_6H_{10}O_5)_n$

Cellulose from wood: 300 – 1700 units

Cotton fibers: 800 – 10 000

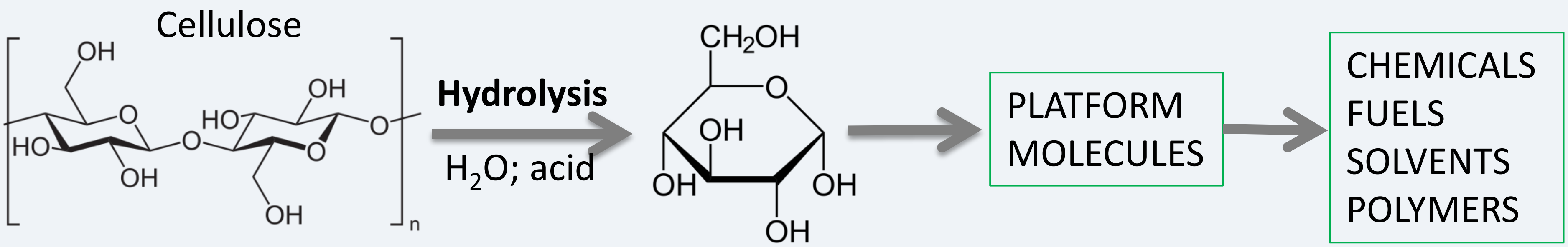


Cellulose consist of **crystalline** and **amorphous** regions.

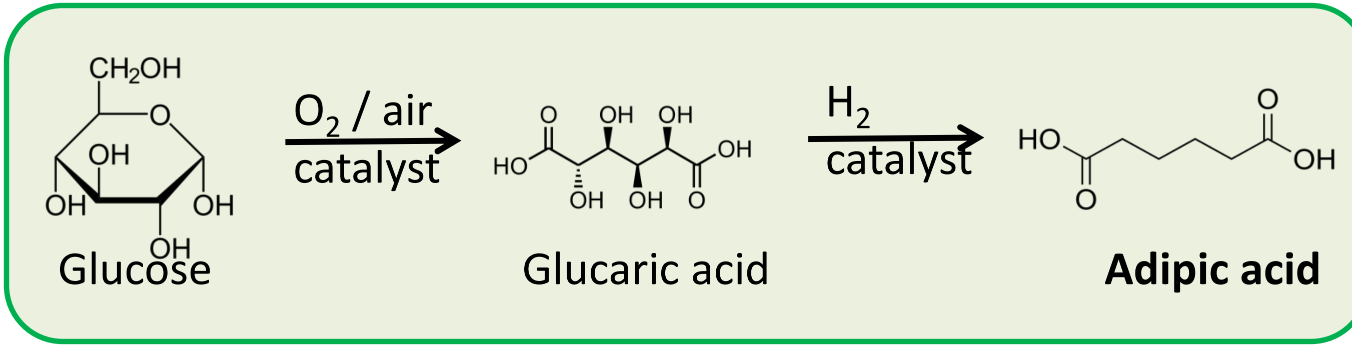
Different **crystalline structures** of cellulose are know → corresponding to the location of **hydrogen bonds** between and within strands.

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

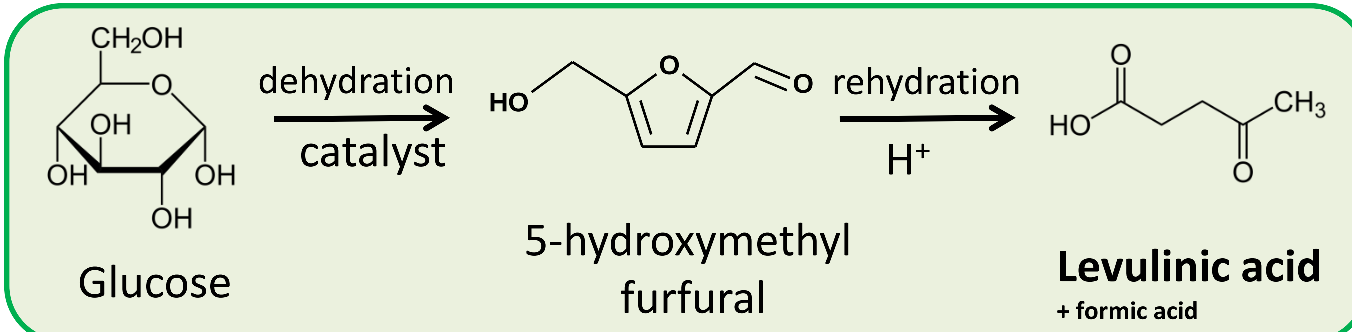
Cellulose conversion



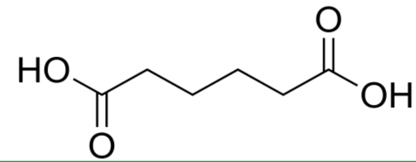
Glucaric acid and **Adipic acid** production from cellulose



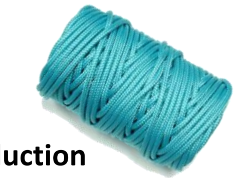
5-HMF and **Levulinic acid** production from cellulose

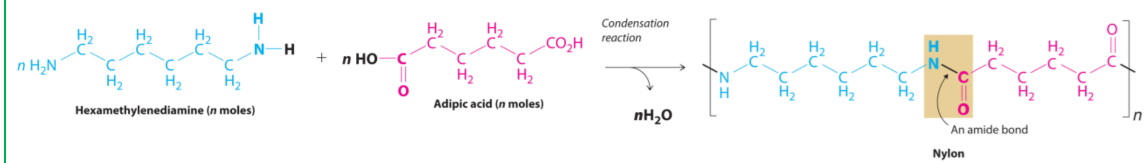


Adipic acid



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

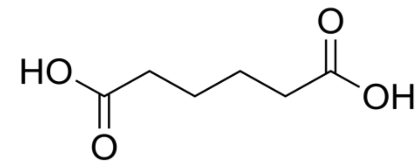




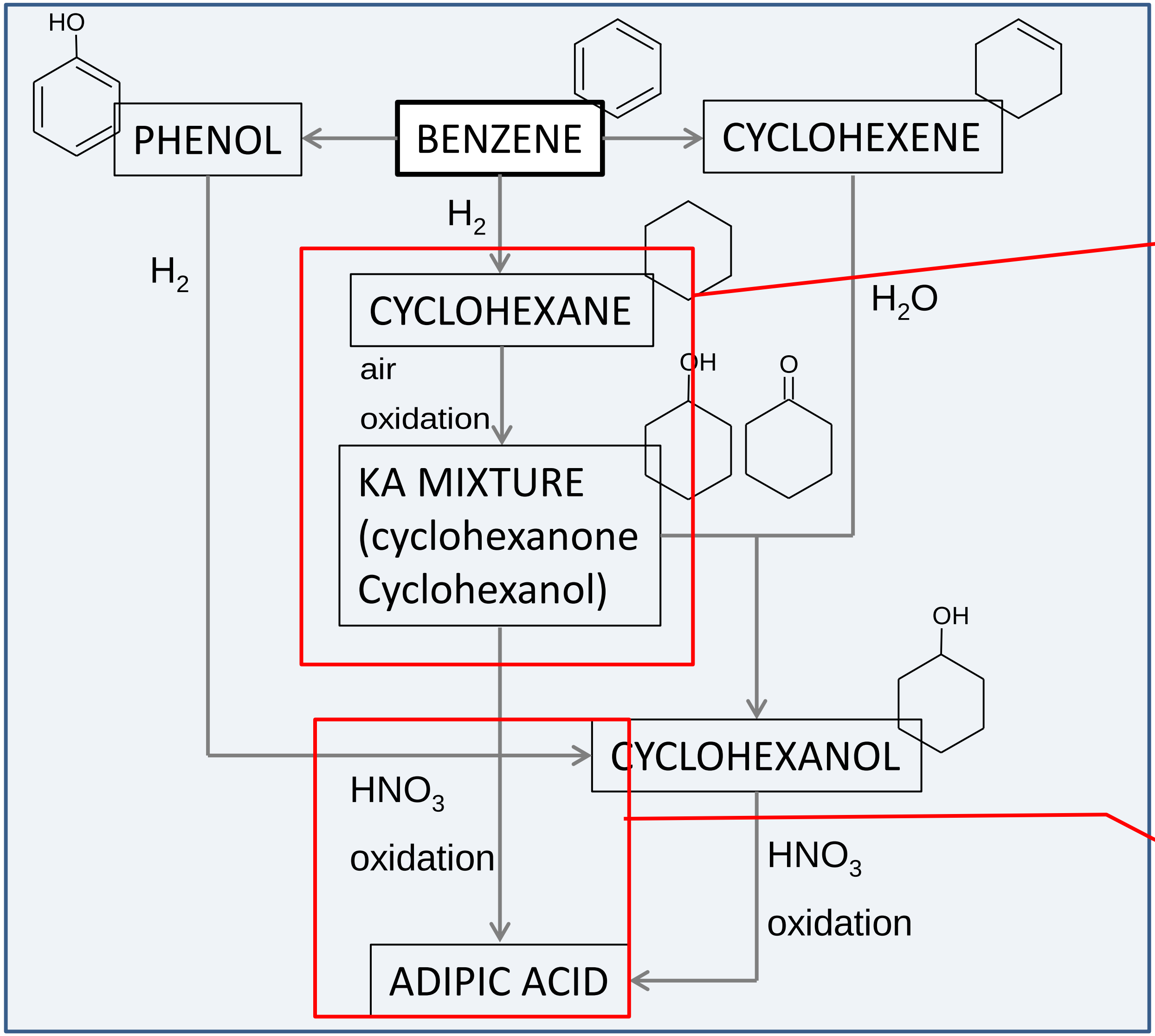
- Used for polyurethanes production, plasticizers, PVC, in medicine,...

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_2O

Adipic acid production



1. Conventional petrochemical process

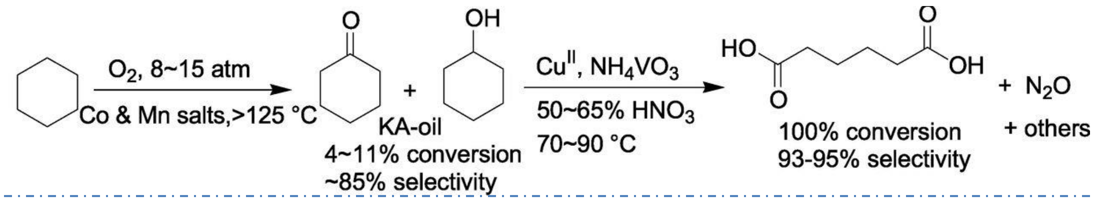


Low conversion (4-11 %)

N_2O & NO_x formation
Exothermic reaction

Adipic acid production

1. Conventional petrochemical process

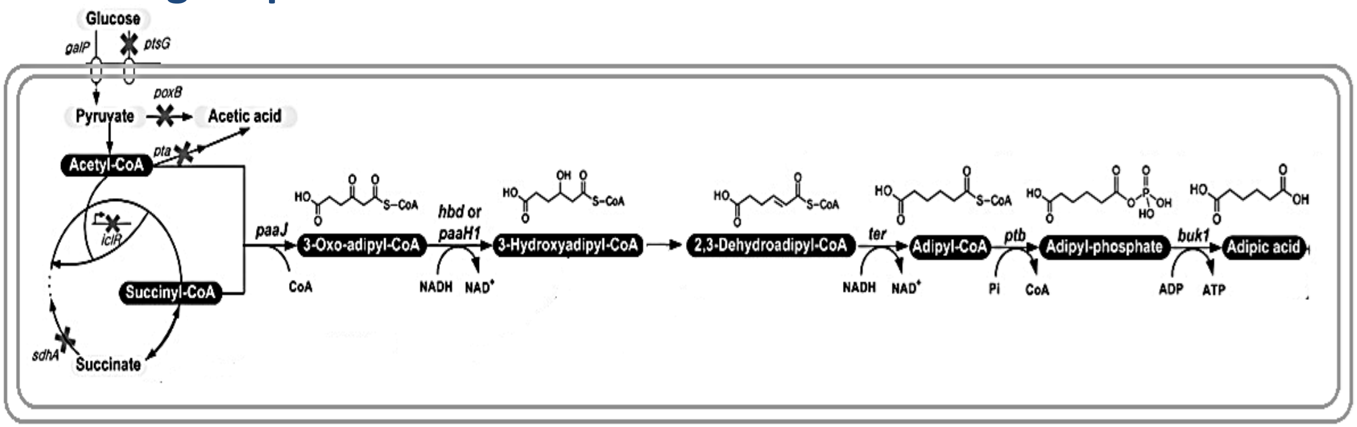


- -crude oil as a feedstock
- -benzene as a reactant
- -low yields
- -runaway exothermic reactions → explosion risk
- - High cost of corrosion resistant equipment

ALTERNATIVE PROCESSES

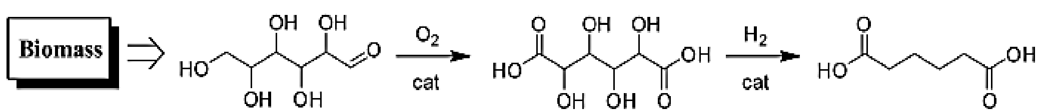
Companies investing on the development of alternative routes:
Amyris, Bioamber, Genomatica, Verdezyne

2. Biological process



- Biobased feedstock
- Selective process
- Mild reaction condition
- Expensive
- Well defined reaction conditions and environment → contamination

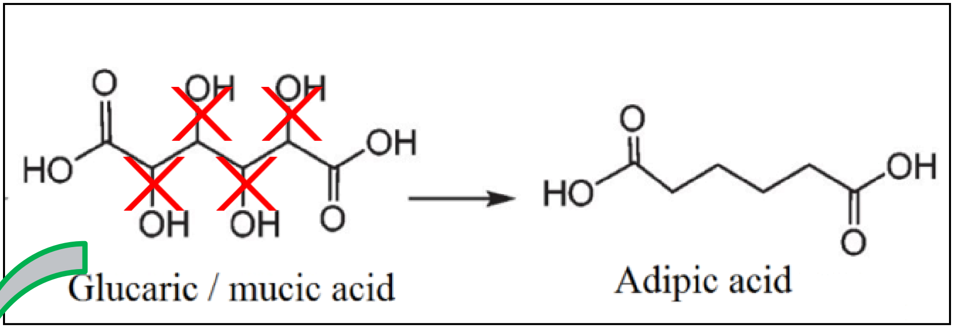
3. Chemical catalytic process



Glucose   Glucaric acid   Adipic acid

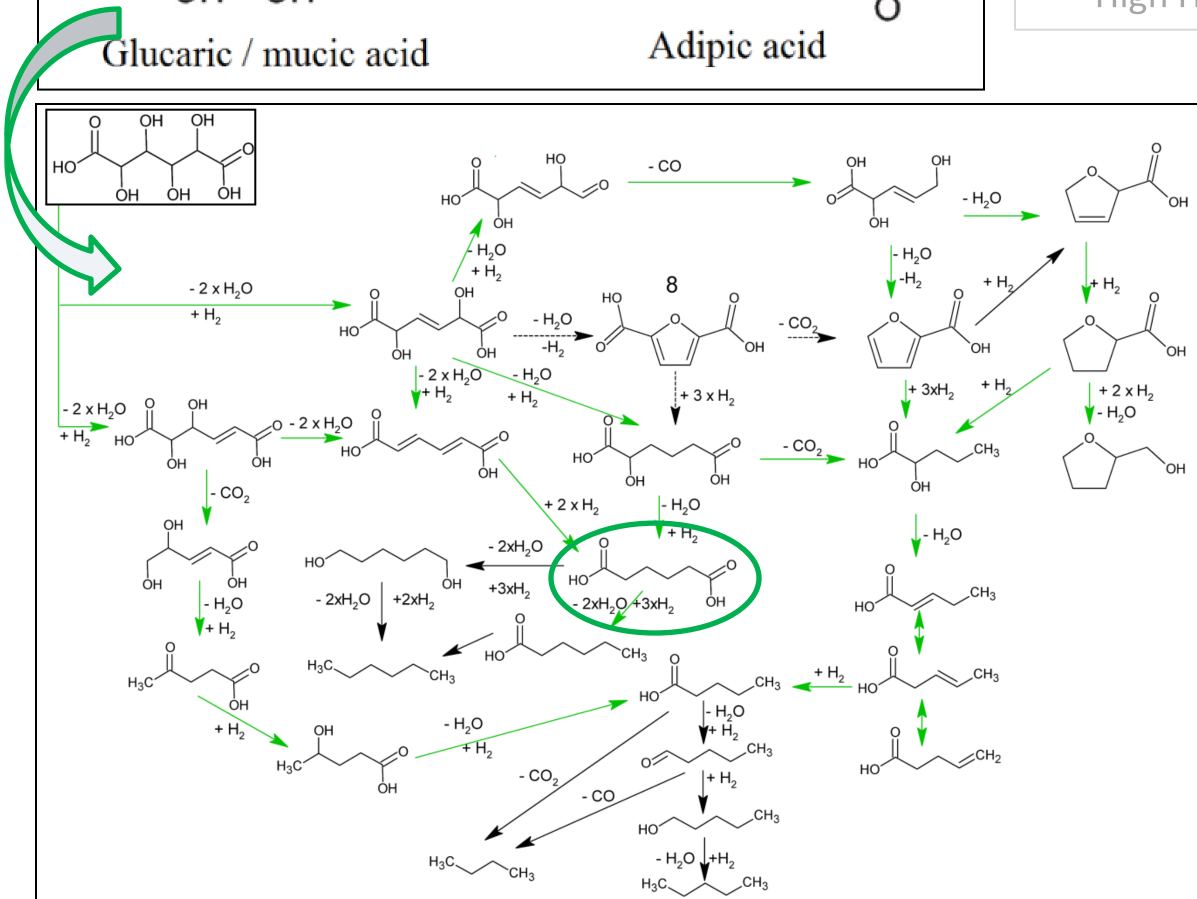
- Biobased feedstock (biowaste)
- Green solvents (water, MeOH, EtOH)
- No GHG emission
- Higher yields (up to 89 %)

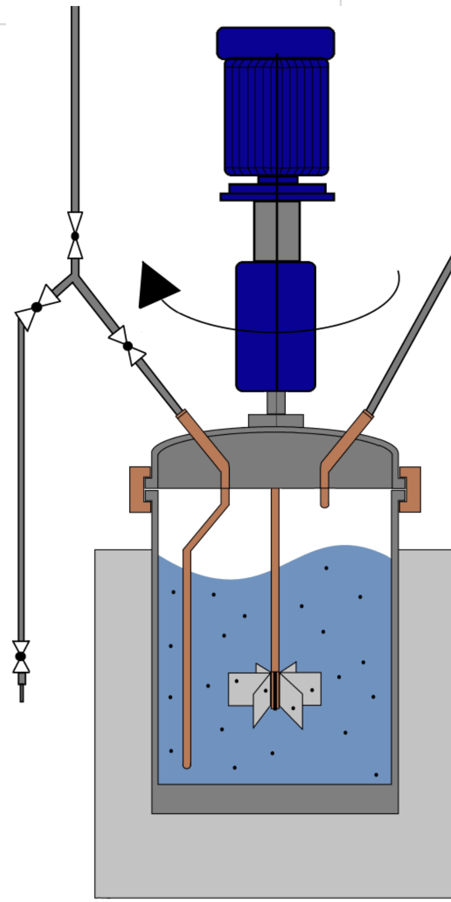
Adipic acid production → Chemical catalytic process



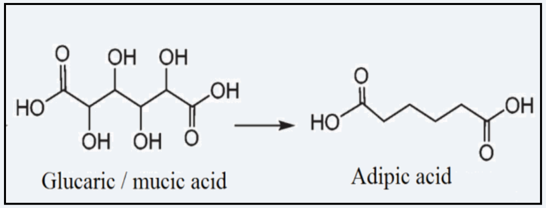
Reaction conditions:

- Green solvent : H_2O
- Heterogeneous metal catalysts
- Moderate temperatures (125-150°C)
- High H_2 pressure



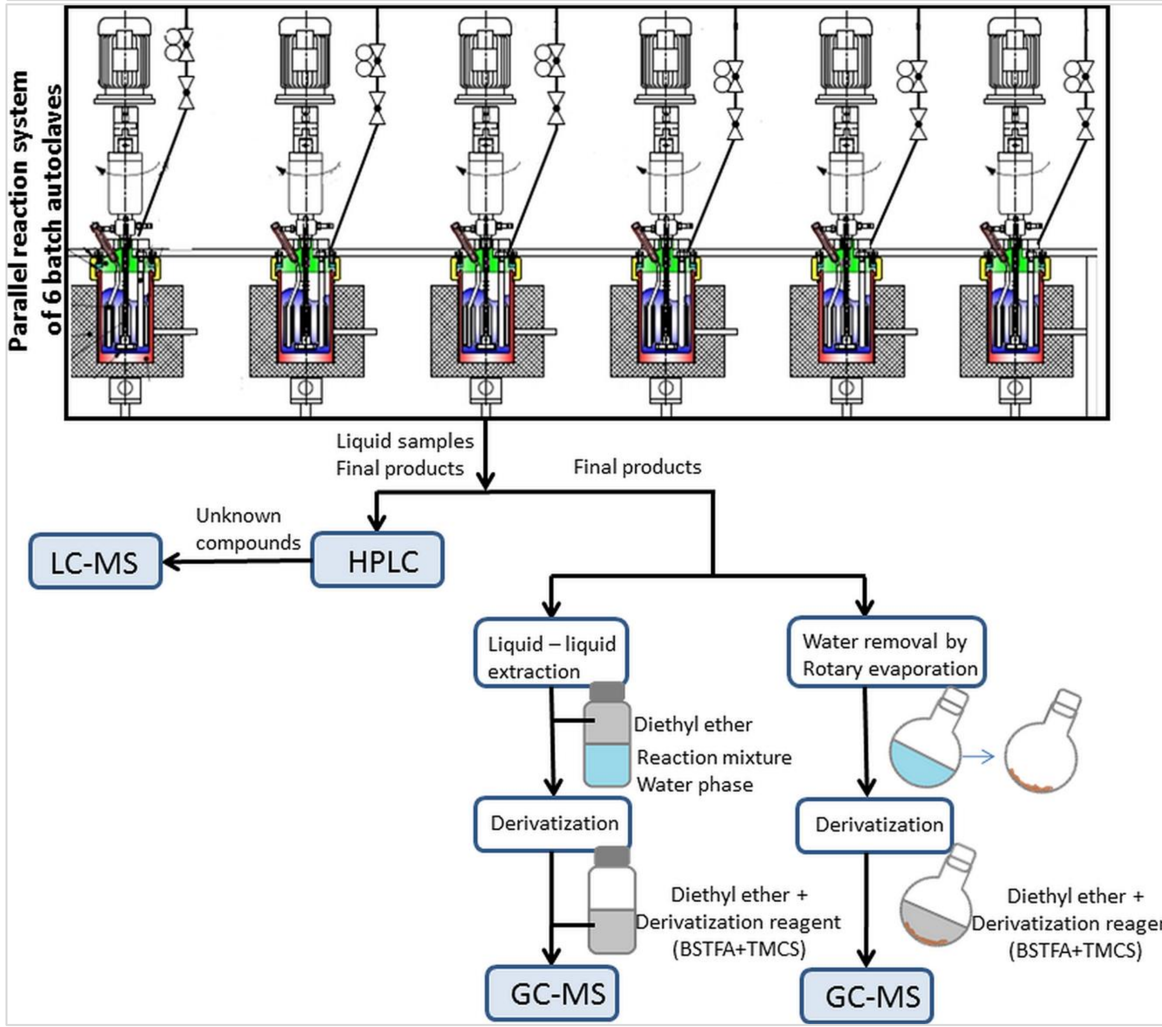


Adipic acid production → Chemical catalytic process



Catalyst type	*T* (°C)
NiMo/γ-Al_2O_3	125,135,150,175, 200,225
Pt/γ-Al_2O_3	125,135,150,175
Ru/SiO_2	125,135,150,175
Rh//SiO_2	125,135,150,175
Ni//SiO_2	125,135,150,175
Pt//SiO_2	125,135,150,175
Ru/C	125,135,150,175
Rh/C	125,135,150,175
Ni/C	125,135,150,175
Pt/C	125,135,150,175

A combination of different analytical methods used for detection of formed products

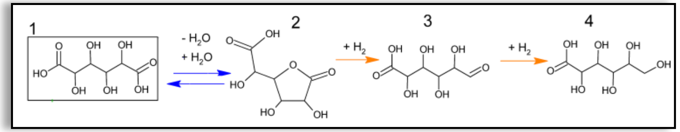


Adipic acid production → Chemical catalytic process

Solvent selection

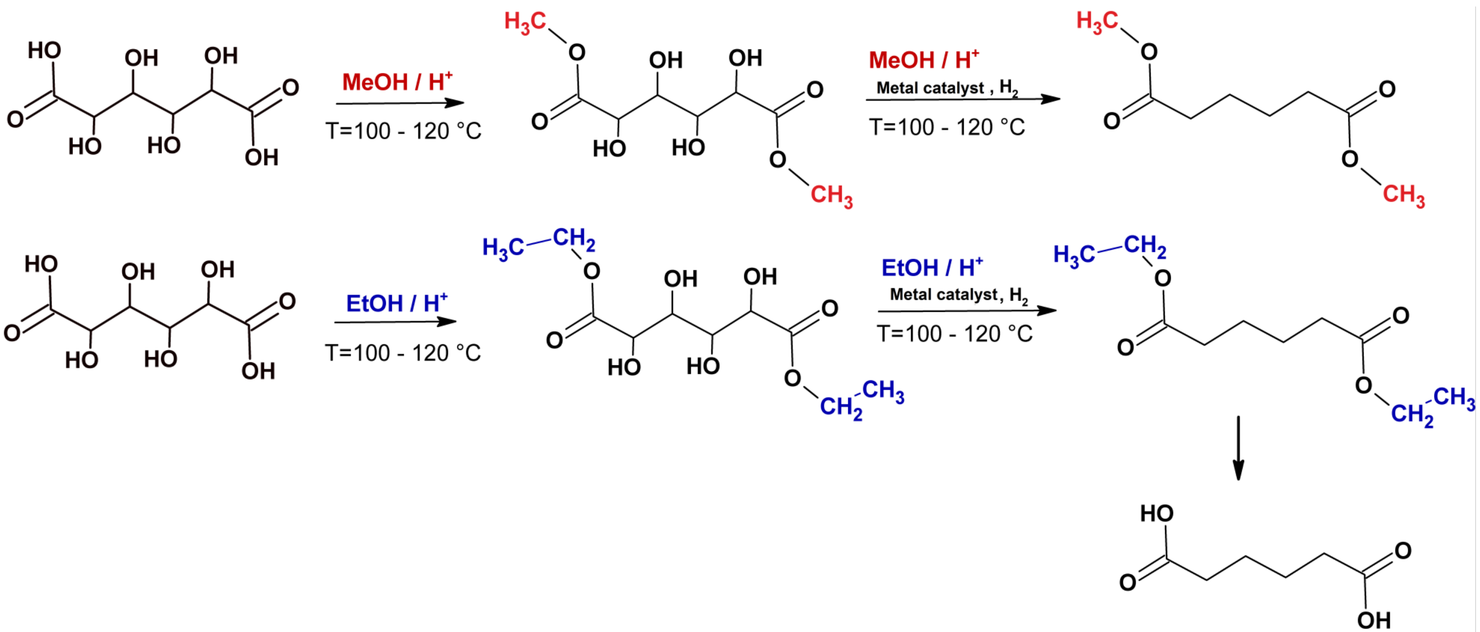
1. Aqueous hydrodeoxygenation of aldaric acids (glucaric/mucic) over transition (Ni, Mo) or noble (Pt, Rh, Ru) metals on neutral or acidic supports

- **Lactone formation** under aqueous conditions



- **Low selectivity** (formation of many products; >30 detected compounds)

2. Esterification of aldaric acid in alcohol (MeOH or EtOH) → as a protection of carboxyl group



Methyl adipate

Ethyl adipate

Adipic acid

Biobased Adipic acid – Our developed processes

Chemocatalytic – in alcohols as solvents

Experimental set-up:

- 250 mL batch reactor
- 120 mL of solvent (MeOH)
- H_2 or N_2 gaseous phase
- 10 mol% of catalyst (regarding to the reactant)
- 200 mg of reactant (mucic acid/glucaric acid)
- RKC T: 100 – 150 °C
- RKC time: 72 h

Homogeneous Re catalyst:

- $MeReO_3$
- $KReO_4$
- $HReO_4$

Homogeneous Re catalyst + heterogeneous hydrogenation catalyst:

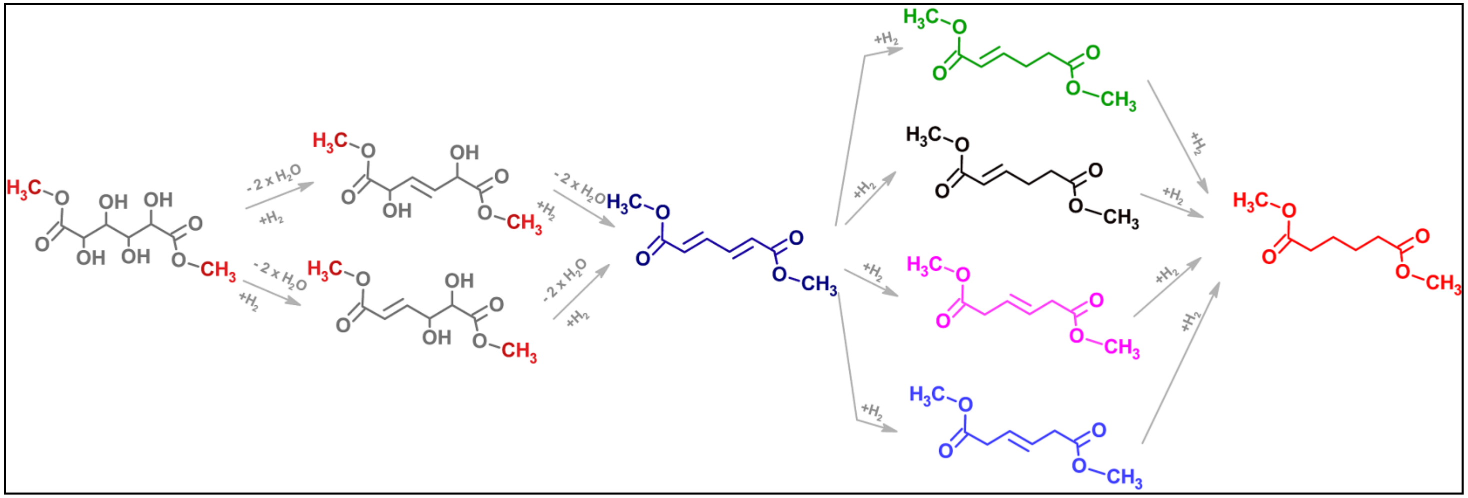
- $MeReO_3$ + Pd/C or Pt/C
- $KReO_4$ + Pd/C or Pt/C
- $HReO_4$ + Pd/C or Pt/C

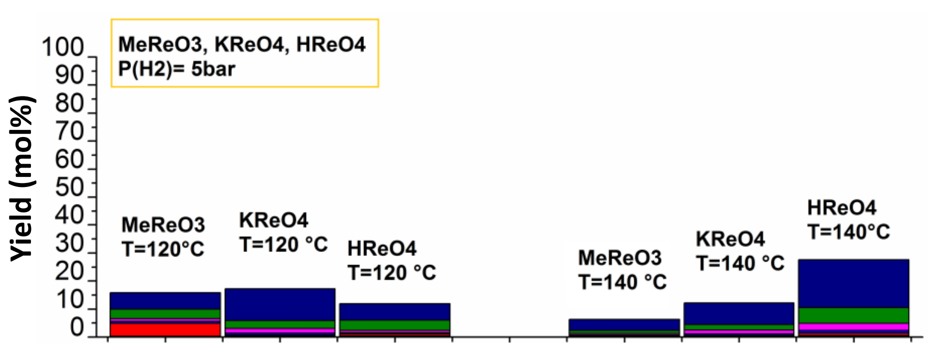
Heterogeneous Re catalyst:

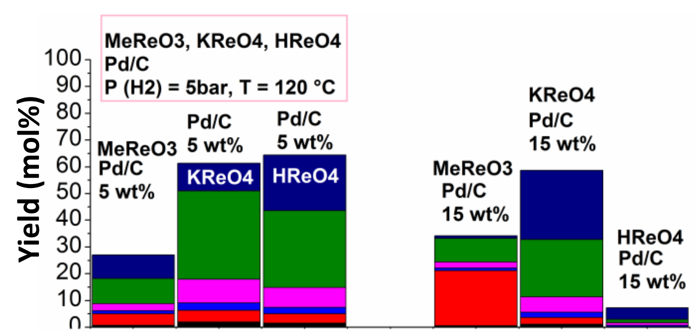
- Re/C
- Re/SiO_2
- Re/Al_2O_3
- Re/C + Pd/C

Biobased Adipic acid – Our developed processes

Chemocatalytic – in alcohols as solvents over homogeneous Re catalysts

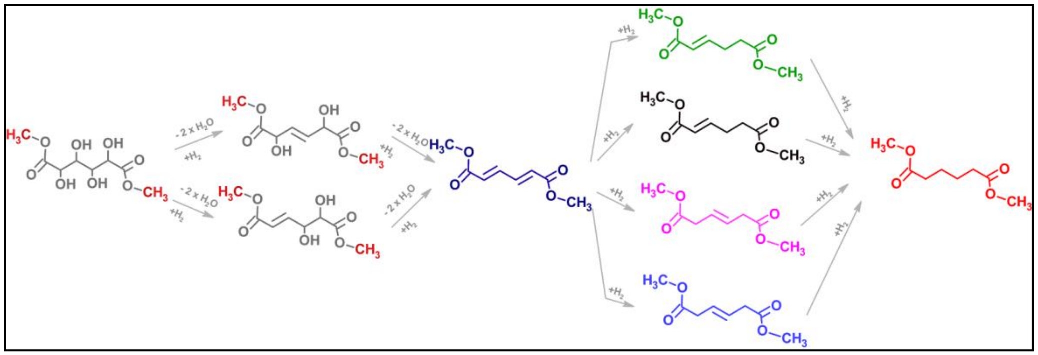


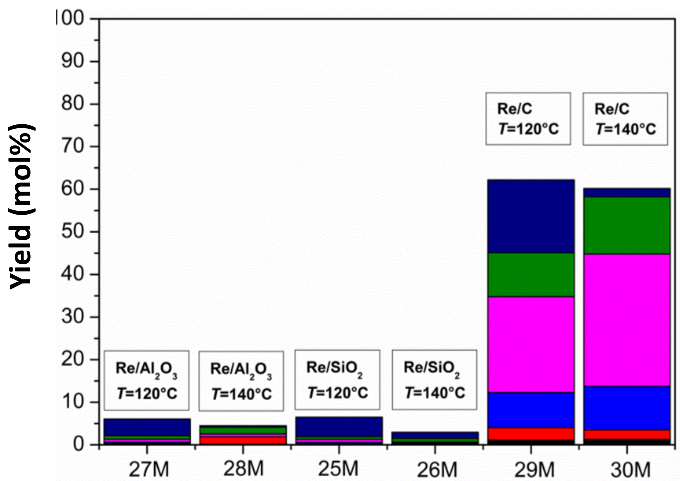


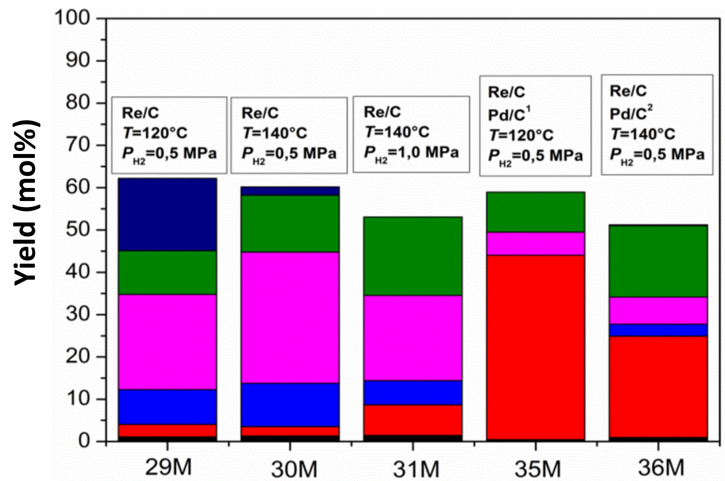


Biobased Adipic acid – Our developed processes

Chemocatalytic – in alcohols as solvents over heterogeneous Re catalysts

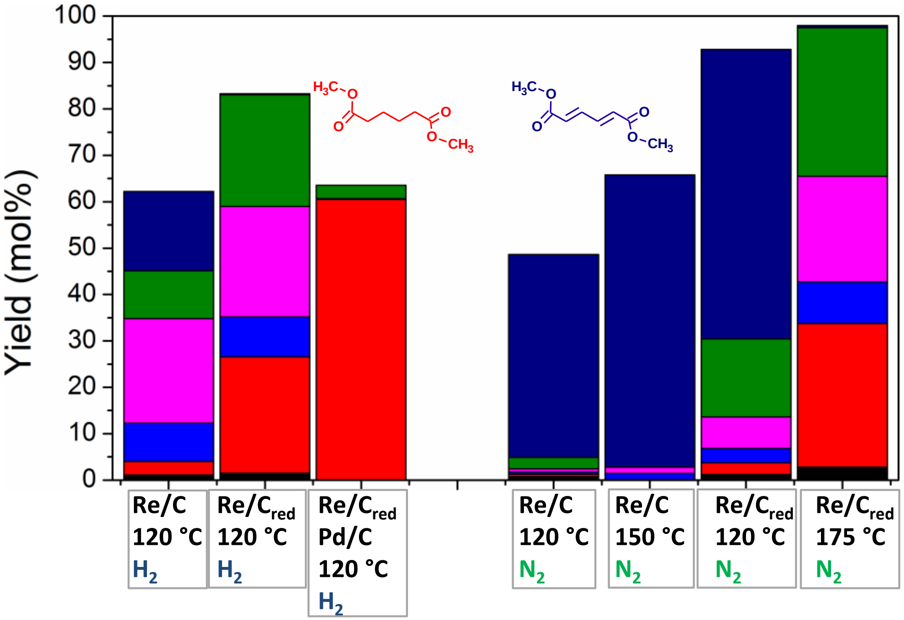






Biobased Adipic acid – Our developed processes

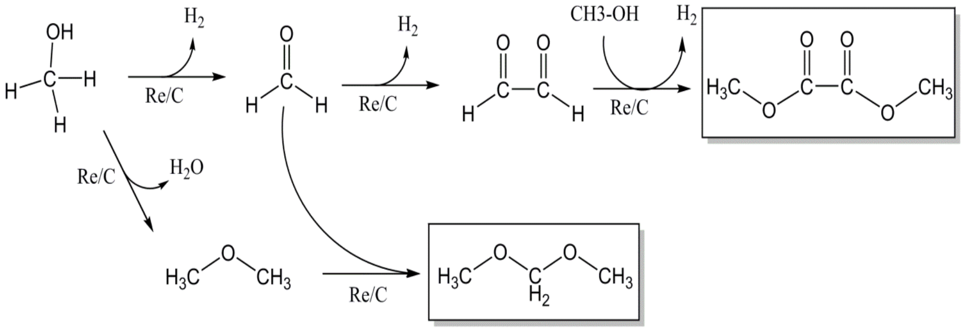
Chemocatalytic – in alcohols as solvents over heterogeneous Re catalysts



Catalyst reduction → increased yield of products

MeOH reduction → formaldehyde + H_2 formation

H_2 formation → hydrogenation of double bonds

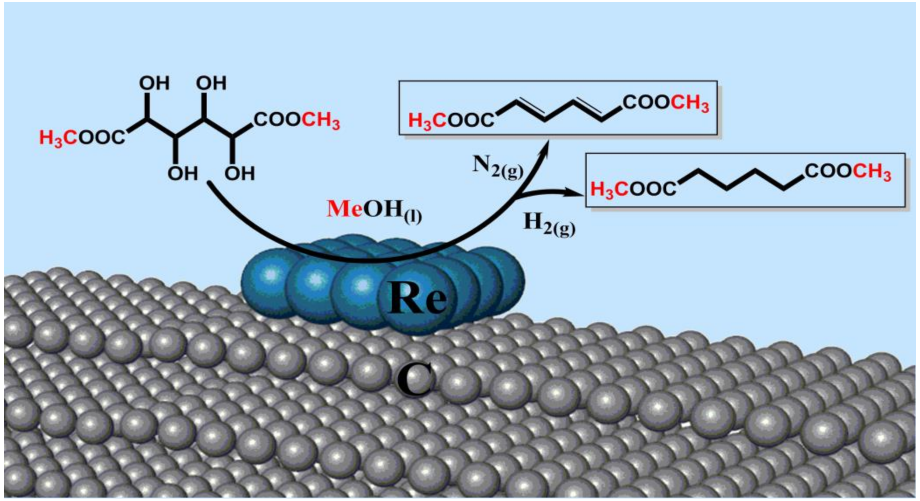


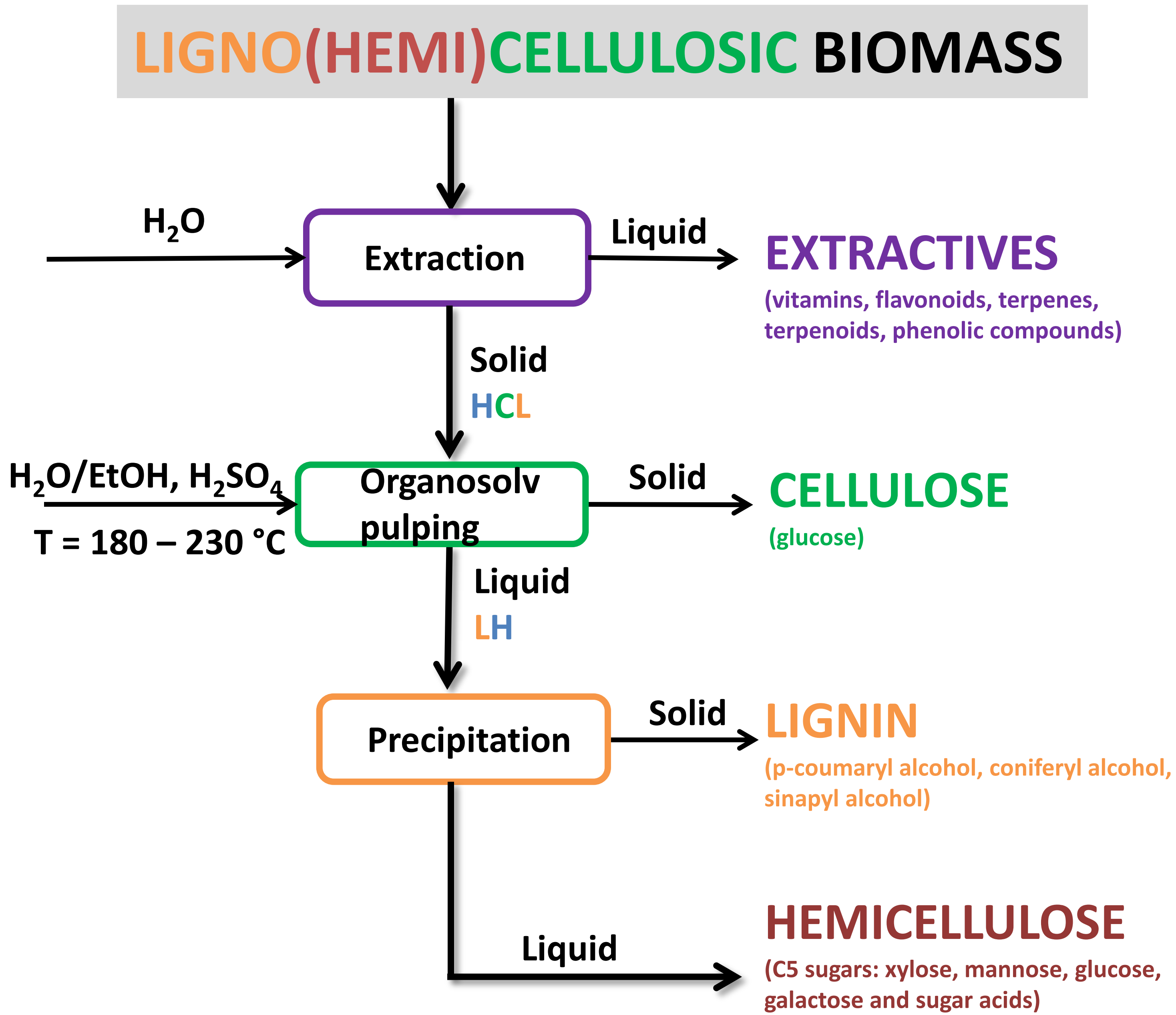
Biobased Adipic acid – Our developed processes

Benefits of the developed process:

- High yields
- No gas emissions
- No harmful side products
- Heterogeneous catalyst
- Easy separation of catalyst
- Reuse of catalyst
- Reuse of solvent
- Easy transition to continuous process

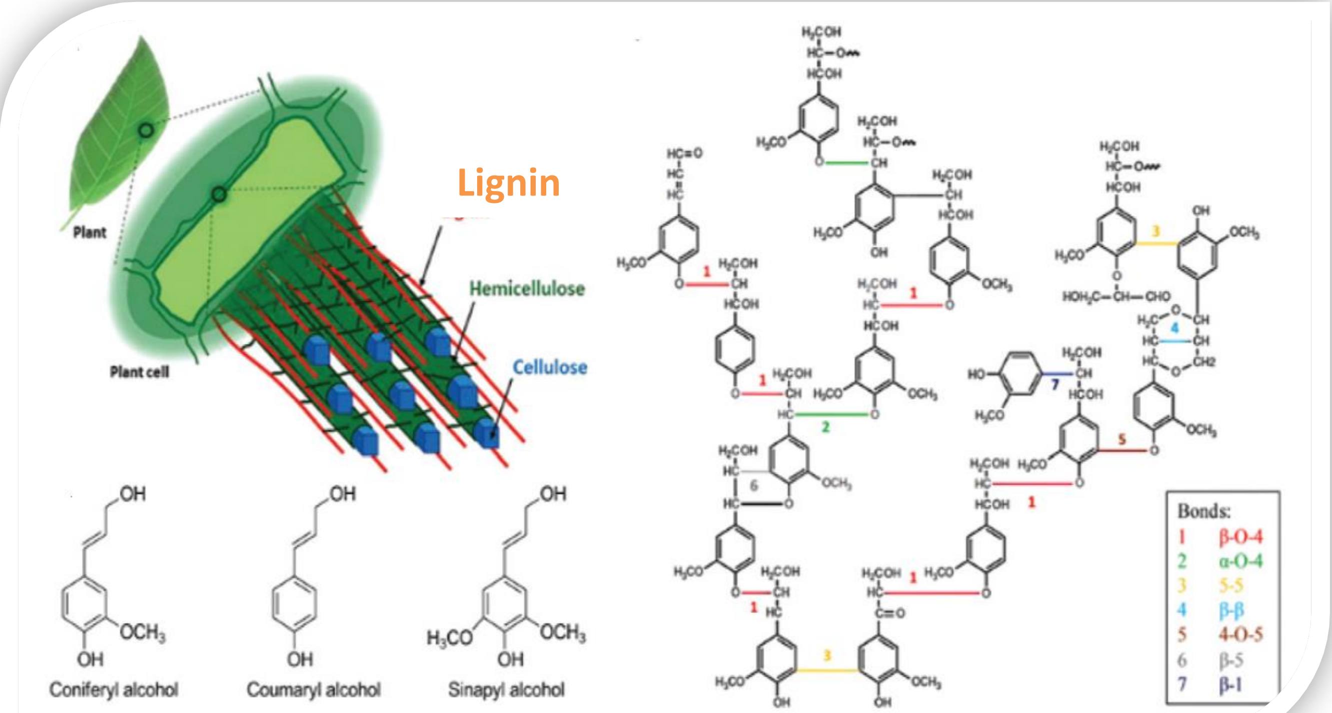
Patent application





LIGNO(HEMI)CELLULOSIC BIOMASS
H2O
Extraction
Liquid
EXTRACTIVES
(vitamins, flavonoids, terpenes, terpenoids, phenolic compounds)
Solid
HCL
H2O/EtOH, H2SO4
T = 180 – 230 °C
Organosolv pulping
Solid
CELLULOSE
(glucose)
Liquid
LH
Precipitation
Solid
LIGNIN
(p-coumaryl alcohol, coniferyl alcohol, sinapyl alcohol)
Liquid
HEMICELLULOSE
(C5 sugars: xylose, mannose, glucose, galactose and sugar acids)

Lignin



Shao-Hai Li et al. The Royal Society of Chemistry 2015

Lignin bio-polymer

- Several types of inter-unit bonds
- Different plats: various ratio of each unit
- SW (21–29 %), HW (18–25 %), HP (15–24 %)
- 5 – 30 % of the weight ~40 % of the energy
- Composed of monomeric aromatic units
- Provides rigidity to plants and protection

Lignin potential

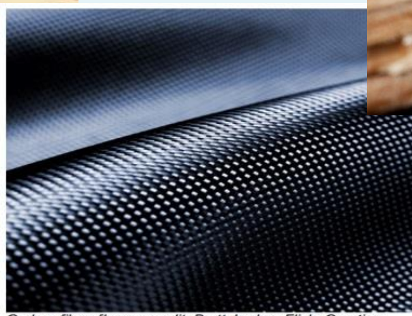
- Rich of functional groups: – OCH_3, – OH
- Cheap & Abundant
- 30% of organic carbon
- Economic necessity of bio-based industries
- Regulations
- To be used as a polymer

Lignin applications

As polymer

Antioxidant

Carbon fibers



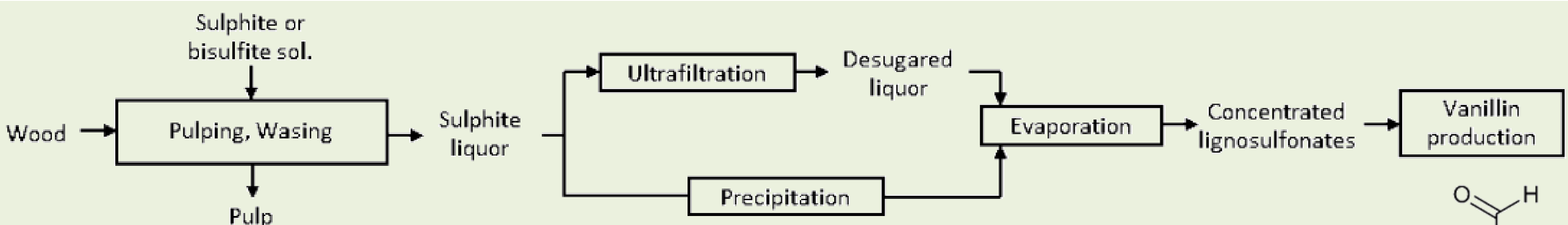
Carbon fiber. [Image credit: Brett Jordan, Flickr Creative Commons]

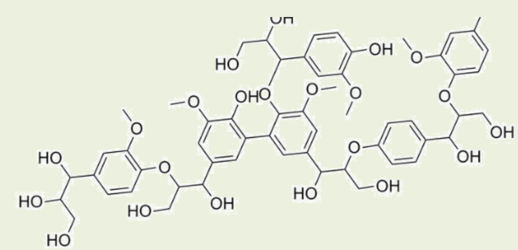
Board binder

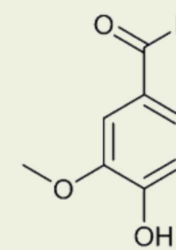
Foams

Dispersants

For chemicals

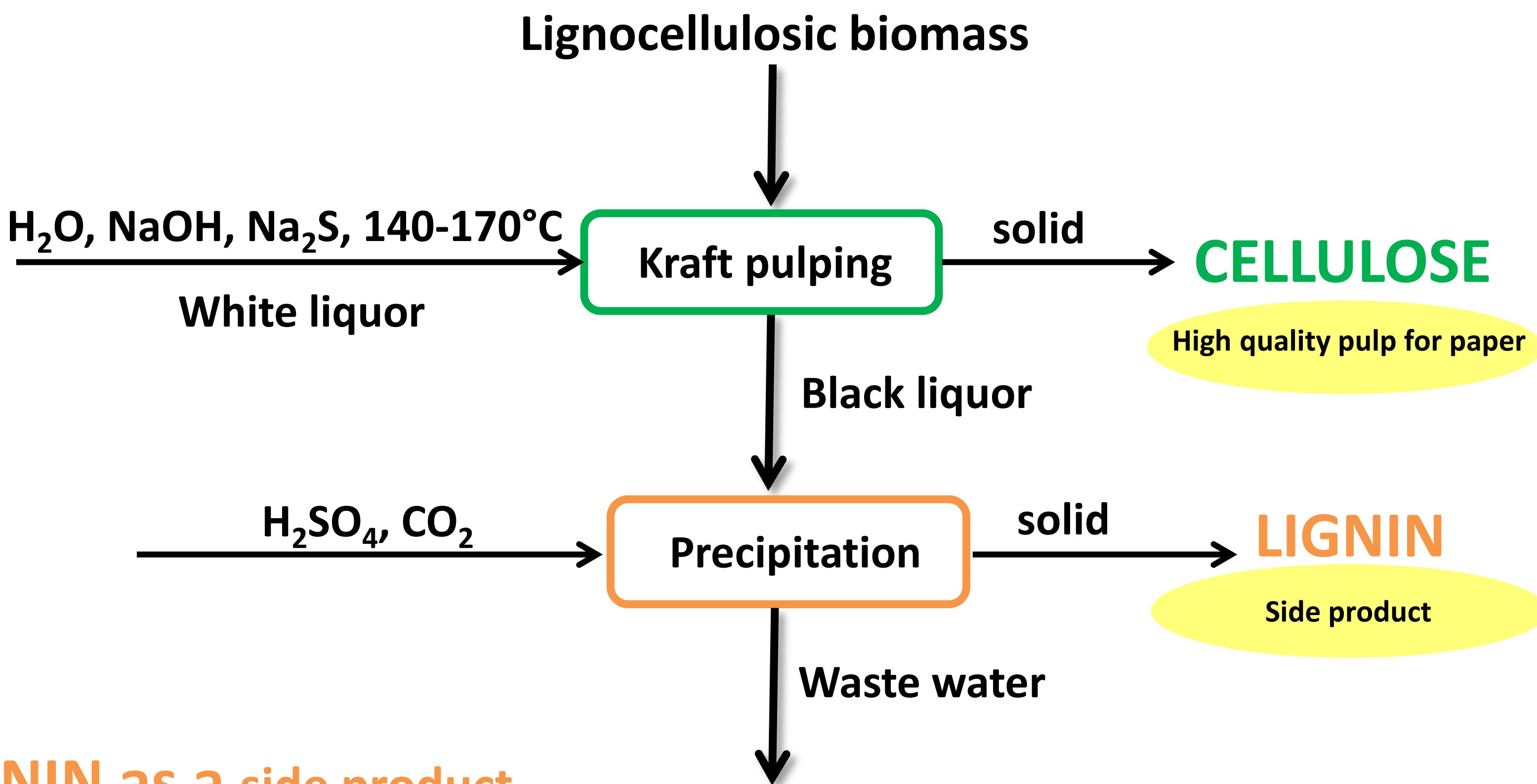






vanillin

Kraft LIGNIN



LIGNIN as a side product

Advantages

High amounts available from the pulp and paper industry - over 70 Mt per year

Disadvantages

Less preserved lignin structure: **β-O-4** linkages are cleaved during the kraft pulping
Lignin structure contains sulfur

Organosolv LIGNIN

Lignocellulosic biomass

$EtOH/H_2O$, H_2SO_4 → **Organosolv pulping** → **solid** → **CELLULOSE**

T= 180 °C

Black liquor

Water → **Precipitation** → **solid** → **LIGNIN**

LIGNIN

High quality

Liquid → **HEMICELLULOSE**

(C5 sugars: xylose, mannose, glucose, galactose and sugar acids)

LIGNIN-first approach

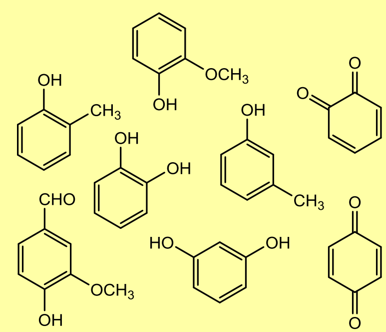
Advantages

- High quality lignin that is suitable for the thermocatalytic conversion into the value-added chemicals such as aromatics
- Most of the **β-O-4** linkages in lignin are preserved

Disadvantages

- Less abundant material in market – production is increasing

Value–added chemicals

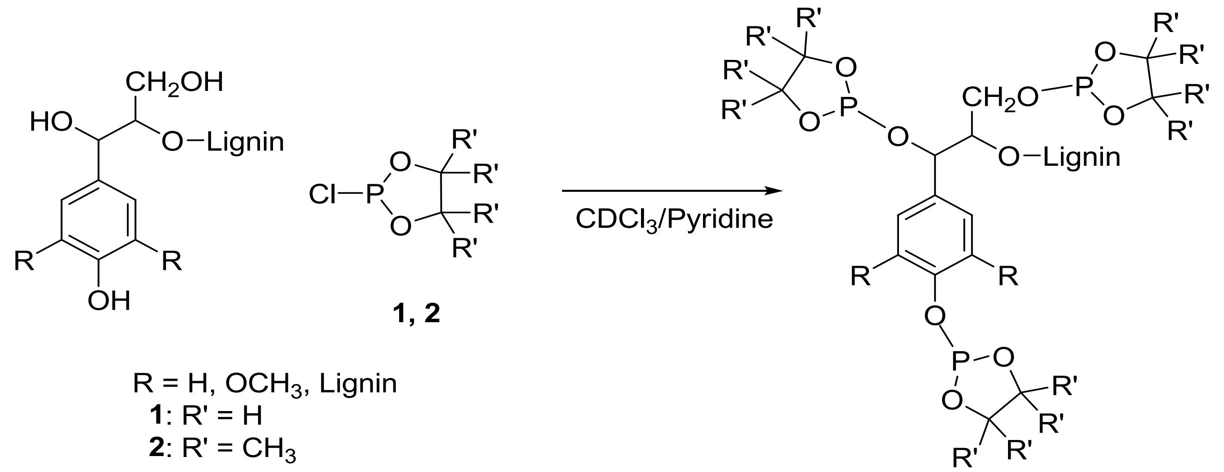


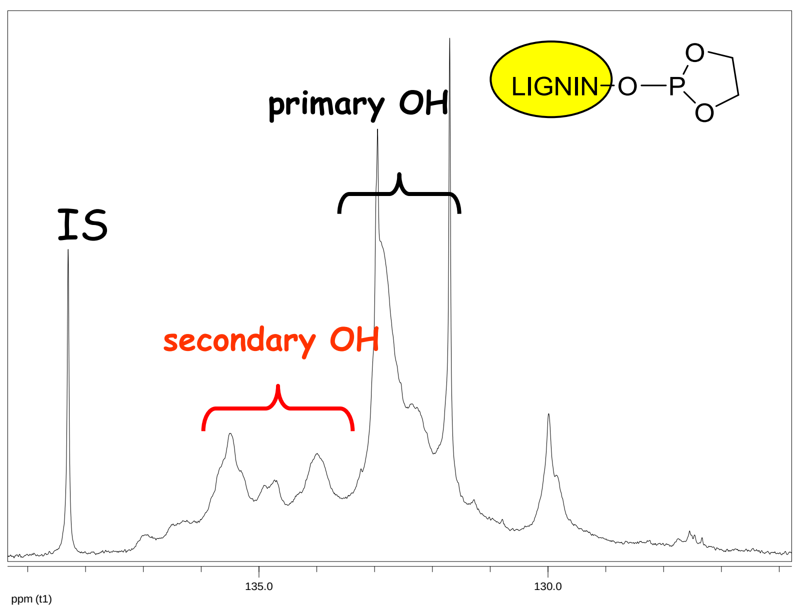
- Cresols
- Catechols
- Resorsinols
- Quinones
- Vanillin
- Guaiacols

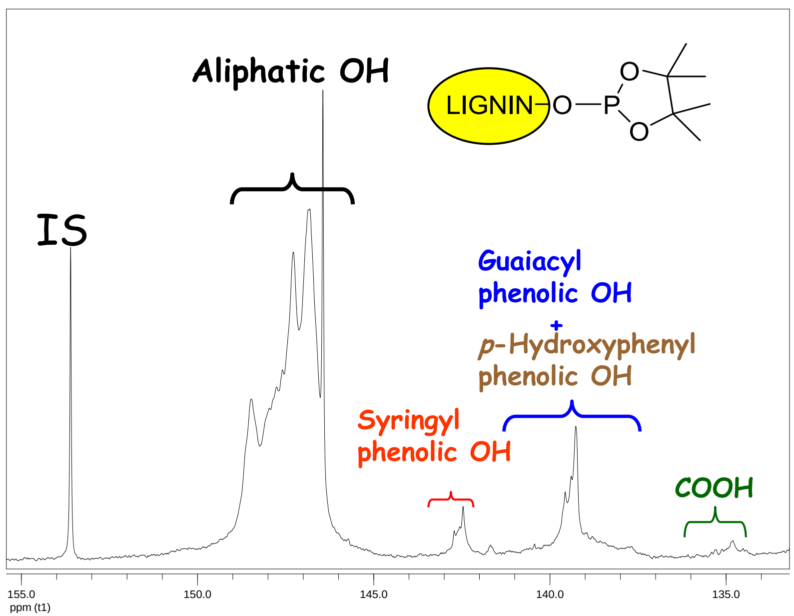
Analytical techniques for the LIGNIN: Quantitative ^{31}P NMR analysis

Identification and quantification of :

- Aliphatic OH groups
  - Primary OH
  - Secondary OH
- Phenolic OH groups
  - Syringyl OH
  - Guaiacyl OH
  - p-Hydroxyphenyl
- Carboxylic OH groups





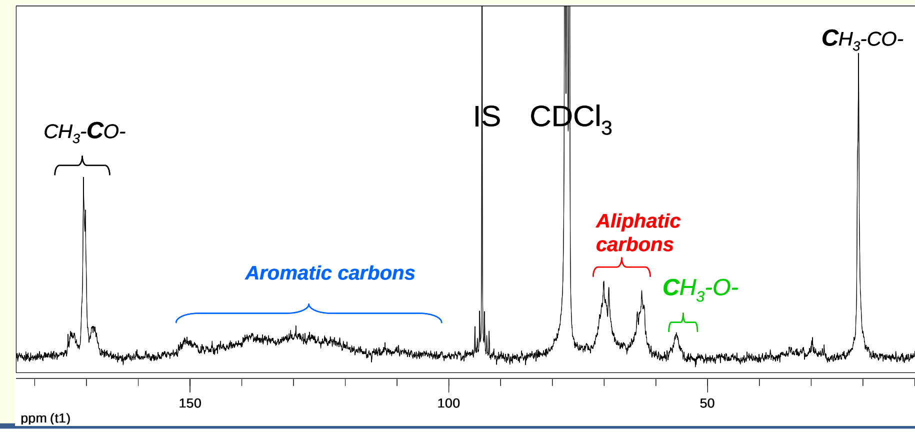


Analytical techniques for the LIGNIN:

Quantitative ^{13}C NMR analysis

Identification and quantification of :

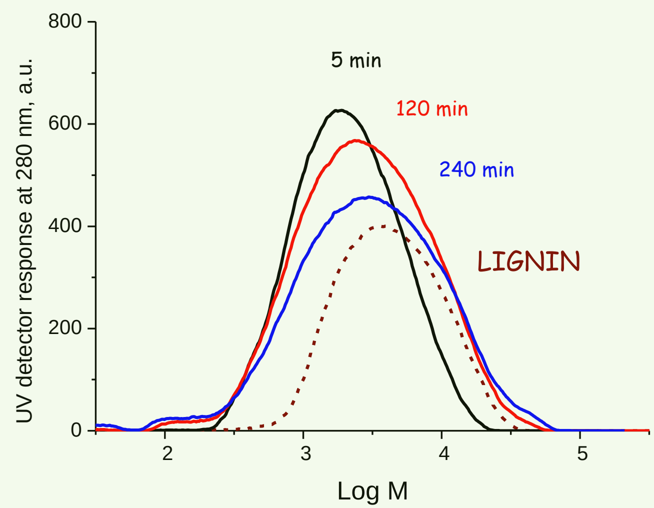
- Aromatic carbons
- Aliphatic carbons
- Methoxy groups



Size-exclusion chromatography

Determination of average molecular weight

UV detector 280 nm
Column: PLgel 5 μm MIXED-E 7.5 x 300 mm
Eluent: THF
Flow rate: 1 mL/min
Injection volume 100 μL



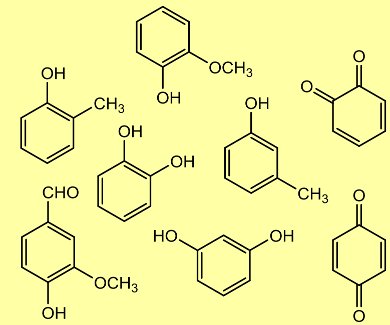
Organosolv LIGNIN isolation

EtOH/H_2O, H_2SO_4

180 °C, 60 min

Conversion

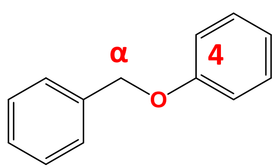
Value–added chemicals



- Cresols
- Catechols
- Resorsinols
- Quinones
- Vanillin
- Guaiacols

Study of α-O-4 linkage cleavage during the organosolv lignin isolation process

Influence of the solvent

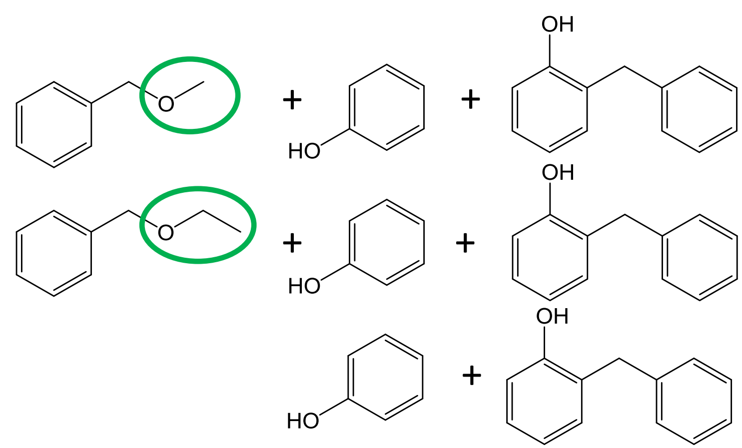


α-O-4 lignin model compound

MeOH, H_2SO_4, 200 °C, 240 min

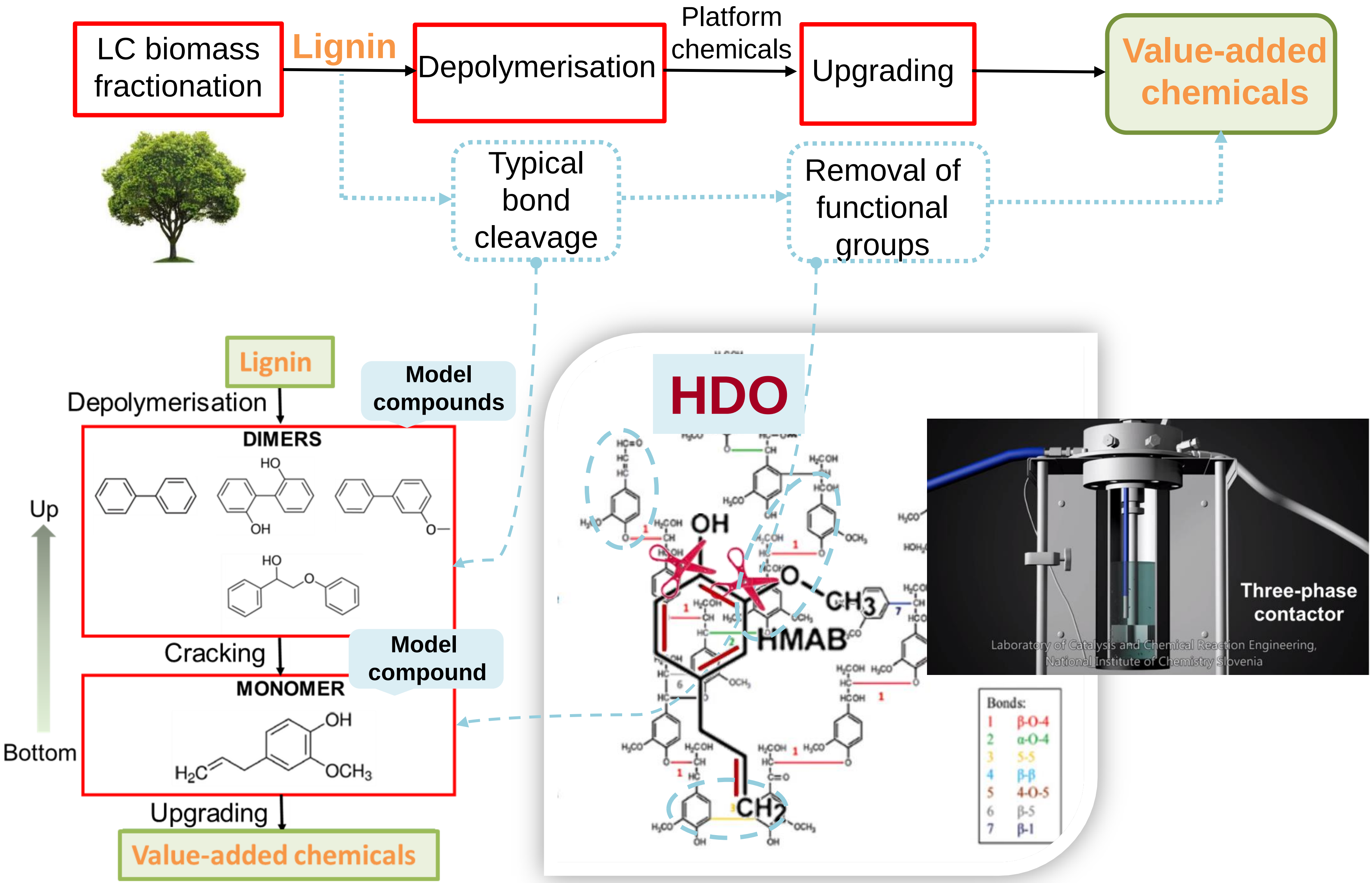
EtOH, H_2SO_4, 200 °C, 240 min

GVL, H_2SO_4, 200 °C, 240 min

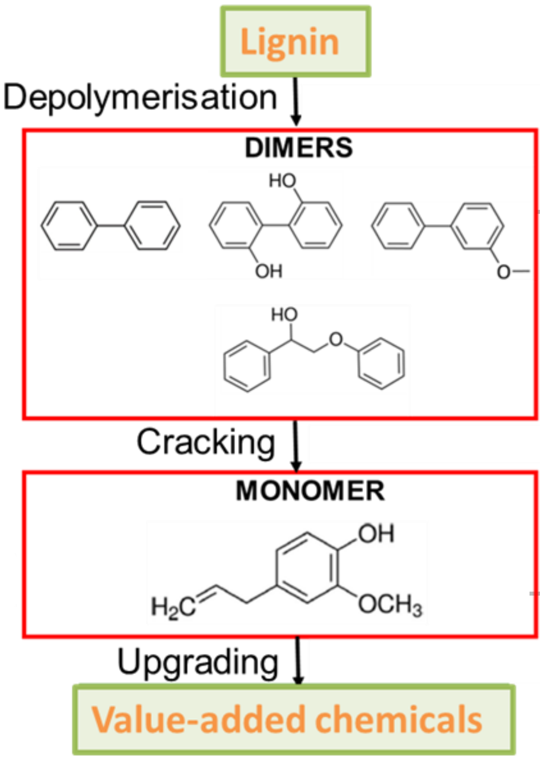


MeOH and **EtOH** acts as a capping agent, while **GVL** is not reactive with reaction intermediates

Lignin processing



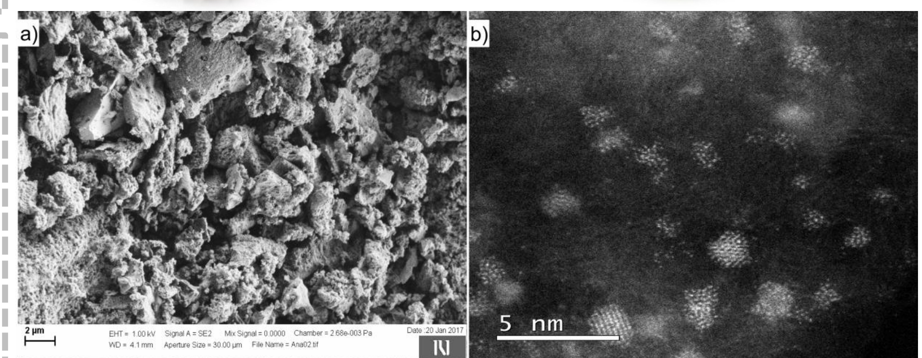
Approach and objectives

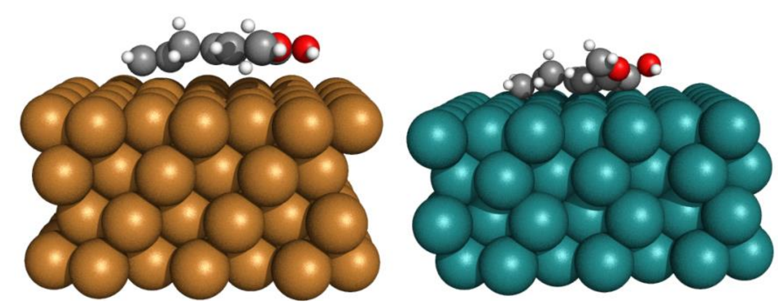


Temperature:
225, 325 °C
Pressure:
5, 7 MPa
Catalysts:
Pt/Al_2O_3, Pt/C,
Ni/Al_2O_3, Cu/Al_2O_3
Catalyst loading:
0.4 wt%
Dimers loading:
up to 2 wt%

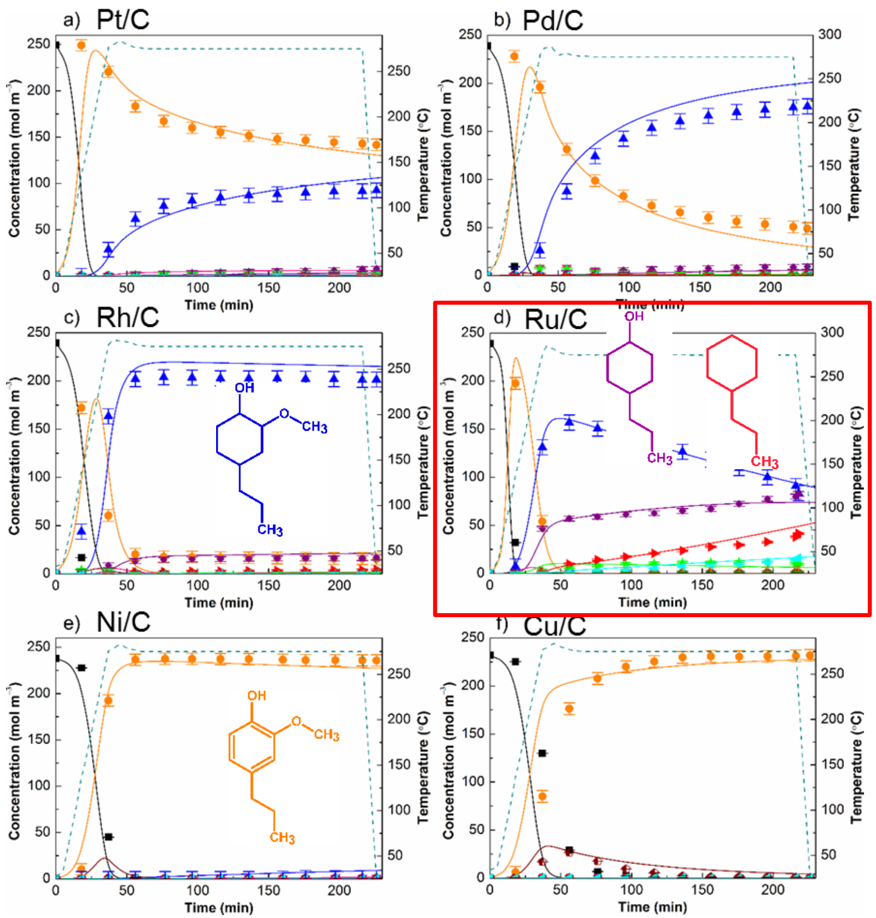
Temperature:
225 – 325 °C
Pressure:
3 – 7 MPa
Carbon supported:
Ru, Pt, Pd, Rh, Ni, Cu
Alumina supported:
Ru, Pt, Pd, Rh, Ni, Cu
Additionally:
Ru/SiO_2, Ru/SiO_2-Al_2O_3,
Ru/TiO_2, Ru/HZSM-5
Catalyst loading:
0 – 0.4 wt%
Eugenol loading:
0 – 5 wt%
Solvent:
Hexadecane

The role of different active sites

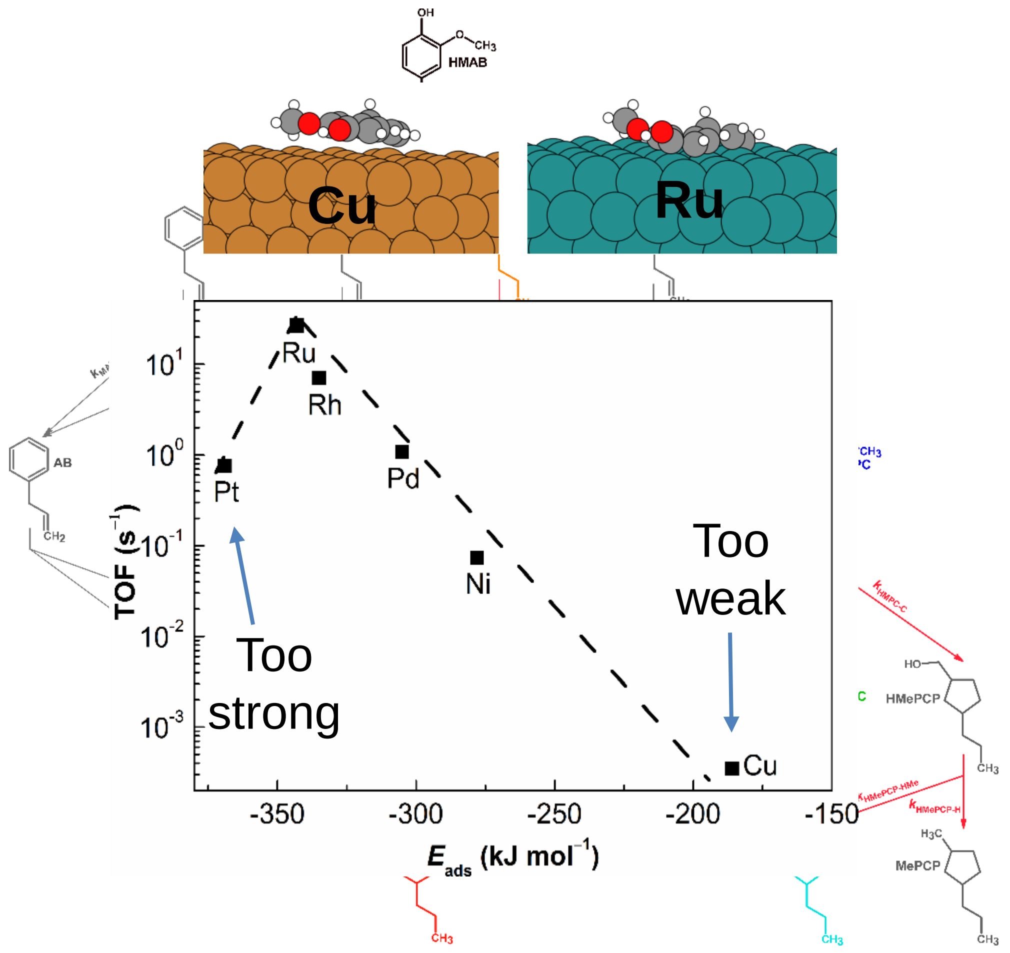




Eugenol HDO over Ru/C: reaction network

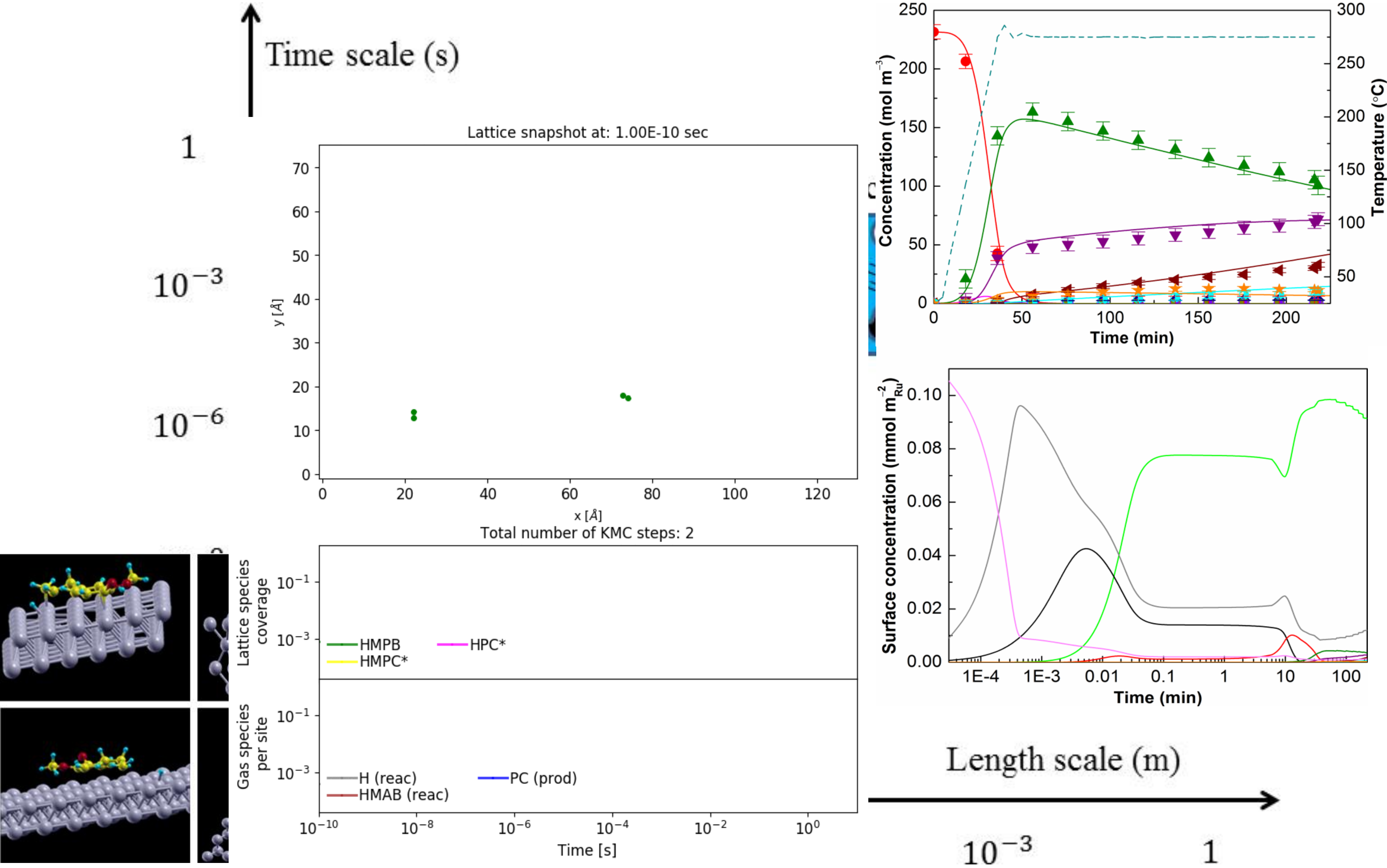


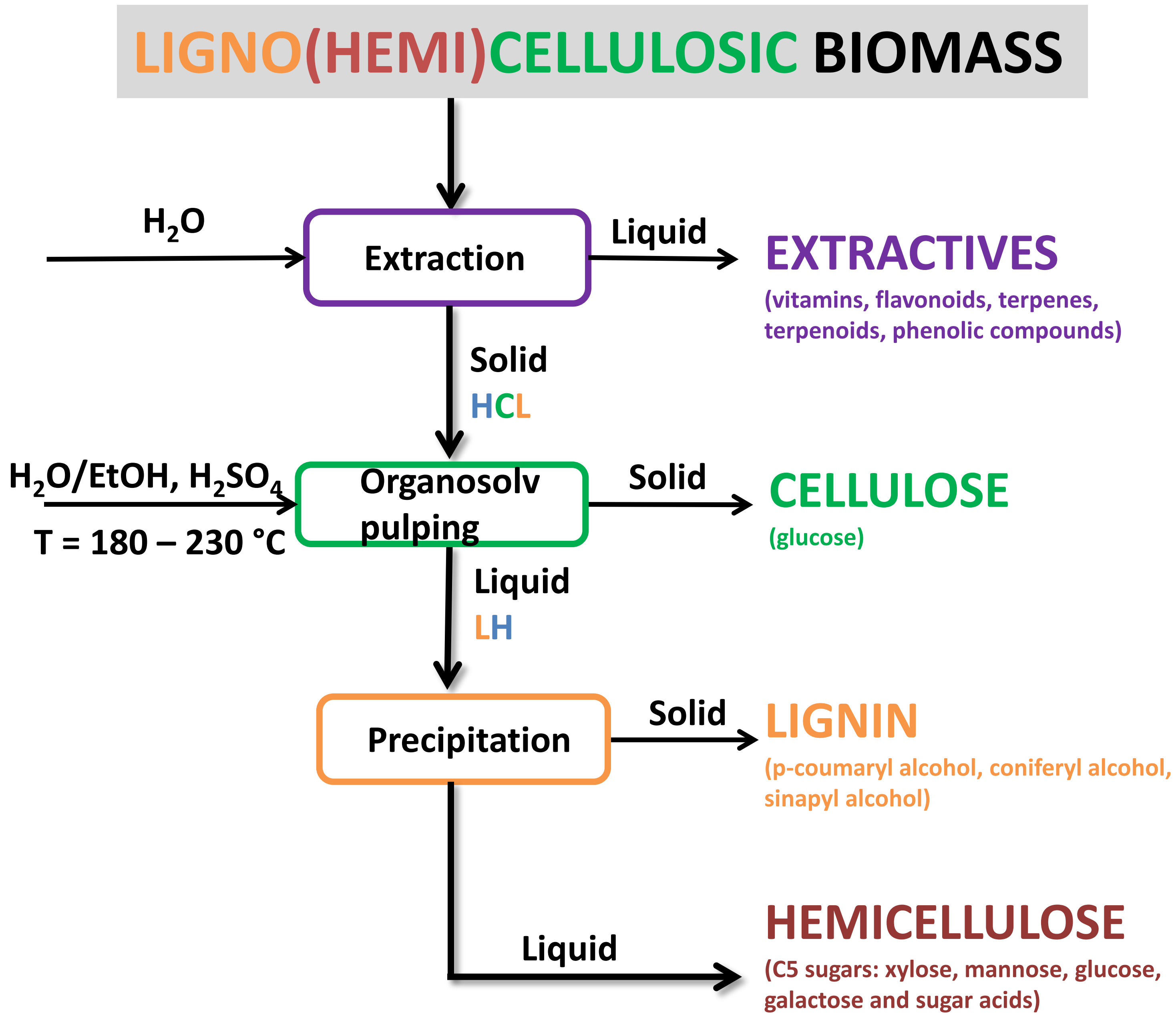
Proposed eugenol HDO reaction network



- Dominant reaction pathway
- Less dominant reaction pathway
- Non-occurred reactions

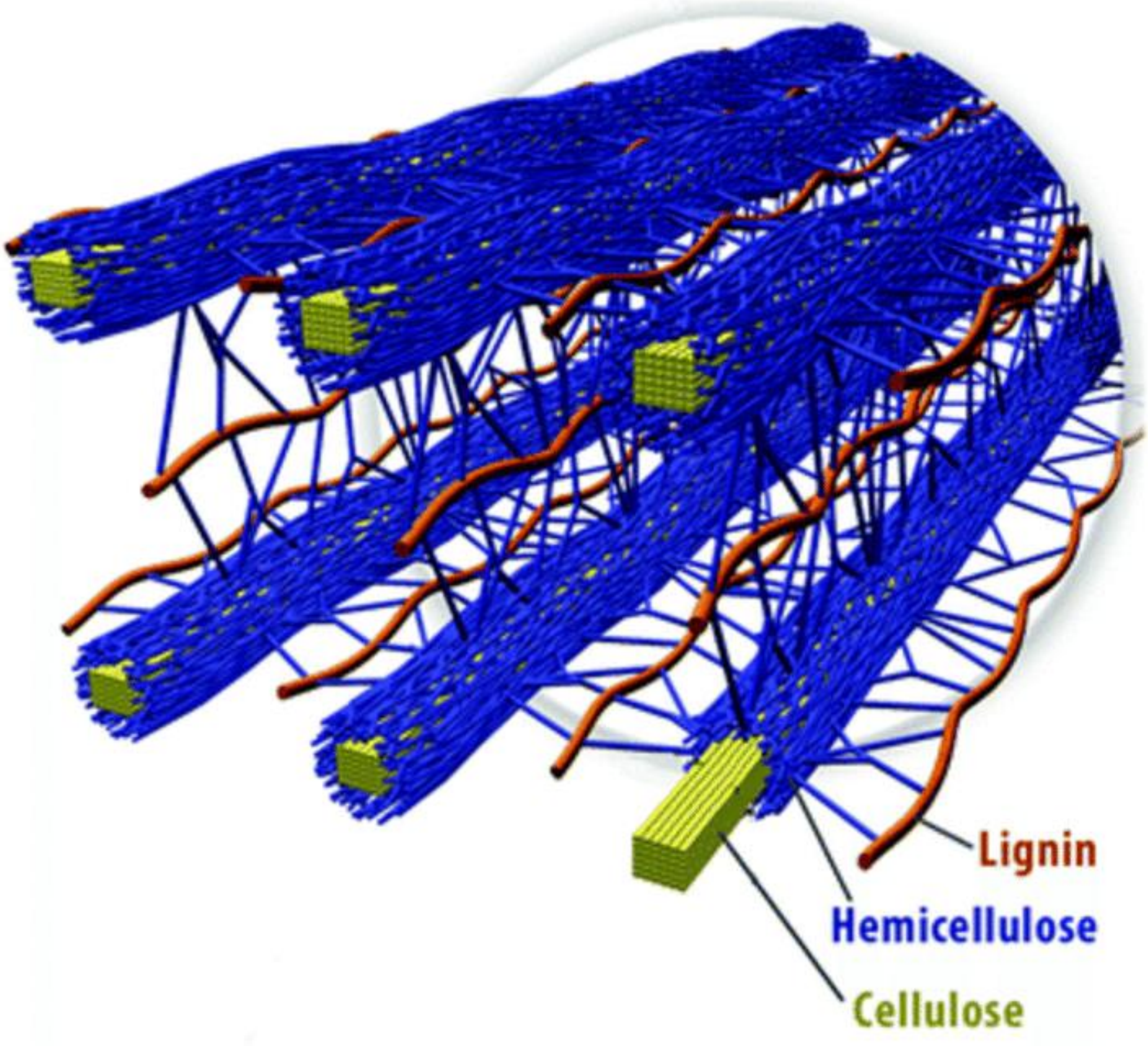
MULTISCALE MODELING: BRIDGING THE GAP





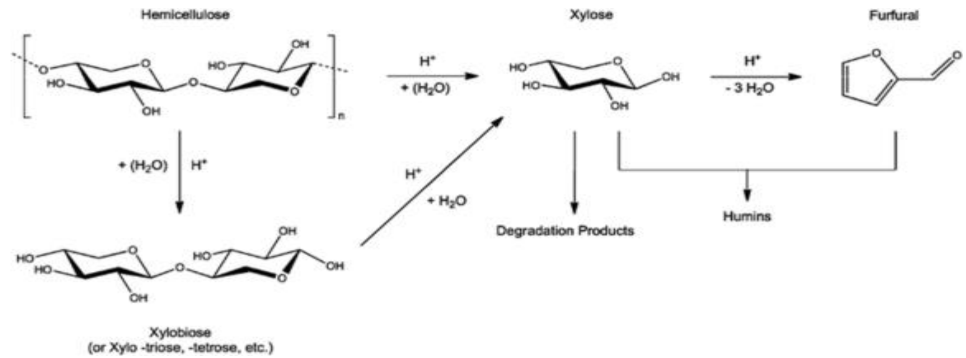
LIGNO(HEMI)CELLULOSIC BIOMASS
H_2O
Extraction
Liquid
EXTRACTIVES
(vitamins, flavonoids, terpenes, terpenoids, phenolic compounds)
Solid
HCL
H_2O/EtOH, H_2SO_4
T = 180 – 230 °C
Organosolv pulping
Solid
CELLULOSE
(glucose)
Liquid
LH
Precipitation
Solid
LIGNIN
(p-coumaryl alcohol, coniferyl alcohol, sinapyl alcohol)
Liquid
HEMICELLULOSE
(C5 sugars: xylose, mannose, glucose, galactose and sugar acids)

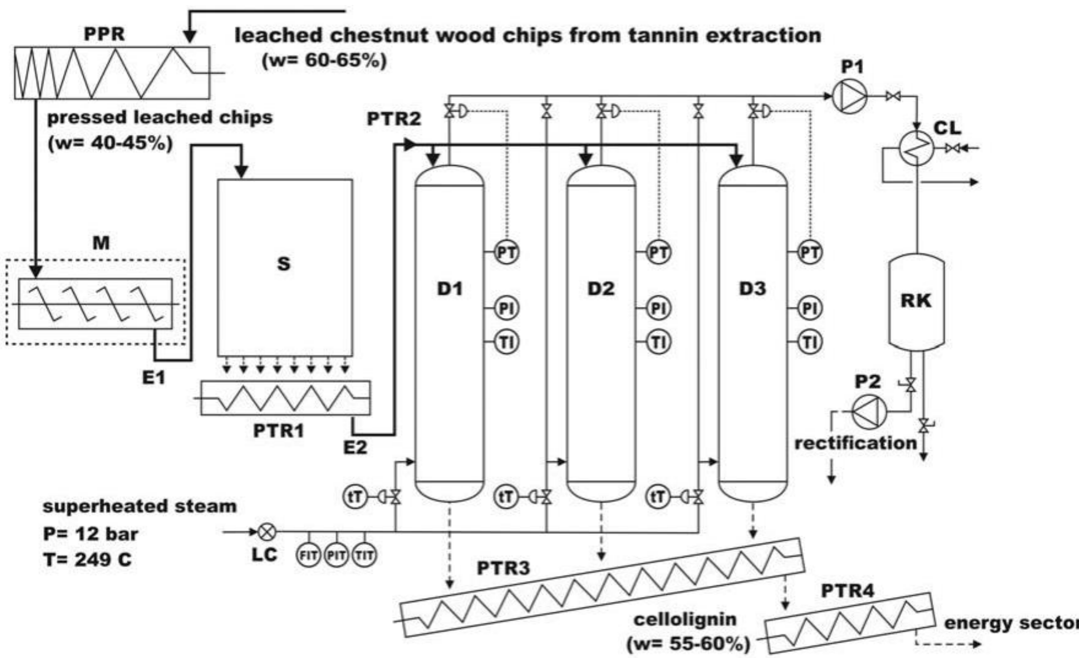
HEMICELLULOSE



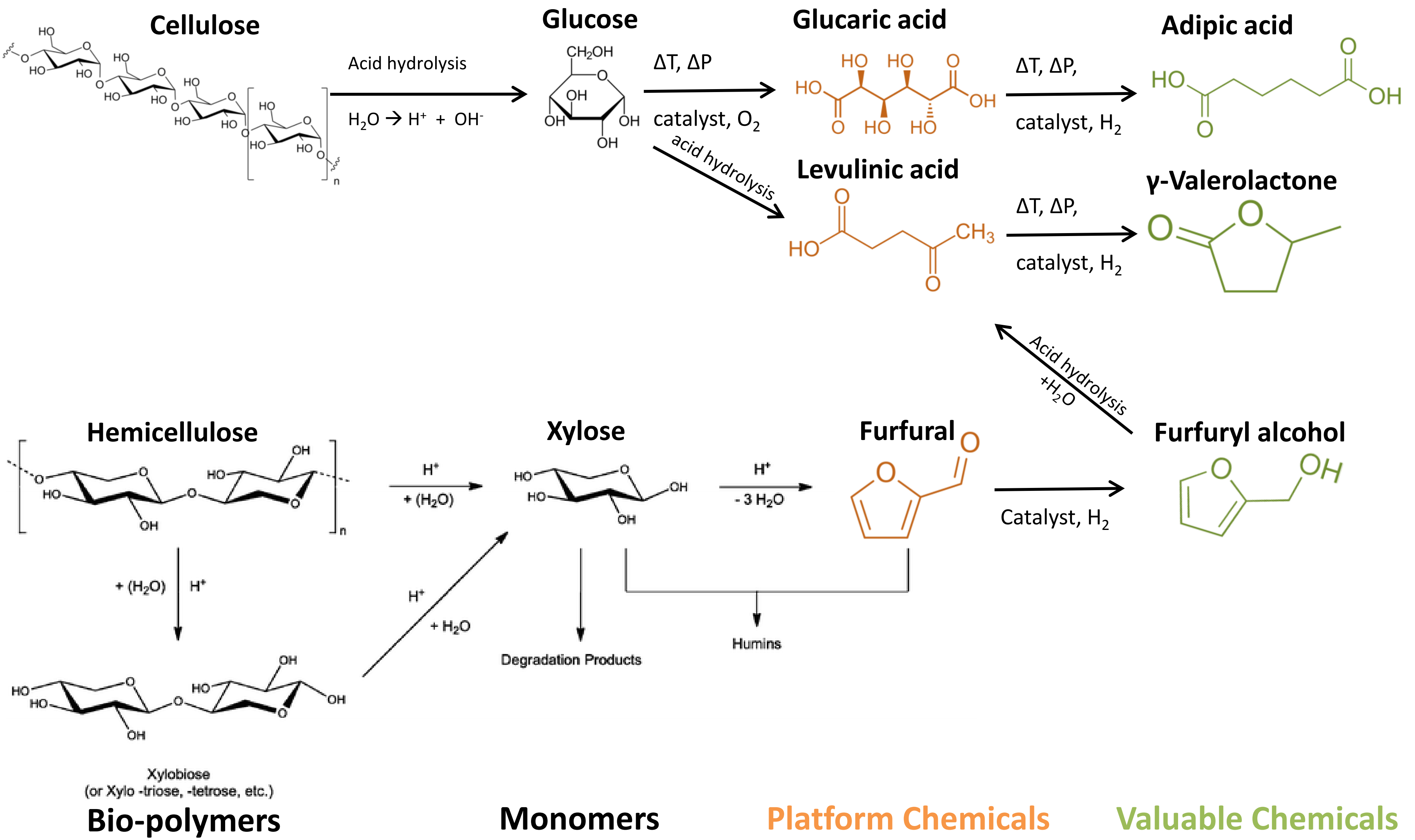
FURFURAL FROM HEMICELLULOSE

Co-operation with industrial partner





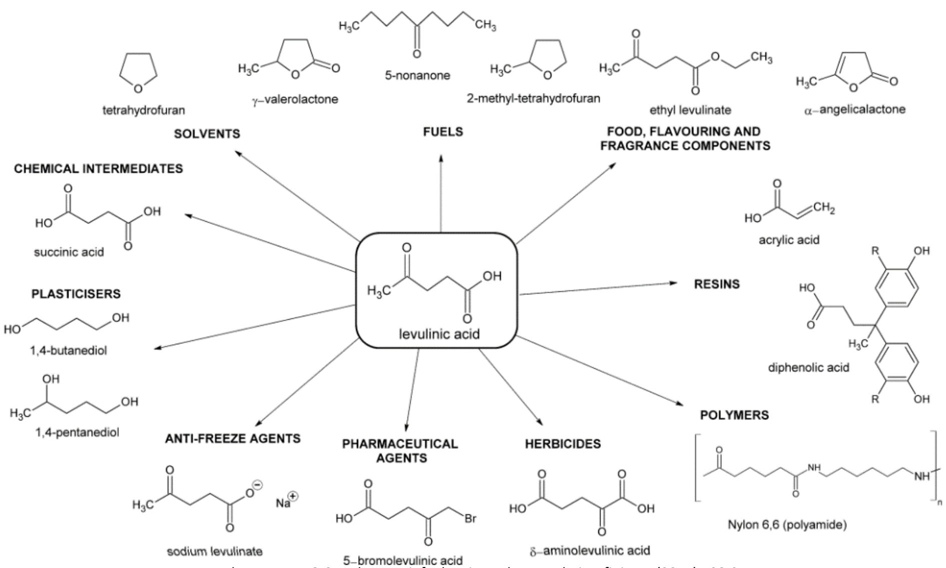
CELLULOSE AND HEMICELLULOSE VALORISATION: TOP – DOWN APPROACH



LEVULINIC ACID: PLATFORM CHEMICAL

AIM:

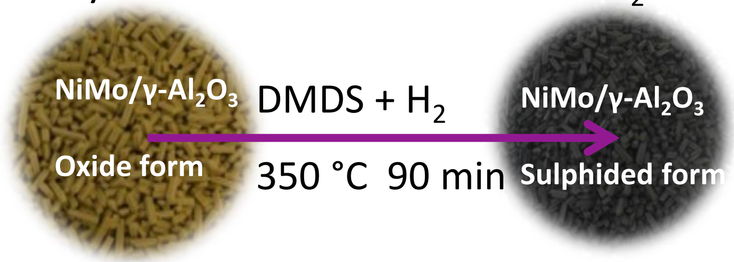
- Added-value biomass-derived products
  - Fuel additives
  - Monomers
  - Flavors
  - Solvents
- Use of cheap transition metal catalysts
- Avoiding the use of solvents
- Reaction mechanism proposal
- Microkinetic model development
- Process bottlenecks identification



D.W. Rackemann, W.O.S. Doherty, Biofuels, Bioproducts and Biorefining 5 (2011) 198-214

LEVULINIC ACID HYDROTREATMENT TESTS:

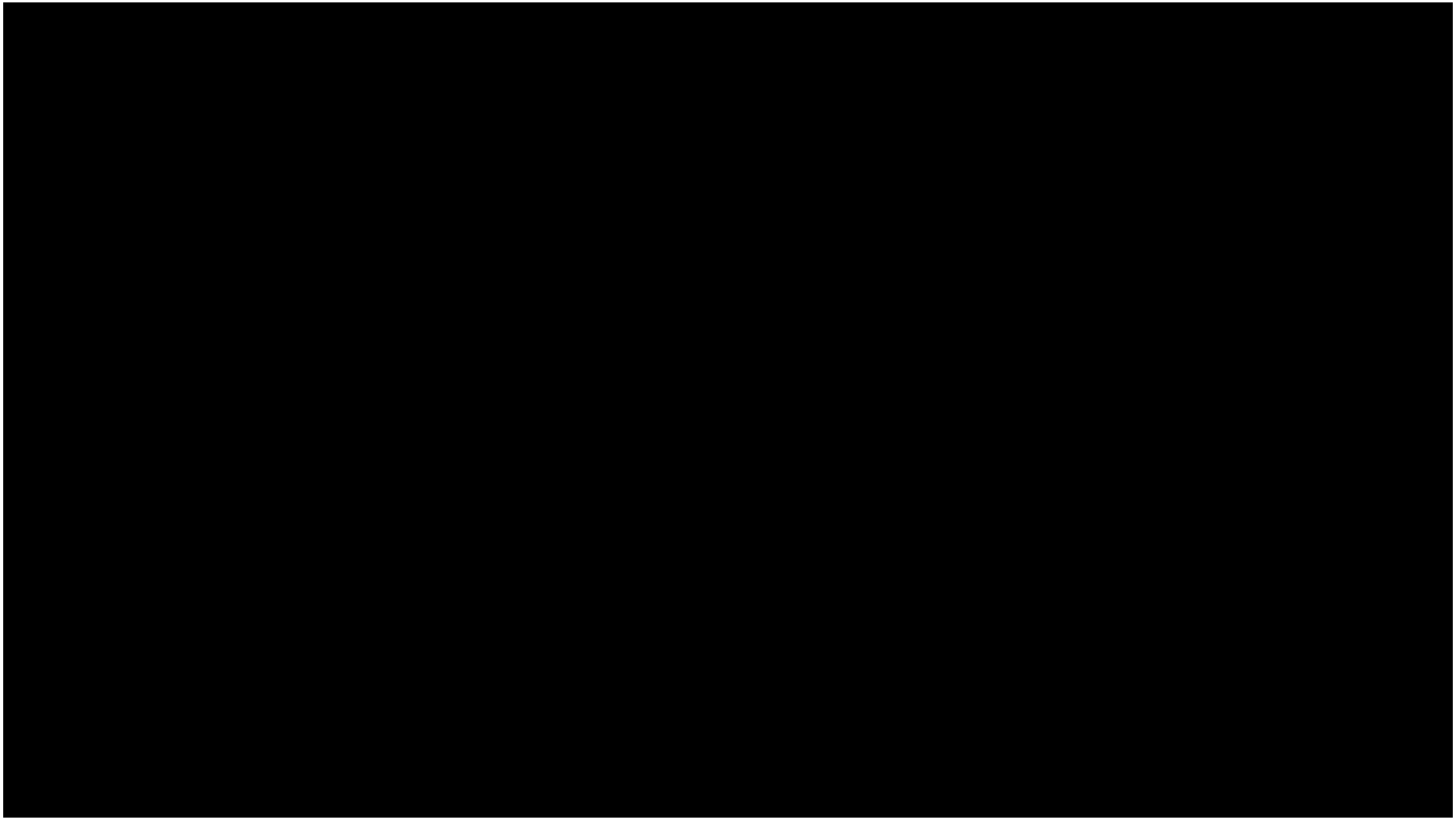
- Solventless conditions
- Hydrogenation agent: gaseous H_2
- Batch regime (S,L), continuous purge of gas phase
- Commercial NiMo/γ-Al_2O_3 catalyst
- Catalyst activation with DMDS and H_2



Run	Temperature (°C)	Pressure (MPa)	Stirring speed (min^{-1})	Catalyst (wt.%)	Particle size
1	**225**	5.0	1000	2	1.5 mm pellets
2	**250**	5.0	1000	2	1.5 mm pellets
3	**275**	5.0	1000	2	1.5 mm pellets
4	275	**2.5**	1000	2	1.5 mm pellets
5	275	**7.5**	1000	2	1.5 mm pellets
6	275	**5.0 (N_2)**	1000	2	1.5 mm pellets
7	250	**5.0 (N_2)**	1000	2	1.5 mm pellets
8	275	5.0	**200**	2	1.5 mm pellets
9	275	5.0	**600**	2	1.5 mm pellets
10	275	5.0	**1400**	2	1.5 mm pellets
11	275	5.0	1000	**0**	1.5 mm pellets
12	250	5.0	1000	**0**	1.5 mm pellets
13	275	5.0	1000	**1**	1.5 mm pellets
14	275	5.0	1000	**4**	1.5 mm pellets
15	275	5.0	1000	2	**500–710 μm**
16	275	5.0	1000	2	**150–250 μm**
17	275	5.0	1000	2	**< 40 μm**
18	275	5.0	1000	2	1.5 Q pellets

LEVULINIC ACID HDO: EXPERIMENTAL SET-UP

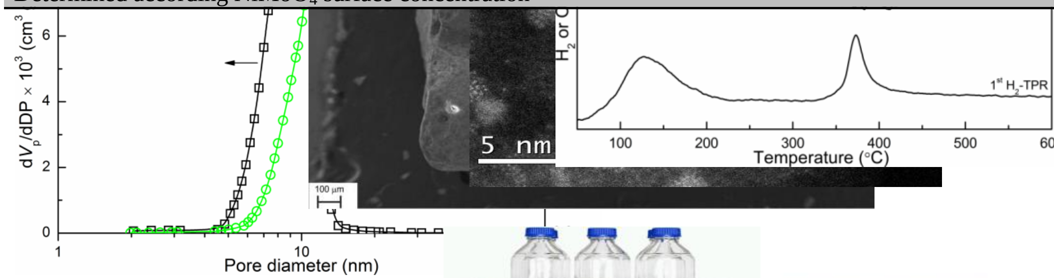
LEVULINIC ACID HDO: EXPERIMENTAL SET-UP



LEVULINIC ACID HDO: ANALYTICS

Catalyst	Metal content (wt. %)	Active Phase	Active sites (µmol m^{-2})	Surface Area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore size (Å)
NiMo/Al_2O_3	3/15[a]	$NiMoS_x$	0.33[b]	170.9	0.471	110.4

[a] As mass content of NiO and MoO_3 respectively for fresh catalyst
[b] Determined according $NiMoO_4$ surface concentration



Solid phase (catalyst):

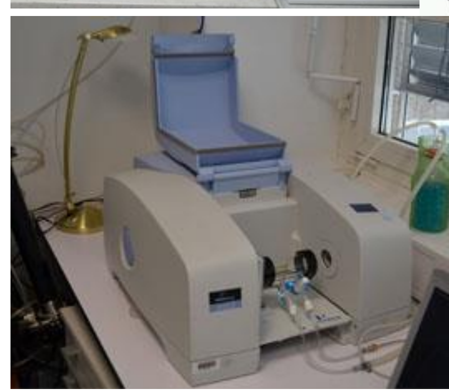
- BET
- TPR-TPO-TPR
- TEM, SEM/EDX
- XRD
- NH_3-TPD

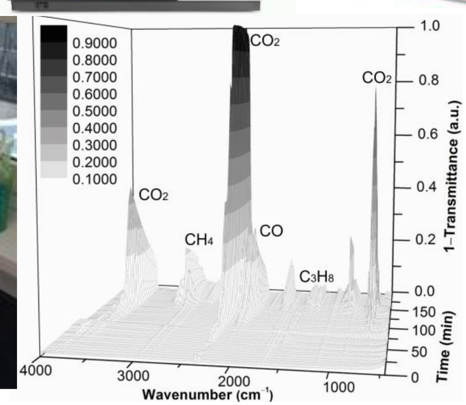
Liquid phase analysis (sampling):

- GC-MS (Identification)
- GC-FID (Quantification)
- UHPLC-FC and Benchtop NMR (New)

Gas phase analysis (online):

- FTIR (flow-through cell)
- µ-GC

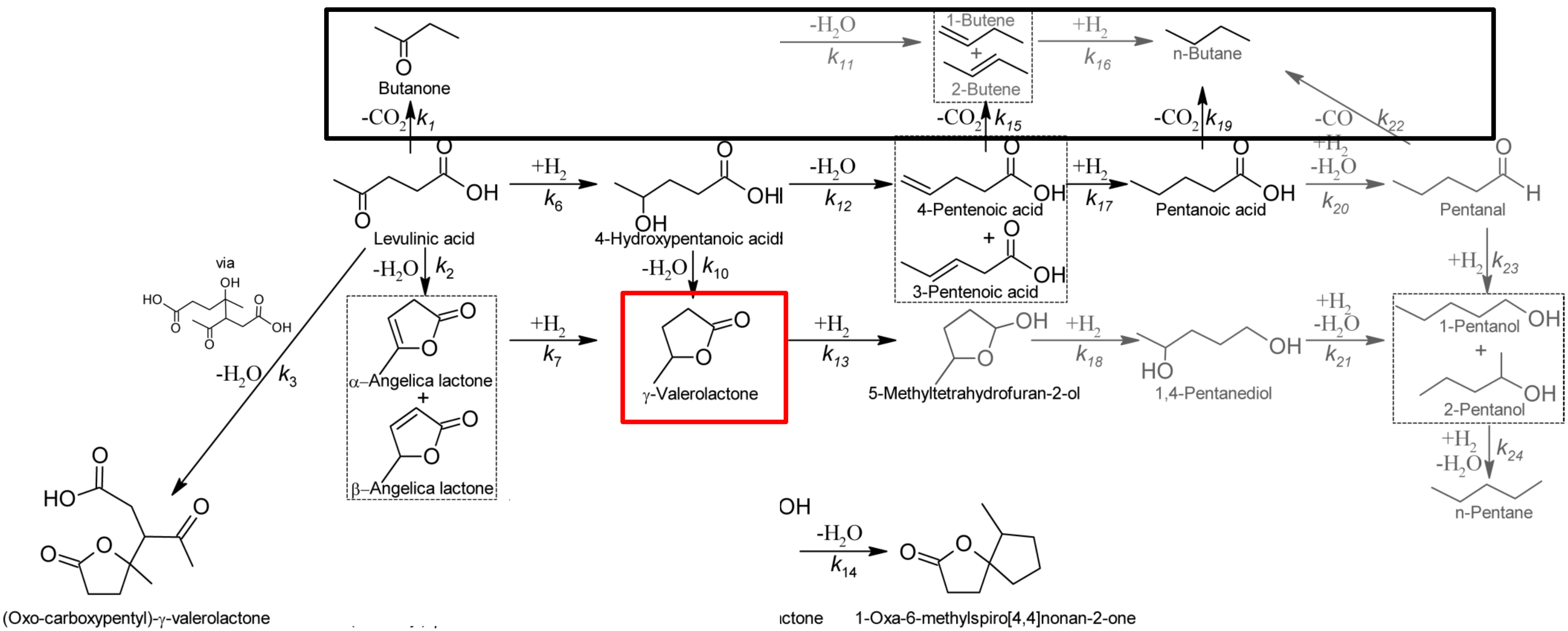




LEVULINIC ACID HDO: REACTION PATHWAY NETWORK

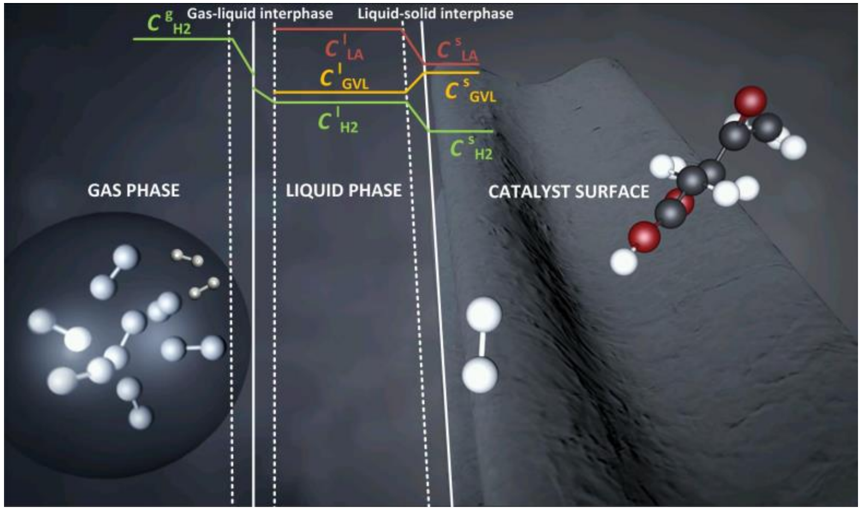
Elementary reactions:

- Decarboxylation
- Ketone group hydrogenation
- Dehydrative cyclisation
- Alkene hydrogenation
- Oligomerization by C-C coupling



LEVULINIC ACID HDO: MICROKINETIC MODEL

- Thermodynamics (VLE-EOS)
- Mass transfer G-L, L-S
- Adsorption & desorption
- Bulk reactions
- Surface reactions



Mass transfer rate through G-L film:

$$r_j^{GL} = k_j^L \cdot A_G \cdot (C_j^{Li} - C_j^L)/V_L$$

$$k_j^L = 0.42 \cdot \left(\frac{\mu_l \cdot g}{\rho_l}\right) \cdot Sc^{-0.5} \cdot \alpha \cdot d_b$$

$$C_j^{Li} = f(P_{tot}, T, y_j)$$

$$A_G = 6 \cdot V_G \cdot \varepsilon_G / d_b$$

$$\varepsilon_G = 0.45 \frac{(N - N^*) \cdot d_t^2}{d_r \cdot (g \cdot d_r)^{0.5}} + 0.31 \cdot \left(\frac{u_G}{\sqrt[4]{\frac{\sigma_l \cdot g}{\rho_l}}}\right)^{2/3}$$

$$d_b = \left(\frac{0.41 \cdot \sigma_l}{g \cdot (\rho_l - \rho_g)}\right)^{0.5}$$

Mass transfer rate through L-S film:

$$r_j^{LS} = k_j^S \cdot A_S \cdot (C_j^L - C_j^{Si})/V_L$$

$$k_j^S = 0.34 \cdot \left(\frac{g \cdot \mu_l \cdot (\rho_s - \rho_l)}{\rho_l^2}\right)^{1/3} \cdot Sc^{-2/3}$$

$$A_S = m_S \cdot a_{BET}$$

Adsorption rate:

$$r_j^A = k_j^A \cdot C_j^{Si} \cdot C_{VS}^*$$

$$C_{VS}^*(t=0) = m_s \cdot a_{BET} \cdot C_{AS}/V_L$$

Desorption rate:

$$r_j^D = k_j^D \cdot C_j^*$$

Homogeneous reaction rate:

$$r_i^H = k_i^H \cdot C_{j1}^L \cdot C_{j2}^L$$

Surface reaction rate:

$$r_i^C = k_i^C \cdot C_{j1}^* \cdot C_{j2}^*$$ **Langmuir-Hinshel.**

$$r_i^C = k_i^C \cdot C_{j1}^* \cdot C_{j2}^{Si}$$ **Eley–Rideal**

Molar balances for component *j*:

$$\frac{dn_j^{G}}{dt} = -r_j^{GL} \cdot V_L \pm \sum \frac{y_j \cdot V \cdot P}{R \cdot T}$$ In gas phase

$$\frac{dC_j^L}{dt} = r_j^{GL} - r_j^{LS} + \sum \pm r_i^H$$ In liquid phase

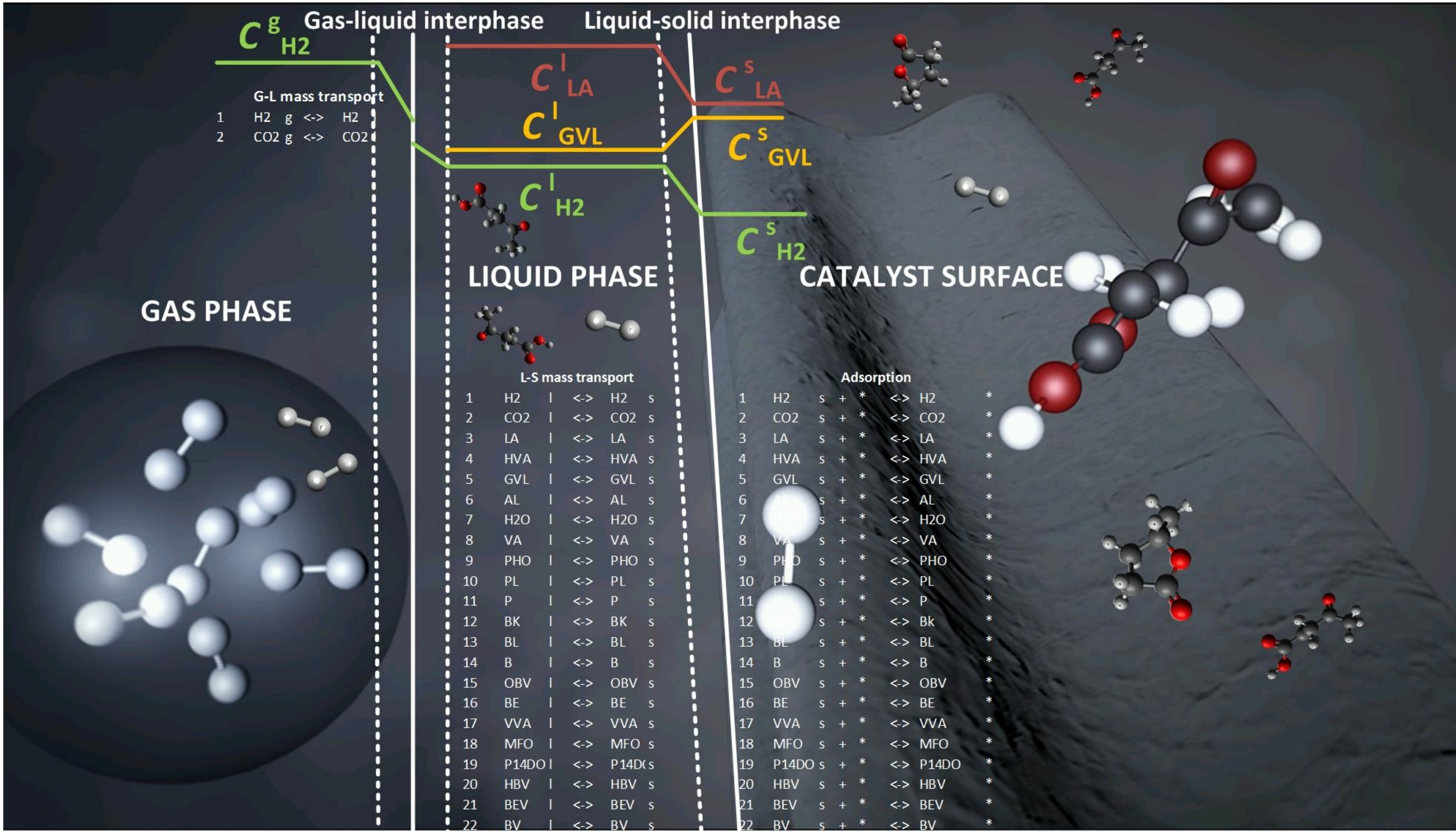
$$\lim_{V_{si} \to 0} \left(V_{si} \frac{dC}{dt}\right) = r_j^{LS} - r_j^{ads} + r_j^{des}$$ On L-S interphase

$$\frac{dC_j^L}{dt} = r_j^{GL} - r_j^{LS} + \sum \pm r_i^H$$ On active sites

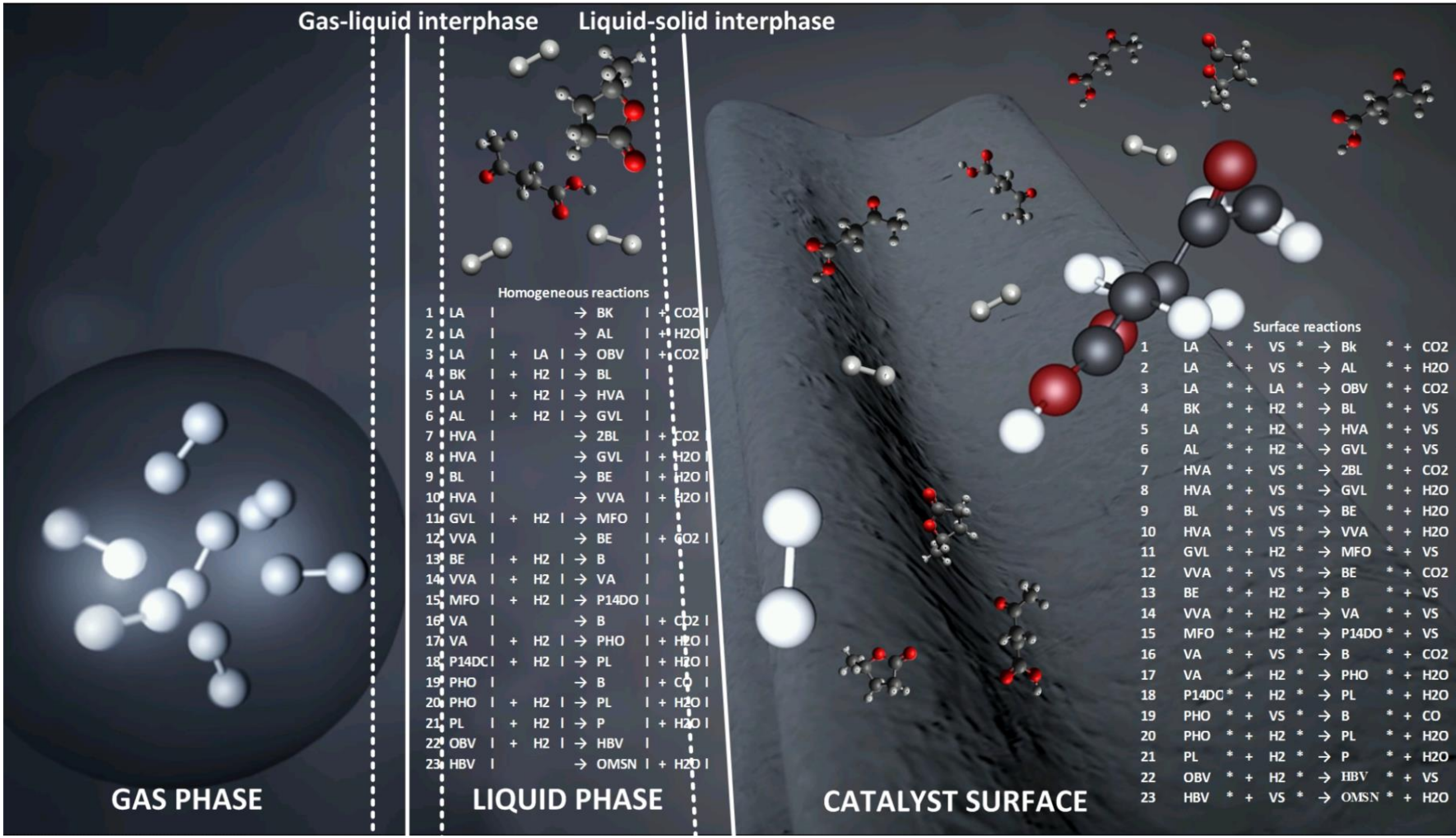
Molar balance for vacant sites:

$$\frac{dC_{VS}^*}{dt} = \sum_{j=1}^{J} r_j^D - \sum_{j=1}^{J} r_j^A + \sum \pm r_i^C$$

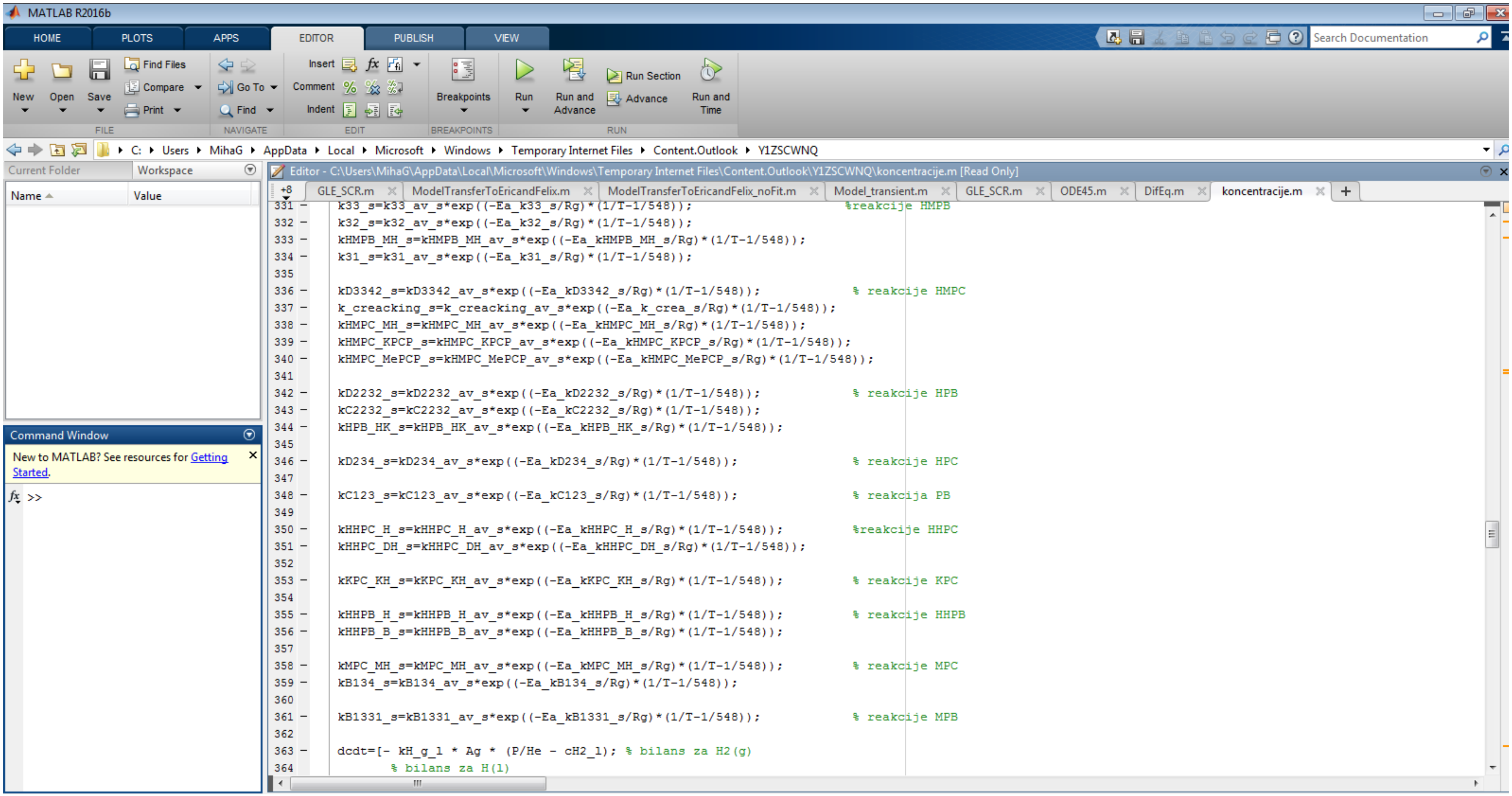
LEVULINIC ACID HDO: MASS TRANSFER



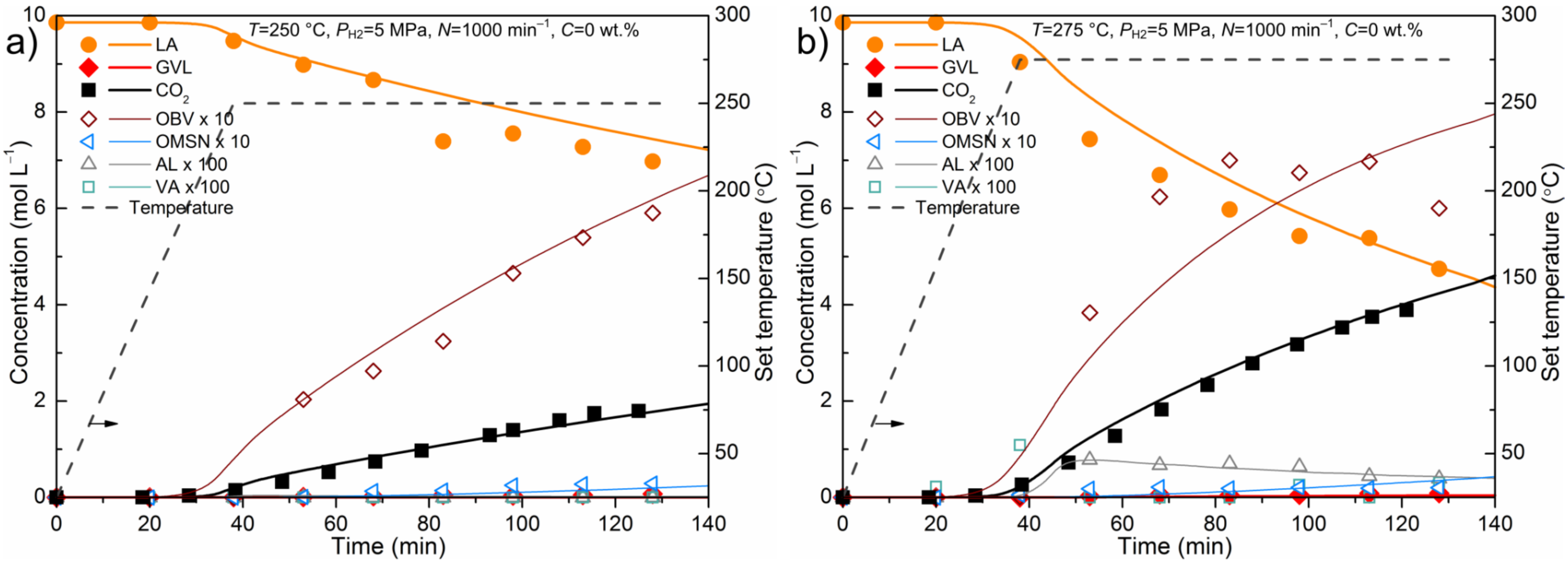
LEVULINIC ACID HDO: HOMOGENEOUS AND CATALYTIC REACTIONS



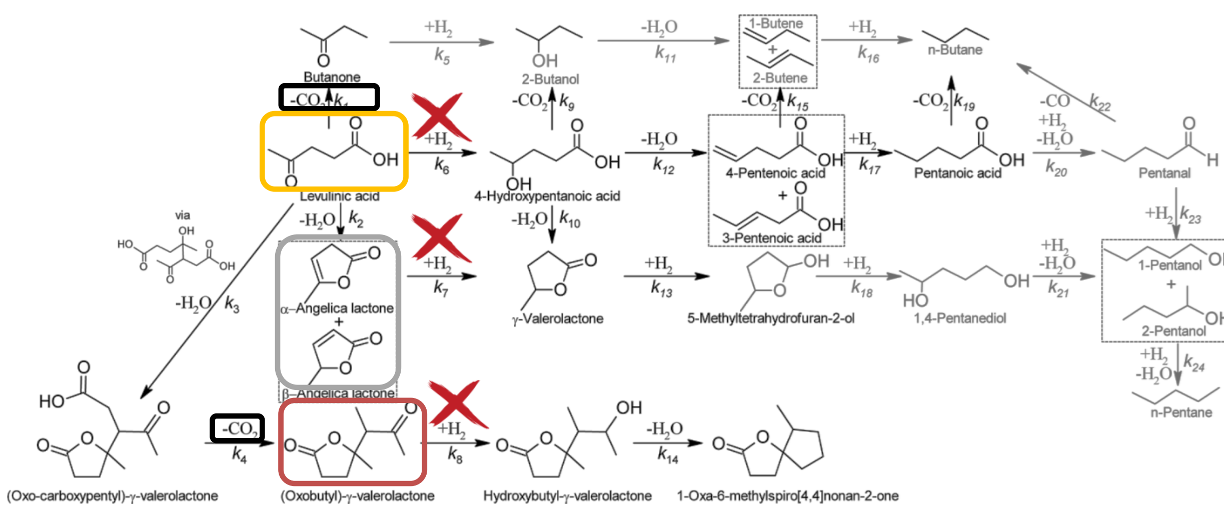
KINETIC MODEL: DIFFERENTIAL EQUATIONS SOLVED NUMERICALLY IN MATLAB



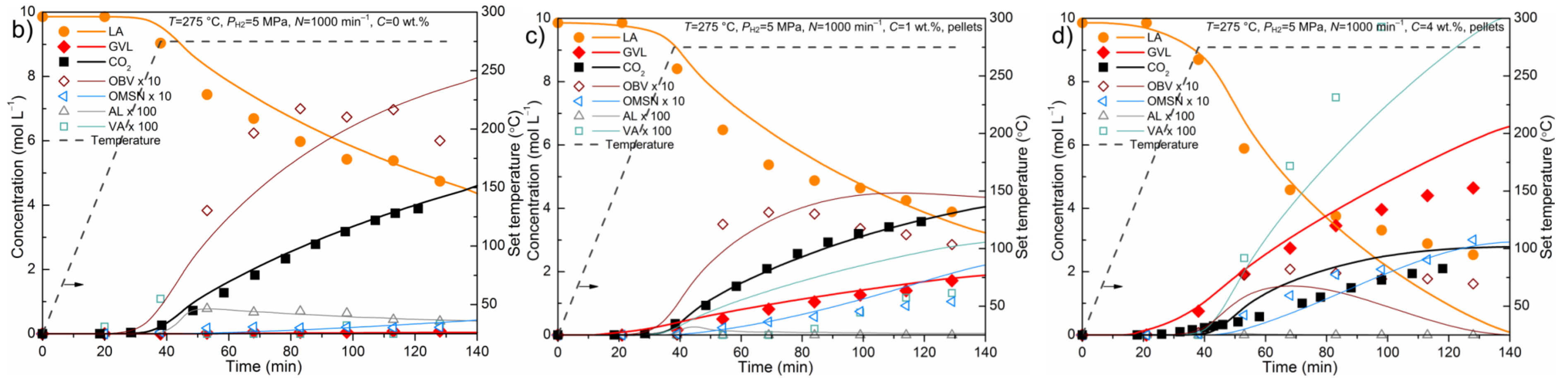
LEVULINIC ACID HDO: HOMOGENEOUS REACTIONS



i	r_i^H	k_i^H at 275 °C	k_i^H unit	Ea_i^H (kJ mol^{-1})
1	$k_1^H [LA^L]$	5.17×10^{-3}	min^{-1}	134
2	$k_2^H [LA^L]$	6.12×10^{-5}	min^{-1}	164
3	$k_3^H [LA^L] [LA^L]$	1.61×10^{-4}	L mol^{-1} min^{-1}	61.3
4	$k_4^H [OCPV^L]$	$>> k_3^H$	min^{-1}	n.a.
5	$k_5^H [BK^L] [H_2^L]$	n.a.	L mol^{-1} min^{-1}	n.a.
6	$k_6^H [LA^L] [H_2^L]$	$< 1.00 \times 10^{-4}$	L mol^{-1} min^{-1}	n.a.
7	$k_7^H [AL^L] [H_2^L]$	3.61×10^{-1}	L mol^{-1} min^{-1}	20.3
8	$k_8^H [OBV^L] [H_2^L]$	3.59×10^{-3}	L mol^{-1} min^{-1}	12.9
9	$k_9^H [HVA^L]$	5.17×10^{-3}	min^{-1}	134
10	$k_{10}^H [HVA^L]$	n.a.	min^{-1}	n.a.
11	$k_{11}^H [BL^L]$	n.a.	min^{-1}	n.a.
12	$k_{12}^H [HVA^L]$	n.a.	min^{-1}	n.a.
13	$k_{13}^H [GVL^L] [H_2^L]$	$< 1.00 \times 10^{-5}$	L mol^{-1} min^{-1}	n.a.
14	$k_{14}^H [HBV^L]$	$>> k_8^H$	min^{-1}	n.a.



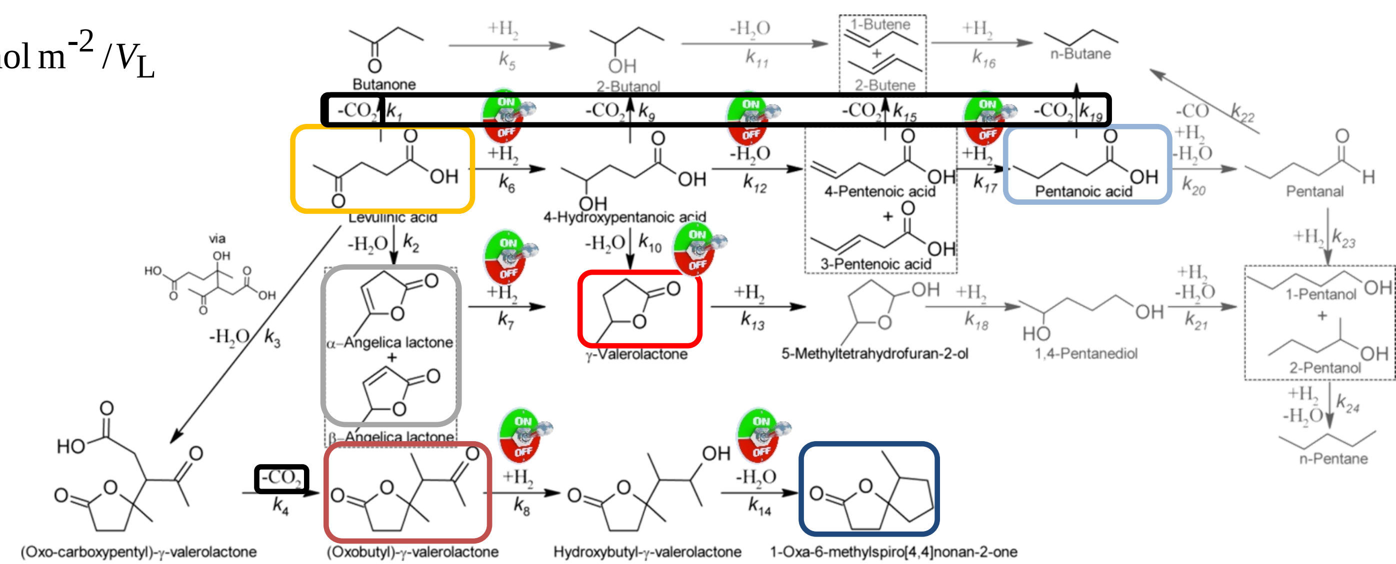
LEVULINIC ACID HDO: CATALYST LOADING



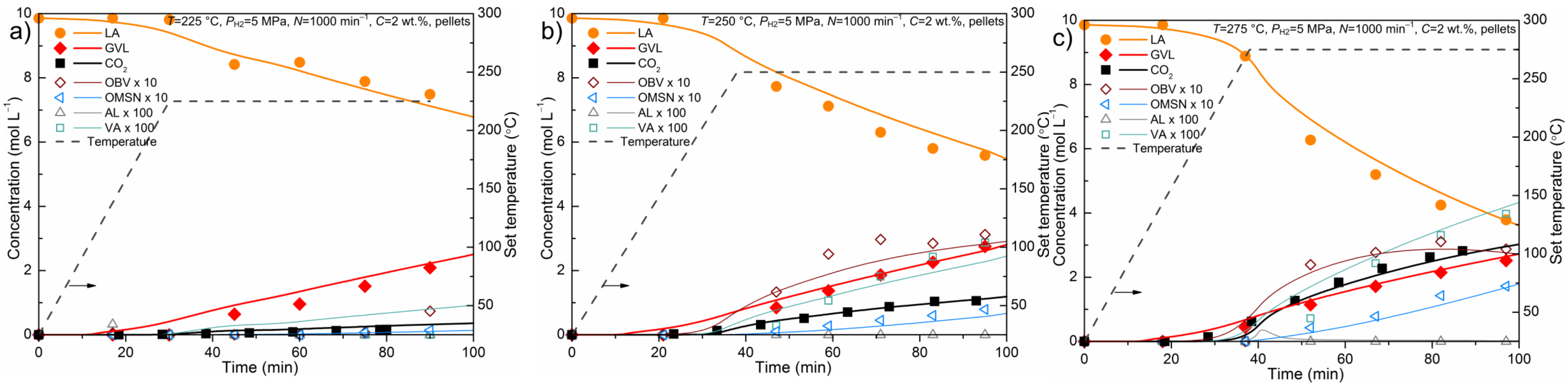
i	r_i^C	k_i^C at 275 °C (L mol^{-1} min^{-1})
1	k_1^C [LA*] [*]	2.15×10^5
2	k_2^C [LA*] [*]	$< 1 \times 10^2$
3	k_3^C [LA*] [LA*]	$< 2 \times 10^3$
4	k_4^C [OCPV*] [*]	n.a.
5	k_5^C [BK*] [H_2*]	n.a.
6	k_6^C [LA*] [H_2*]	2.02×10^9
7	k_7^C [AL*] [H_2*]	7.58×10^{11}
8	k_8^C [OBV*] [H_2*]	3.60×10^9
9	k_9^C [HVA*] [*]	2.15×10^5
10	k_{10}^C [HVA*] [*]	$>> k_6^C$
11	k_{11}^C [BL*] [*]	n.a.
12	k_{12}^C [HVA*] [*]	$k_{10}^C \times 2.04 \times 10^{-2}$
13	k_{13}^C [GVL*] [H_2*]	$< 1 \times 10^5$
14	k_{14}^C [HBV*] [*]	$>> k_8^C$
15	k_{15}^C [VVA*] [*]	2.15×10^5
16	k_{16}^C [BE*] [H_2*]	n.a.
17	k_{17}^C [VVA*] [H_2*]	$>> k_{12}^C$
18	k_{18}^C [MFO*] [H_2*]	n.a.
19	k_{19}^C [VA*] [*]	2.15×10^5
20	k_{20}^C [VA*] [H_2*]	$< 1 \times 10^5$
21	k_{21}^C [PDO*] [H_2*]	n.a.
22	k_{22}^C [PHO*] [*]	n.a.

$.33 \mu mol\, m^{-2} / V_L$

$_i^C$



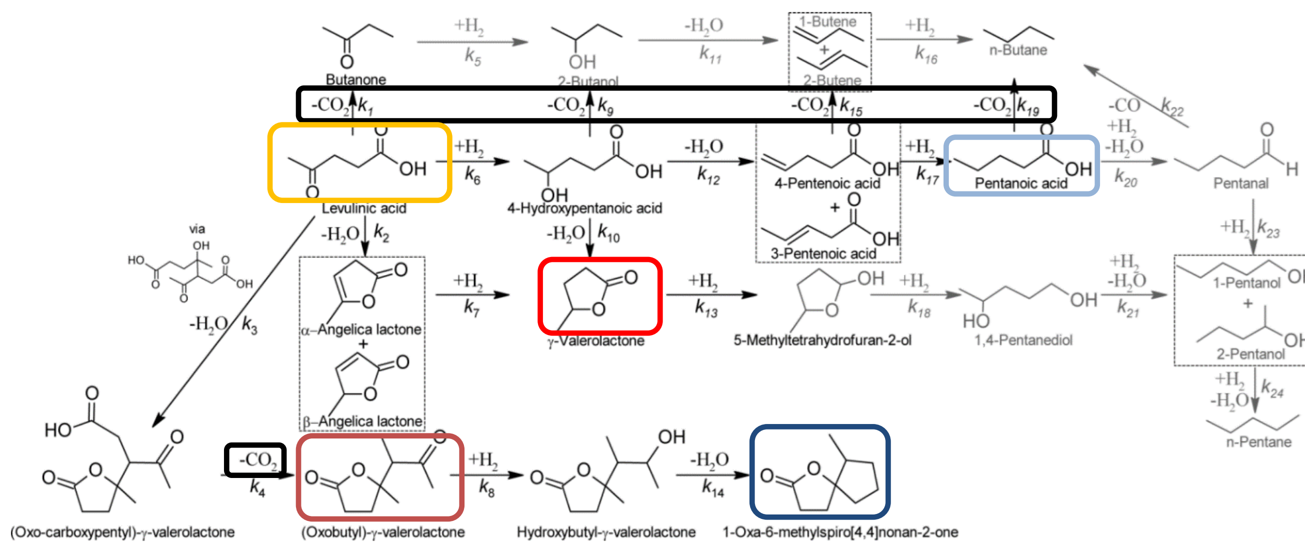
LEVULINIC ACID HDO: TEMPERATURE



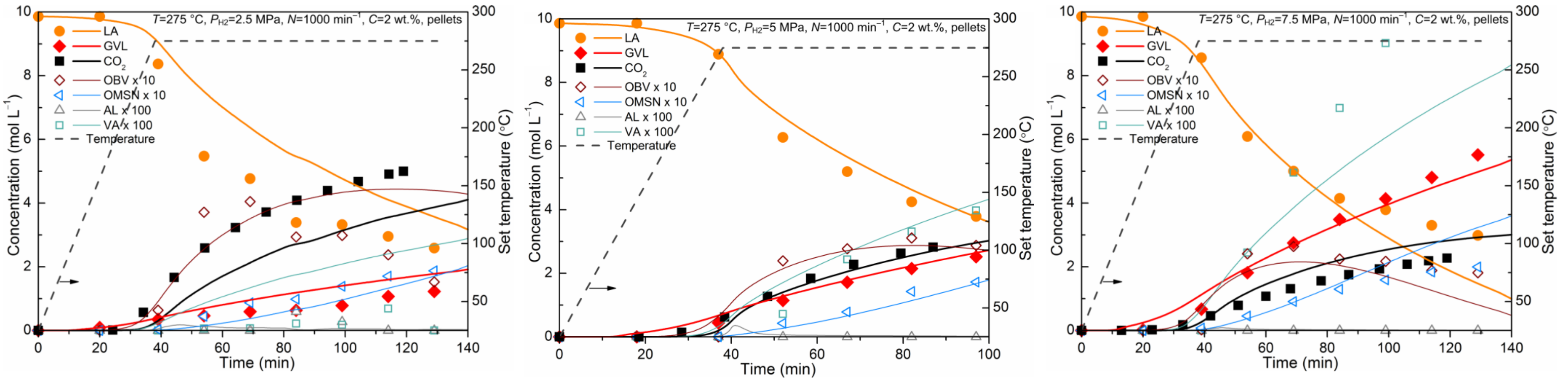
i	r_i^C	k_i^C at 275 °C (L mol^{-1} min^{-1})	Ea_i^C (kJ mol^{-1})
1	k_1^C [LA*] [*]	2.15×10^5	113
2	k_2^C [LA*] [*]	$< 1 \times 10^2$	n.a.
3	k_3^C [LA*] [LA*]	$< 2 \times 10^3$	n.a.
4	k_4^C [OCPV*] [*]	n.a.	n.a.
5	k_5^C [BK*] [H_2*]	n.a.	n.a.
6	k_6^C [LA*] [H_2*]	2.02×10^9	19.9
7	k_7^C [AL*] [H_2*]	7.58×10^{11}	80.0
8	k_8^C [OBV*] [H_2*]	3.60×10^9	89.9
9	k_9^C [HVA*] [*]	2.15×10^5	113
10	k_{10}^C [HVA*] [*]	$>> k_6^C$	n.a.
11	k_{11}^C [BL*] [*]	n.a.	n.a.
12	k_{12}^C [HVA*] [*]	$k_{10}^C \times 2.04 \times 10^{-2}$	150
13	k_{13}^C [GVL*] [H_2*]	$< 1 \times 10^5$	n.a.
14	k_{14}^C [HBV*] [*]	$>> k_8^C$	n.a.
15	k_{15}^C [VVA*] [*]	2.15×10^5	113
16	k_{16}^C [BE*] [H_2*]	n.a.	n.a.
17	k_{17}^C [VVA*] [H_2*]	$>> k_{12}^C$	n.a.
18	k_{18}^C [MFO*] [H_2*]	n.a.	n.a.
19	k_{19}^C [VA*] [*]	2.15×10^5	113
20	k_{20}^C [VA*] [H_2*]	$< 1 \times 10^5$	n.a.
21	k_{21}^C [PDO*] [H_2*]	n.a.	n.a.
22	k_{22}^C [PHO*] [*]	n.a.	n.a.

$$k_i^H(T(t)) = k_i^H(T_P)\cdot\exp\left(-\frac{Ea_i^H}{R}\left(\frac{1}{T(t)}-\frac{1}{T_P}\right)\right)$$

$$k_i^C(T(t)) = k_i^C(T_P)\cdot\exp\left(-\frac{Ea_i^C}{R}\left(\frac{1}{T(t)}-\frac{1}{T_P}\right)\right)$$



LEVULINIC ACID HDO: H_2 PRESSURE

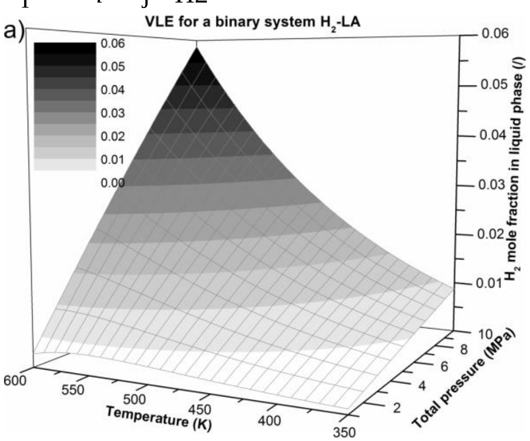


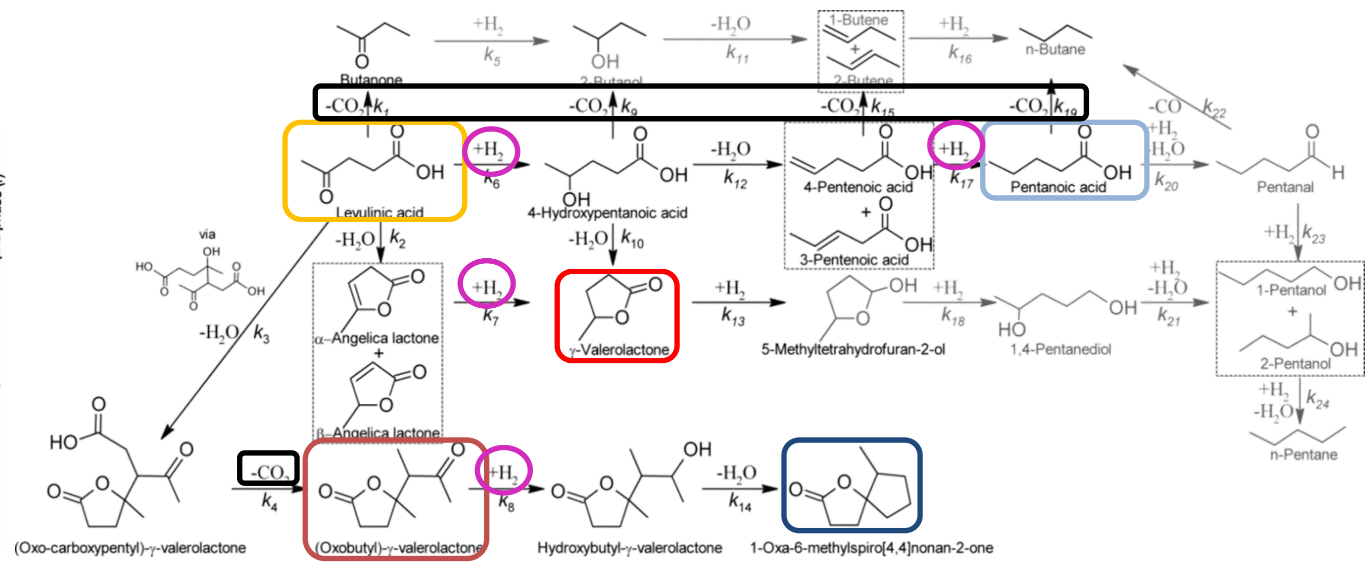
$$r_j^{GL} = k_j^L \cdot A_G \cdot (C_j^{Li} - C_j^L)/V_L$$

$$r_j^{LS} = k_j^S \cdot A_S \cdot (C_j^L - C_j^{Si})/V_L$$

$$r_j^A = k_j^A \cdot C_j^{Si} \cdot C_{VS}^*$$

$$r_i^C = k_i^C C_j^* C_{H2}^*$$





LEVULINIC ACID HDO: STIRRING SPEED

- Mass transfer rate through G-L film becomes limiting between 600 and 1000 rpm: $k_j^L \cdot a_G << k_j^S \cdot a_S$

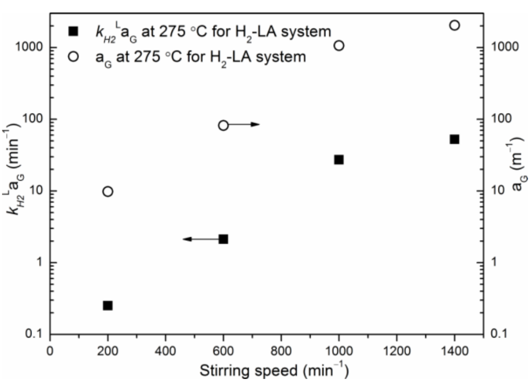
$$r_j^{GL} = k_j^L \cdot A_G \cdot (C_j^{Li} - C_j^L)/V_L$$

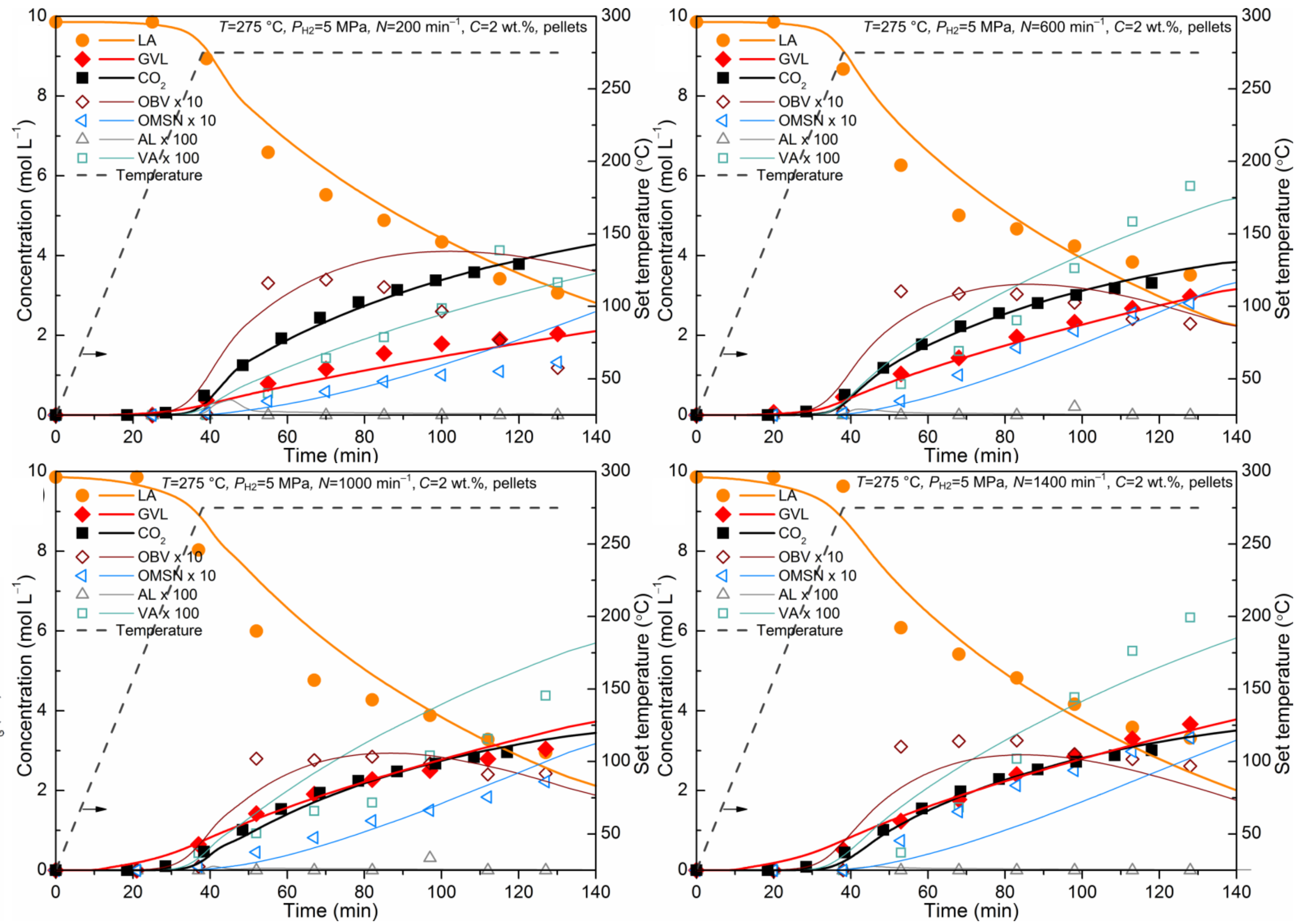
$$k_j^L = 0.42 \cdot \left(\frac{\mu_l \cdot g}{\rho_l}\right) \cdot Sc^{-0.5} \cdot \alpha \cdot d_b$$

$$A_G = 6 \cdot V_G \cdot \varepsilon_G / d_b$$

$$\varepsilon_G = 0.45 \frac{(N - N^*) \cdot d_t^2}{d_r \cdot (g \cdot d_r)^{0.5}} + 0.31 \cdot \left(\frac{u_G}{\sqrt[4]{\frac{\sigma_l \cdot g}{\rho_l}}}\right)^{2/3}$$

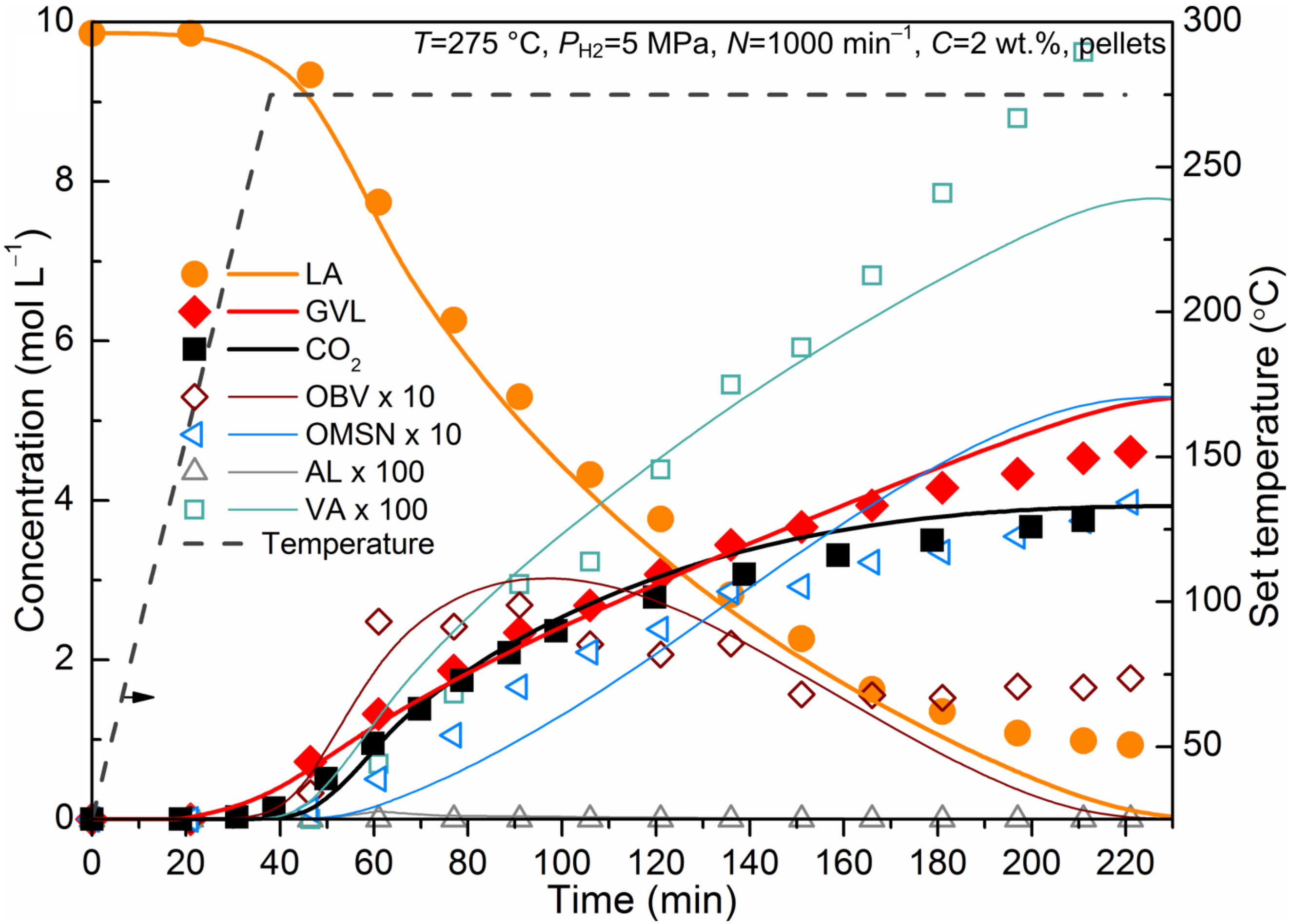
$$d_b = \left(\frac{0.41 \cdot \sigma_l}{g \cdot (\rho_l - \rho_g)}\right)^{0.5}$$





LEVULINIC ACID HDO: VALIDATION EXPERIMENT

- Experiment prolonged to 220 min.
- Two times higher catalyst and levulinic acid mass (ratio remained unchainged).
- Very good agreement within 180 min, some discrepancies in last 30 min.



LEVULINIC ACID HDO: A LIST OF KINETIC PARAMETERS

Grilc, Likozar, Chemical Engineering Journal, Vol. 330, 2017, P. 383-397

Regression analysis:

- k_i^H at 275 °C, Ea_i^H
- k_i^C at 275 °C, Ea_i^C
- k_j^A, k_j^D

Empirical correlations:

- k_j^L, k_j^S
- a^G

Catalyst characterisation:

- a^S, C_{VS}^*

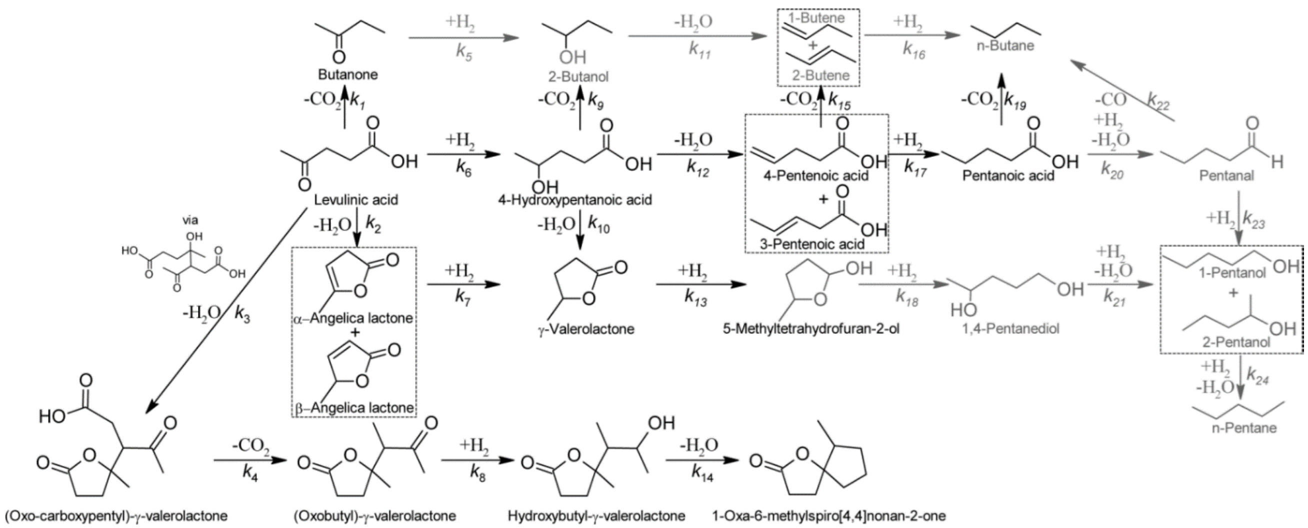
Parameter	Value	Unit
$k^A_{H_2}$	5.47×10^3	L mol^{-1} min^{-1}
k^A_{Liq}	5.57×10^4	L mol^{-1} min^{-1}
$k^D_{H_2}$	2.22×10^4	min^{-1}
k^D_{Liq}	1.96×10^4	min^{-1}
$k^L_{H_2\,(T=275°C)}$	2.56×10^{-2}	m min^{-1}
$k^S_{H_2\,(T=275°C)}$	2.43×10^{-2}	m min^{-1}
$k^S_{LA\,(T=275°C)}$	1.28×10^{-2}	m min^{-1}
$a_G = A_G / V_L$	1.06×10^3	m^{-1}
$a_S = A_S / V_L$	4.43×10^6	m^{-1}

i	r_i^H	k_i^H at 275 °C	k_i^H unit	Ea_i^H (kJ mol^{-1})
1	k_1^H [LA^L]	5.17×10^{-3}	min^{-1}	134
2	k_2^H [LA^L]	6.12×10^{-5}	min^{-1}	164
3	k_3^H [LA^L] [LA^L]	1.61×10^{-4}	L mol^{-1} min^{-1}	61.3
4	k_4^H [$OCPV^L$]	$>> k_3^H$	min^{-1}	n.a.
5	k_5^H [BK^L] [H_2^L]	n.a.	L mol^{-1} min^{-1}	n.a.
6	k_6^H [LA^L] [H_2^L]	$< 1.00 \times 10^{-4}$	L mol^{-1} min^{-1}	n.a.
7	k_7^H [AL^L] [H_2^L]	3.61×10^{-1}	L mol^{-1} min^{-1}	20.3
8	k_8^H [OBV^L] [H_2^L]	3.59×10^{-3}	L mol^{-1} min^{-1}	12.9
9	k_9^H [HVA^L]	5.17×10^{-3}	min^{-1}	134
10	k_{10}^H [HVA^L]	n.a.	min^{-1}	n.a.
11	k_{11}^H [BL^L]	n.a.	min^{-1}	n.a.
12	k_{12}^H [HVA^L]	n.a.	min^{-1}	n.a.
13	k_{13}^H [GVL^L] [H_2^L]	$< 1.00 \times 10^{-5}$	L mol^{-1} min^{-1}	n.a.
14	k_{14}^H [HBV^L]	$>> k_8^H$	min^{-1}	n.a.
15	k_{15}^H [VVA^L]	n.a.	min^{-1}	n.a.
16	k_{16}^H [BE^L] [H_2^L]	n.a.	L mol^{-1} min^{-1}	n.a.
17	k_{17}^H [VVA^L] [H_2^L]	n.a.	L mol^{-1} min^{-1}	n.a.
18	k_{18}^H [MFO^L] [H_2^L]	n.a.	L mol^{-1} min^{-1}	n.a.
19	k_{19}^H [VA^L]	n.a.	min^{-1}	n.a.
20	k_{20}^H [VA^L] [H_2^L]	n.a.	L mol^{-1} min^{-1}	n.a.
21	k_{21}^H [PDO^L] [H_2^L]	n.a.	L mol^{-1} min^{-1}	n.a.
22	k_{22}^H [PHO^L]	n.a.	min^{-1}	n.a.

i	r_i^C	k_i^C at 275 °C (L mol^{-1} min^{-1})	Ea_i^C (kJ mol^{-1})
1	k_1^C [LA*] [*]	2.15×10^5	113
2	k_2^C [LA*] [*]	$< 1 \times 10^2$	n.a.
3	k_3^C [LA*] [LA*]	$< 2 \times 10^3$	n.a.
4	k_4^C [OCPV*] [*]	n.a.	n.a.
5	k_5^C [BK*] [H_2*]	n.a.	n.a.
6	k_6^C [LA*] [H_2*]	2.02×10^9	19.9
7	k_7^C [AL*] [H_2*]	7.58×10^{11}	80.0
8	k_8^C [OBV*] [H_2*]	3.60×10^9	89.9
9	k_9^C [HVA*] [*]	2.15×10^5	113
10	k_{10}^C [HVA*] [*]	$>> k_6^C$	n.a.
11	k_{11}^C [BL*] [*]	n.a.	n.a.
12	k_{12}^C [HVA*] [*]	$k_{10}^C \times 2.04 \times 10^{-2}$	150
13	k_{13}^C [GVL*] [H_2*]	$< 1 \times 10^5$	n.a.
14	k_{14}^C [HBV*] [*]	$>> k_8^C$	n.a.
15	k_{15}^C [VVA*] [*]	2.15×10^5	113
16	k_{16}^C [BE*] [H_2*]	n.a.	n.a.
17	k_{17}^C [VVA*] [H_2*]	$>> k_{12}^C$	n.a.
18	k_{18}^C [MFO*] [H_2*]	n.a.	n.a.
19	k_{19}^C [VA*] [*]	2.15×10^5	113
20	k_{20}^C [VA*] [H_2*]	$< 1 \times 10^5$	n.a.
21	k_{21}^C [PDO*] [H_2*]	n.a.	n.a.
22	k_{22}^C [PHO*] [*]	n.a.	n.a.

LEVULINIC ACID HDO: CONCLUSIONS

- **225 °C slow but selective LA HDO**
- **Above 225 °C competitive non-catalytic DCX overdominates catalytic HDO**
- ***Ea* DCX 134 kJ mol^{-1}, dimerization 61 kJ mol^{-1}, HDO 19 kJ mol^{-1}**
- **HDO selectivity ↗ H_2 pressure and catalyst loading**
- **Mass transfer does not play major role, as long as gas hold-up is sufficient (> 800 rpm)**
- **Microkinetic model accounts process parameters well (*T*, *p*, catalyst loading, stirring, geometry)**



TAKE-HOME MESSAGE: BIOMASS IS A SUSTAINABLE SOURCE OF CHEMICALS

STEP 1

- **Fractionation of LC Biomass:** Cellulose, hemicellulose, lignin, extractives

STEP 2

- **Depolymerisation** of bio-polymers into building blocks (platform chemicals)

STEP 3

- **Selective (catalytic) conversion** of building blocks into added-value chemicals
- **Hydrotreatment** (treatment with H_2) is only one among many possible transformation routes

OUR INVESTIGATION APPROACH GUIDELINES

High-throughput experimental measurements
- Fast experimental screening
- Systematic experimental design
- Online process analysis

No

Enough measured data?

Yes

No

Clear?

Yes

- Used catalyst well characterized
- Structure–activity correlation
- Structure–selectivity correlation
- Reaction/process mechanism
- Effect/sensitivity of process conditions
- Identification of bottlenecks

Analytics
- Identification
- Quantification
- Processing

Mechanism
- Intermediates
- Pathways
- Reactions

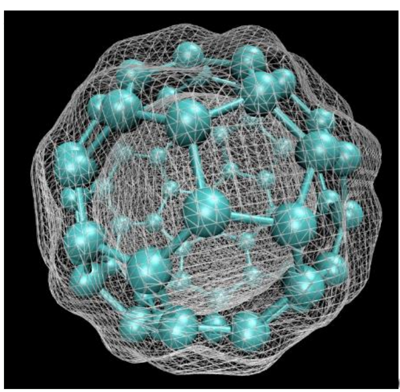
Model
- Mass transfer (gas-liquid-solid)
- Adsorption/desorption processes on material surface
- Surface reactions based on elementary steps

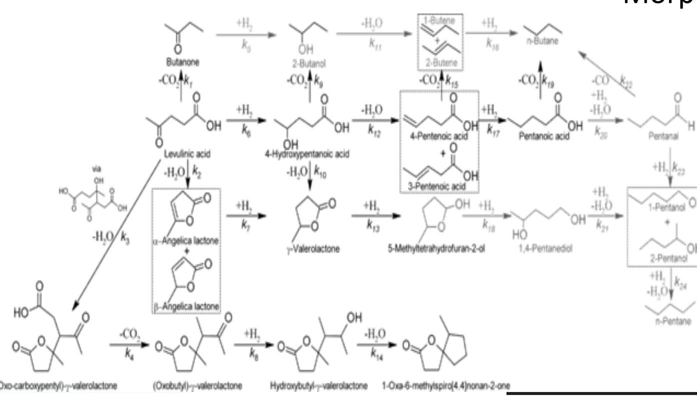
Kinetic Monte Carlo

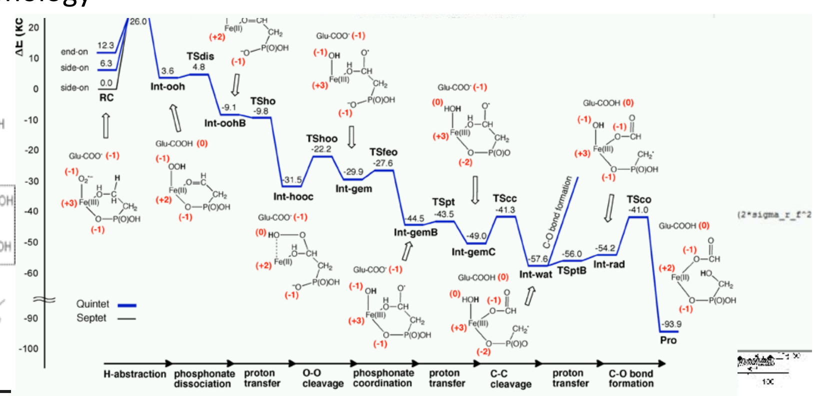
Density functional theory

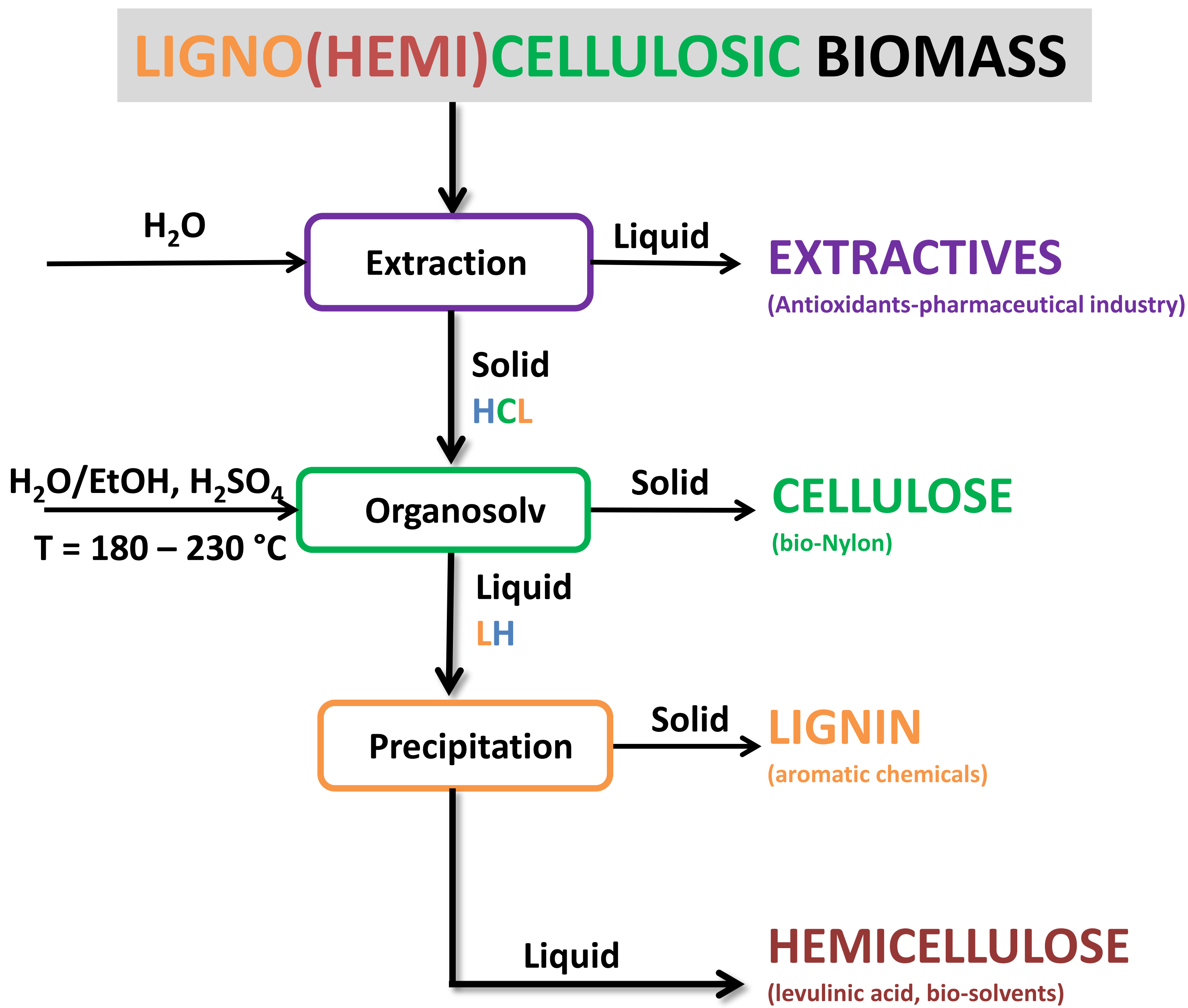
Characterisation
- Composition
- Structure
- Morphology

Thermodynamics









LIGNO(HEMI)CELLULOSIC BIOMASS
H_2O
Extraction
Liquid
EXTRACTIVES
(Antioxidants-pharmaceutical industry)
Solid
HCL
H_2O/EtOH, H_2SO_4
T = 180 – 230 °C
Organosolv
Solid
CELLULOSE
(bio-Nylon)
Liquid
LH
Precipitation
Solid
LIGNIN
(aromatic chemicals)
Liquid
HEMICELLULOSE
(levulinic acid, bio-solvents)

Mar3bio

ERA-Marine Biotech 2016-2019

MarineBiotech

Fresh raw materials

Access to samples and waste streams from large scale macroalgae processing plant

The marine biomasses used in Mar3Bio are brown algae and crustacean byproducts which are sources of the marine polysaccharides alginate and chitosan.

NTNU SINTEF KTH VETENSKAP OCH KONST matís

Current technology for marine biomass processing is:

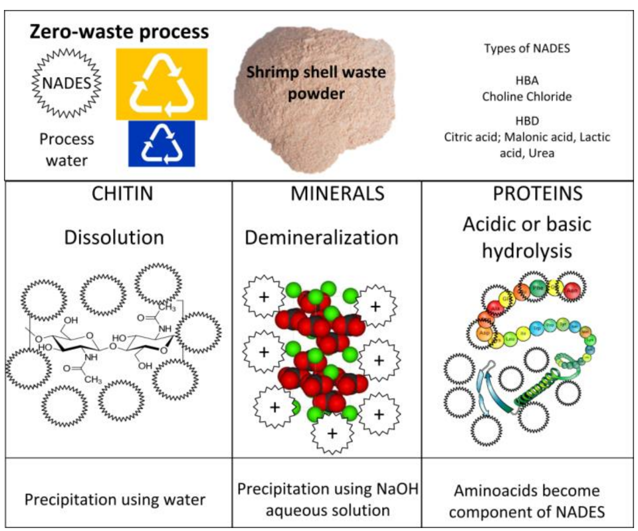
- not useful for cost efficient separation/recovery of products.
- The knowledge about structure and composition of marine biomass not good enough to suggest good enzyme assisted strategies for treatment and fractionation.
- The enzyme toolbox for processing of marine biomass is not yet developed for industrial utilization.
- Products are poorly characterized.
- Some of the products lack good applications.

Green Chemistry in Biomass Processing

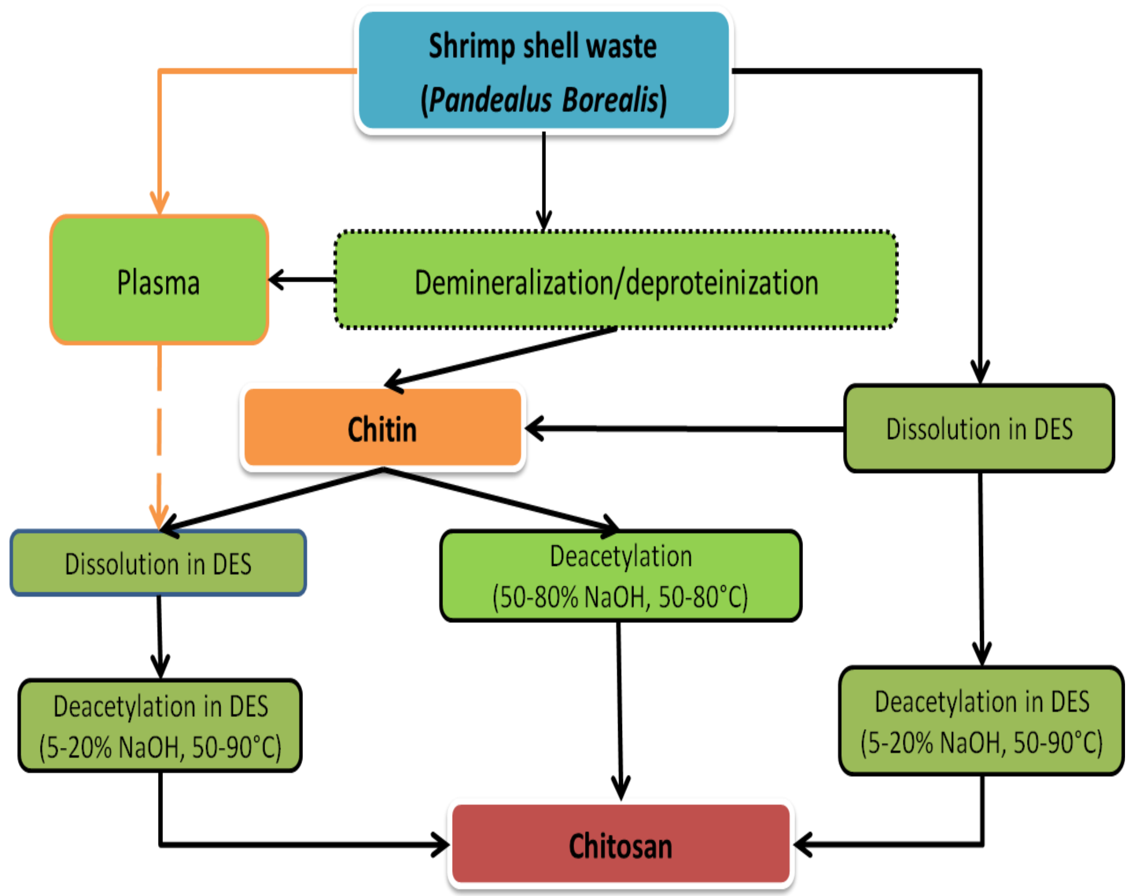
A new „green“ lab-scale pretreatment pipeline reducing the harsh conditions currently used for deprotonating and demineralization of the shells and the subsequent deacetylation of chitin to obtain chitosan.

Special focus:

- ❑ DBD Plasma treatment of shrimp shells
- ❑ Chitin dissolution and extraction using deep eutectic solvents (DES)
- ❑ Kinetics and mechanism of chitin N-deacetylation (heterogeneous and homogeneous)



Chitin/chitosan pipeline



BioApp in numbers

Duration: 30 months

Start: 01. 10. 2017

End: 31. 03. 2020

No. of partners: 5

Budget:
1.265.587,29€

European Regional Development Fund contribution:
1.075.749,20€

www.ita-slo.eu/BioApp

PROJECT COORDINATOR

National Institute of Chemistry,
Department of Catalysis and Chemical Reaction Engineering

Hajdrihova 19
1000 Ljubljana

Uroš Novak, phD
01 476 0 283
uros.novak@ki.si

YouTube

Interreg

UNIONE EUROPEA
EVROPSKA UNIJA

ITALIA-SLOVENIJA

BioApp

Progetto standard co-finanziato dal Fondo europeo di sviluppo regionale
Standardni projekt sofinancira Evropski sklad za regionalni razvoj

Overall Objective of the Project:

To establish a **new technological platform** aimed at strengthening the collaboration between research institutions and the main economic actors in order to **develop pilot technologies** for advanced biopolymers. With the technological platform, which will lay the groundwork for innovative business initiatives, while at the same time **promoting** the necessary **exchange of knowledge**, technology and innovation, the project will make a positive contribution to the cross-border cooperation program's specific objectives.

BioApp

Interreg
ITALIA-SLOVENIJA
UNIONE EUROPEA
EVROPSKA UNIJA
BioApp
Progetto standard co-finanziato dal Fondo europeo di sviluppo regionale
Standardni projekt sofinancira Evropski sklad za regionalni razvoj

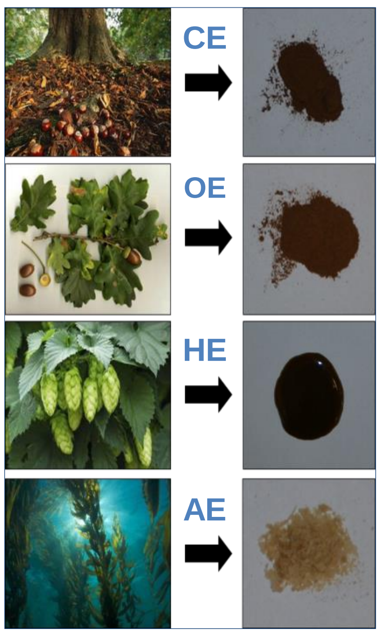
1. EXTRACTS
food grade
antibacterial
antioxidant

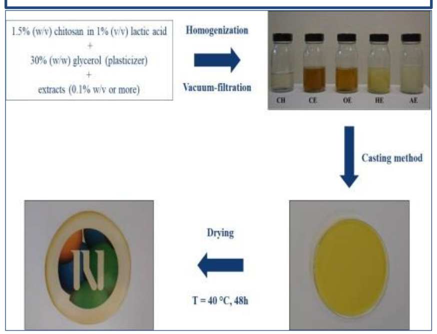
2. PREPARATION
high molecular weight CH
DD > 75%
glycerol - plasticizer

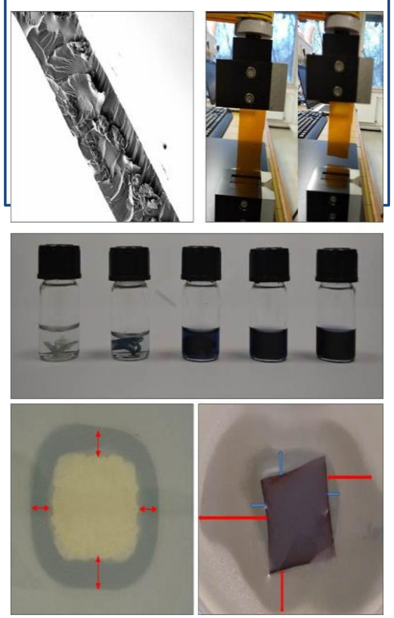
3. EVALUATION
morphology/water content
optical transmittance
mechanical properties
total phenolic

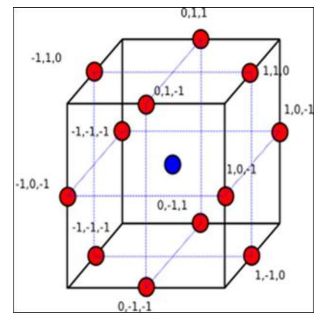
4. OPTIMIZATION
composition of FFS
Box–Behnken
realease

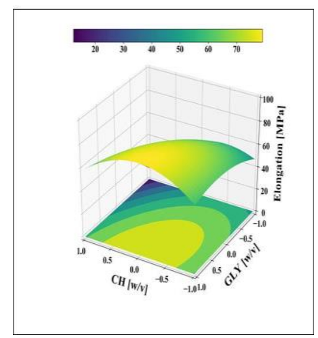
5. APPLICATION
active packagings
bags/sachets
wrappings

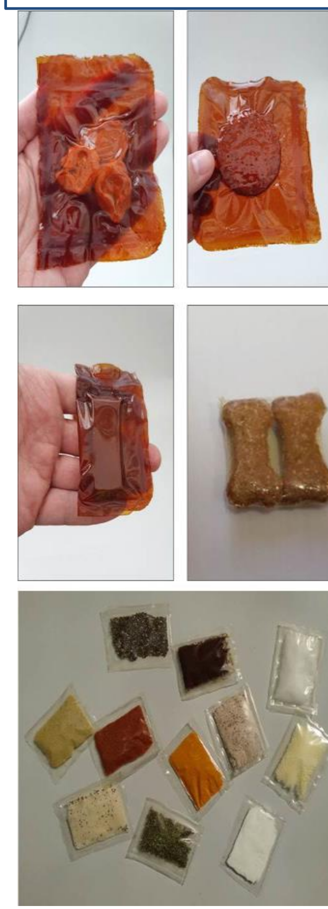












CE – Chestnut extract
OE – Oak extract
HE – Hop extract
AE – Algal extract

Chitosan-based films development process