# RHODOLIVE Kick-off meeting

## Presentation of partners: National Institute of Chemistry

dr. Miha Grilc


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Milan
Venice
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Ljubljana
Zagreb
Pécs
Osijek
Koper
Rijeka
CROATIA
Novi Sad
Toulouse
200 km
Genoa
Bucharest
Bologna
Marseille
Nice
BOSNIA AND HERZEGOVINA
Belgrade
SERBIA
Florence
Zadar
Zaragoza
Split
Sarajevo
500 km
ITALY
Niš
BULGARIA
SPAIN
Barcelona
Mostar
MONTE-NEGRO
Pristina
Dubrovnik
KOSOVO
Sofia
Rome
Podgorica
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800 km
Valencia
MACEDONIA
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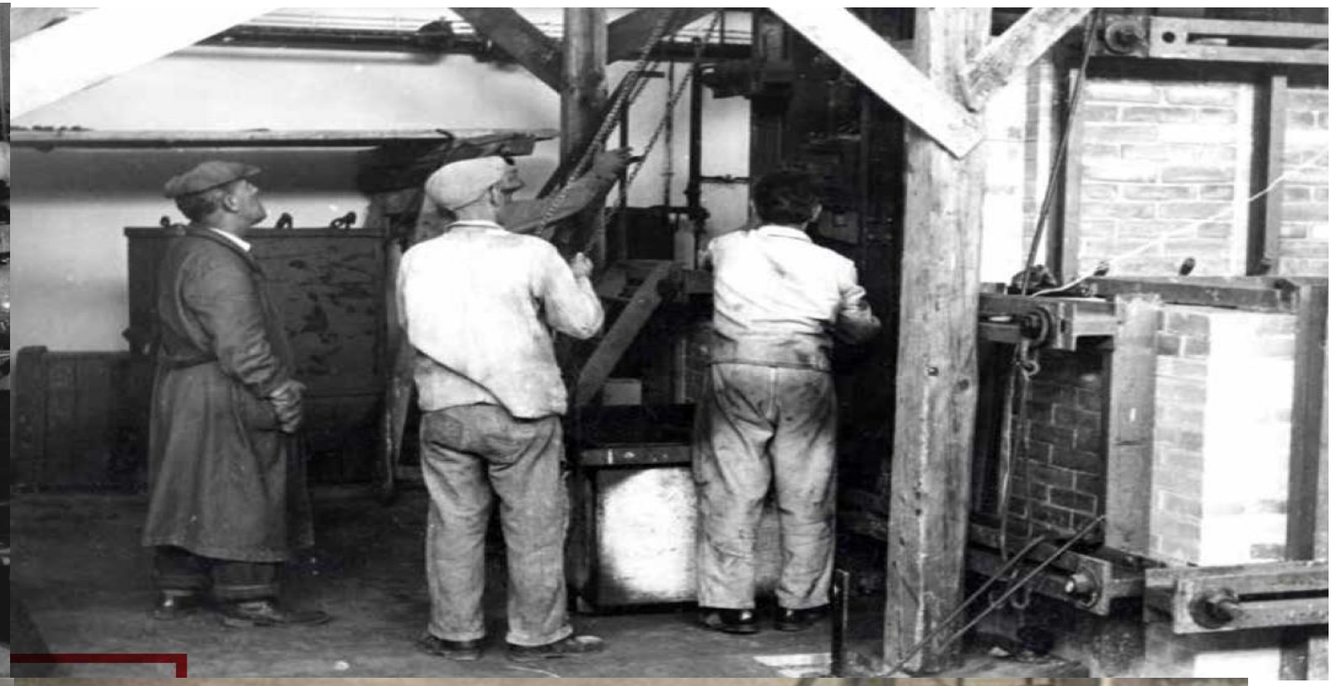
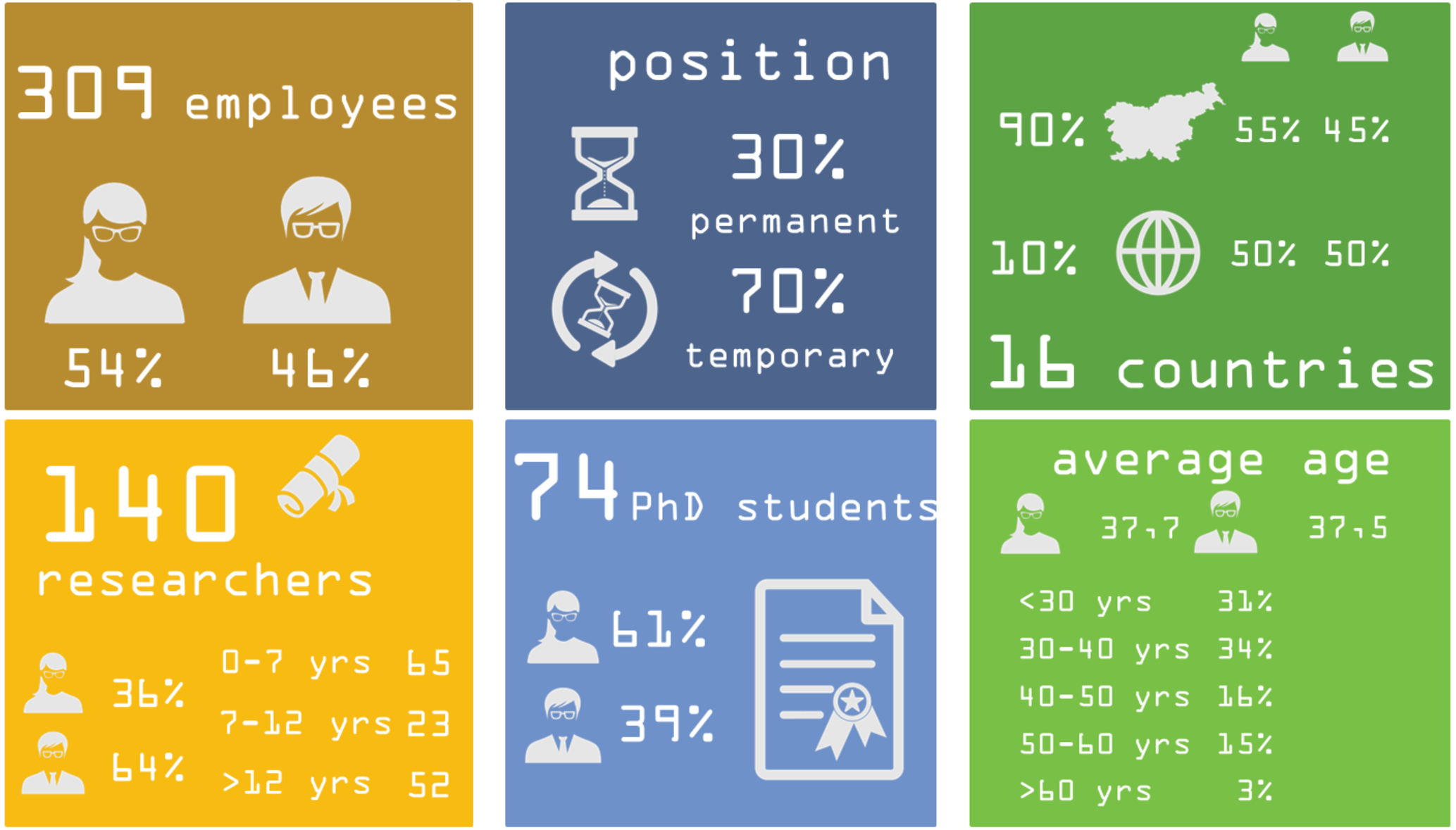
# more than 70 years of tradition

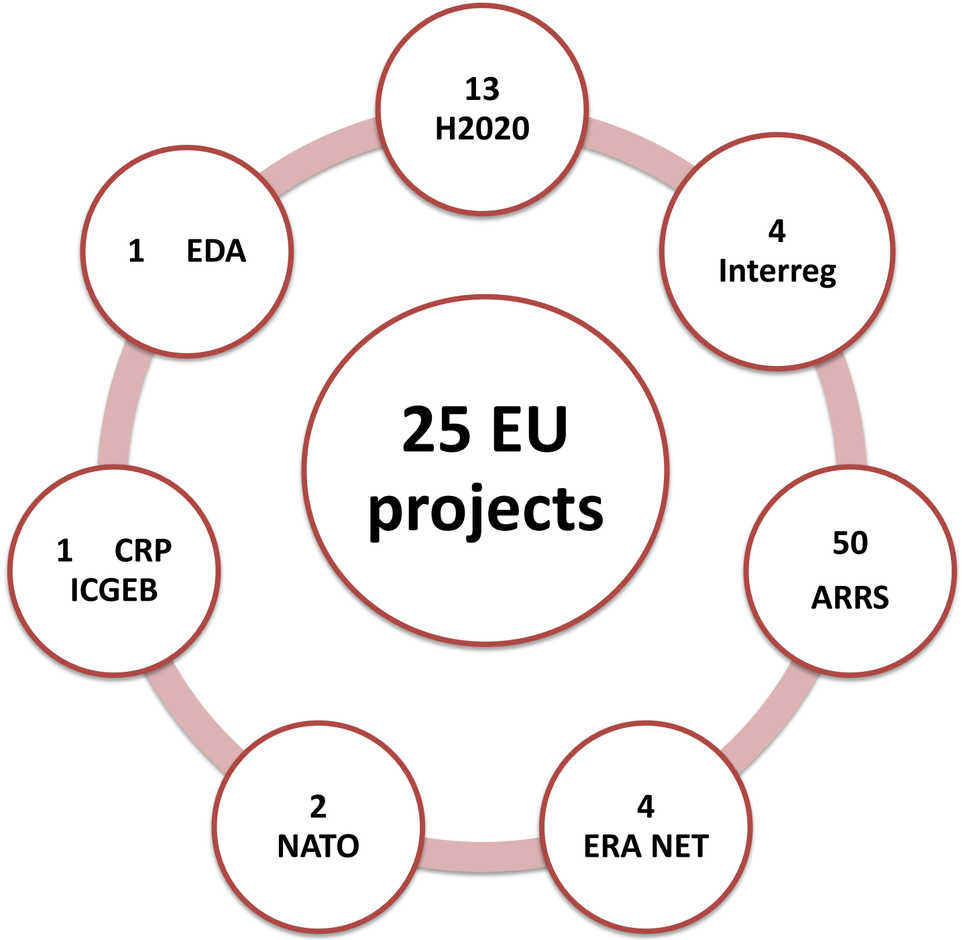


# National Institute of Chemistry



# National institute of Chemistry in collaboration with stakeholders

**Expanding knowledge of chemistry and associated studies**
**Transferring knowledge to younger generations**
**Applying newly acquired knowledge to industry**



# 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**

## Ongoing projects

**Horizon 2020:**

- MefCO2, Synthesis of Methanol from Captured Carbon Dioxide Using Surplus Electricity (SPIRE-02-2014)
- Fresme, Methanol from CO2 Blast Furnace gasses to be used as ship transportation fuel
- ADREM, Adaptable Reactors for Resource- and Energy-Efficient Methane Valorisation (SPIRE-05-2015)
- nextBioPharmDSP, Next-generation Biopharmaceutical Downstream Process (BIOTEC-4-2014)

**ERA-NET:**

- Mar3Bio, Biorefinery and Biotechnological Exploitation of Marine Biomasses (MarineBiotech - Marine Biotechnology ERA-NET)
- RHODOLIVE, Biovalorization Of Olive Mill Wastewater To Microbial Lipids And Other Products

**NATO SPS:**

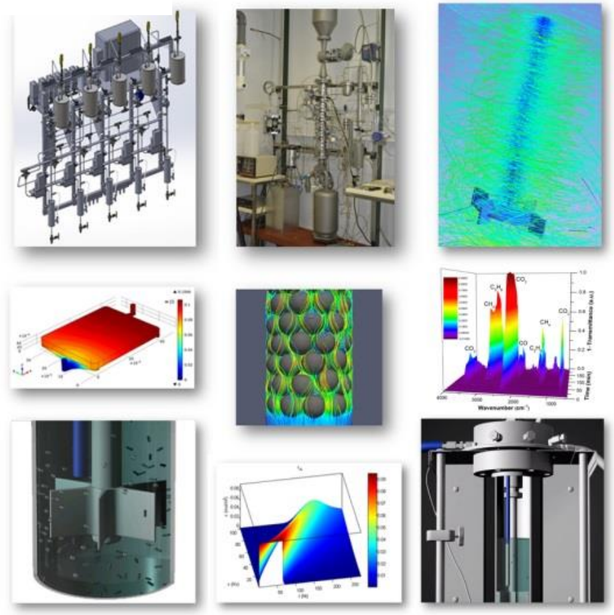
- 984738, Enhanced Portable Energetically Self-sustained Devices for Military Purposes (ESCD - Emerging Security Challenges Division); coordinator

**COST Actions:** 3

**Members of EERA – European Energy Research Alliance**

**Slovenian Research Agency projects:** 1

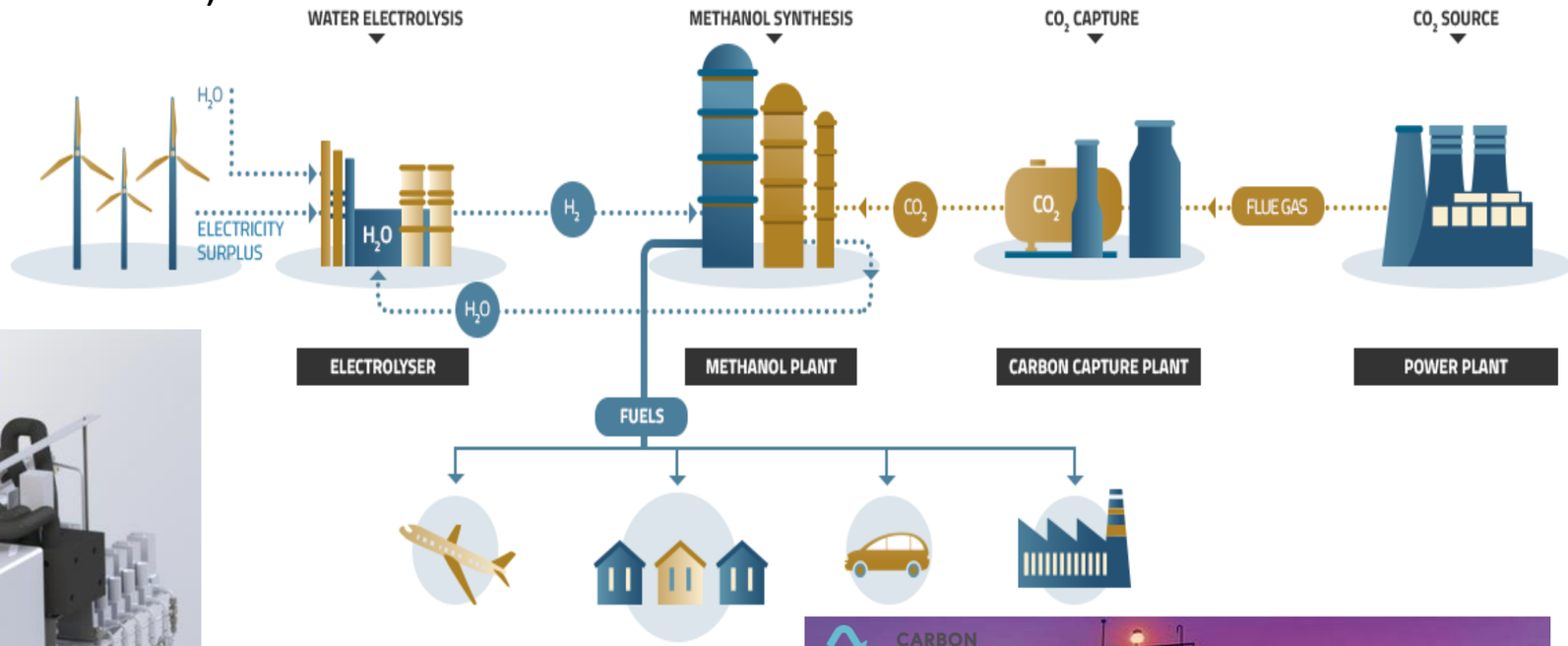
**Bilateral cooperation projects:** 2

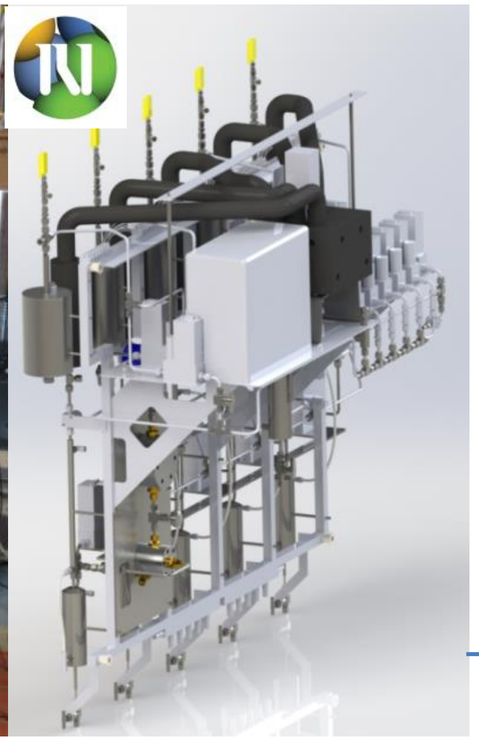


# Methanol fuel from $CO_2$

Horizon 2020 (*MefCO2*, **2014-2018**, *11 mil. EUR in total*)

**Mef$CO_2$** aims to produce green methanol as energy vector from captured **$CO_2$** and hydrogen produced using surplus renewable energy. Goal 2018: 1 ton / day

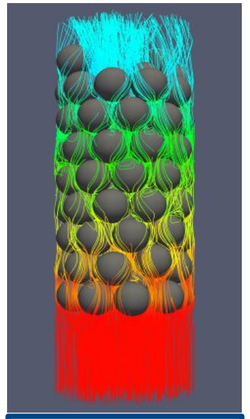


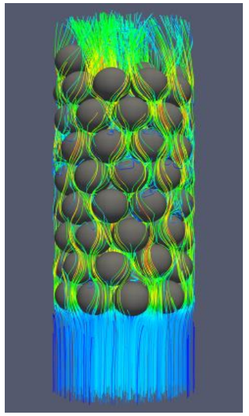
Optimisation
Scale-up

# Research subfield: Carbon dioxide activation –Computational fluid dynamics

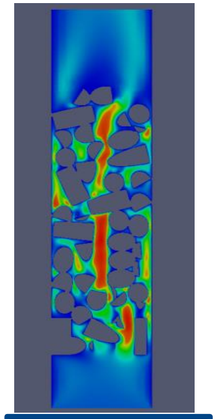
- generation of packed bed reactors' random and realistic geometry model
- generation of models for various packing sizes and shapes
- CFD simulations of flow inside generated models for various Reynolds numbers
- kinetic Monte Carlo simulations of adsorption, desorption and surface chemical reactions



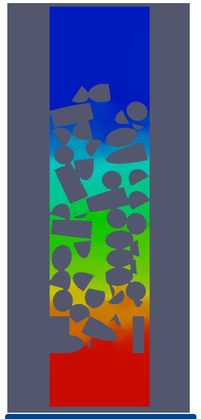
Packed bed with 100 spheres: turbulent streamline profile with pressure field.



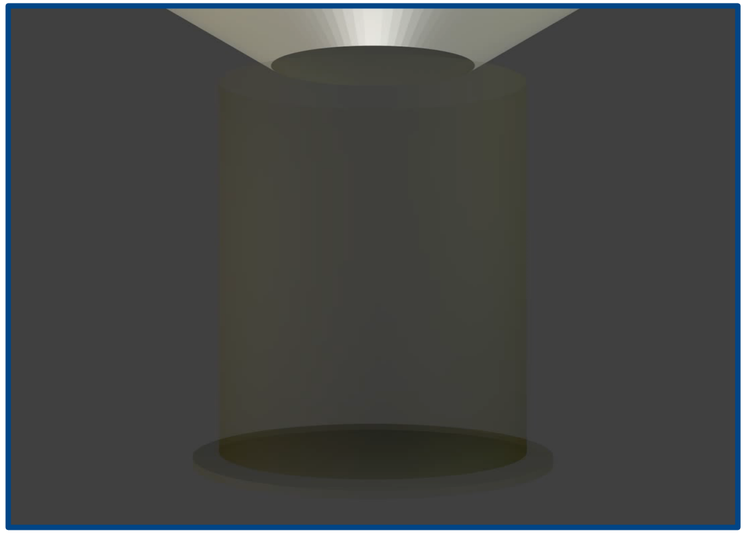
Packed bed with 100 spheres: turbulent streamline profile with pressure field.



Packed bed with 99 cylinders: central slice with laminar velocity field.



Packed bed with 99 cylinders: central slice with pressure field.

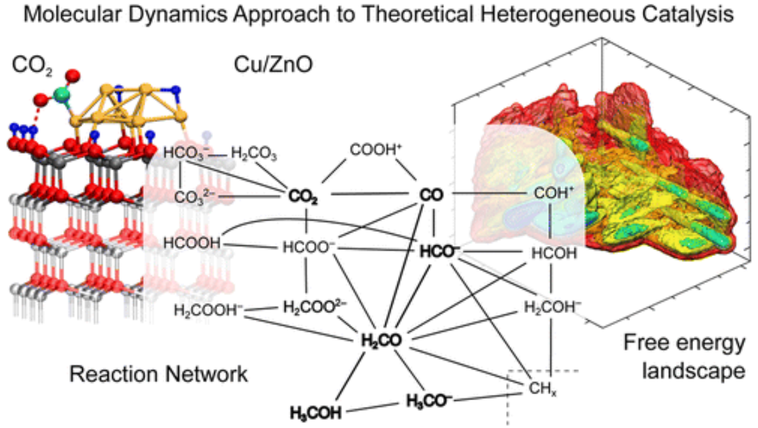


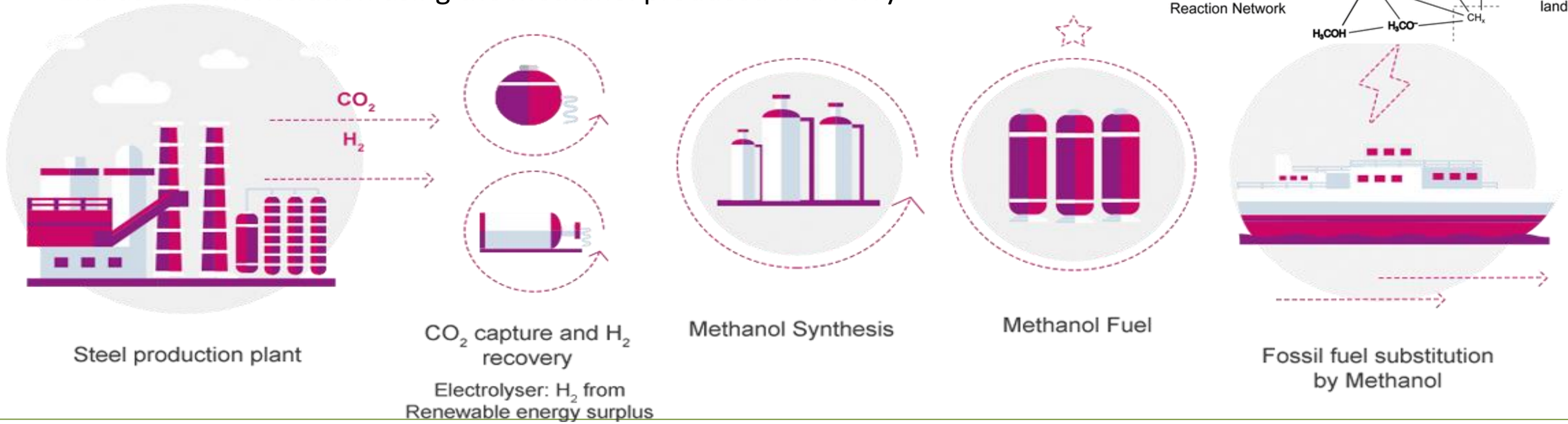
# From Residual Steel Gases ($CO_2$) to Methanol

FReSMe

Horizon 2020 (*FReSMe*, **2016-2020**, *11.4 mil. EUR in total*)

- Lab developments supporting the technology improvement
- Modelling and simulation in order to optimize the processes
- Pilot plant construction and test campaigns implementation
- Life cycle analysis to evaluate the actual reduction achieves on GHG emissions
- End user demonstration using the methanol produced in a Ferry

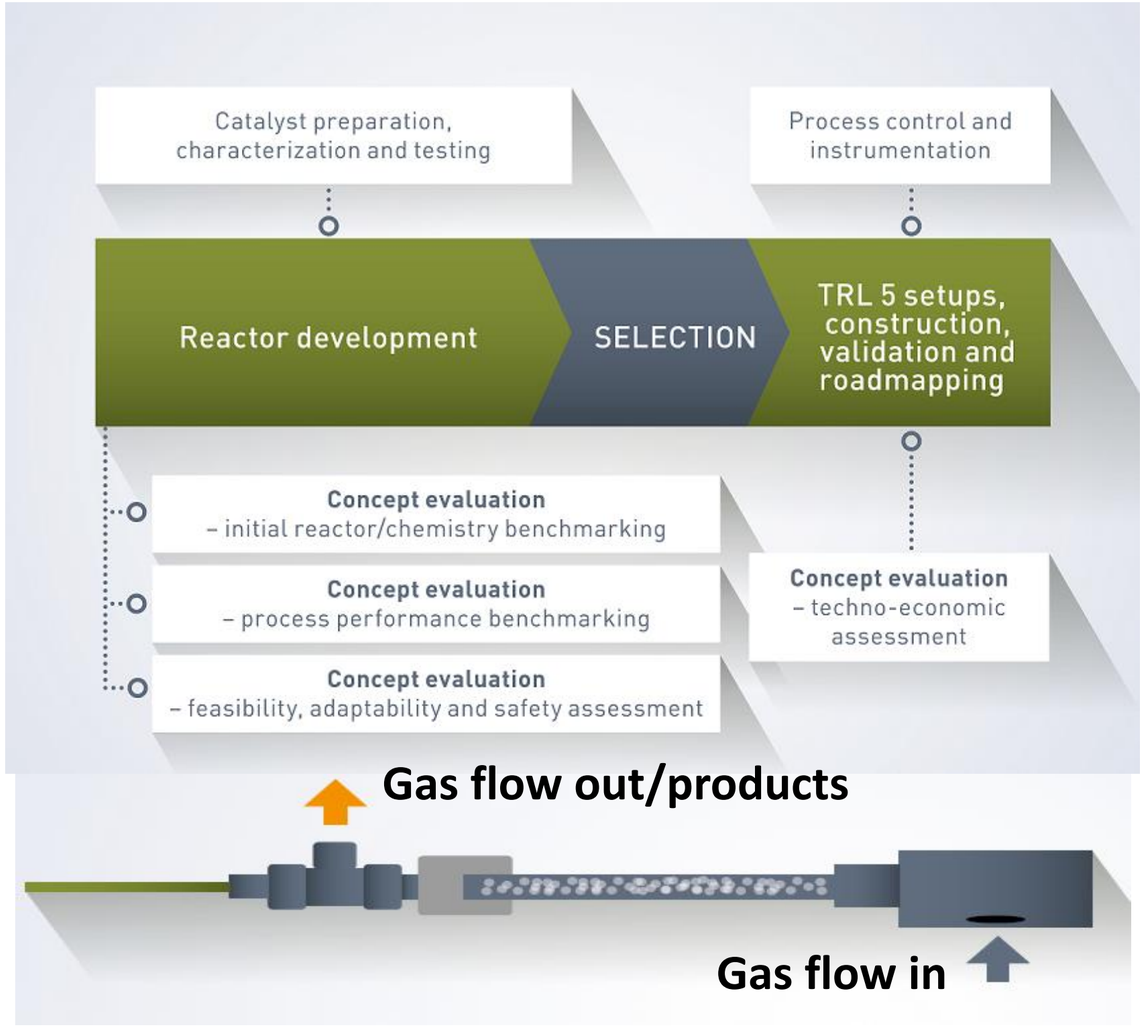


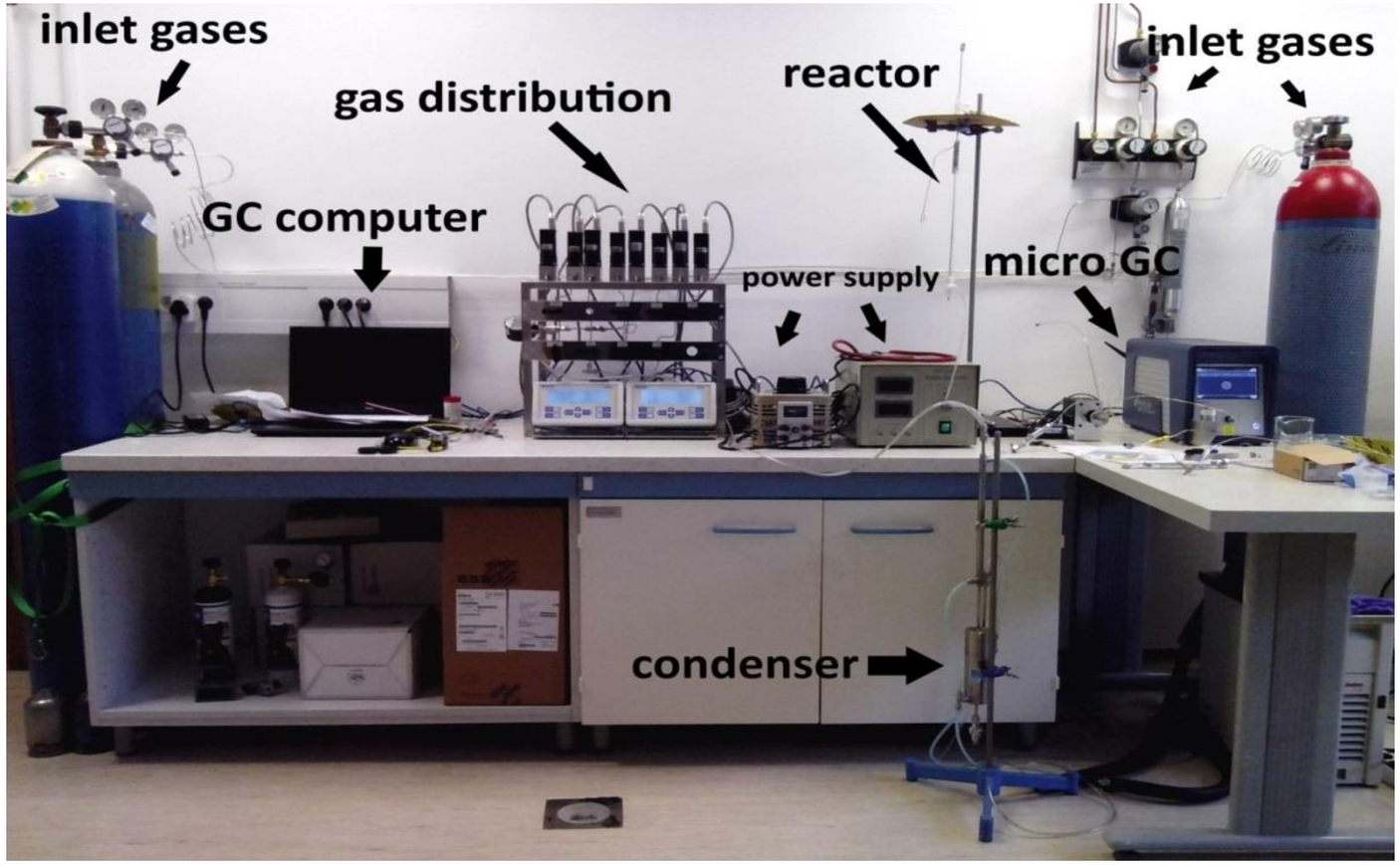
# Adaptable Reactors for **Methane Valorisation**

Horizon 2020 (*ADREM*, **2015-2019**, *6 mil. EUR in total*)

ADREM
Adaptable Reactors for Resource- and Energy-Efficient Methane Valorisation



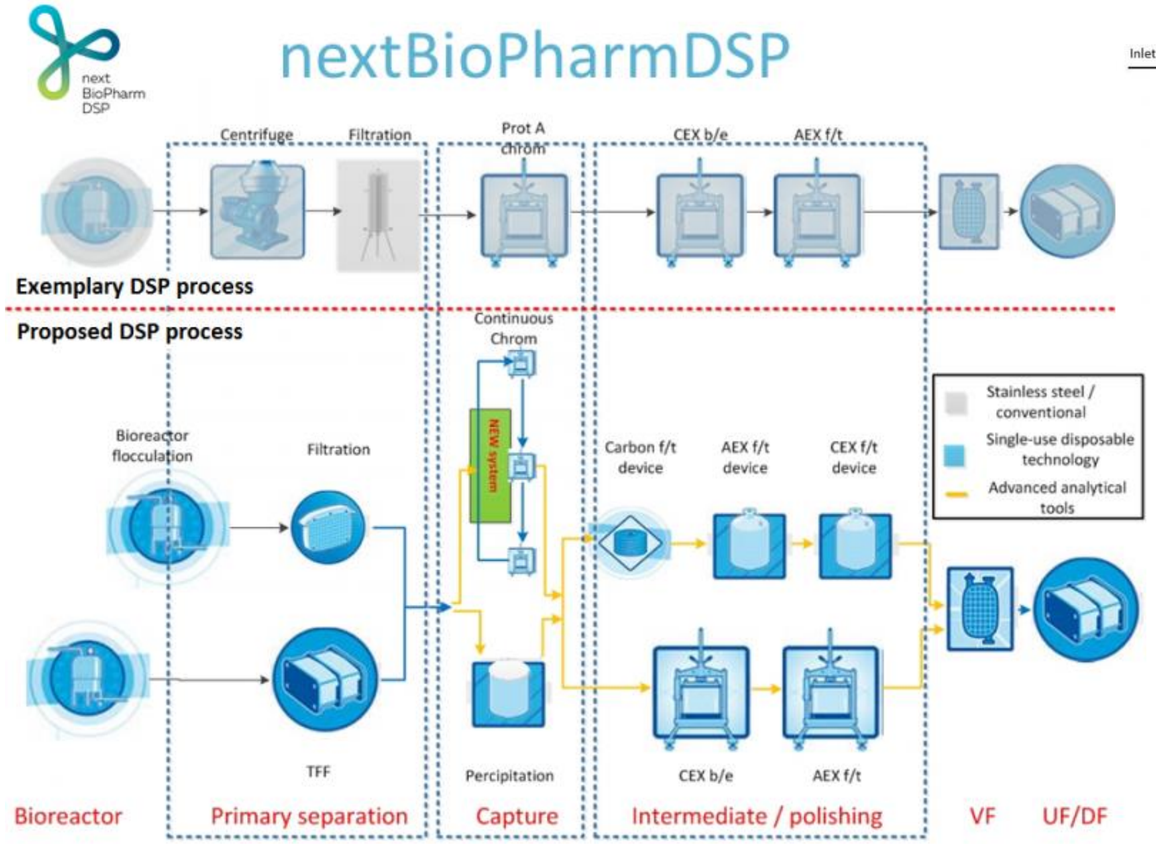

Development of plasma-activated (catalytic) systems for enhanced methane coupling processes

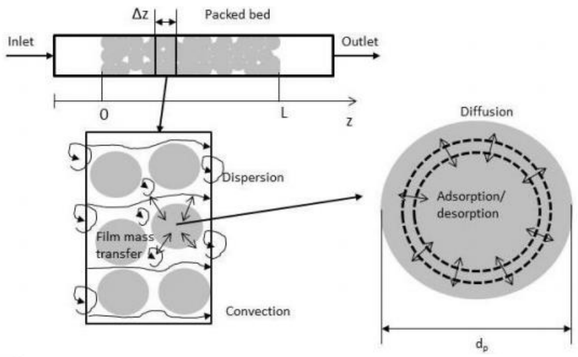


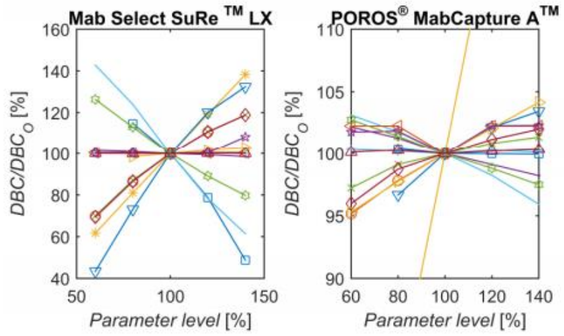
# Next-generation biopharmaceutical **downstream process**

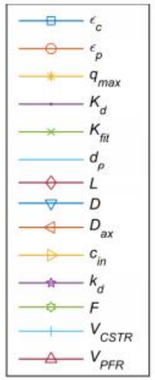
Horizon 2020 (nextBioPharm *LEIT*, **2015-2019**, *11 mil. EUR in total)*

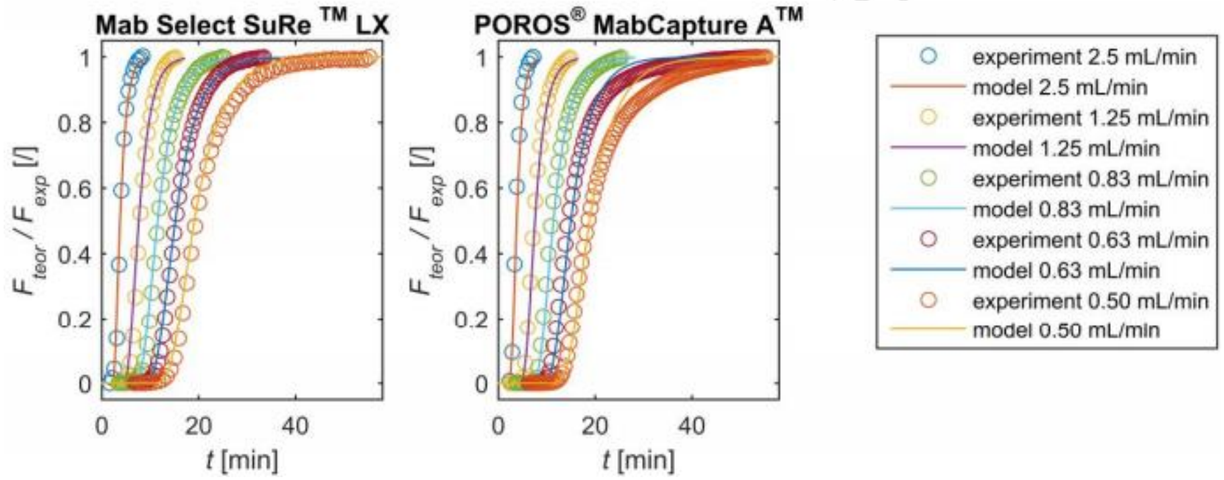
- *Chromatography modelling (adsorption/desorption, mass transfer, thermodynamics)*



# Biomass-derived building blocks subgroup

- 8 Postdocs, 5 PhD students

## Ongoing activities

**LIGNOCELLULOSIC BIOMASS:**

- Fractionation
- Liquefaction
- Furfural synthesis from hemicellulose
- Adipic acid synthesis from glucose
- Isolation of flavonoids from fir bark
- Levulinic acid valorisation by HDO
- Lignin valorisation by HDO

**MARINE BIOMASS:**

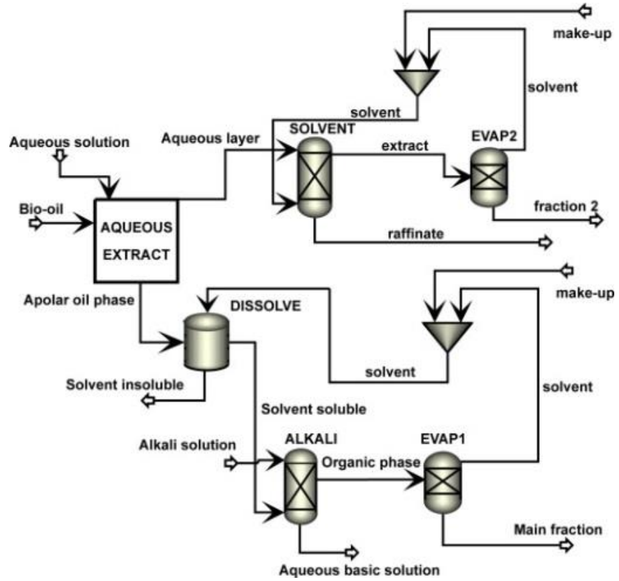
Biorefinery and Biotechnological Exploitation of Marine Biomasses (MarineBiotech - Marine Biotech. ERA-NET)

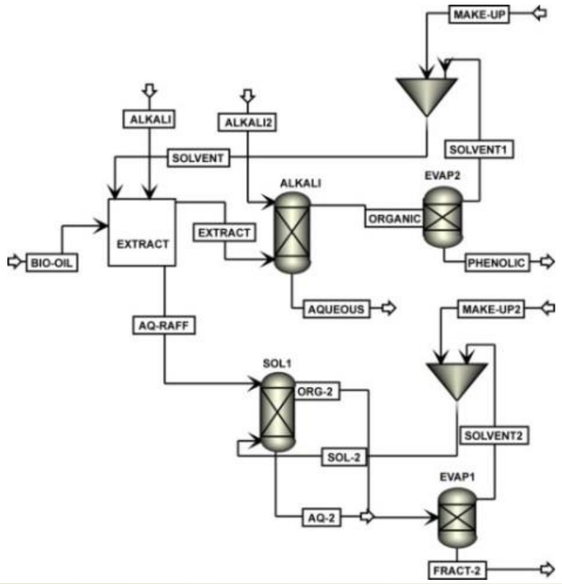
- Extraction of chitin from crustaceans
- Chitin conversion into chitosan and chitlac
- Isolation of oligosacharides from algae

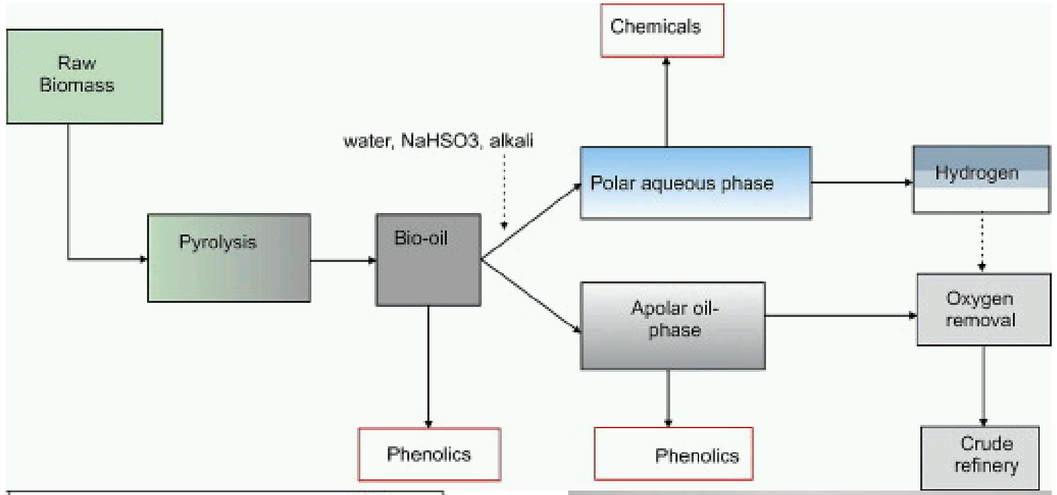
# Research subfield: Biomass-derived building blocks – Extraction of valuable bio-chemicals

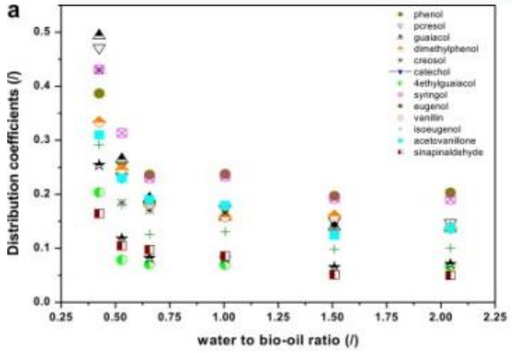
- BIO COUP Project: Co-processing of upgraded Bio-Liquids in Standard Refinery Units (17 partners, 8 countries)
- Isolation and fractionation technology for the production of discrete target oxygenated compounds or defined fractions
- Utilization of these compounds to derive industrial chemicals and products, evaluated by companies (CHIMAR Hellas, Greece)

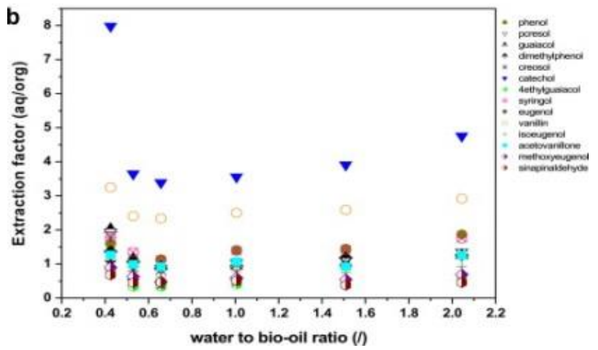

1. Ljudmila Fele Žilnik, Alma Jazbinšek, *Sep. Purif. Technol.*, **2012**, 86, 157.
2. EU project (*BIOCOUP-Contract no 518312 (SES6)*, **2006,** 5 years, **7.7 MEur)**

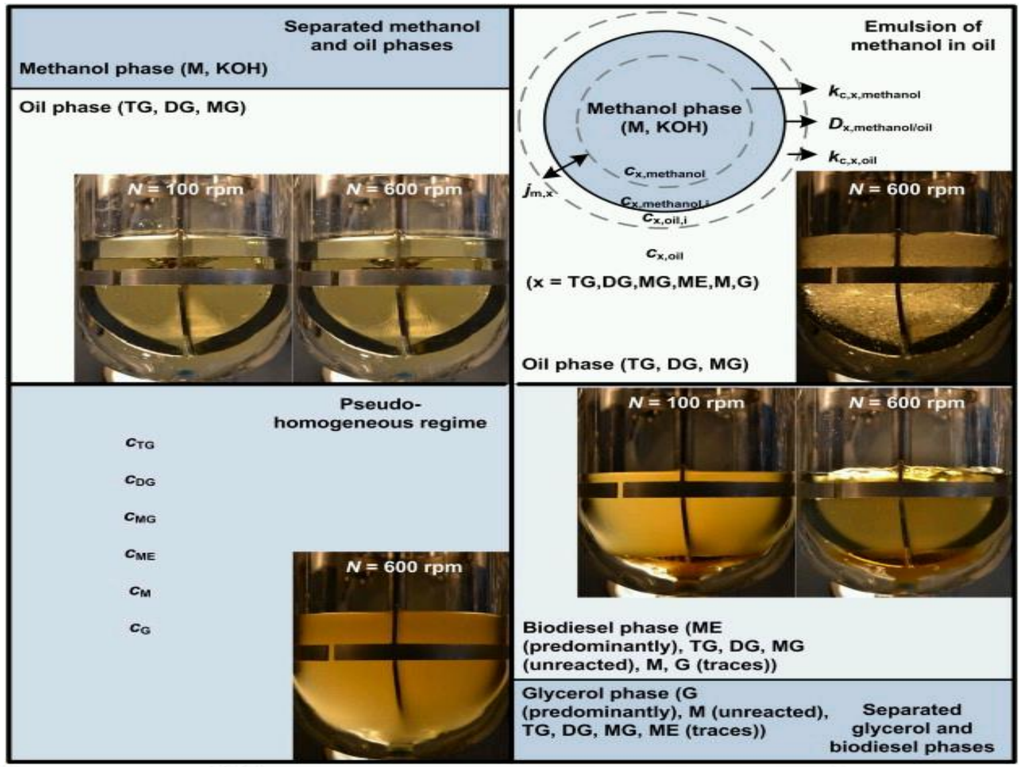



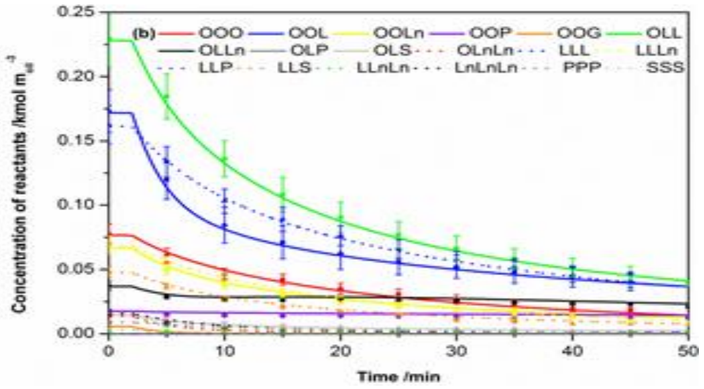

# Research subfield: Biomass-derived building blocks – 1st generation lipid biofuels

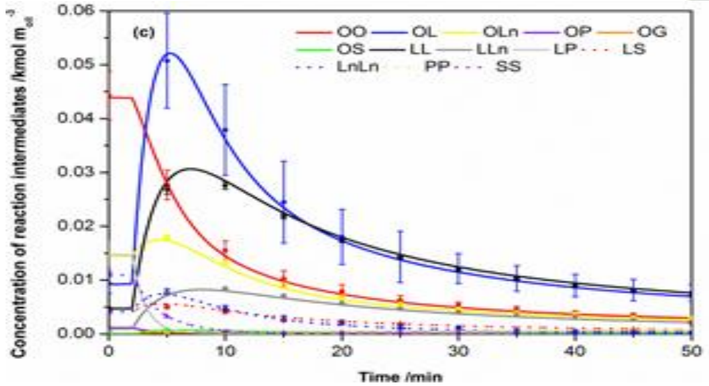
- transesterification of vegetable oils
- novel kinetic model based on different glyceride and fatty acid ester composition
- integration of thermodynamics, fluid mechanics, transport phenomena and chemical kinetics
- batch, continuous and membrane reactor operation using homogeneous, heterogeneous inorganic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

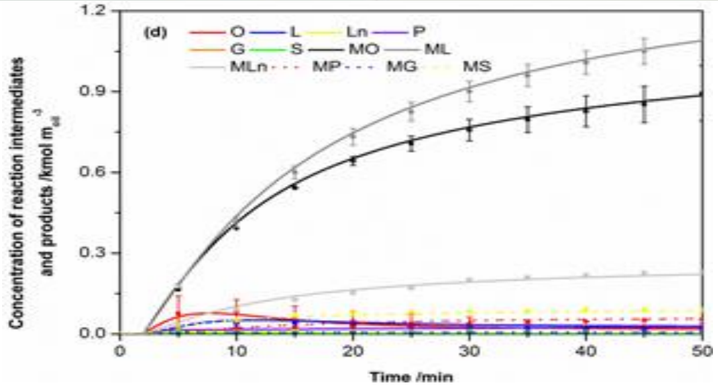




1. Blaž Likozar *et al.*, *Fuel Process Technol.*, **2016**, *142*, 326.
2. Blaž Likozar and Janez Levec, *Appl. Energ.*, **2014**, *123*, 108.
3. Blaž Likozar and Janez Levec, *Fuel Process Technol.*, **2014**, *122*, 30.

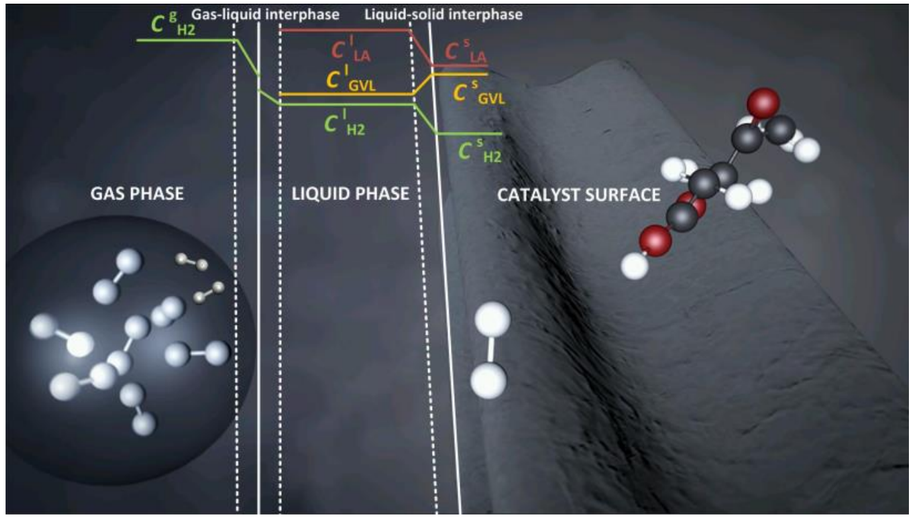



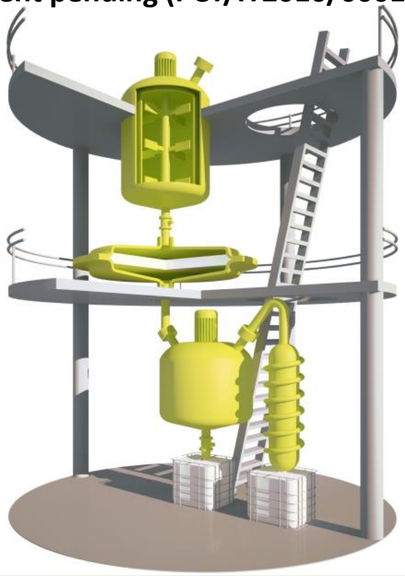



# Research subfield: Biomass-derived building blocks – 2nd generation lignocellulosic biofuels

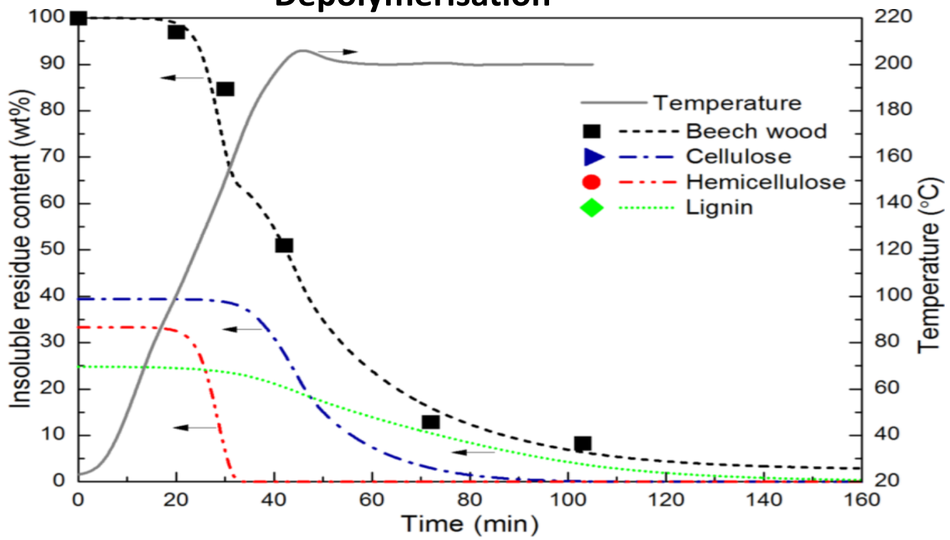
- selective fractionation processes
- depolimerisation of whole lignocellulosic biomass
- catalytic conversion of liquefied biomass to fuel
- kinetic models developed for decomposition and HDO
- screening of 30 synthetized and commercial HDO catalysts



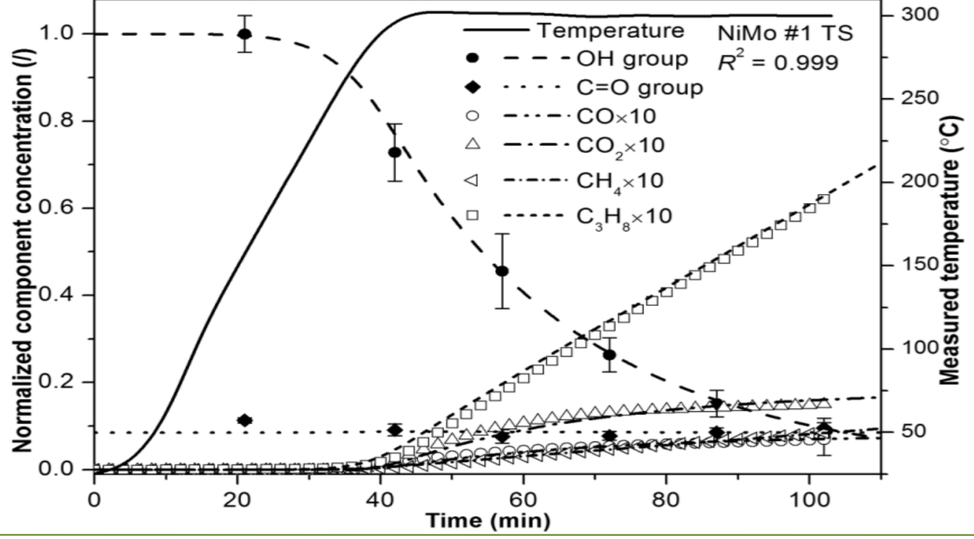

Patent pending (PCT/IT2016/000140)



**Depolymerisation**




**Hydro-deoxygenation (HDO)**



## Research subfield: Biomass-derived building blocks – Discarded potentials of lignocellulosic biomass

CELCYCLE Discarded potentials of biomass

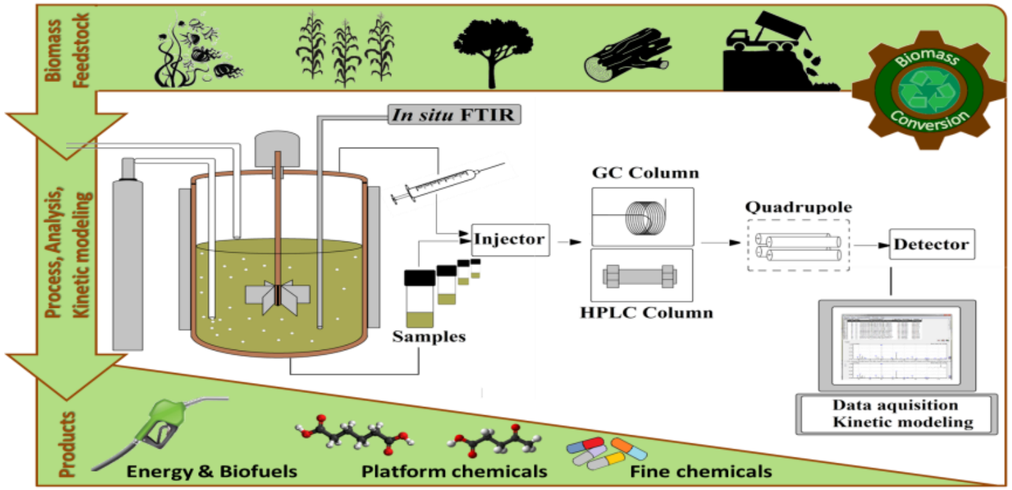
Slovenian smart specialization strategy (CELCYCLE, 2016-2020, 8.6 mil. € in total)

**5 conceptual sections:**

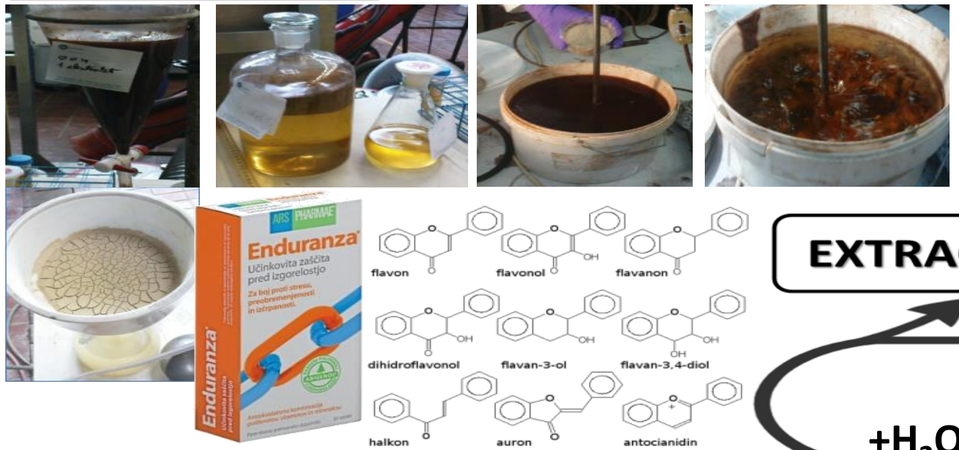
1. **Valorisation of biomass potential and development of bio-based products: nanocellulose and green chemicals**
2. Development of advanced and multifunctional materials with integrated nanocellulose and environmentally acceptable additives: paper, board and yarn
3. Development of products with higher proportion of bio-based components and improved functionalities: construction, automotive, textile and electrical industry
4. **Development of procedures for biological and mechanical processing of solid waste into products with added value**
5. Development of innovative system for energy recovery from waste

**Intersectoral and social networking with emphasis on local production circles – new value chains**

Biomass-derived building block and products



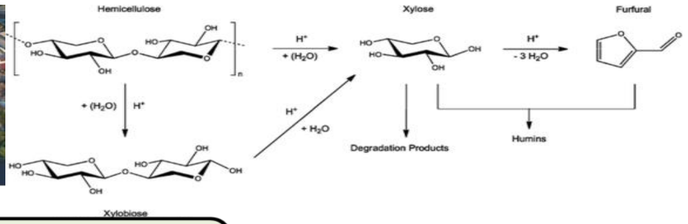
## PHARMACEUTICALS FROM EXTRACTIVES




Co-operation with industrial partner




## INDUSTRIAL FURFURAL PRODUCTION FROM HEMICELLULOSE




Co-operation with industrial partner

**EXTRACTIVES**

**HEMICELLULOSE**

$+H_2O$, $H^+$

$+H_2O$

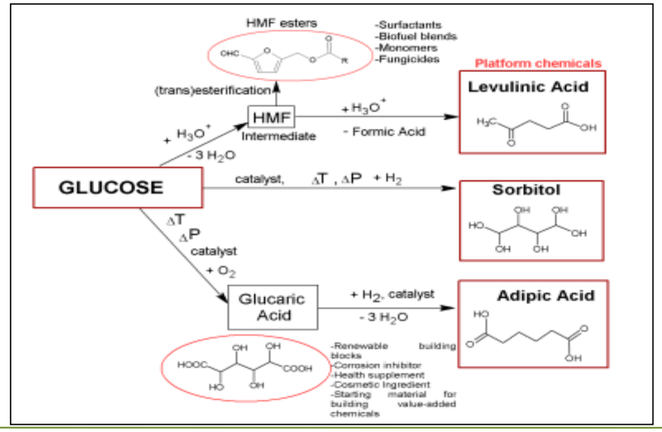
**Lignocellulosic Biomass**

+Solvent, $H^+$

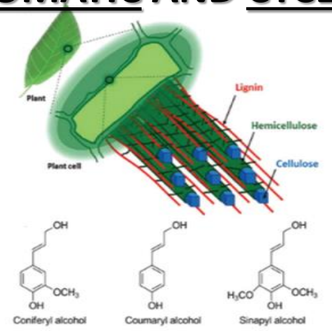
**CELLULOSE**

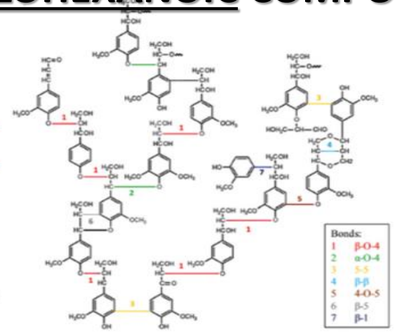
**LIGNIN**

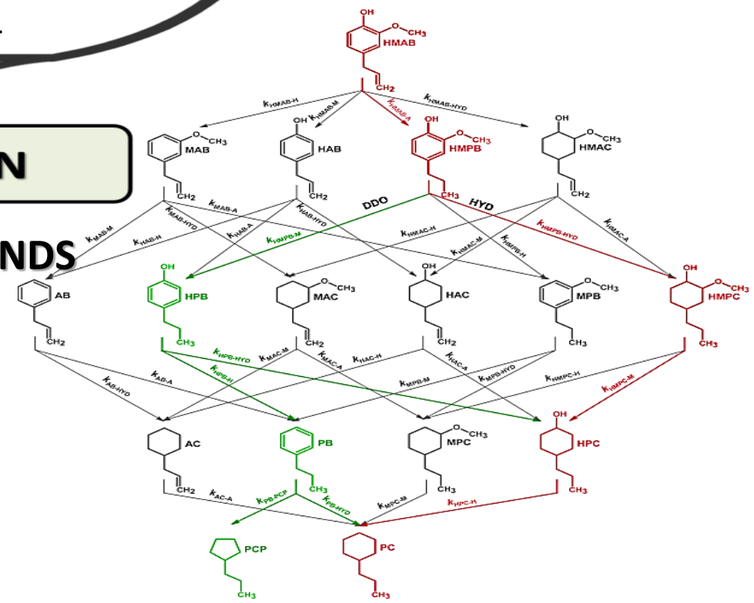
**LEVULINIC ACID**
**γ-VALEROLACTONE**
**PENTANEDIOL (1,2; 1,4; 1,5)**
**GLUCARIC ACID**
**ADIPIC ACID**
**SORBITOL**




## AROMATIC AND CYCLOHEXANOIC COMPOUNDS



# High-throughput experimenta-*in silico* approach

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

Enough measured data?
- No
- Yes

Clear?
- No
- Yes

- Characterized developed material
- Structure–activity correlation
- Structure–selectivity correlation
- Reaction/process mechanism
- Effect of process conditions
- Micro-scale process model

Analytics
- Identification
- Quantification
- Processing

Mechanism
- Intermediates
- Pathways
- Reactions

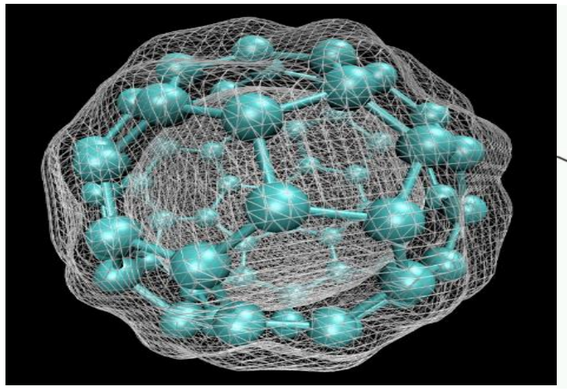
Model
- Mass transfer (gas-liquid-solid)
- Adsorption/desorption processes on material surface
- Surface reactions based on elementary steps

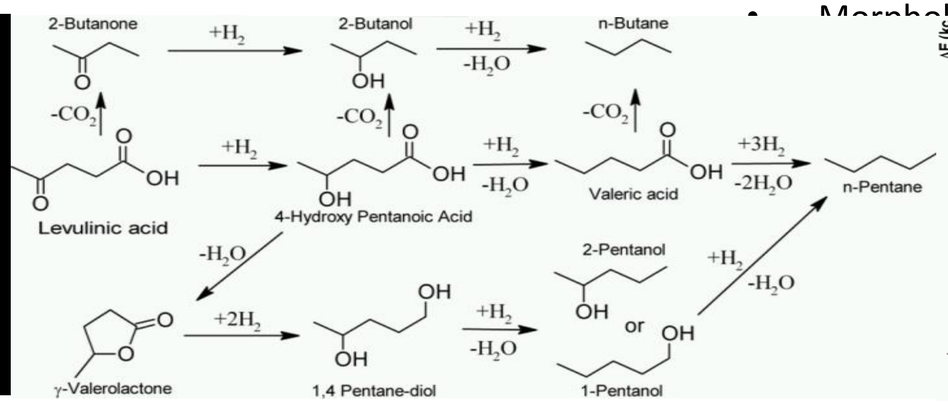
Kinetic Monte Carlo

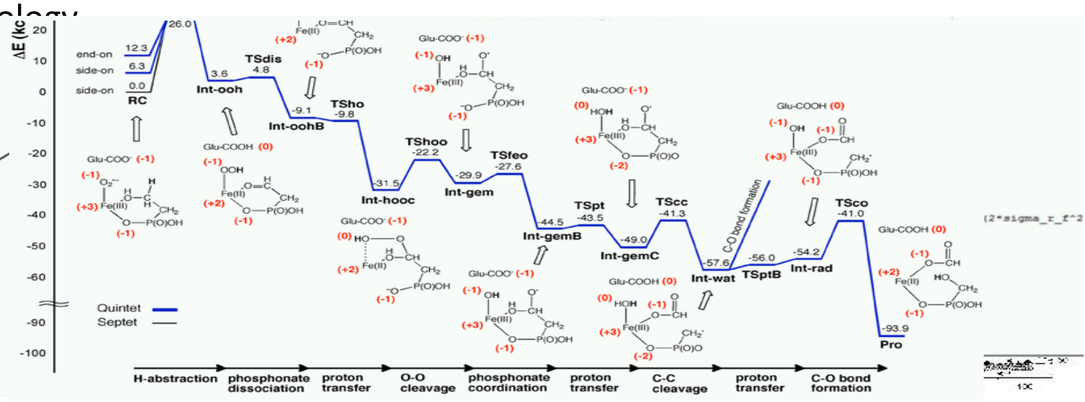
Density functional theory

Characterisation
- Composition
- Structure
- Morphology

Thermodynamics





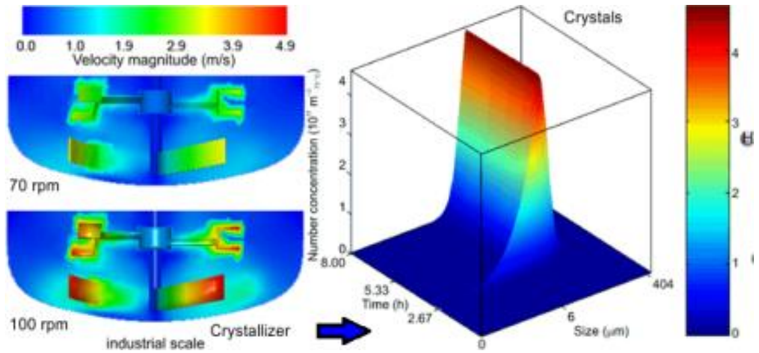
## Our profile:

- R&D on a lab scale
- Scale-up (based on combined experimental and *in-silico* studies)
- R&D on a pilot scale
- Unit operations
- Kinetic modeling, parameter estimation and sensitivity analysis
- Process simulation and optimization (CFD, DFT, Monte-Carlo, Aspen+)
- Downstream processing

## Our role in a Rhodolive:

- WP 2
- Separation process development (lipids, carotenoids, biophenols)
- Pre-treatment, extraction, isolation, purification, solvent recovery
- Experimental screening of operating conditions
- Modelling of thermodynamics and mass transfer kinetics
- Sensitivity analysis and process optimization

- Purified VCP‘s to AIDISA
- Isolated phenolics to UNI Kassel



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### AVAILABLE RESEARCH INFRASTRUCTURE:

**High-throughput high-pressure reactor systems:**

5 x parallel continuous fixed-bed reactors (in-house fabricated)
6 x parallel fully-automatized stirred reactors (Amar)
6 × parallel carousel Plus Reaction Station (Radleys)

**Individual high-pressure reactor equipment:**

1 x Fully automatized fixed bed or trickle bed reactor (PID Eng&Tech)
2 x 1700 mL stirred reactors (Parr, SS-316 and Titanium)
1 x 300 mL stirred reactor (Autoclave engineers)
1 x Reactor equipped with a scale for thermogravimetric analysis (Rubotherm)
1 x RC1e calorimeter with *in-situ* FTIR and FBRM probes (Metler Toledo)
1 x Fully automatized view-cell with highly-precise T and P sensors (in-house fabr.)

**Analytical equipment:**

4 x Two-module μ-GC (2 x Agilent, 2 x Inficon)
4 x GC–TCD (2 x SRI, 2 x Agilent)
2 x GC–MS/FID (1 x Agilent, 1 x Shimadzu)
1 x GC–FID (Thermo Scientific)
2 x HPLC/DAD (HP/Agilent, Thermo Scientific)
1 x UHPLC/DAD–RI (model known in May)
2 x FTIR with DRIFT, ATR liquid–probe & gas–cell modules
1 x UV-VIS spectrophotometer (Perkin–Elmer)
1 x Benchtop NMR (Magritec)

**Glass apparatus:**

1 x Labmax (Metler Toledo)
1 x Ebuliometer (Fischer Sci)
2 x Pilot scale adsroption and destilation units

**Characterization equipment:**

1 x Physisorption analyzer (Micromeritics ASAP 2020)
1 x Chemisorption analyzer with MS (Mircromeritics AutoChem)
1 x Co-owners of scanning electron microscope (Carl Zeiss)

Various reactor configurations

Separation unit operation

Various scales of operation

# High-throughput reactor systems

6 × parallel carousel Plus Reaction Station

- Radleys
- 100 ml
- Tmax =180 °C

5 x parallel high-throughput packed bed reactor

- In-house built
- 5 mL, SS-316
- Max *P* = 200 bar
- Max *T* = 500 °C

6 x parallel stirred autoclave system

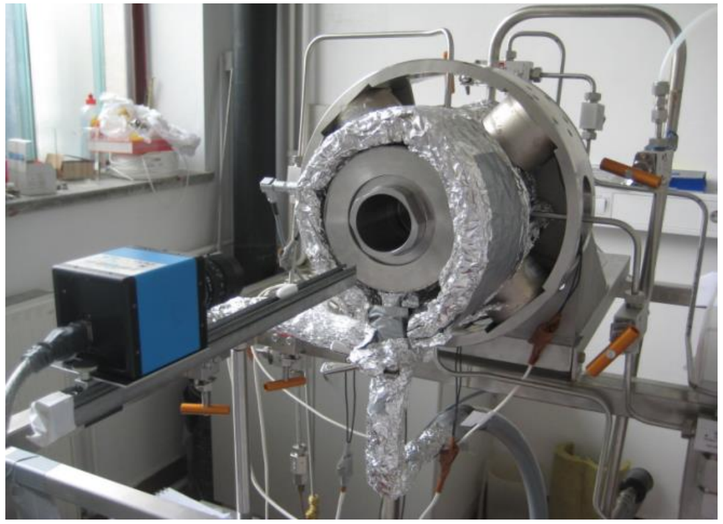
- Amar Equipments
- 250 ml
- Max *T* = 350 °C
- Max *P* = 200 bar
- SCADA software (fully automatized)

# Individual reactor systems

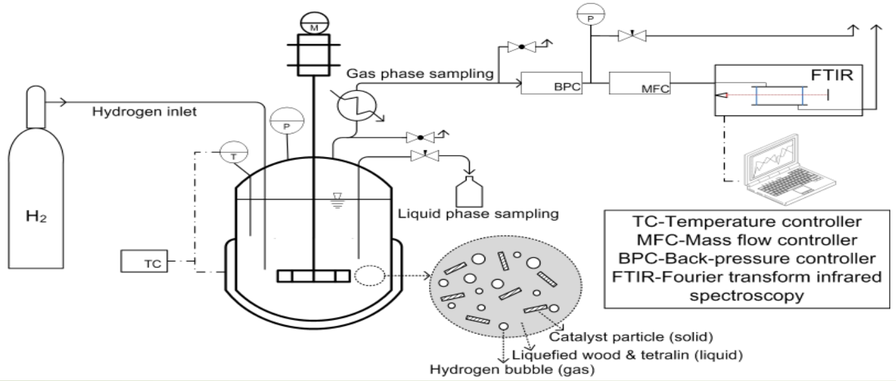
Autoclave engineers, 300 mL, SS-316,
Max *P* = 345 bar, Max *T* = 510 °C

Parr instruments, 1900 mL, Ti & SS-316,
Max *P* = 200 bar, Max *T* = 400 °C

High pressure phase-equilibrium cell
(In-house made)



- Batch, Semi-batch, CSTR mode
- G-L, G-S, L-S, G-L-S reactions
- Reactions, (supercritical) extraction
- Online GC and FTIR analysis



# RC1e reactor/calorimeter with *in-situ* FTIR and FBRM (Mettler Toledo)

3L and 200 ml

In situ FTIR and FBRM probes


FBRM -Focused Beam Reflectance Measurement

# Analytical equipment

- UHPLC–DAD/RI and fraction collector (Thermo Fisher Scientific)
- 2x HPLC–DAD (Agilent; Thermo Fisher Scientific)
- 2x FTIR/DRIFT/ATR (gaseous/liquid/solid) (PerkinElmer)
- UV–Vis (liquid/solid) (PerkinElmer)
- 2x GC–MS/FID (1 × Agilent, 1 × Shimadzu)
- 4x GC–TCD (2 × Agilent; 2 × SRI Instruments)
- Micro GC (2 × Agilent; 1 × Inficon)
- TOC
- High pressure TG-GC-MS
- Benchtop NMR (Magritek)
- FBRM (Metler Toledo)

UV-Vis Spectrophotometer

UHPLC


Micro-GC

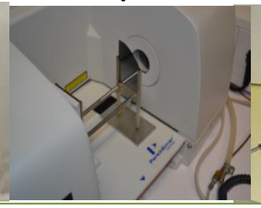
GC-MS

In-situ FTIR and FBRM

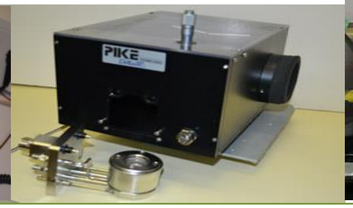
**FTIR**

Gases

Liquids



Solids



# Thank you for your attention!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