Valorisation of lignocellulosic (LC) biomass by catalytic hydrotreatment

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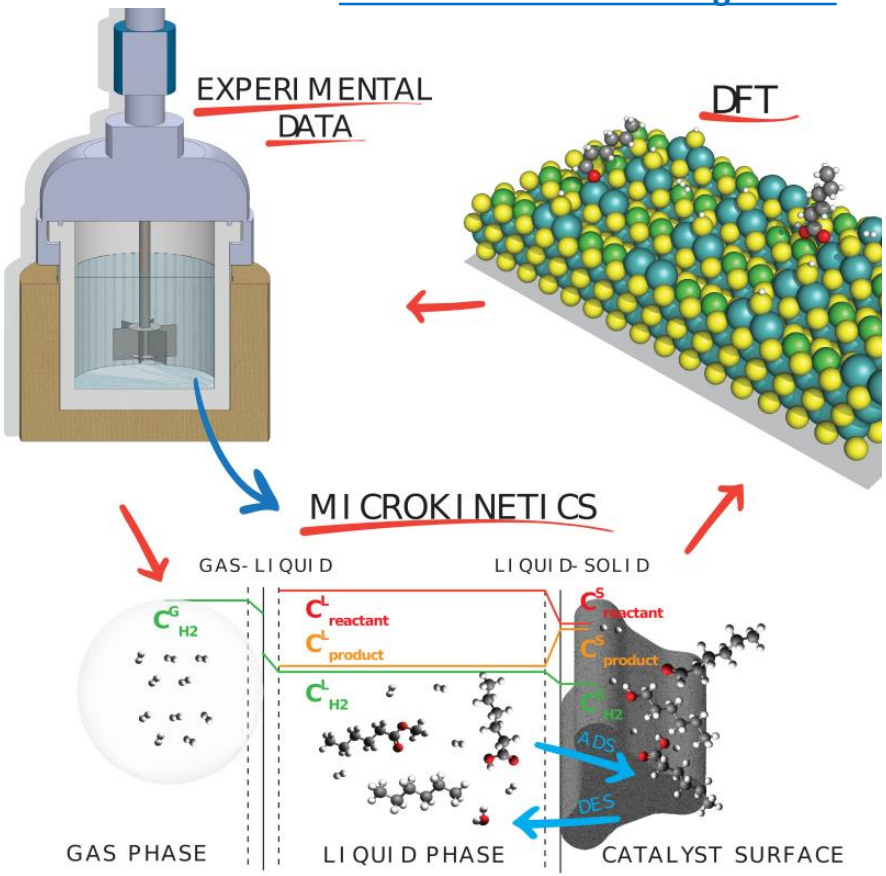
Research topics

- 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 CO_2 Using Surplus Electricity (SPIRE-02-2014)
- FReSMe, Methanol from CO_2 Blast Furnace gasses (LCE-25-2016)
- ADREM, Adaptable Reactors for Resource- and Energy-Efficient Methane Valorisation (SPIRE-05-2015)
- nextBioPharmDSP, Next-generation Biopharmaceutical Downstream Process (BIOTEC-4-2014)
- CONVERGE, CarbON Valorisation in Energy-efficient Green fuels (H2020-LC-SC3-2018)
- BIZEOLCAT, Bifunctional Zeolite based Catalysts and Innovative process for Sustainable HC Transformation (H2020-NMBP-2018)
- ReaxPro Software Platform for Multiscale Modelling of Reactive Materials and Processes (Reax Pro, H2020-NMBP-TO-IND-2018)

ERA-NET:

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

NATO SPS:

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

INTERREG (Italy-Slovenia):

- BIOAPP, Transregional platform for transfer of advanced biopolymers from lab to market

COST Actions: 3

Slovenian Research Agency programmes/projects: 5

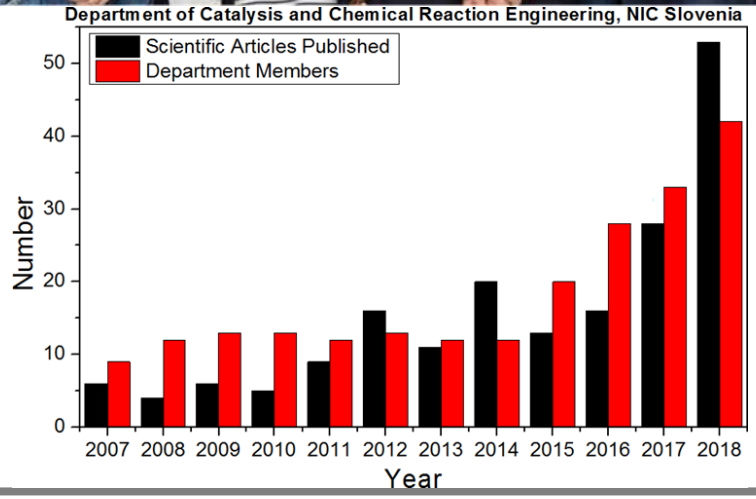
Bilateral cooperation projects: 6

Department of Catalysis and Chemical Reaction Engineering

Then and now

2012

2019



SUBGROUP: BIOMASS-DERIVED BUILDING BLOCKS

- 9 Postdocs, 8 PhD students, 12 MSc students
- 1 Interreg, 2 ERA-NET, 1 Horizon 2020 project
- 2 Postdoctoral projects (ARRS)
- 2 COST actions

Ongoing activities

LC Biomass and Catalysis (Miha):
- Liquefaction
- Fractionation
- Furfural synthesis from **hemicellulose**
- Adipic acid synthesis from **cellulose**
- Isolation of **extractives** (flavonoids)
- **Lignin** valorisation by HDO
- **Levulinic acid** valorisation by HDO

Marine Biomass and Product Eng. (Uroš):
- Edible bio-based packaging material
- Biorefinery and Biotechnological Exploitation of Marine Biomasses
- Extraction of chitin from crustaceans
- Chitin conversion into chitosan and chitlac
- Isolation of oligosacharides from algae

SUBGROUP: BIOMASS-DERIVED BUILDING BLOCKS

Then and now (2013-2019)

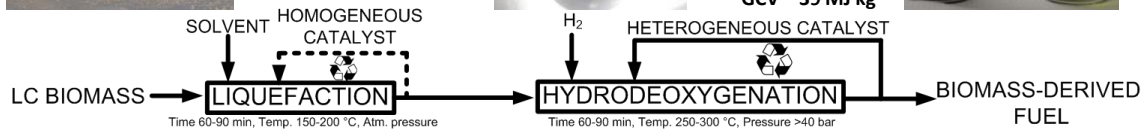
PAST WORK: 2ND GENERATION BIOFUELS

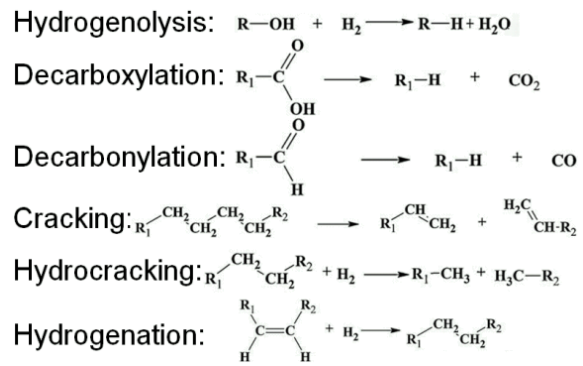
SOLVOLYSIS AND HYDRODEOXYGENATION OF LC BIOMASS

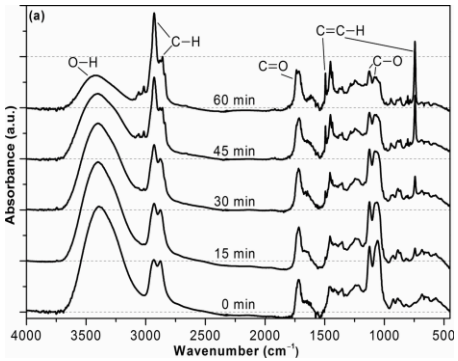
- Depolymerization and solubilization of lignocellulosic biomass
- Catalytic conversion of liquefied biomass to fuel
- Lumped kinetic models developed for solvolysis and HDO
- Screening of 30 synthetized and commercial HDO catalysts

Liquefied biomass
Polar
Density ~ 1.2 kg L^{-1}
GCV ~ 21 MJ kg^{-1}

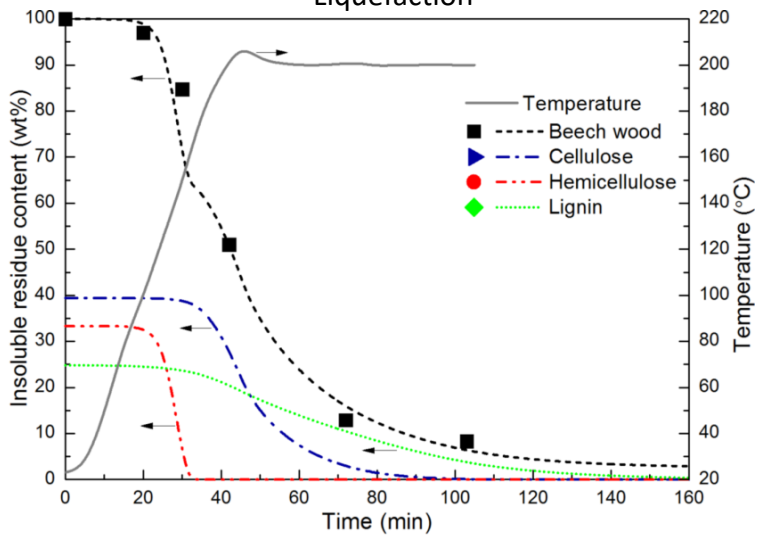
Non-polar (oil) phase
Non-polar
Alkanes, Alkenes
Density ~ 0.85 kg L^{-1}
GCV ~ 39 MJ kg^{-1}



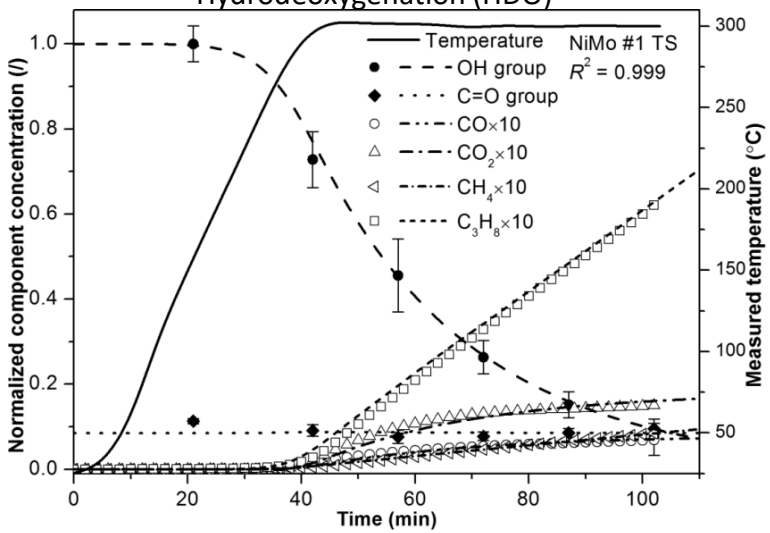




Liquefaction

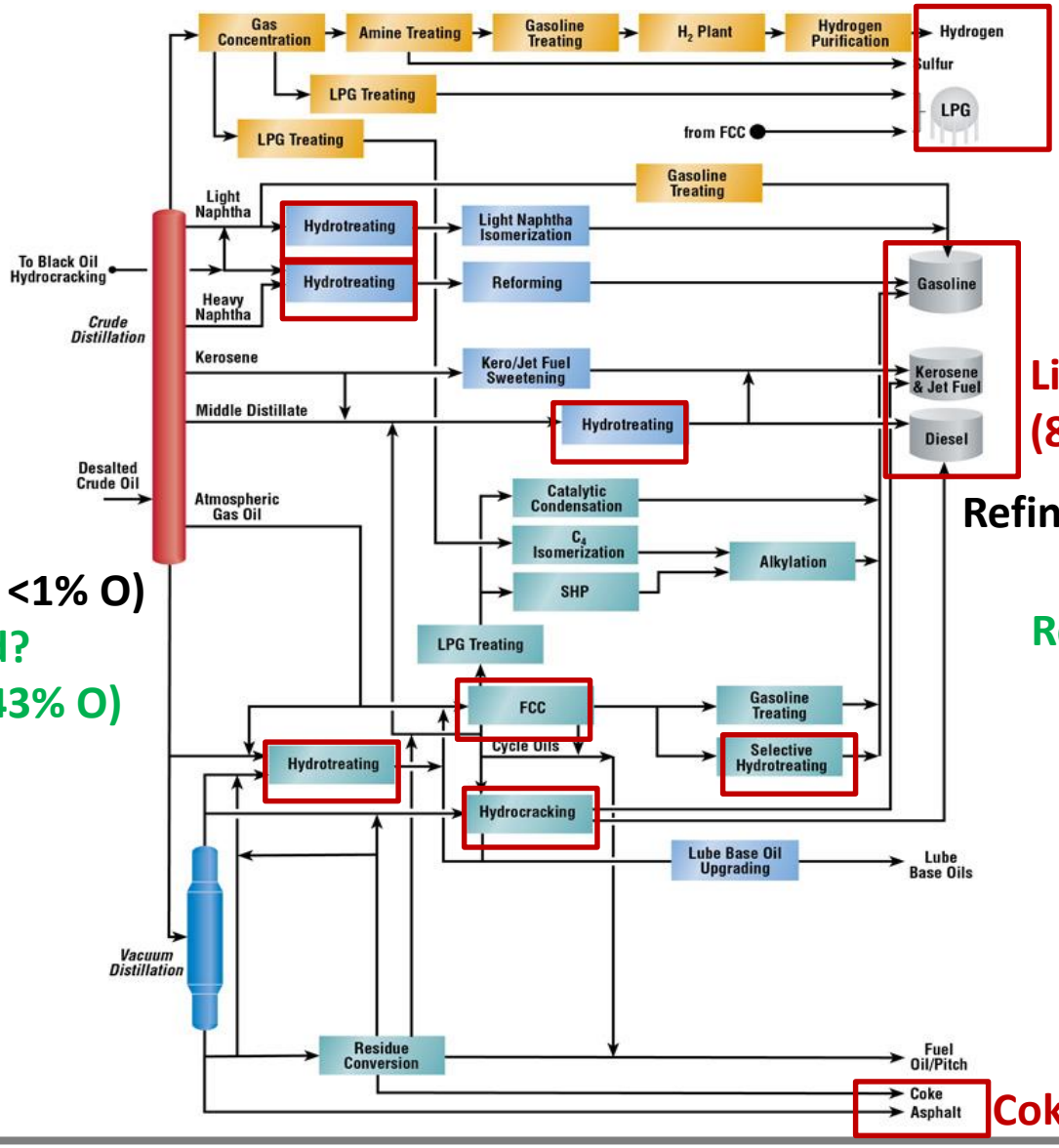


Hydrodeoxygenation (HDO)



1. Miha S. Grilc *et al.*, *Biomass Bioenerg.*, **2014**, *63*, 300. Highly Cited Paper
2. Miha S. Grilc *et al.*, *Appl. Catal. B.*, **2014**, *150*, 275. Highly Cited Paper
3. Miha S. Grilc, *et al.*, *Appl. Catal. B.*, **2015**, *163*, 467. Highly Cited Paper
4. Miha S. Grilc *et al.*, *Catal. Today.*, **2015**, *256*, 302.
5. Miha S. Grilc *et al.*, *ChemCatChem.*, **2016**, *8*, 180.
6. Miha S. 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 (LW):
600 €/ton

CONCEPT: BIOREFINERY

LIGNO(HEMI)CELLULOSIC BIOMASS

H_2O → **Extraction** → Liquid → **EXTRACTIVES**
(vitamins, flavonoids, terpenes, terpenoids, phenolics)

Solid
HCL

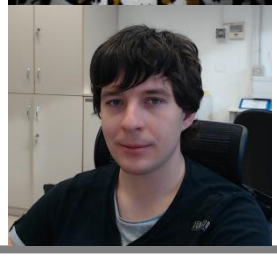
$H_2O/EtOH, H_2SO_4$
T = 180 – 230 °C

Pulping → Solid → **CELLULOSE**
(glucose)

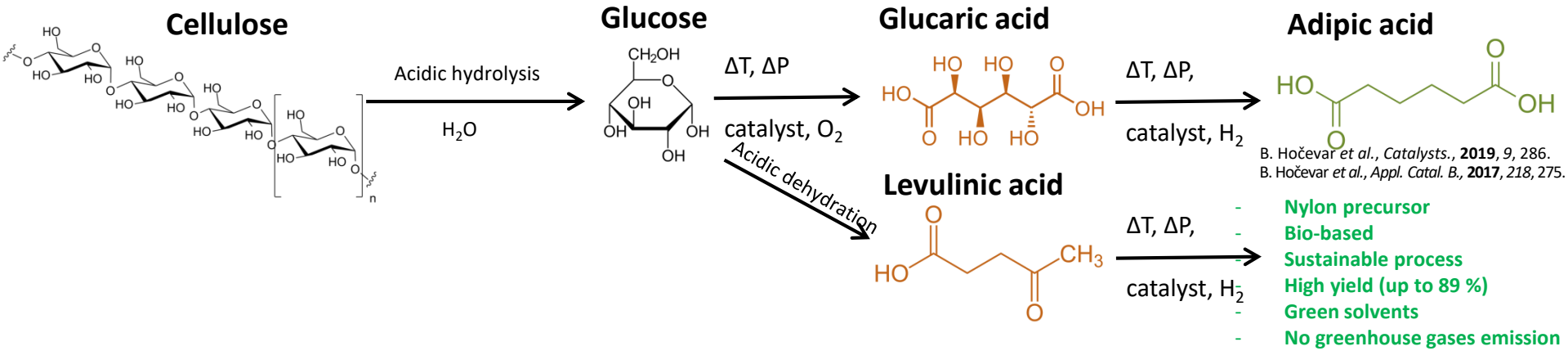
Liquid
LH

Precipitation → Solid → **LIGNIN**
(p-coumaryl alcohol, coniferyl alcohol, sinapyl alcohol)

Liquid → **HEMICELLULOSE**
(C5 sugars: xylose, mannose, glucose, galactose and sugar acids)



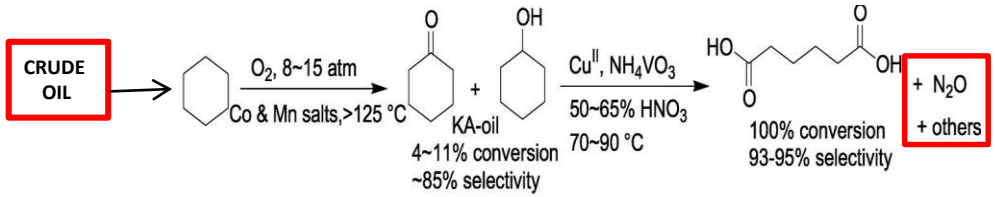
CELLULOSE AND HEMICELLULOSE VALORISATION: TOP – DOWN APPROACH



B. Hočevar *et al.*, *Catalysts.*, **2019**, *9*, 286.
B. Hočevar *et al.*, *Appl. Catal. B.*, **2017**, *218*, 275.

- Nylon precursor
- Bio-based
- Sustainable process
- High yield (up to 89 %)
- Green solvents
- No greenhouse gases emission

Conventional petrochemical process

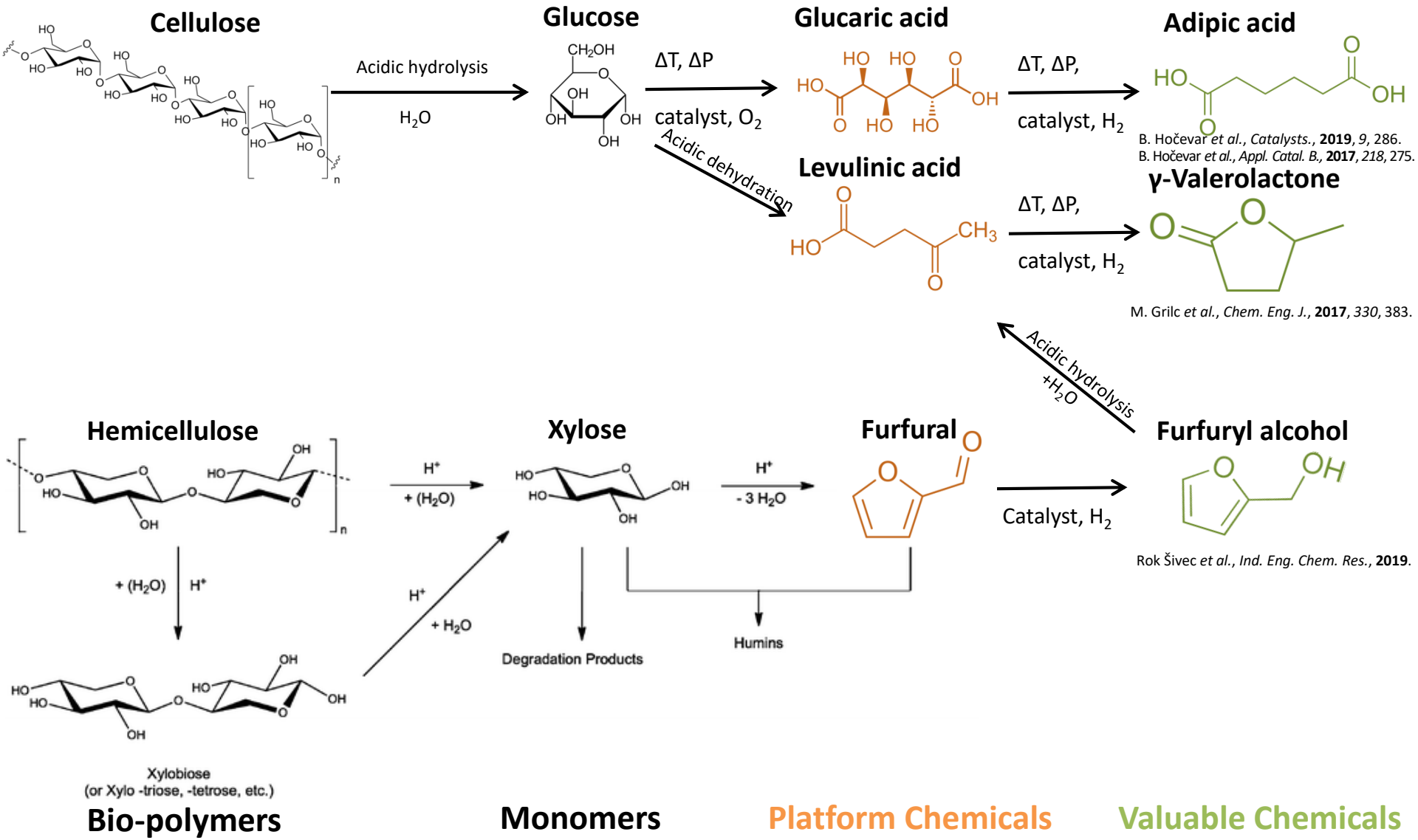


Rok Šivec *et al.*, *Ind. Eng. Chem. Res.*, **2019**.

- Low yield of KA oil
- NOx emission

Bio-polymers **Monomers** **Platform Chemicals** **Valuable Chemicals**

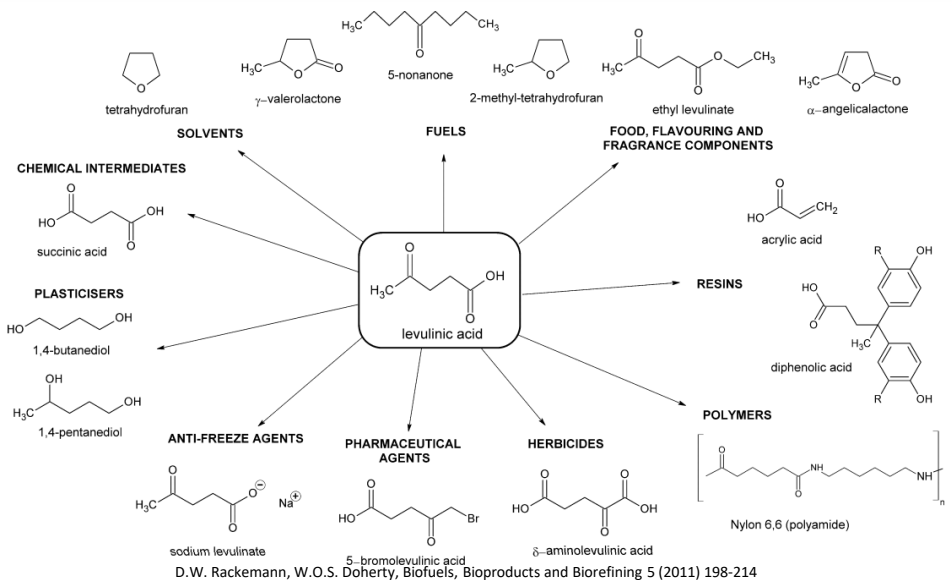
CELLULOSE AND HEMICELLULOSE VALORISATION: TOP – DOWN APPROACH



LEVULINIC ACID: PLATFORM CHEMICAL

AIM:

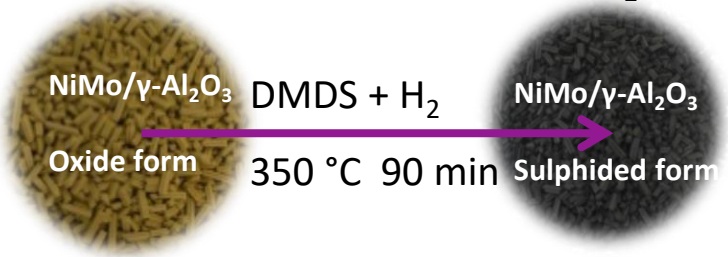
- Added-value biomass-derived products
  - Fuel additives
  - Monomers
  - Flavors
  - Solvents
- Use of cheap transition metal catalysts
- Avoiding the use of solvents
- Reaction mechanism proposal
- Microkinetic model development
- Process bottlenecks identification



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

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LEVULINIC ACID HDO: EXPERIMENTAL SET-UP

LEVULINIC ACID HDO: ANALYTICS

Solid phase (catalyst):

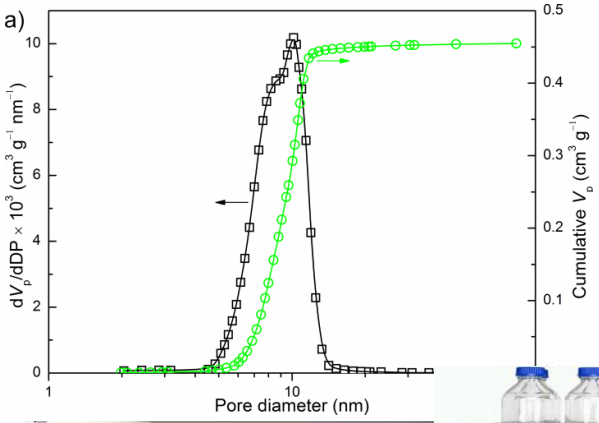
- N_2-Physisorption
- TPR-TPO-TPR
- TEM, SEM/EDX
- XRD
- NH_3-TPD

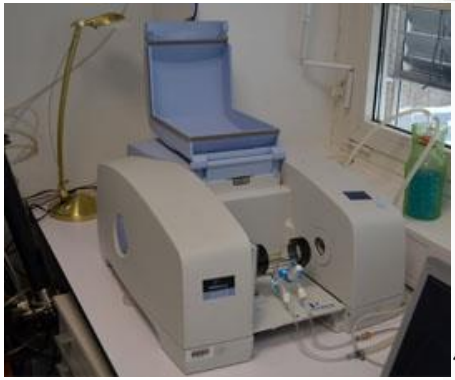
Liquid phase analysis (sampling):

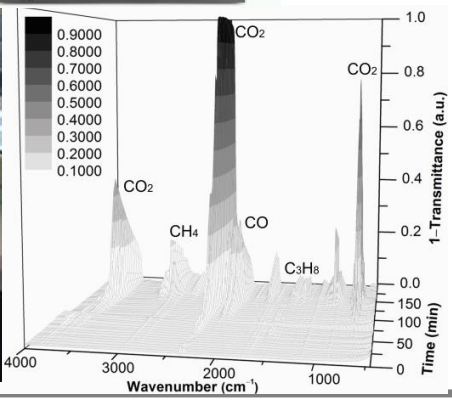
- GC-MS (Identification)
- GC-FID (Quantification)
- UHPLC-FC and 3D Benchtop NMR

Gas phase analysis (online):

- FTIR (flow-through cell)
- µ-GC







LEVULINIC ACID HDO: ANALYTICS

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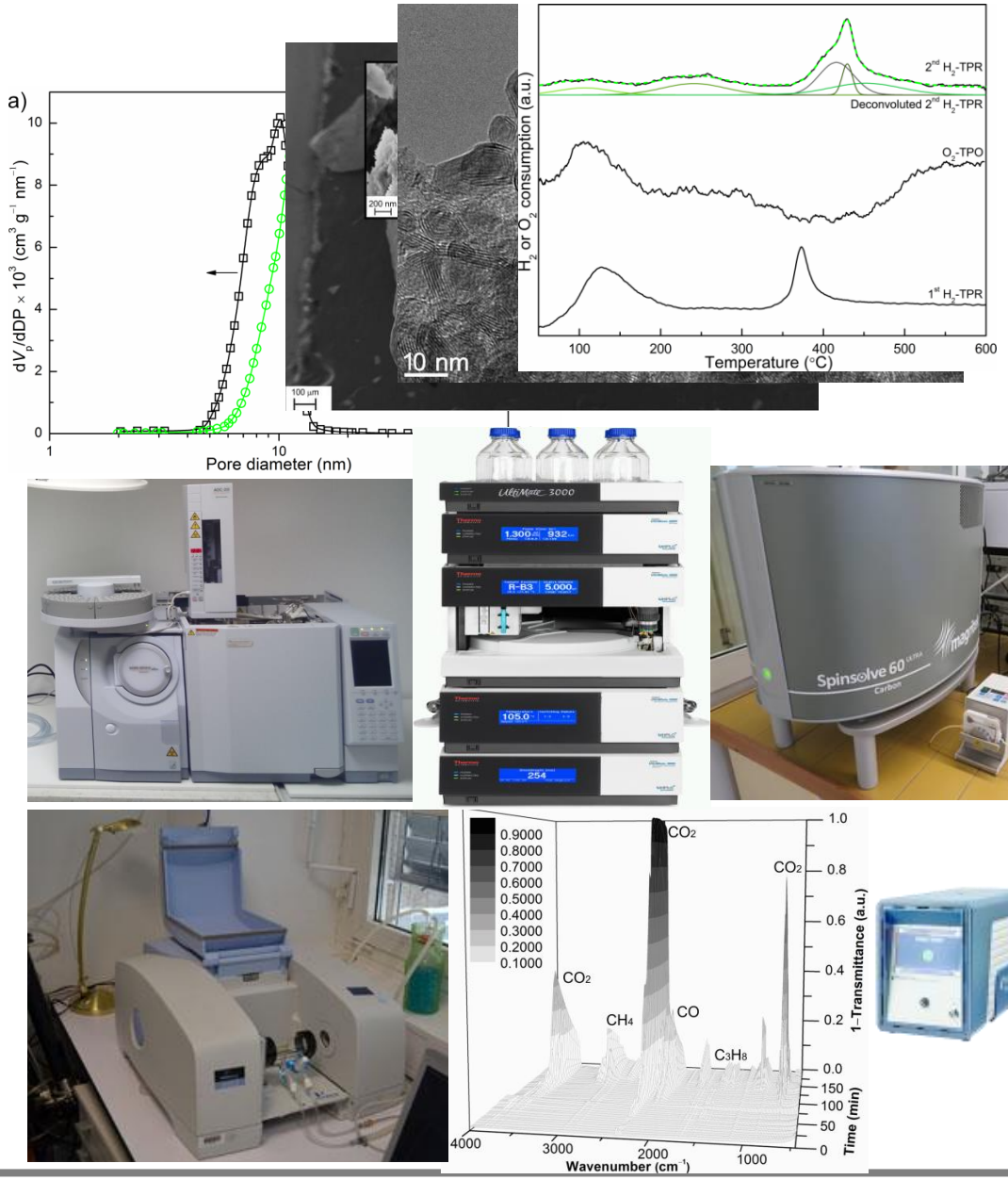

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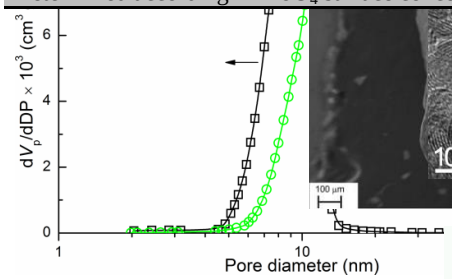
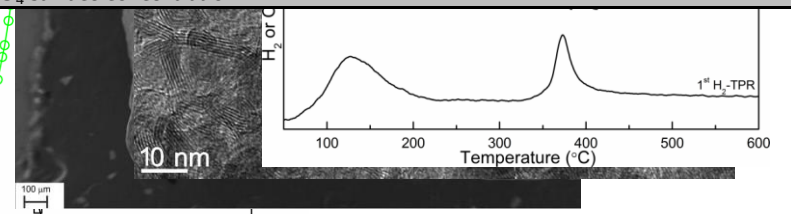
Gas phase analysis (online):

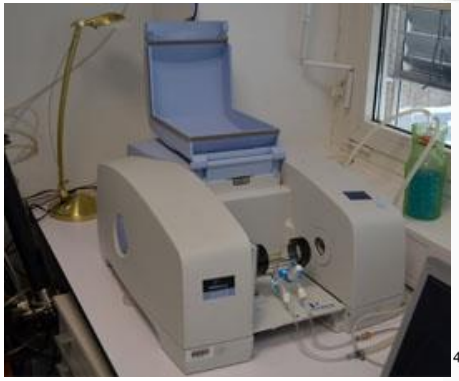
- FTIR (flow-through cell)
- µ-GC

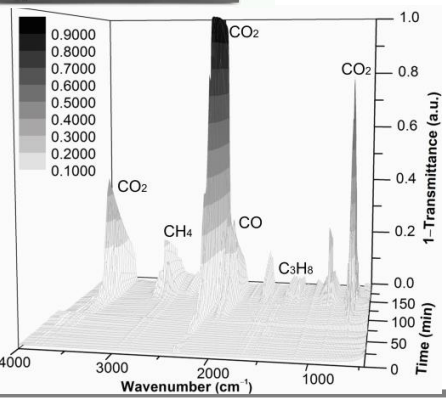
Catalyst	Metal content (wt. %)	Active Phase	Active sites (µmol m^{-2})	Surface Area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore size (Å)
$NiMo/Al_2O_3$	3/15[a]	$NiMoS_x$	0.33[b]	170.9	0.471	110.4

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





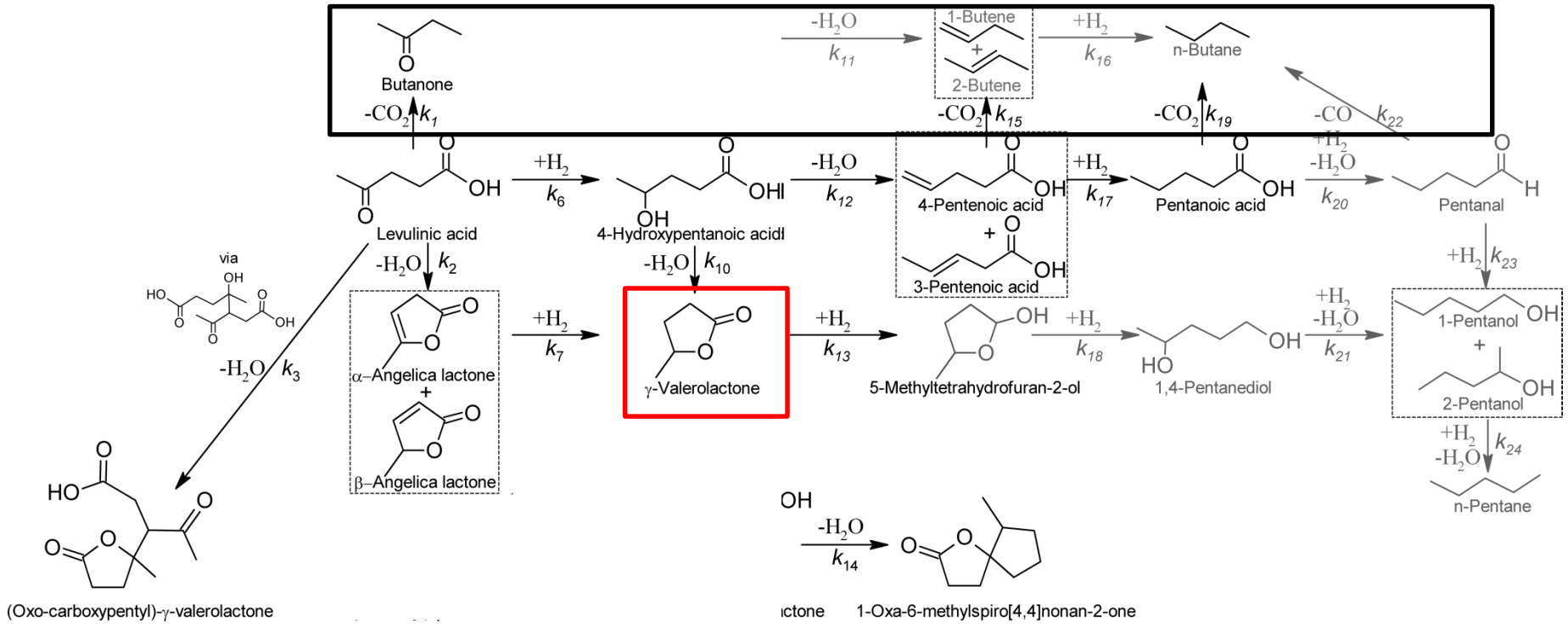




LEVULINIC ACID HDO: REACTION PATHWAY NETWORK

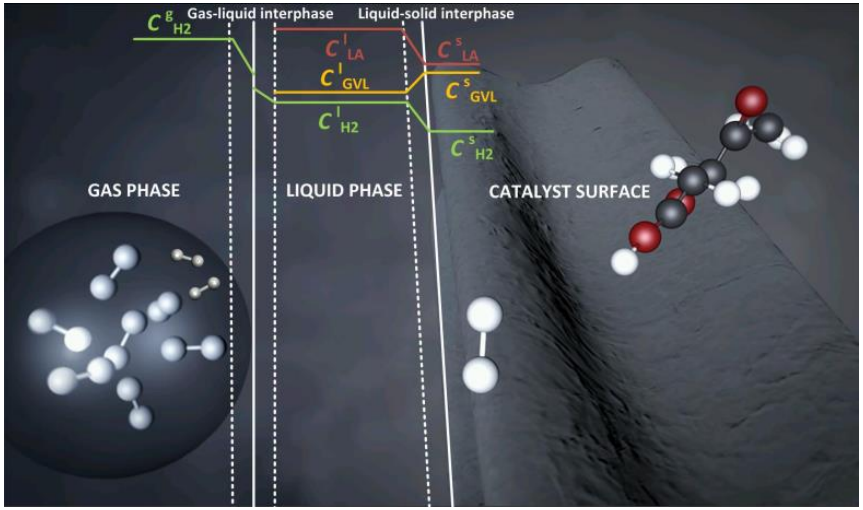
Elementary reactions:

- 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:

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

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

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

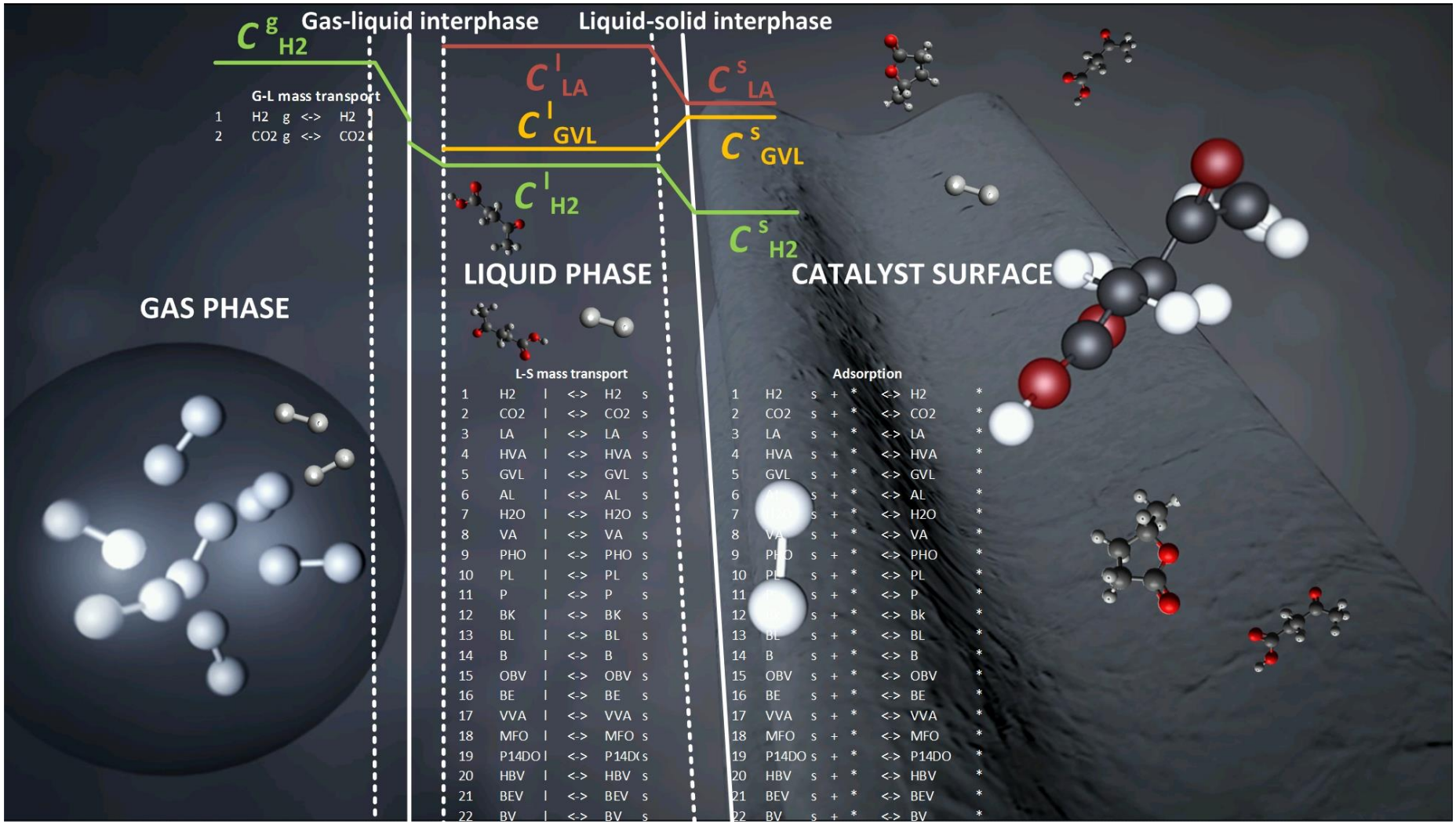
$$\lim_{V_{si} \to 0} \left(V_{si} \frac{dC}{dt}\right) = r_j{}^{LS} - r_j^{ads} + r_j^{des}$$ On L-S interphase

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

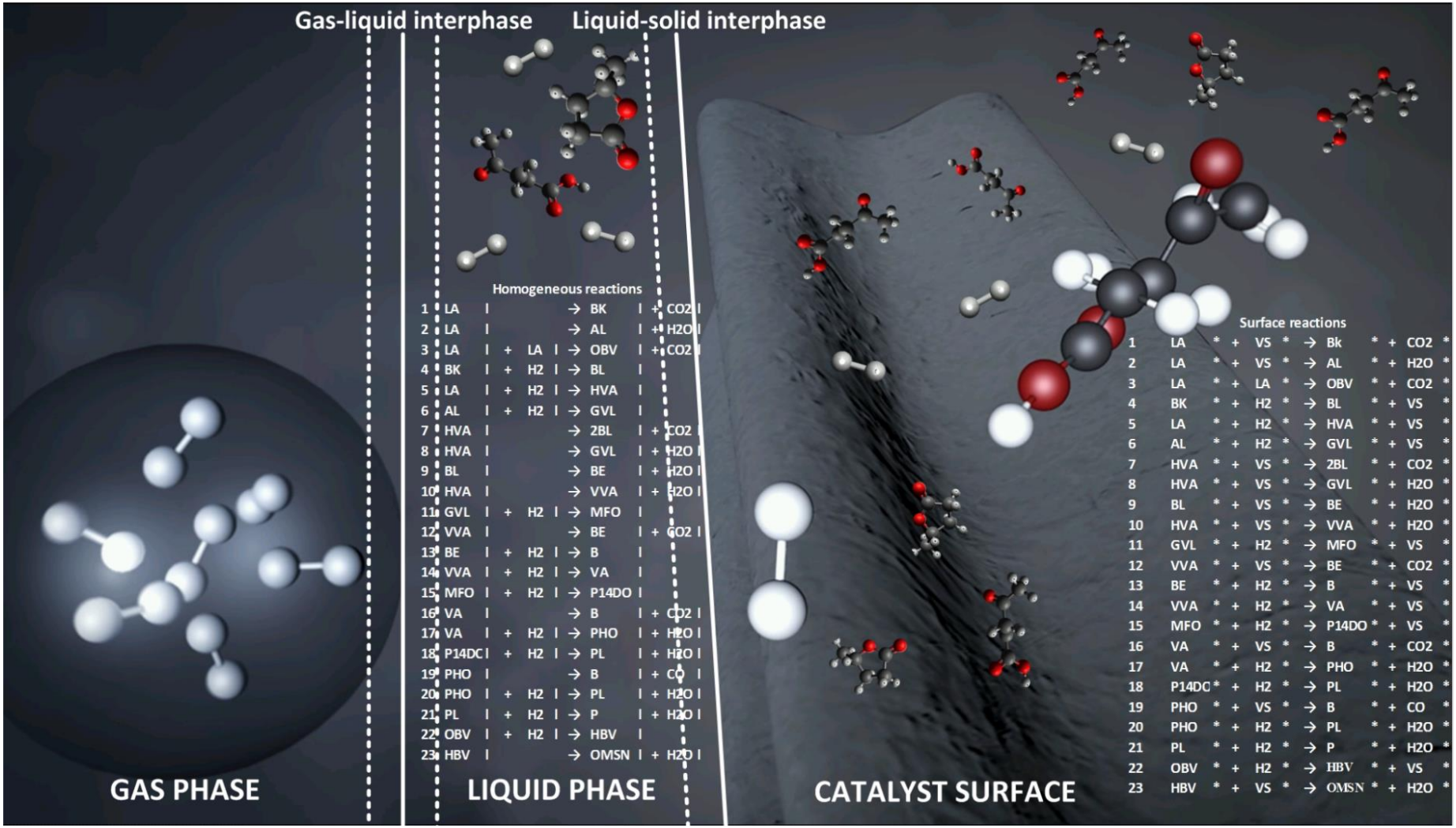
Molar balance for vacant sites:

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

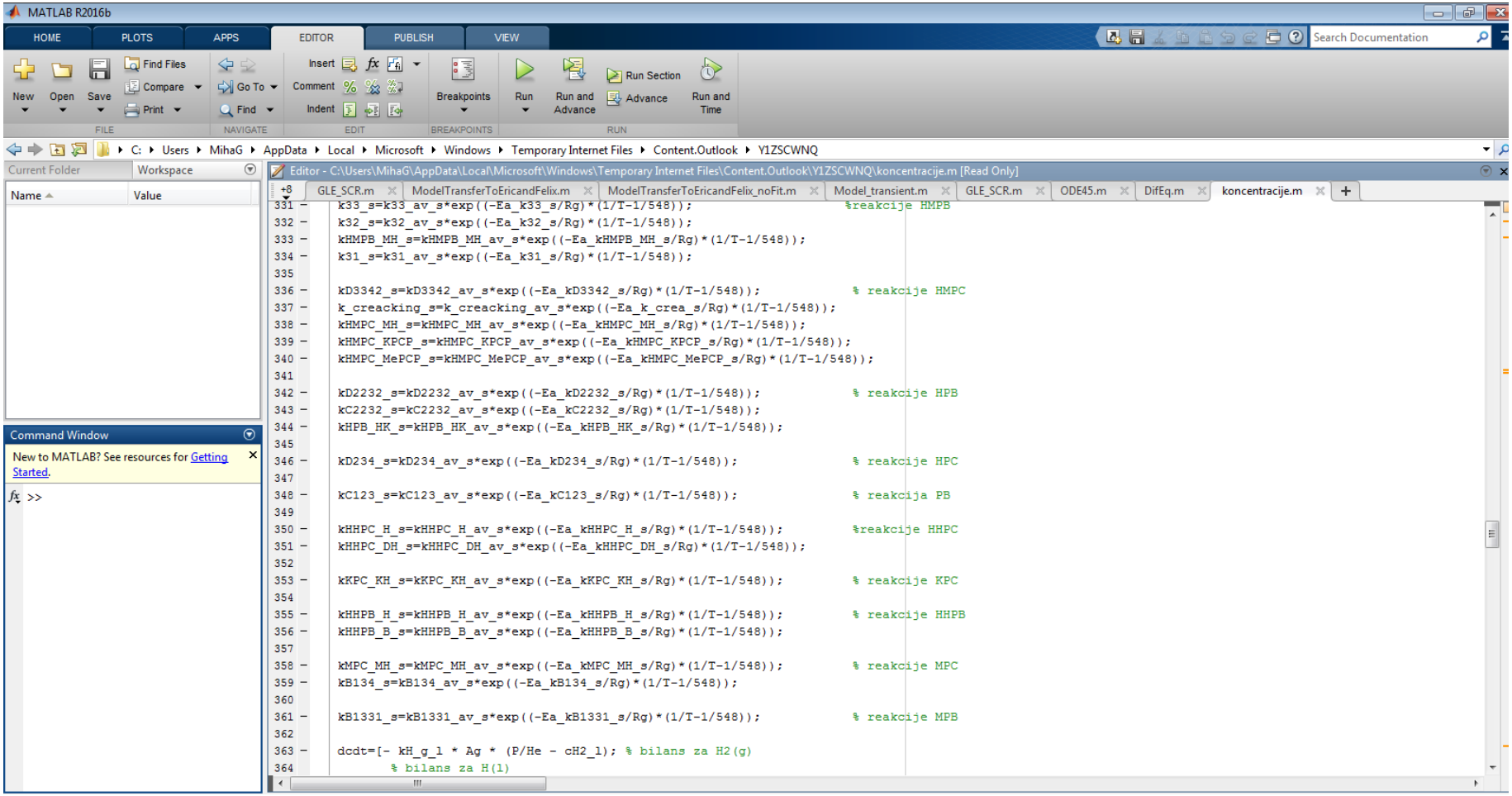
LEVULINIC ACID HDO: MASS TRANSFER



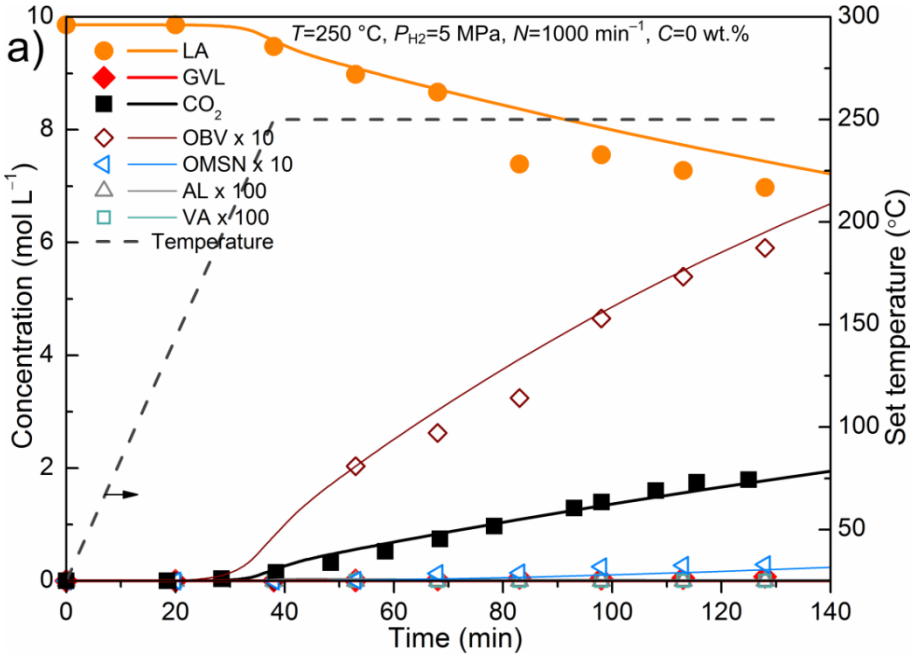
LEVULINIC ACID HDO: HOMOGENEOUS AND CATALYTIC REACTIONS

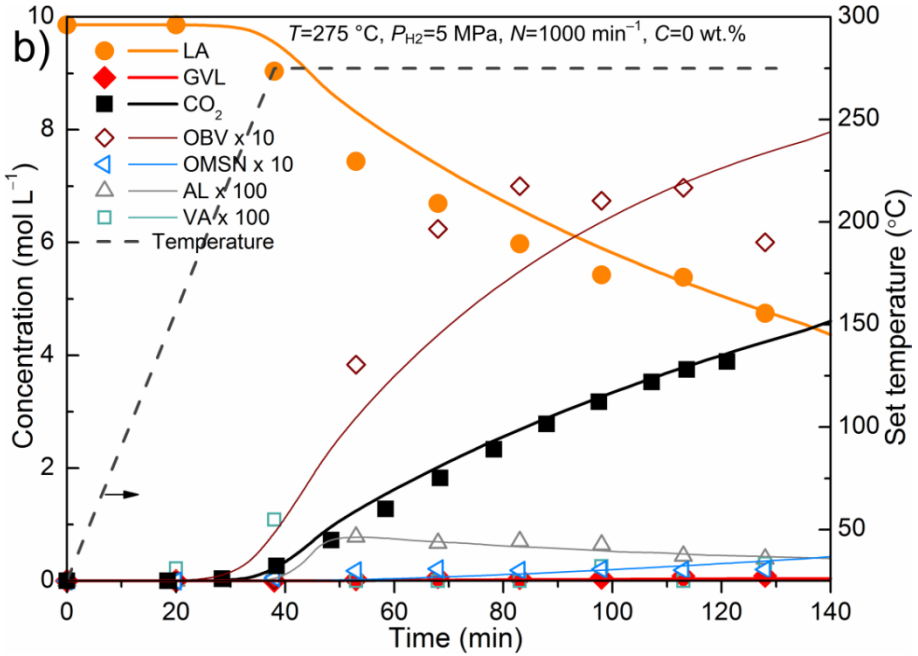


KINETIC MODEL: DIFFERENTIAL EQUATIONS SOLVED NUMERICALLY IN MATLAB



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.
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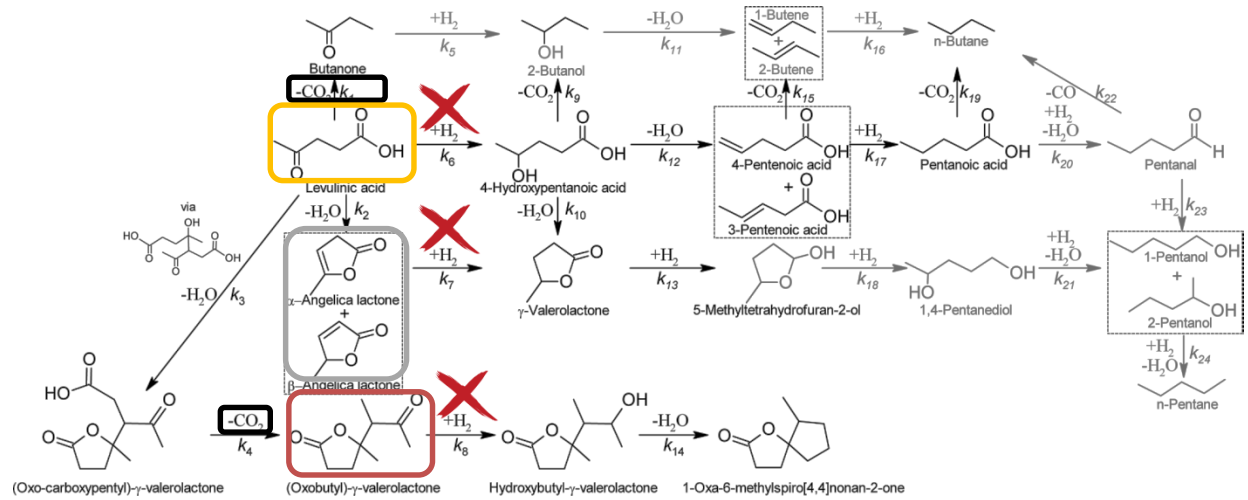

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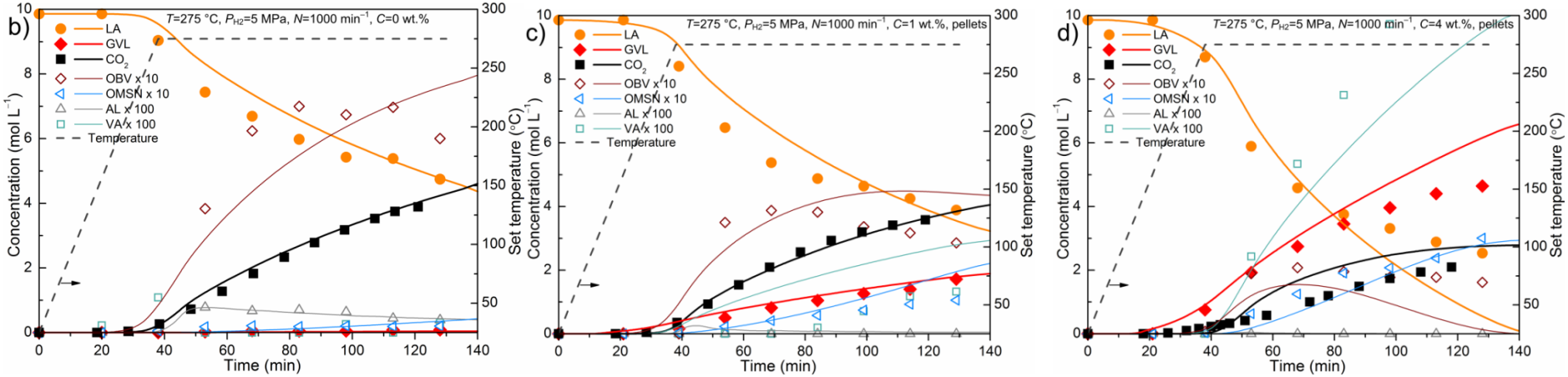
LEVULINIC ACID HDO: CATALYST LOADING

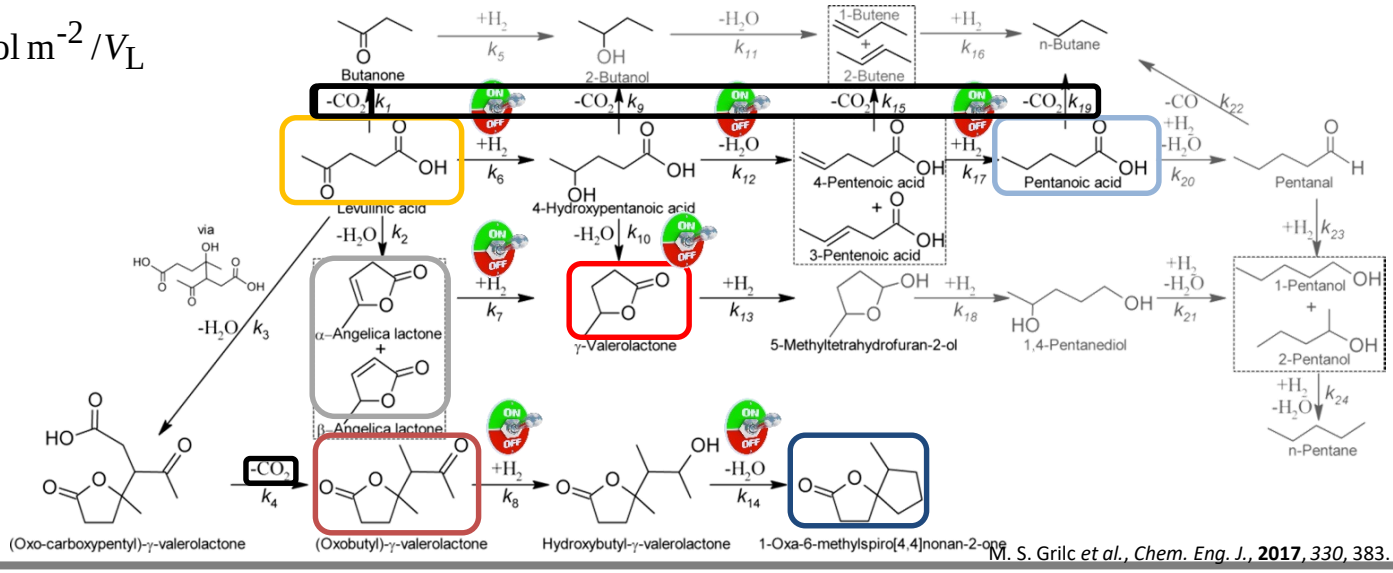


$$C^*_{VS}(t=0) = m_S \cdot a_{BET} \cdot 0.33 \mu\text{mol m}^{-2} / V_L$$

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

$$\frac{dC^*_j}{dt} = r_j^A - r_j^D + \sum \pm r_i^C$$

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



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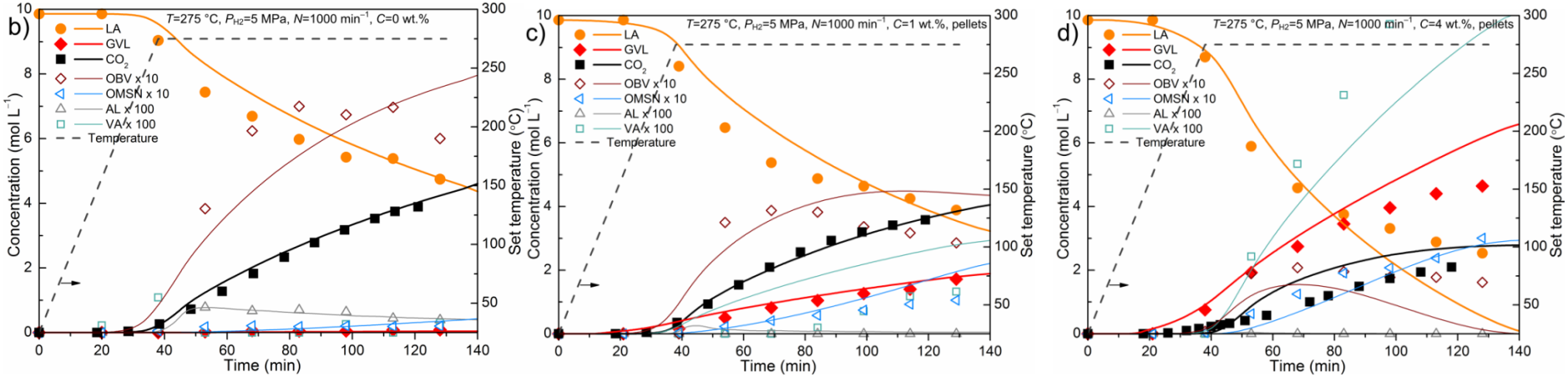

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3	k_3^C [LA*] [LA*]	$< 2 \times 10^3$
4	k_4^C [OCPV*] [*]	n.a.
5	k_5^C [BK*] [H_2*]	n.a.
6	k_6^C [LA*] [H_2*]	2.02×10^9
7	k_7^C [AL*] [H_2*]	7.58×10^{11}
8	k_8^C [OBV*] [H_2*]	3.60×10^9
9	k_9^C [HVA*] [*]	2.15×10^5
10	k_{10}^C [HVA*] [*]	$>> k_6^C$
11	k_{11}^C [BL*] [*]	n.a.
12	k_{12}^C [HVA*] [*]	$k_{10}^C \times 2.04 \times 10^{-2}$
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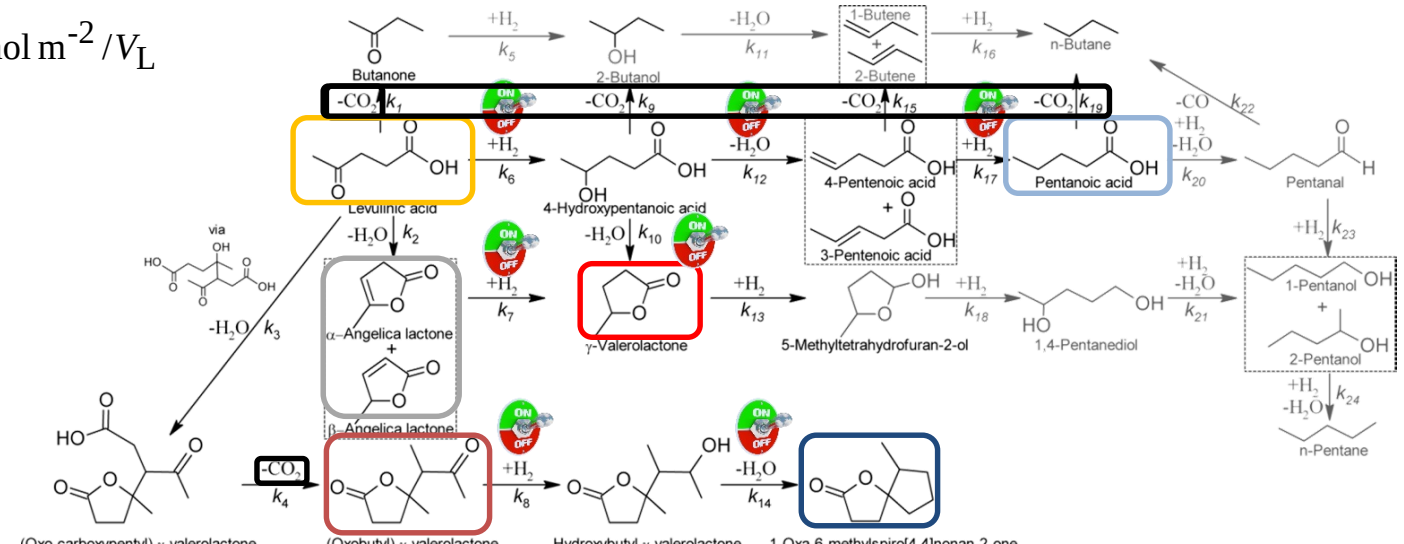
17	k_{17}^C [VVA*] [H_2*]	$>> k_{12}^C$
18	k_{18}^C [MFO*] [H_2*]	n.a.
19	k_{19}^C [VA*] [*]	2.15×10^5
20	k_{20}^C [VA*] [H_2*]	$< 1 \times 10^5$
21	k_{21}^C [PDO*] [H_2*]	n.a.
22	k_{22}^C [PHO*] [*]	n.a.

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

C



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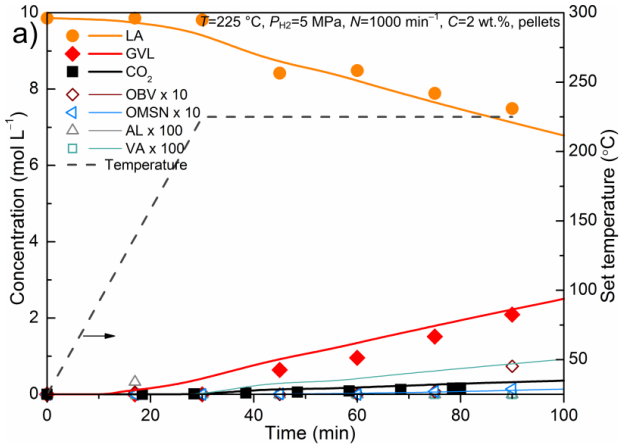
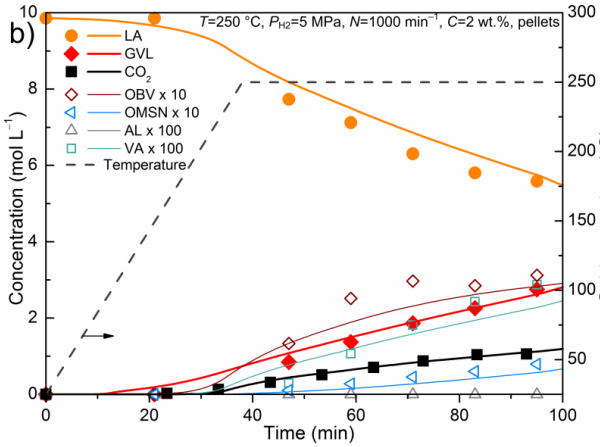
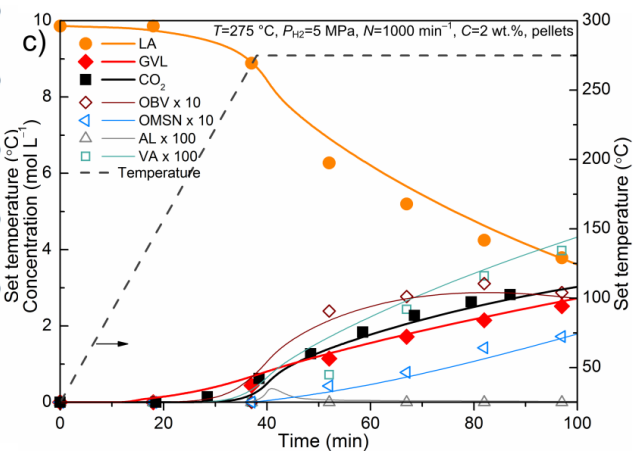
LEVULINIC ACID HDO: TEMPERATURE







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12	k_{12}^C [HVA*] [*]	$k_{10}^C \times 2.04 \times 10^{-2}$	150
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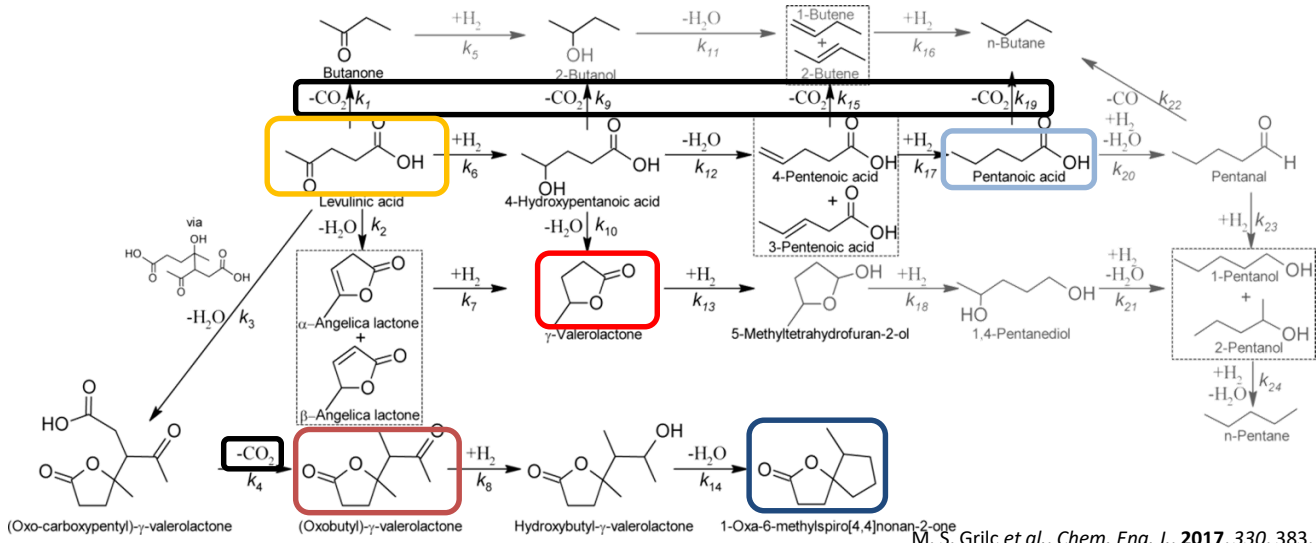
17	k_{17}^C [VVA*] [H_2*]	>> k_{12}^C	n.a.
18	k_{18}^C [MFO*] [H_2*]	n.a.	n.a.
19	k_{19}^C [VA*] [*]	2.15×10^5	113
20	k_{20}^C [VA*] [H_2*]	$< 1 \times 10^5$	n.a.
21	k_{21}^C [PDO*] [H_2*]	n.a.	n.a.
22	k_{22}^C [PHO*] [*]	n.a.	n.a.

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

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



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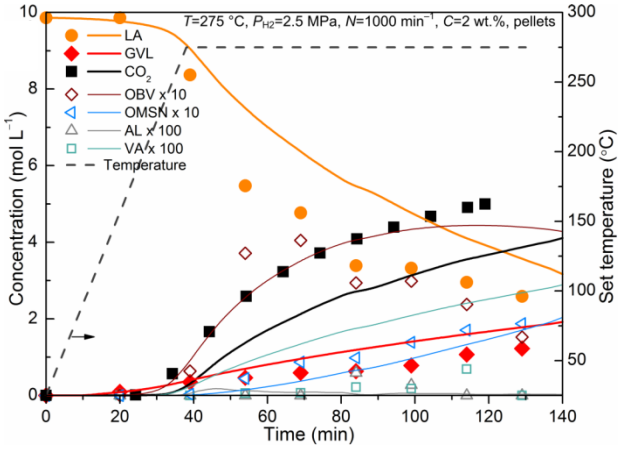
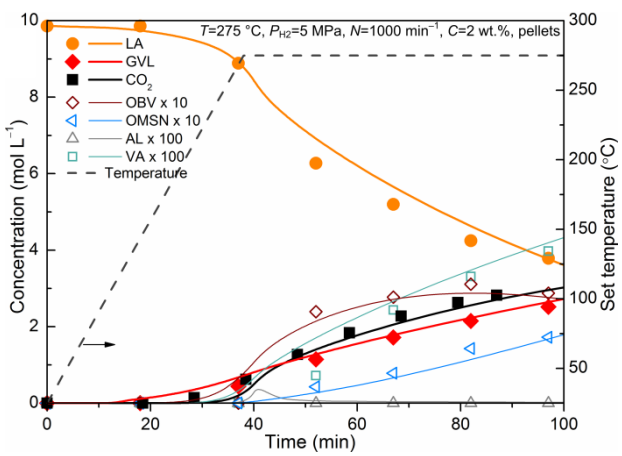
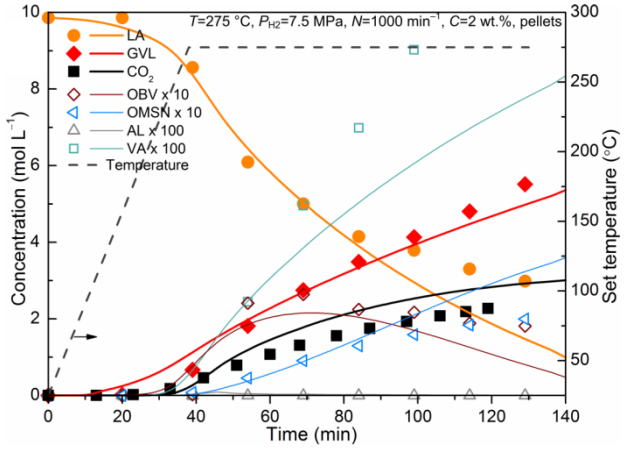
LEVULINIC ACID HDO: H_2 PRESSURE





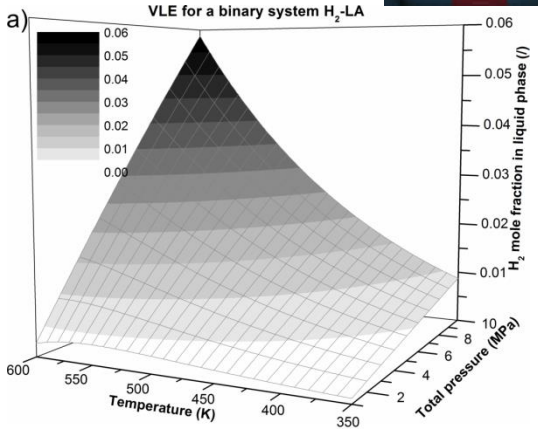


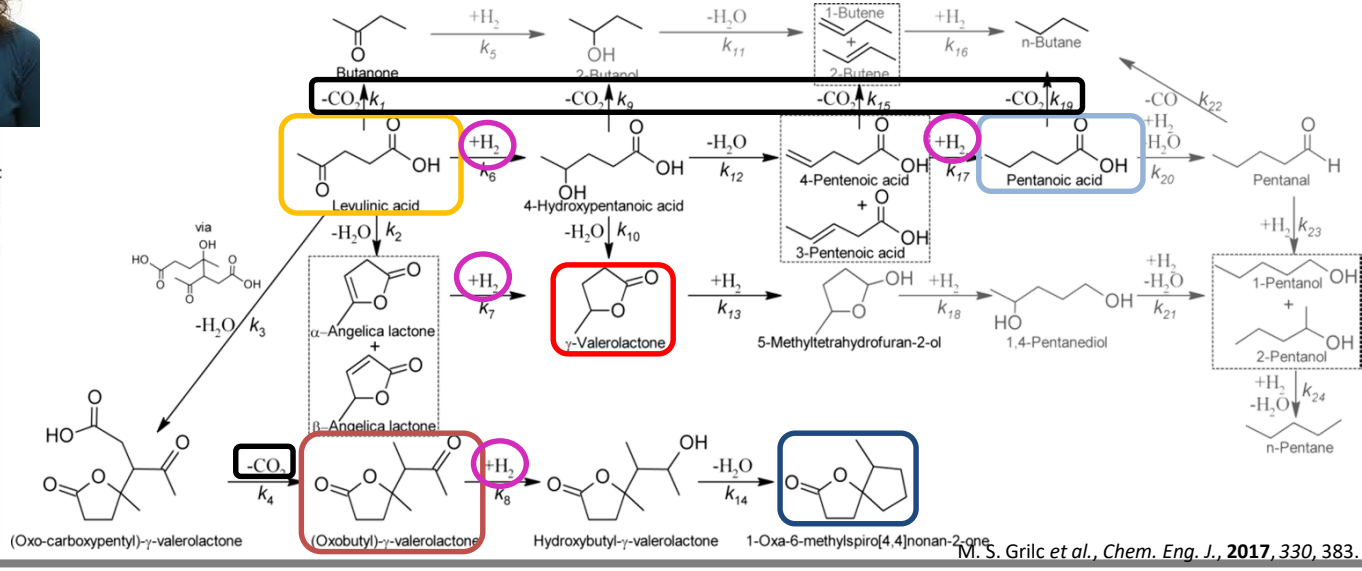
$$r_j^{GL} = k_j^L \cdot A_G \cdot (C_j^{Li} - C_j^L)/V_L$$

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

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

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





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LEVULINIC ACID HDO: STIRRING SPEED

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

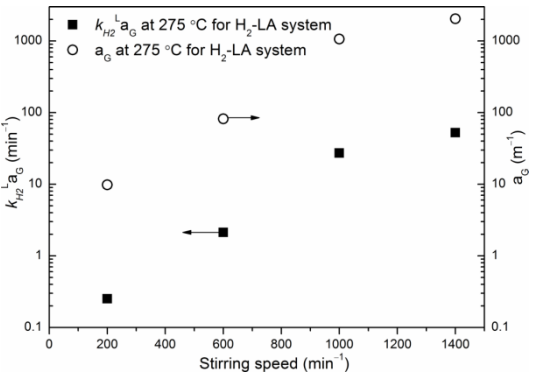
$$r_j^{GL} = k_j^L \cdot A_G \cdot (C_j^{Li} - C_j^L)/V_L$$

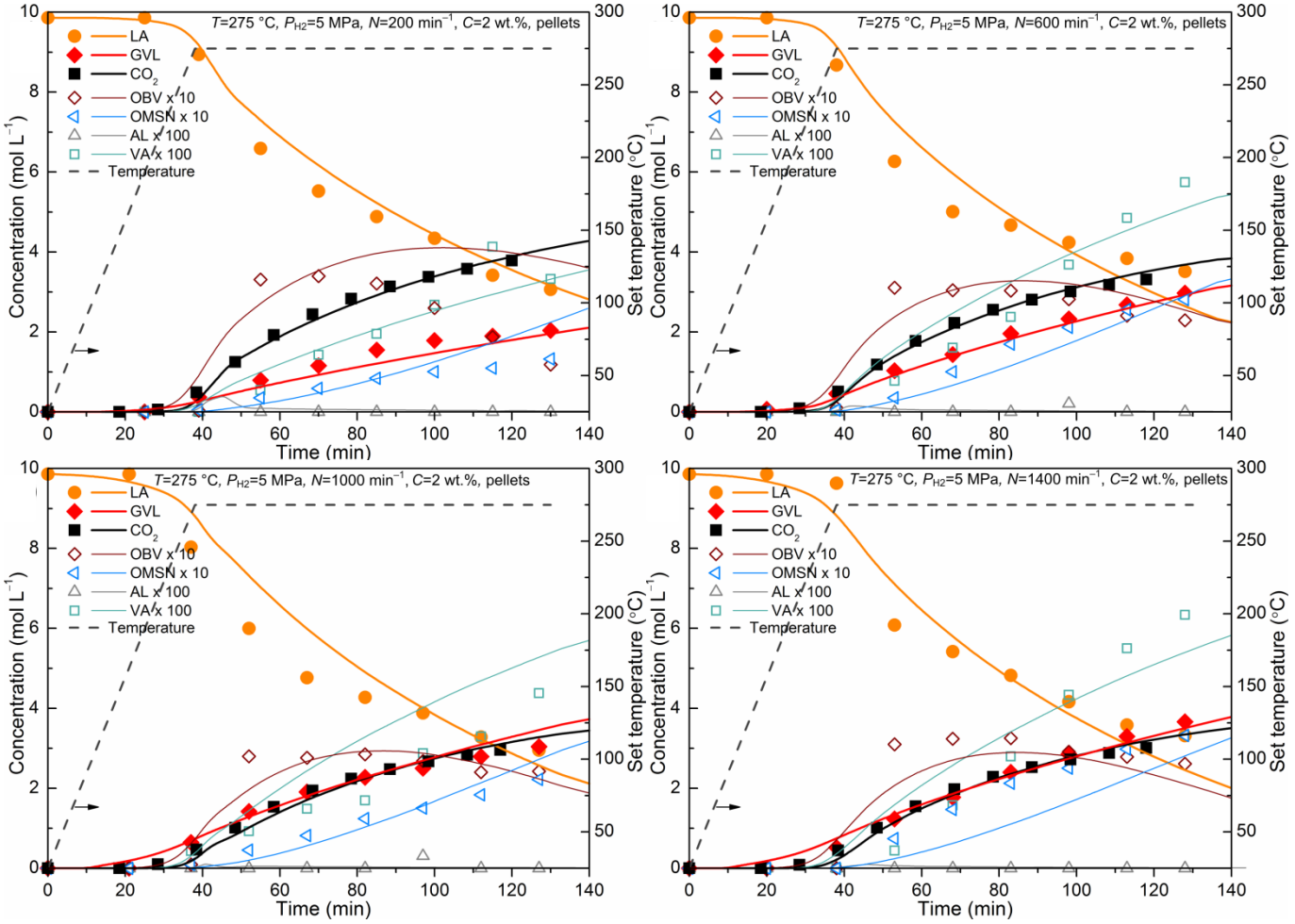
$$k_j^L = 0.42 \cdot \left(\frac{\mu_l \cdot g}{\rho_l}\right) \cdot Sc^{-0.5} \cdot \alpha \cdot d_b$$

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

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

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





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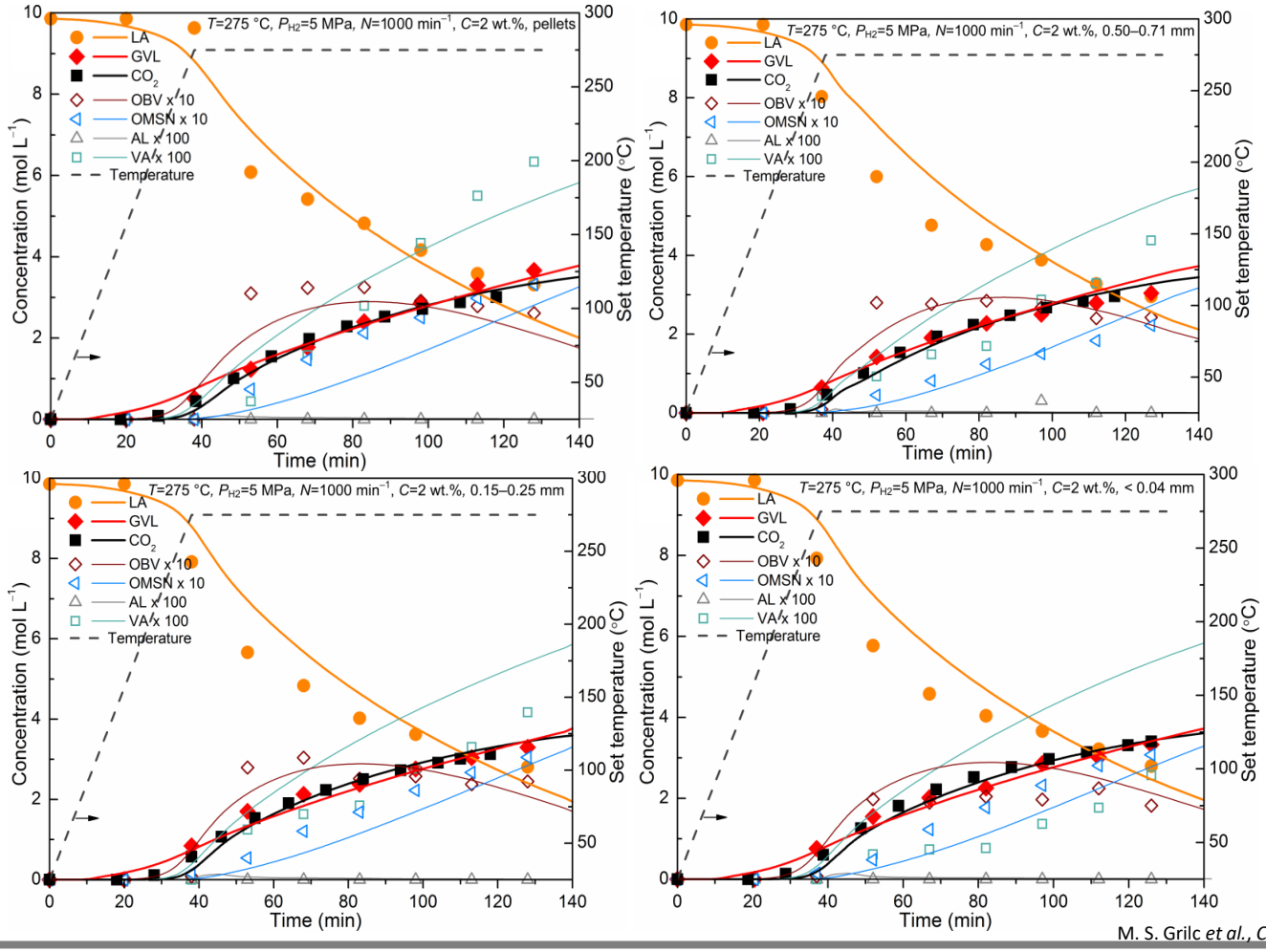
LEVULINIC ACID HDO: CATALYST PARTICLE SIZE

- Catalyst particle size from <0.04 mm powder to 1.5 mm pellets had no significant effect.
- Internal mass transfer has a negligible effect on the global reaction rates.



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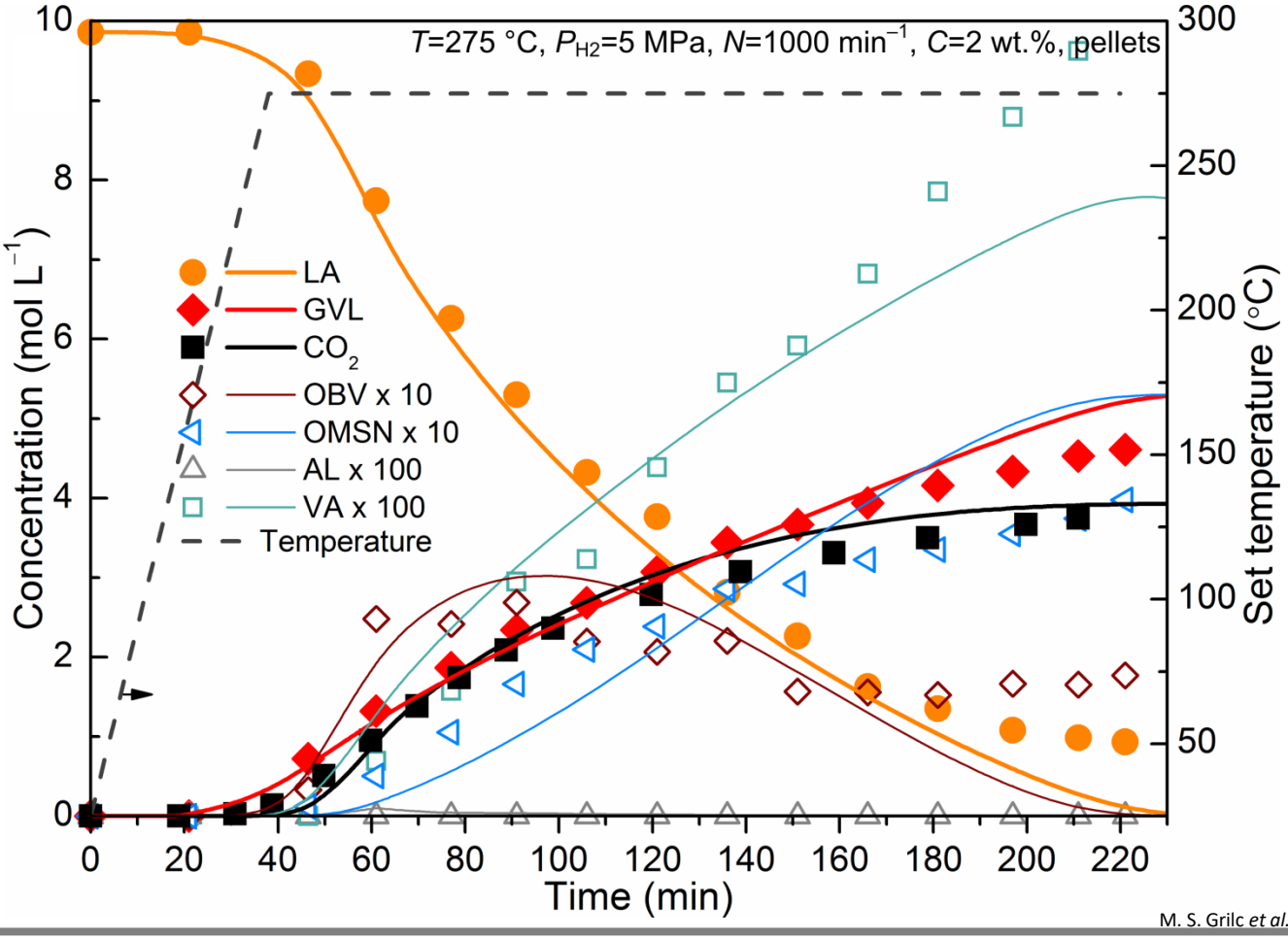
LEVULINIC ACID HDO: VALIDATION EXPERIMENT

- 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.



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LEVULINIC ACID HDO: A LIST OF KINETIC PARAMETERS

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}

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

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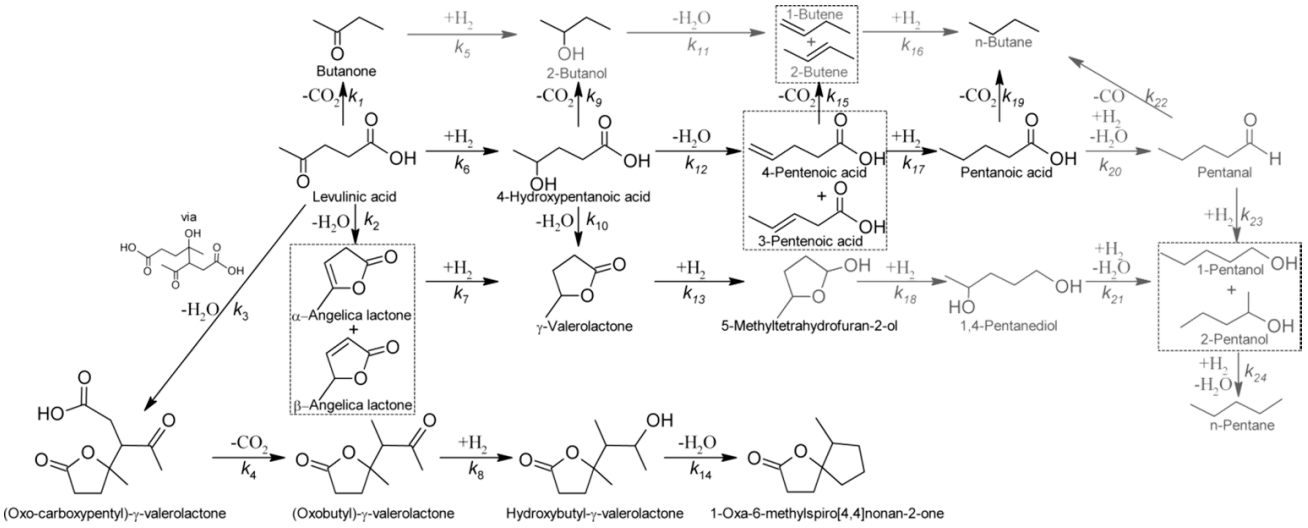
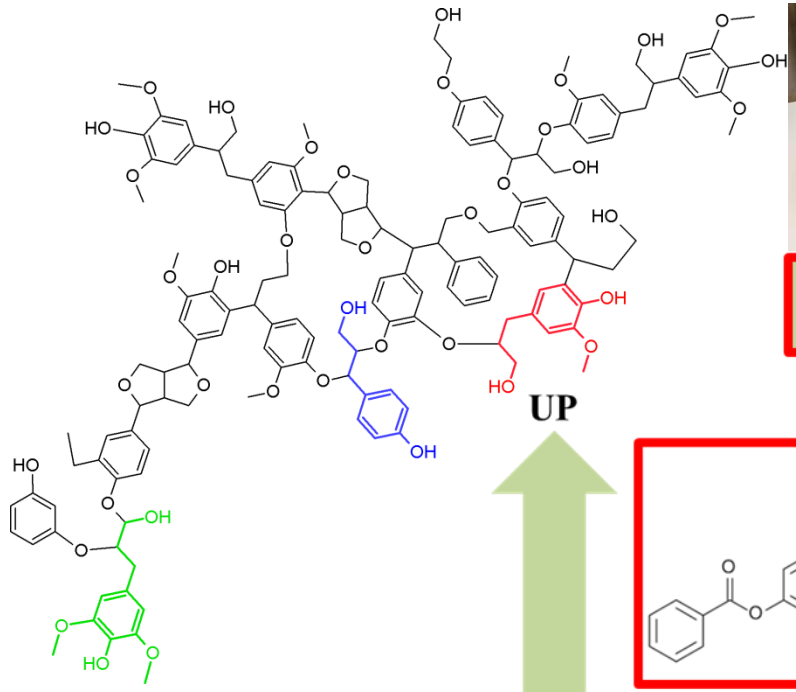
LEVULINIC ACID HDO: CONCLUSIONS

- **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)**



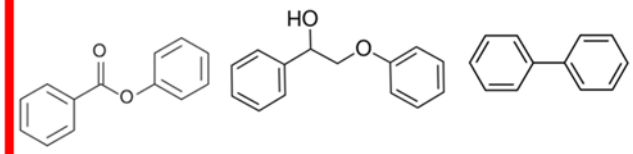
LIGNIN VALORIZATION: BOTTOM-UP APPROACH



LIGNIN

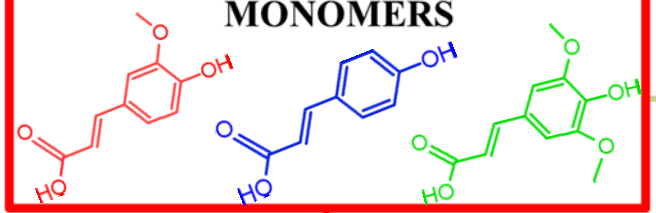
Depolymerization

OLIGOMERS



Cracking

MONOMERS



Hydrotreatment

FINE CHEMICALS

UP

BOTTOM

Breaking cross-linking bonds
Re-condensation
Softening
Cracking of –O– bridges
Cracking of C–C bridges
Cracking of loops
Hydrogenation of double bonds
Hydrogenation of aromatic ring
Hydrodeoxygenation of –OH
Hydrodeoxygenation of – O –
Isomerisation

Cracking of –O– bridges
Cracking of C–C bridges
Cracking of loops
Hydrogenation of double bonds
Hydrogenation of aromatic ring
Hydrodeoxygenation of –OH
Hydrodeoxygenation of – O –
Isomerization

Hydrogenation of double bonds
Hydrogenation of aromatic ring
HDO of –OH group
HDO of – O – group
Isomerization

AIM: UNDERSTANDING CATALYTIC HYDROTREATMENT THROUGH KINETIC MODELLING

CATALYST SCREENING:

1.) Metals on neutral support (C):
Ru, Pt, Pd, Rh, Ni, Cu

2.) Metals on acidic support (Al_2O_3):
Ru, Pt, Pd, Rh, Ni, Cu

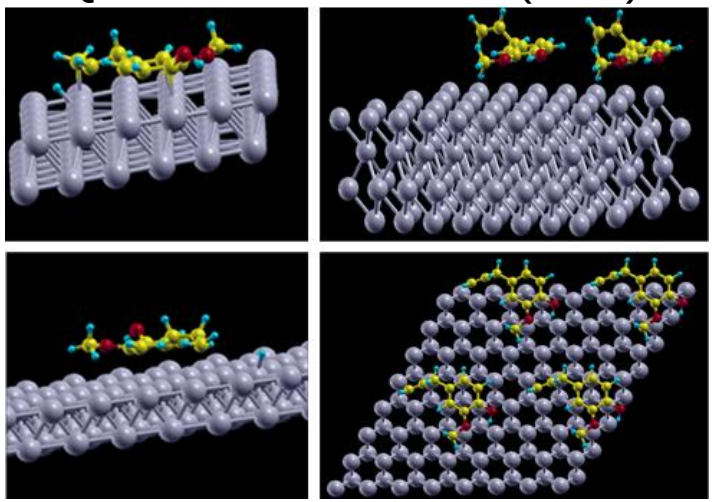
3.) Variation of acidic supports:
SiO_2, SiO_2-Al_2O_3, TiO_2, HZSM-5

KINETIC MODELLING:

- Mass transfer
- Reactions in bulk phase
- Adsorption/desorption kinetics
- Surface reactions on metallic sites
- Surface reactions on acidic sites

MODELLING SUPPORT:

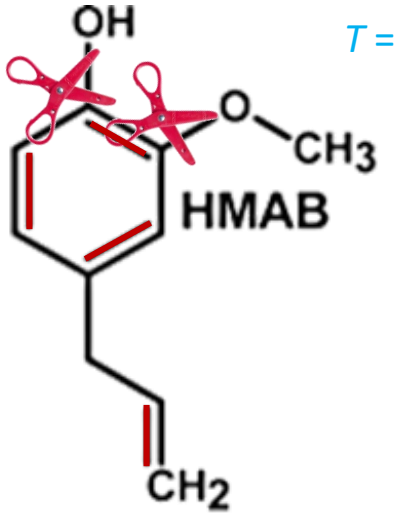
- Quantum mechanics (DFT)



Lignin monomers: more than 150 catalytic tests, 3600 samples, 54000 exp. points processed.

LIGNIN MONOMER MODEL COMPOUND: EUGENOL

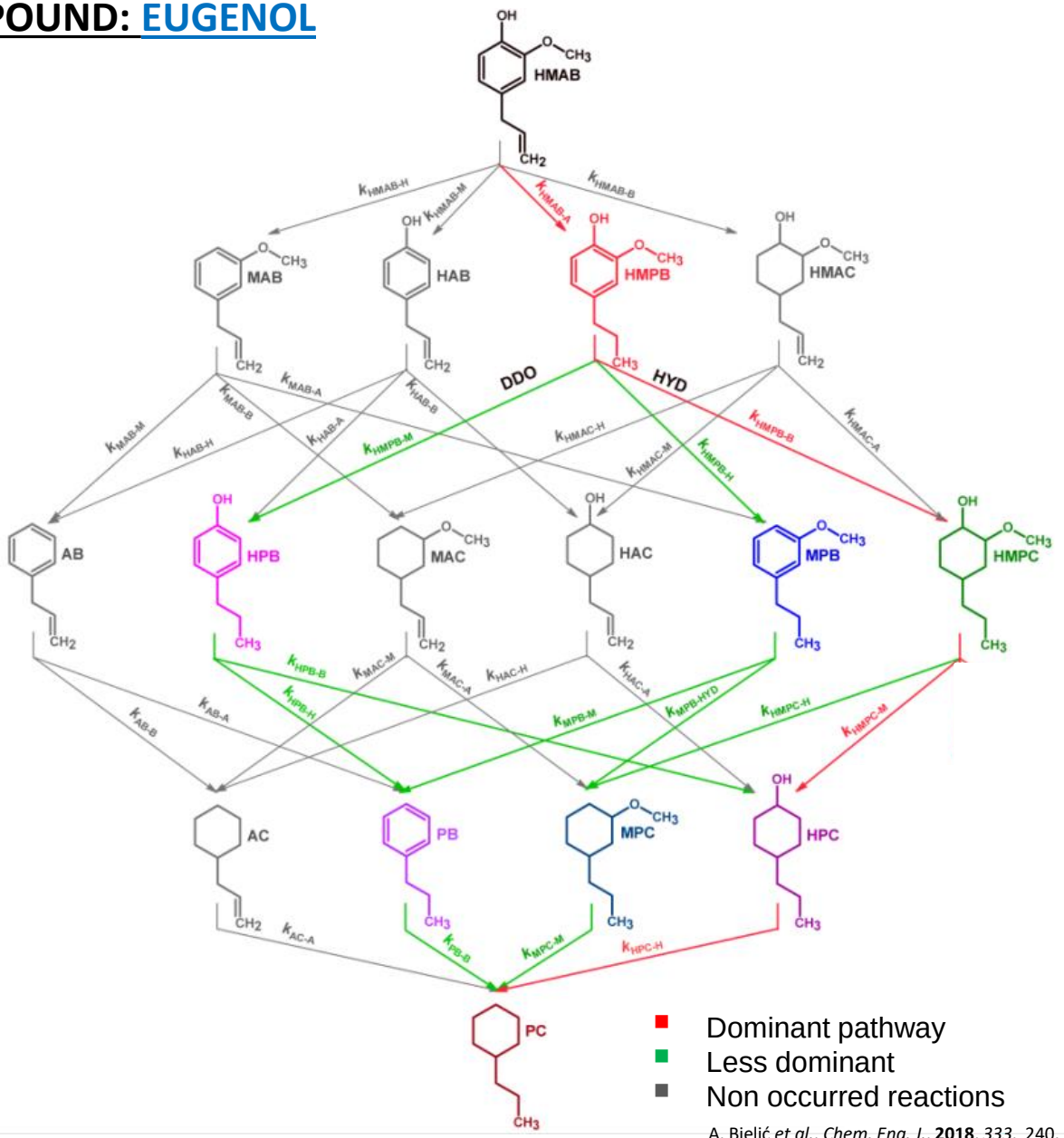
Ru/C



T = 300 °C

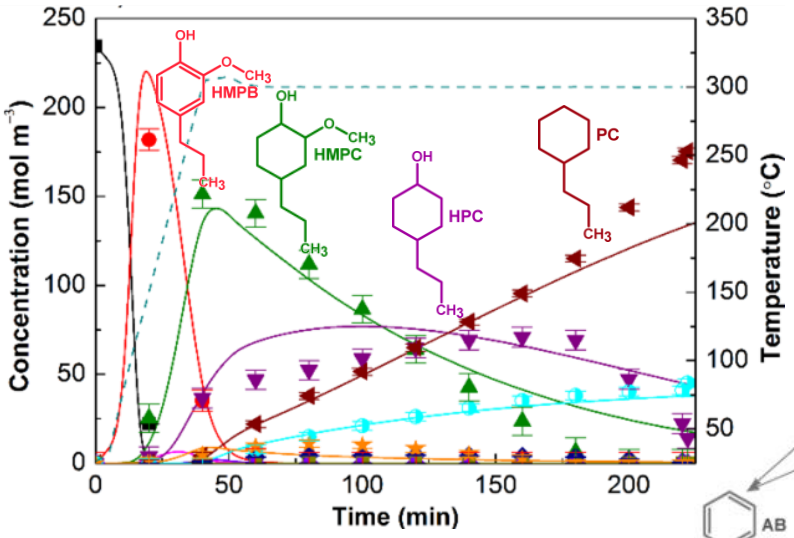
Representative lignin monomer

- Hydroxyl group (H)
- Methoxyl group (M)
- Allyl group (A)
- Benzene ring (B)



A. Bjelić *et al.*, *Chem. Eng. J.*, **2018**, *333*, 240.

LIGNIN MONOMER MODEL COMPOUND: EUGENOL



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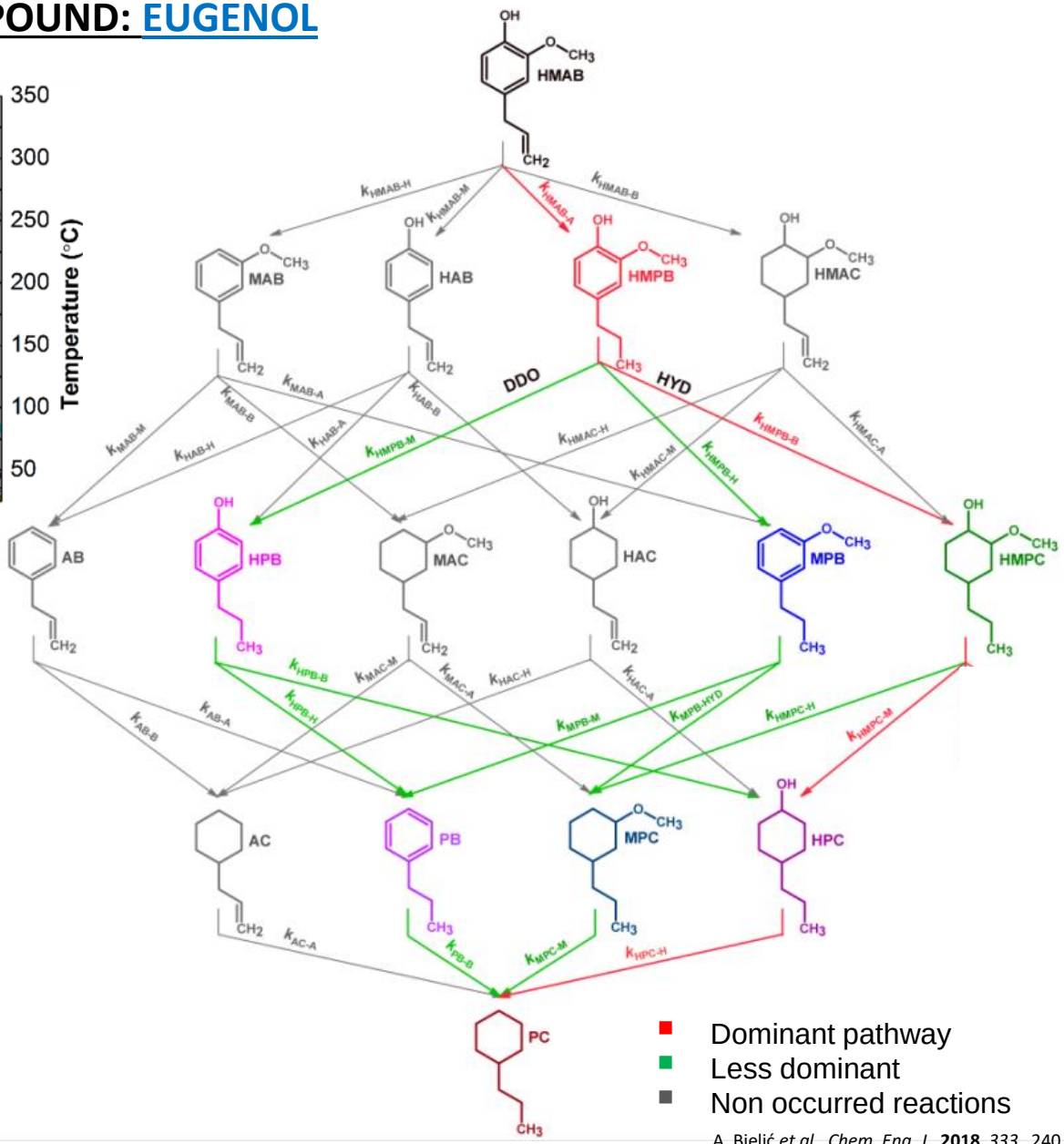


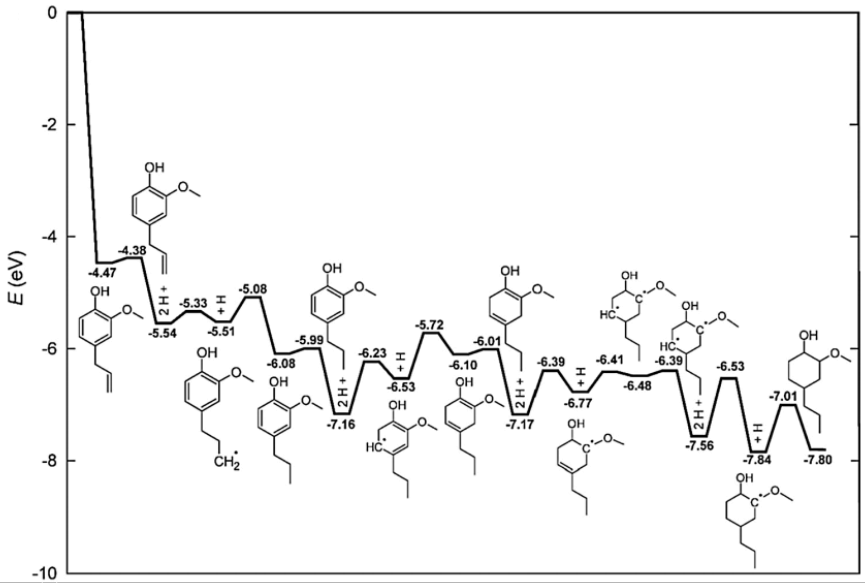
A. Bjelić *et al.*, *Chem. Eng. J.*, **2018**, *333*, 240.

DENSITY FUNCTIONAL THEORY: Ru(0001)

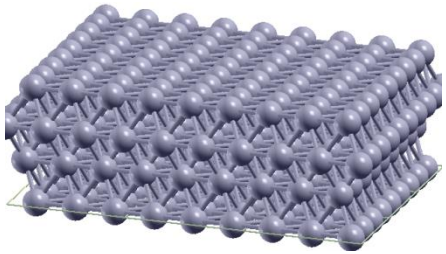
Open-source software:
- Quantum Espresso

Computationally cheap approach used:
- PW DFT with PBE + Grimme-D2
- Unit cell: 4x6x4 (96 Ru atoms)
- 500 structures calculated

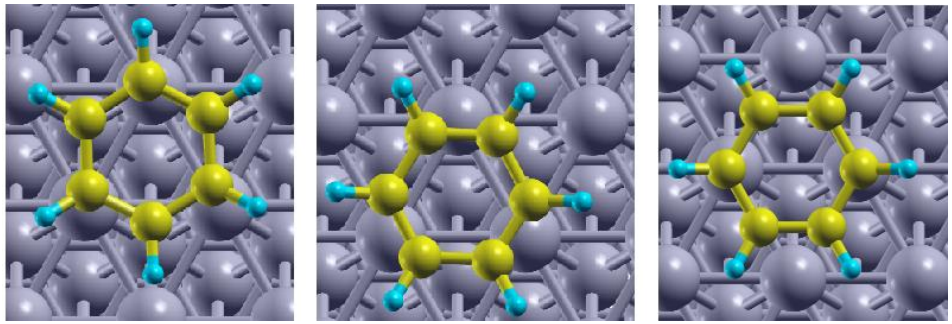
Ru(0001) sites occupied at adsorption:
- Propyl-benzene/C6: 6 –OH/–OCH_3 : +1
- H : 1



Calculations on bulk metal

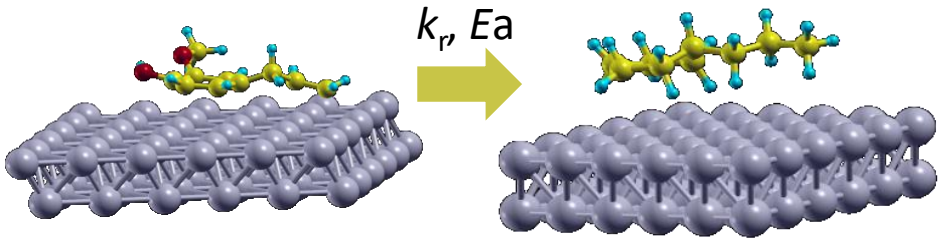


Adsorption configurations



$$\Delta E_{ads} = E_{adsorbed} - E_{catalyst} - E_{species}$$

Homogeneous and surface reactions



$$E_A = E_{TS} - E_{reactant}$$

$$\Delta E = E_{product} - E_{reactant}$$

CATALYST CHARACTERISATION: Ru/C

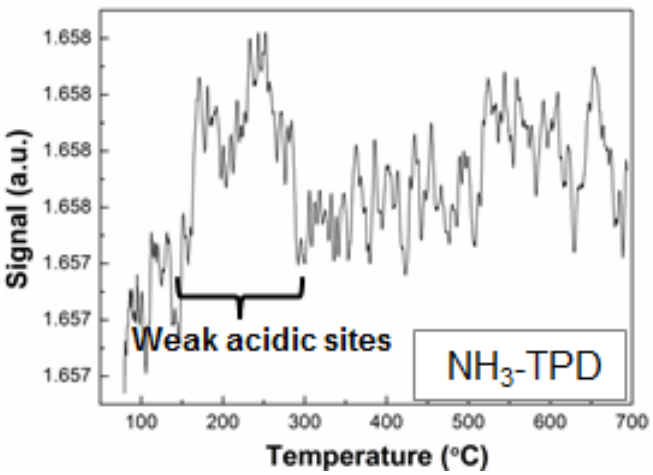
- N_2-physisorption

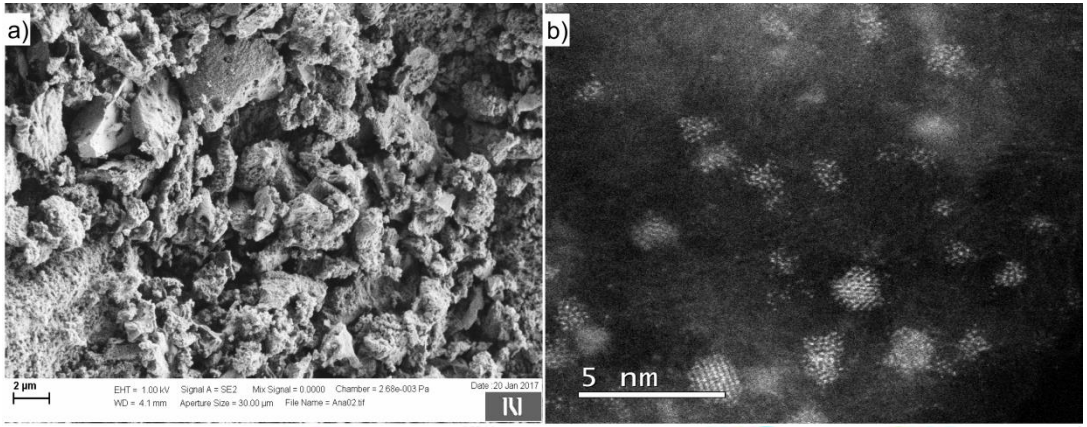
S_{BET}, ($m^2\ g^{-1}$)	V_{pores}, ($cm^3\ g^{-1}$)	Pore size, (Å)
648	0.792	48.8

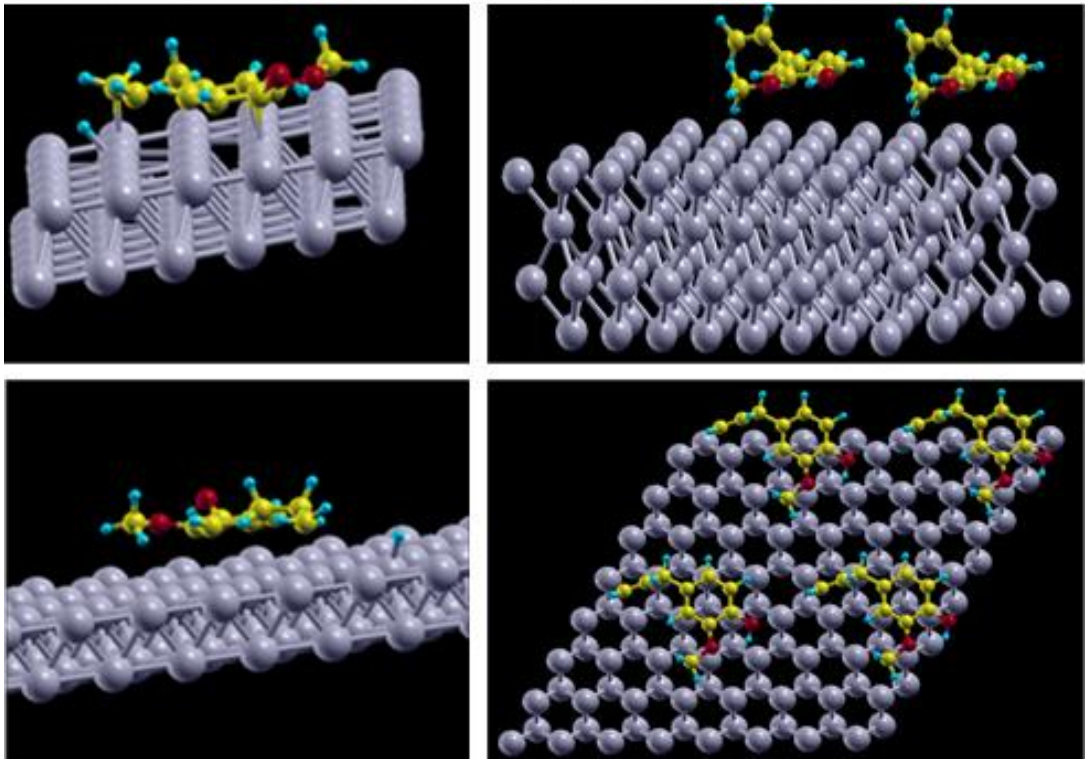
- CO-chemisorption

  $C_{desCO} \approx C_{Ru}$ = 38 µmol g^{-1}

- NH_3-chemisorption







- 1 adsorbed eugenol molecule covers 8 Ru(0001) atoms

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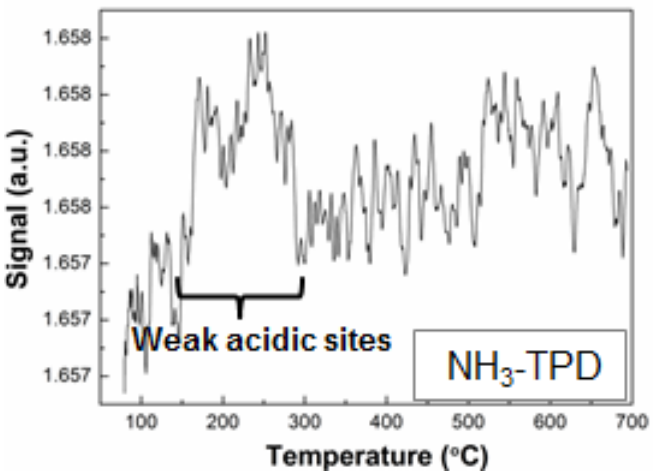
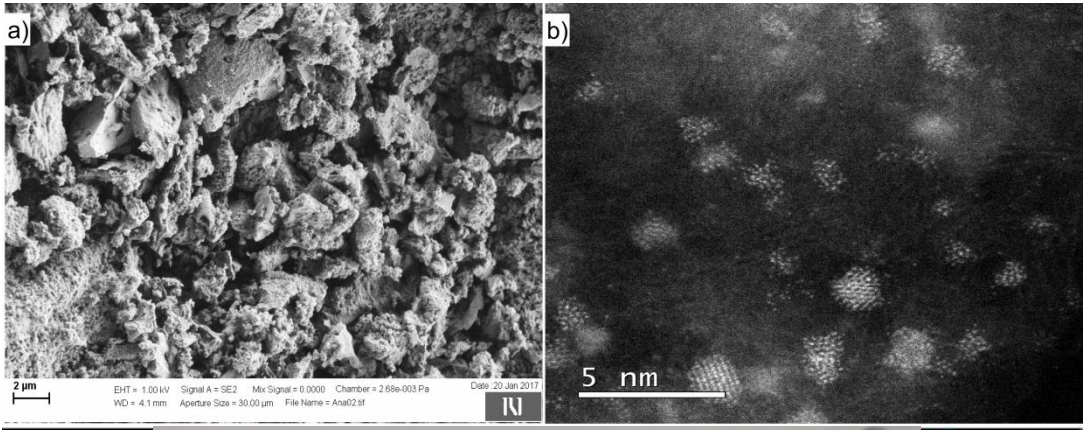
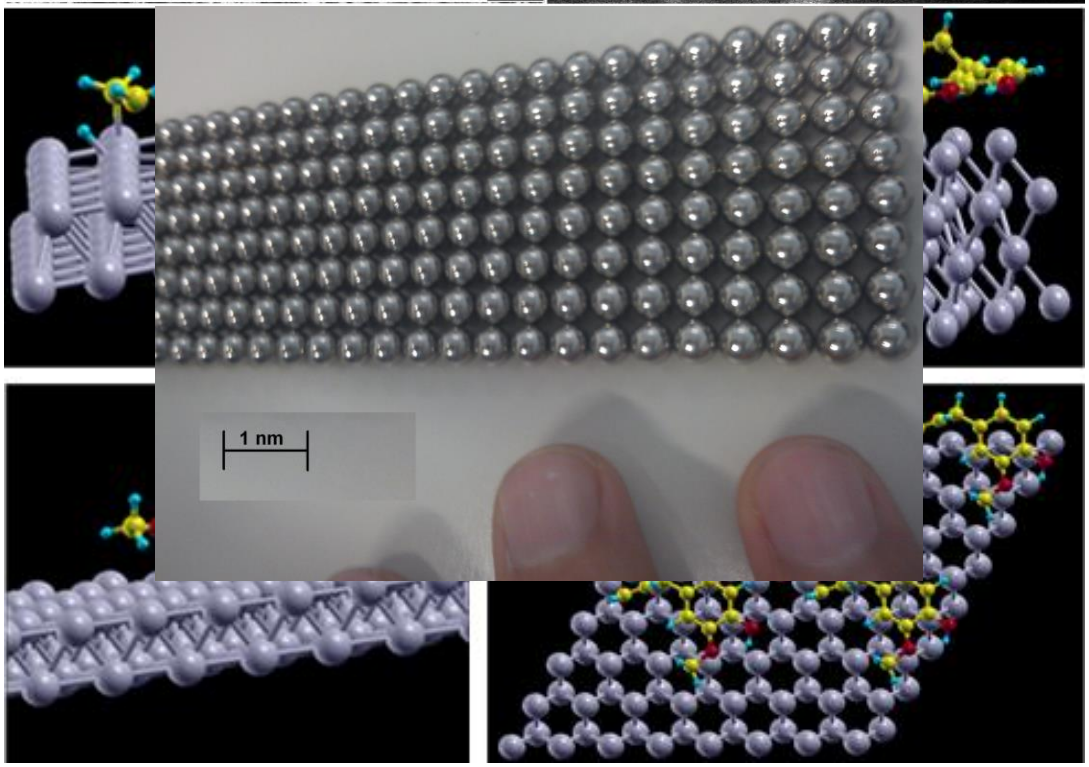


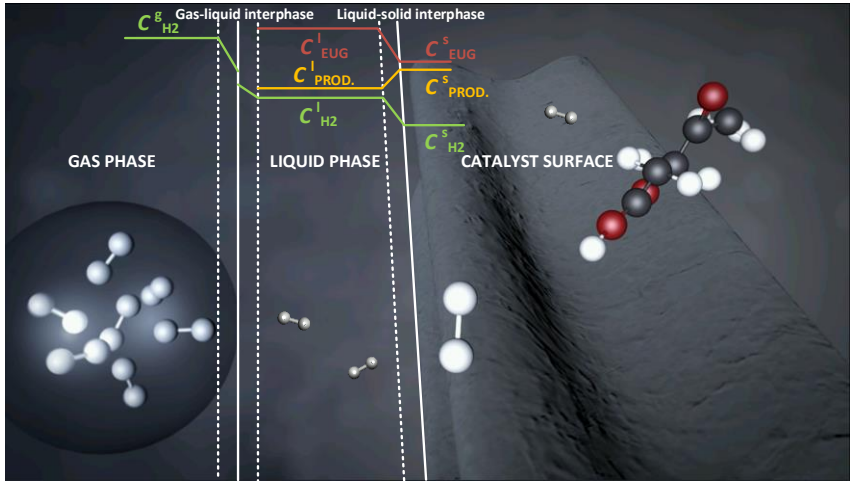




- 1 adsorbed eugenol molecule covers 8 Ru(0001) atoms

MICROKINETICS: MATLAB

- Thermodynamics (VLE-EOS)
- Mass transfer
- 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:

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

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

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:

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

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

Molar balances for component *j*:

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

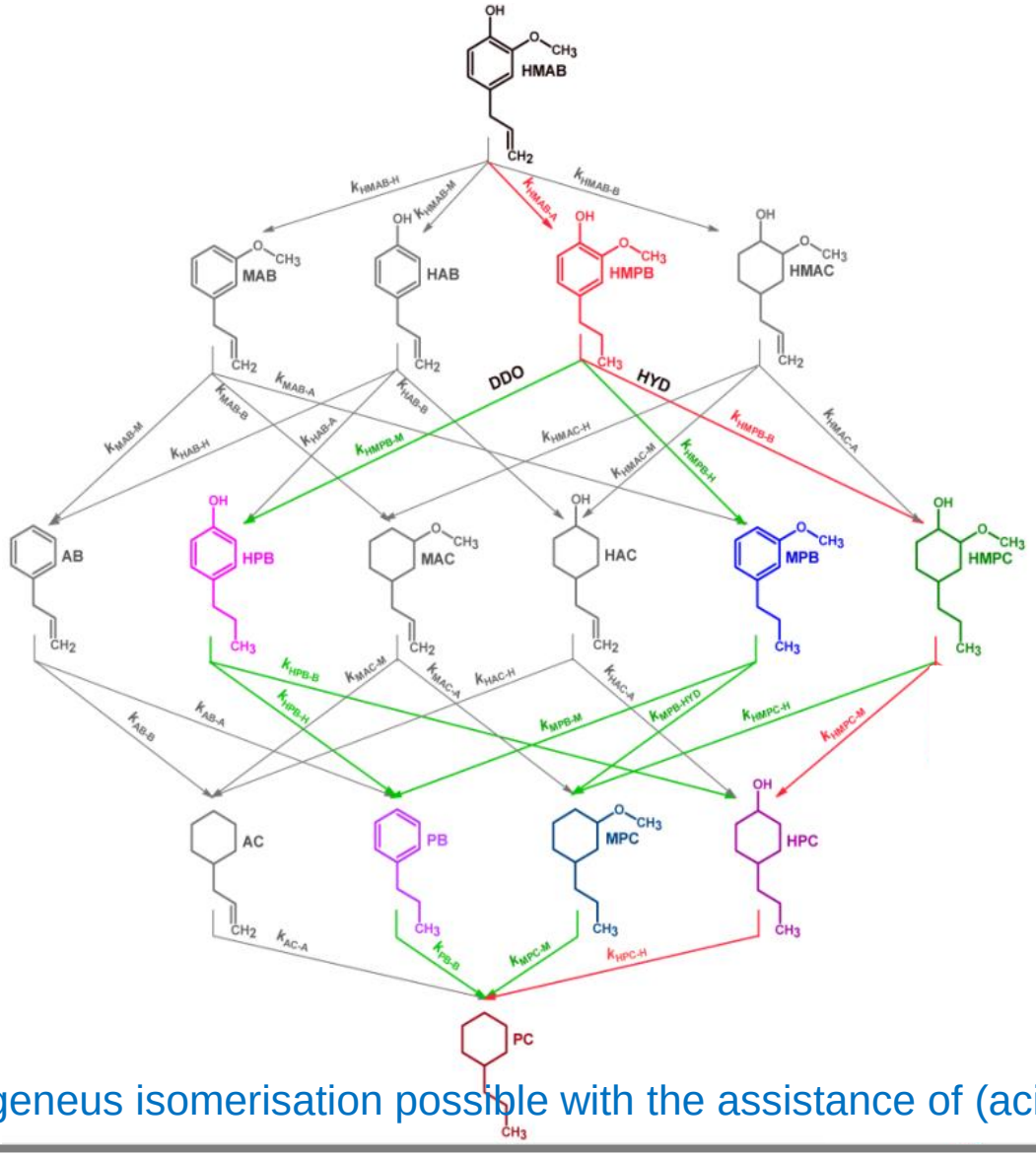
Molar balance for vacant sites:

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

Parameters based on characterization or DFT

HOMOGENEOUS REACTIONS: ISOMERISATION AND HYDROGENATION

275 °C

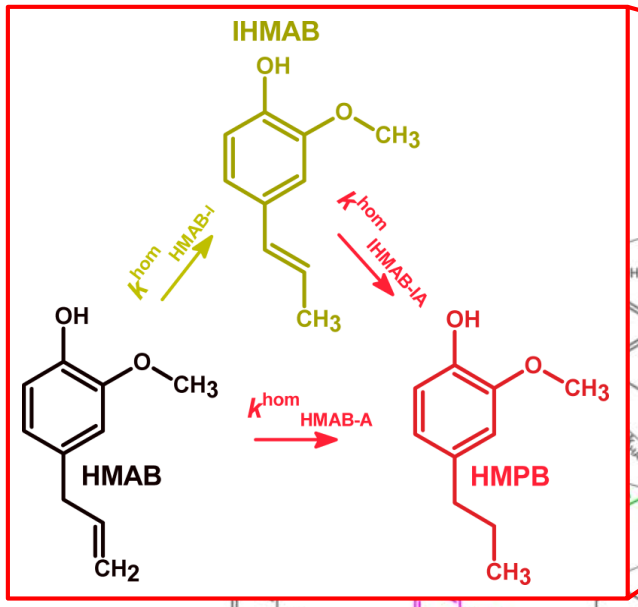


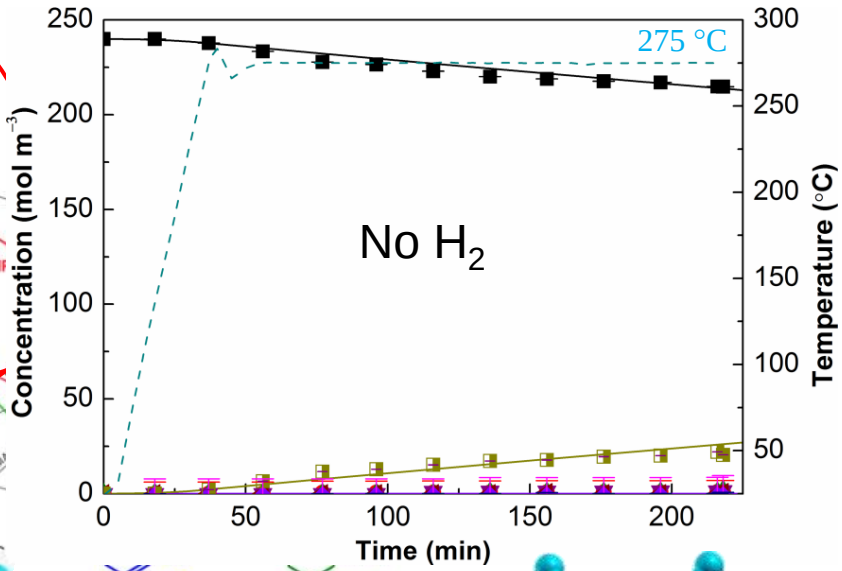
- Homogeneus isomerisation possible with the assistance of (acidic) phenolic group

M. Huš *et al.*, *J. Catal.*, **2018**, *358*, 8.

T=275 °C, $p(N_2)$=5 MPa, No cat, *N*=1000 min^{-1}

HOMOGENEOUS REACTIONS: ISOMERISATION AND HYDROGENATION





Bimolecular homog. isomerisation
Ea =1.80 eV (173 kJ mol^{-1})

Unimolecular homog. isomerisation
Ea = 2.84 eV (275 kJ mol^{-1})

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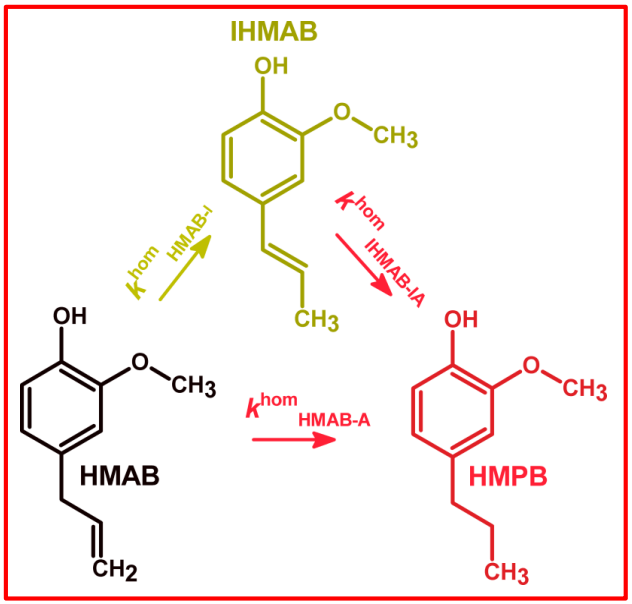
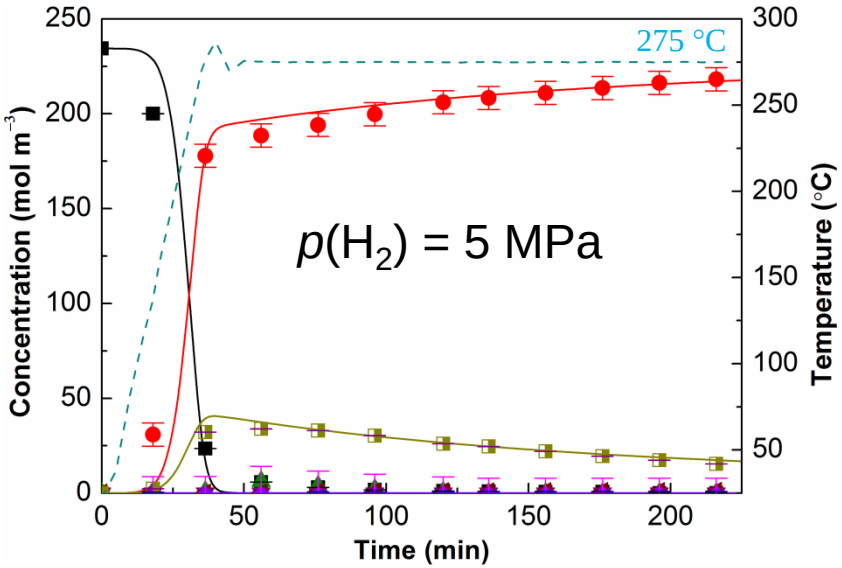
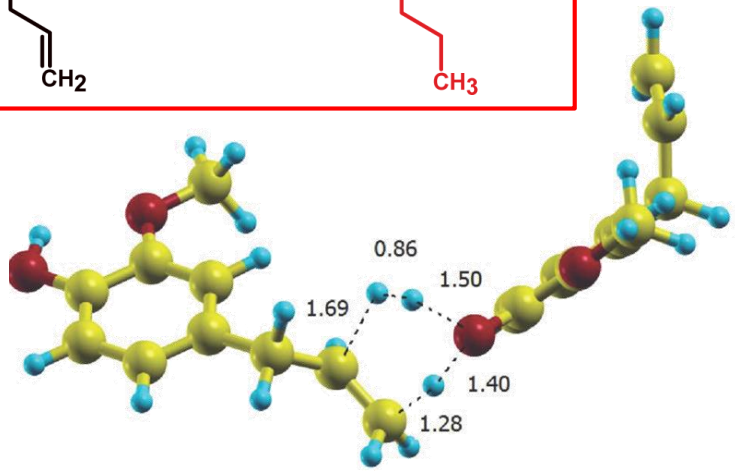
M. Huš *et al.*, *J. Catal.*, **2018**, *358*, 8.

T=275 °C, $p(N_2)$=5 MPa, No cat, *N*=1000 min^{-1}

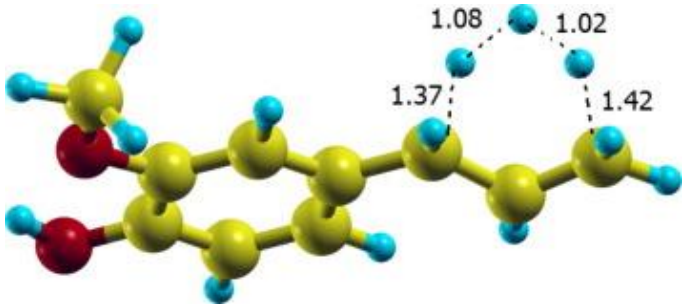
HOMOGENEOUS REACTIONS: ISOMERISATION AND HYDROGENATION







Acid-assisted homogenous hydrogenation
Ea = 1.96 eV (189 kJ mol^{-1})



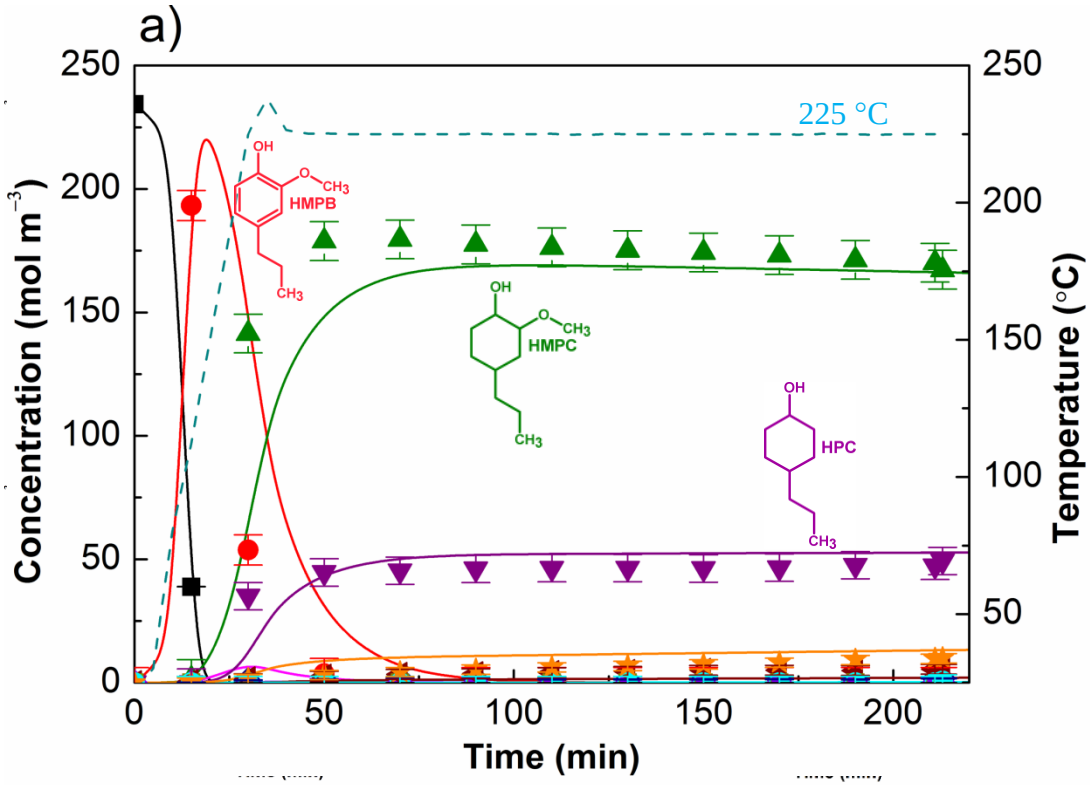
H_2-assisted homogenous isomerisation
Ea = 1.46 eV (140 kJ mol^{-1})

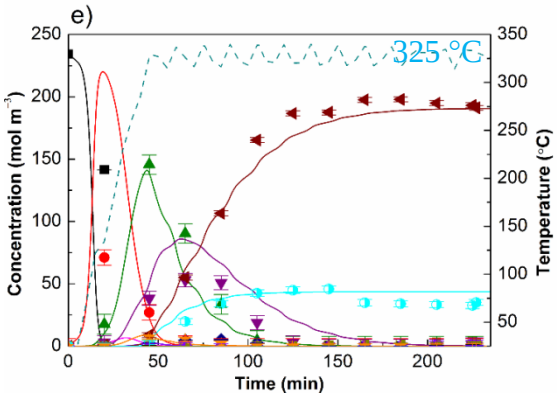
- Homogeneous hydrogenation not possible (SPIN!) without assistance of an acidic phenolic group

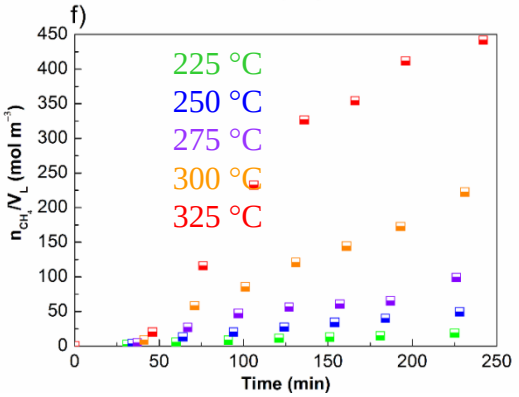
M. Huš *et al.*, *J. Catal.*, **2018**, *358*, 8.

T=275 °C, $p(H_2)$=5 MPa, No cat, *N*=1000 min^{-1}

CATALYTIC TESTING OF Ru/C: KINETIC PARAMETERS BY REGRESSION ANALYSIS





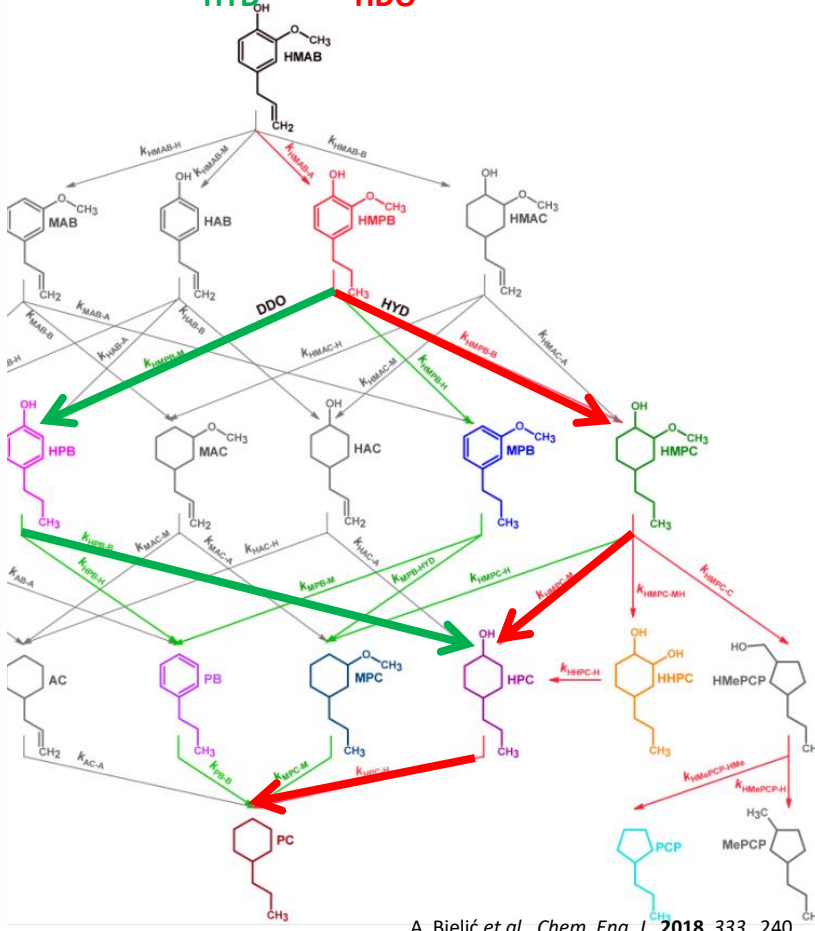


Competitive HDO and HYD

$k_{HDO} < k_{HYD}$

$k_{HDO\ (alyl)} << k_{HDO\ (aryl)}$

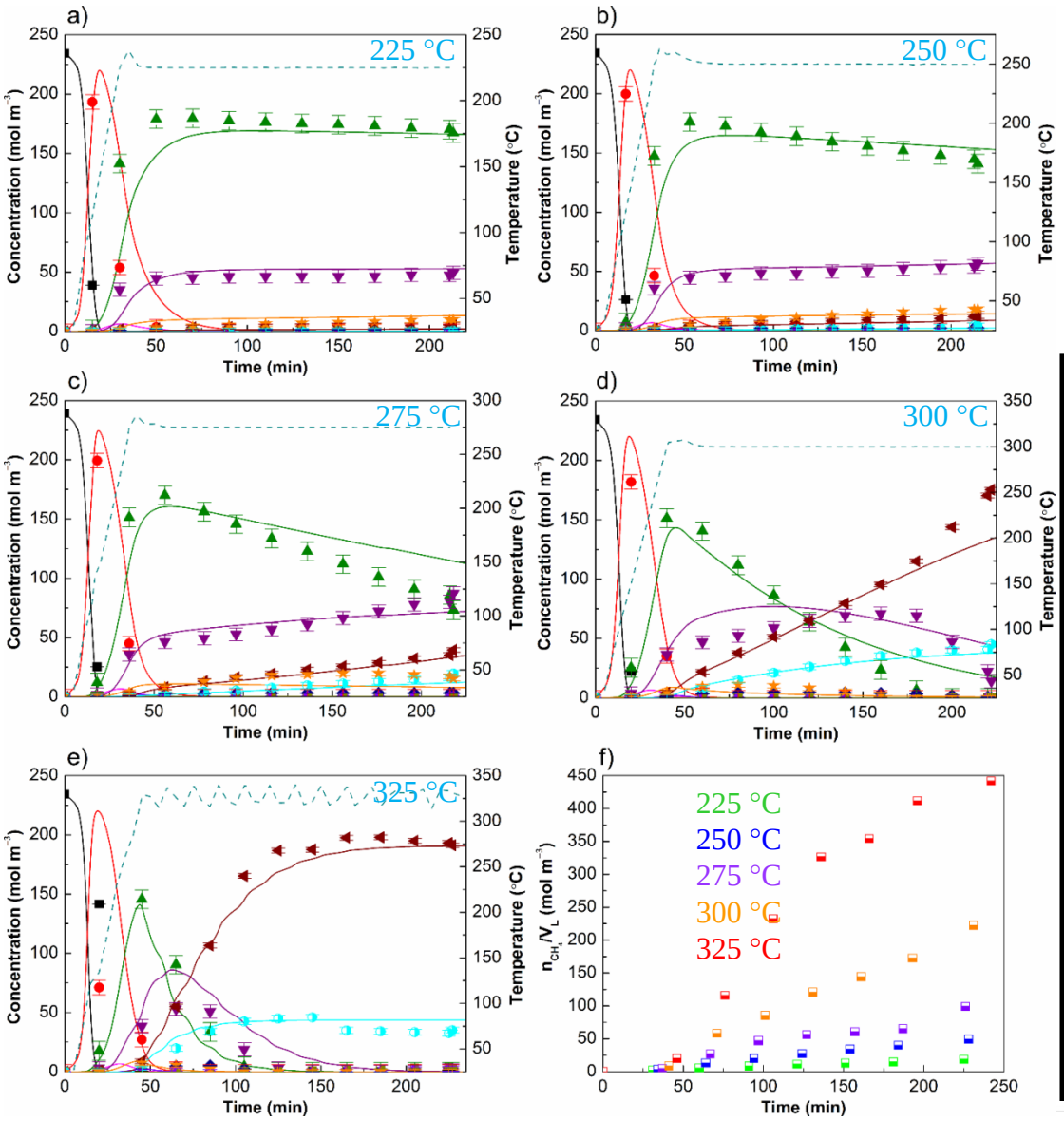
$Ea_{HYD} < Ea_{HDO}$



A. Bjelić *et al.*, *Chem. Eng. J.*, **2018**, *333*, 240.

Reaction condition: p=5 MPa, m_{cat}/m_{EUG}=4.5%, N=1000 min^{-1}

CATALYTIC TESTING OF Ru/C: KINETIC PARAMETERS BY REGRESSION ANALYSIS



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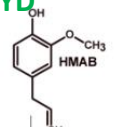
$Ea_{HYD} < Ea_{HDO}$



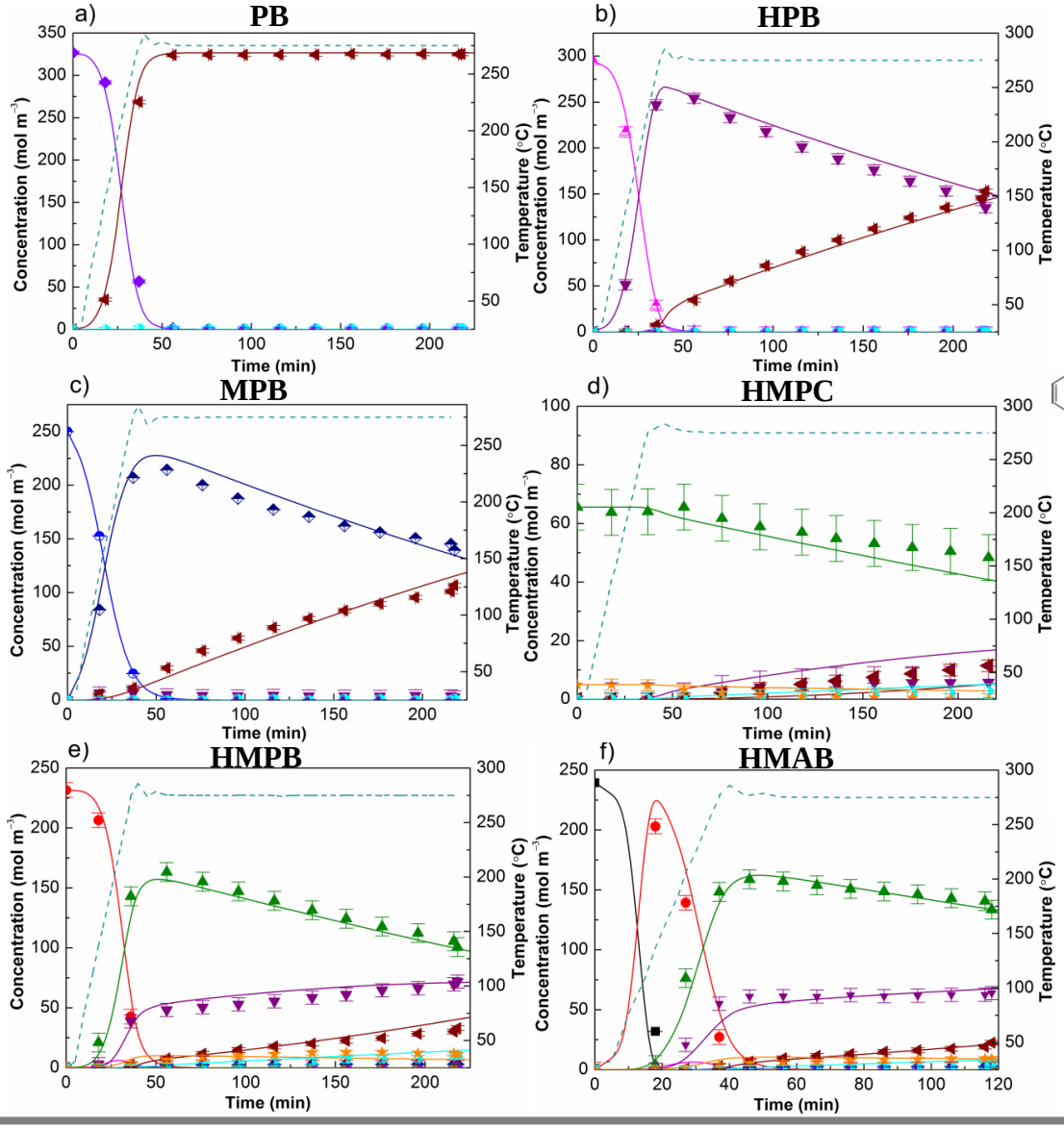
Adsorption and desorption constants			
k_{ads} $m^3\ mol^{-1}\ min^{-1}$	$k_{ads(H)}$ $m^3\ mol^{-1}\ min^{-1}$	k_{des} min^{-1}	$k_{des(H)}$ min^{-1}
$\geq 5.5\times10^3$	$\geq 3.0\times10^6$	$k_{ads} \times 31.7$	$k_{ads(H)} \times 3.15$

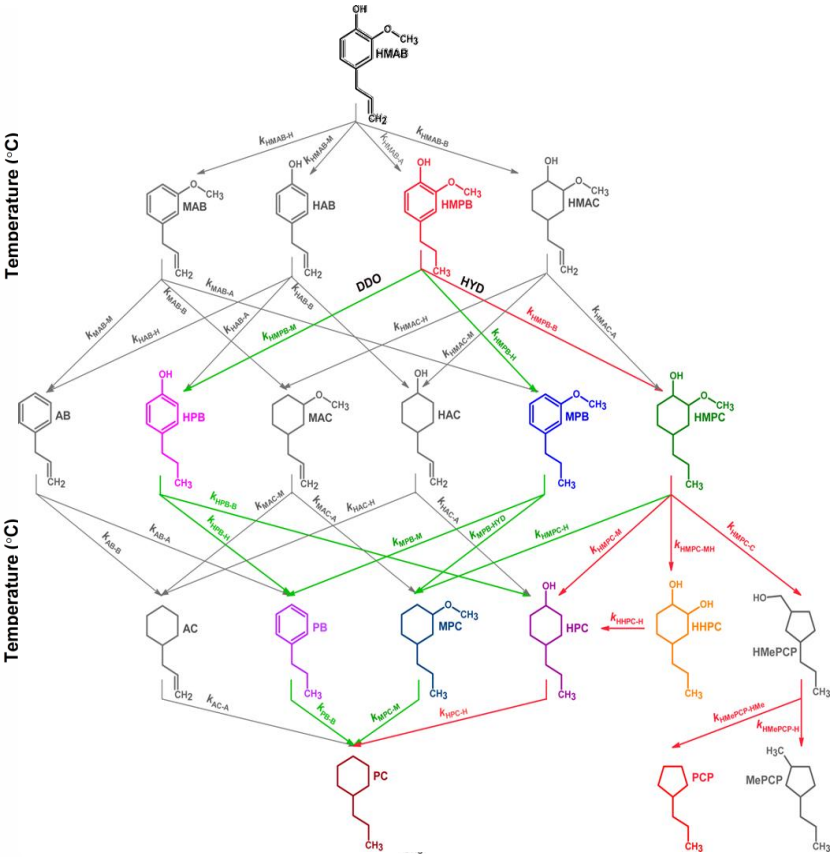
Heterogeneous reactions			
Reaction rate constants at 275 °C, $m^3\ mol^{-1}\ min^{-1}$		Activation energies, $J\ mol^{-1}$	
$k_{HMAB\text{-}A}$	1.34×10^8	$Ea_{HMAB\text{-}A}$	5.77×10^4
$k_{IHMAB\text{-}IA}$	1.34×10^8	$Ea_{IHMAB\text{-}IA}$	5.77×10^4
$k_{HMPB\text{-}B}$	2.04×10^5	$Ea_{HMPB\text{-}B}$	3.72×10^4
$k_{HMPB\text{-}M}$	6.99×10^4	$Ea_{HMPB\text{-}M}$	4.07×10^4
$k_{HMPC\text{-}M}$	1.91×10^3	$Ea_{HMPC\text{-}M}$	2.05×10^5
$k_{HPB\text{-}B}$	5.54×10^5	$Ea_{HPB\text{-}B}$	2.79×10^4
$k_{HPB\text{-}H}$	1.86×10^5	$Ea_{HPB\text{-}H}$	1.25×10^5
$k_{HPC\text{-}H}$	4.37×10^3	$Ea_{HPC\text{-}H}$	1.83×10^5
$k_{PB\text{-}B}$	3.47×10^5	$Ea_{PB\text{-}B}$	3.16×10^4
$k_{HMPC\text{-}MH}$	1.30×10^3	$Ea_{HMPC\text{-}MH}$	8.00×10^4
$k_{HHPC\text{-}H}$	2.30×10^4	$Ea_{HHPC\text{-}H}$	1.50×10^5
$k_{MPB\text{-}B}$	2.03×10^5	$Ea_{MPB\text{-}B}$	1.6×10^4
$k_{MPC\text{-}M}$	4.30×10^3	$Ea_{MPC\text{-}M}$	1.00×10^4
$k_{HMPC\text{-}C}$	8.28×10^2	$Ea_{HMPC\text{-}C}$	1.64×10^5
$k_{HMePCP\text{-}HMe}$	$> 10^6$	$Ea_{HMePCP\text{-}HMe}$	n.a.
$k_{HMePCP\text{-}H}$	$<< k_{HMePCP\text{-}HMe}$	$Ea_{HMePCP\text{-}H}$	n.a.

A. Bjelić *et al.*, *Chem. Eng. J.*, **2018**, *333*, 240.

Reaction condition: p=5 MPa, m_{cat}/m_{EUG}=4.5%, N=1000 min^{-1}

EUGENOL HYDROTREATMENT: EXPERIMENTS WITH INTERMEDIATES (275 °C, 5 MPa)

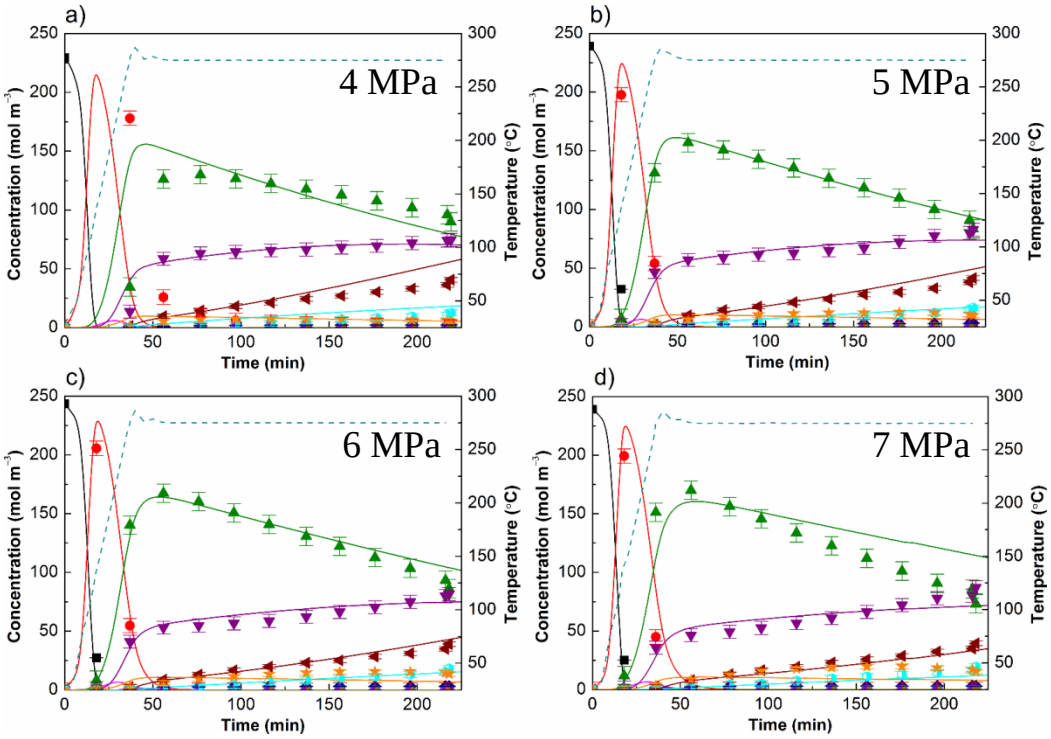


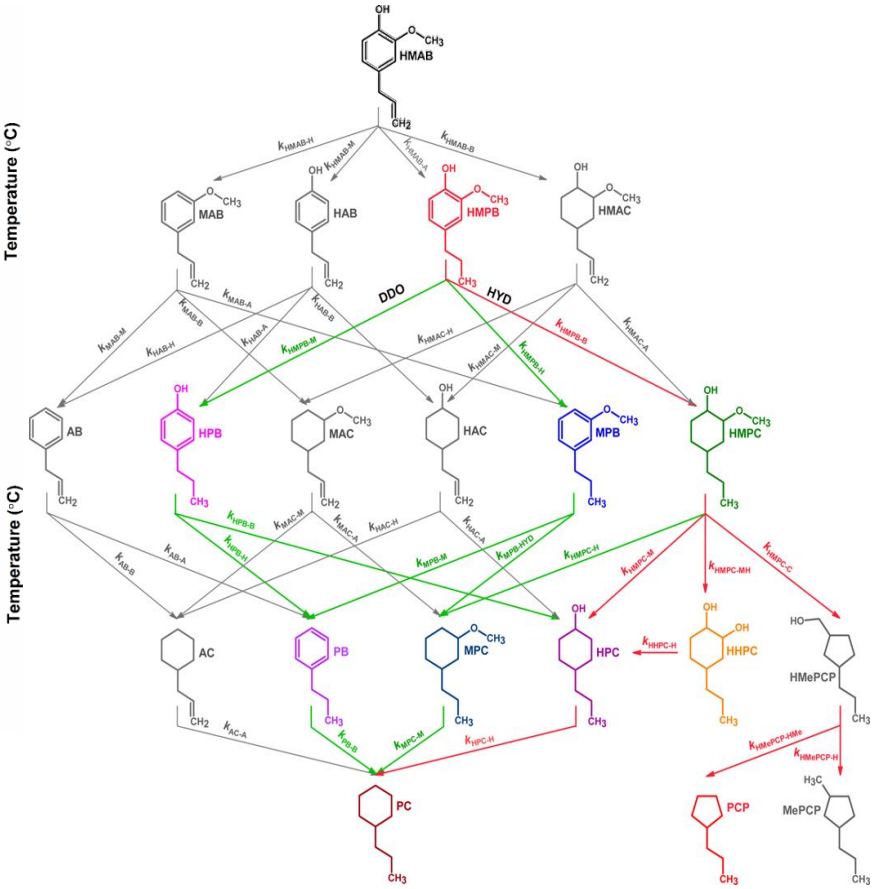


- Dominant pathway
- Less dominant
- Non occurred reactions

A. Bjelić *et al.*, *Chem. Eng. J.*, **2018**, *333*, 240.

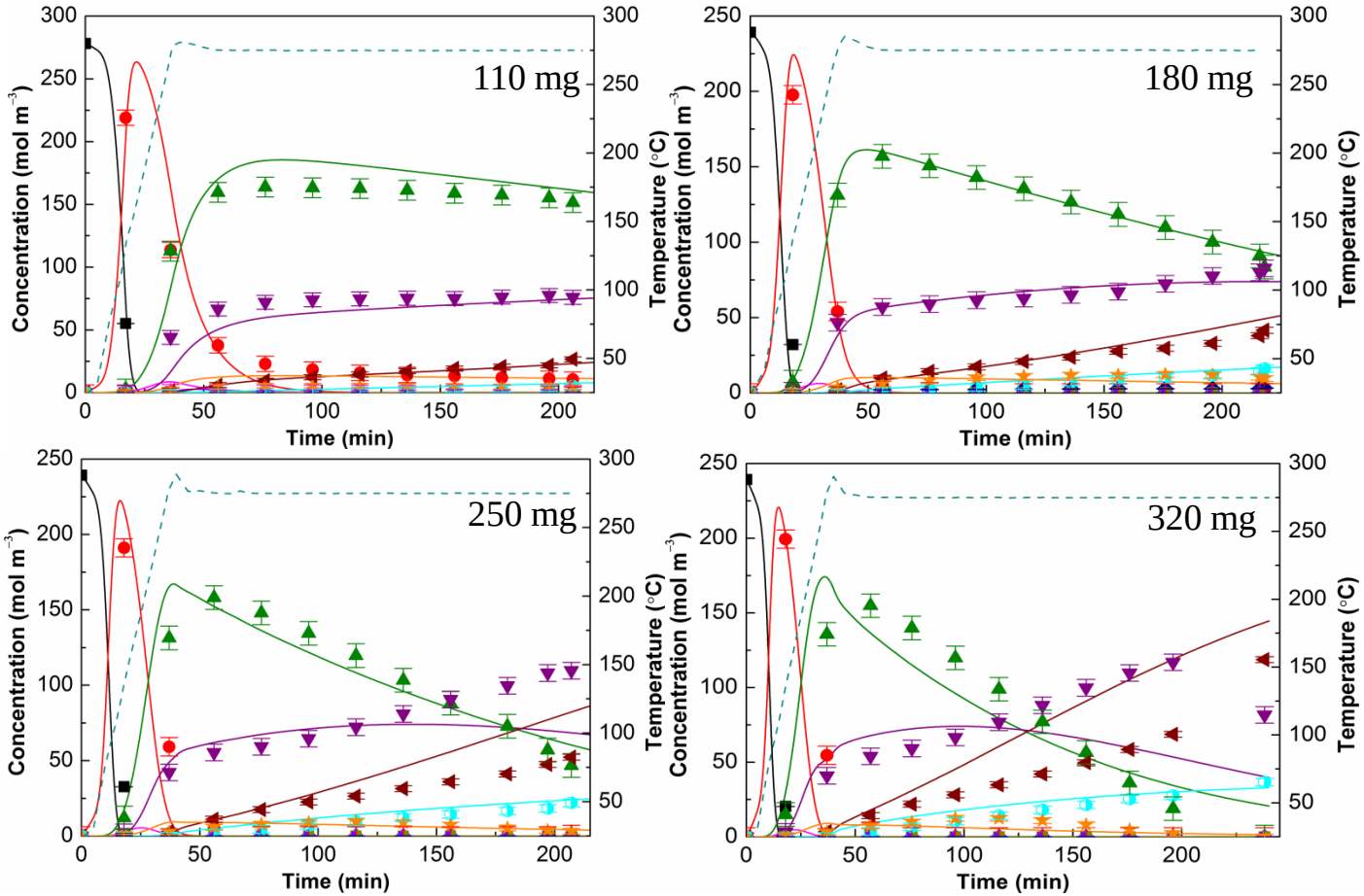
EUGENOL HYDROTREATMENT: INFLUENCE OF PRESSURE (275 °C)





A. Bjelić *et al.*, *Chem. Eng. J.*, **2018**, *333*, 240.

EUGENOL HYDROTREATMENT: INFLUENCE OF Ru/C CATALYST LOADING (275 °C, 5 MPa)



A. Bjelić *et al.*, *Chem. Eng. J.*, **2018**, *333*, 240.

EUGENOL HYDROTREATMENT: KINETIC PARAMETERS BASED ON REGRESSION ANALYSIS

$Ea_{HYD} < Ea_{HDO}$

Adsorption and desorption constants			
k_{ads} $m^3\ mol^{-1}\ min^{-1}$	$k_{ads(H)}$ $m^3\ mol^{-1}\ min^{-1}$	k_{des} min^{-1}	$k_{des(H)}$ min^{-1}
$\geq 5.5\times10^3$	$\geq 3.0\times10^6$	$k_{ads}\times31.7$	$k_{ads(H)}\times3.15$
Heterogeneous reactions			
Reaction rate constants at 275 °C, $m^3\ mol^{-1}\ min^{-1}$		Activation energies, $J\ mol^{-1}$	
$k_{HMAB\text{-}A}$	1.34×10^8	$Ea_{HMAB\text{-}A}$	5.77×10^4
$k_{IHMAB\text{-}IA}$	1.34×10^8	$Ea_{IHMAB\text{-}IA}$	5.77×10^4
$k_{HMPB\text{-}B}$	2.04×10^5	$Ea_{HMPB\text{-}B}$	3.72×10^4
$k_{HMPB\text{-}M}$	6.99×10^4	$Ea_{HMPB\text{-}M}$	4.07×10^4
$k_{HMPC\text{-}M}$	1.91×10^3	$Ea_{HMPC\text{-}M}$	2.05×10^5
$k_{HPB\text{-}B}$	5.54×10^5	$Ea_{HPB\text{-}B}$	2.79×10^4
$k_{HPB\text{-}H}$	1.86×10^5	$Ea_{HPB\text{-}H}$	1.25×10^5
$k_{HPC\text{-}H}$	4.37×10^3	$Ea_{HPC\text{-}H}$	1.83×10^5
$k_{PB\text{-}B}$	3.47×10^5	$Ea_{PB\text{-}B}$	3.16×10^4
$k_{HMPC\text{-}MH}$	1.30×10^3	$Ea_{HMPC\text{-}MH}$	8.00×10^4
$k_{HHPC\text{-}H}$	2.30×10^4	$Ea_{HHPC\text{-}H}$	1.50×10^5
$k_{MPB\text{-}B}$	2.03×10^5	$Ea_{MPB\text{-}B}$	1.6×10^4
$k_{MPC\text{-}M}$	4.30×10^3	$Ea_{MPC\text{-}M}$	1.00×10^4
$k_{HMPC\text{-}C}$	8.28×10^2	$Ea_{HMPC\text{-}C}$	1.64×10^5
$k_{HMePCP\text{-}HMe}$	$> 10^6$	$Ea_{HMePCP\text{-}HMe}$	n.a.
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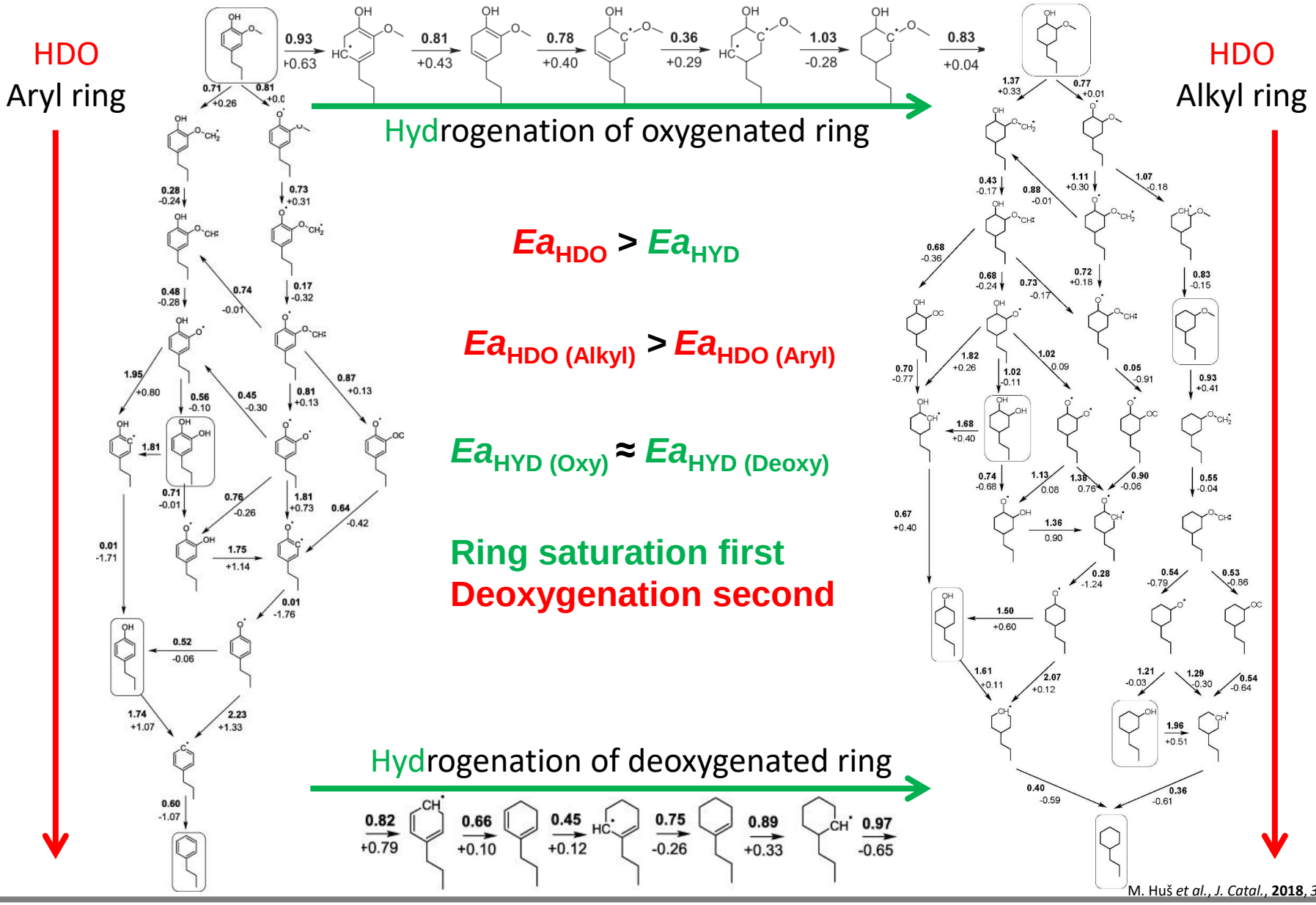
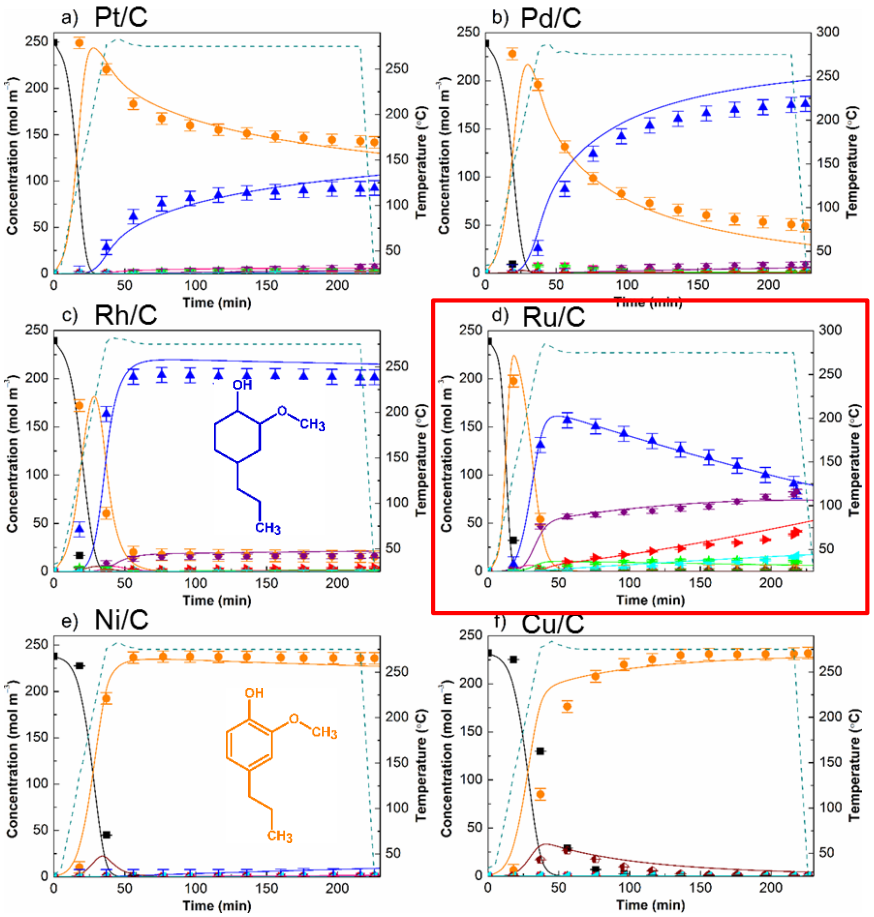
A. Bjelić *et al.*, *Chem. Eng. J.*, **2018**, *333*, 240.

DFT CALCULATION: ENERGY BARRIERS

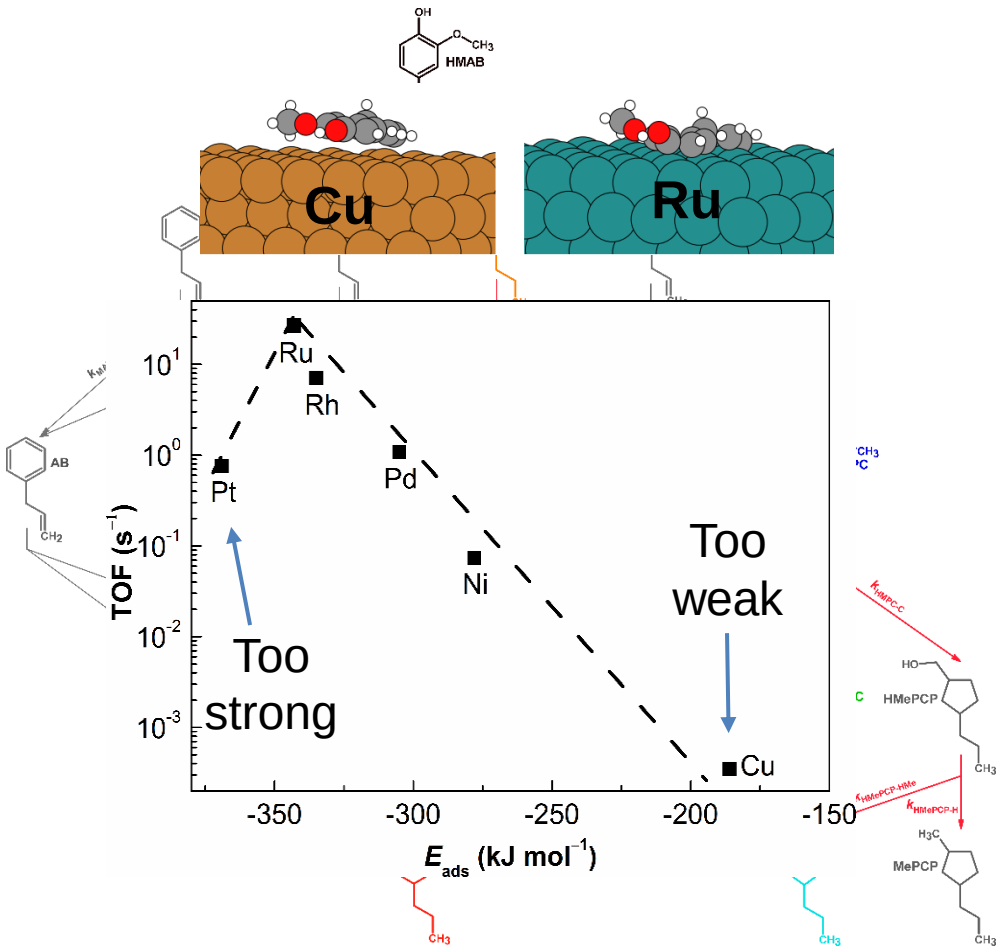


M. Huš *et al.*, *J. Catal.*, **2018**, *358*, 8.

CATALYST SCREENING: VARIATION OF METALS ON CARBON



Proposed eugenol HDO reaction network

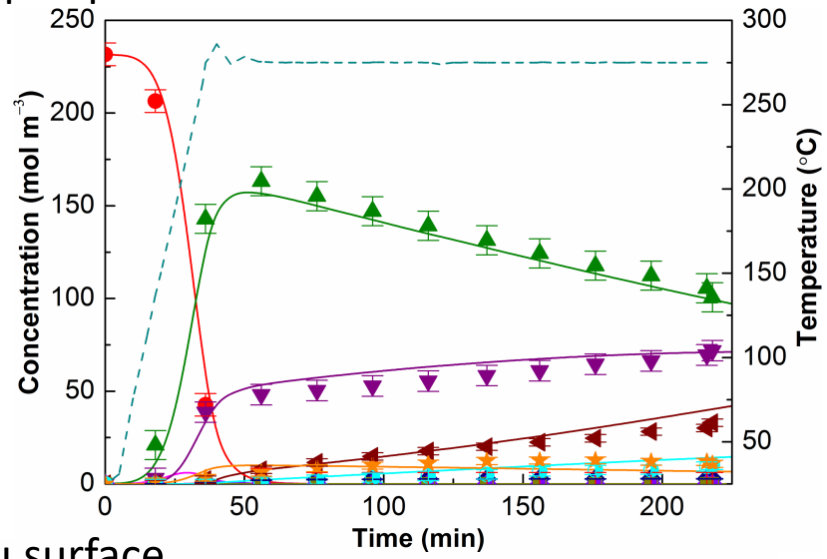


- Dominant reaction pathway
- Less dominant reaction pathway
- Non-occurred reactions

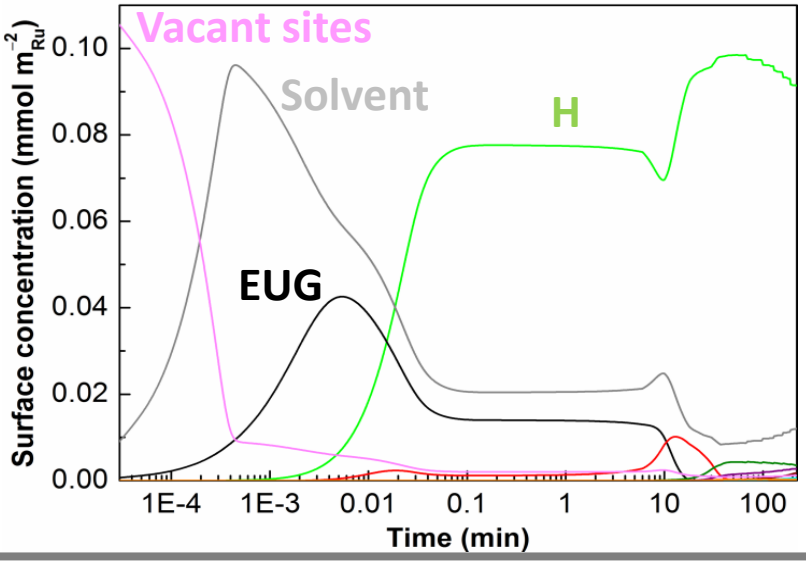
A. Bjelić *et al.*, *Chem. Eng. J.*, **2019**, 359, 305.

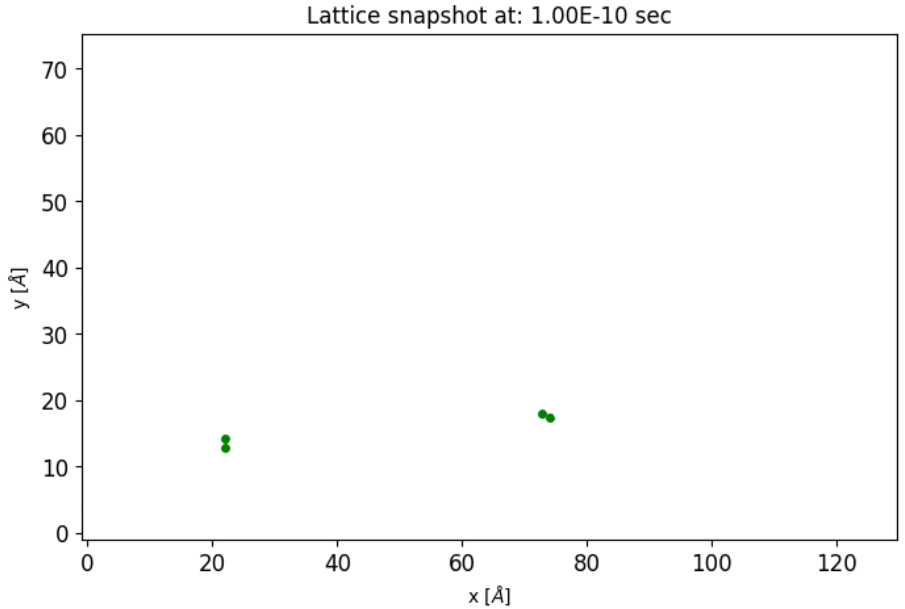
CURRENT WORK: LINKING SCALES (DFT, KMC, MEAN-FIELD)

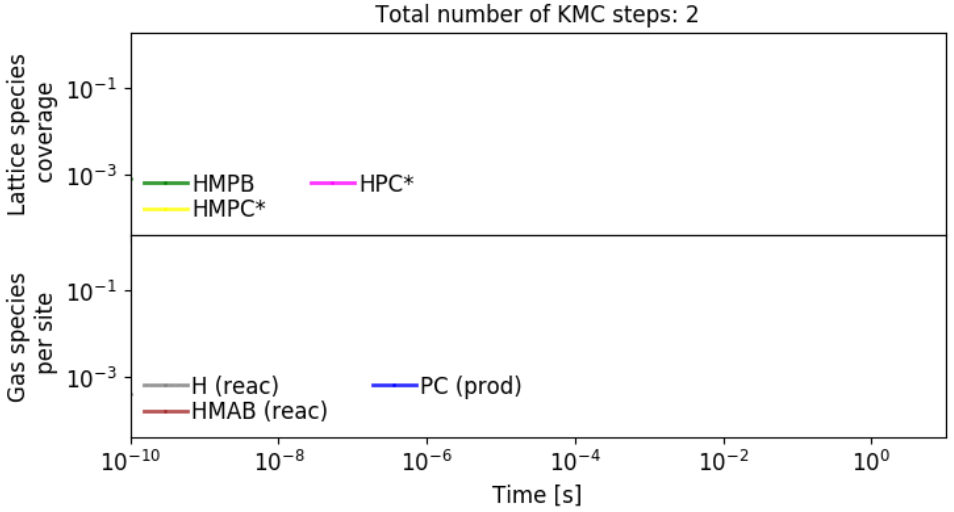
Liquid phase



Ru surface

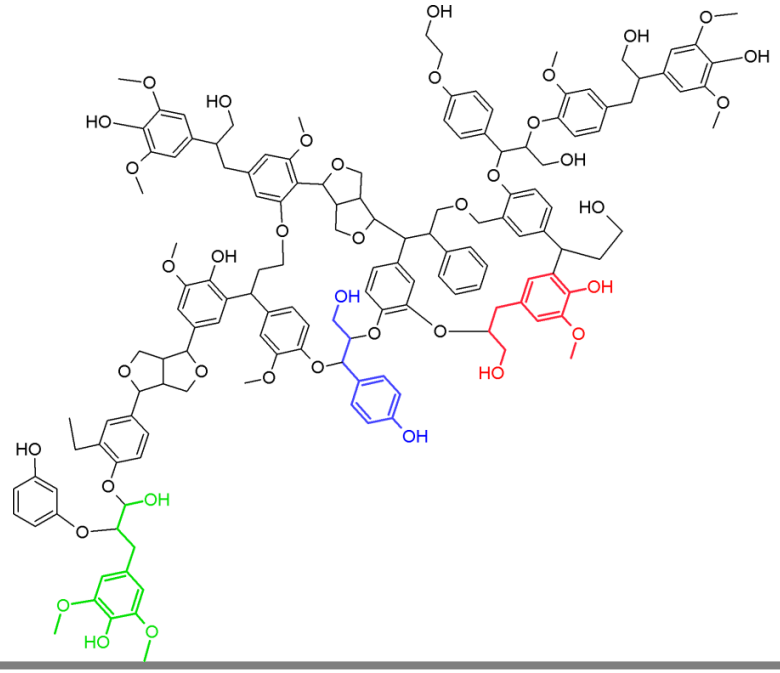






LIGNIN VALORISATION: CONCLUSIONS

- **Lignin is a complex molecule to start a process with**
- **Depolymerisation leads to various monomeric units**
- **Hydrotreatment: competition between aromatic ring saturation and oxygen removal**
- **Activation energy of HDO is higher than for hydrogenation over noble metals**
- **Noble metals should be used to convert lignin into cyclohexanolic species**



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

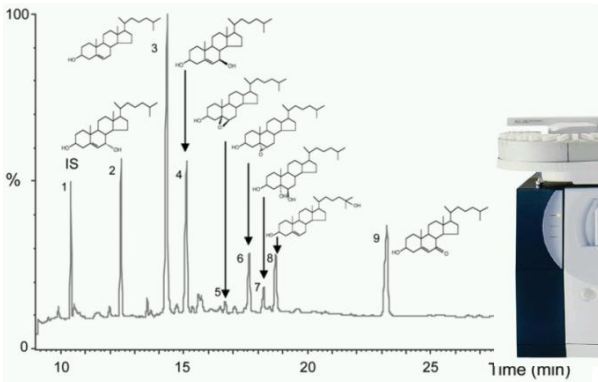
Model
- Mass transfer (gas-liquid-solid)
- Adsorption/desorption processes on material surface
- Surface reactions based on elementary steps

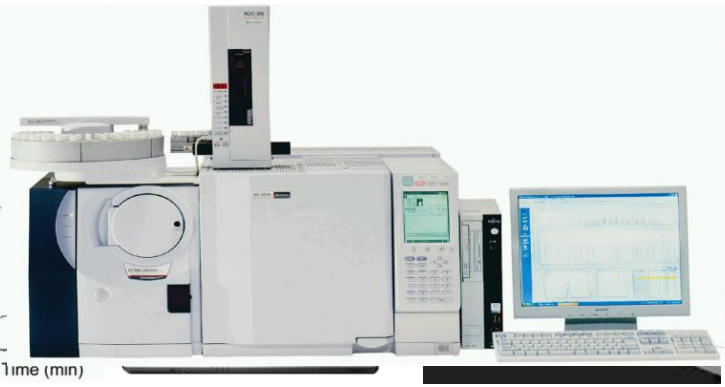
Kinetic Monte Carlo

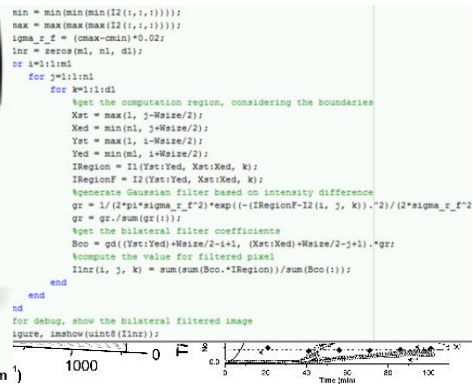
Density functional theory

Characterisation
- Composition
- Structure
- Morphology

Thermodynamics







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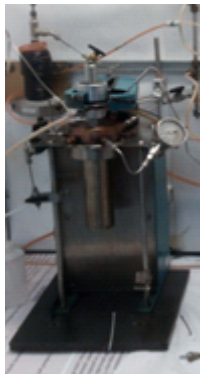

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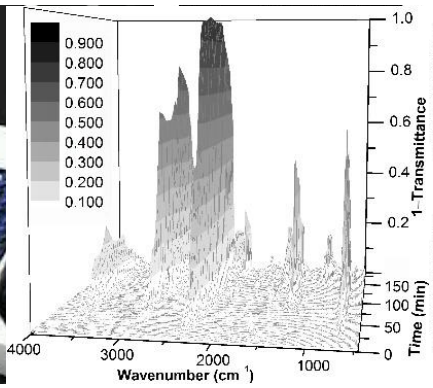

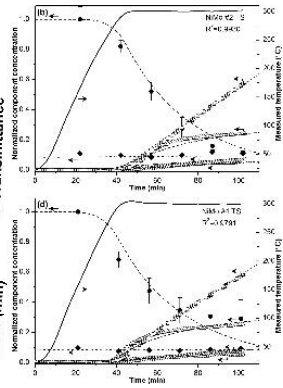

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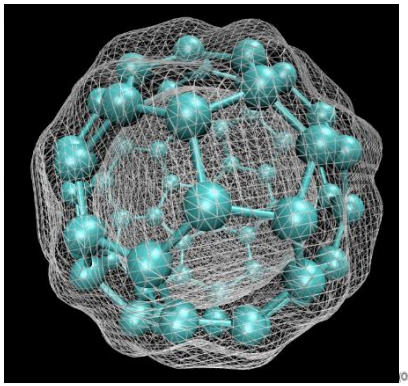
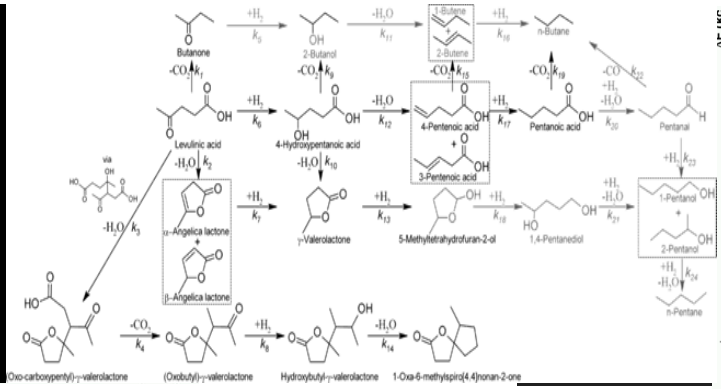
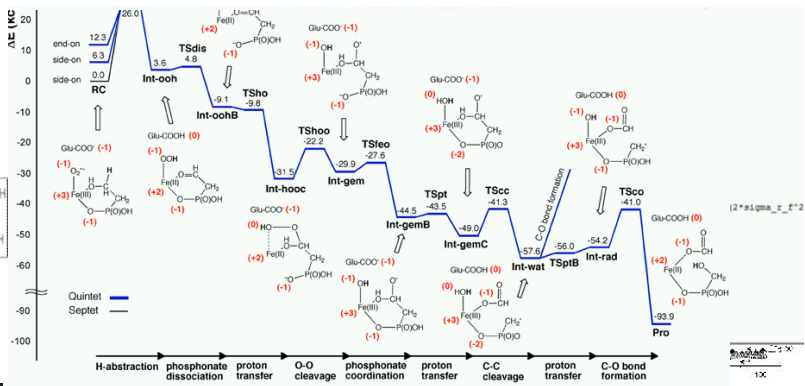






TAKE-HOME MESSAGE: BIOMASS IS A SUSTAINABLE SOURCE OF CHEMICALS

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**

Thank you for your attention!

Acknowledgements:


Dr. Ana Bjelić

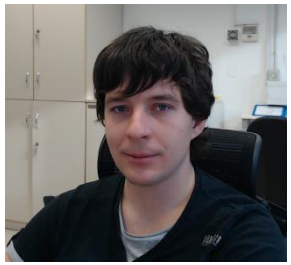

Ms. Brigita Hočevar


Dr. Matej Huš


Mr. Matic Grojzdek


Catalyst synthesis


Fractionation


Good behavior


Thermodynamics


Catalyst synthesis


Modelling challenges

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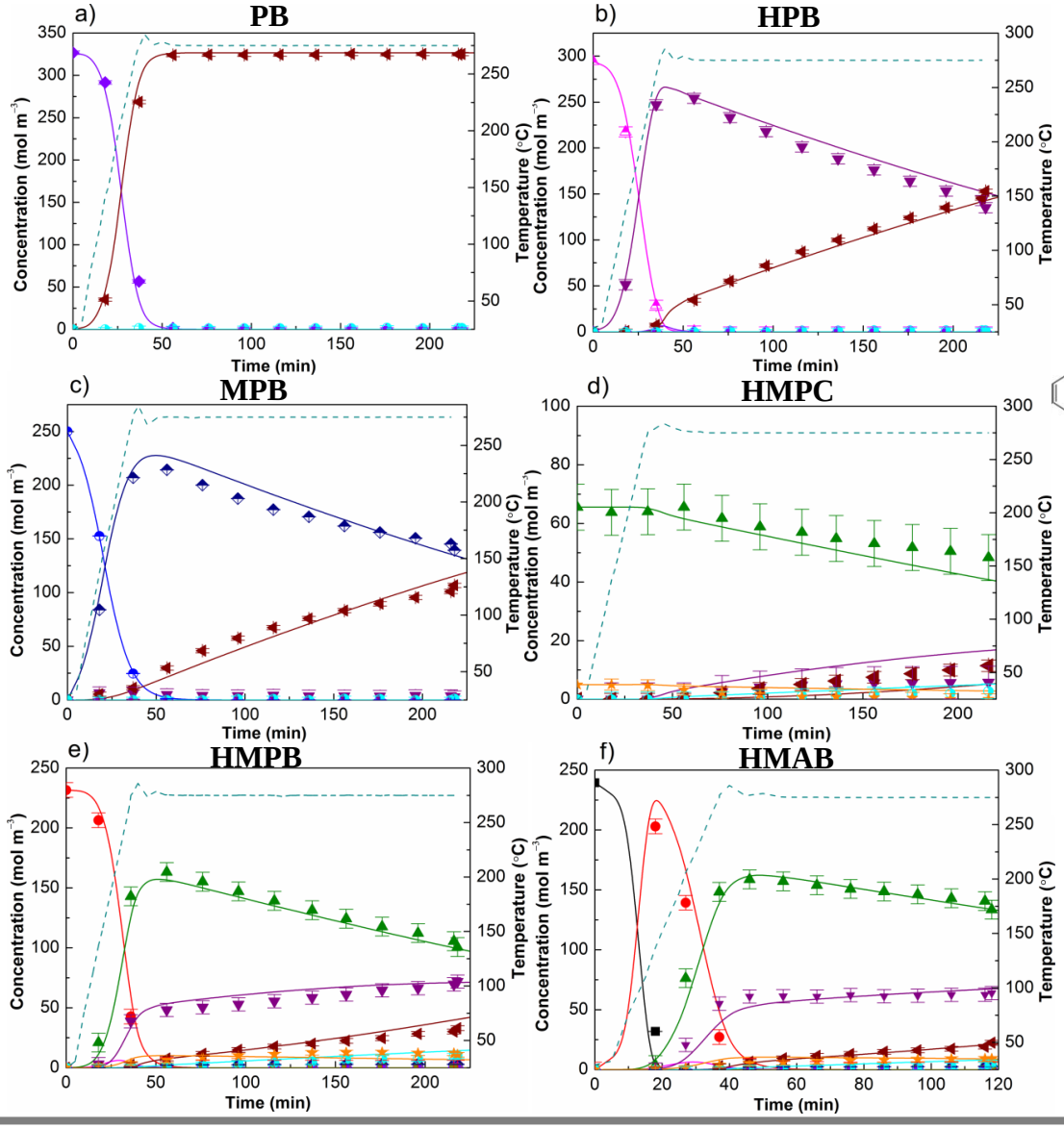
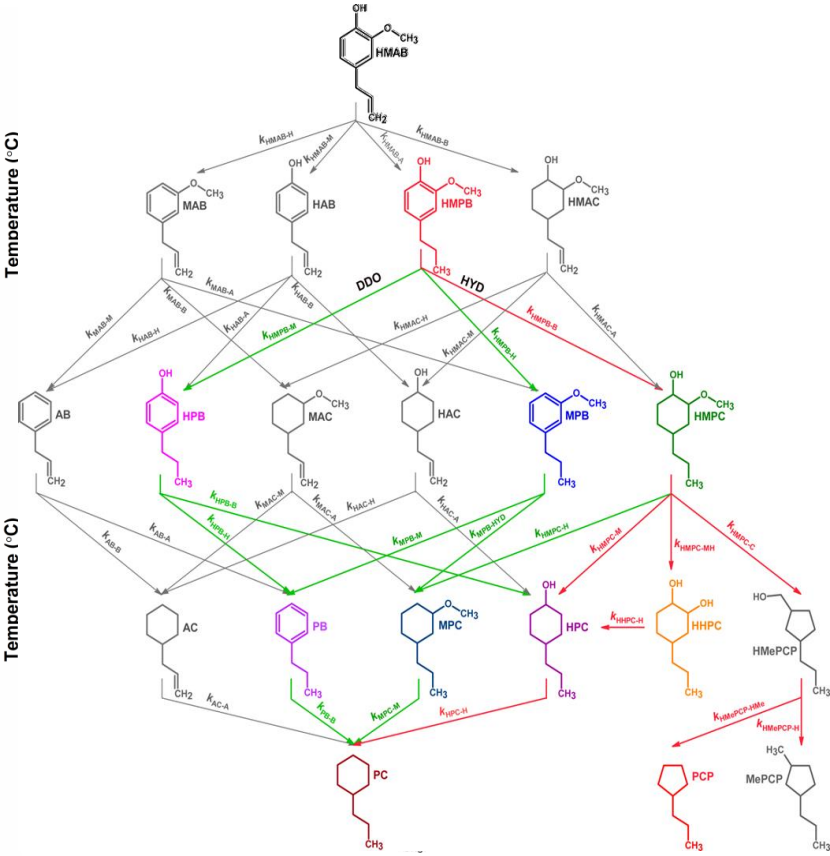
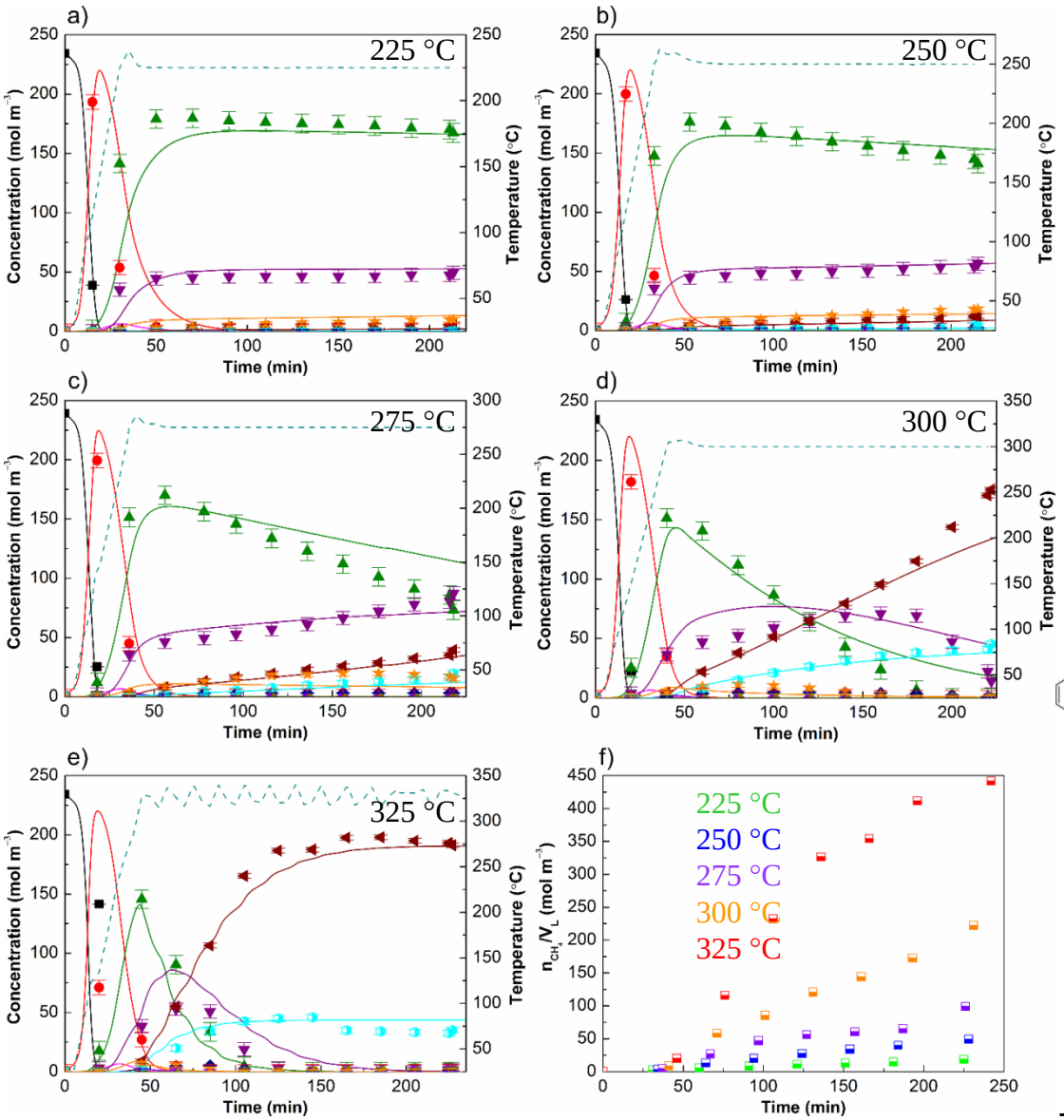
EUGENOL HYDROTREATMENT: CATALYSED REACTIONS WITH INTERMEDIATES (275 °C, 5 MPa)



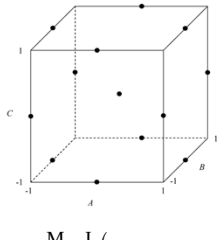


- Dominant pathway
- Less dominant
- Non occurred reactions

EUGENOL HYDROTREATMENT: INFLUENCE OF TEMPERATURE (5 MPa)



Box–Behnken alghorithm for initial approximations (739 combinations in total)



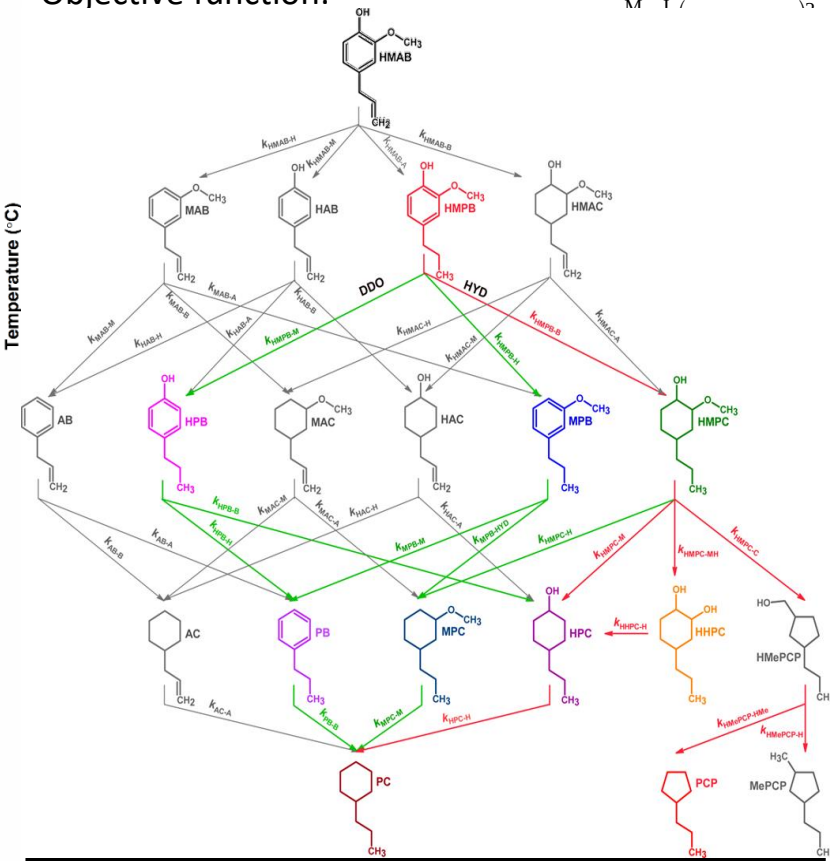
Temperature profile:

$$T(t) = T(t=0) + ht \qquad \forall T \le T_{final}$$

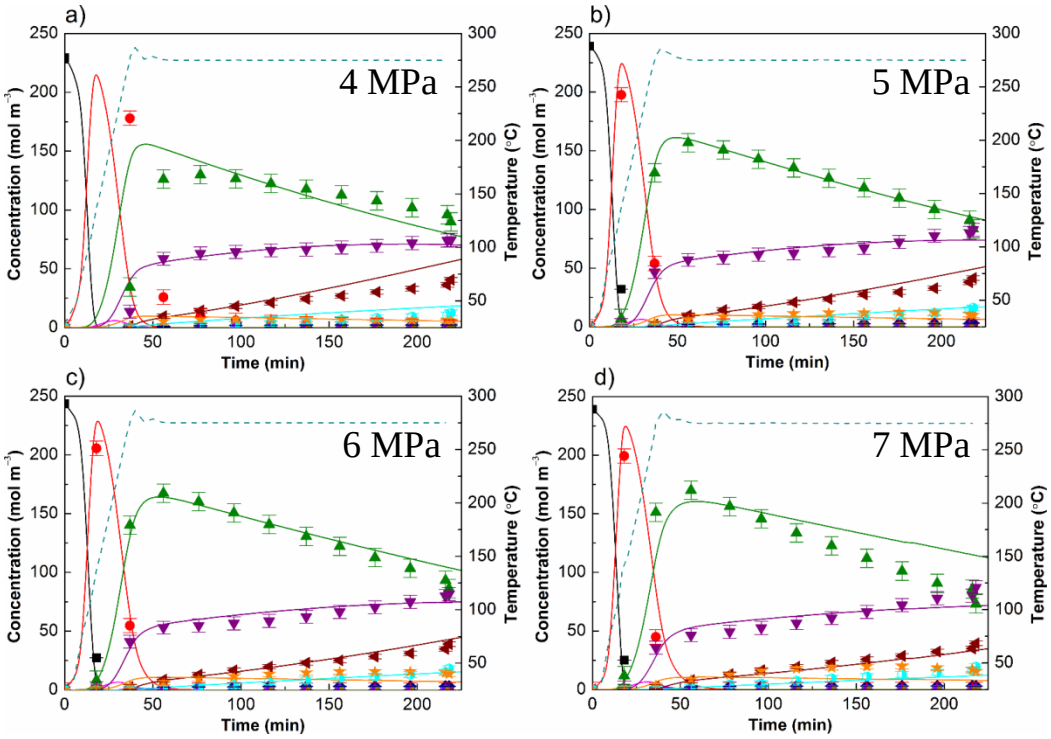
Modified Arrhenious law:

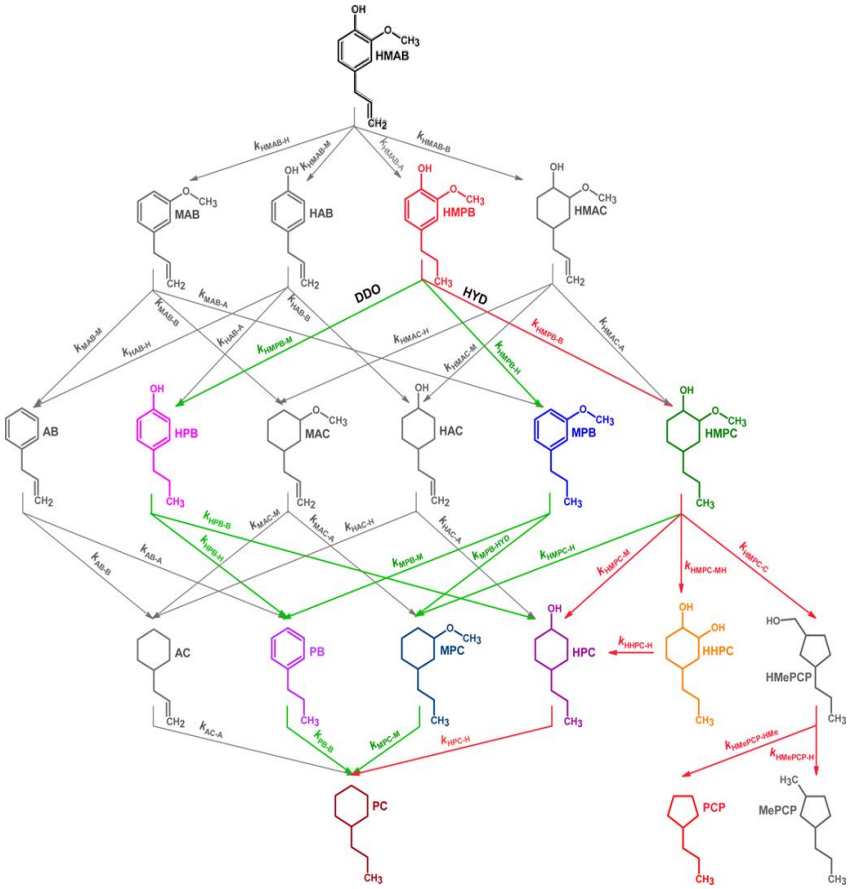
$$k_i^C(T(t)) = k_i^C(T_P) \cdot \exp\left(-\frac{Ea_i^C}{R}\left(\frac{1}{T(t)} - \frac{1}{T_P}\right)\right)$$

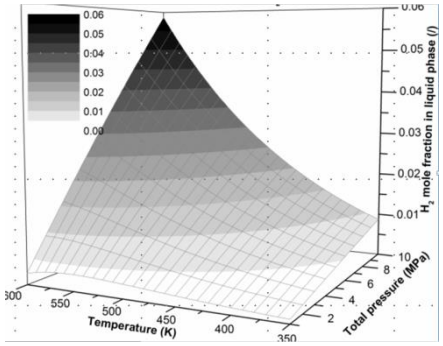
Objective function:



EUGENOL HYDROTREATMENT: INFLUENCE OF PRESSURE (275 °C)







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

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

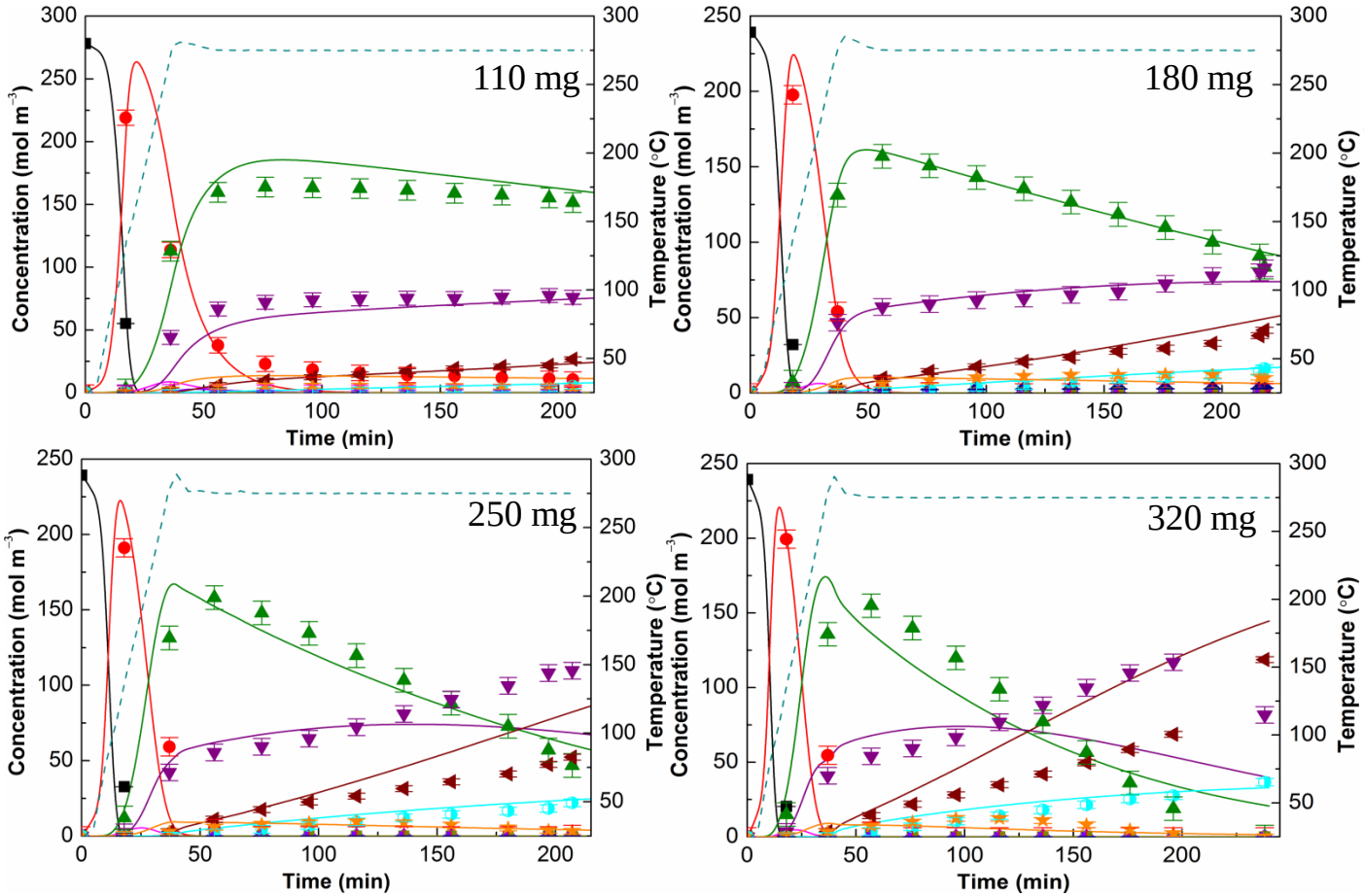
$$r_j^A = k_j^A \cdot C_j^{Si} \cdot C_{VS}^*$$

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

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

$$\underbrace{V_{Si}\frac{dC_j^{Si}}{dt}}_{\to 0} = r_j^{LS} - r_j^A + r_j^D$$

EUGENOL HYDROTREATMENT: INFLUENCE OF Ru/C CATALYST LOADING (275 °C, 5 MPa)



$$N_{AS} = 38\ \mu\text{mol g}^{-1}$$

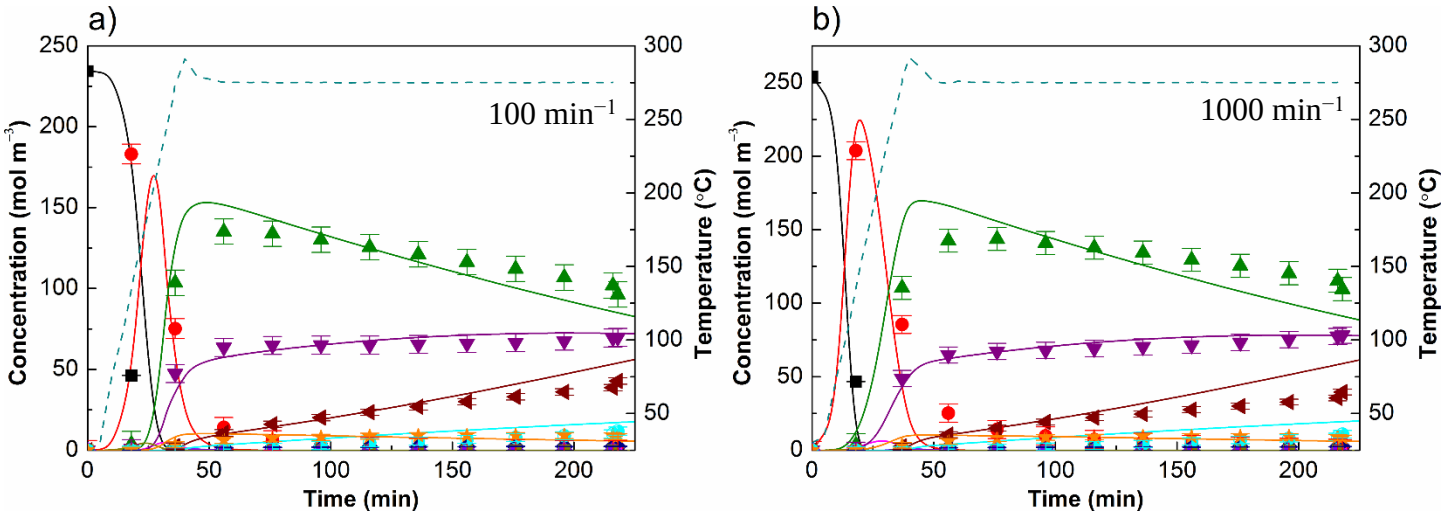
$$C^*_{VS}(t=0) = N_{AS}\, m_{CAT} / V_L$$

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

$$\frac{dC_j^*}{dt} = r_j^A - r_j^D + \sum \pm r_i^C$$

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

EUGENOL HYDROTREATMENT: INFLUENCE OF STIRRING SPEED (275 °C, 5 MPa)



External mass transfer had no influence on global reaction rate.

$$r_{H_2}^{GL} = \frac{k_l A_g \left(\frac{p_{H_2}}{He} - c_{H_2(l)}\right)}{V_l}$$

$$r_j^{LS} = \frac{k_s A_s \left(c_{j(l)} - c_{j(s)}\right)}{V_l}$$

$$k_l = 0.42 \times \left(\frac{\mu_s a}{\rho_s}\right)^{1/3} Sc^{-1/2} \alpha d_b$$

$$k_s = 0.13 \times \left(\frac{W \mu_s}{V_L \rho_s^2}\right)^{1/4} Sc^{-2/3}$$

$$A_g = \frac{6 V_g \varepsilon_g}{d_b}$$

$$\varepsilon_g = 0.45 \times \frac{\left(N - N^*\right) d_a^2}{d_r \left(a d_r\right)^{1/2}}$$

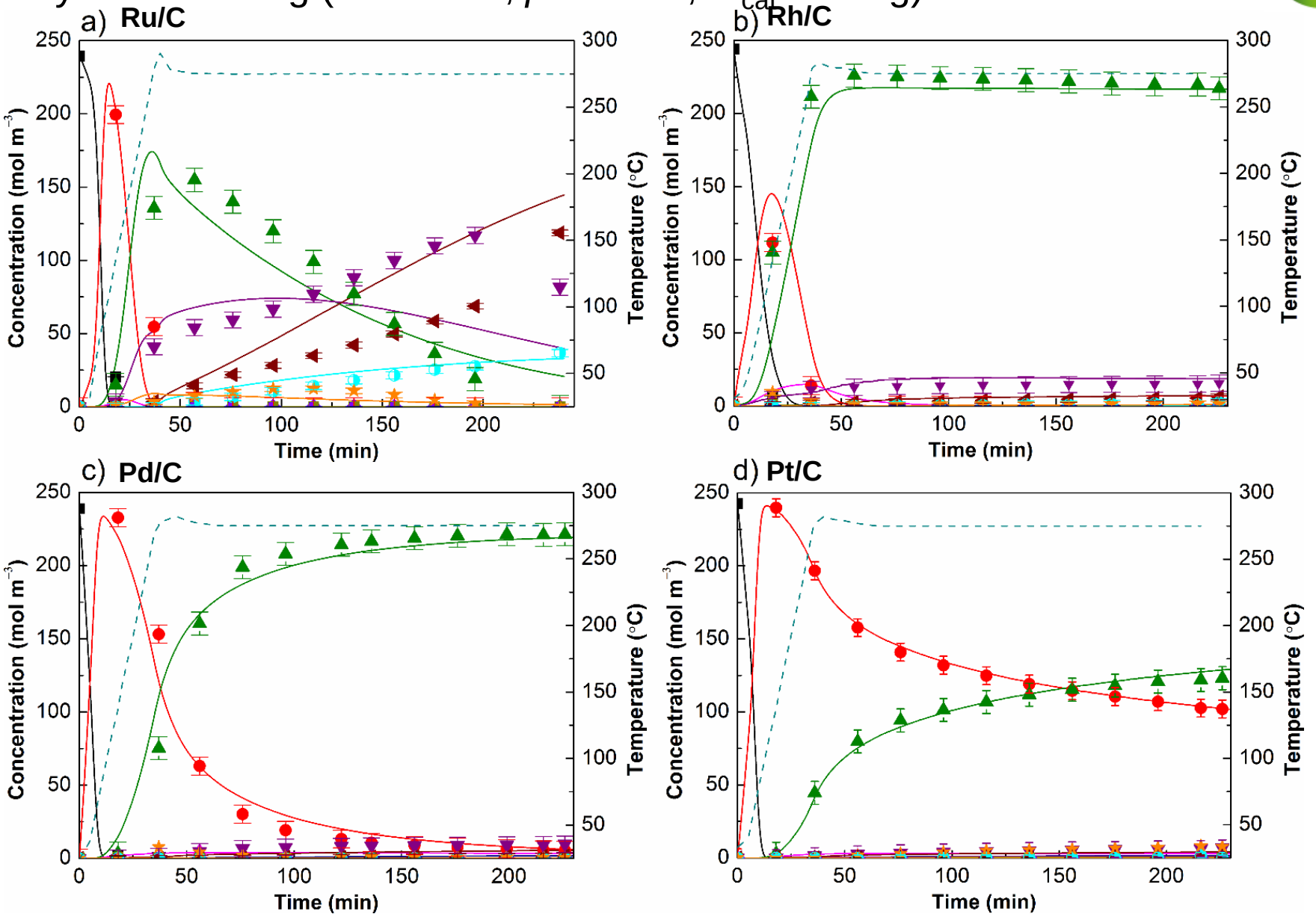
$$W = \frac{N_p \rho_s N^3 d_r^5}{a}$$

$$A_s = m_{cat} \times a_s$$

CONCLUSION:

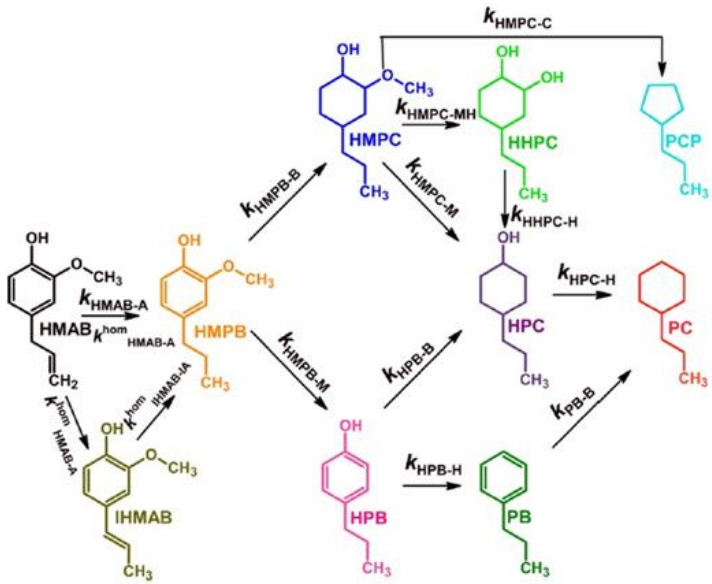
adsorption > mass transfer >> surface reaction rate

Catalysts screening (T=275 °C, p=5 MPa, m_{cat}=0.31 g)



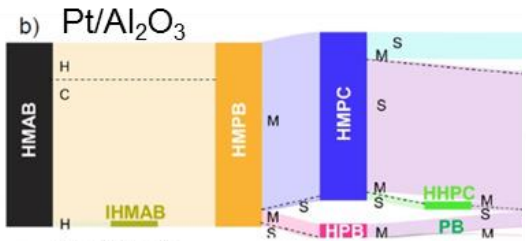
FURTHER CATALYST SCREENING: METALS & SUPPORTS

a) Eugenol HDO reaction network

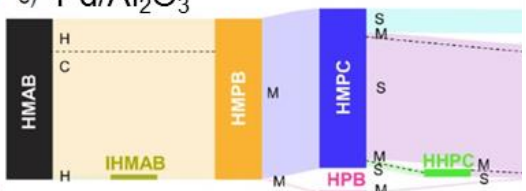


Variation of metals

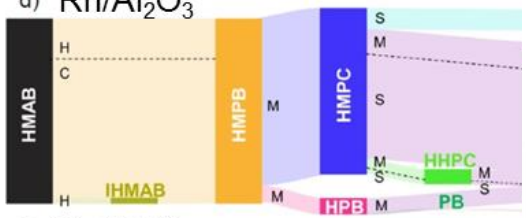
b) Pt/Al_2O_3



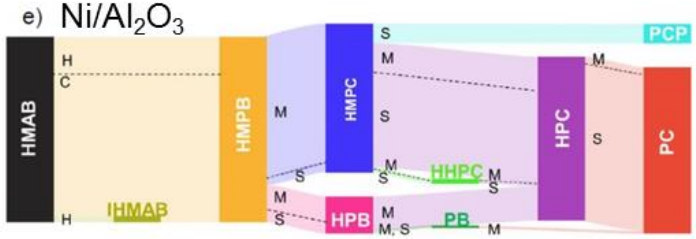
c) Pd/Al_2O_3



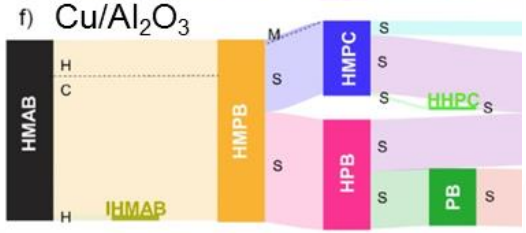
d) Rh/Al_2O_3



e) Ni/Al_2O_3

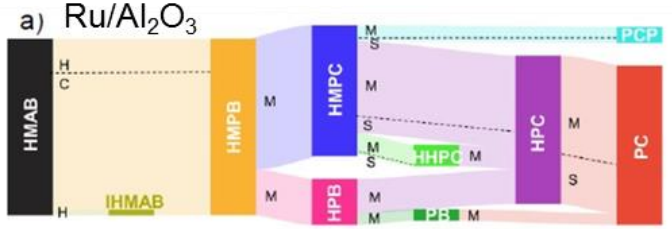


f) Cu/Al_2O_3

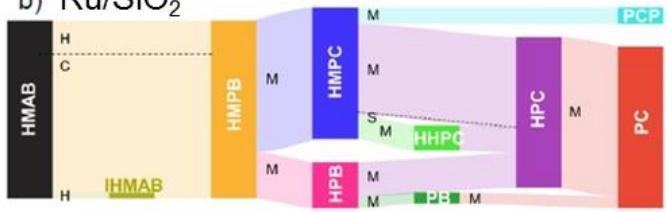


Variation of supports

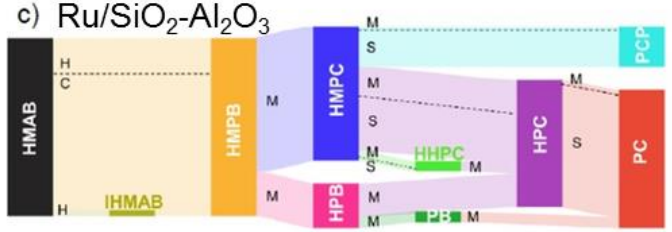
a) Ru/Al_2O_3



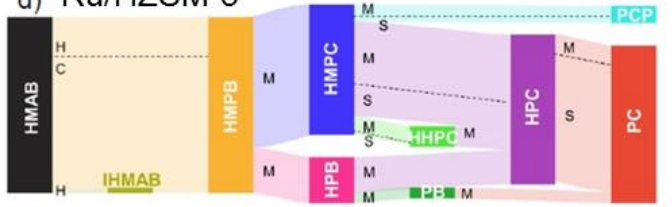
b) Ru/SiO_2



c) Ru/SiO_2-Al_2O_3



d) Ru/HZSM-5



e) Ru/TiO_2

Adsorption and desorption constants

k_{ads} m^3 mol^{-1} min^{-1}	$k_{ads(H)}$ m^3 mol^{-1} min^{-1}	k_{des} min^{-1}	$k_{des(H)}$ min^{-1}
$\geqslant 5.6 \times 10^3$	$\geqslant 3.2 \times 10^3$	$k_{ads} \times (32 \pm 4)$	$k_{ads(H)} \times (3.2 \pm 0.2)$

Heterogeneous reactions

Reaction rate constants at 275 °C, m^3 mol^{-1} min^{-1}		Activation energies, J mol^{-1}	
$k_{HMAB\text{-}A}$	$(1.3411 \pm 0.0002) \times 10^8$	$Ea_{HMAB\text{-}A}$	$(5.8 \pm 0.5) \times 10^4$
$k_{HMAB\text{-}IA}$	$(1.3411 \pm 0.0002) \times 10^8$	$Ea_{HMAB\text{-}IA}$	$(5.8 \pm 0.5) \times 10^4$
$k_{HMPB\text{-}B}$	$(2.0 \pm 0.1) \times 10^5$	$Ea_{HMPB\text{-}B}$	$(3.7 \pm 0.1) \times 10^4$
$k_{HMPB\text{-}M}$	$(7.0 \pm 0.8) \times 10^4$	$Ea_{HMPB\text{-}M}$	$(4.1 \pm 0.2) \times 10^4$
$k_{HMPC\text{-}M}$	$(1.9 \pm 0.4) \times 10^3$	$Ea_{HMPC\text{-}M}$	$(2.1 \pm 0.1) \times 10^5$
$k_{HPB\text{-}B}$	$(5.5 \pm 0.2) \times 10^5$	$Ea_{HPB\text{-}B}$	$(2.8 \pm 1.6) \times 10^4$
$k_{HPB\text{-}H}$	$(1.7 \pm 0.3) \times 10^5$	$Ea_{HPB\text{-}H}$	$(1.3 \pm 0.2) \times 10^5$
$k_{HPC\text{-}H}$	$(4.4 \pm 0.5) \times 10^3$	$Ea_{HPC\text{-}H}$	$(1.5 \pm 0.1) \times 10^5$
$k_{PB\text{-}B}$	$(3.5 \pm 0.1) \times 10^5$	$Ea_{PB\text{-}B}$	$(3 \pm 2) \times 10^4$
$k_{HMPC\text{-}MH}$	$(1.3 \pm 0.6) \times 10^3$	$Ea_{HMPC\text{-}MH}$	$(8 \pm 1) \times 10^4$
$k_{HHPC\text{-}H}$	$(2.3 \pm 0.8) \times 10^4$	$Ea_{HHPC\text{-}H}$	$(1.5 \pm 0.2) \times 10^5$
$k_{MPB\text{-}B}$	$(2.0 \pm 0.4) \times 10^5$	$Ea_{MPB\text{-}B}$	$(1.6 \pm 0.3) \times 10^4$
$k_{MPC\text{-}M}$	$(4.3 \pm 0.6) \times 10^3$	$Ea_{MPC\text{-}M}$	$(1 \pm 1) \times 10^4$
$k_{HMPC\text{-}C}$	$(8 \pm 1) \times 10^2$	$Ea_{HMPC\text{-}C}$	$(1.9 \pm 0.1) \times 10^5$
$k_{HMePCP\text{-}HMe}$	$> 10^6$	$Ea_{HMePCP\text{-}HMe}$	n.a.
$k_{HMePCP\text{-}H}$	$\ll k_{HMePCP\text{-}HMe}$	$Ea_{HMePCP\text{-}H}$	n.a.

A. Bjelić *et al.*, *Chem. Eng. J.*, **2018**, *333*, 240.