

Most Abundant Bio Feedstocks

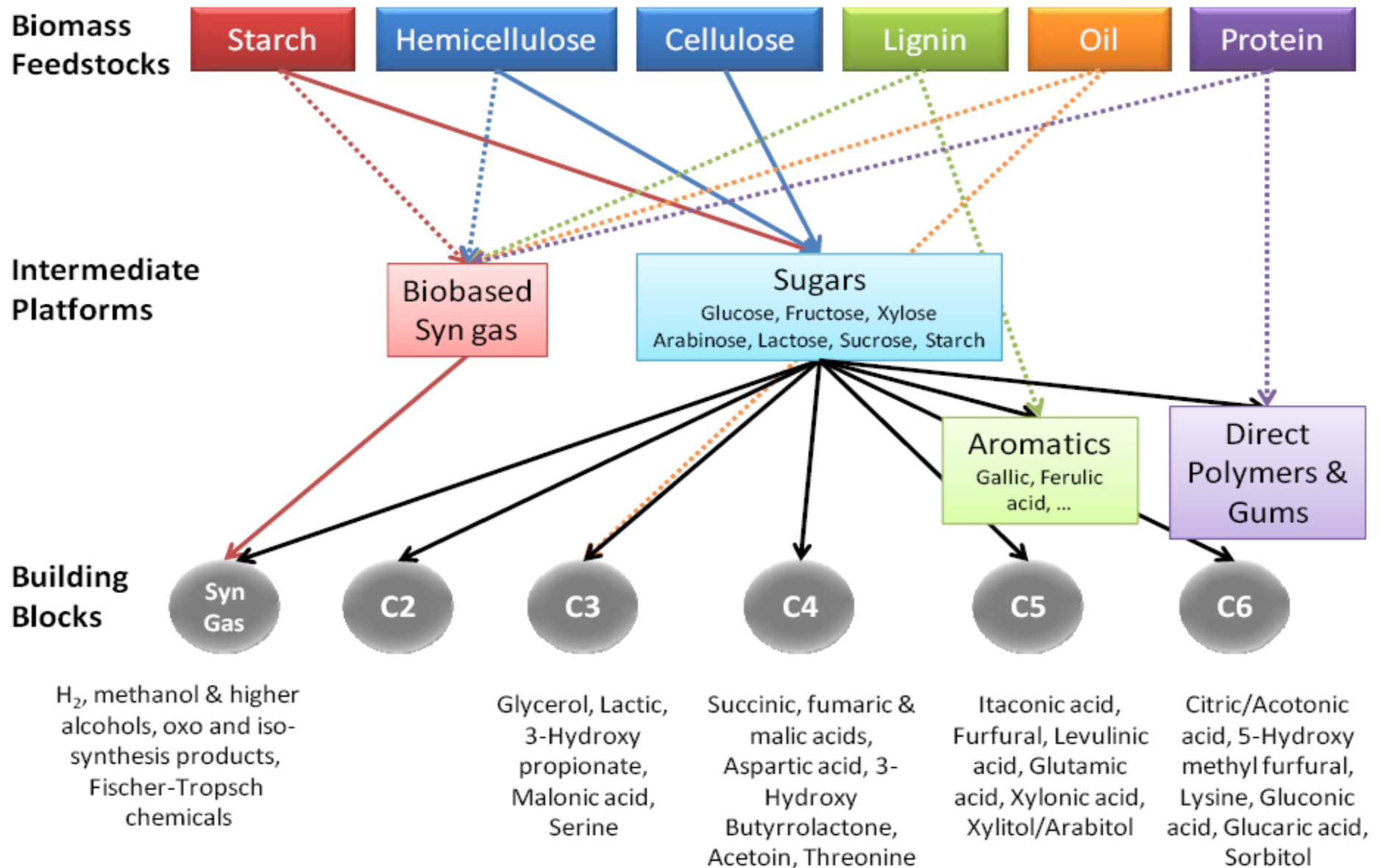
– depending on geographical location and local politics

- Trees
- Forest residues
- Grasses
- Agricultural crops
- Animal waste
- Municipal waste
- Algae (Alger, Levä)

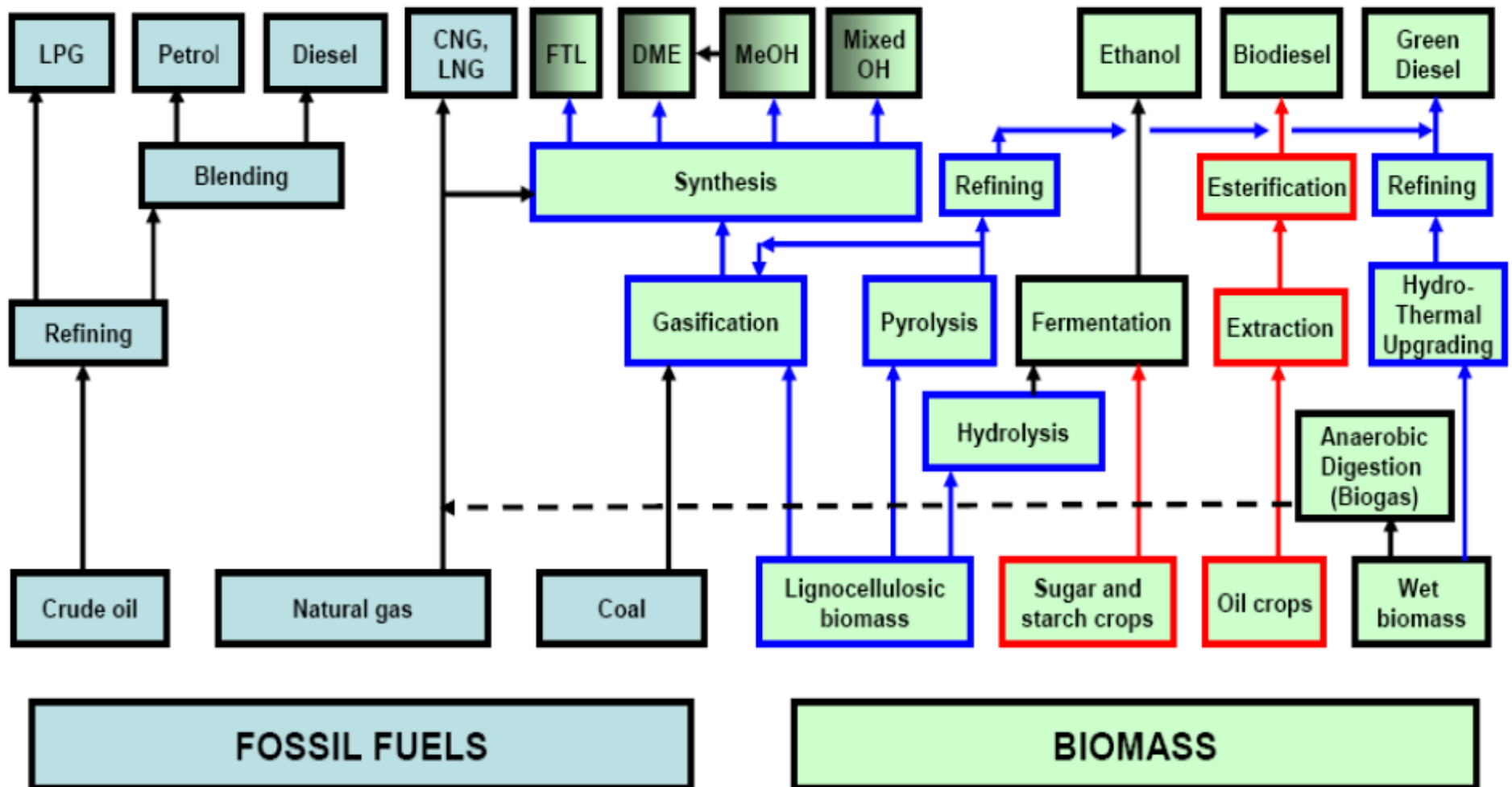
[www.cifor.cgiar.org/publications/
pdf_files/Books/ForestPerspective.pdf](http://www.cifor.cgiar.org/publications/pdf_files/Books/ForestPerspective.pdf)



Product flow-chart for biomass feedstocks



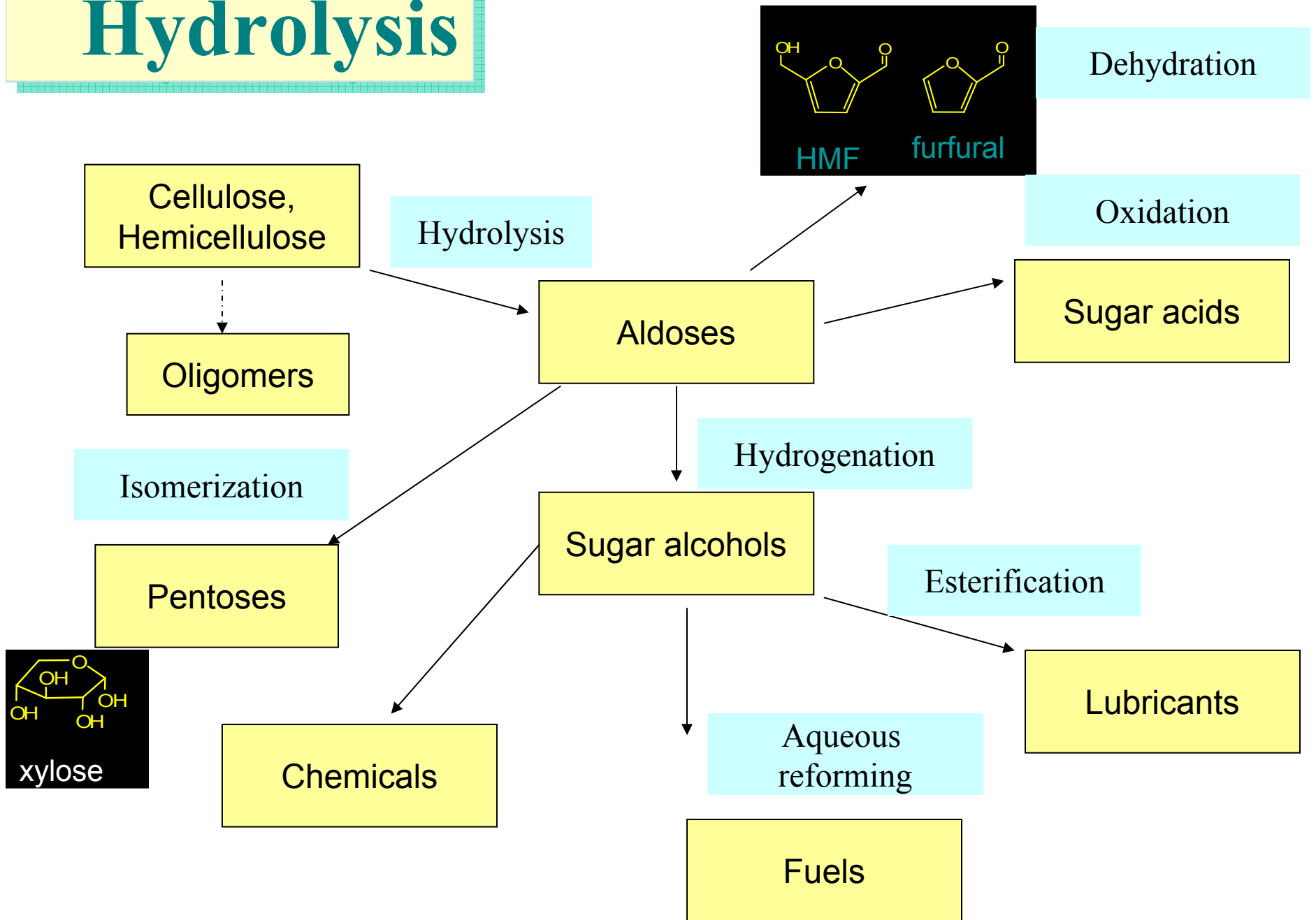
Biofuel production pathways



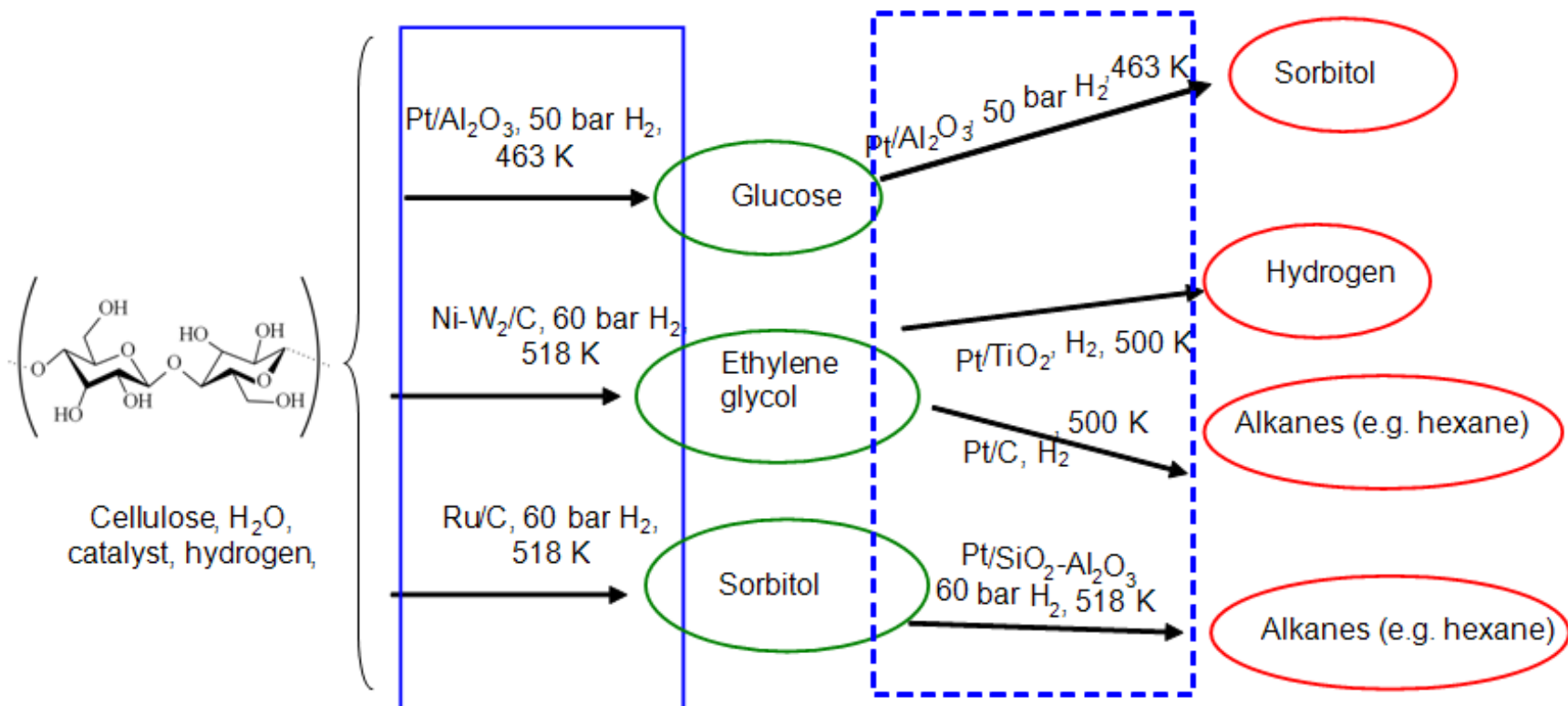
Treatment of wood

- **Gasification**
- **Pyrolysis**
- **Depolymerization** to get low molecular mass components (sugars, phenols, furfural, etc.), e.g. **building blocks**
- **Delignification (cellulose, derivatives, paper)**
- **Extraction of valuable chemicals (bioactive components)**

Hydrolysis

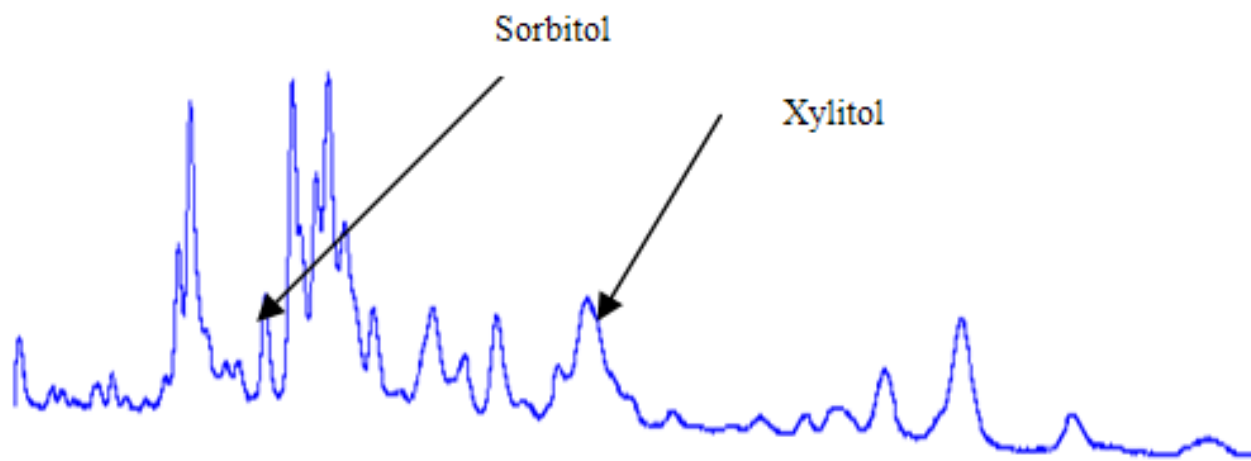


Hydrolytic hydrogenation



A. Fukuoka, P.L. Dhepe, *Angew. Chem. Int. Ed.* **2006**, 45, 5161

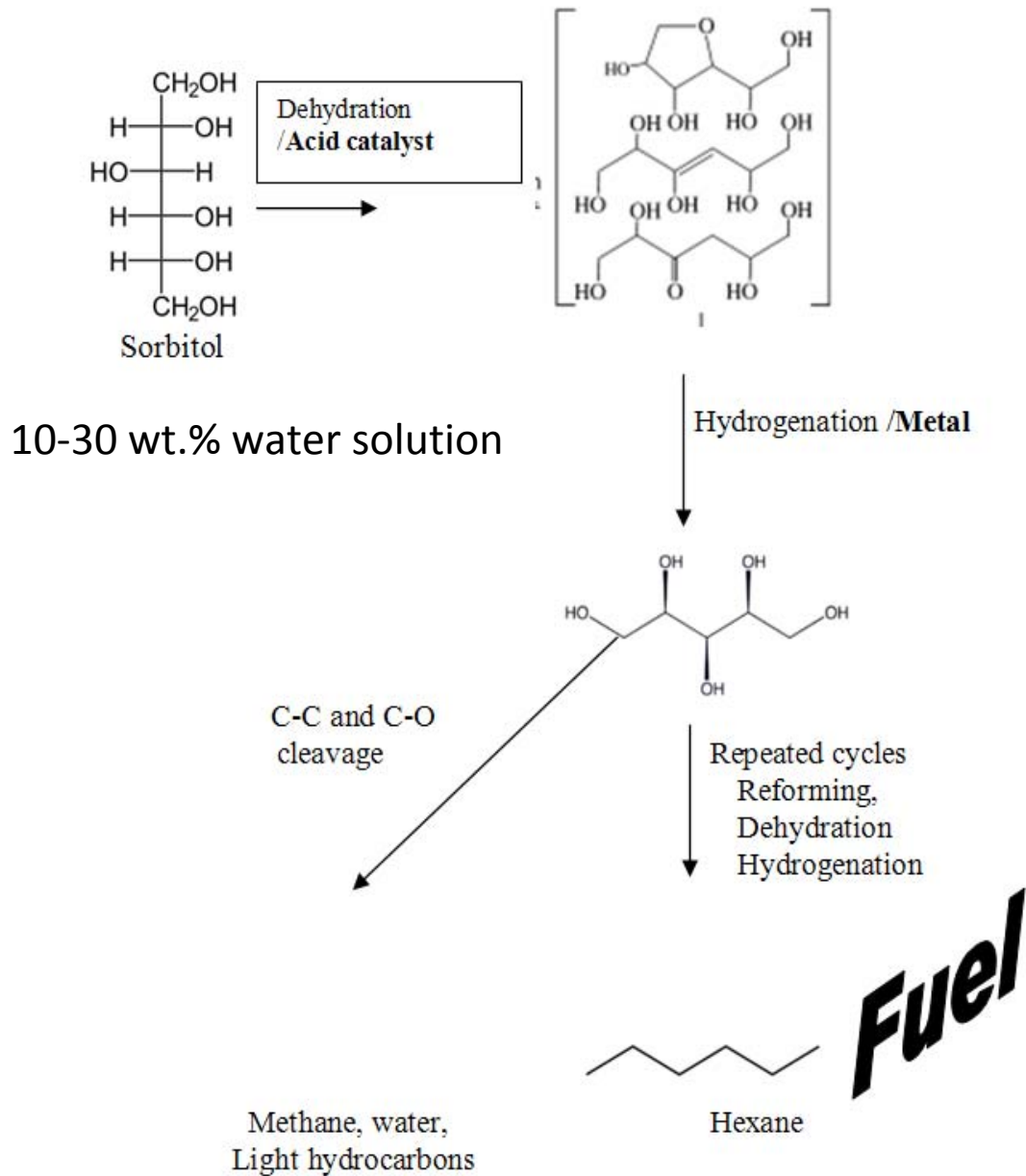
A. A. Balandin, N.A. Vasyunina, S.V. Chepigo, G. S. Barysheva, *Doklady Akademii Nauk SSSR*, **1959**, 128, 941



Hydrolytic hydrogenation of cellulose on Pt-MCM-48

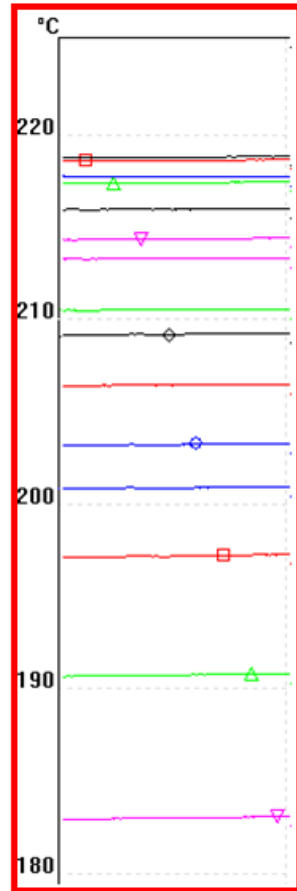
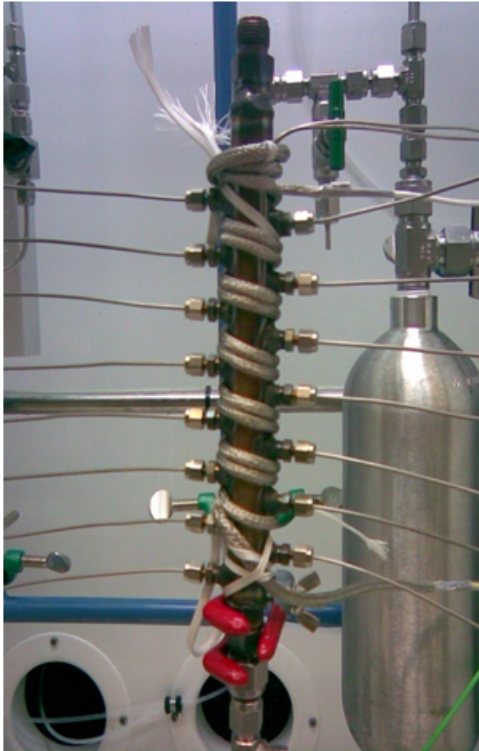
M. Kälström

Aqueous phase reforming

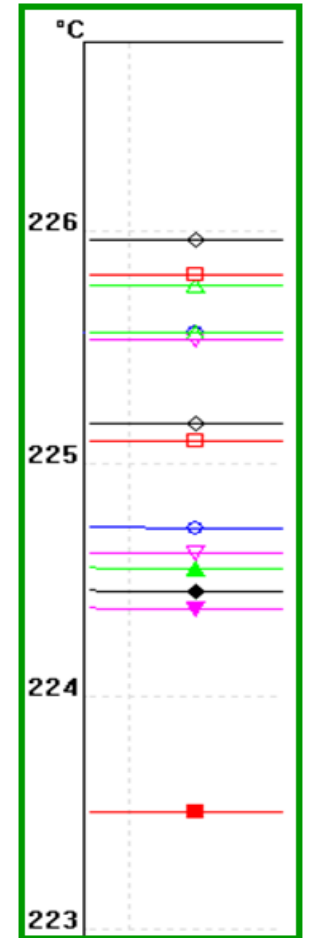


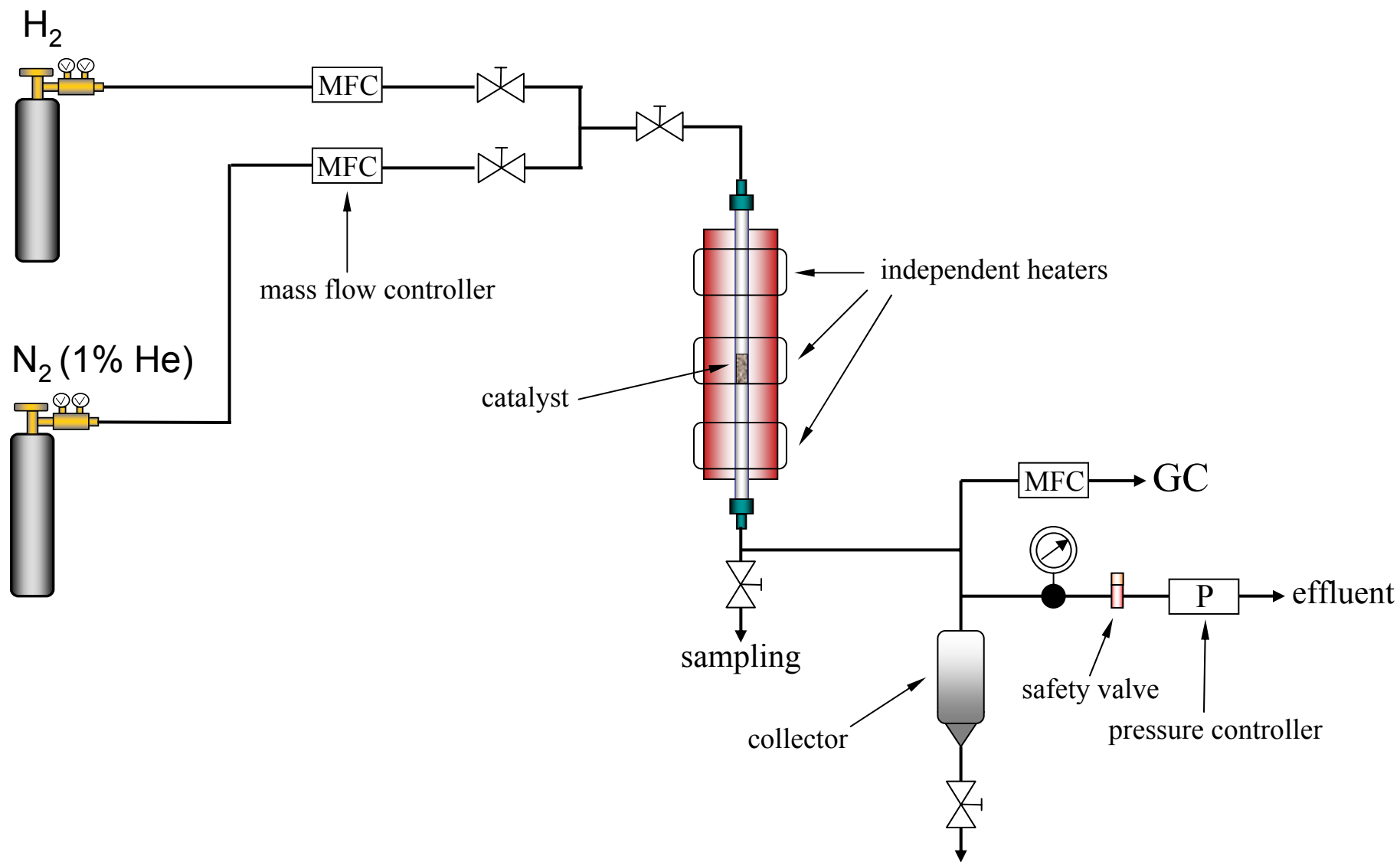
A. Tokarev, A. Kirilin

Initial state: 1 heater



Current state:
3 independent heaters

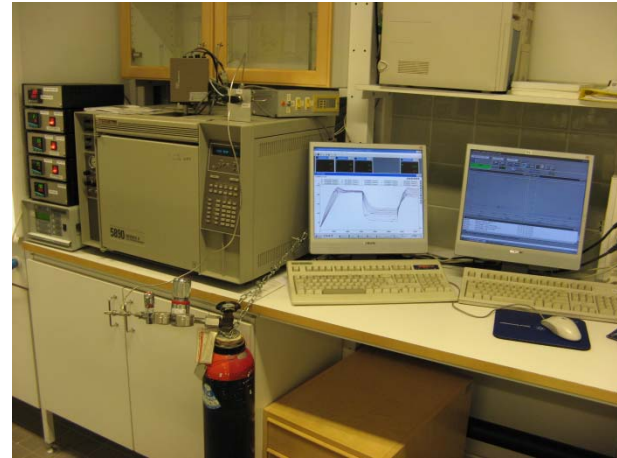




Analysis of products



3rd version



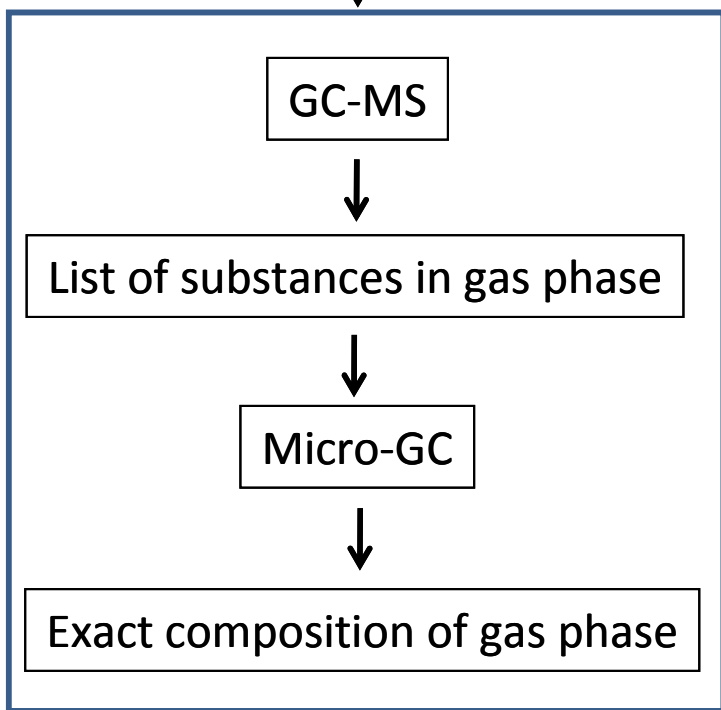
On-line



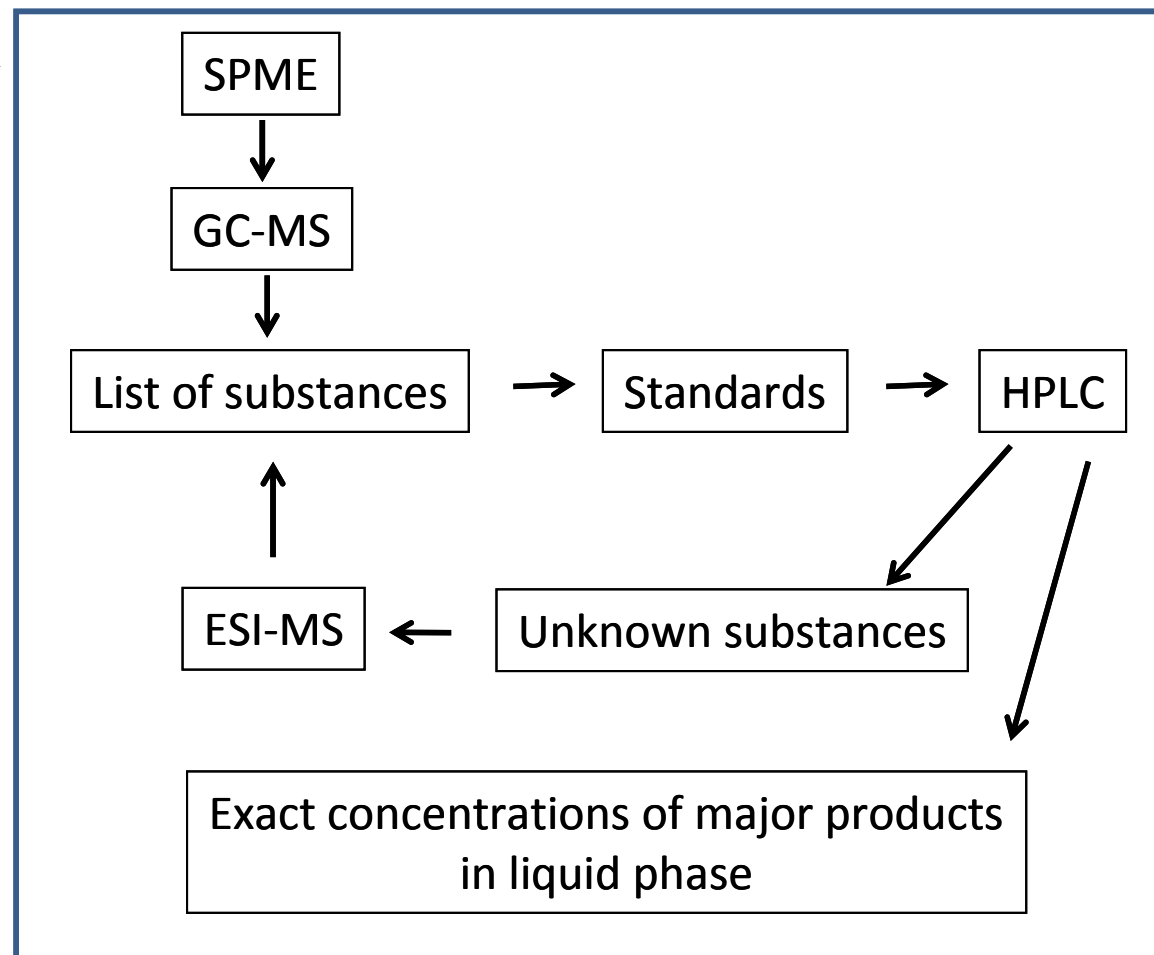
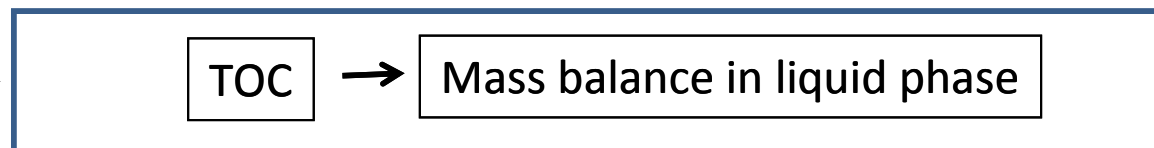
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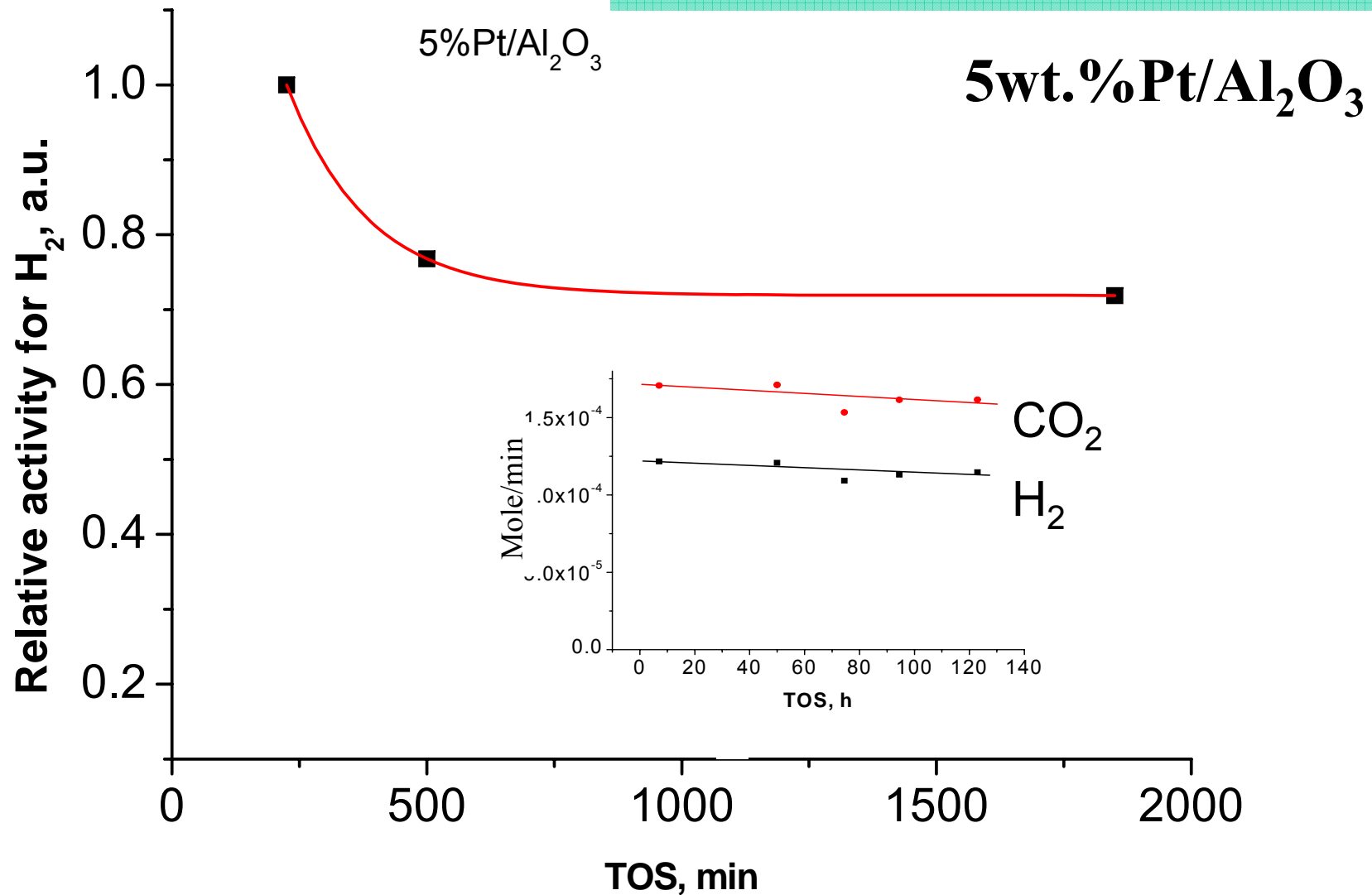
APR products



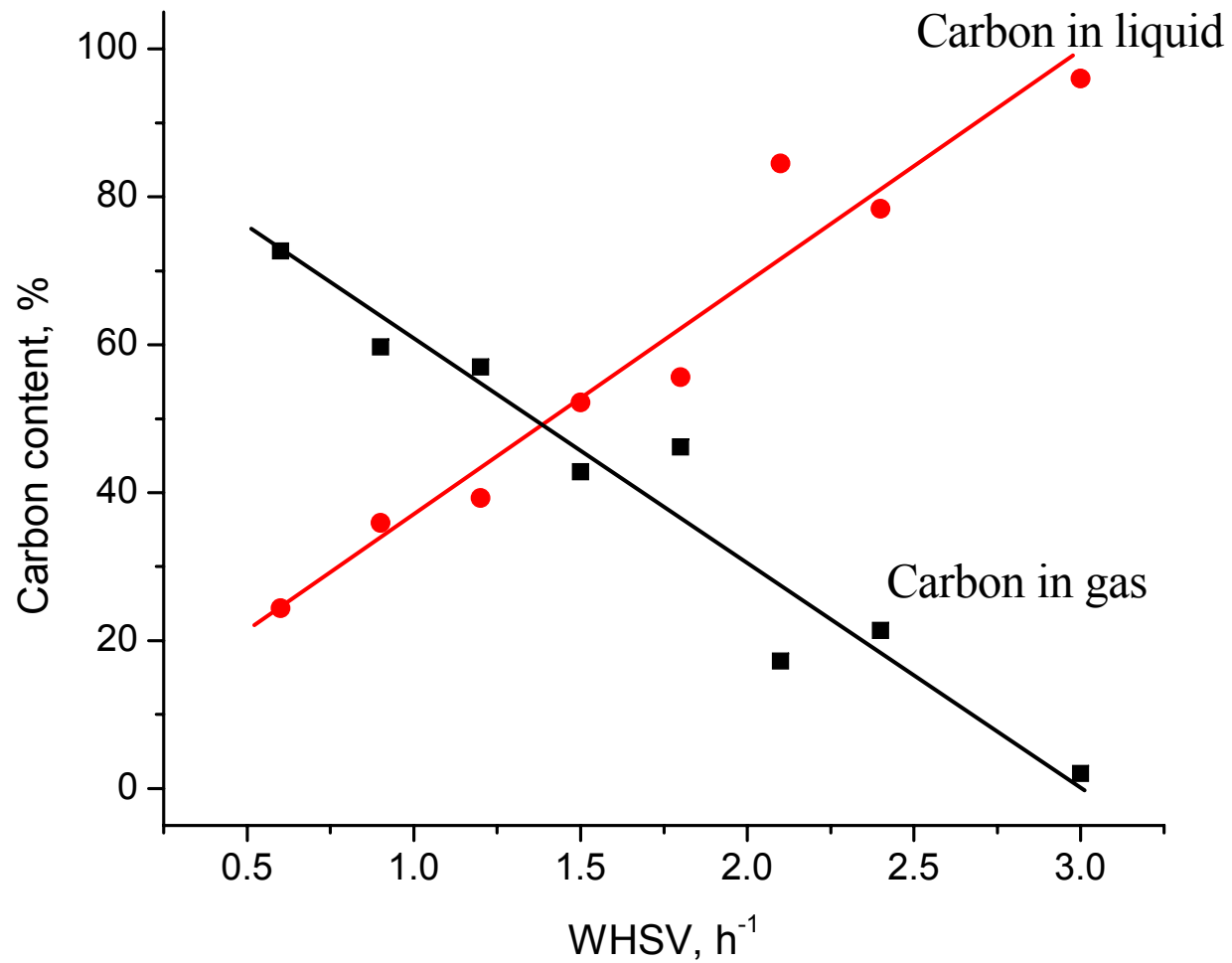
HPLC



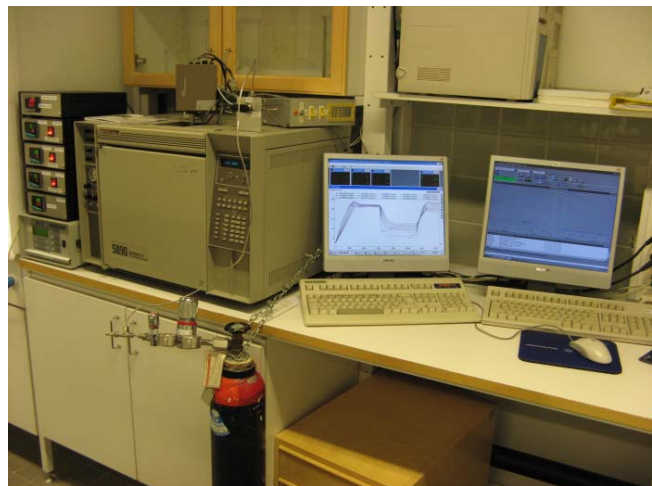
Time-on-stream



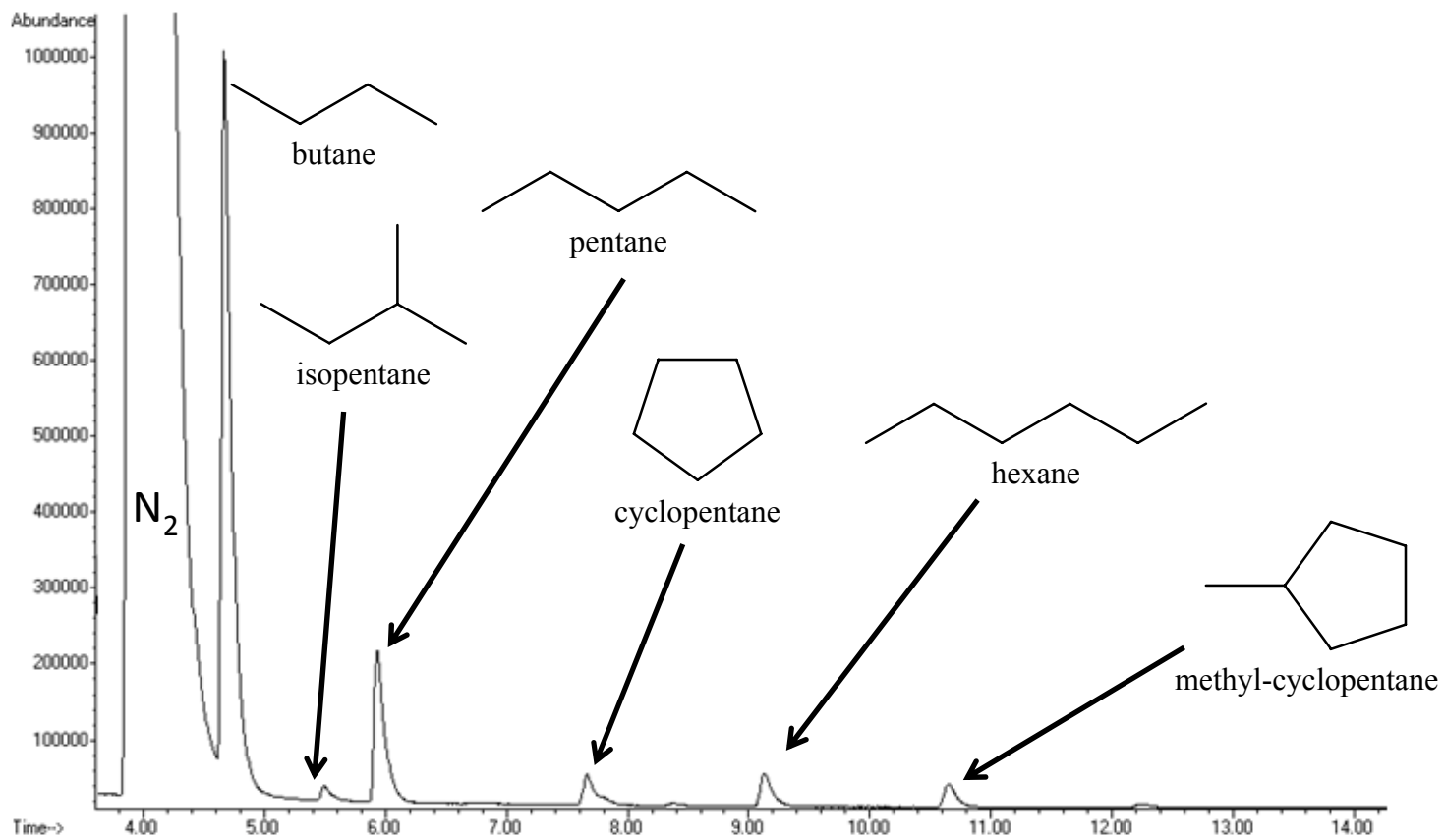
In-situ reduction at 250°C. V'(sorbitol) = 0.1ml/min, V'(N₂) = 30 ml /min, 225°C



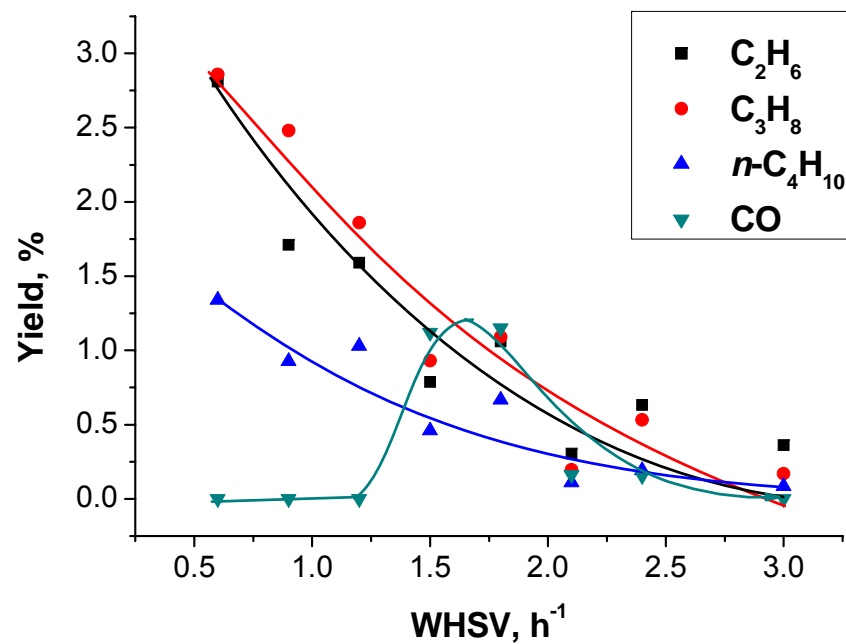
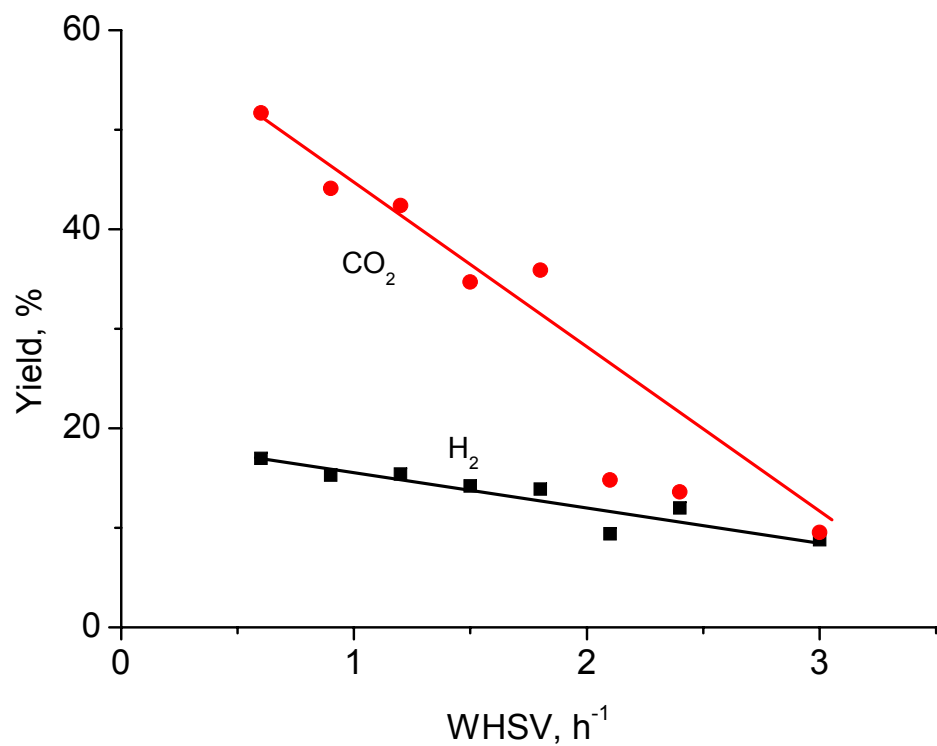
225°C, 29.3 bar, 10 wt.% sorbitol solution, 30 ml/min nitrogen flow rate. Pt/Al₂O₃



Gas-phase

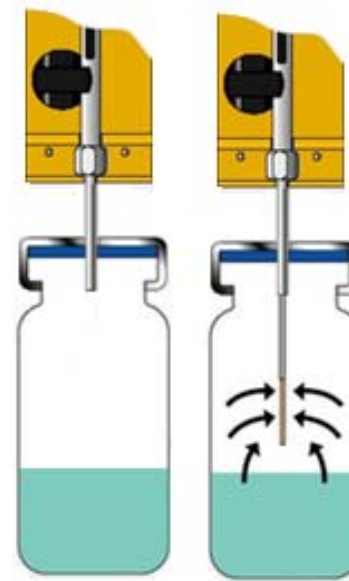
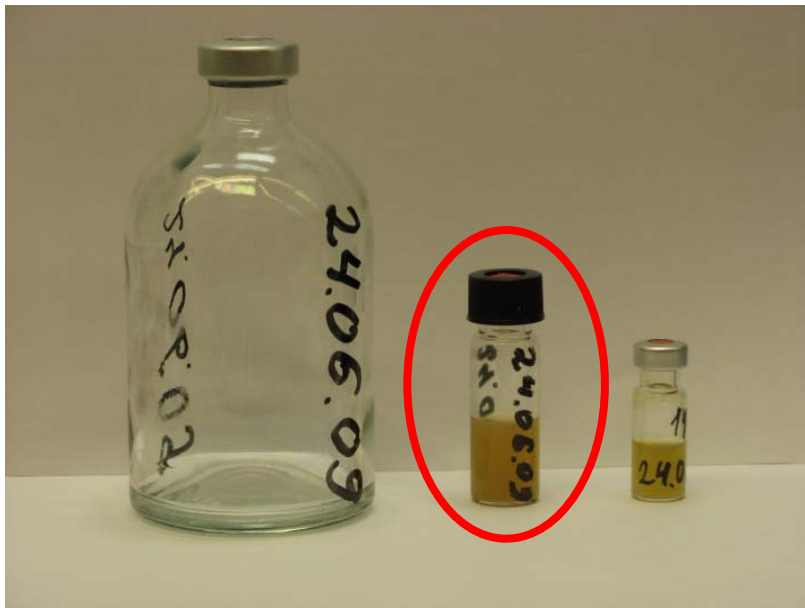


A. Tokarev

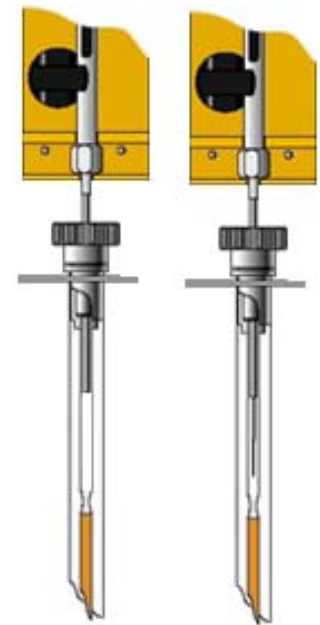


225°C, 29.3 bar, 10 wt.% sorbitol solution, 30 ml/min nitrogen flow rate. $\text{Pt}/\text{Al}_2\text{O}_3$

Soild phase micro extraction

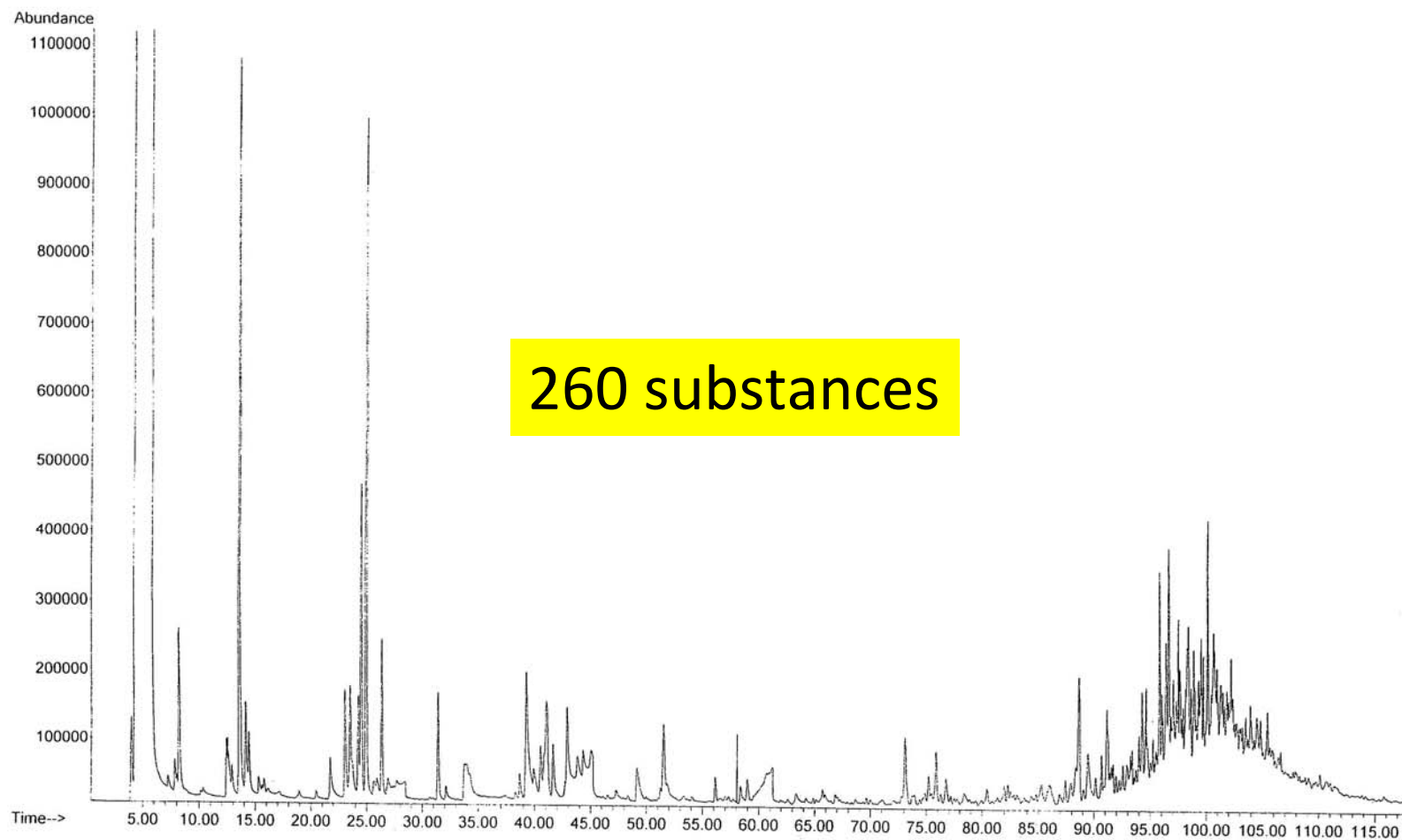


Adsorption
magnet stirrer
50 °C, 30 min

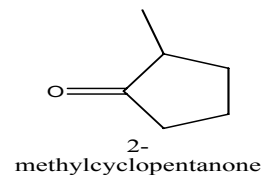
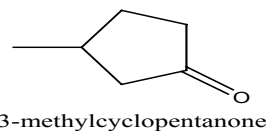
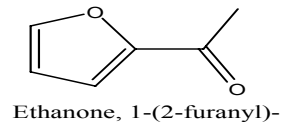
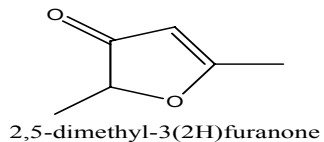
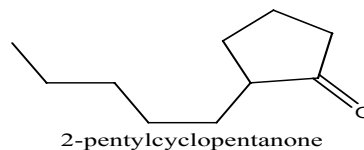
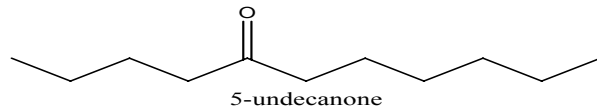
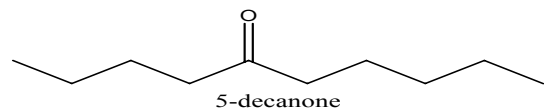
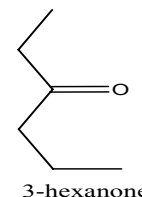
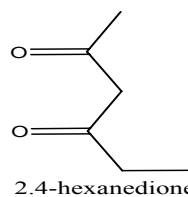
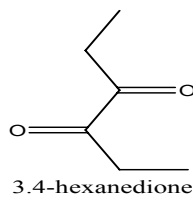
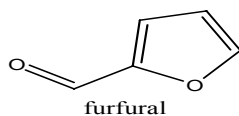
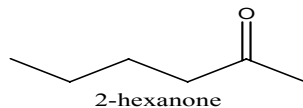
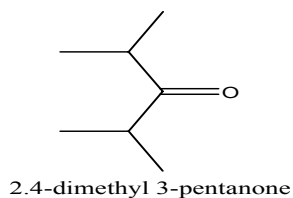
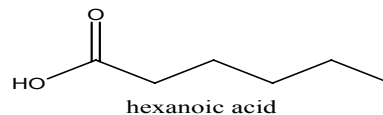
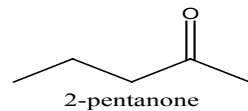
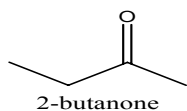
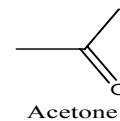
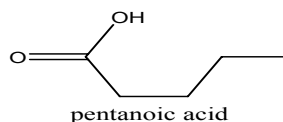
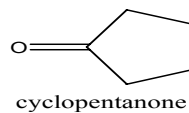
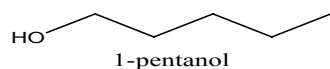
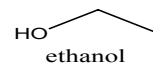
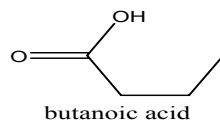
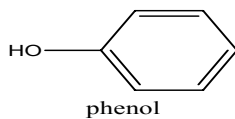
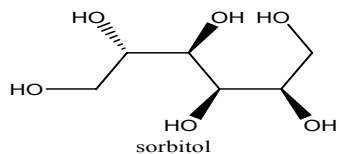


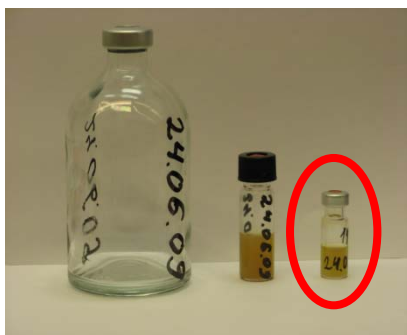
Desorption
T-ramp from 30 to
200 °C in 30 min

SPME & GC-MS

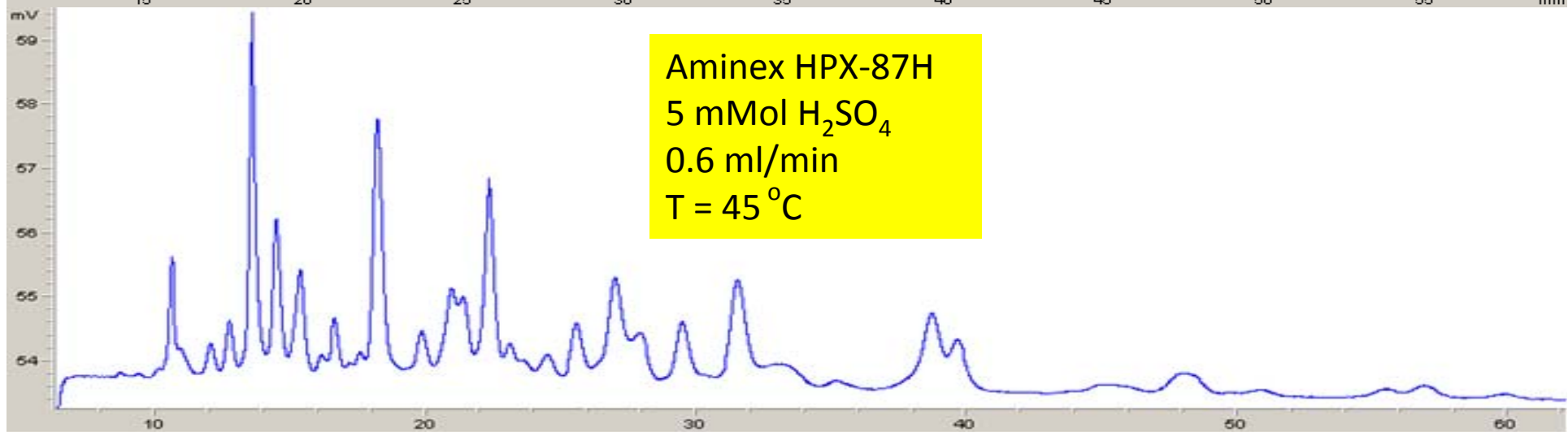
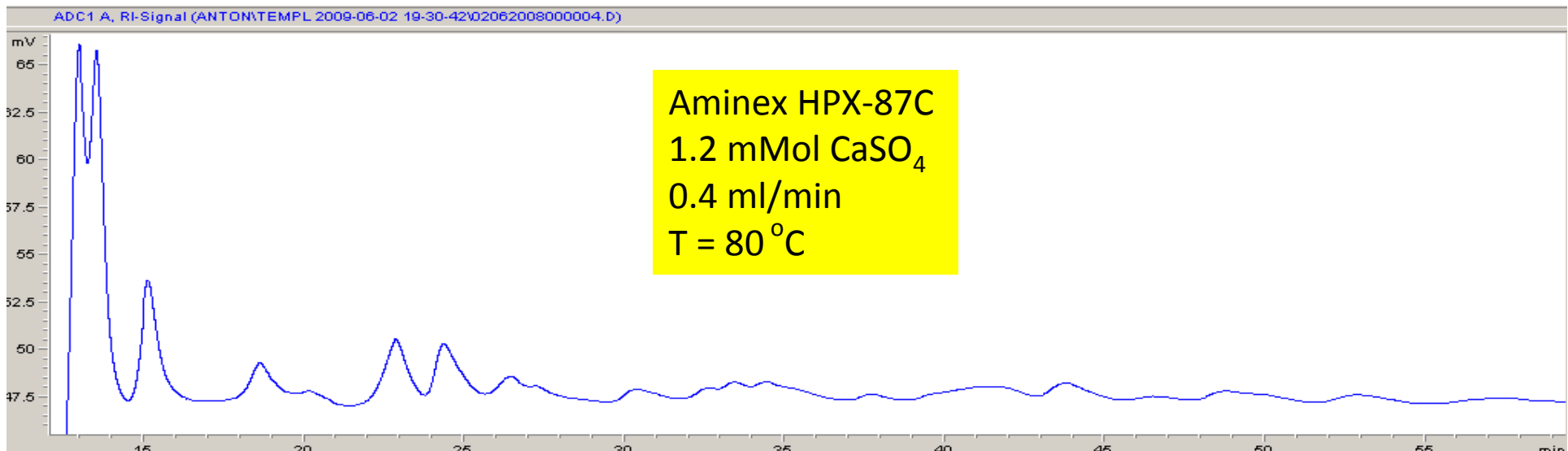


SPME & GC-MS: Top 25

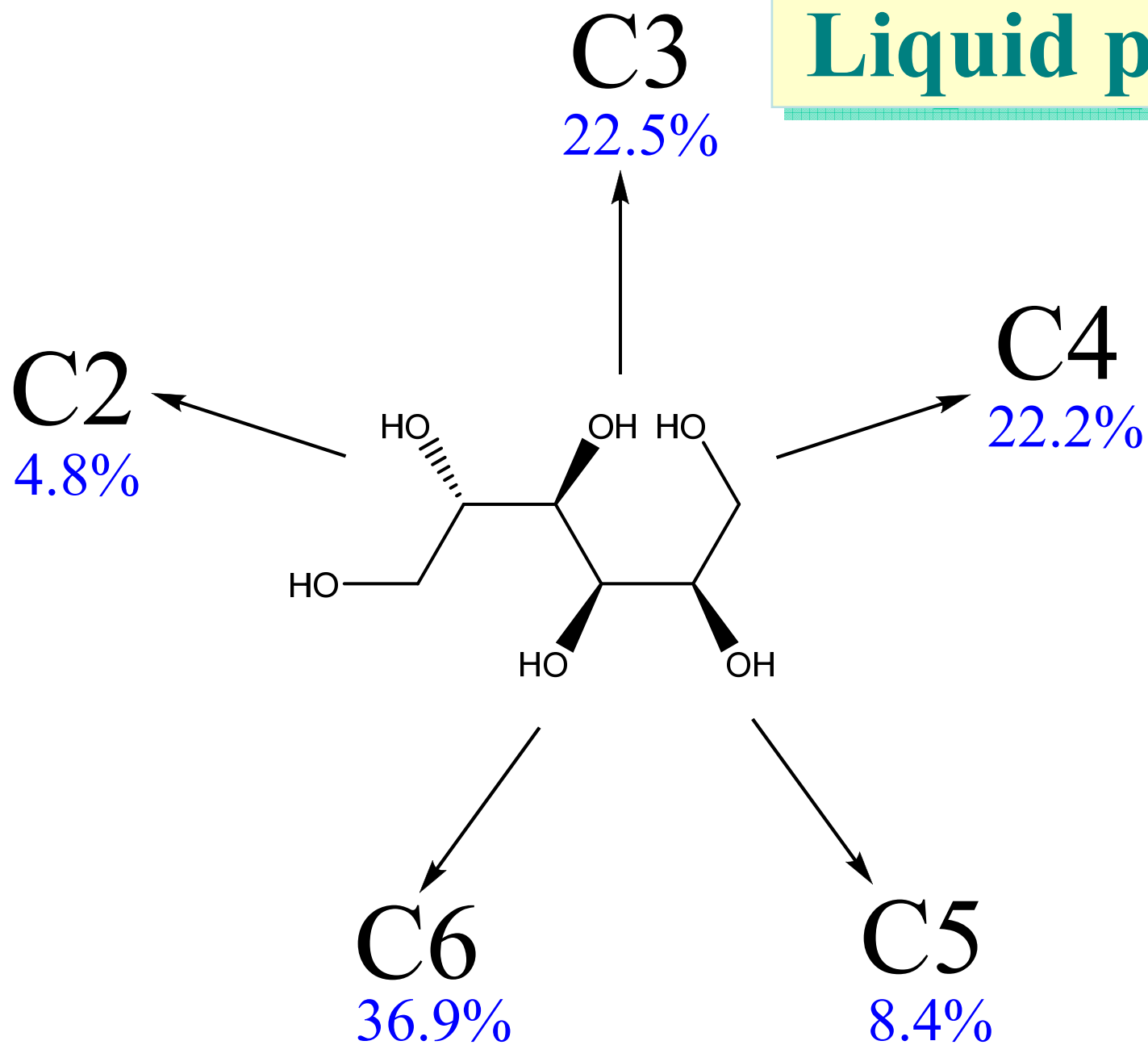




HPLC



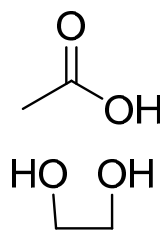
Liquid phase



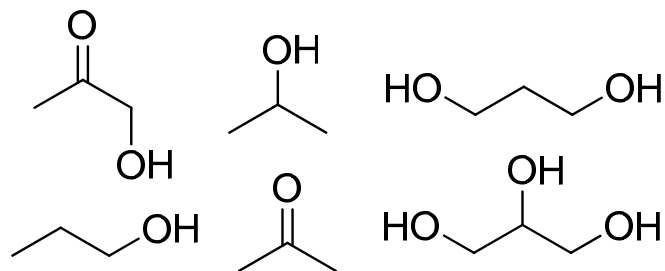
A. Kirilin

Liquid phase

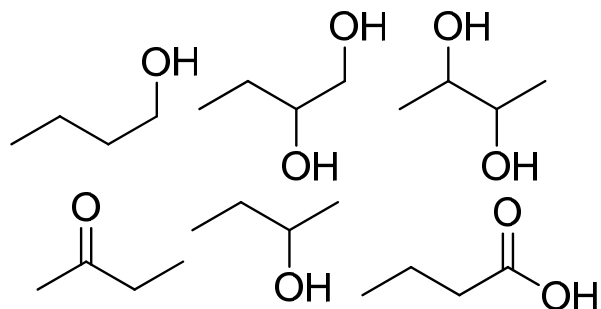
C2



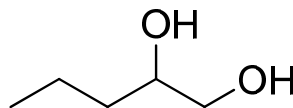
C3



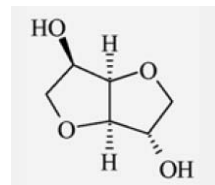
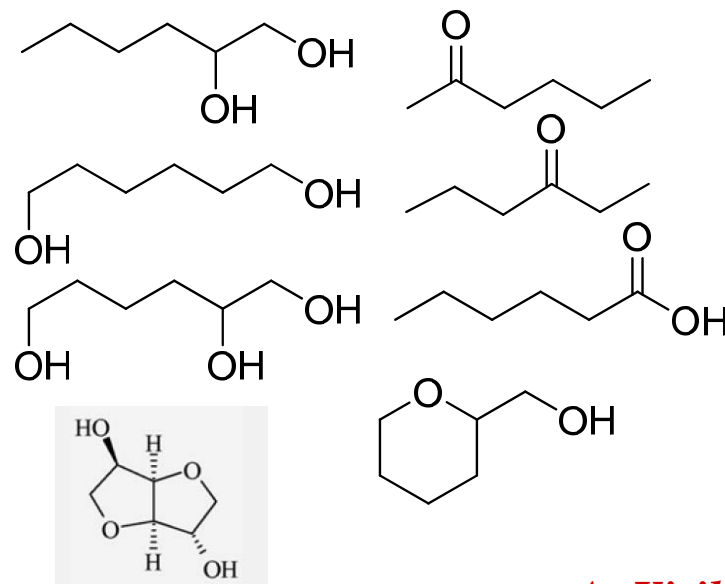
C4



C5



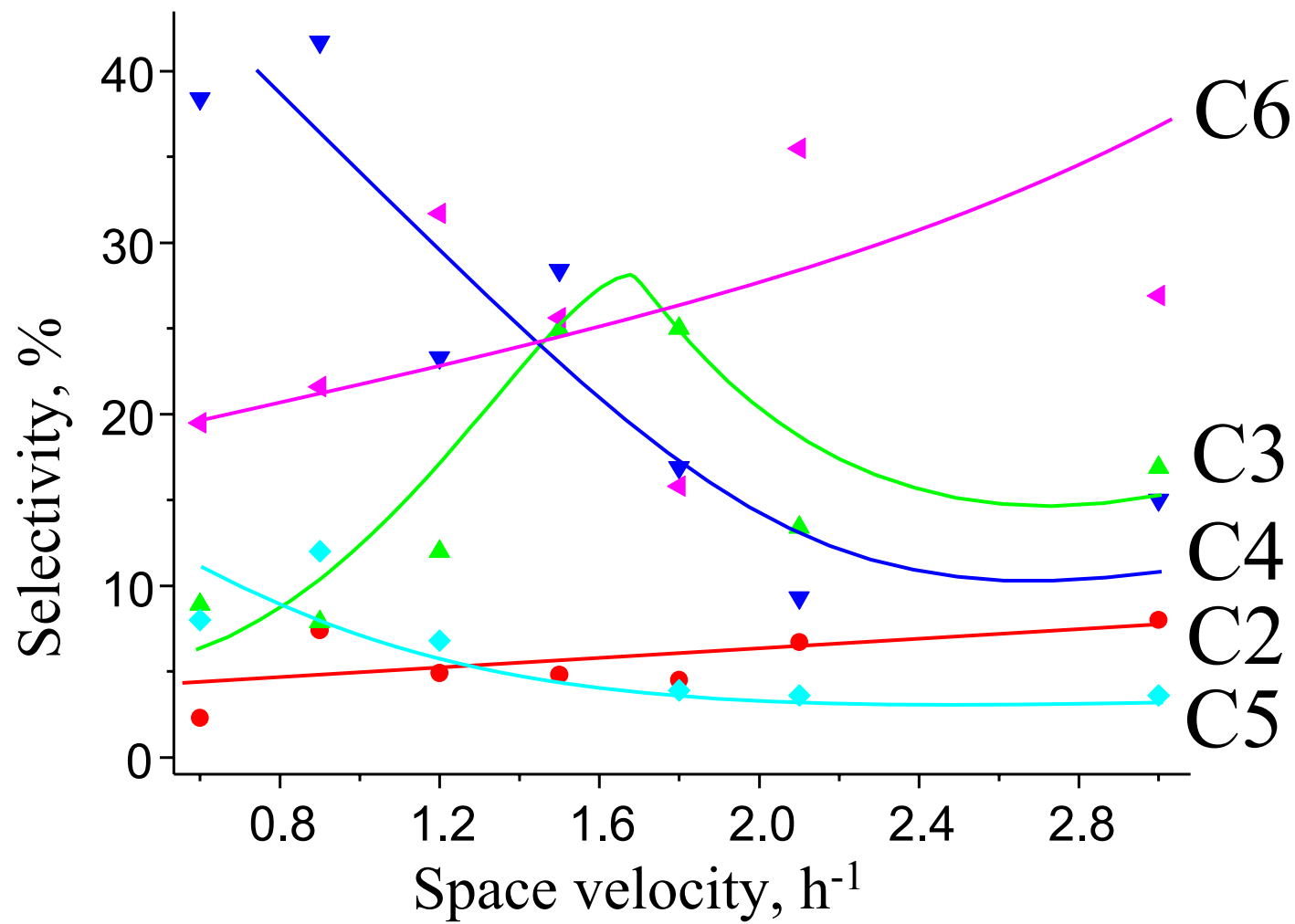
C6



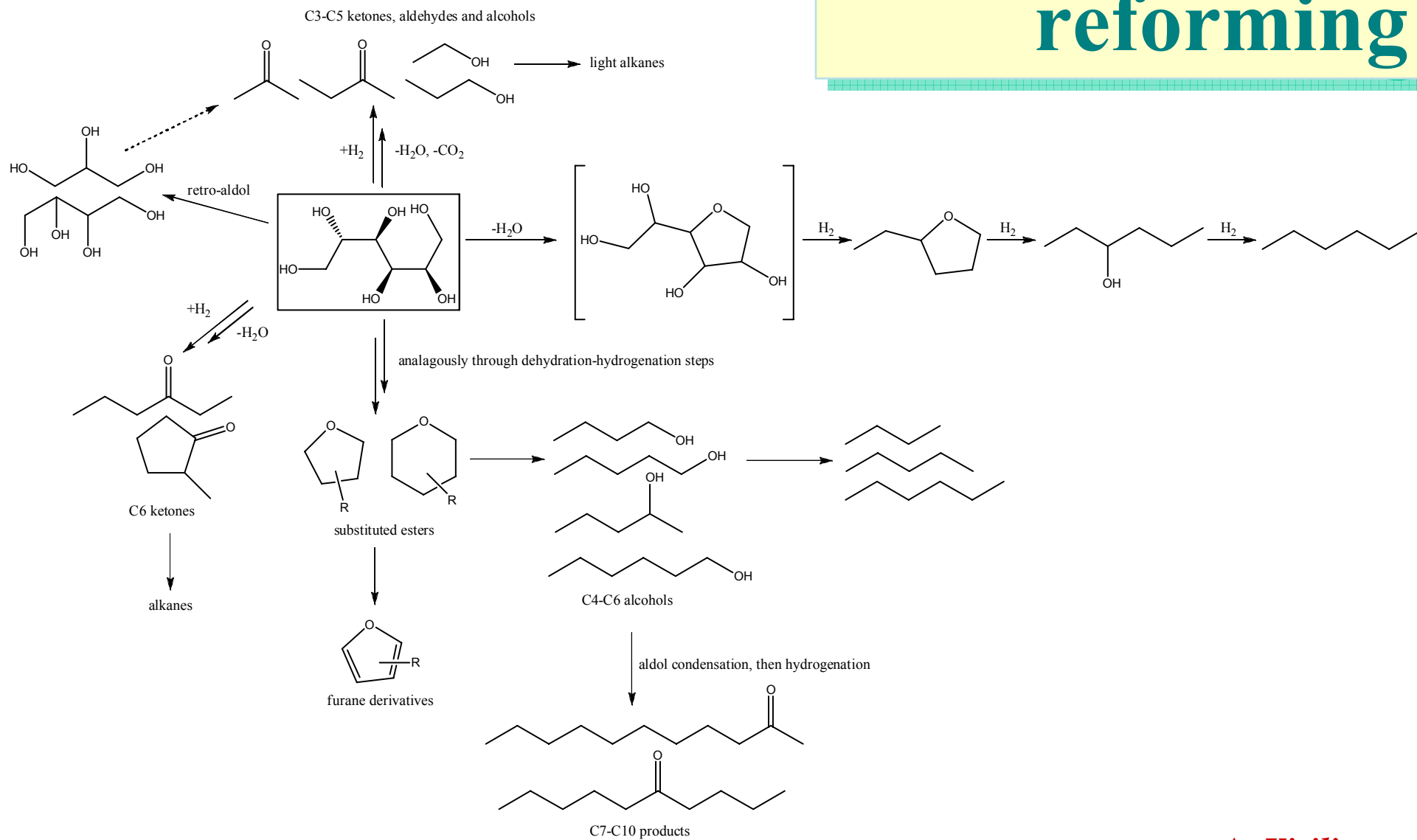
isosorbide

A. Kirilin

Liquid phase



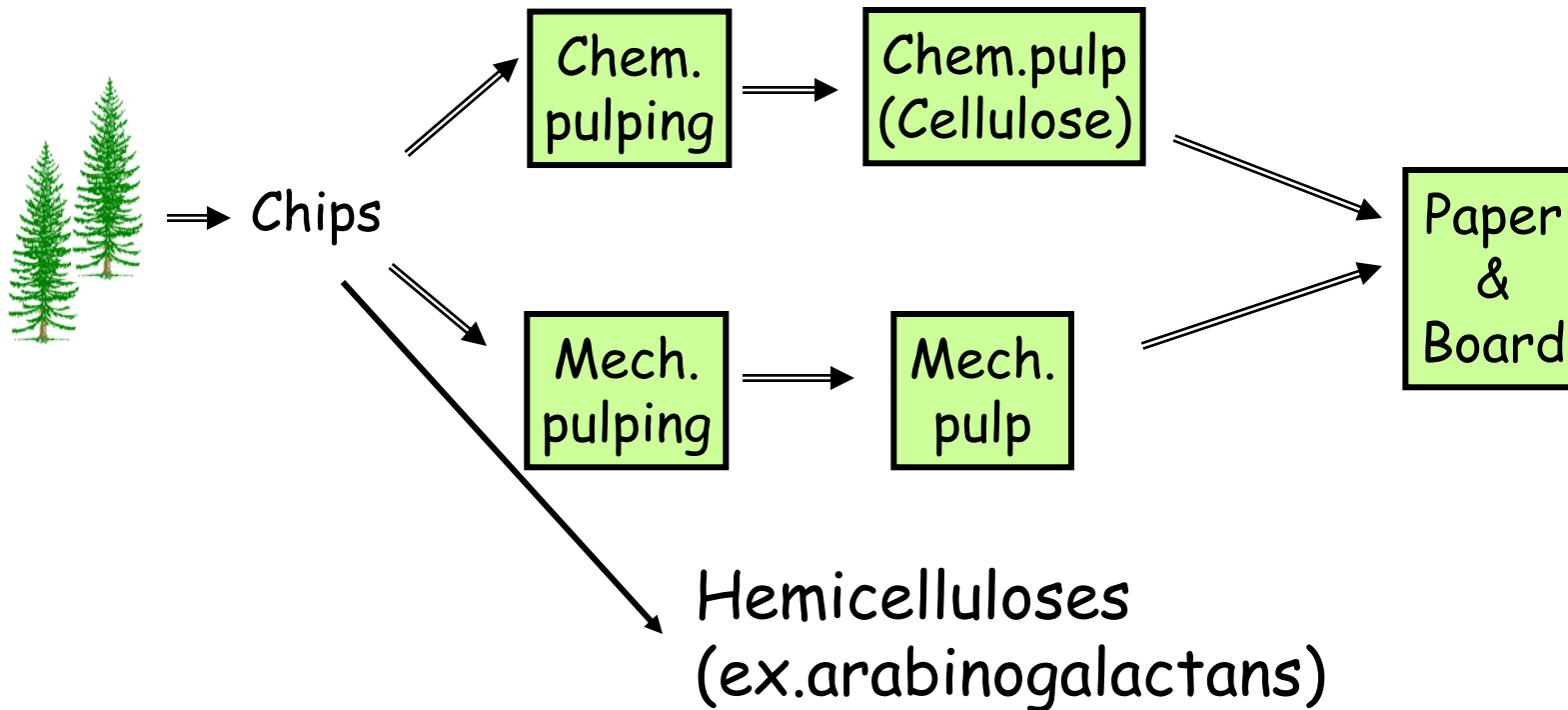
Aqueous phase reforming



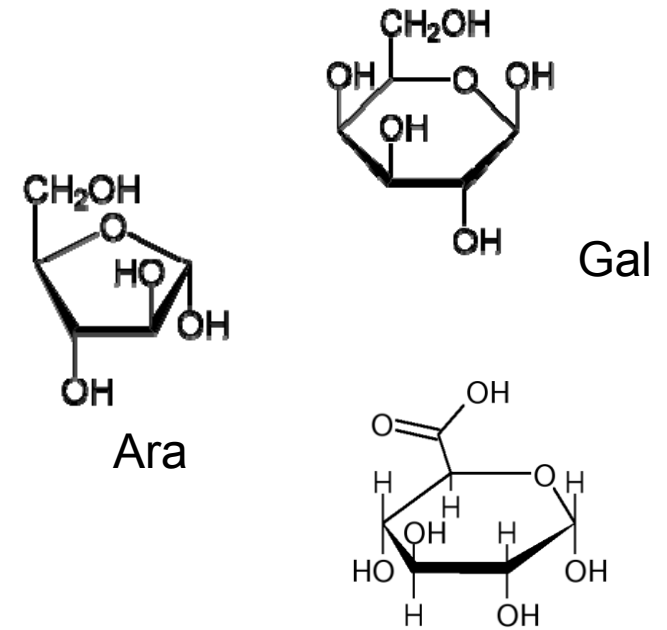
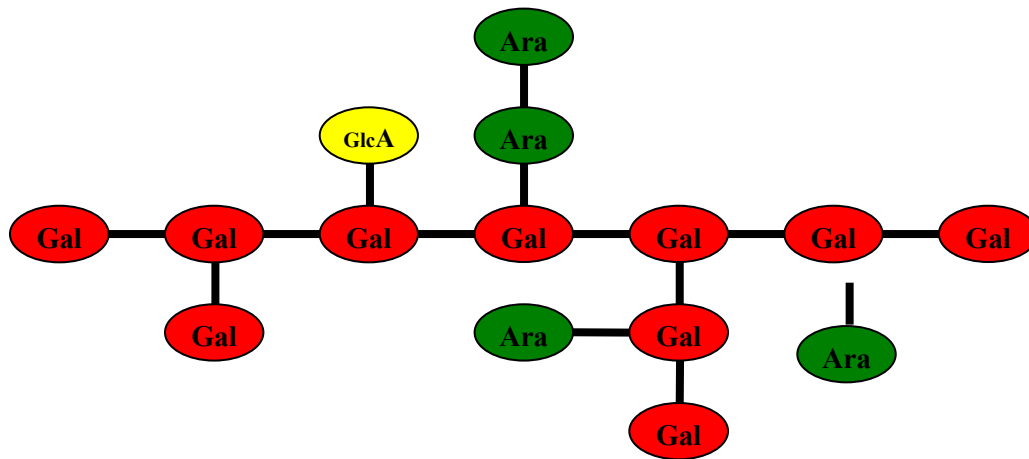
A. Kirilin

Hemicellulose

Many opportunities



Arabinogalactans



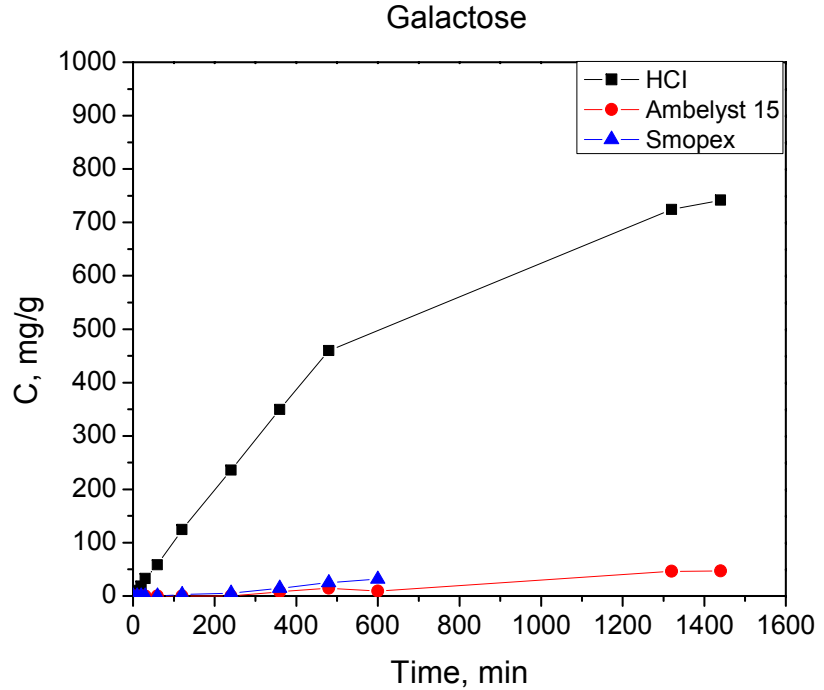
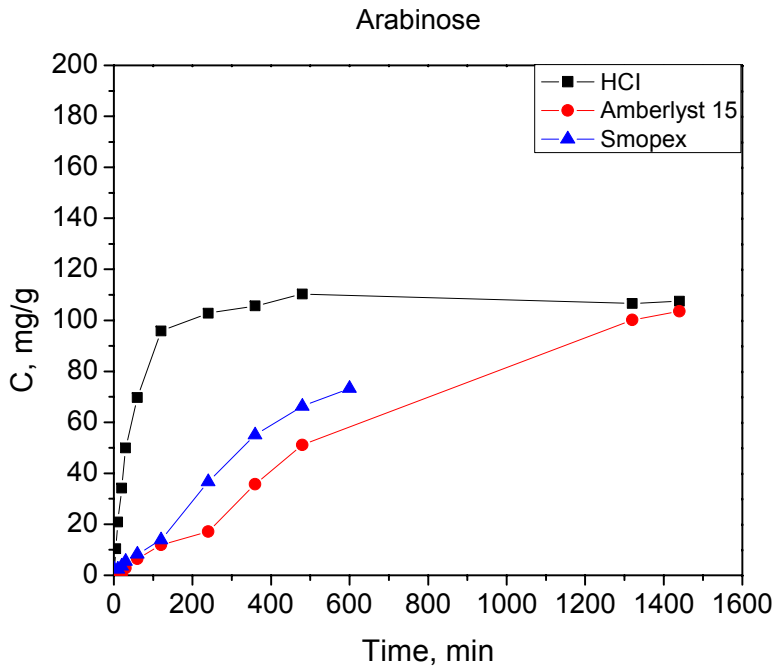
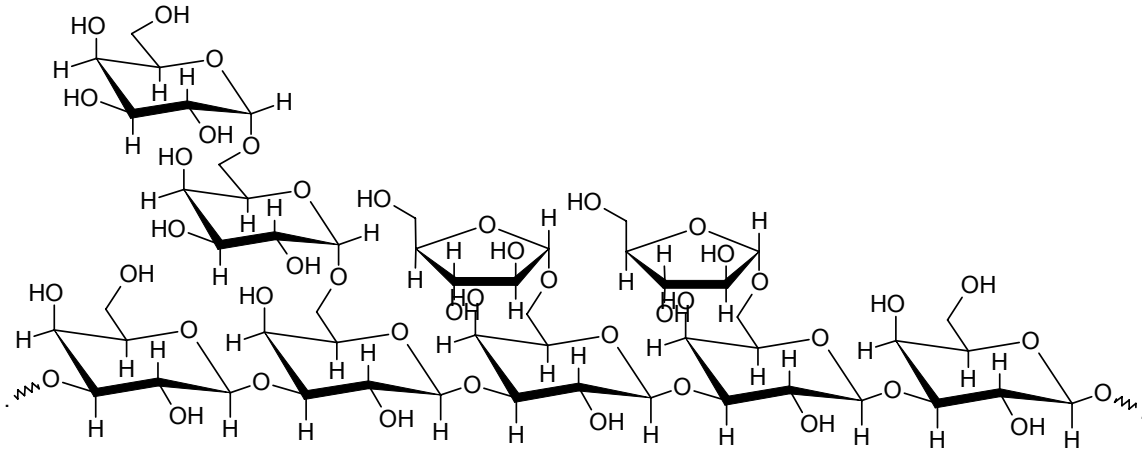
- Backbone: β -galactopyranose
- D-galactopyranose, L-arabinofuranose and D-glucuronic acid side chains.

- **Potential for many products !**

Ara:Gal:GlcA ~ 19:80:2

Molar mass 20,000 – 100,000

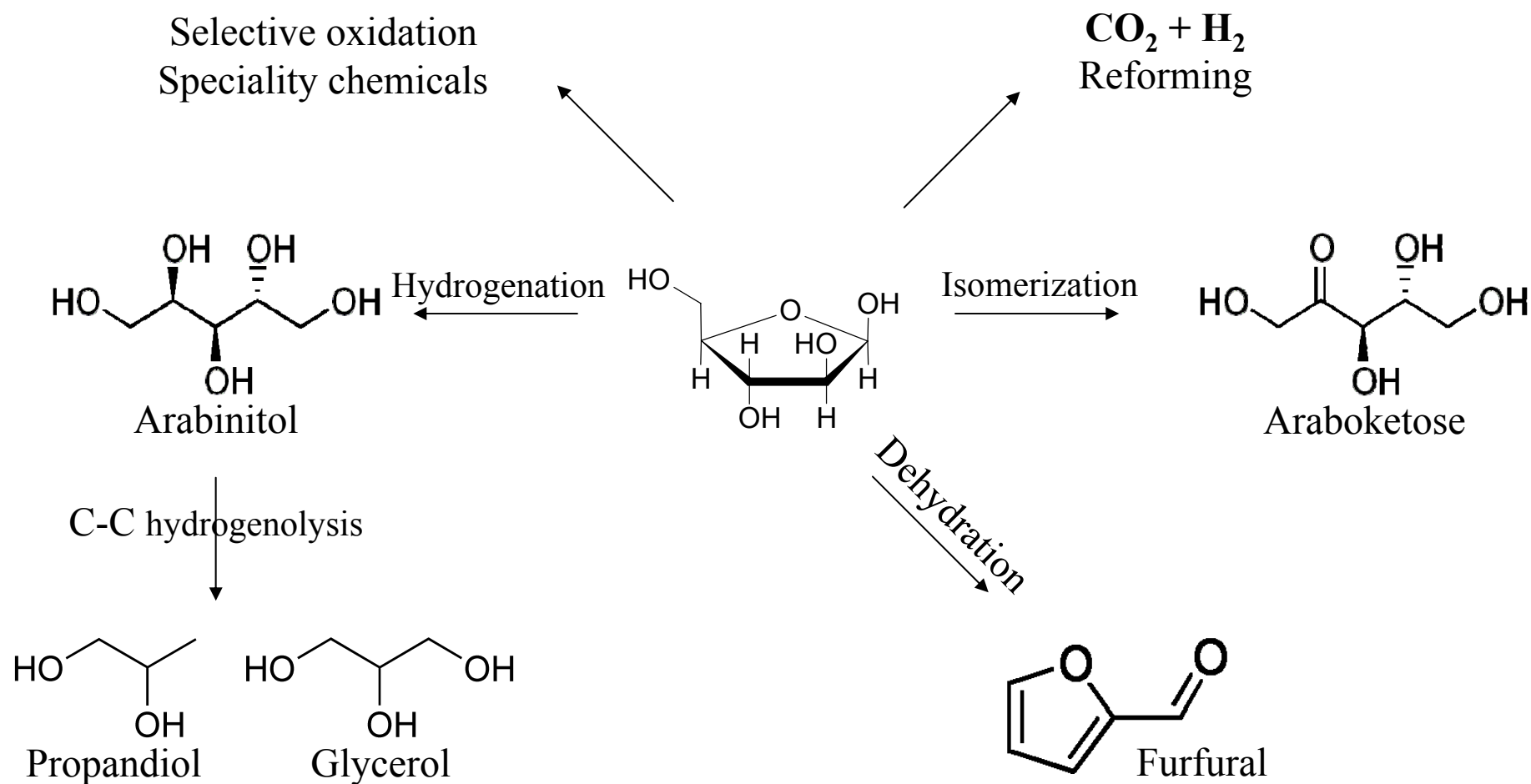
Hydrolysis



Selective cleavage

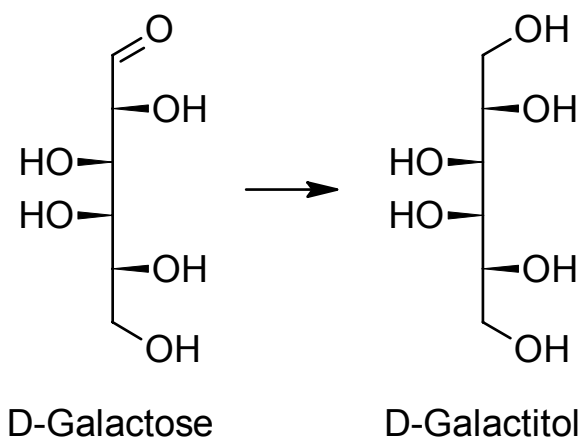
B. Kusema

Transformation of monomers



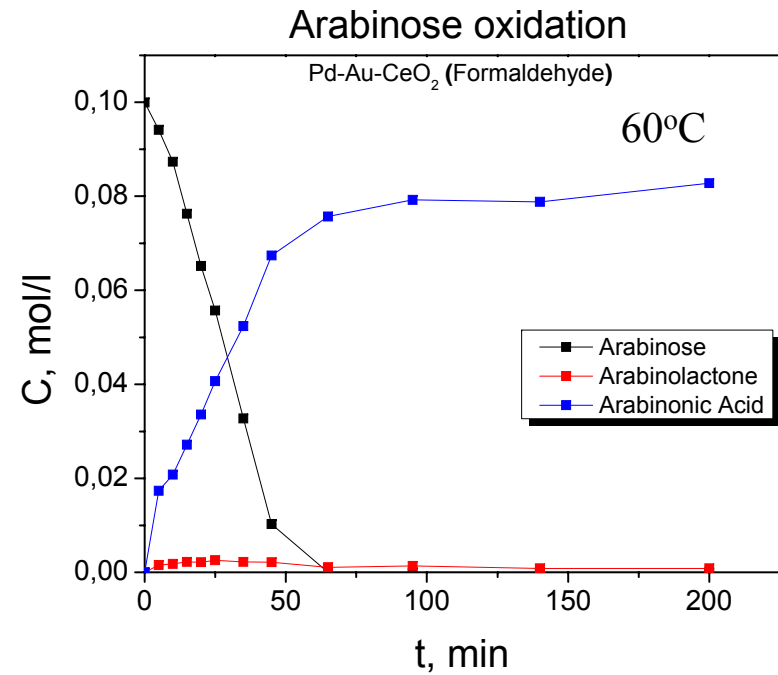
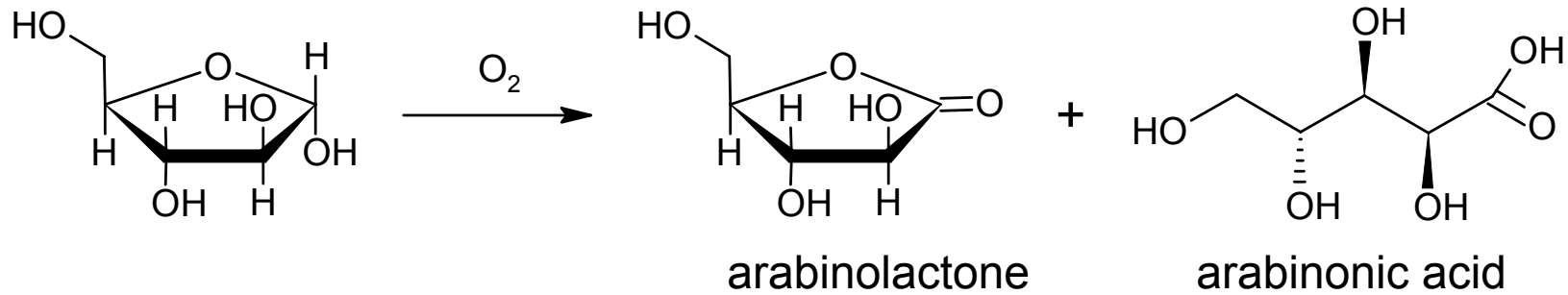
Hydrogenation

Ru/C (Sibunit)



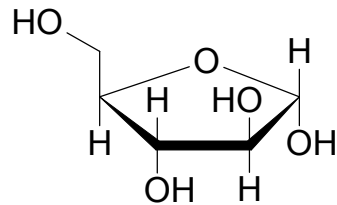
V. Sifontes

Arabinose oxidation

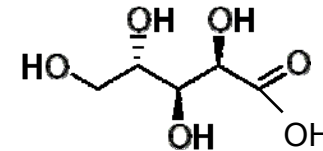


B. Kusema

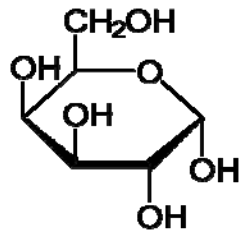
Oxidation of aldehydes/alcohols



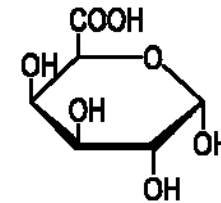
Arabinose



Arabinonic acid



Galactose



Galacturonic acid

- Temperature 60°C
- pH 6 - 10
- O₂ flow rate 2.5 ml/min
- P atm.

Preparation

Impregnation: **Not Good!**

Au has a lower melting point and a lower affinity for metal oxides than Pd and Pt.

Also, during calcination of HAuCl_4 , chloride ion markedly enhances the coagulation of gold particles

Preparation

- **Co-precipitation**: well-mixed precursors, for example, hydroxide, oxide, with the metal component of the support by coprecipitation.
- These precursor mixtures are then transformed during calcination in air at temperatures above 550K into metallic Au particles strongly attached to the crystalline metal oxides such as Fe_2O_3 , Co_3O_4 .

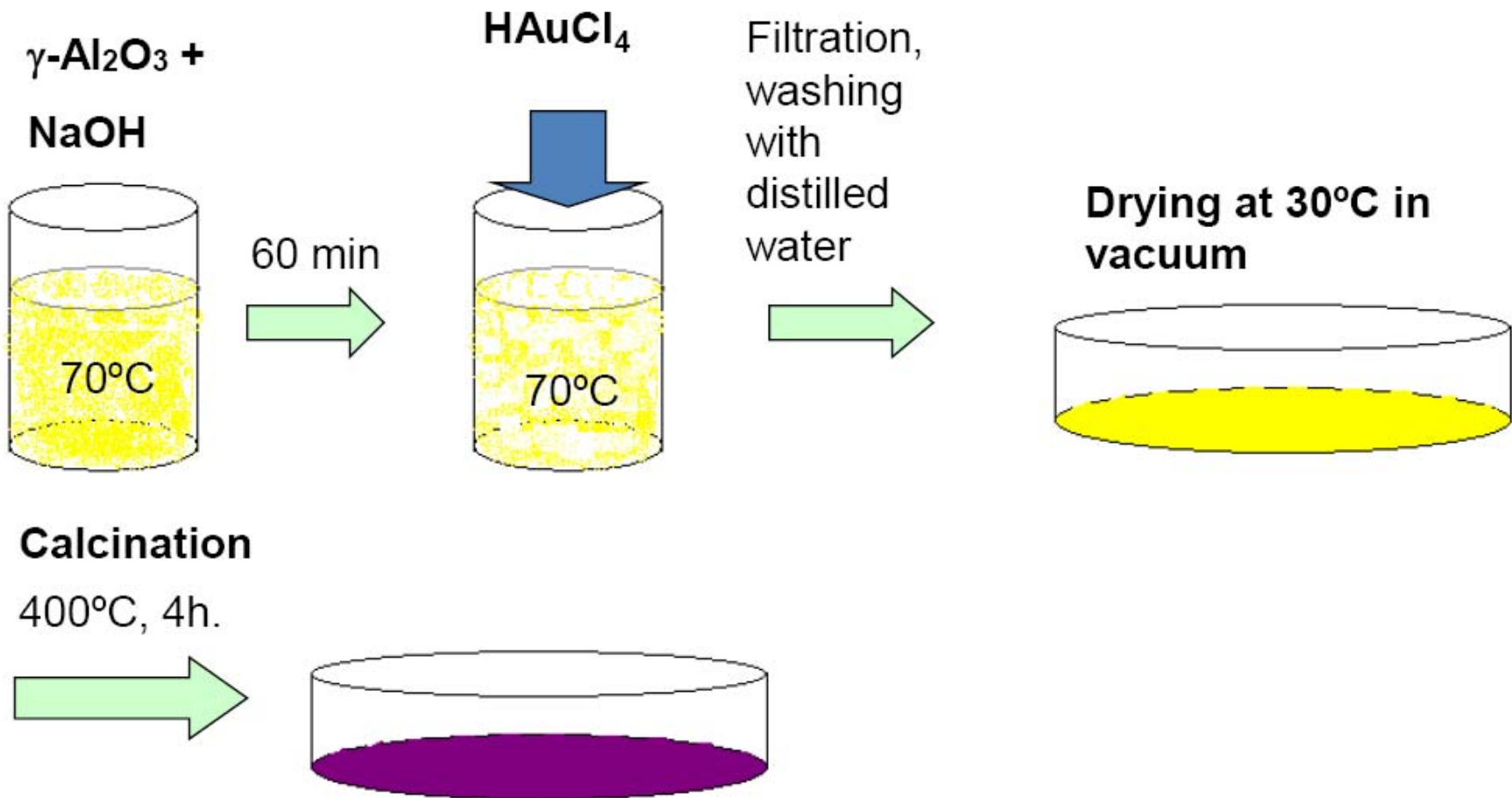
Deposition-precipitation

- Deposition of Au compounds, Au hydroxide, to the surface of a metal oxide
- Due to the amphoteric properties of $\text{Au}(\text{OH})_3$, the pH of aqueous HAuCl_4 solution is adjusted at a fixed point in the range of 6 to 10, and is selected primarily based on the isoelectric points (IEP) of the metal oxide supports.

Deposition-precipitation

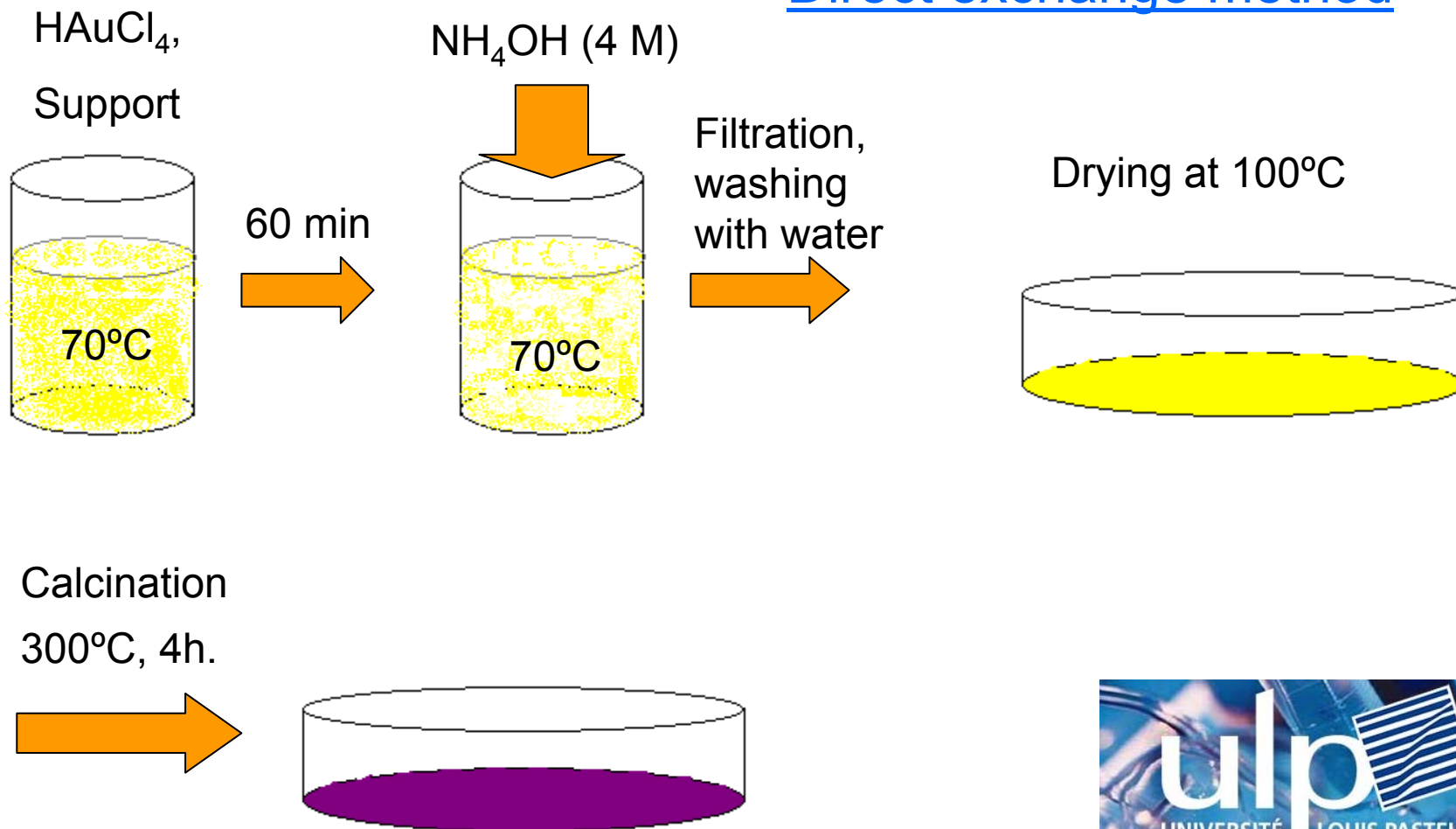
- Deposition of Au compounds, Au hydroxide, to the surface of a metal oxide
- It is not applicable to metal oxides, the IEPs of which are below 5, and to activated carbon. Gold hydroxide cannot be deposited on SiO_2 (IEP=2); $\text{SiO}_2\text{-Al}_2\text{O}_3$ (IEP=1).

Conventional DP



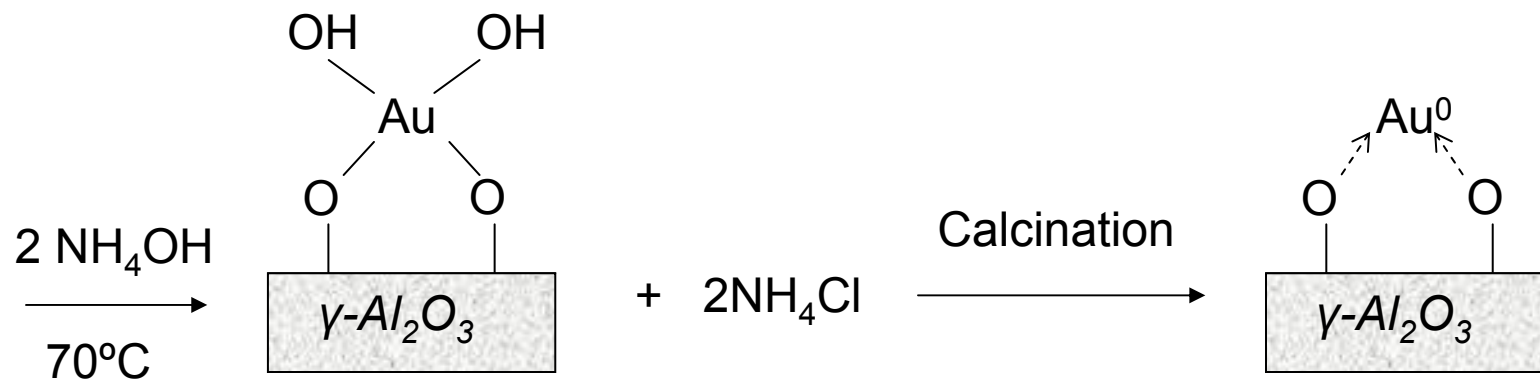
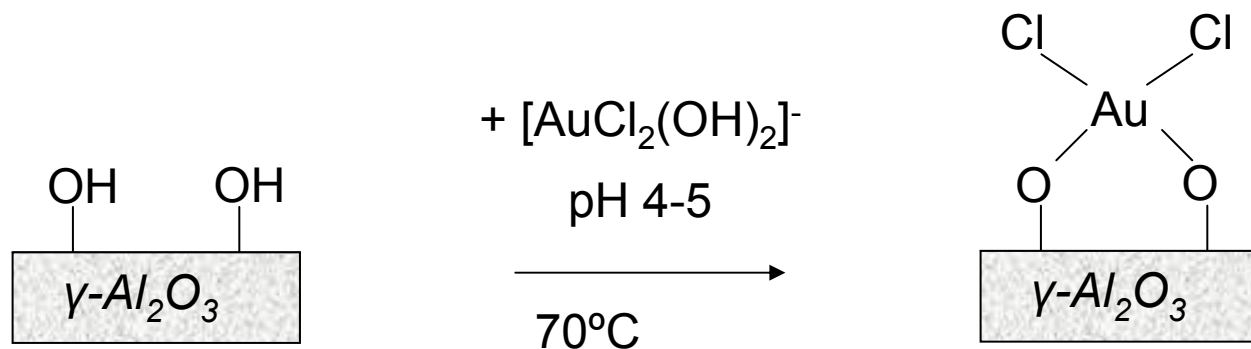
Gold on metal oxides

Direct exchange method



Direct exchange

Scheme of the active component formation

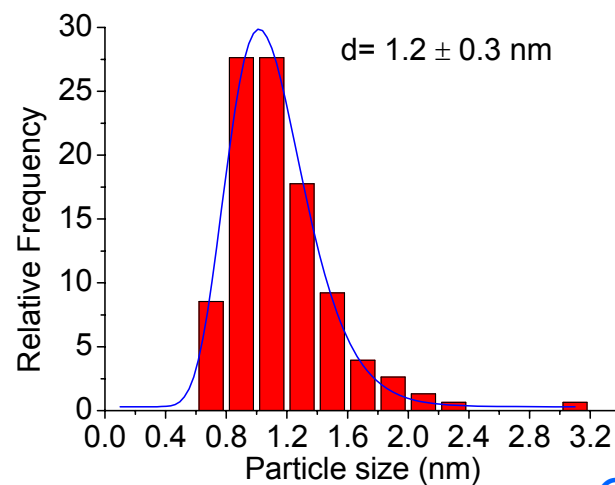
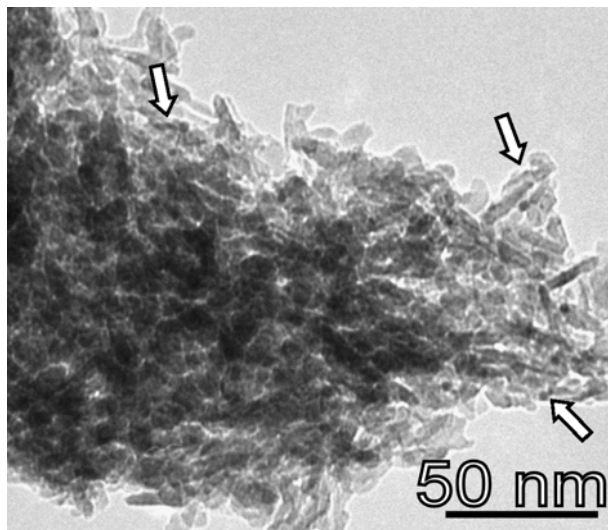
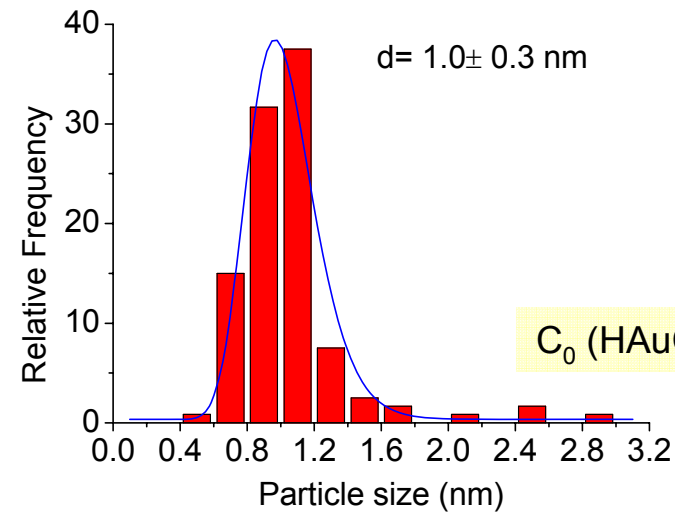
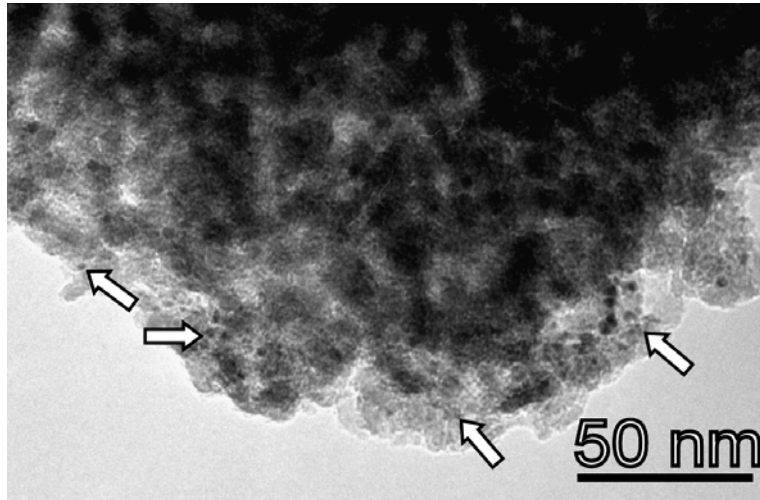


+ Complexes of ammonia with gold

Can be applied for Al_2O_3 , TiO_2 , CeO_2 , ZrO_2 only

Changing dispersion

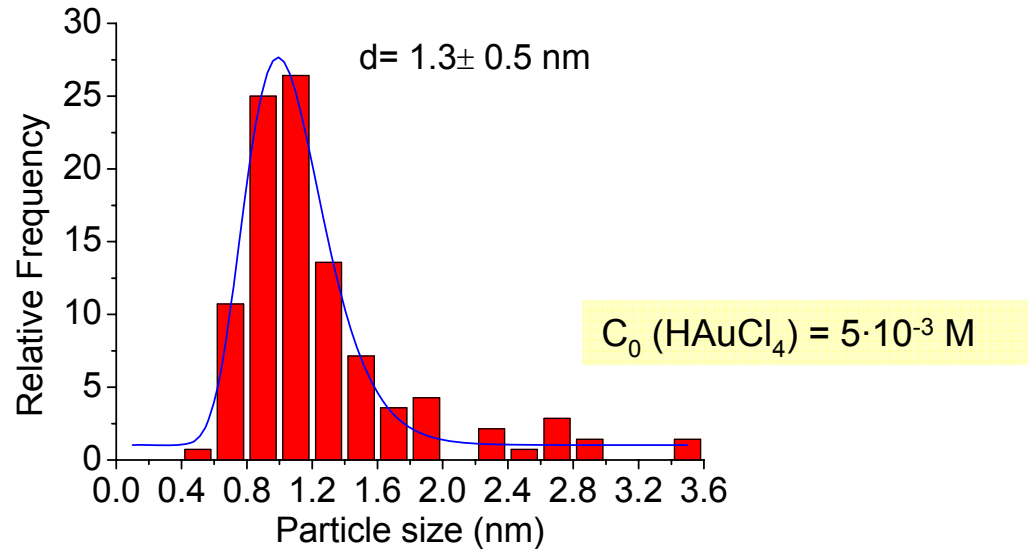
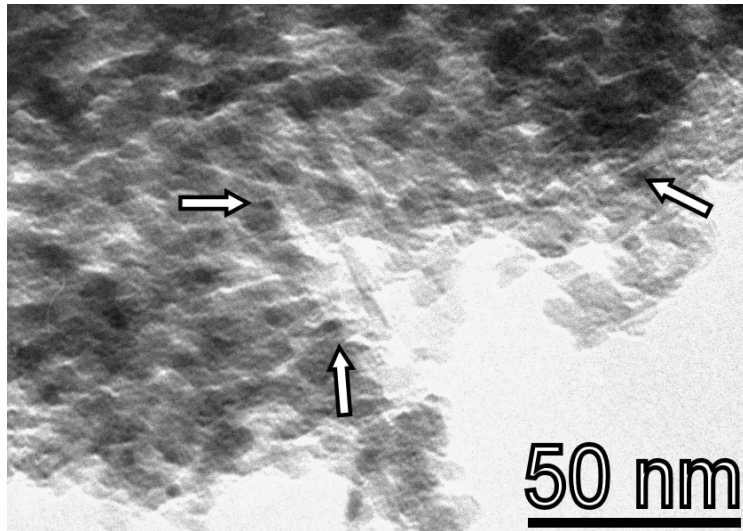
2 wt. % Au/Al₂O₃



Olga Simakova, 2009

Changing dispersion

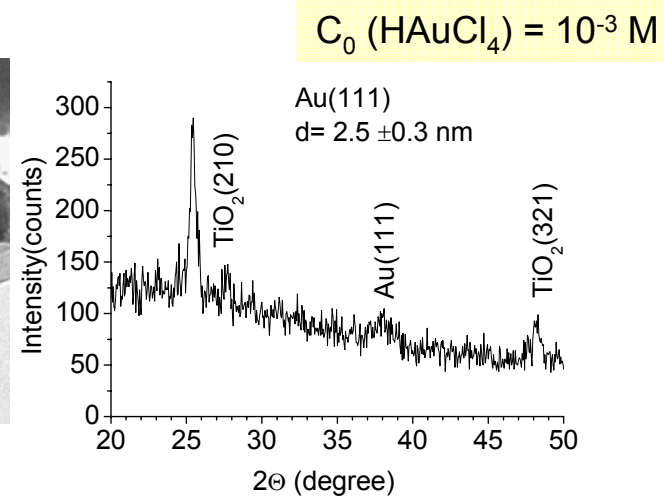
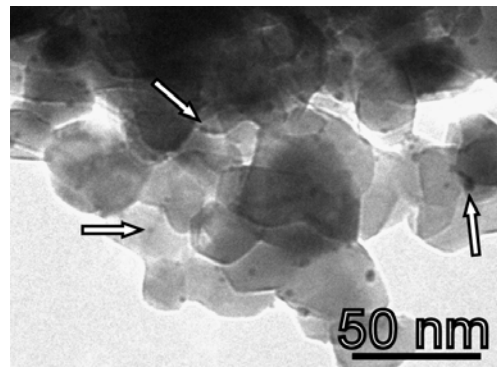
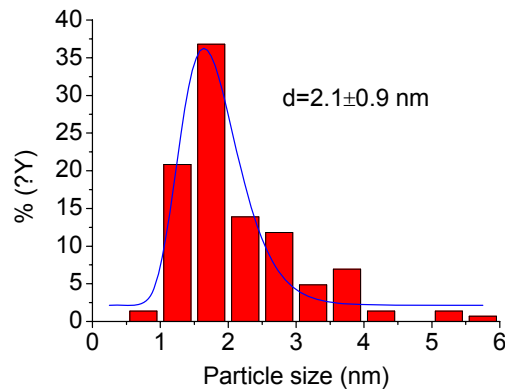
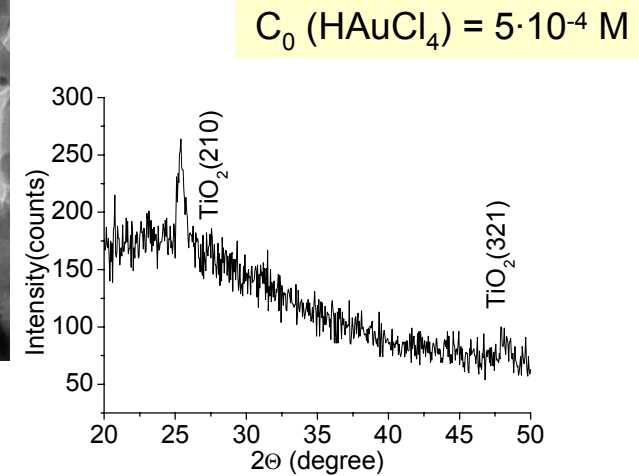
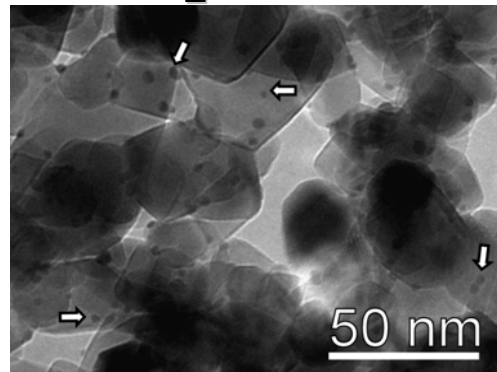
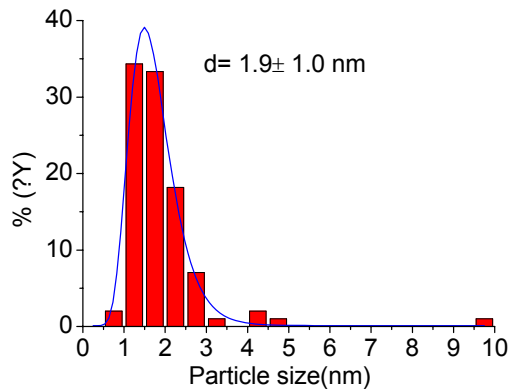
2 wt. % Au/Al₂O₃



Increasing of concentration of HAuCl₄ solution results in increasing of supported gold particle size

Changing dispersion

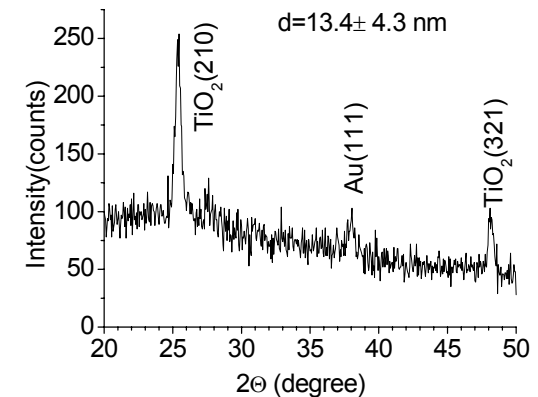
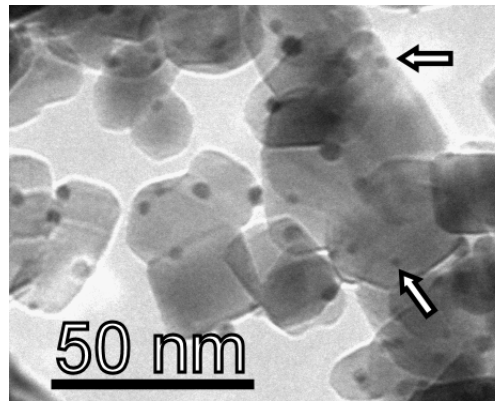
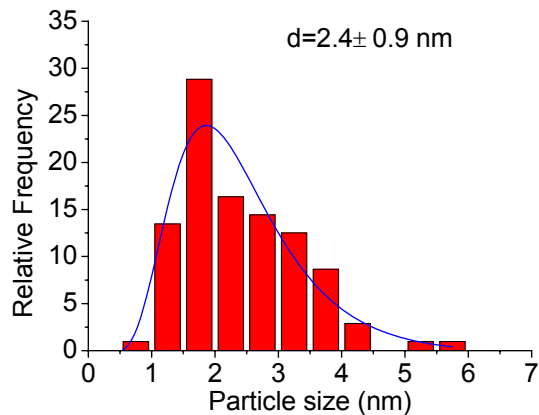
2 wt. % Au/TiO₂



Changing dispersion

2 wt. % Au/TiO₂

$C_0(\text{HAuCl}_4) = 5 \cdot 10^{-3} \text{ M}$

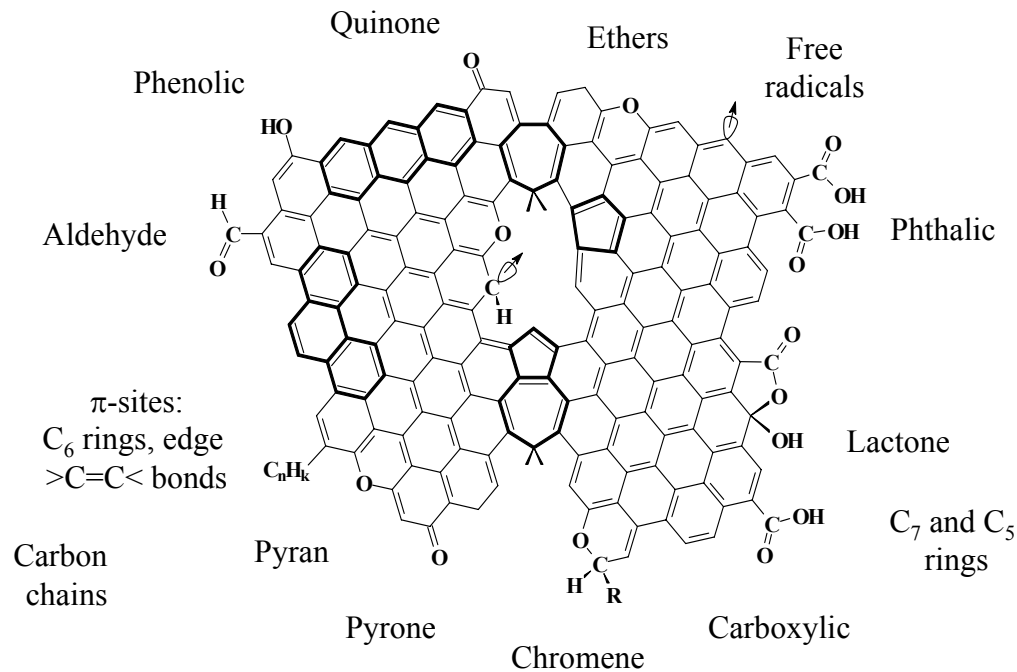


Increasing of concentration of HAuCl₄ solution results in increasing of supported gold particle size

Gold on carbon

Mesoporous carbon material Sibunit
($S_{\text{BET}} = 450 \text{ m}^2/\text{g}$, micropore area $37.7 \text{ m}^2/\text{g}$)

**Surface chemical groups
specific to polycrystalline quasi-graphitic carbons**

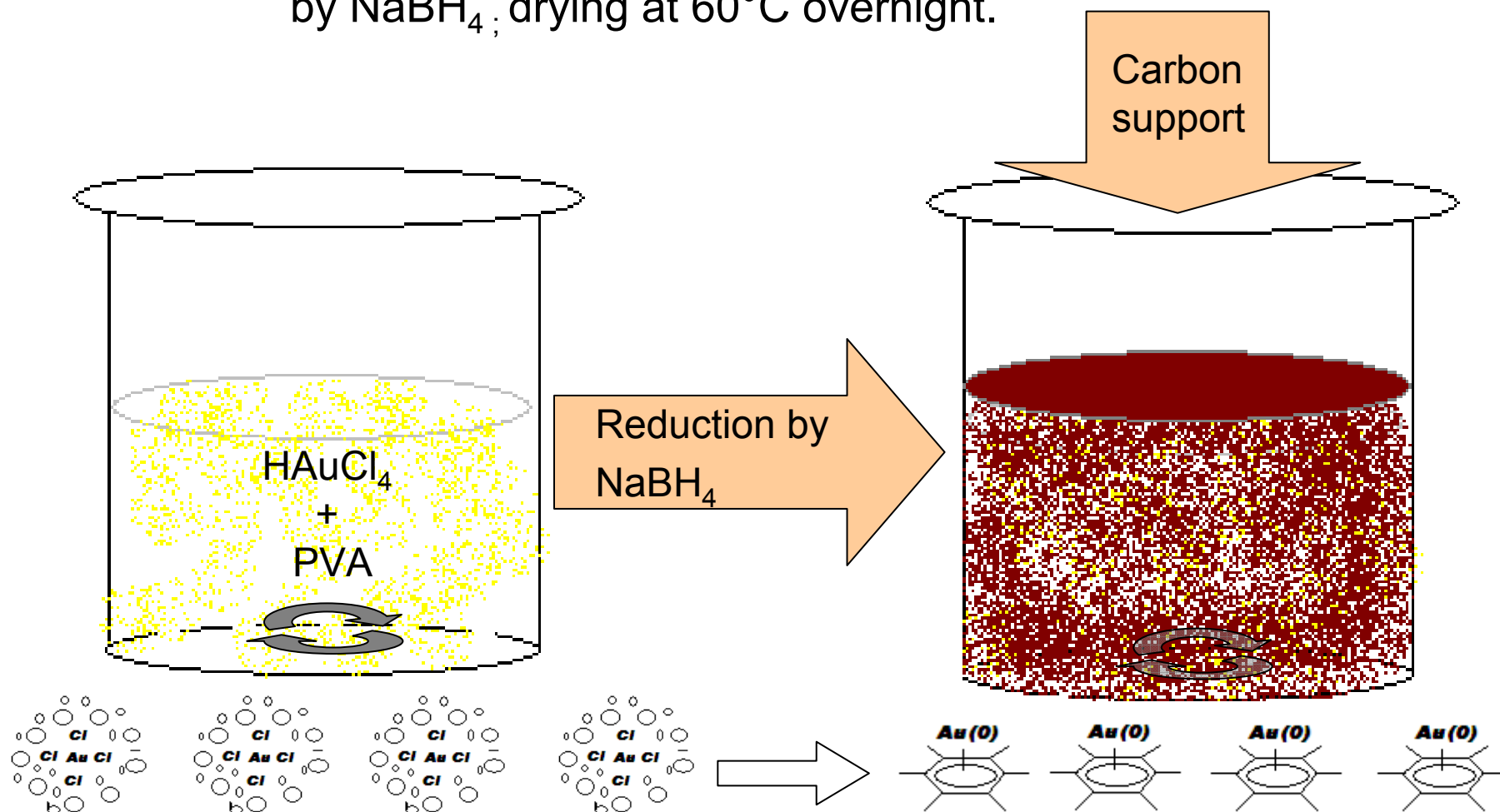


Oxidation of carbon by
5 wt. % HNO_3 12h, at 25°C

Olga Simakova, 2009

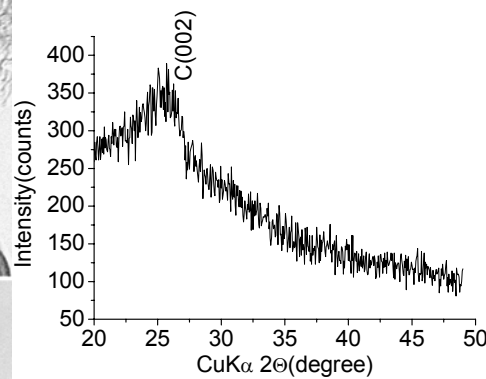
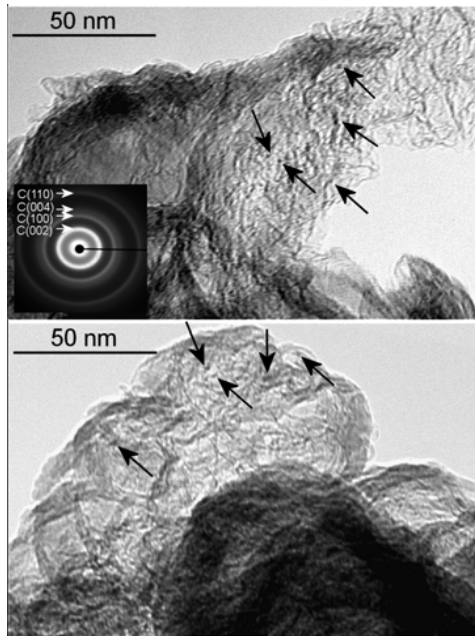
1 wt% Au/carbon

- Gold sols formation with polyvinyl alcohol (PVA); reduction by NaBH_4 ; drying at 60°C overnight.

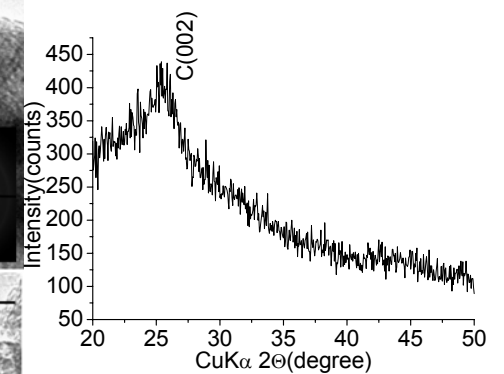
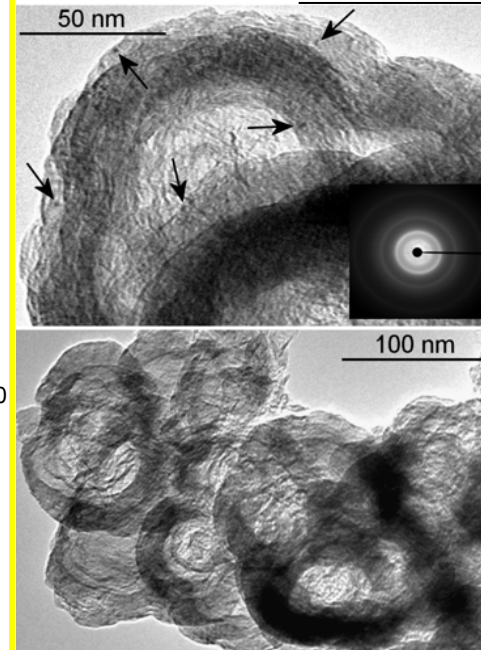


1 wt% Au/carbon

1 wt. % Au/Non-oxidized carbon



1 wt. % Au/Oxidized carbon



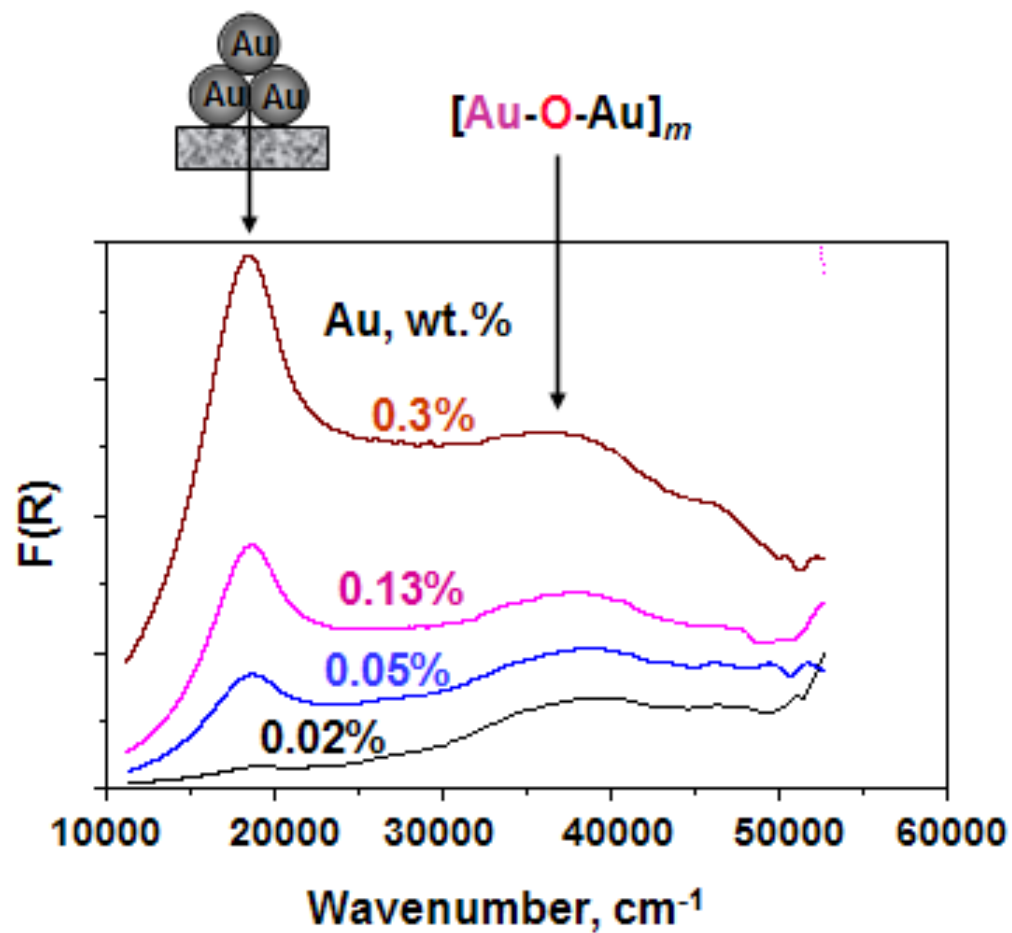
The same size of supported
gold particles

$$d_{\text{Au}} = 1-2 \text{ nm}$$

Characterization

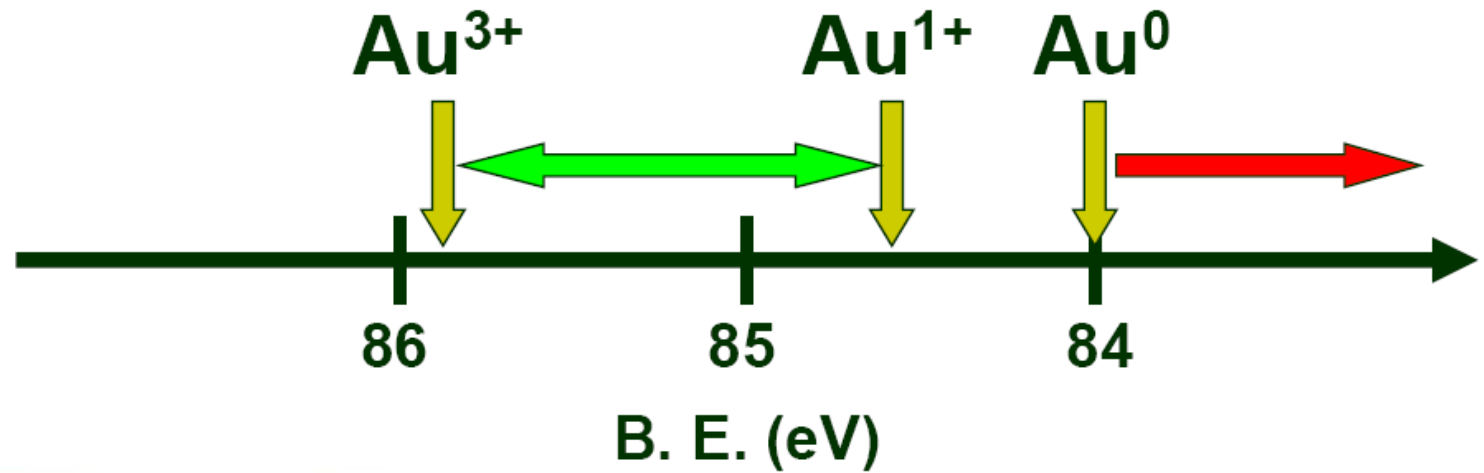
- XPS
- UV-vis
- TEM
- Chemisorption does not work!

UV-vis



Au 4f

XPS

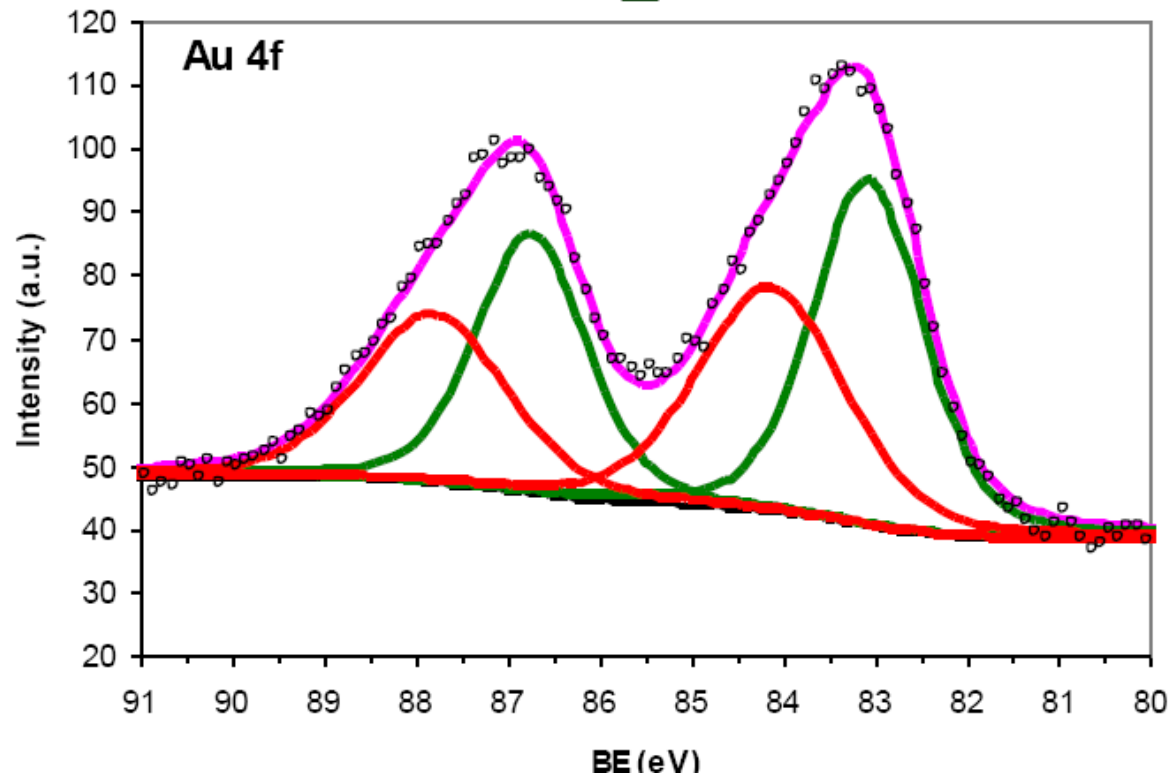


PHI Quantum 2000 Scanning ESCA
Microprobe spectrometer with Al
anode

Betiana Campo, 2009

1% Au/SiO₂

XPS

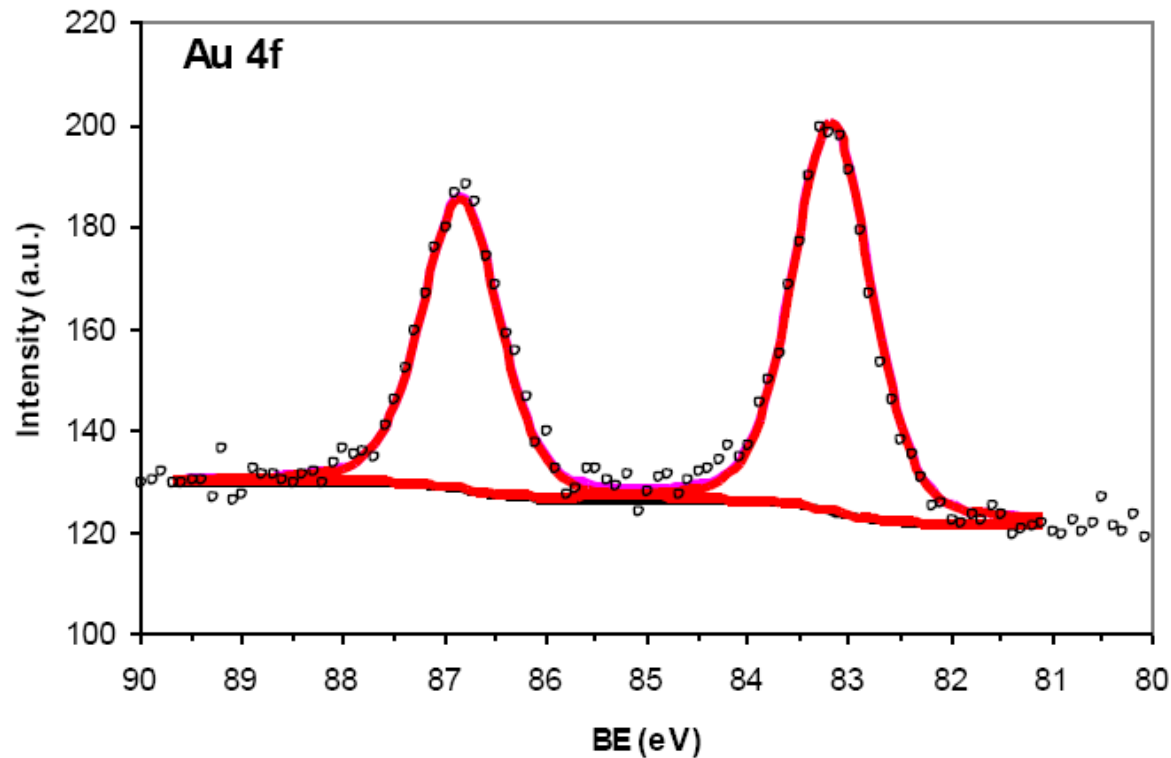


Particle size
lower than 2 nm

	Position (eV)	
	4f _{5/2}	4f _{7/2}
Au ⁰	87.8	84.1
Au ^{δ-}	86.7	83.0

1% Au/TiO₂

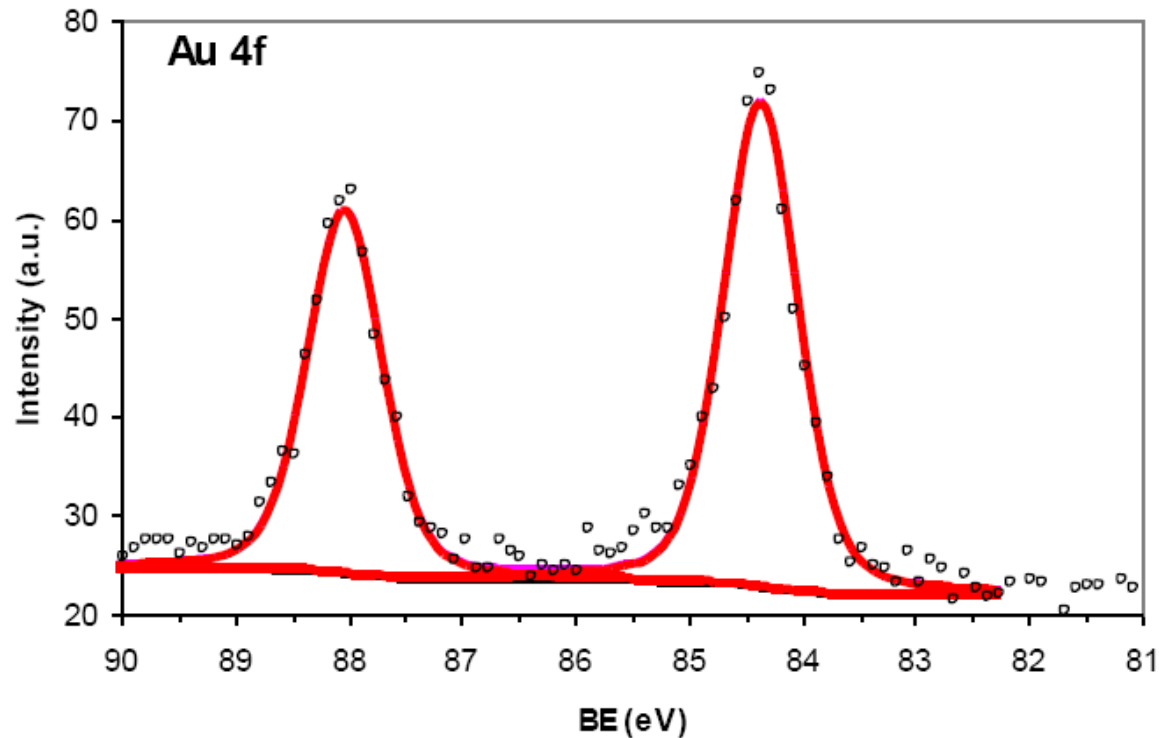
XPS



	Position (eV)	
	4f _{5/2}	4f _{7/2}
Au ^{δ-}	86.9	83.2

1% Au/C (PVA)

XPS



	Position (eV)	
	4f _{5/2}	4f _{7/2}
Au ⁰	88.0	84.3

Catalysts: cluster size

- 2% Au/Al₂O₃ Direct ion exchange (DIE)
Deposition-precipitation with urea (DPU)
Impregnation
- Calcination temperature (DIE) 300°C
400°C
500°C
600°C

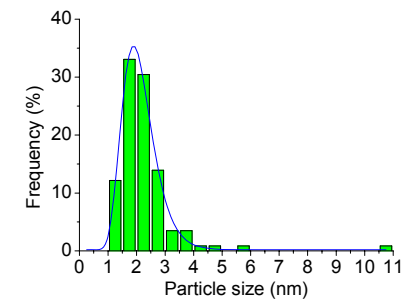
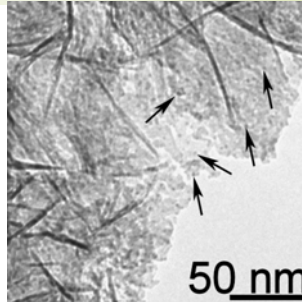
Characterization

- Size of particles (TEM)
 - average Au particles 1-20 nm
- Metal loading (ICP)
 - 2.0 wt. % Au
- Electronic state of gold species (XPS)
 - metallic gold species
- Catalytic activity in sugar oxidation

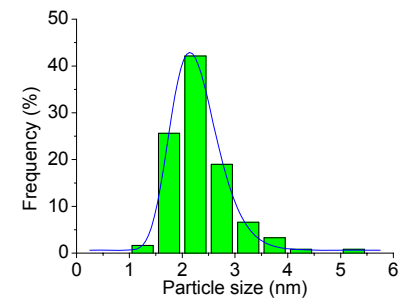
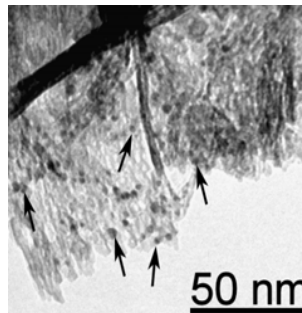
Olga Simakova, Bright Kusema, Betiana Campo

2% Au/Al₂O₃

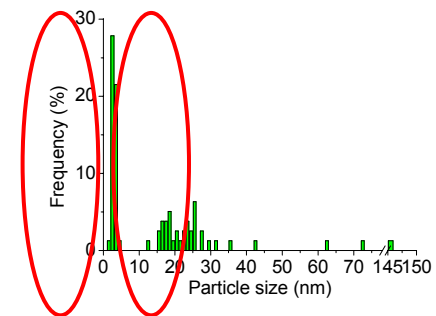
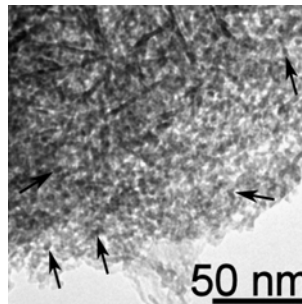
DIE 2.2 ± 1.0 nm



DPU 2.3 ± 0.6 nm.



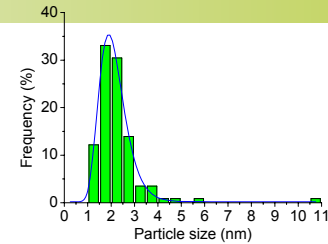
IMP 2.9 ± 0.6 nm
28.1 ± 22.9 nm



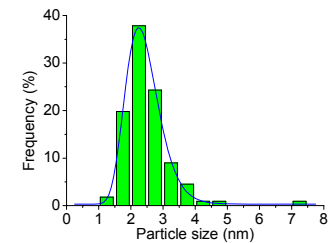
Olga Simakova, Bright Kusema, Betiana Campo

2% Au/Al₂O₃

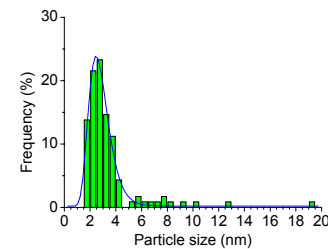
DIE 300°C 2.2 ± 1.0 nm



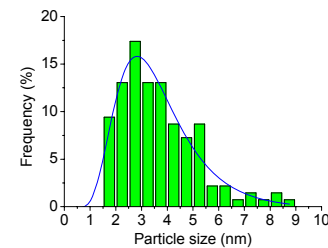
DIE 400°C 2.7 ± 0.7 nm



DIE 500°C 3.4 ± 2.3 nm

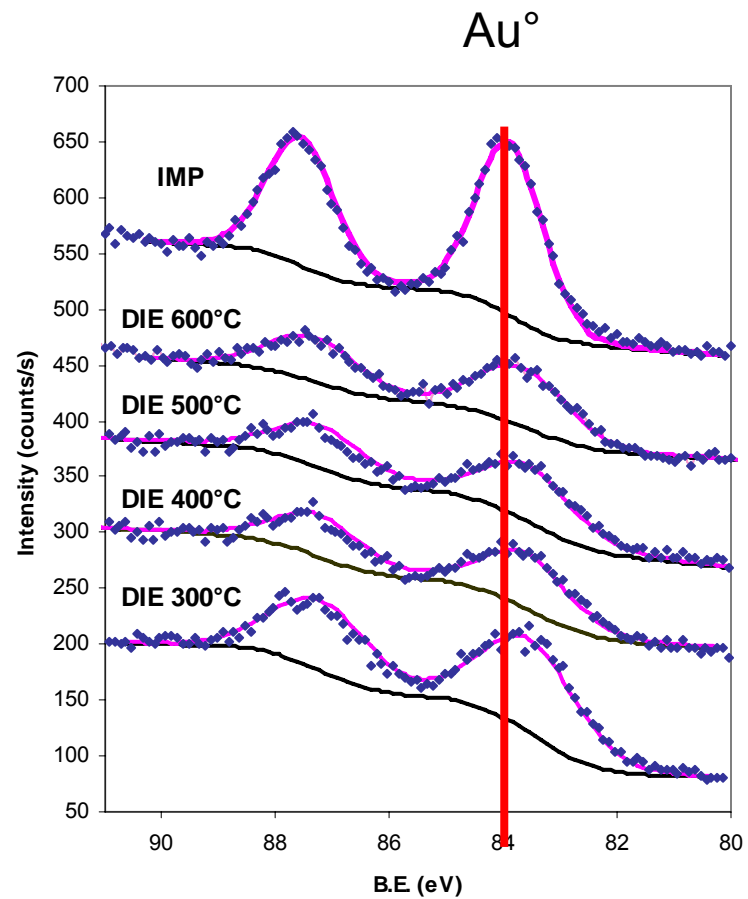


DIE 600°C 3.7 ± 1.5 nm

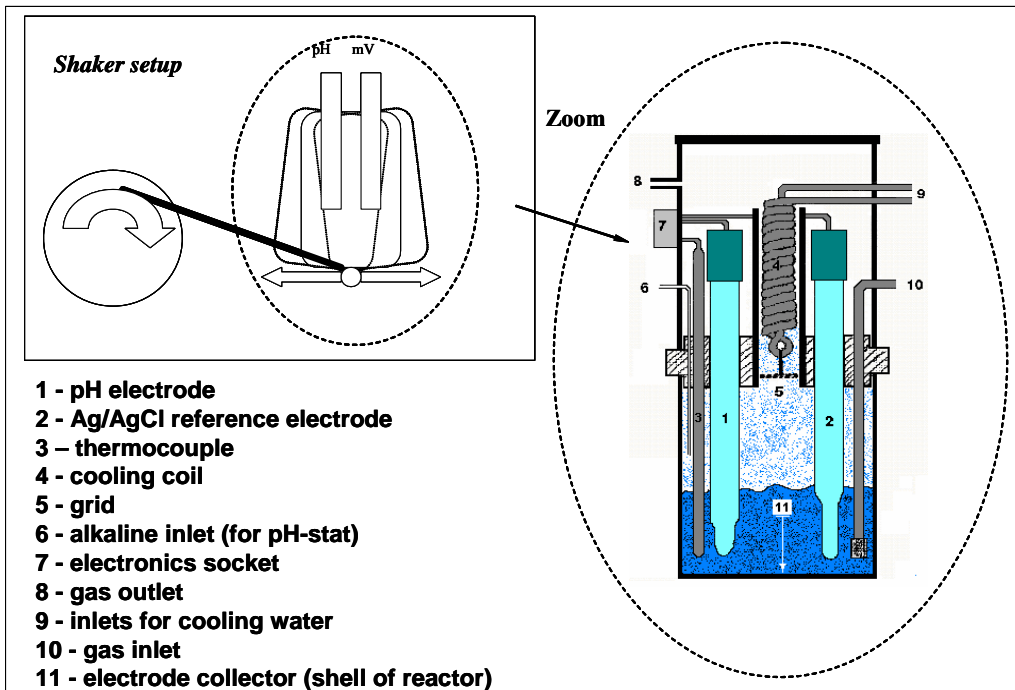


Olga Simakova, Bright Kusema, Betiana Campo

XPS – Fresh catalyst

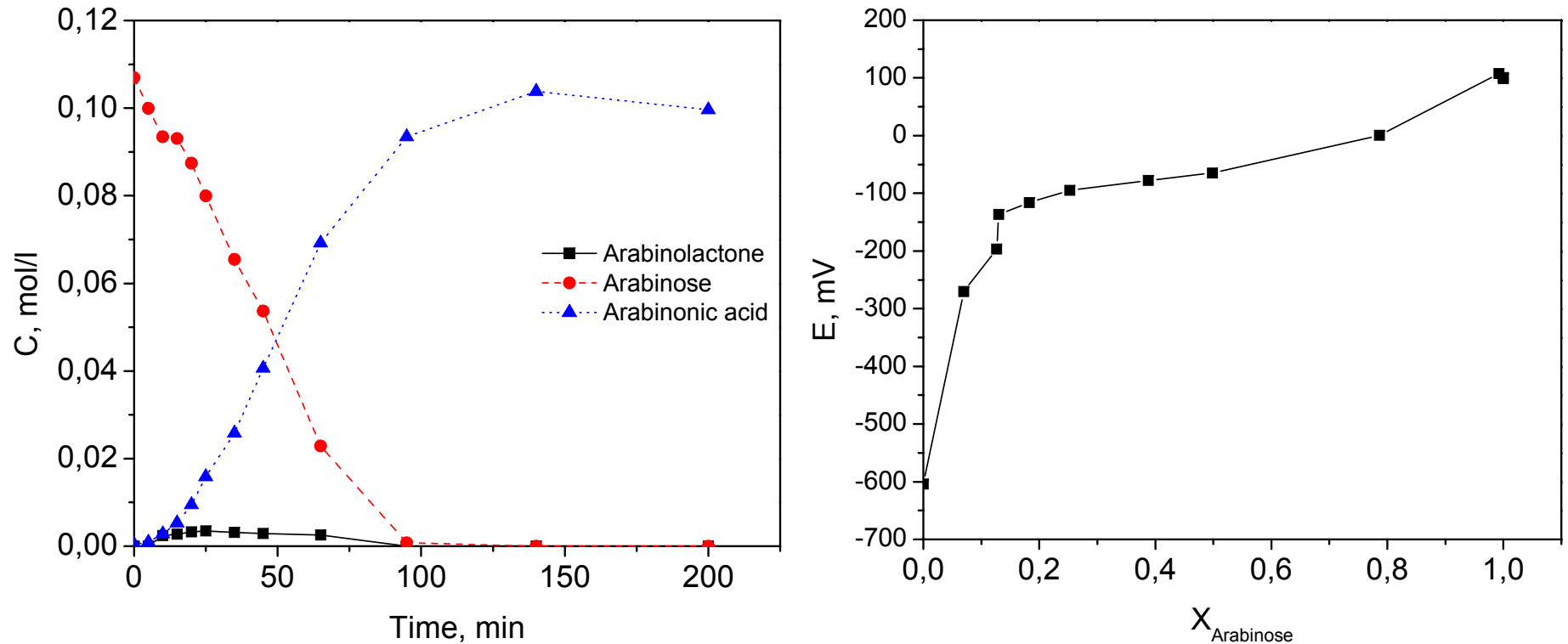


Olga Simakova, Bright Kusema, Betiana Campo



Bright Kusema

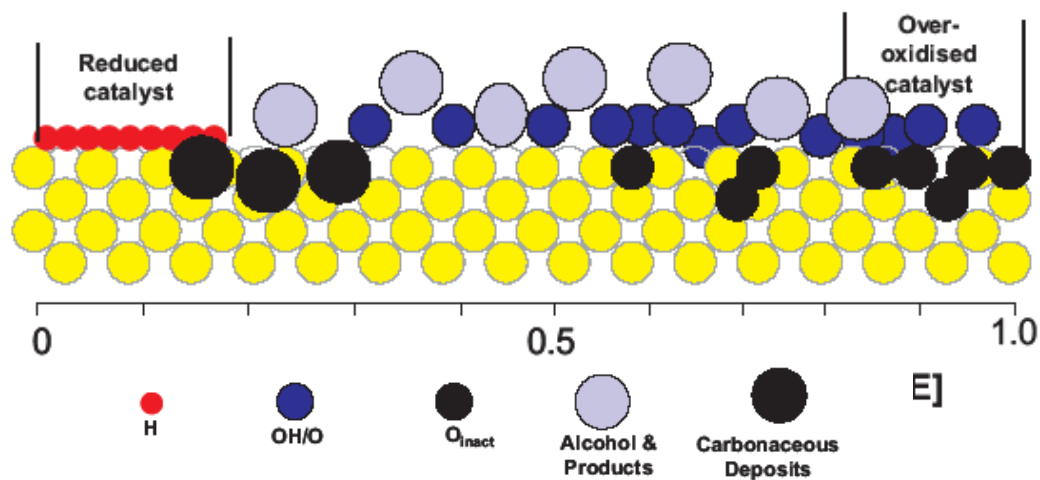
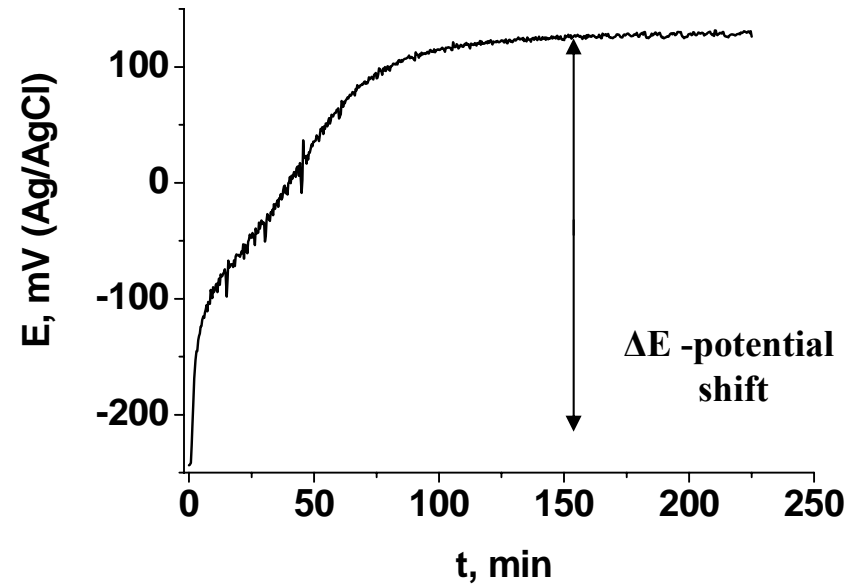
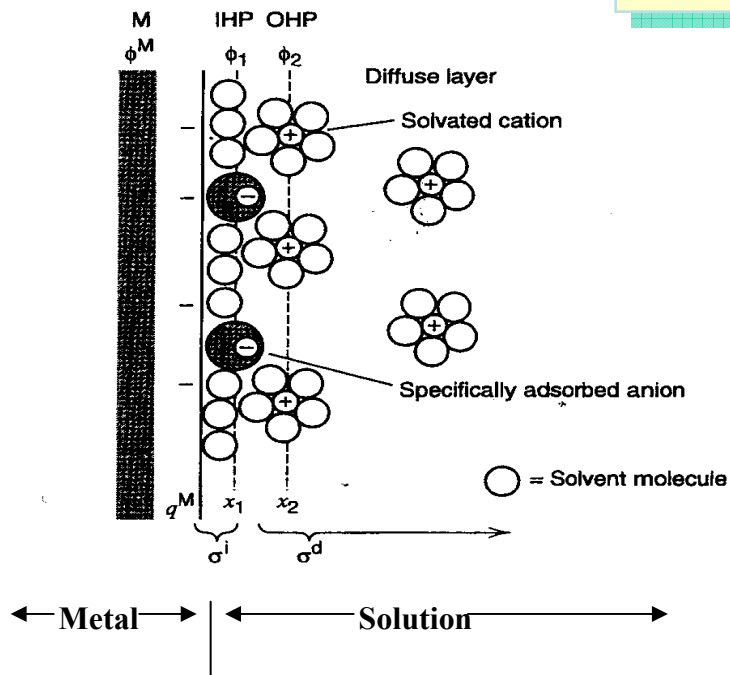
Results



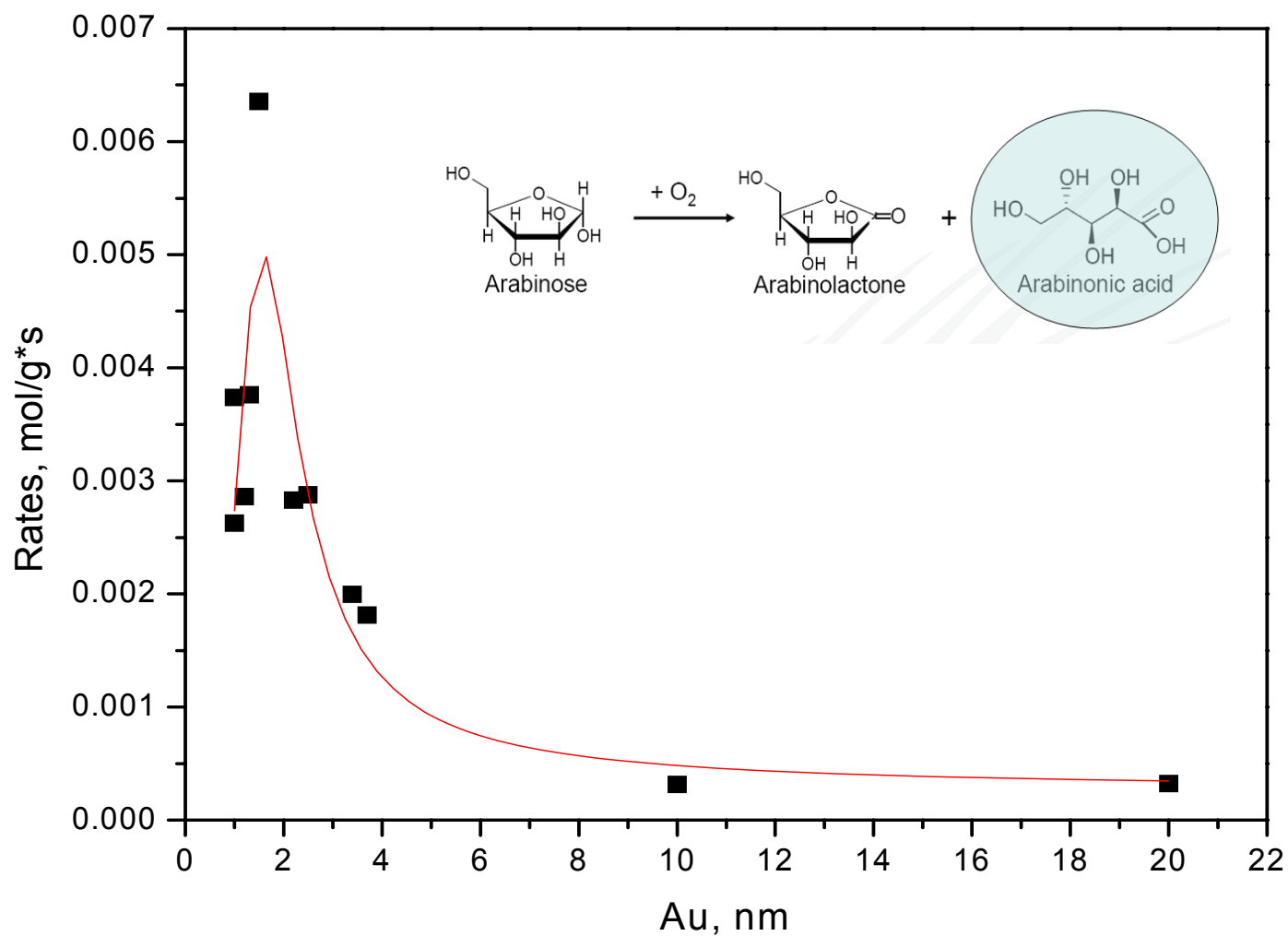
➤ Kinetic curves; E (mV) vs. $X_{\text{Arabinose}}$

➤ 2% Au/Al₂O₃, $T = 60^\circ\text{C}$, pH 8, O₂ 2.5 ml/min.

Catalyst potential



Dependence of activity on cluster size



Olga Simakova, Bright Kusema, Betiana Campo

Treatment of wood

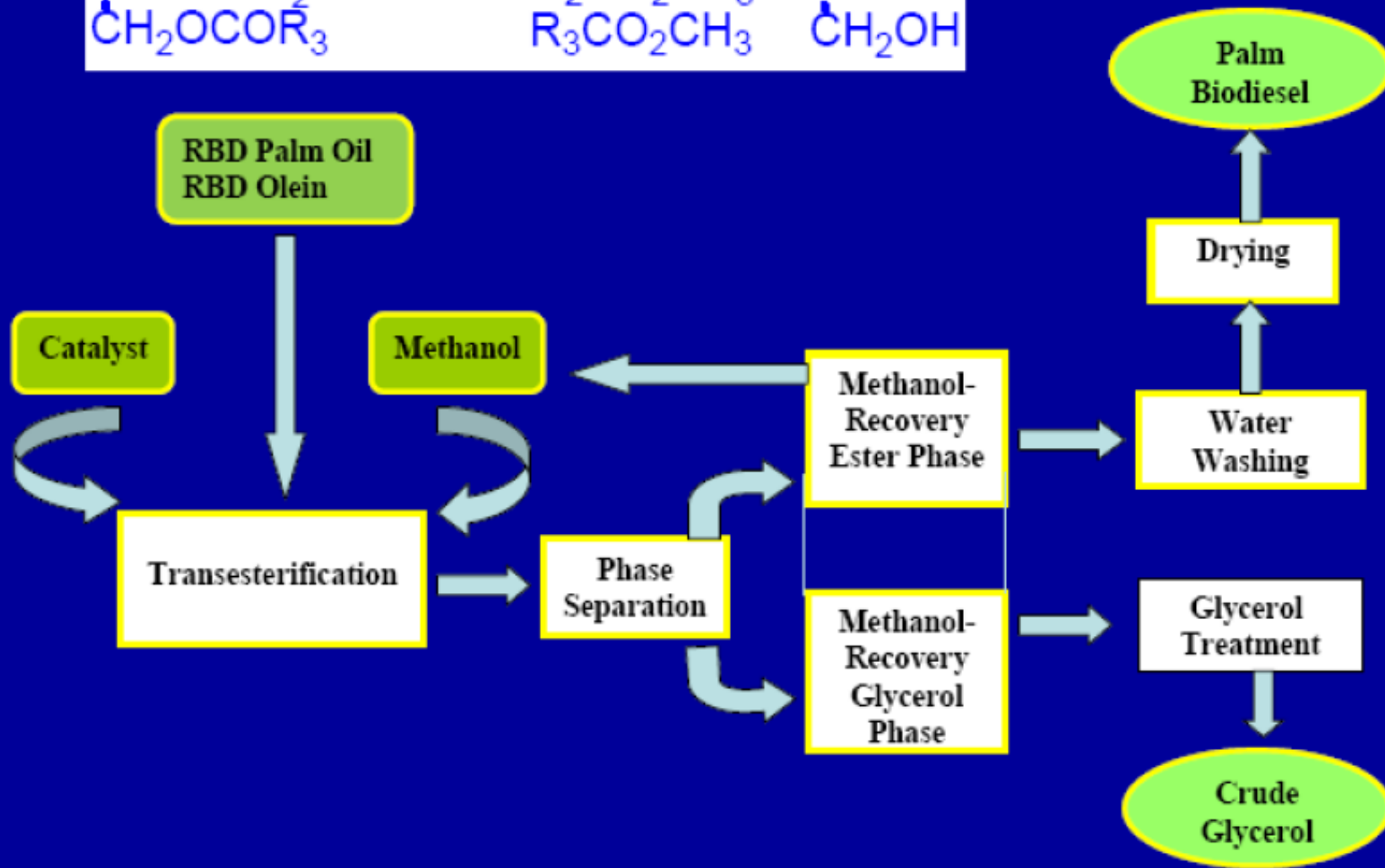
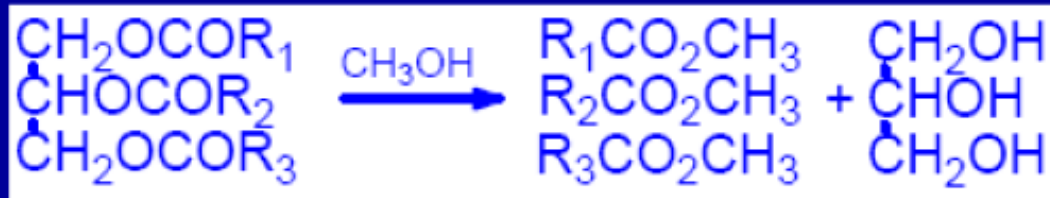
- **Gasification**
- **Pyrolysis**
- **Depolymerization** to get low molecular mass components (sugars, phenols, furfural, etc.), e.g. **building blocks**
- **Delignification** (cellulose, derivatives, paper)
- **Extraction of valuable chemicals (bioactive components)**



The use of vegetable oils as engine fuels may seem insignificant today but the such oils may become, in the course of time, as important as petroleum and the coal tar products of the present time.

-Rudolph Diesel, 1912

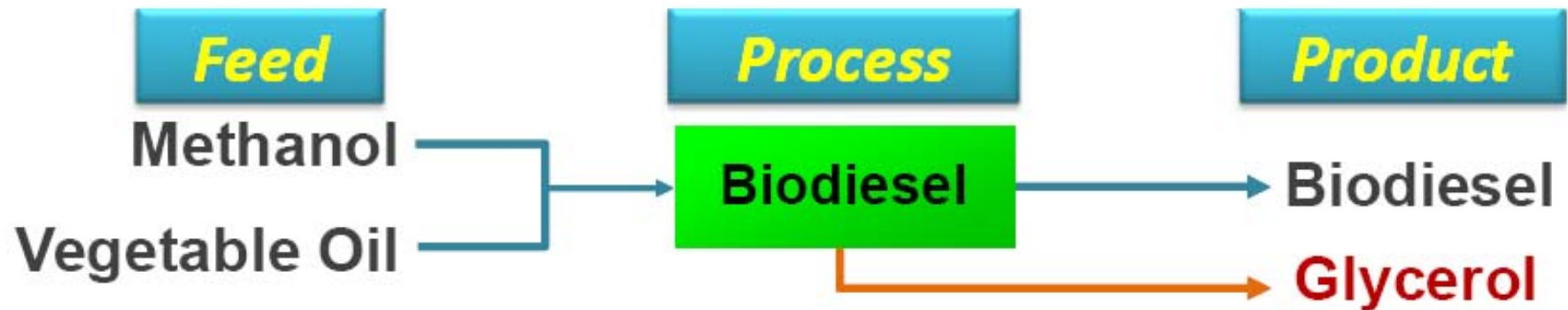
Biodiesel process chart



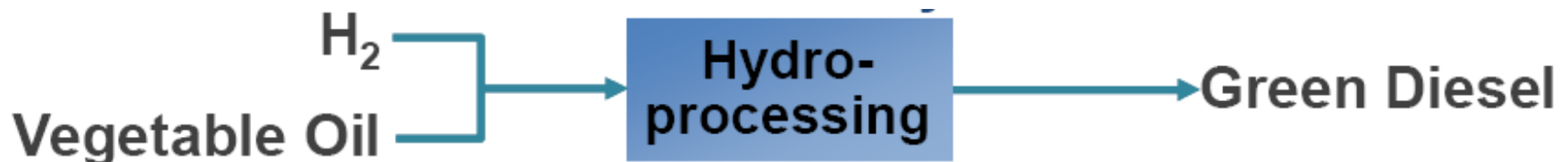
Biodiesel technology

- **Transesterification reaction** – Predominantly uses homogeneous base catalysts e.g. sodium methoxide, sodium hydroxide and potassium hydroxide.
- **Differences between commercial processes:**
 - *Reactor Design:* Continuous Stirred Tank Reactor (CSTR), Loop Reactor, Tubular Reactor.
 - *Purification Step:* Residual catalysts and soap need to be removed from biodiesel and glycerol. (**main drawback**)
- **Purification processes:** Water washing process and adsorbent treatment process (water-free process):
 - *Water washing process* – need waste water treatment plants.
 - *Evaporate and recover water for re-use:* energy intensive.
 - *Adsorbent treatment process e.g. Magnesium Silicate* – high cost of adsorbent and disposal of spent adsorbents
- **Eliminate catalyst cleaning up step and simplify biodiesel and glycerol purification (solid catalysts, enzymatic transesterification)**

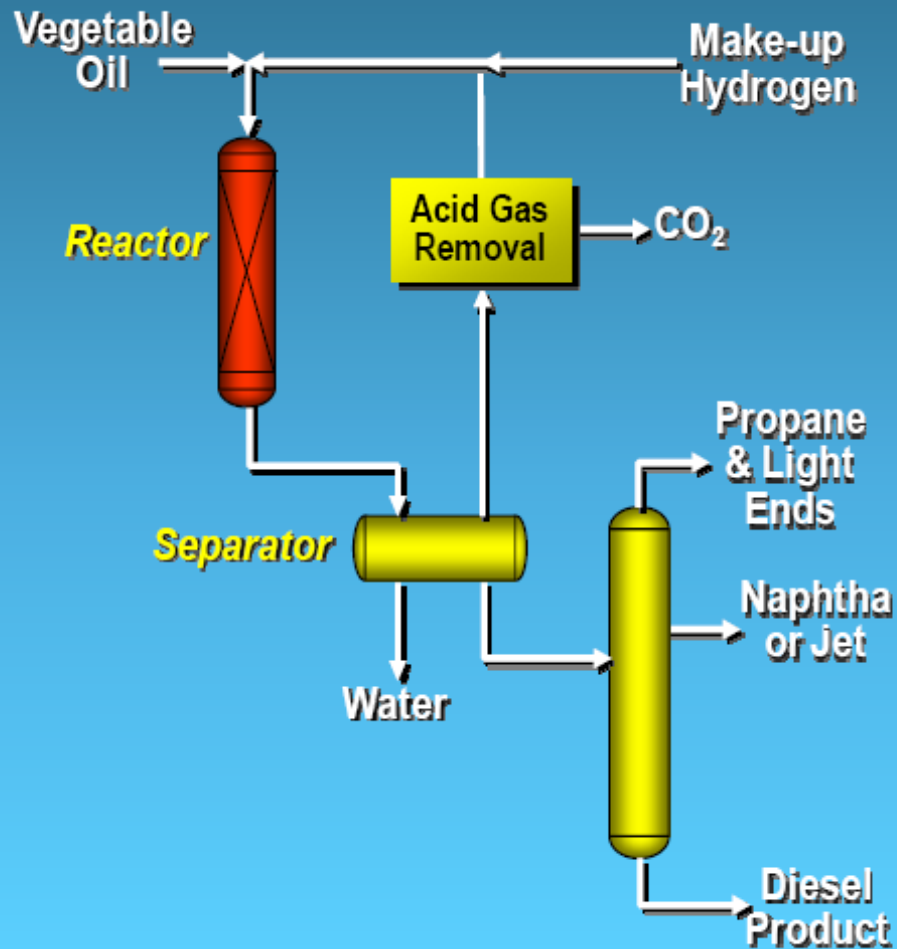
Green diesel



- 8 vol-% of product is low value glycerol
- Requires methanol as a feedstock, higher priced vegetable oil

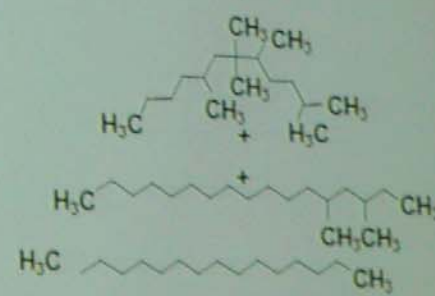
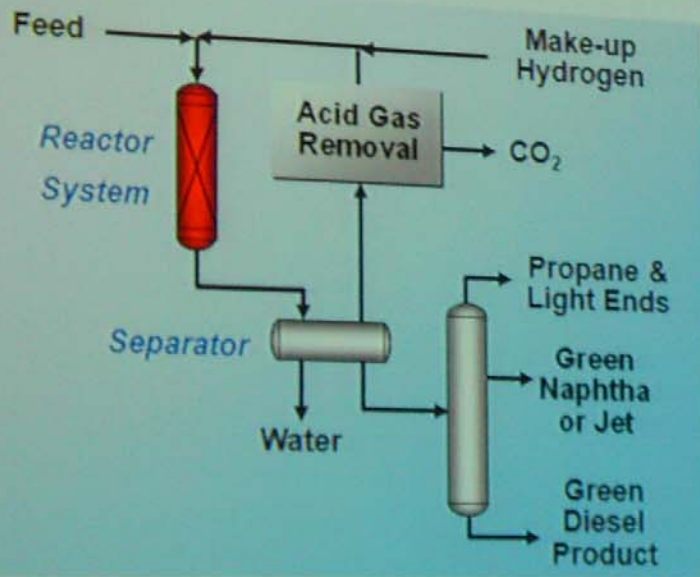
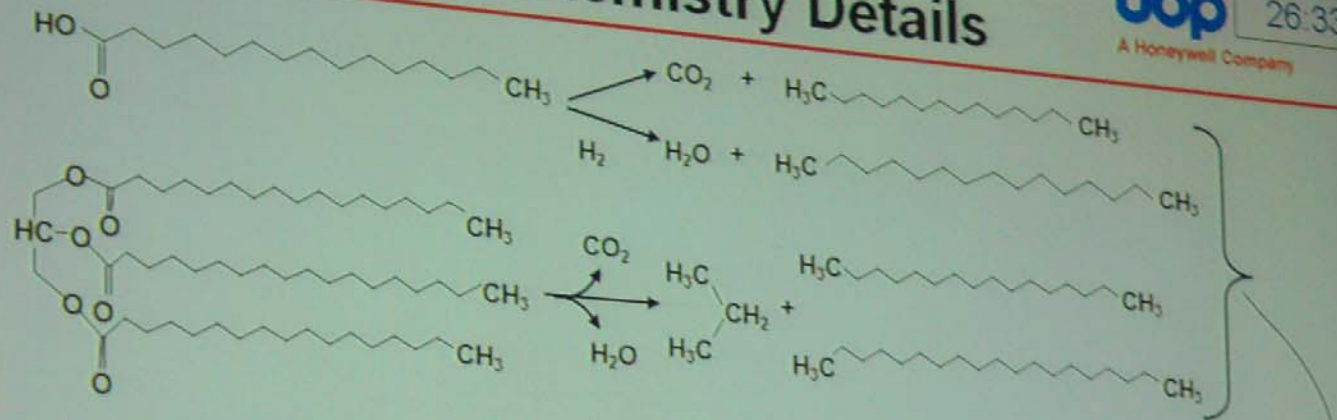


- Equivalent volume yield of diesel fuel
- Uses available hydrogen as a feedstock
- No low value liquid by-products
- Can process fatty acids in lower cost vegetable oils



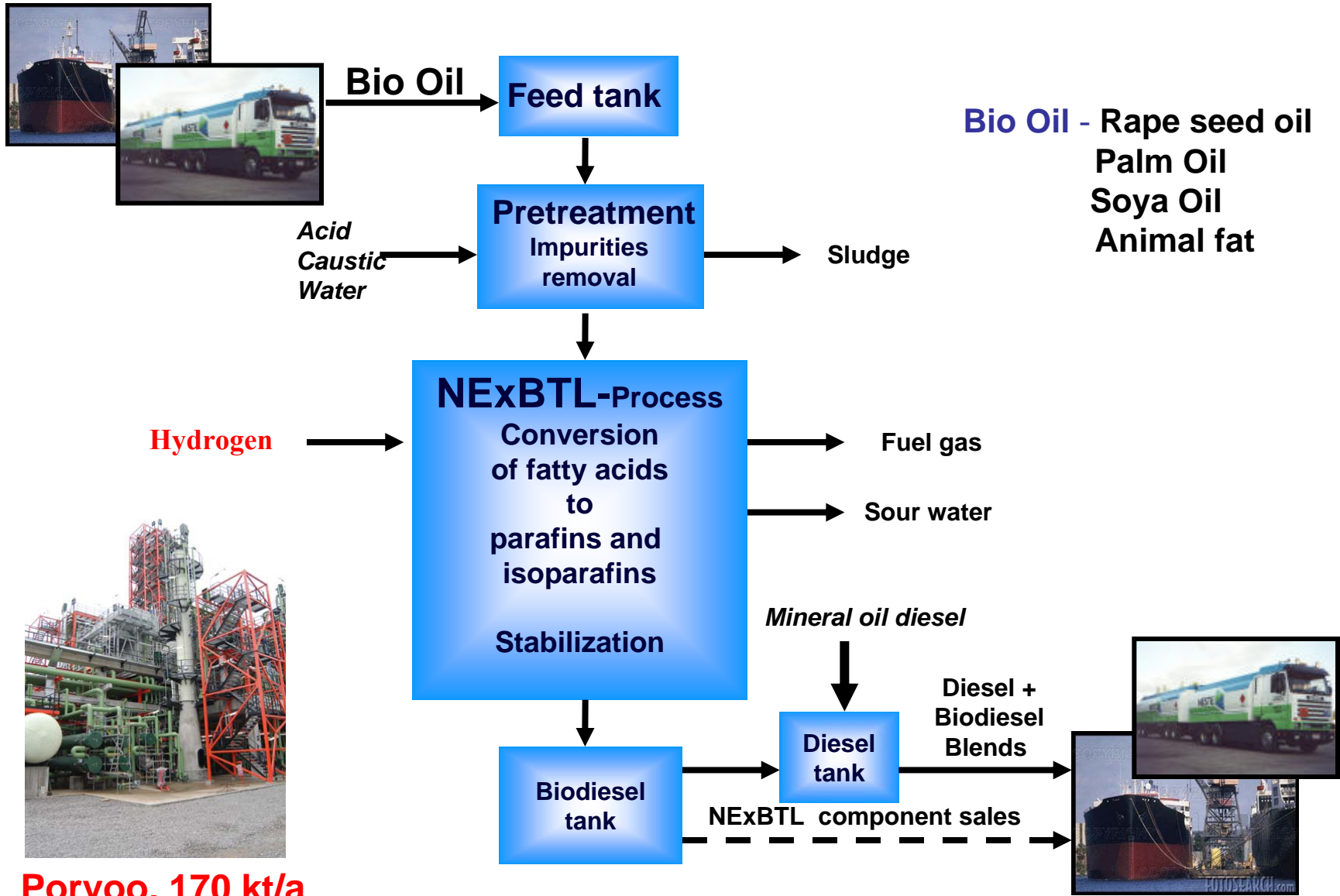
- Upgrade vegetable oil using hydroprocessing
- Product is an high cetane diesel blending component
- Hydrocarbon product, not an oxygenated compound
- Co-production of propane, naphtha, and high quality jet fuel possible

Ecofining Process Chemistry Details



Ecofining Feed Testing Program – Soy, Rapeseed, Palm, Jatropha, Algal, Tallow, ...

REFINERY BASED NEXBTL UNIT



Fuel Property comparison

	NExBTL	GTL	FAME (RME)	Sulfur free Diesel fuel (summer)
Density at +15°C (kg/m ³)	775 ... 785	770 ... 785	≈ 885	≈ 835
Viscosity at +40°C (mm ² /s)	2.9 ... 3.5	3.2 ... 4.5	≈ 4.5	≈ 3.5
Cetane number	≈ 84 ... 99 *	≈ 73 ... 81	≈ 51	≈ 53**
Cloud point (°C)	≈ - 5 ... - 30	≈ 0 ... - 25	≈ - 5	≈ - 5
Heating value (lower) (MJ/kg)	≈ 44	≈ 43	≈ 38	≈ 43
Heating value (MJ/l)	≈ 34	≈ 34	≈ 34	≈ 36
Polyaromatic content (wt-%)	0	0	0	≈ 4
Oxygen content (wt-%)	0	0	≈ 11	0
Sulfur content (mg/kg)	< 10 (< 1)	< 10	< 10	< 10
Carbon / hydrogen	≈ 5.6	≈ 5.6		≈ 6.0

*) Blending cetane number

***) ASTM specification > 40

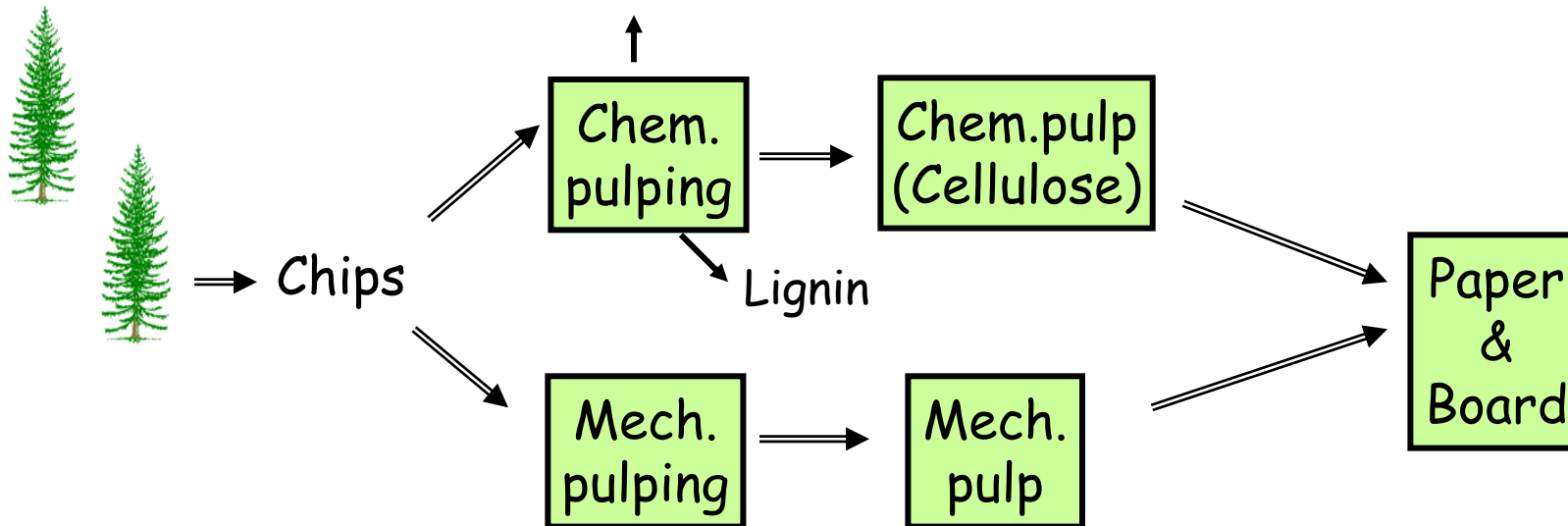


Feedstocks: bio-oil

Feedstock	Oil yield / ha	1 ton biodiesel to vegetable oil	ha equivalent
Rapeseed EU25	1.18	1	0.85
Soybean Oil	0.49	1	2.02
Palm Oil	4.05	1	0.25
Sunflower Oil	0.62	1	1.63

Feedstocks: wood based oil

Tall Oil



Tall oil

Resinous yellow-black oily liquid composed mainly of a mixture of **rosin acids, fatty acids and sterols**; obtained as a byproduct in the treatment of pine pulp.



Rauma, Finland

DEOXYGENATION CHEMICAL PROCESSES



Renewable source

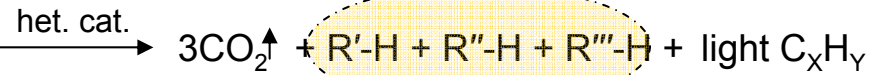
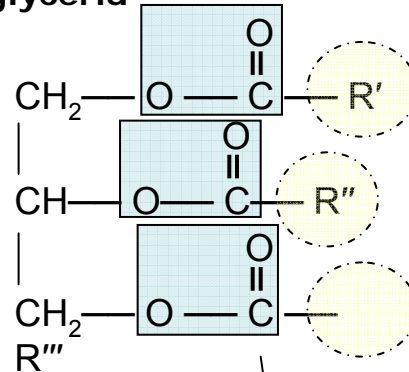


Wood

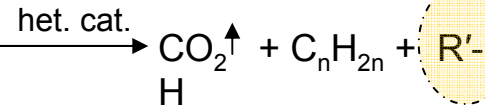
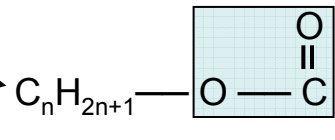
Animal fats & vegetable oils



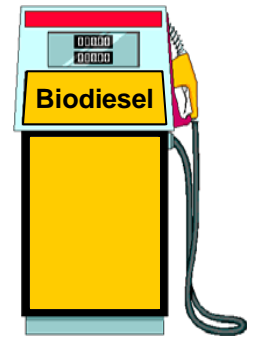
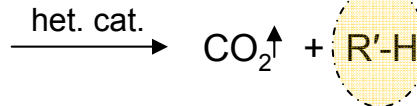
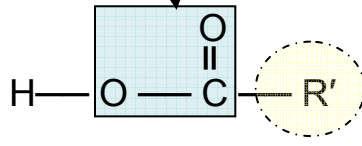
Triglyceride



Fatty acid ester



Fatty acid

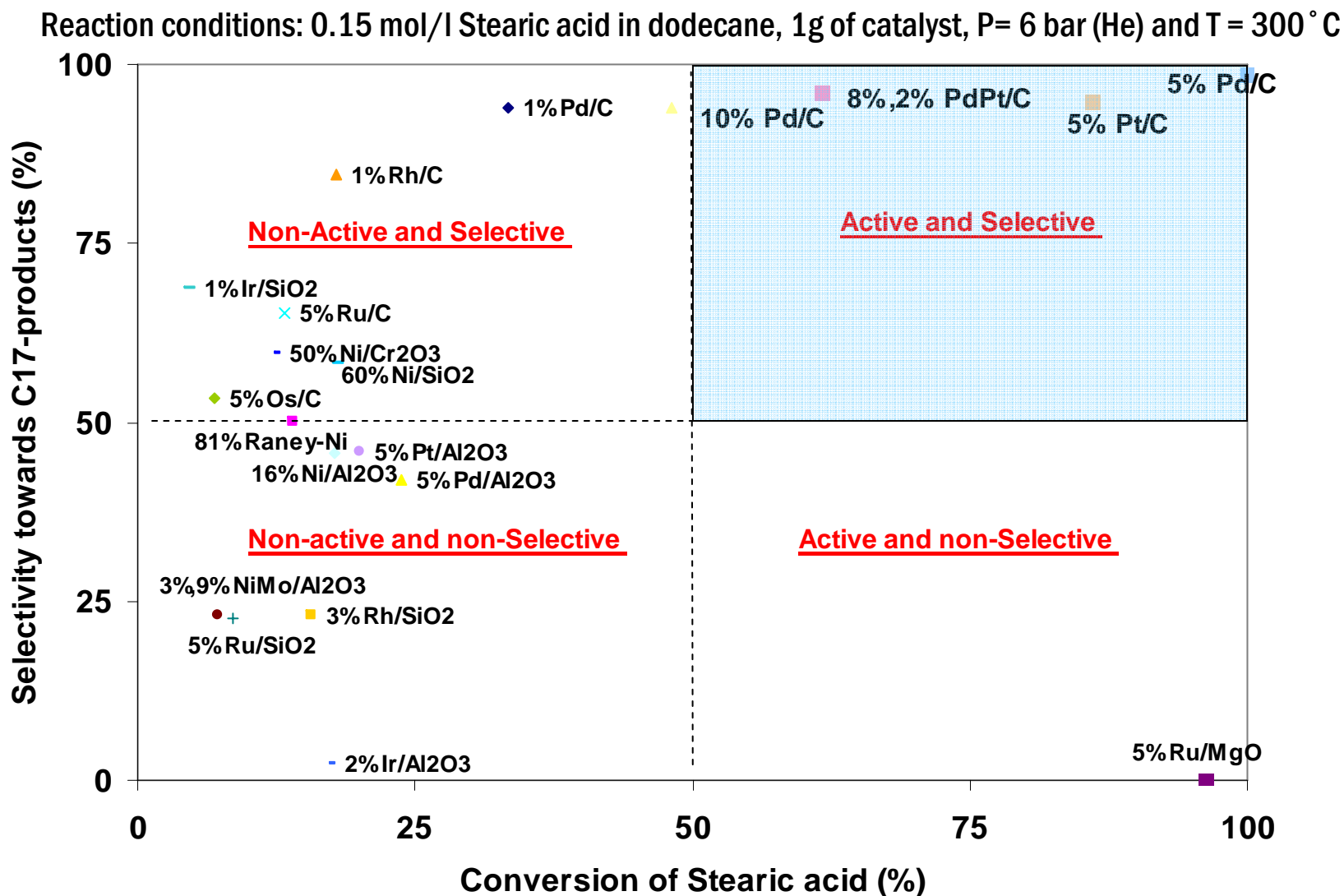


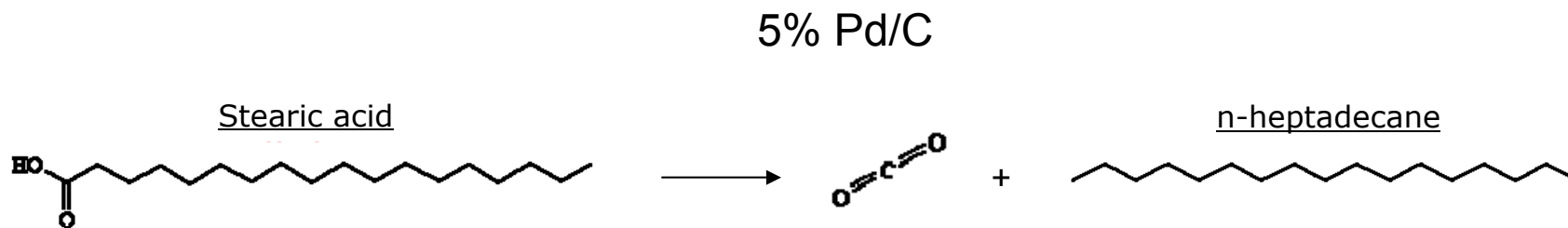
$\text{C}_n\text{H}_{2n+1}$ = Ester alkyl group (C1-C4)

R' , R'' , R''' = Fatty acid alkyl chain, (saturated and unsaturated, C5-C23)

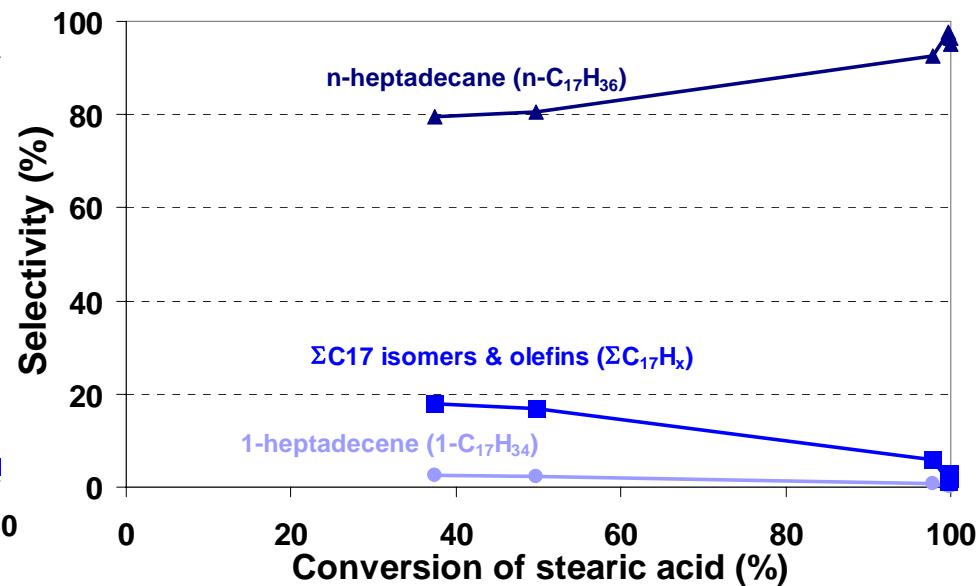
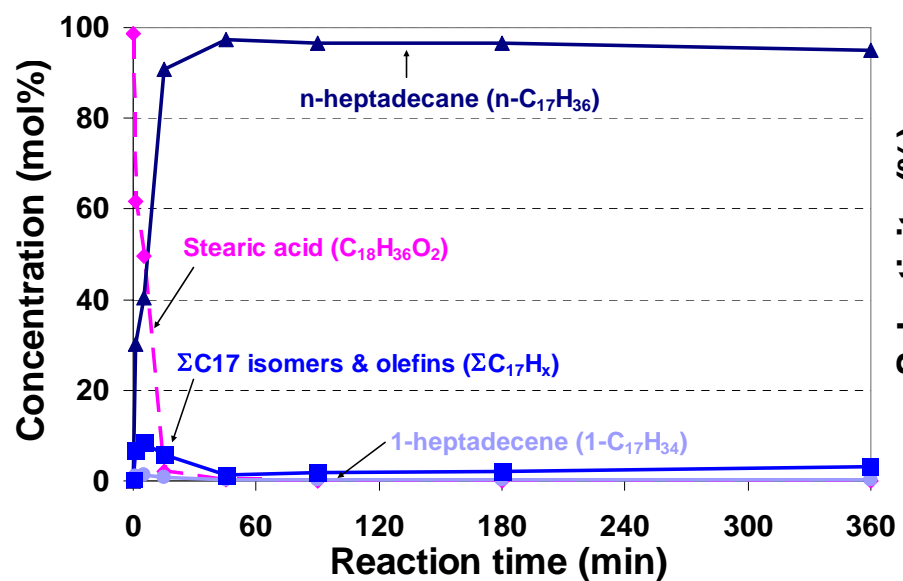
- Over 70 tested catalysts
 - with a wide variety of metal and support combinations
 - metals
 - Pd, Pt, Rh, Os, Ni, Mo, Ru and Ir
 - support
 - metal oxides (Cr_2O_3 , Al_2O_3 , SiO_2 and MgO)
 - zeolites (ZSM-5, Mordenite, BETA and Y)
 - mesoporous materials (MCM-21 and MCM-41)
 - carbonaceous material (activated carbons and carbon cloths)
 - with different metal contents

Catalyst screening in the deoxygenation of stearic acid





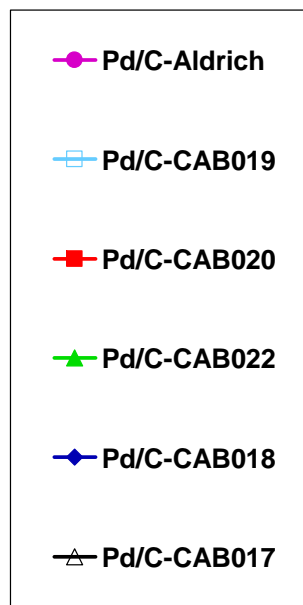
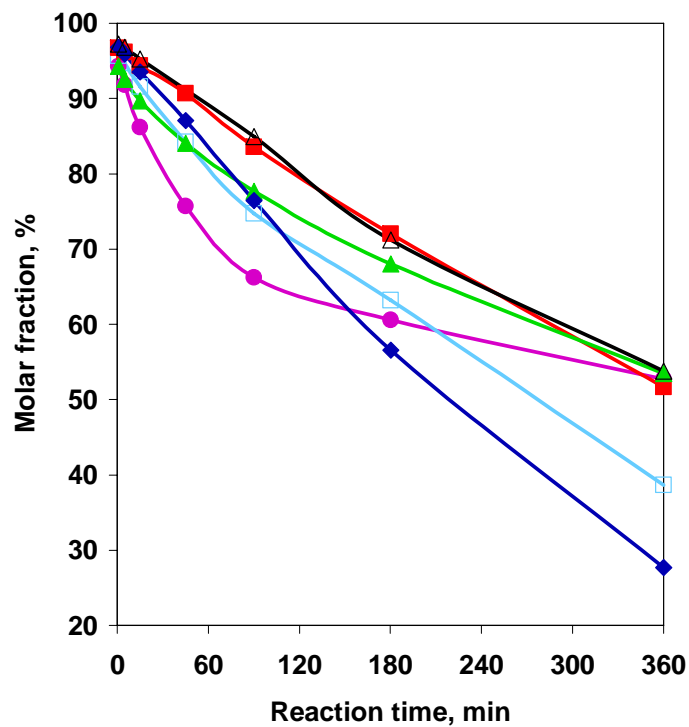
Reaction conditions: 0.15 mol/l Stearic acid in dodecane, 1g Pd/C, P= 6 bar (He) and T=300 °C



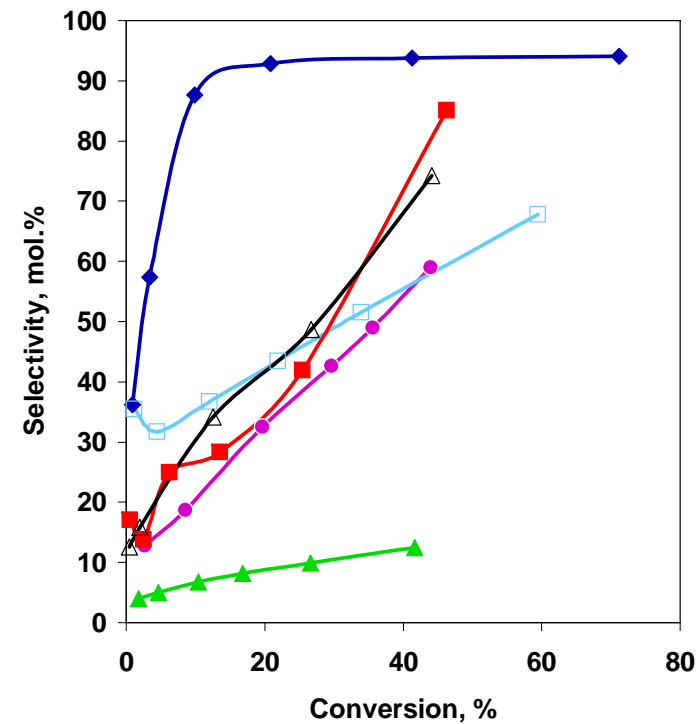
Catalyst development

- over 20 prepared 5% Pd/C catalysts
 - with different activated carbon supports
 - birch, peat and coal based
 - with a wide variety of preparation techniques
 - metal deposition (impregnation and precipitation)
 - carbon activation (heat and chemical treatment)

Ethyl stearate



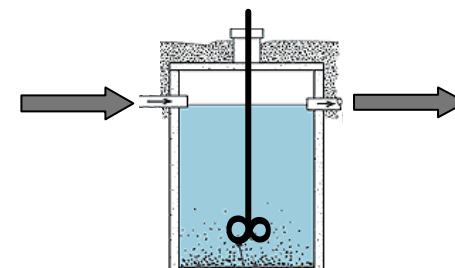
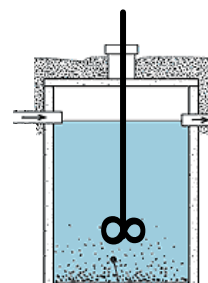
n-heptadecane

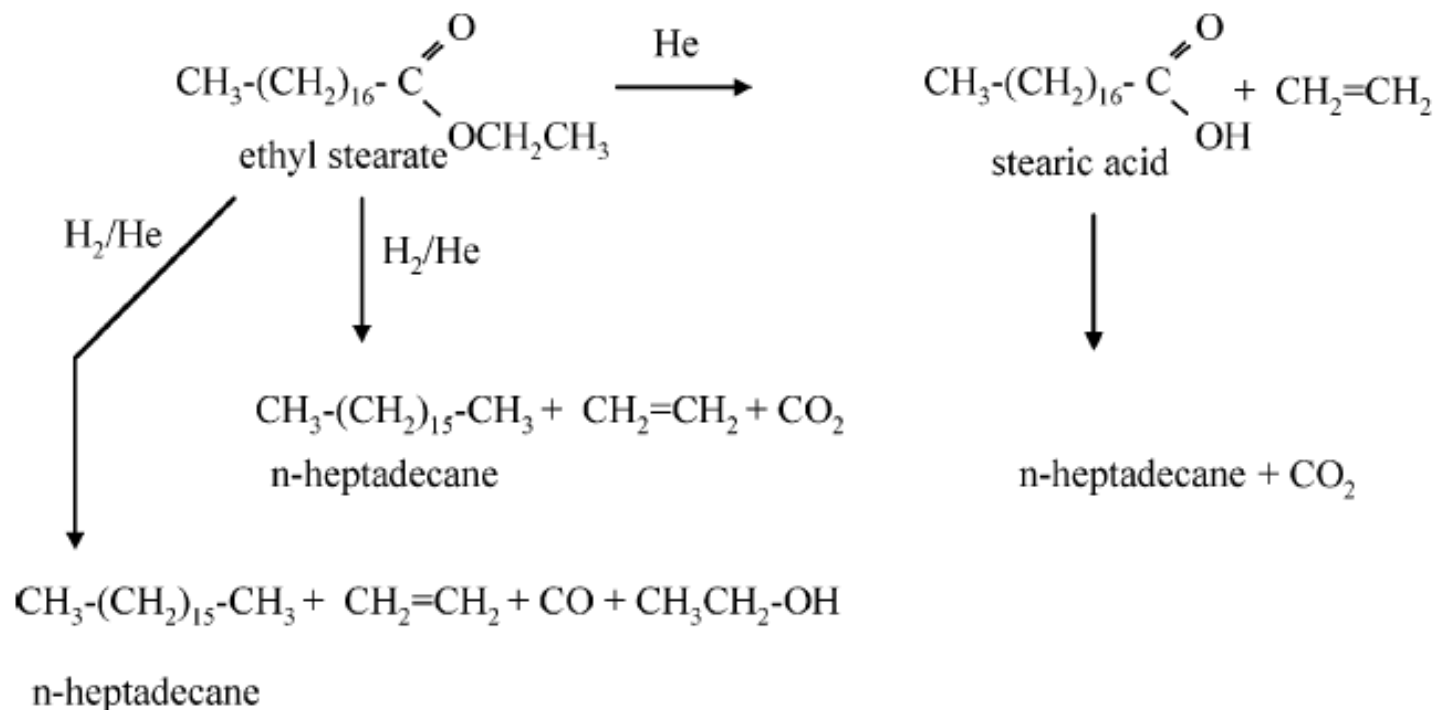


Reaction conditions: 0.1 mol/l Ethyl stearate in dodecane, 1g Pd/C, P= 7.5 bar (H₂) and T=320 °C

Optimization

- Effect of
 - temperature
 - pressure
 - reactant concentration
 - solvent
 - atmosphere
 - catalyst mass and metal content
 - catalyst pretreatment



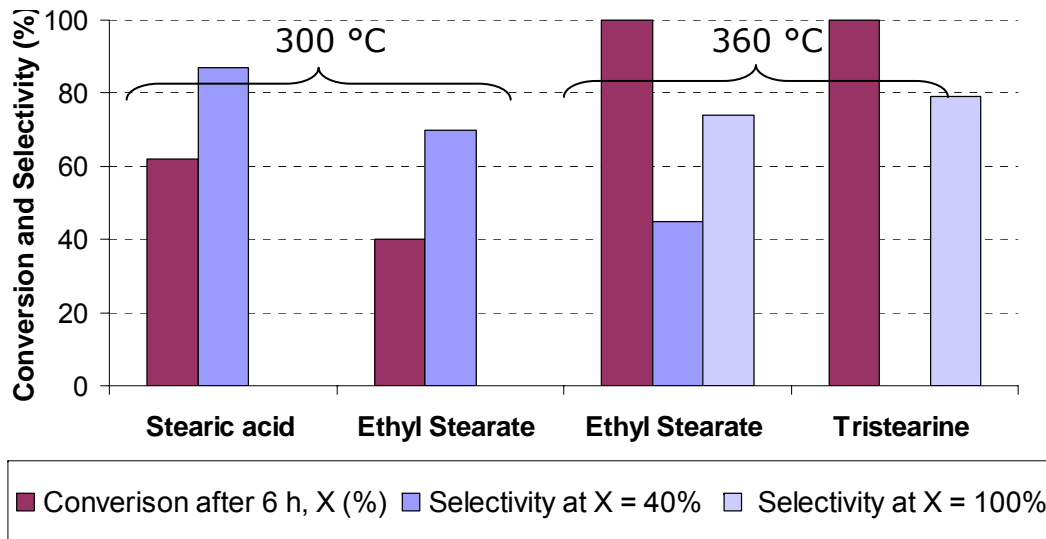
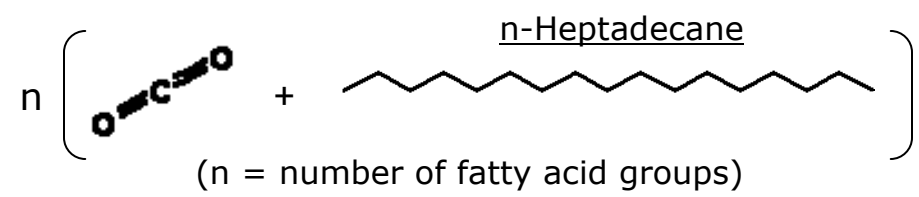
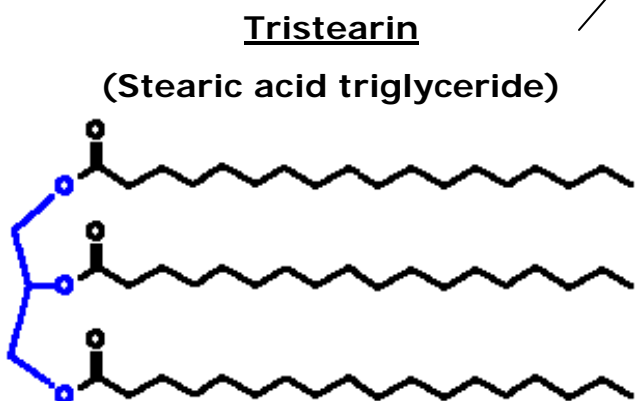
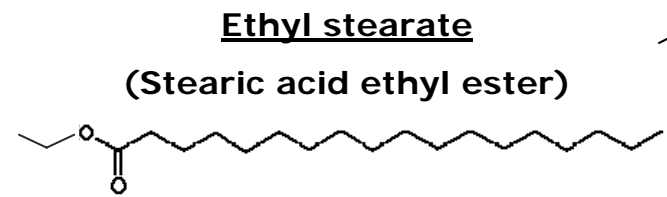
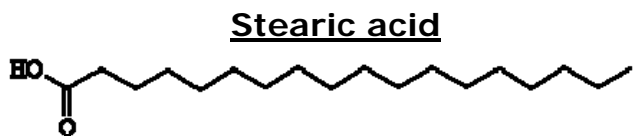


Energy & Fuels 2007, 21, 30–41

Catalytic Deoxygenation of Fatty Acids and Their Derivatives

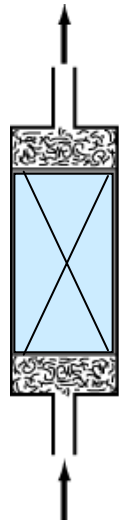
Päivi Mäki-Arvela, Iva Kubickova, Mathias Snåre, Kari Eränen, and Dmitry Yu. Murzin*

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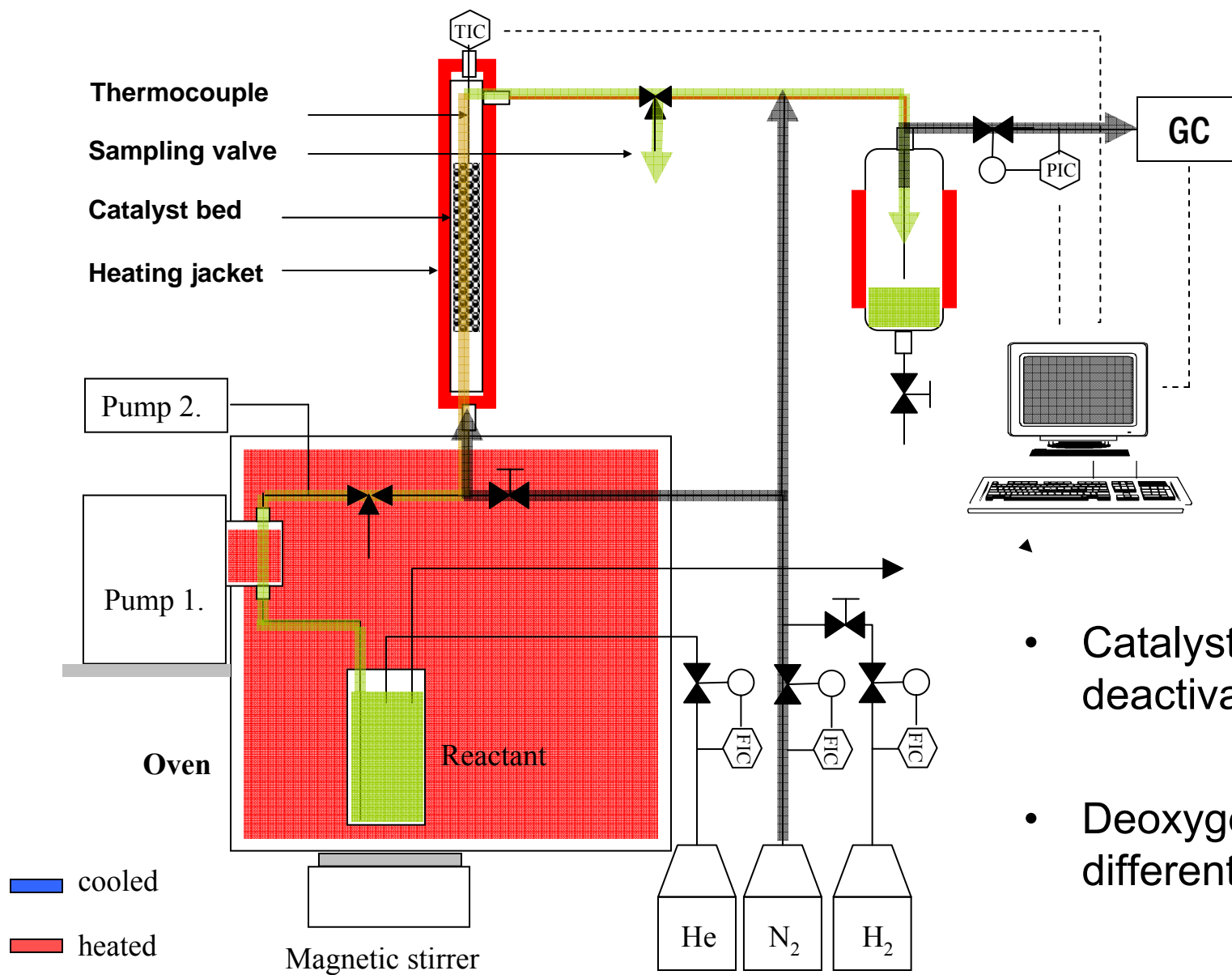


Reaction conditions: 1.6 mol/l feed in dodecane, 1g Pd/C, $P_{300^\circ\text{C}} = 17$, $P_{360^\circ\text{C}} = 40$ bar in Ar + H₂(5%) atmosphere

Fixed bed reactor

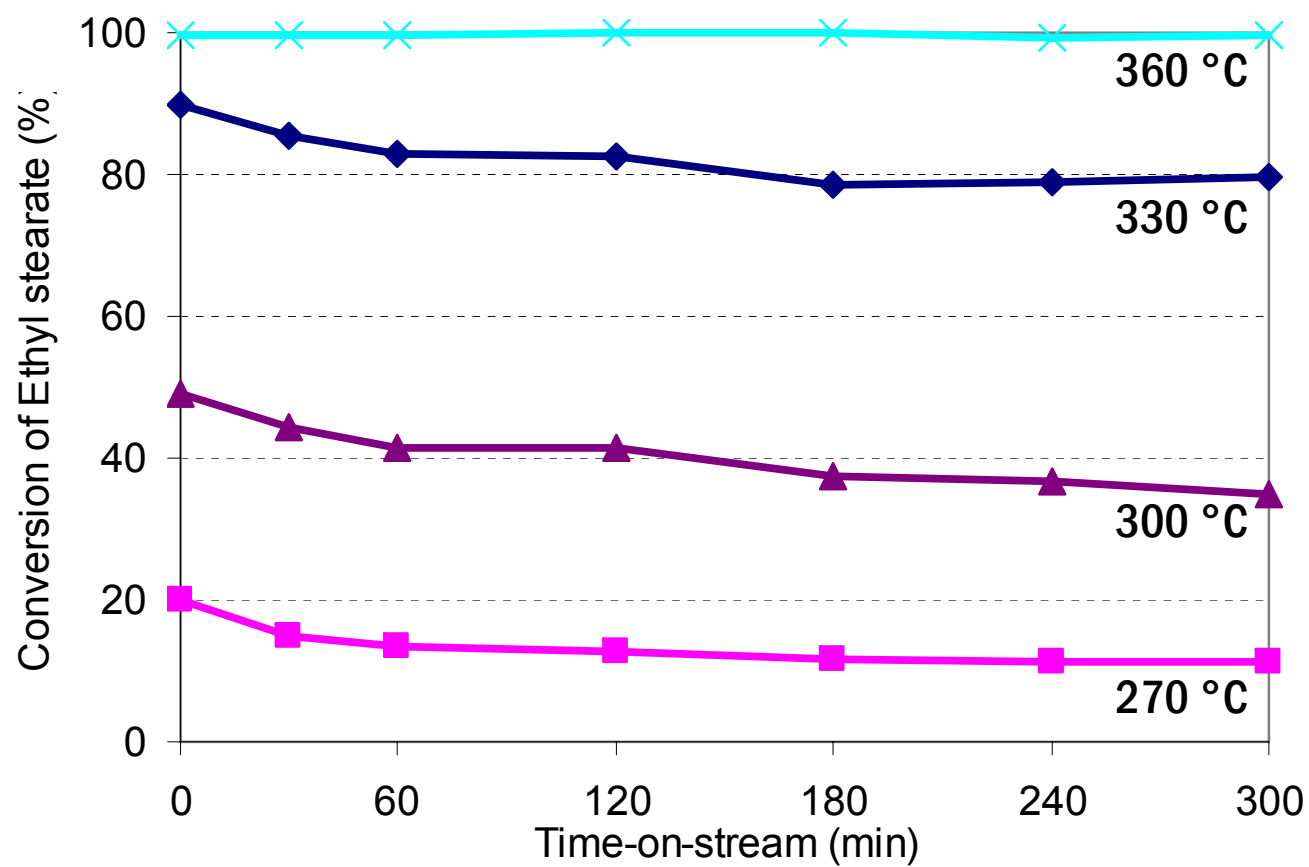


Deactivation?
Mass transfer?



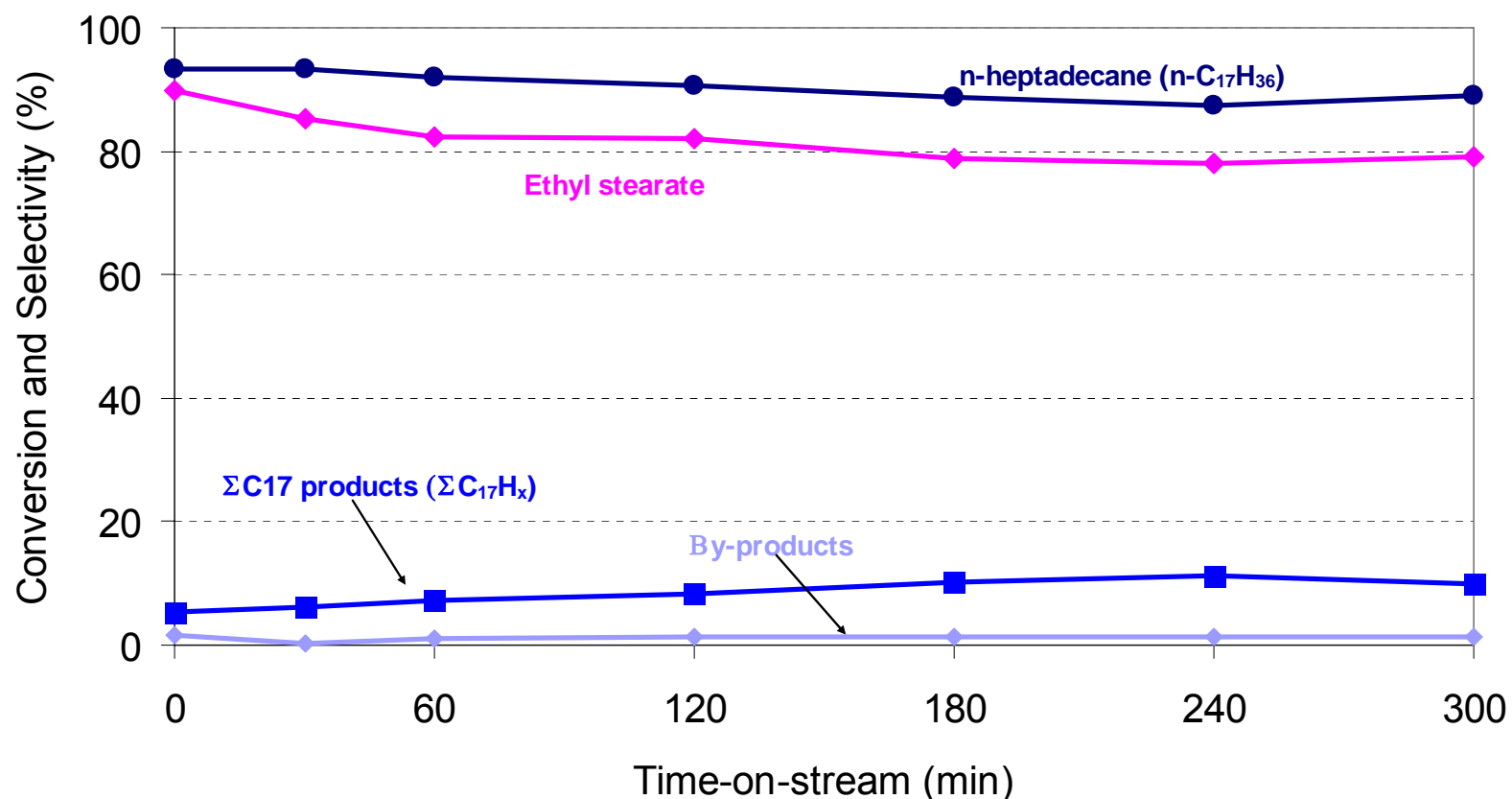
- Catalyst stability and deactivation
- Deoxygenation of different feedstocks

Continuous decarboxylation of ethyl stearate



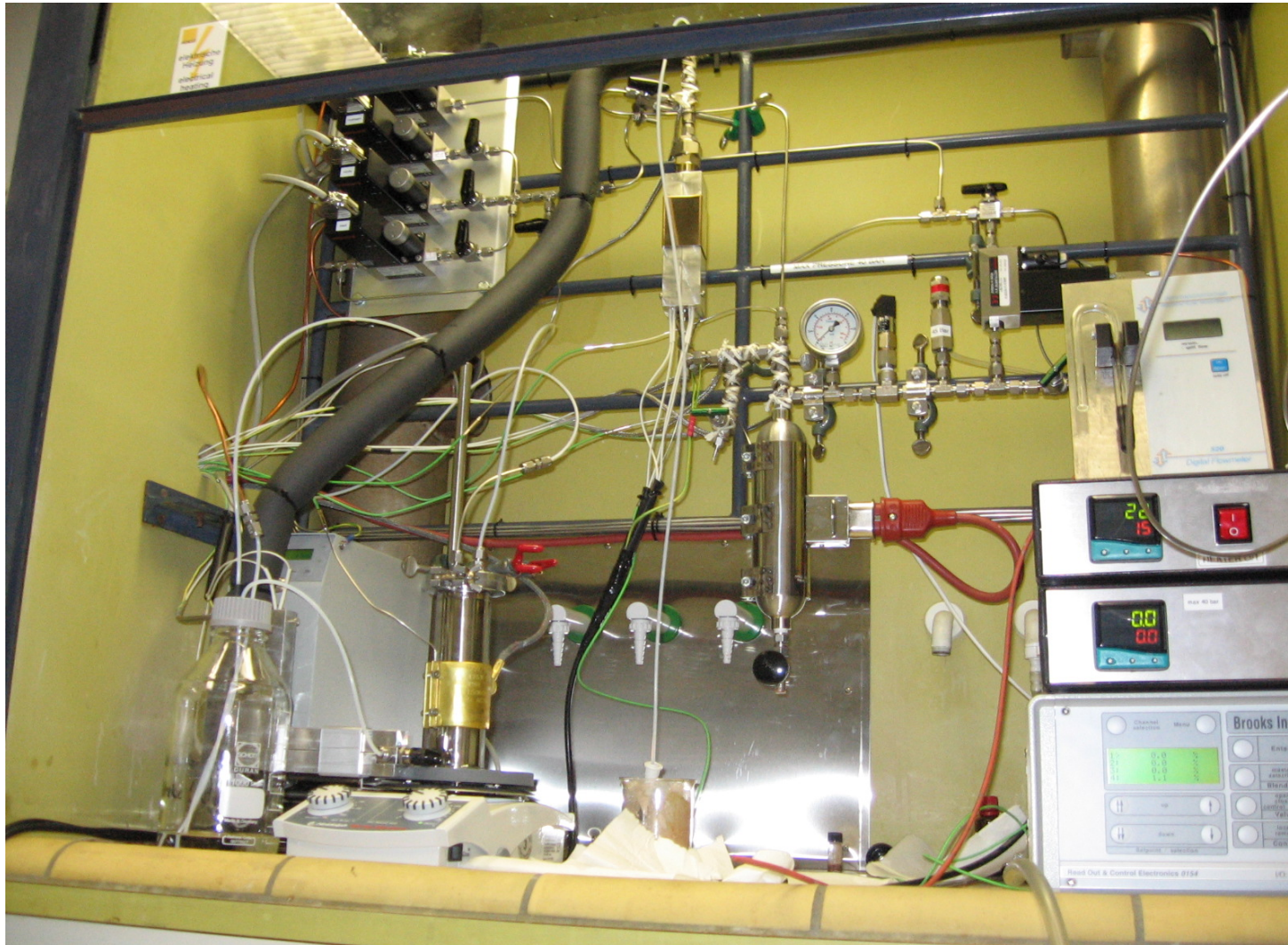
Reaction conditions: 0.16 mol/l Ethyl stearate in hexadecane, 0.4g Pd/C, $V'=0.1$ ml/min

Continuous decarboxylation of ethyl stearate

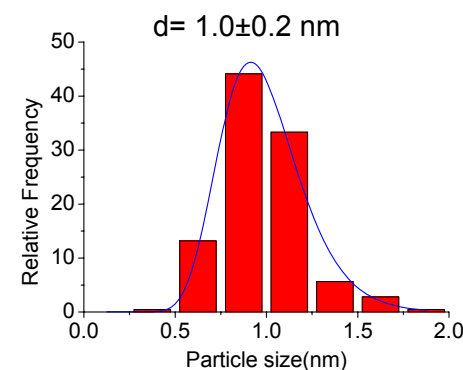
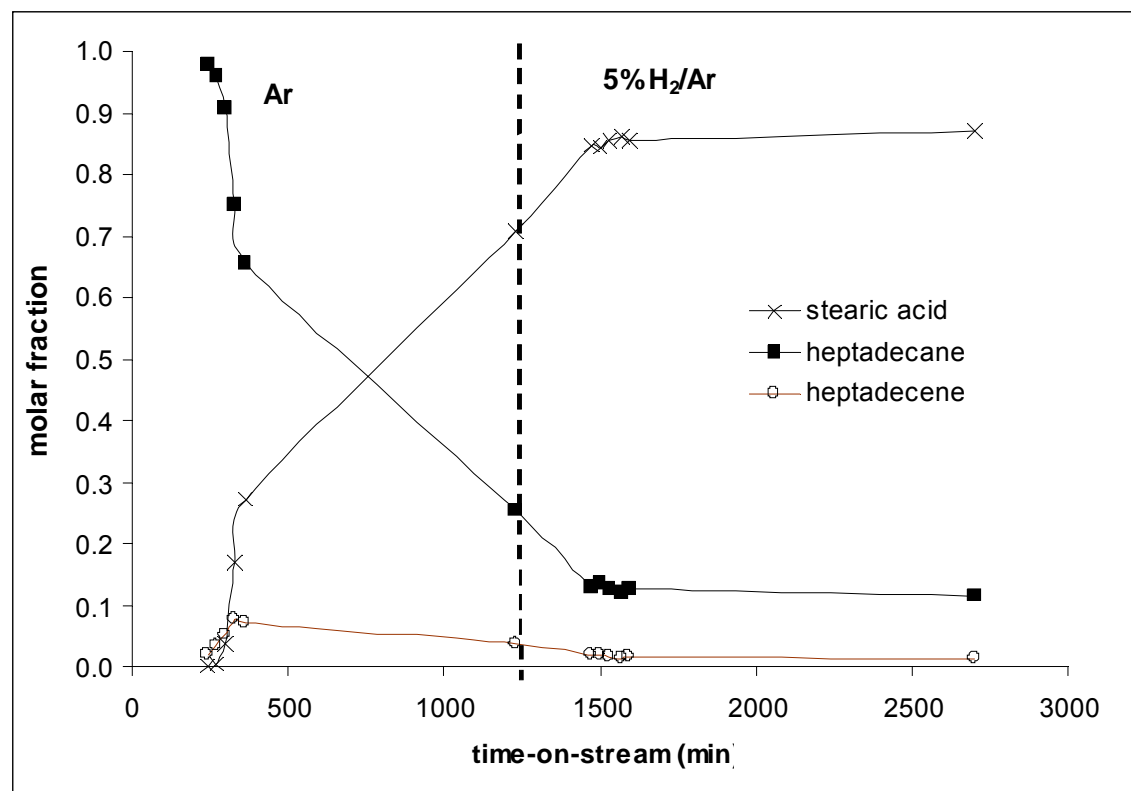


Reaction conditions: 0.16 mol/l Ethyl stearate in hexadecane, 0.4g Pd/C, V'=0.1 ml/min, T = 330° C and P = 5 bar

Trickle bed



Deoxygenation: neat stearic acid



5 wt-% Pd/Sibunit, reaction temperature 360 °C, reaction pressure 10 bar (first argon, then 5% hydrogen in argon), volumetric flow rate of stearic acid 0.075 ml/min.

S. Lestari, P. Mäki-Arvela, H. Bernas, O. Simakova, R. Sjöholm, J. Beltramini, G.Q. Max Lu, J. Myllyoja, I. Simakova, D.Yu. Murzin, Catalytic deoxygenation of stearic acid in a continuous reactor over a mesoporous carbon Pd catalyst, *Energy and Fuels*, **2009**, 23, 3842-3845.

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(54) Title: METHOD FOR THE MANUFACTURE OF HYDROCARBONS

(57) Abstract: Feedstock originating from renewable sources is converted to hydrocarbons in diesel fuel distillation range by contacting with a supported catalyst comprising VIII group metal/metals, whereby the consumption of hydrogen is decreased.