

# Possibilities of the utilization of second-generation bioethanol for the production of monomers and fuel additives

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**Blažej Horváth**

Slovak University of Technology in Bratislava

**Project meeting**

**„Joint chemical laboratory for the service of bioeconomy in the Slovak-Hungarian border region”**

**Interreg, SKHU/1902/4.1/001/Bioeconomy**

**Research Centre for Natural Sciences,  
Magyar tudósok körútja 2, Budapest H-1117, Hungary**

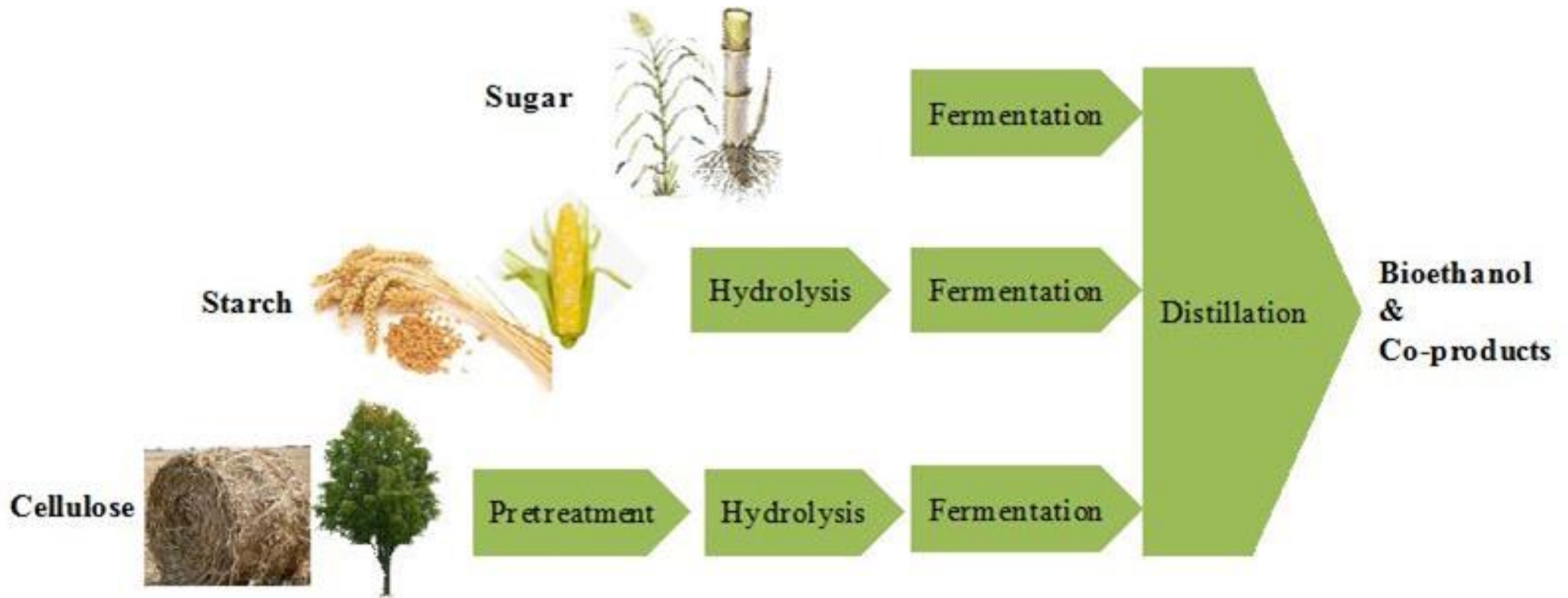
22 September, 2021



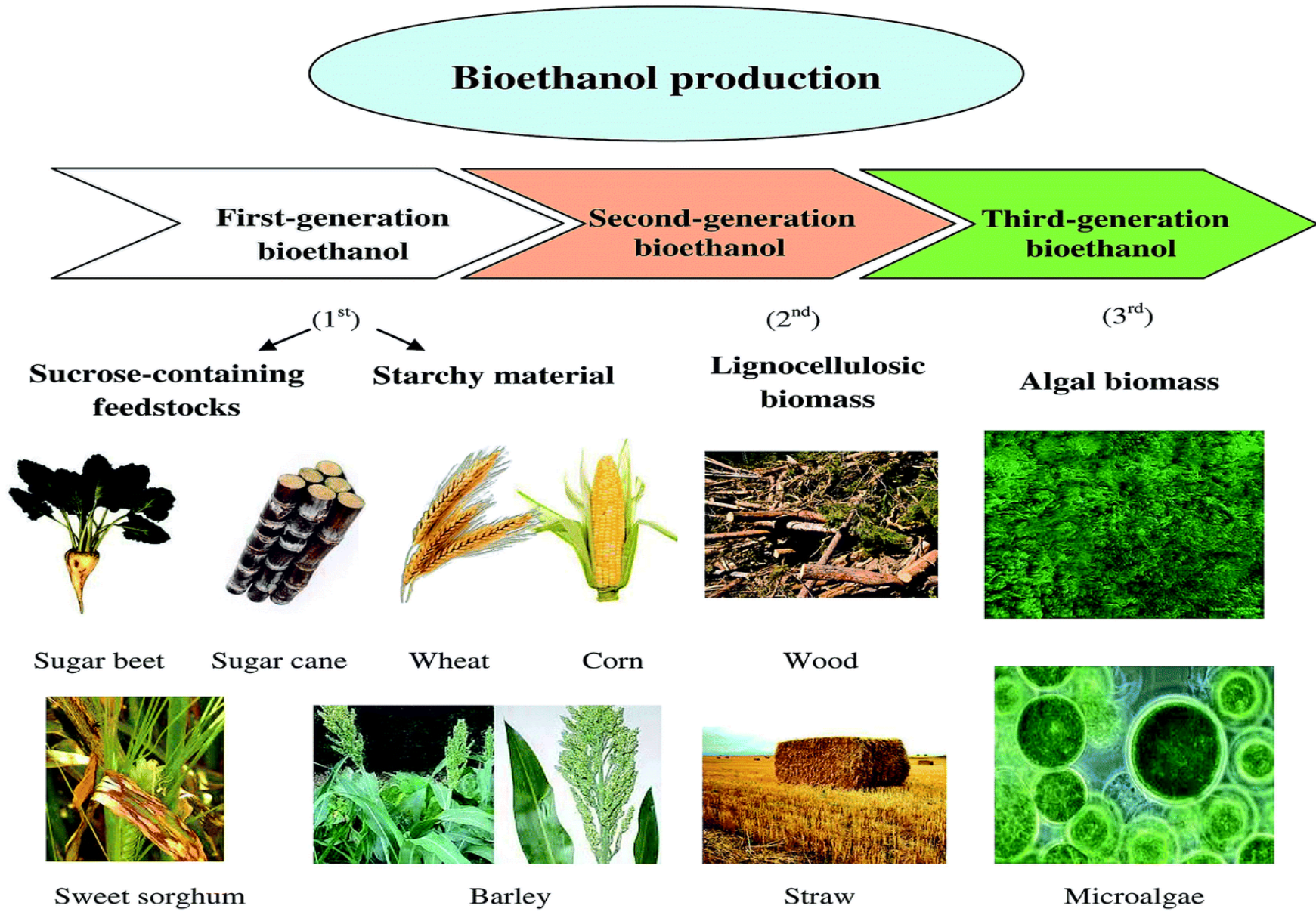
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# Possible transformations of sacharides to bioethanol



# The sources of ethanol



# The sources of ethanol

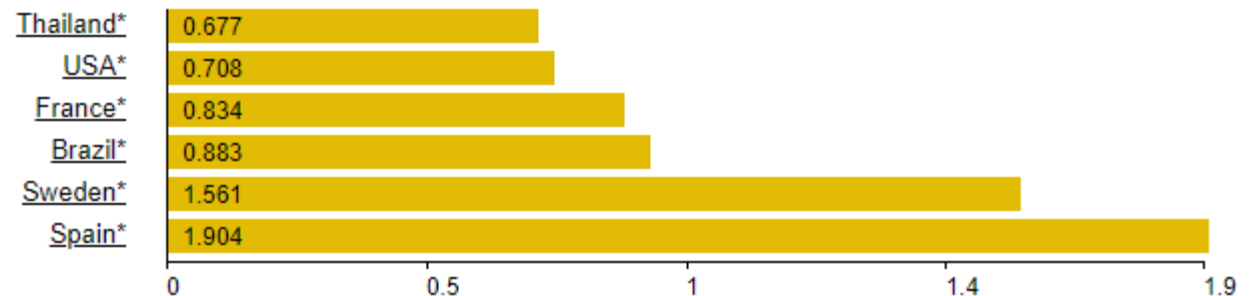


- **First generation:**
  - Pure sugars: up to 15% of ethanol concentration, simple fermentation in one step. The yeasts utilize **nitrogen**.
  - Sugar by-products: molasses. A secondary gain: nitrogen in **alkylpyrazines** (taste and aroma of cocoa, baked goods, coffee, etc.)
  - Starch: potatoes historically, corn in modern agroindustry. There is a necessity of **enzymatic pre-hydrolysis**.
- **Second generation:**
  - Lignocellulosic materials contain both pentoses and hexoses. Their co-fermentation is practically solved.
  - A challenging problem: a formation of **fermentation-retardants** during enzymatic hydrolysis. There is a necessity of a further research to find tolerant yeasts.
- **Third generation:**
  - Algae: abundant, difficult to harvest. In contrast with more developed plants there is a necessity of assisted irradiation.
  - Genetically modified algae produce oils.

# Ethanol prices in the world

- 20-Sep-2021: The average price of ethanol around the world is 1.09 U.S. Dollar per litre.
- However, there is substantial difference in these prices among countries.
- As a general rule, richer countries have higher prices while poorer countries and the countries that produce and export oil have significantly lower prices.
- One notable exception is the U.S. which is an economically advanced country but has low gasoline prices.
- The differences in prices across countries are due to the various taxes and subsidies for gasoline.
- All countries have access to the same petroleum prices of international markets but then decide to impose different taxes. As a result, the retail price of ethanol is different.

Ethanol prices, 20-Sep-2021  
(litre, U.S. Dollar)



The prices of ethanol are comparable to that of petrol

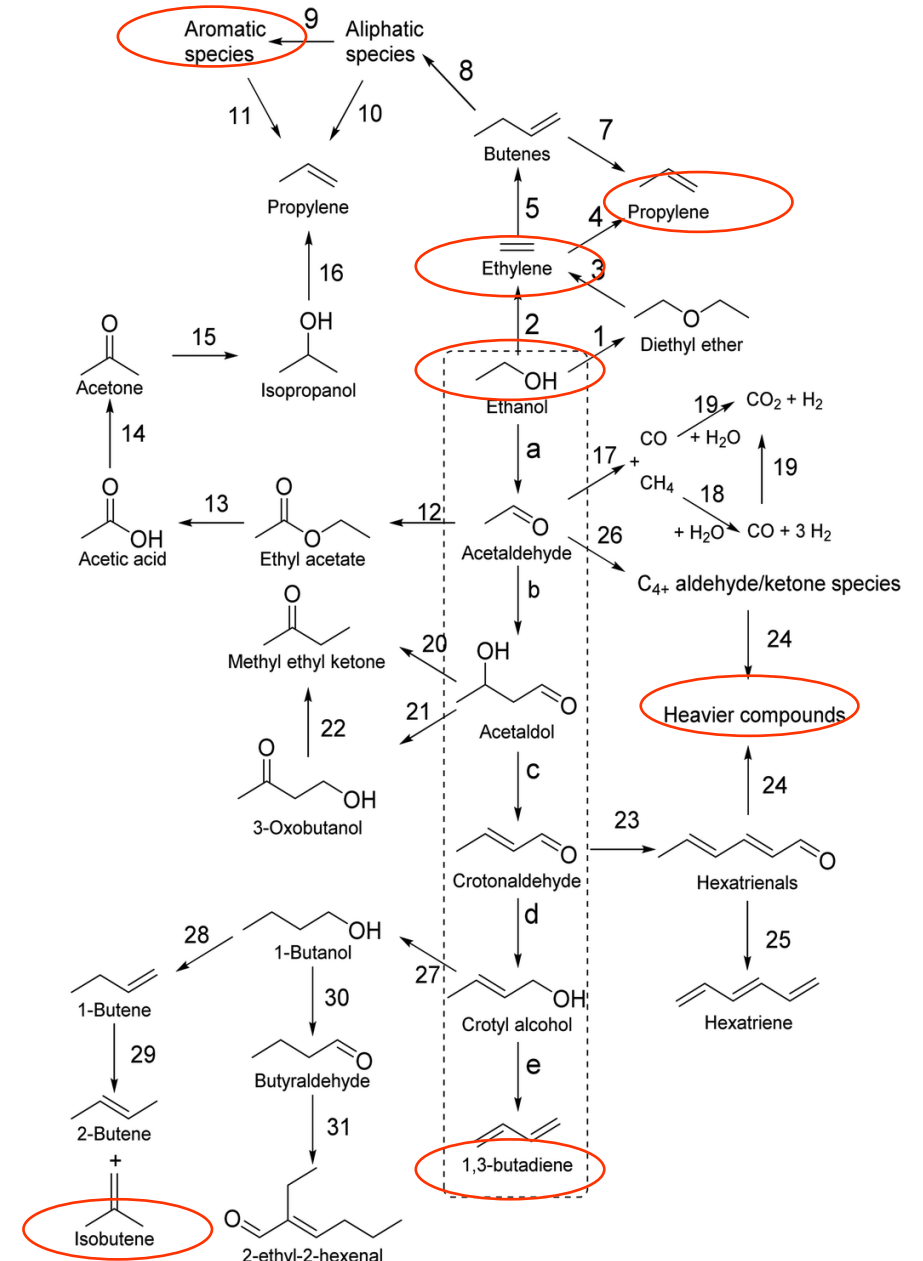
[https://www.globalpetrolprices.com/ethanol\\_prices/#:~:text=Ethanol%20prices%2C%2010-Aug-2020%3A%20The%20average%20price%20of%20ethanol,produce%20and%20export%20oil%20have%20significantly%20lower%20prices.](https://www.globalpetrolprices.com/ethanol_prices/#:~:text=Ethanol%20prices%2C%2010-Aug-2020%3A%20The%20average%20price%20of%20ethanol,produce%20and%20export%20oil%20have%20significantly%20lower%20prices.)



# The reaction scheme of ethanol conversion to alkenes

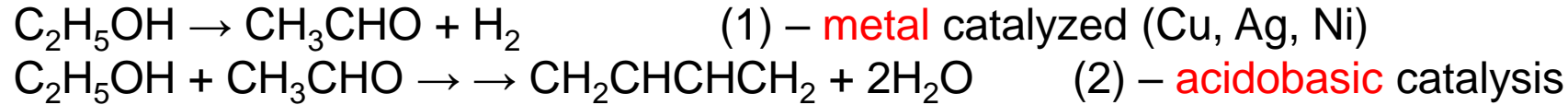


- There is a complex reaction pathway with different possible products
- The majority of the reactions is acidobasically catalyzed, along with metal-catalyzed reactions.
- The reactions can proceed in a single-bed or a double-bed reactor.
- There is a crucial role of the catalysts.
- Temperatures 300 – 550 °C.
- Worth to note that the formation of butadiene is thermodynamically more preferred at higher temperatures.



# Experimental briefly

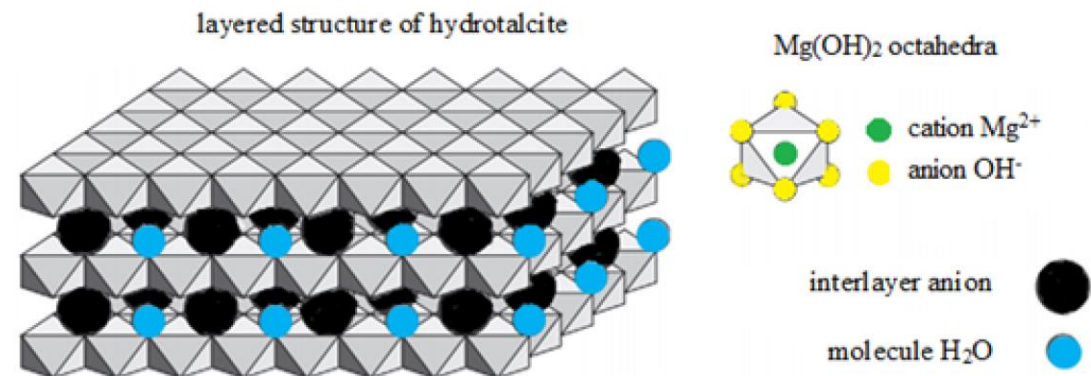
## The simplified reaction pathway leading to butadiene



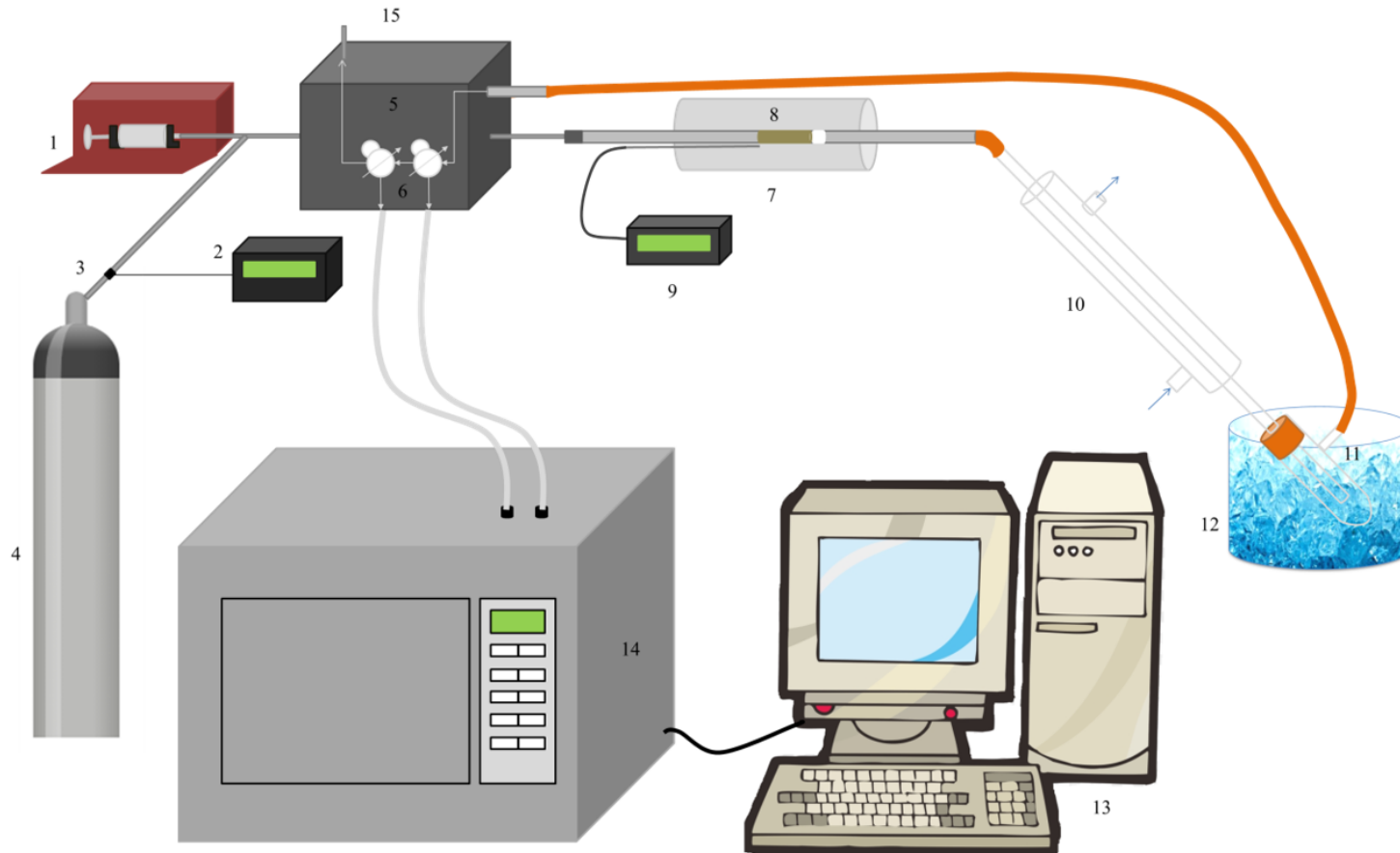
Our research has been mainly focused on finding suitable basic nanostructured catalysts, especially hydrotalcites and sepiolites. For the sake of completeness, zeolitic catalysts were briefly tested as well.

- We didn't focus on the first reaction. Is it possible to carry it out with >95 % selectivity.
- For the second reaction we tested:
  - Zeolites
  - Sepiolite
  - Hydrotalcites

**Main focus on hydrotalcites**



# Experimental



**Temperature: 300 –  
400 – 500 and 550 °C**

**LHSV: 1-5 h<sup>-1</sup>**

**Carrier: N<sub>2</sub> 70ml.min<sup>-1</sup>**

**Ethanol/acetaldehyde  
ratio: 100/0 to 50/50**

1 syringe pump; 2 PID controller; 3 solenoid valve;  
4 nitrogen cylinder; 5 heated chamber; 6 six-way valves;  
7 reactor; 8 catalyst in the reactor; 9 temperature controller;  
10 condenser; 11 liquid products collector; 12 pot with ice;  
13 computer; 14 gas chromatograph; 15 off-gas.



# Zeolites

The preferred product is ethylene – acid-catalysed dehydration.

Catalyst / yields %	ethylene	propylene	butadiene	acetaldehyde
MCM-22	31.5	4.2	1.6	8.8
SDUSY	35.3	2.5	0.8	5.2
Y13	47.2	3.5	1.8	1.4
Y13 – 5Mg	14.3	2.6	2.3	9.7
Y13 – 5Cu	38.8	4.8	4.0	22.7
Y13 – 5Mg – 5Zn	12.7	8.2	12.6	6.7
Y13 – 5Cu – 5Zn	35.5	7.2	18.5	7.4

- **Doping with alkaline earth metals suppresses the formation of ethylene with no significant effect on the yield of butadiene**
- **Interestingly there is a formation of phenols and aromatics in the liquid phase**

# Zeolites

Several physico – chemical data

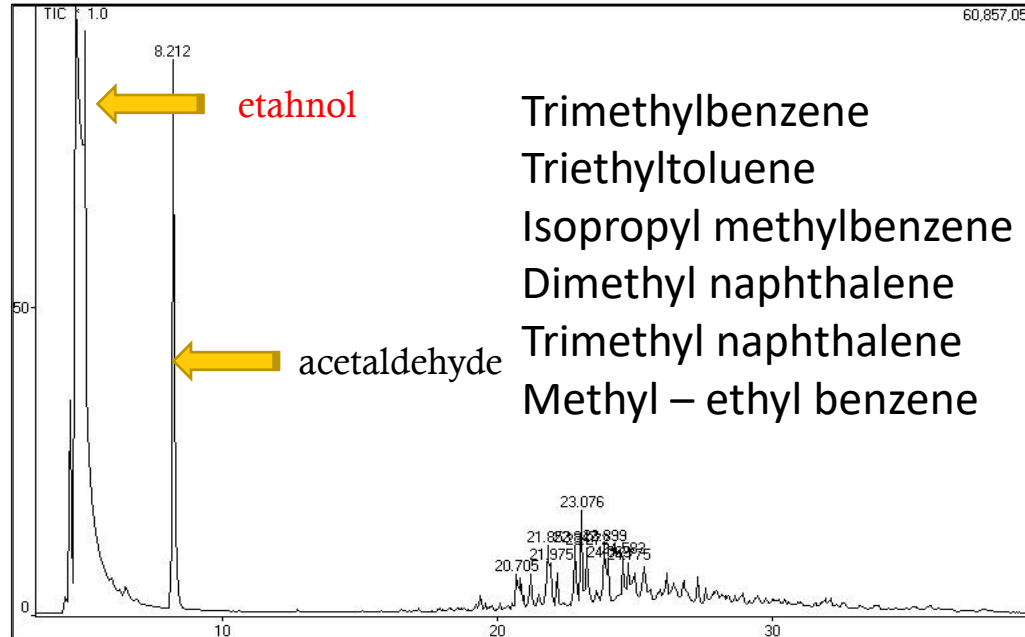


Parameter / Sample	MCM-22		USY
$S_{\text{BET}} / \text{m}^2\text{g}^{-1}$	547		685
$S_{\text{EXT}} / \text{m}^2\text{g}^{-1}$	158		84
$V_{\text{micro}} / \text{cm}^3\text{g}^{-1}$	0.19		0.27
$V_{\text{tot}} / \text{cm}^3\text{g}^{-1}$	0.43		0.38
$B_{\text{ac}} / \mu\text{molg}^{-1}$	390		480
$L_{\text{ac}} / \mu\text{molg}^{-1}$	310		1010

- The more acidic USY gave lower yields of butadiene
- The acidity enhances the dehydration of ethanol

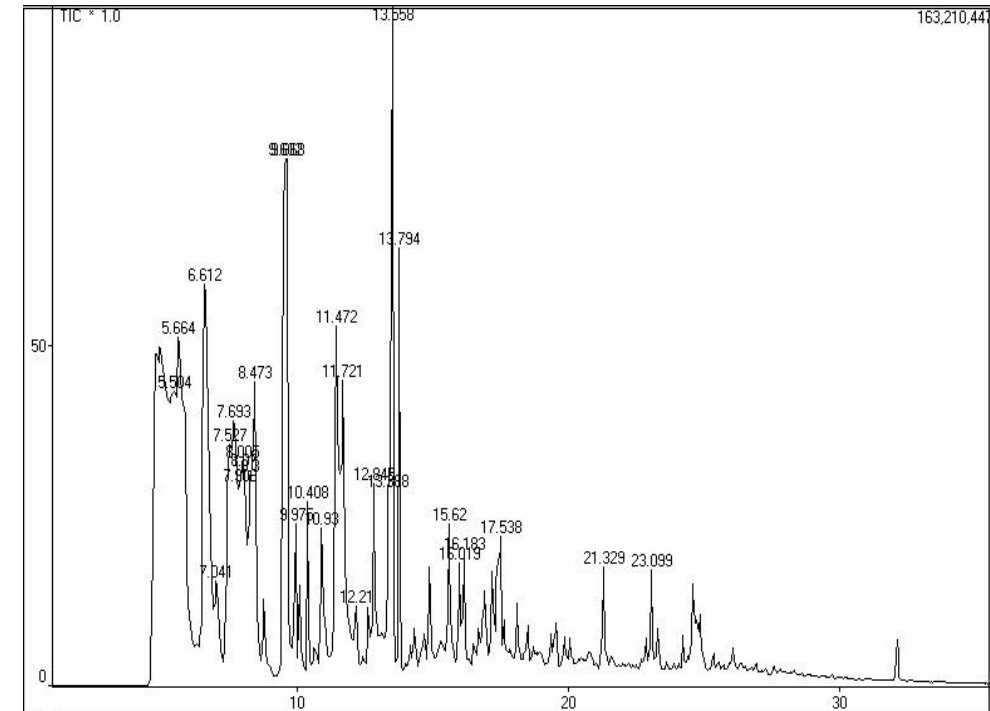
# Zeolites

5%Zr / ZSM-5



+ Cu

GC/MS



- Various oxygenates
- Guerbet reaction
- Aromatics

The aqueous products are more complex than the gaseous ones

# Hydrotalcites

Hydrotalcites:  $M^{2+}_{1-x}M^{3+}_x(OH)_2(A^{n-})_{x/n} \cdot mH_2O$ , where  $M^{2+}$  and  $M^{3+}$  are divalent (e.g., Mg, Ni, Zn, Cu, Mn) and trivalent (e.g., Al, Fe, Cr) metal ions,  $A^{n-}$  is an anion (most commonly  $(CO)_3^{2-}$ , but also  $(SO)_4^{2-}$ ,  $(NO)_3^{3-}$ ,  $Cl^-$ ,  $OH^-$ ), and the value of  $x$  is 0.1 - 0.5.

## **Coprecipitation method**

Inorganic Mg and Al salts at increasing pH or at constant pH.

## **Urea hydrolysis**

Urea hydrolyses slowly at elevated temperature.

## **Sol-gel method**

Hydrolysis of metal-organic compound occurs in organic solvents at elevated or room temperature.

## **Combustion Synthesis**

During combustion synthesis an explosive decomposition of organometallic precursors take place.

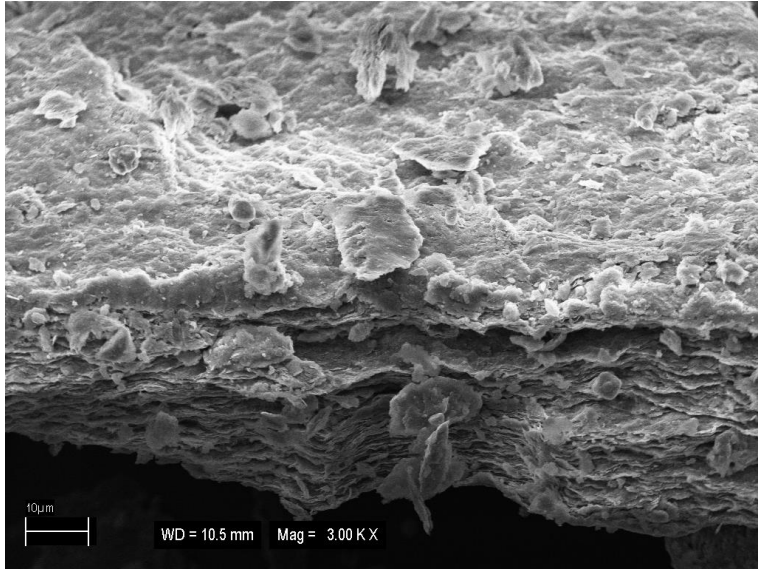
## **Microwave treatment**

Not only reduces the synthesis time but also decreases the crystallite size.

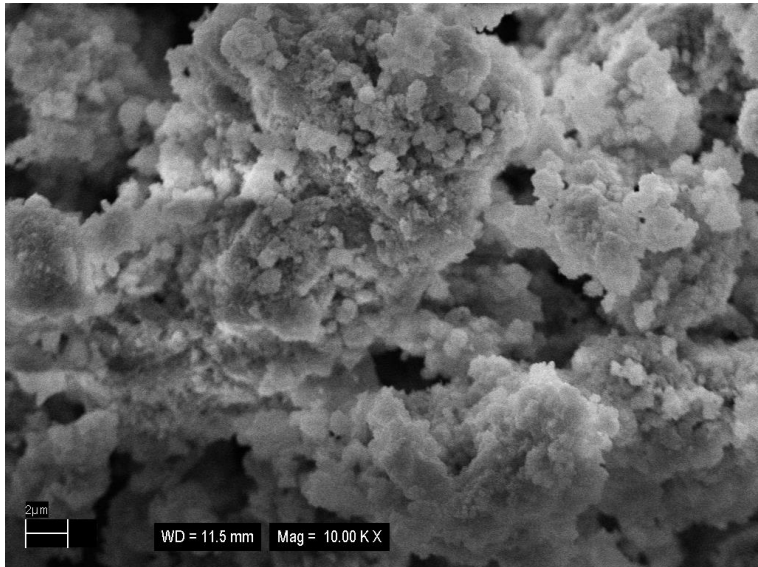
## **Hydrothermal Treatment**

In the presence of water vapor - improves the crystal sizes of hydrotalcites.

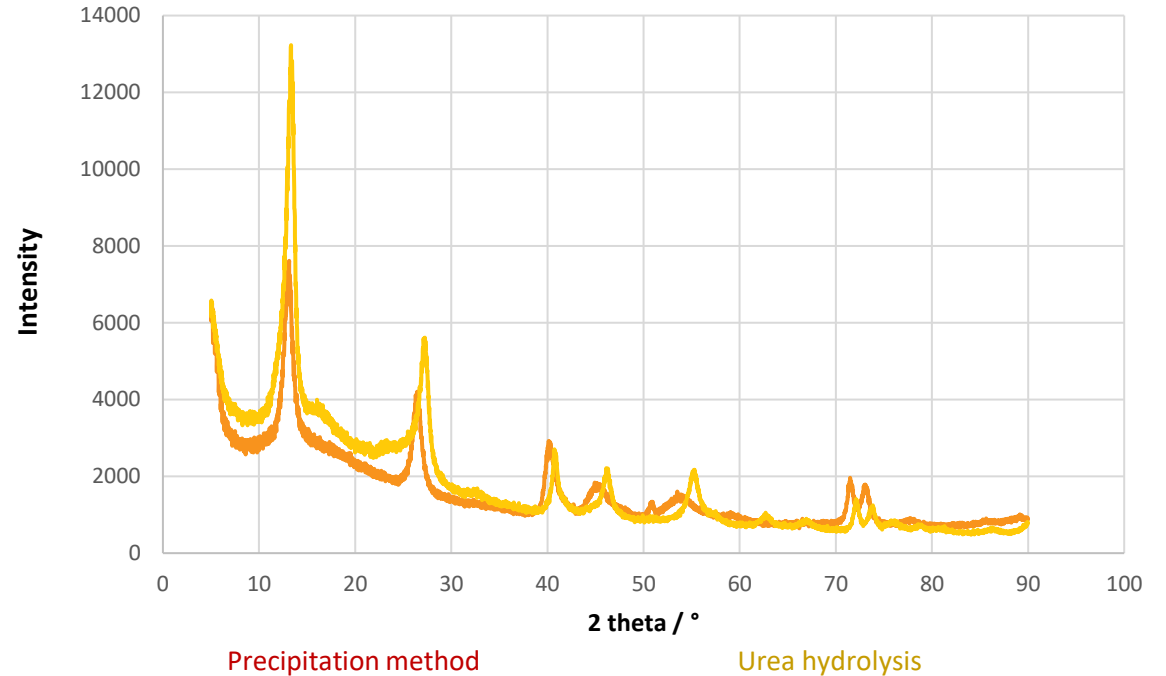
# The effect of the preparation method



Urea method



Precipitation

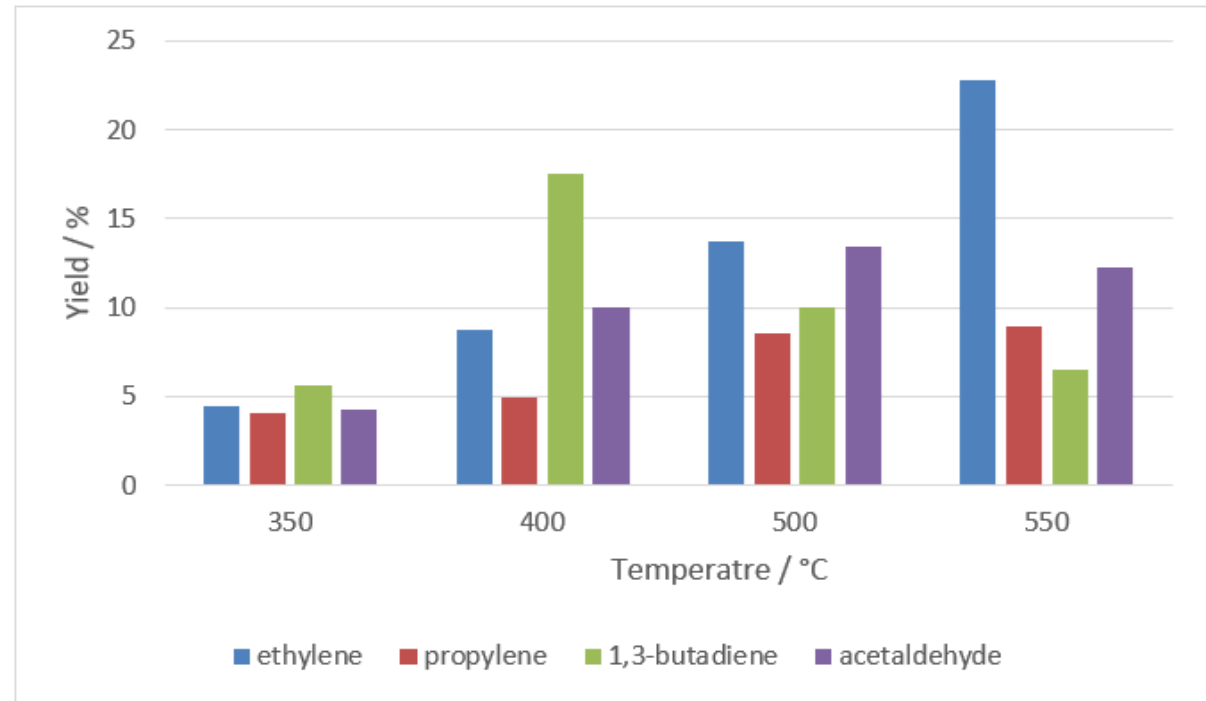
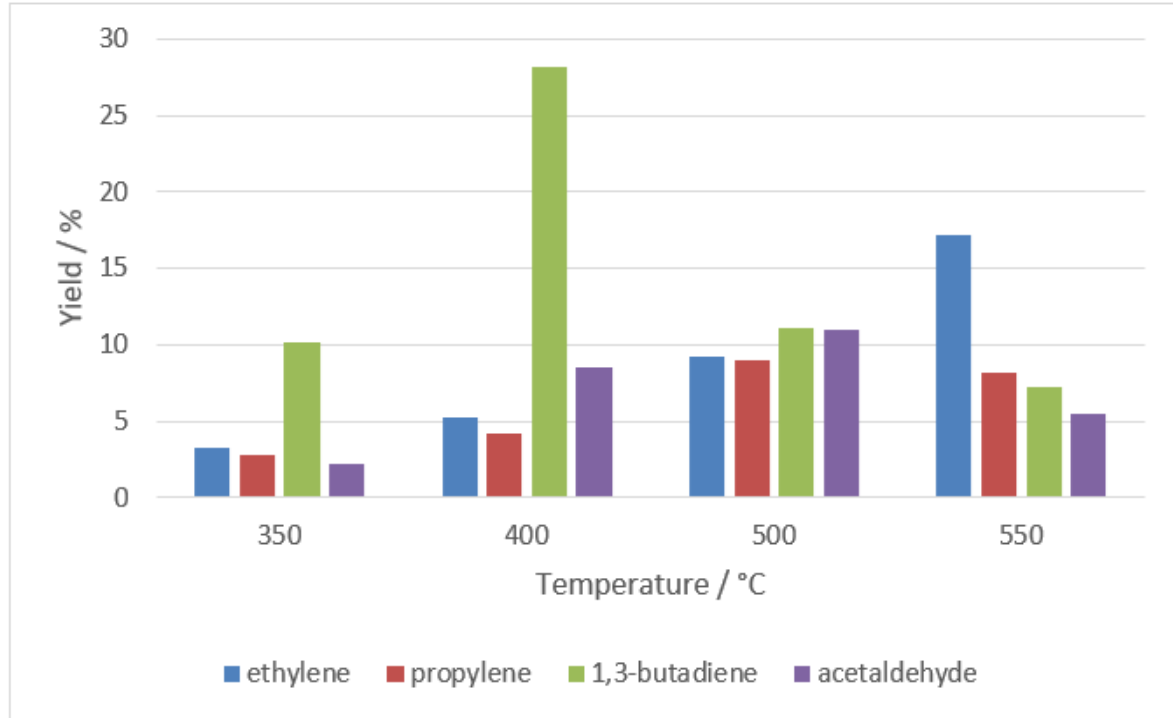


- More pronounced crystallinity in the case of urea hydrolysis
- No significant differences in the XRD patterns – they are both hydroxylapatites

# Differences in the activity

Catalytic performance of the urea-precipitated sample

Catalytic performance of the  $\text{Na}_2\text{CO}_3$ -precipitated sample



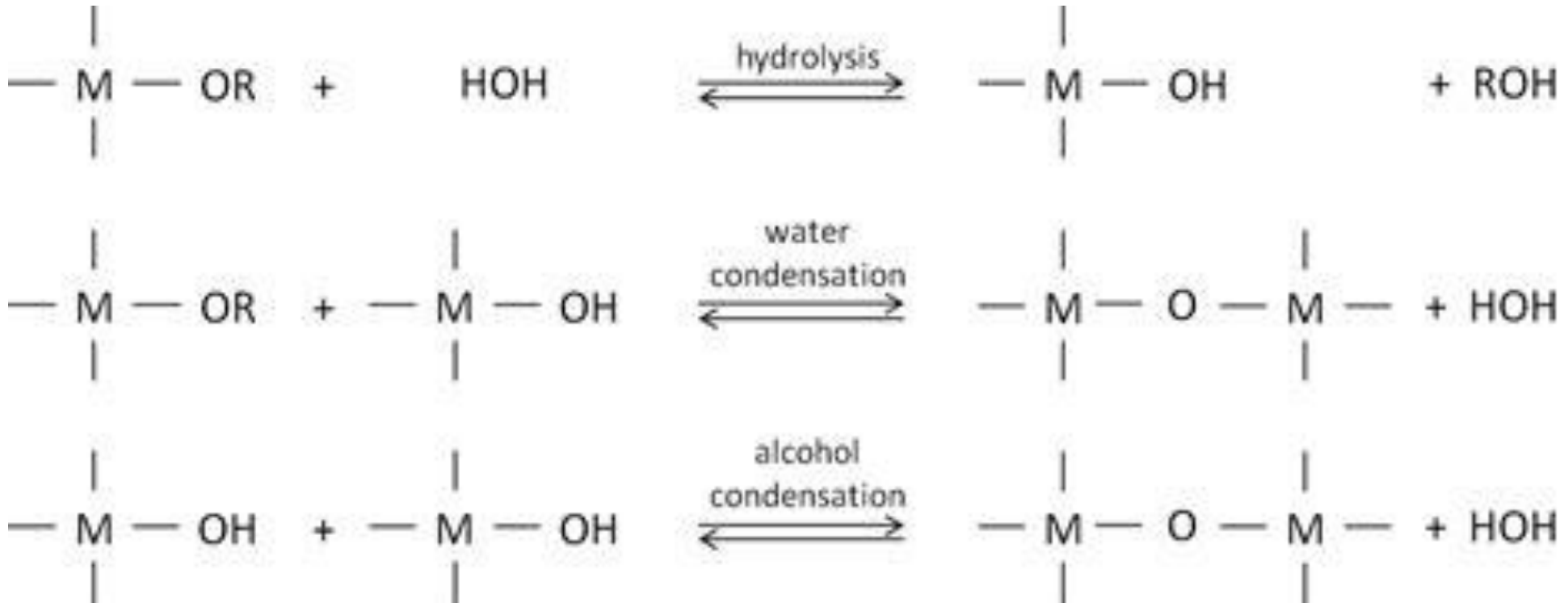
- **The urea – precipitation suppresses the ethylene formation while promoting the formation of butadiene.**
- **Highest butadiene yields at about 400 °C.**



# Preparation of Mg-Al materials with sol-gel method



A matrix of hydrolysis reactions

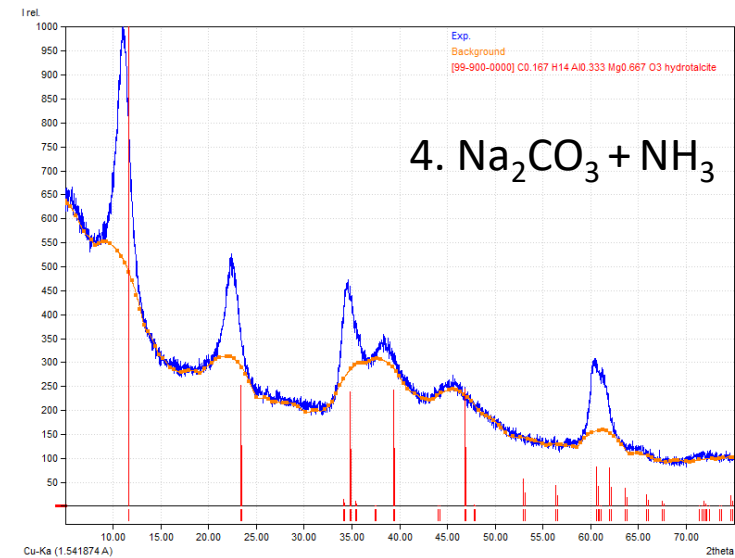
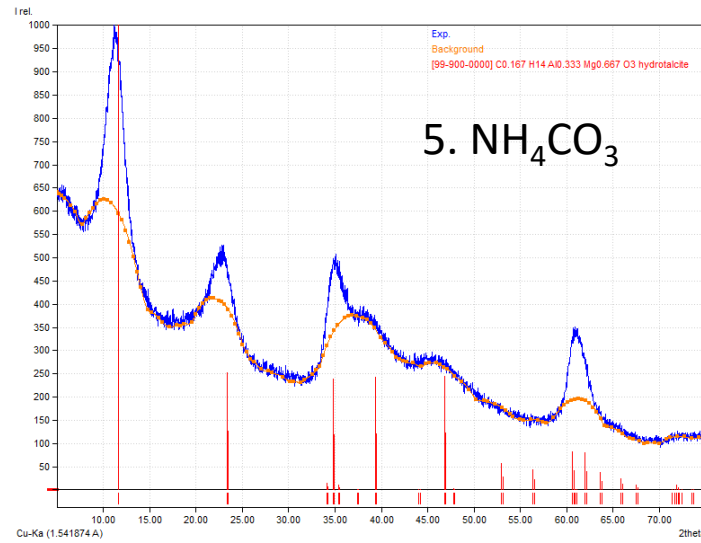
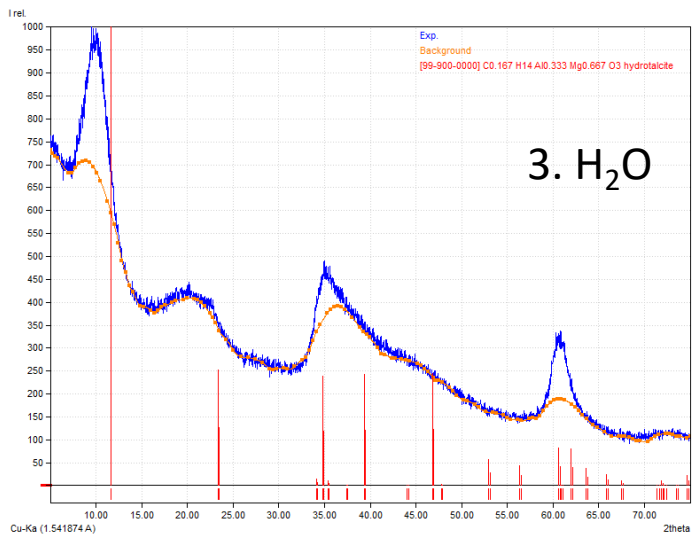
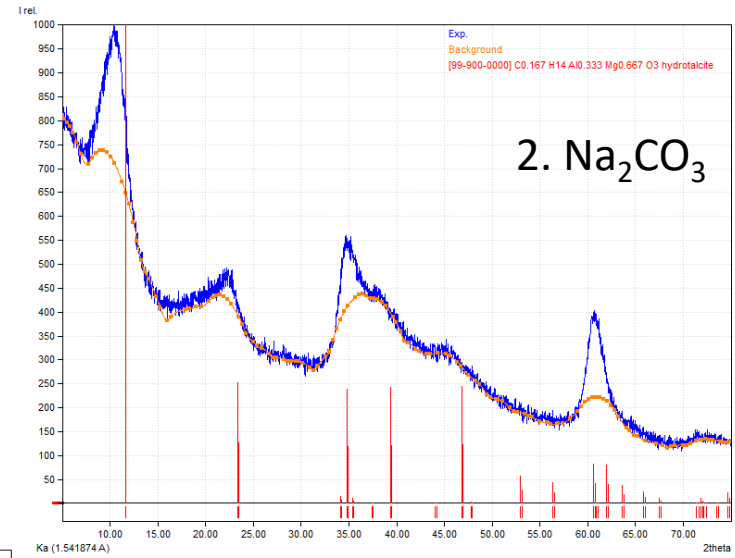
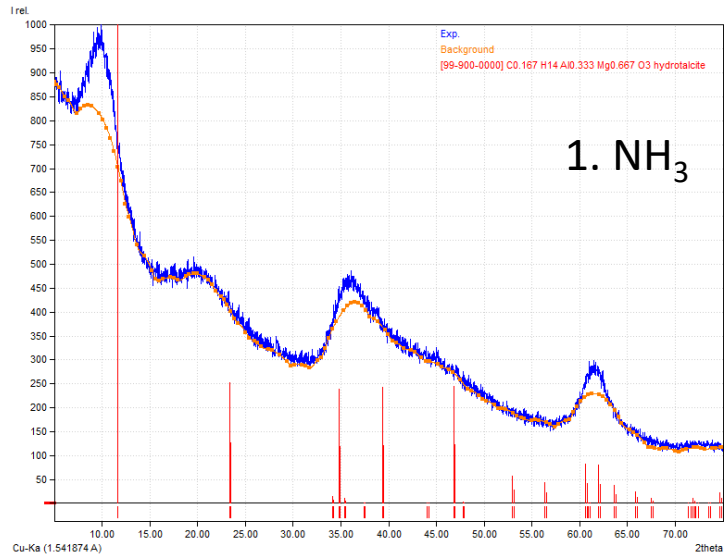


**Alkoxides are usually soluble in their own alcohols, e.g. (BuO)<sub>3</sub>Al is soluble in butanol.**

Some have lower **solubility** e.g. the solubility of (EtO)<sub>2</sub>Mg in ethanol is 0,9%, in methanol 3,1%.

We used methanol as a solvent and tested several hydrolysis agents.

# XRD – not yet been tested

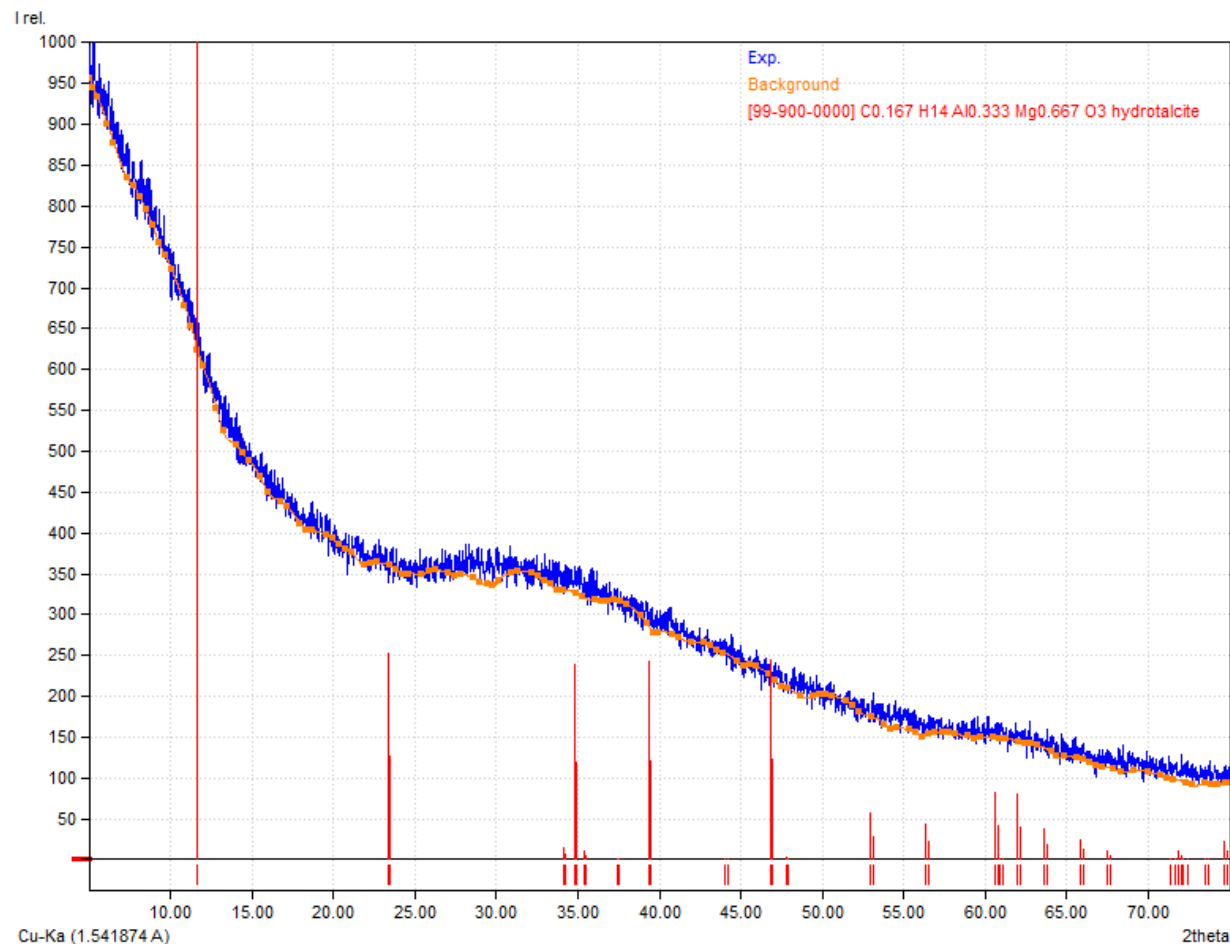


There is a possibility to prepare hydroxalcites in **less polar environment**.

# Sample in perfluoroheptane

- Preparation procedure:
- 2,4632 g (sek.BuO)<sub>3</sub>Al in 12 ml BuOH
- + 39.1 ml 10% methanol solution of Mg - methoxycarbonate
- + 80 ml **perfluoroheptane**
- Ageing for 5 days
- Evaporation of the solvent

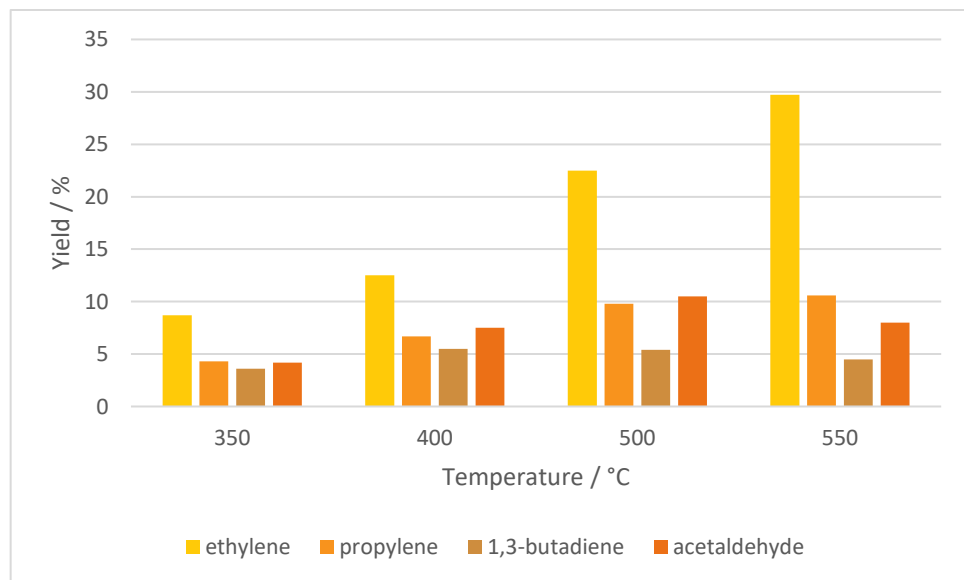
**The resulting material is completely amorphous**



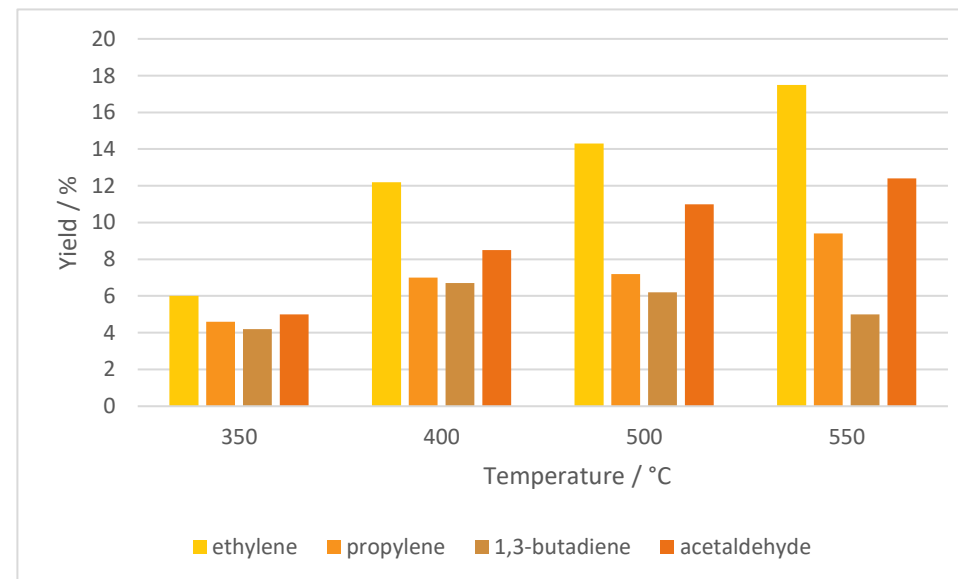
# Sepiolites

Sepiolite, being in fact a hydrous magnesium silicate clay mineral, formally  $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$  can be considered as a promising catalyst for the transformation of ethanol.

## Parent



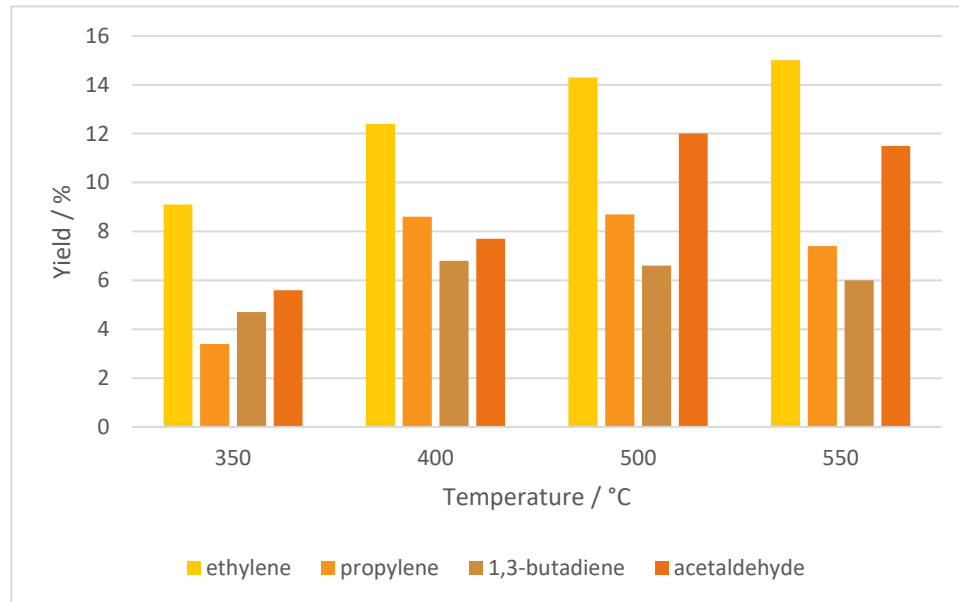
## K-doped



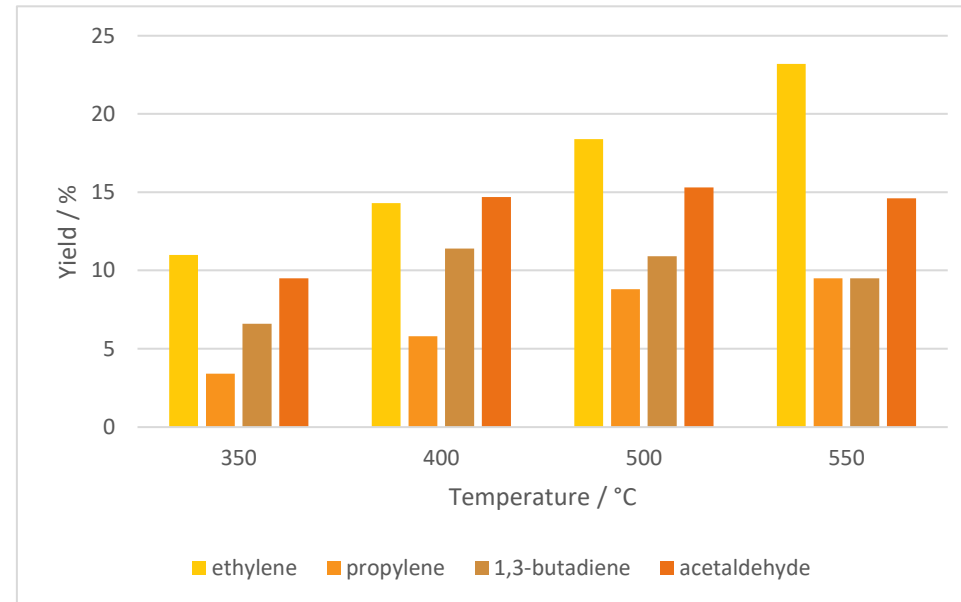
- the main product is ethylene
- In aim to increase the basicity, potassium was introduced.
- K slightly suppresses the dehydration

# Sepiolites

## Sr doped



## Mn-doped



- Sr further suppresses the dehydration, but does not increase the yield of other alkenes, however, leads to product distribution shifted to heavier alkenes
- Mn at 400 °C gives similar ethylene yield as Sr, but in the other hand gives the highest yield of butadiene

# The strong necessity of the further transformations

The intermediates derived from ethanol need to be processed further

- **The main products derived from ethanol:**
  - **Bioethylene: polyethylene from renewable sources; all the other products otherwise made from ethylene**
  - **Butadiene: the Lebedev process – rubber from renewables**
  - **Aromatics: a wide range of useful alkylbenzenes and alkylnaphtalenes; phenols**
  - **Propylene**
- **Propylene:**
  - **Polypropylene**
  - **Acrolein**
  - **Acetone**
  - **Propylene oxide:**
    - **Polyurethanes**
    - **Thermodynamically possible, however there is a need for a catalyst**



# Ethylation of glycerol by ethanol

- combination of **two raw materials** from renewable sources

H-Beta zeolite

**1. Ethylation:** bioethanol + bioglycerol  $\longleftrightarrow$  glycerol ethyl ethers

200 ° C **S (Di- + Tri- ethyl ethers  $\approx$  50 % )**

**2. Consecutive tert. butylation:** glycerol ethyl ethers + isobutylene

Purolite CT, 80° C

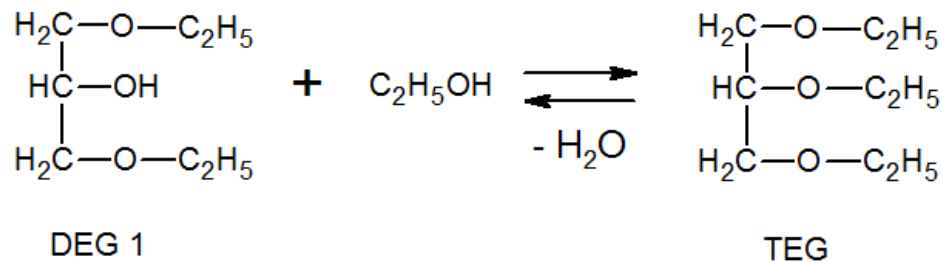
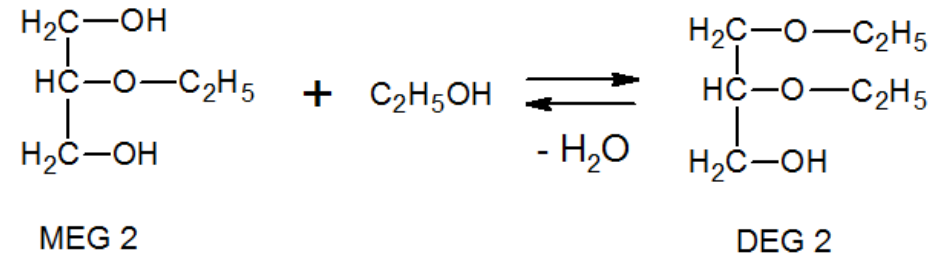
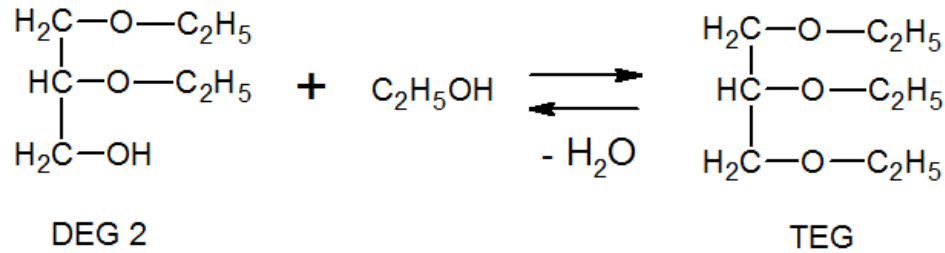
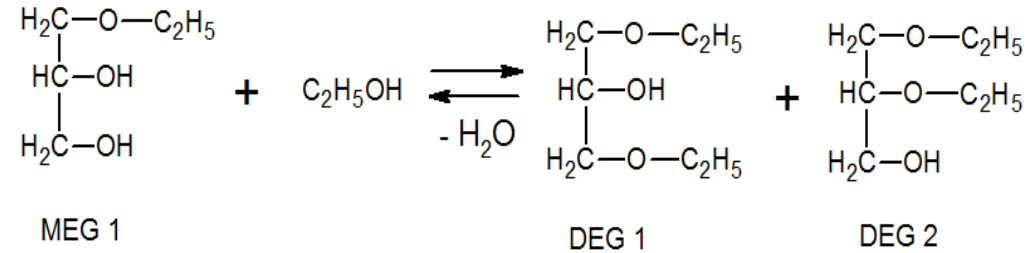
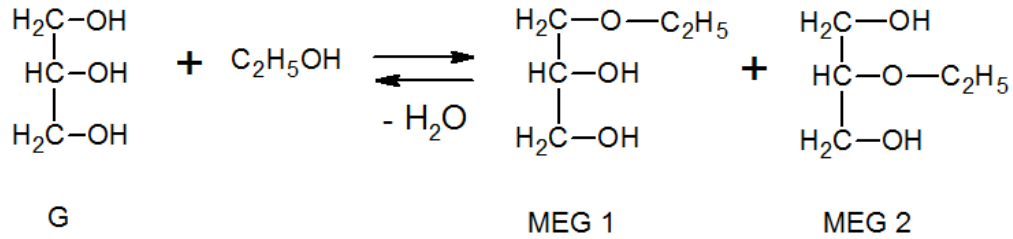


Mixture of ethyl-, tert. butyl-, mixed ethyl- tert.butyl

ethers of glycerol with **S (Di- + Tri- alkyl ethers)  $\approx$  93 %**

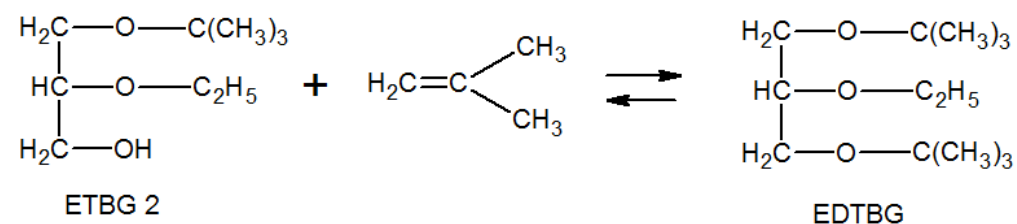
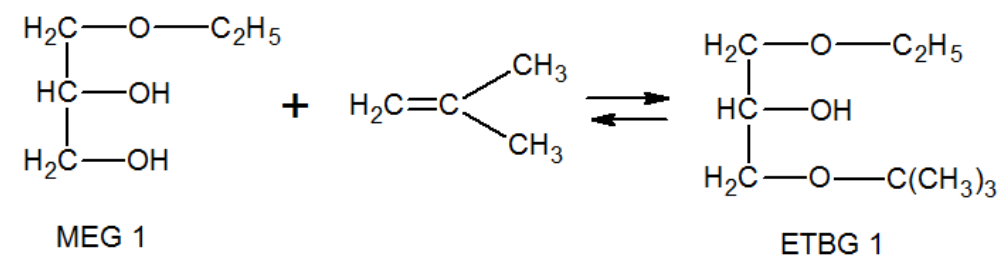
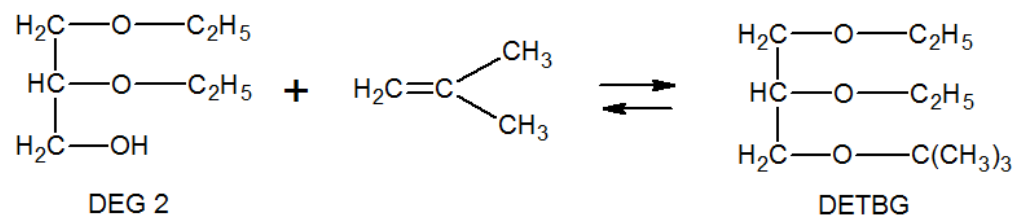
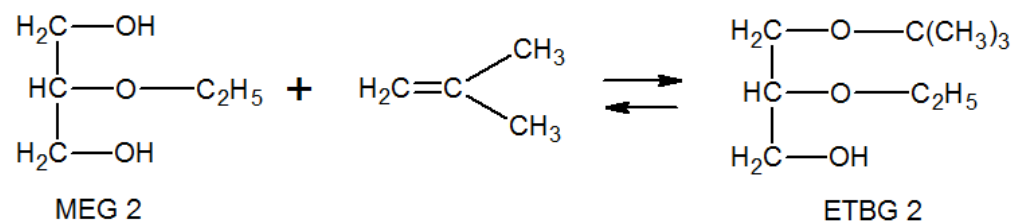
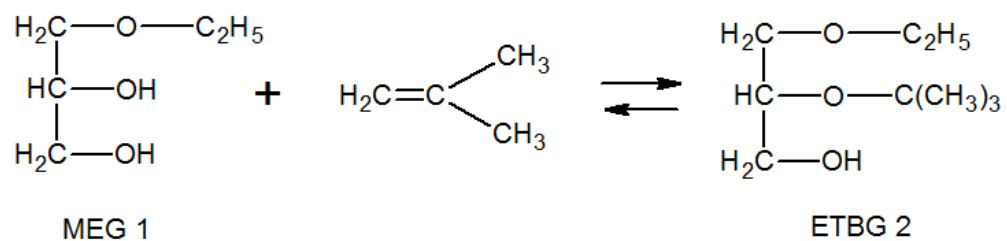
# Ethylation of glycerol

- Reaction steps



- The dehydration reactions usually need higher temperatures (ca. 200 °C)
- At higher temperatures there is a pronounced formation of by-products.

# Consecutive tert-butylation



- There is no dehydration step.
- The alkylation with alkenes doesn't require temperatures above 100 °C (80 °C). No need to withdraw water.

# Basic findings

- Zeolites usually work at **elevated** temperatures. For the condensation of glycerol with ethanol over H-Beta (modules 10 -100) the appropriate temperature is  $\sim 200$  °C. At such temperatures zeolites are surely stable. Ethanol can be replaced by diethylether.
- The consecutive alkylation with isobutylene can proceed at lower temperature ( $\sim 80$  °C). Ion-exchange resins are stable up to 180 °C.
- Problems with the solubility: monomethylethers are poorly soluble in gasoline.
- **Hence, a further alkylation enhances their solubility.**
- However, diethylether is poorly miscible with the glycerine phase.
- **For that reason, we suppose a two-step alkylation process.**
- The two-step process eliminates the drawbacks of the limited solubilities.

# Ethylation of glycerol

Temperature (° C )	180	200
Distribution of products ( wt.% )		
TEG	0,2	1,7
DEG 1	2,1	10
DEG 2	2,0	6,6
MEG 1	20,8	12,9
MEG 2	4,3	2,1
G	70,6	66,6
Conversion (X), selectivity(S) and yield (Y) ( % )		
X (G)	24,5	25,7
S (D+T)	12,1	48,9
Y (D+T)	3,0	12,5
S (M)	87,9	51,1

The effect of reaction temperature to product distribution: (catalyst H- Beta, 10 wt.% of glycerol in ethanol) Reaction conditions: molar ratio EtOH/G = 15, M, D ,T –mono, di-and tri ethers, reaction time 8 h.

# Consecutive tert-butylation of glycerol ethylation products

	Ethylation	Tert.butylation	Tert.butylation
Catalyst	H-Beta	Purolite CT 169	Amberlyst 35 Dry
Molar ratio	EtOH/G=10/1	i-Bu/-OH=2/1	i-Bu/-OH=2/1
Temperature (° C)	200	80	80
Distribution of products	( wt. % )		
TEG	2,2	1,1	1,1
EDTBG		11,3	12,0
DETBG		14,3	13,6
TTBG		4,7	3,5
DEG 1	6,3	1,6	1,7
ETBG 1		10,3	9,4
DTBG 1		10,5	7,5
DEG 2	4,6	0,3	0,4
ETBG 2		1,4	1,3
DTBG 2		1,3	0,7
MTBG 1		1,3	1,3
MTBG 2		0,7	0,2
MEG 1	15,6	0,5	0,7
MEG 2	2,6	0,2	0,2
G	68,7	40,3	46,4
Conversion, selectivities and yield ( % )			
X (G)	23,1	41	34,9
S (D+T)	37,1	93,3	93,5
Y (D+T)	8,5	38,3	32,6
S (M)	62,9	6,7	6,5

- H-Beta gave a conversion of ~23% in the Ethylation step.
- The consecutive alkylation with isobutylene nearly doubled the conversion, while shifting the product distribution to multialkylated products.
- Ethanol can be replaced by diethylether (the absorption of water).
- A two-step process utilizing two different catalysts.
- Good miscibility of multialkylated glycerol with naphtha.
- We suggest a two-step alkylation process.



# Conclusions

- Ethanol is a renewable raw material
- A versatile raw
- On its own, it can be transformed to alkenes or aromatics
- Those of particular interest are **ethylene, propylene and butadiene**.
- **Propylene can be transformed to several industrially important intermediates, as polyurethanes or other polyether polyols**
- **Some catalysts give valuable liquid products**
- **The acidobasic features of the catalyst significantly affect the product distribution**
- **Isobutylene is more reactive than ethanol or butanol in glycerol alkylation**
- **Several zeolites were tested for the Ethylation. The optimal Si/Al ratio was found ca. 25**
- **Diethylether formed in the course of the alkylation with ethanol can be recycled with a beneficial effect on the ethanol conversion.**

# Thank You for your attention

## Acknowledgement

European Regional Development Fund (Interreg, SKHU/1902/4.1/001/Bioeconomy)  
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