Transesterification of alternative sources over mixed oxides to produce biodiesel

Ing. Miroslava Mališová
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

ttk Interreg Slovakia-Hungary Building Partnership STU Slovak University of Technology in Bratislava

Transesterification of alternative sources over mixed oxides to produce biodiesel

Ing. Miroslava Mališová
Slovak University of Technology in Bratislava

Content

01 **Biofuels**
- Definition, divison

02 **Sources of biofuels**
- Vagetable oils, animal fats

03 **Vagetable oil**
- Kinds of vagetable oils

04 **Camelina sativa**
- Properties, composition

05 **Transesterification**
- Homogeneous, heterogeneous

06 **Hydrotalcites – mixed oxides**
- Štruktúra, vlastnosti

07 **Obtained results**

Biofuels

„ liquid fuel made from biomass for transport“ EU 2018/2001

1800 — 1 bilion people in the world

1927 — 2 bilion people in the world

1960 — 3 bilion people in the world

1974 — 4 bilion people in the world

1987 — 5 bilion people in the world

2000 — 6,1 bilion people in the world

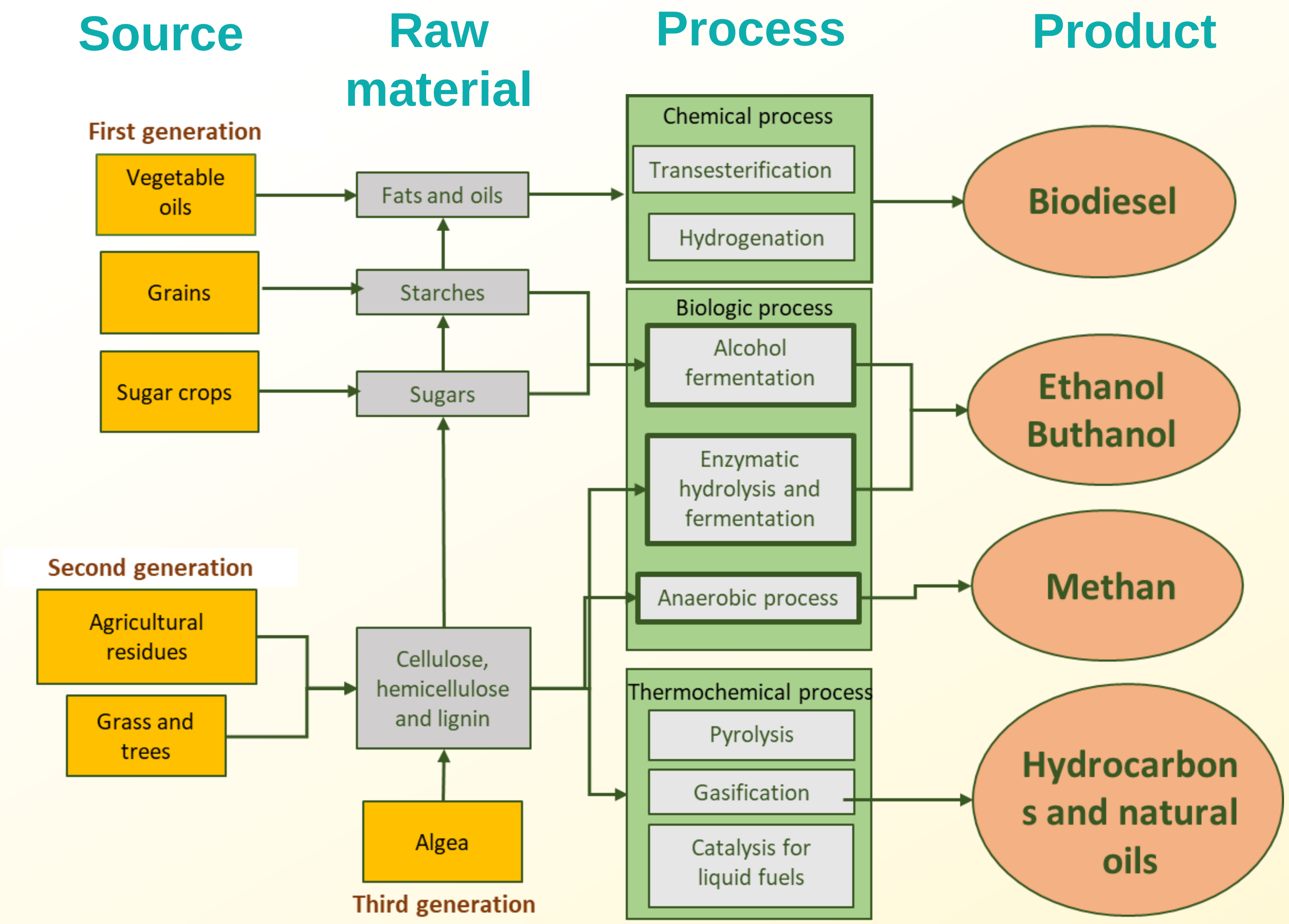
2021 — 7,8 bilion people in the world

1996 — 670 milion cars

2019 — 1,32 bilion

2036 — 2,8 bilion?

2018 – 2020
97 -100 million barrels of oil per day
One person - 5 barrels of oil (596 liters) per year
Verified oil reserves - 50 years

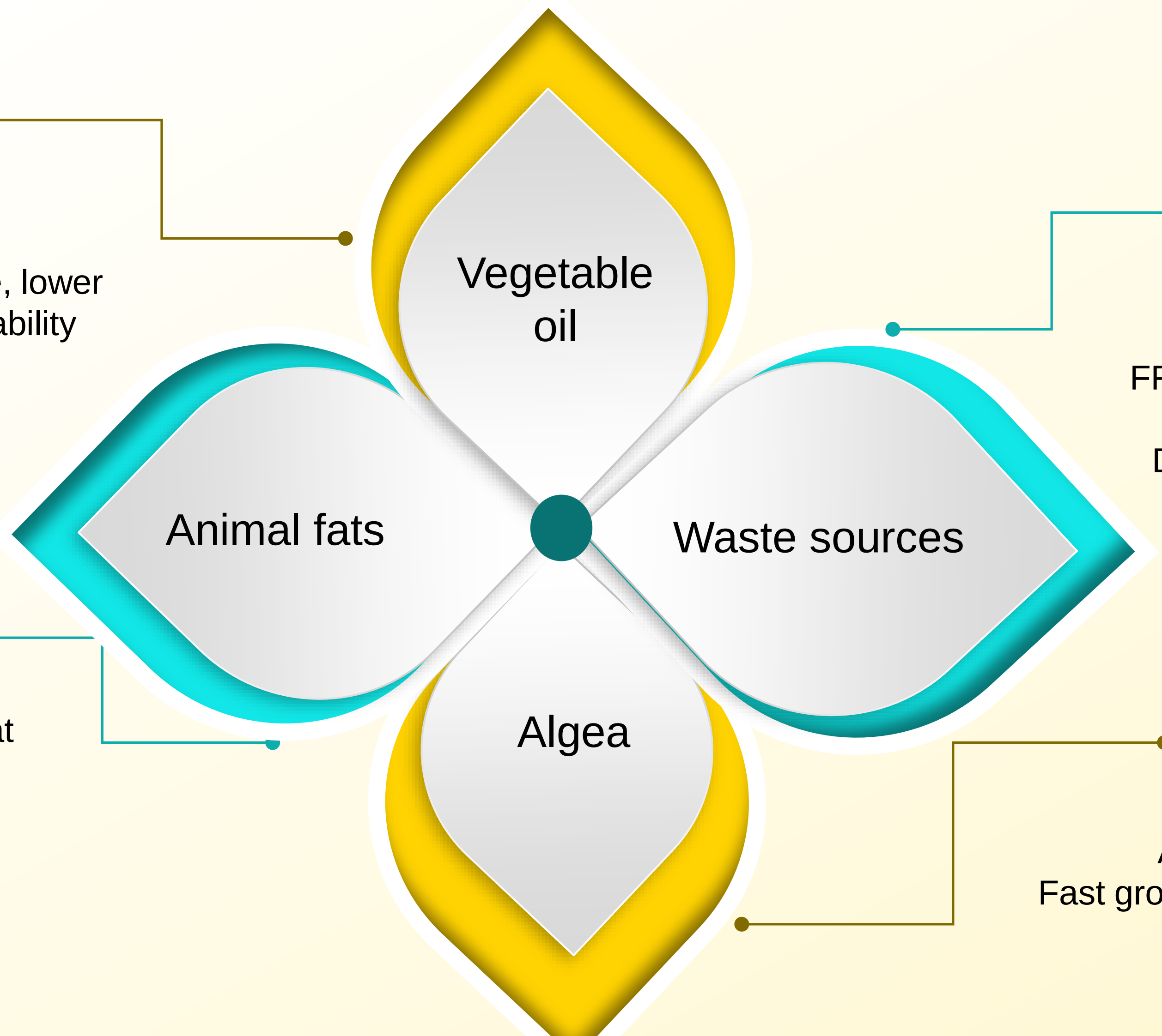

Source
Raw material
Process
Product
First generation
Vegetable oils
Grains
Sugar crops
Fats and oils
Starches
Sugars
Chemical process
Transesterification
Hydrogenation
Biologic process
Alcohol fermentation
Enzymatic hydrolysis and fermentation
Anaerobic process
Thermochemical process
Pyrolysis
Gasification
Catalysis for liquid fuels
Biodiesel
Ethanol
Buthanol
Methan
Hydrocarbons and natural oils
Second generation
Agricultural residues
Grass and trees
Cellulose, hemicellulose and lignin
Algea
Third generation

Biodiesel – sources of biodiesel

Alternative fuel for diesel engines - replacement of conventional diesel
Monoalkyl esters of fatty acids
Production from renewable sources, biodegradable, emission reduction

Vegetable oil

Edible / inedible oils
Adventages :
Liquidity, availability, renewable, lower sulfur content and biodegradability
Disadvantages:
Place to grow



Waste sources

Waste cooking oil, animal fats
Advantages:
FFA content 40 -100%, utilization of waste source
Disadvantages: impurities, water content,

Animal fats

Lard, tallow, fish oil, poultry fat
Advantages:
Availability
Disadvantages:
Solid at room temperature

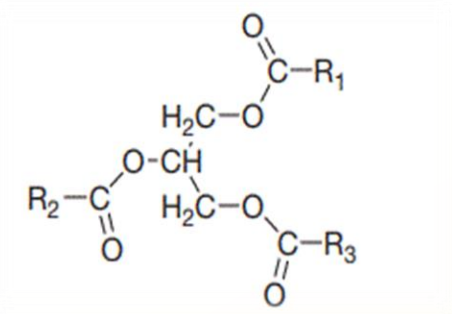
Algea

Microalgae
Advantages:
Fast growth, high oil content

Vegetable oils

Saponifiable fraction (98% oil)

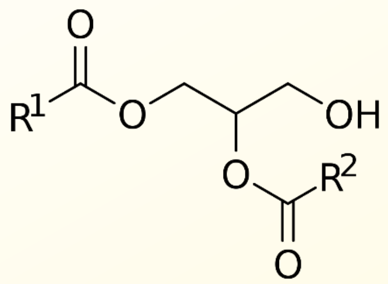
Triglycerids



Triacylglycerol - consists of glycerol esterified with fatty acids
R1, R2, and R3 - fatty acid chains

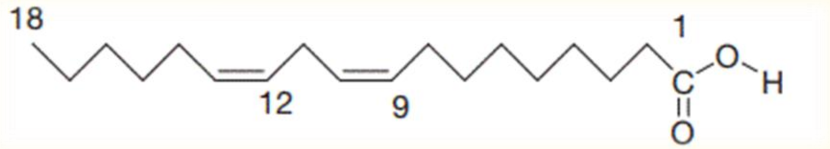
Partial glycerides

Hydrolysis of triglycerides leads to the formation of diacylglycerides (diacylglycerol) and monoglycerides (acylglycerol).



Free fatty acids

Naturally occurring fatty acids - carboxylic acids with a straight chain and an even number of carbons



Other ingredients - vegetable waxes and phosphates

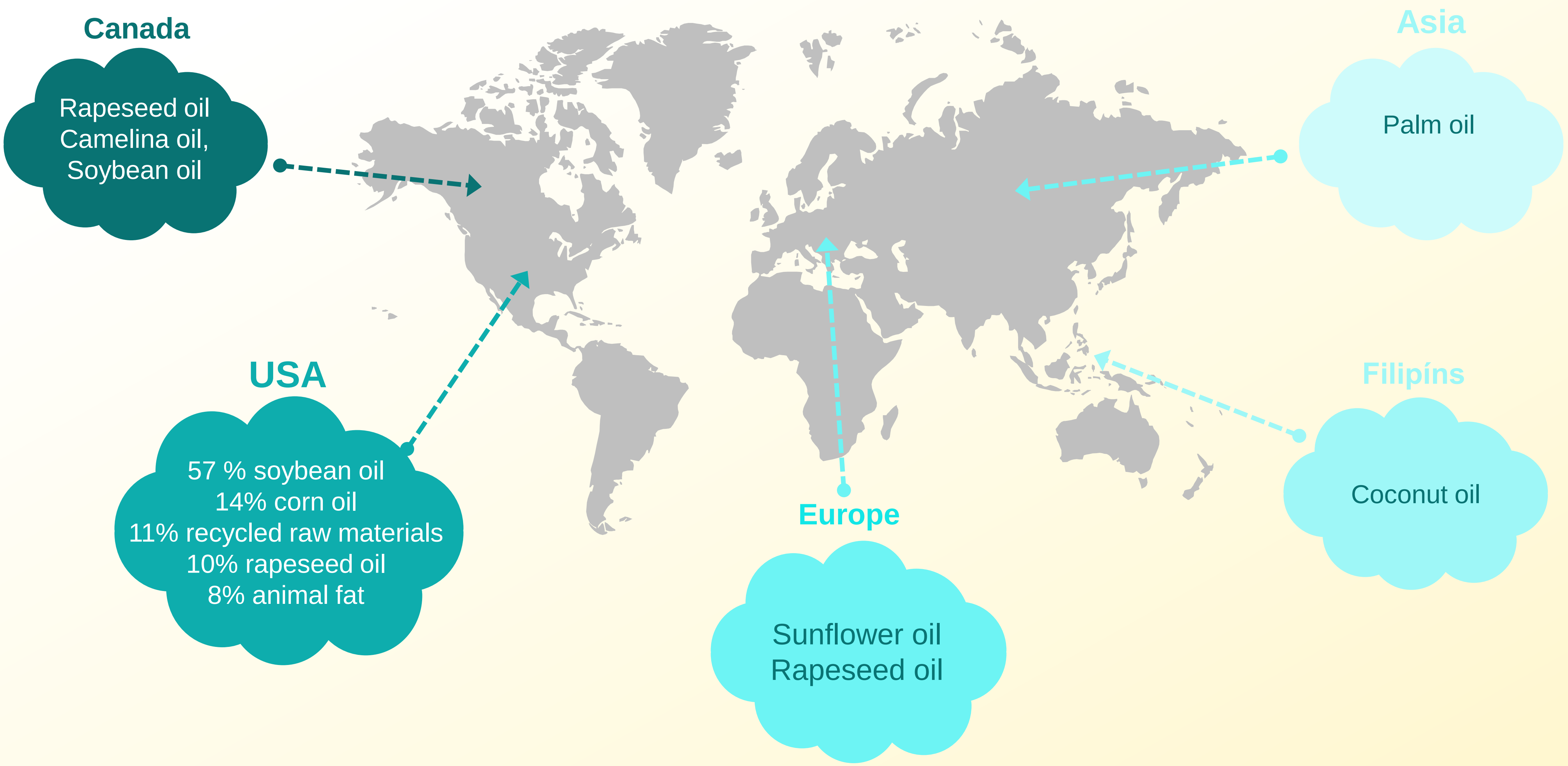
Unsaponifiable fraction (2%)

Tococerols a tocotrienols

natural antioxidants that protect mono- and polyunsaturated fatty acids from oxidation.

Other ingredients - phytosterols, substances that add color to oil

Most common used vegetable oils



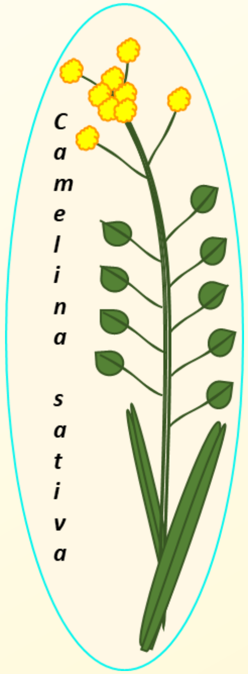
„False flax“

Camelina sativa

„Gold of pleasure“

Cultivation

- Annual summer crop / winter semi - annual crop
- Relatively drought resistant
- Possibility of growing on contaminated soils

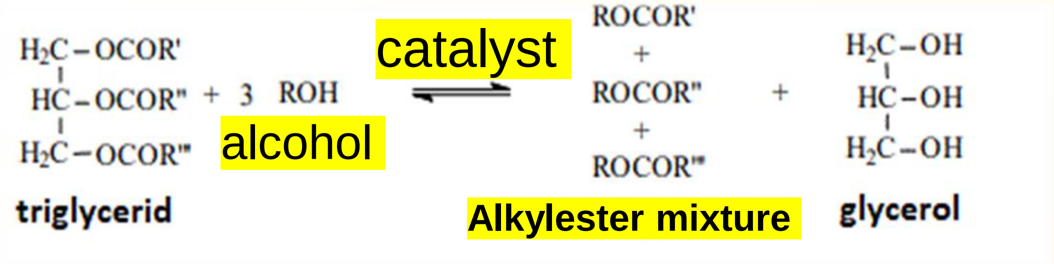


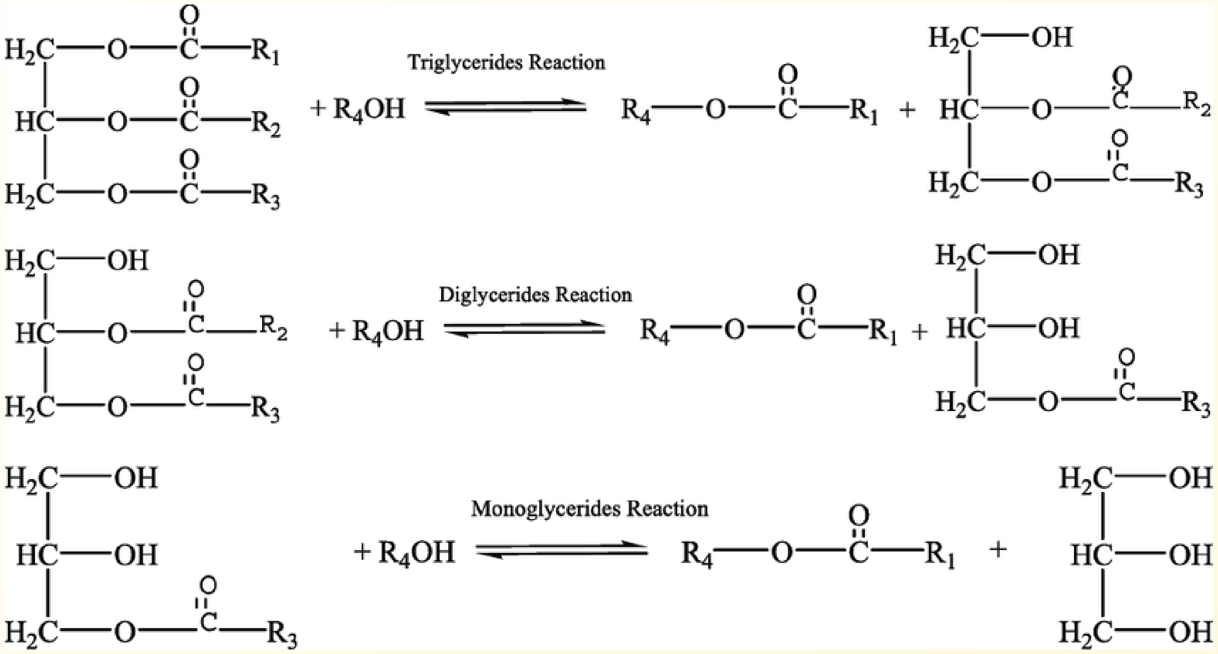
- It is possible to obtain 30 to 40% of oil from the seeds of camelina
- 32 - 46% of unsaturated fatty acids
- High content of natural antioxidants - tocopherols

Oil type	Tocoferol content (mg/kg)	Iodine number (mgI2/g oil)	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0
Camelina oil	700 – 1200	150-153	0.0	6.0	2.9	18.4	19.4	34.2	1.4
Palm oil	650	50-55	1.0	44.4	4.1	39.4	10.2	0.3	0.3
Soya oil	960	120-143	0.1	11.0	4.0	23.4	53.2	7.8	0.3
Sunflower oil	550	110143	6.1	3.9	3.9	42.6	46.4	1.0	0.0
Olive oil	220	79-88	0.0	13.7	2.5	71.1	10.0	0.6	0.9
Rapeseed oil	850	94-120	0.2	3.5	0.9	64.4	22.3	8.2	0.0

Transestericaion

Transesterification (alcoholysis) - reaction of triglycerides with alcohol in the presence of a catalyst to form alkyl esters of fatty acids and glycerol





Catalysts

Homogeneous

Heterogeneous

Parameters affecting transesterification:
Alcohol
Reaction time
Temperature
Catalyst
Oil composition
Pressure

Homogeneous transesterification

Benefits

- Low reaction temperature,
- Atmospheric pressure
- High conversion in minimal time
- Good availability of catalysts

Disadvantages

- Challenging separation
- Need to wash out catalyst
- The catalyst cannot be reused
- Two-step process with high FFA content

Heterogeneous transesterification

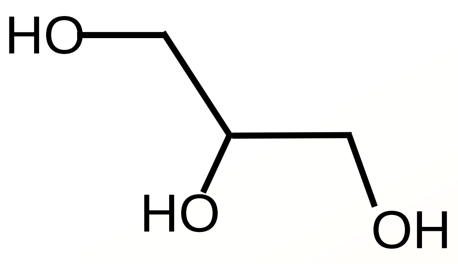
Benefits

- Possibility of catalyst regeneration and reuse
- Easy separation
- Also for oils with a high content of FFA and water
- No soaps are

Disadvantages

- Longer reaction time required to achieve conversion
- Higher reaction temperatures

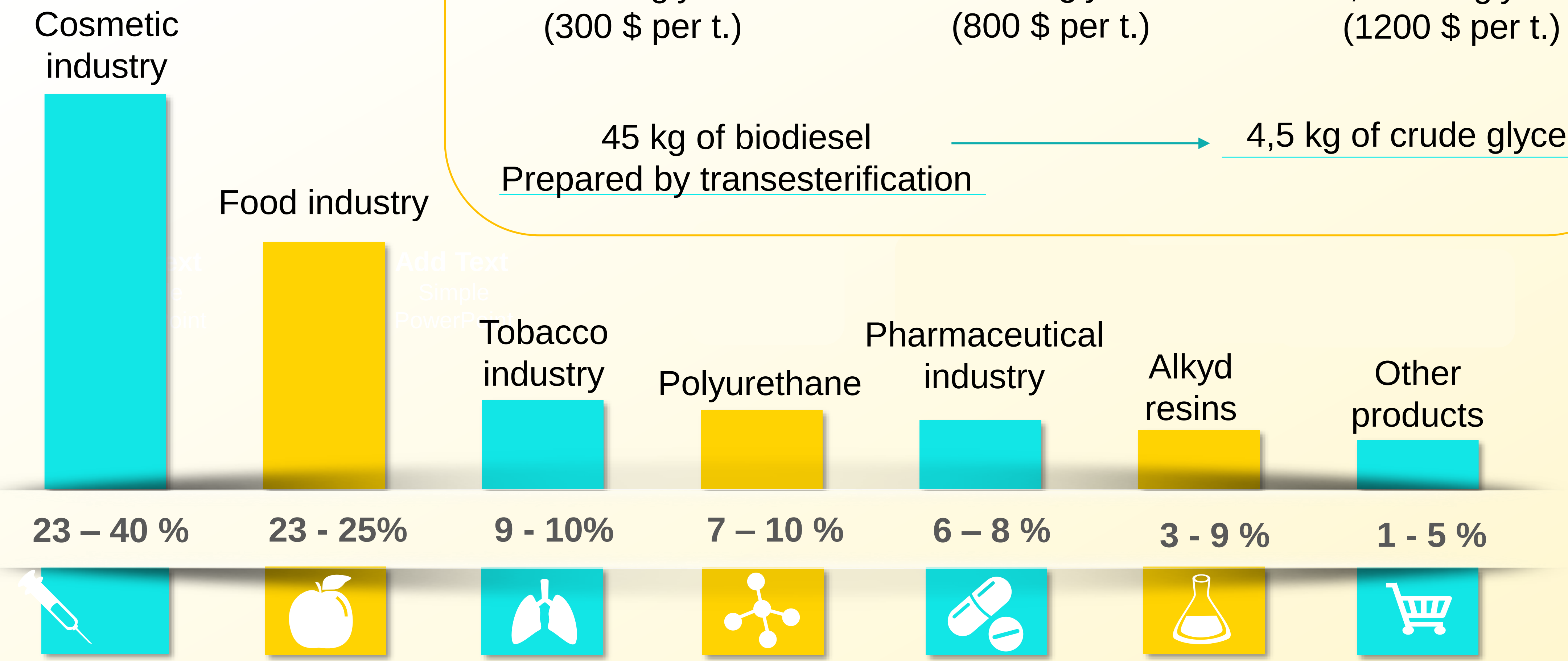
Glycerol



(1,2,3 – propantriol)

Crude glycerine	**Technicál glycerine**	**Purified glycerine**
80 wt.% glycerol	95 wt.% glycerol	99,7 wt.% glycerol
(300 $ per t.)	(800 $ per t.)	(1200 $ per t.)

45 kg of biodiesel
Prepared by transesterification → 4,5 kg of crude glycerol

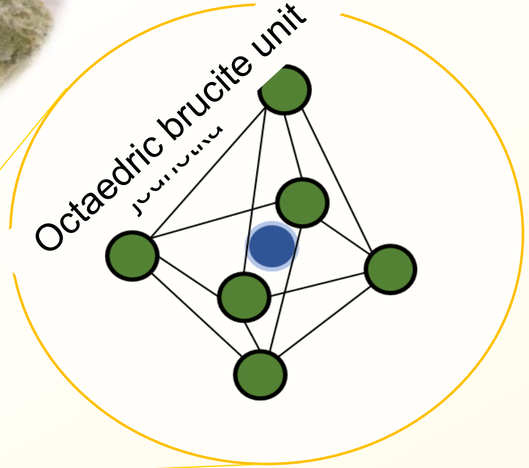


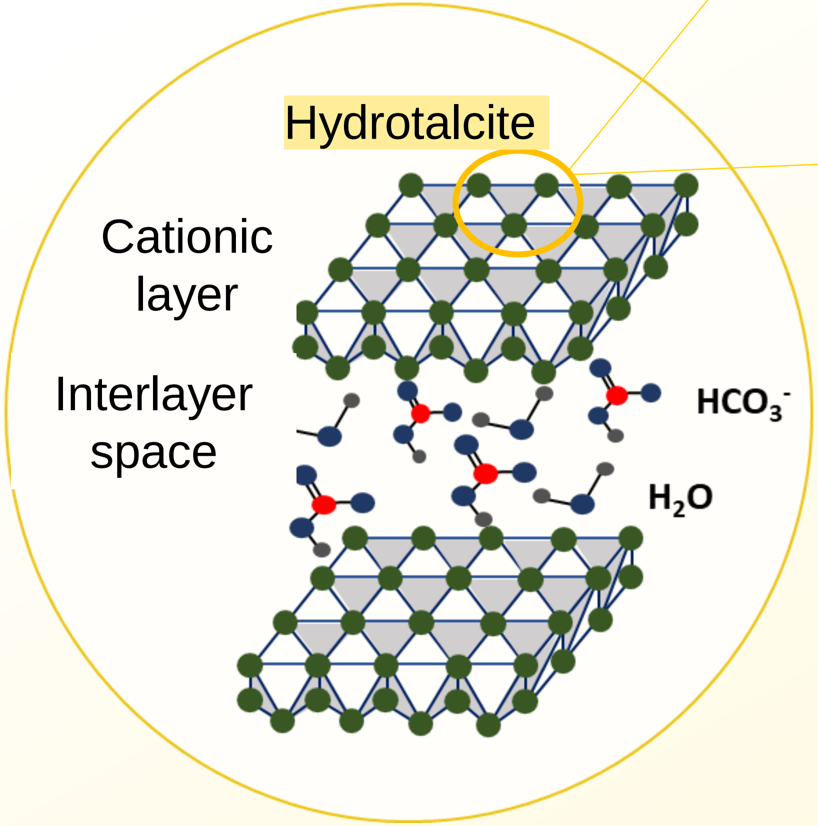
Glycerine application

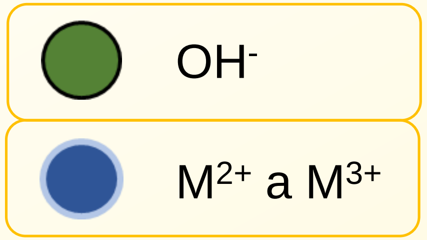
Hydrotalcite

Layered double hydroxides (LDH)

$$[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}_{x/n}mH_2O]$$







Hydrotalcite layered structure

Layered structure:

<u>Cationic lyer</u>

M^{2+} : Cu, Ni, Mn, Ca, alebo Zn

M^{3+} : Al, Fe,Cr

<u>Interlayer space</u>

Possible to built in:

- Inorganic anions

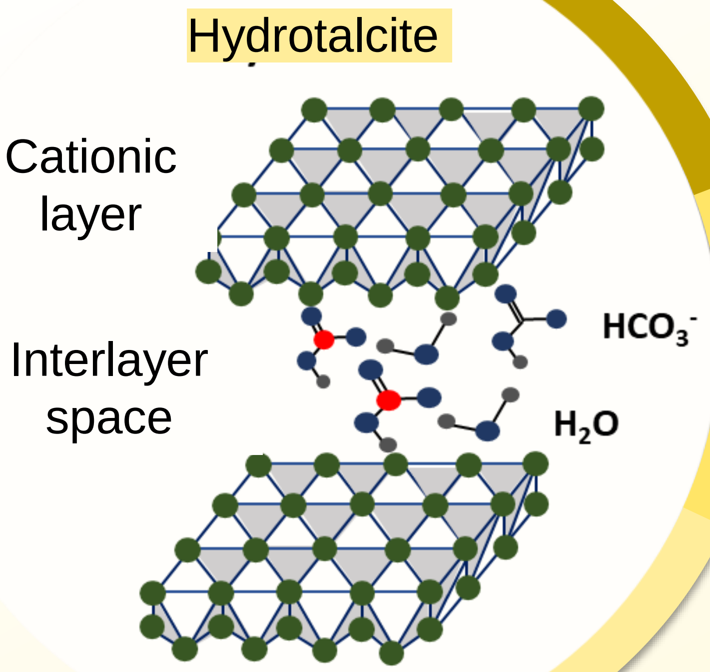
Cl^-, F^-, Br^-, $(SO_4)^{2-}$, $(CO_3)^{2-}$, (OH^-), $(HCO_3)^-$ and others

- Heteropolyacids

$(PMo_{12}O_{40})^{3-}$, $(PW_{12}O_{40})^{3-}$ and others

- Organic acids

Hydrotalcite preparation



Co-precipitation

- Most common used method
- Precipitation from cation and anion solutions

Hydrothermal synthesis

- Better crystallinity
- Treatment in the presence of water vapor, at a temperature below the hydrotalcite scale

Urea method

- High crystallinity and stability of crystals
- The addition of urea leads to agglomeration of the particles

Sol - gel synthesis

Preparation of amorphous gel and subsequent rehydration at low temperatures

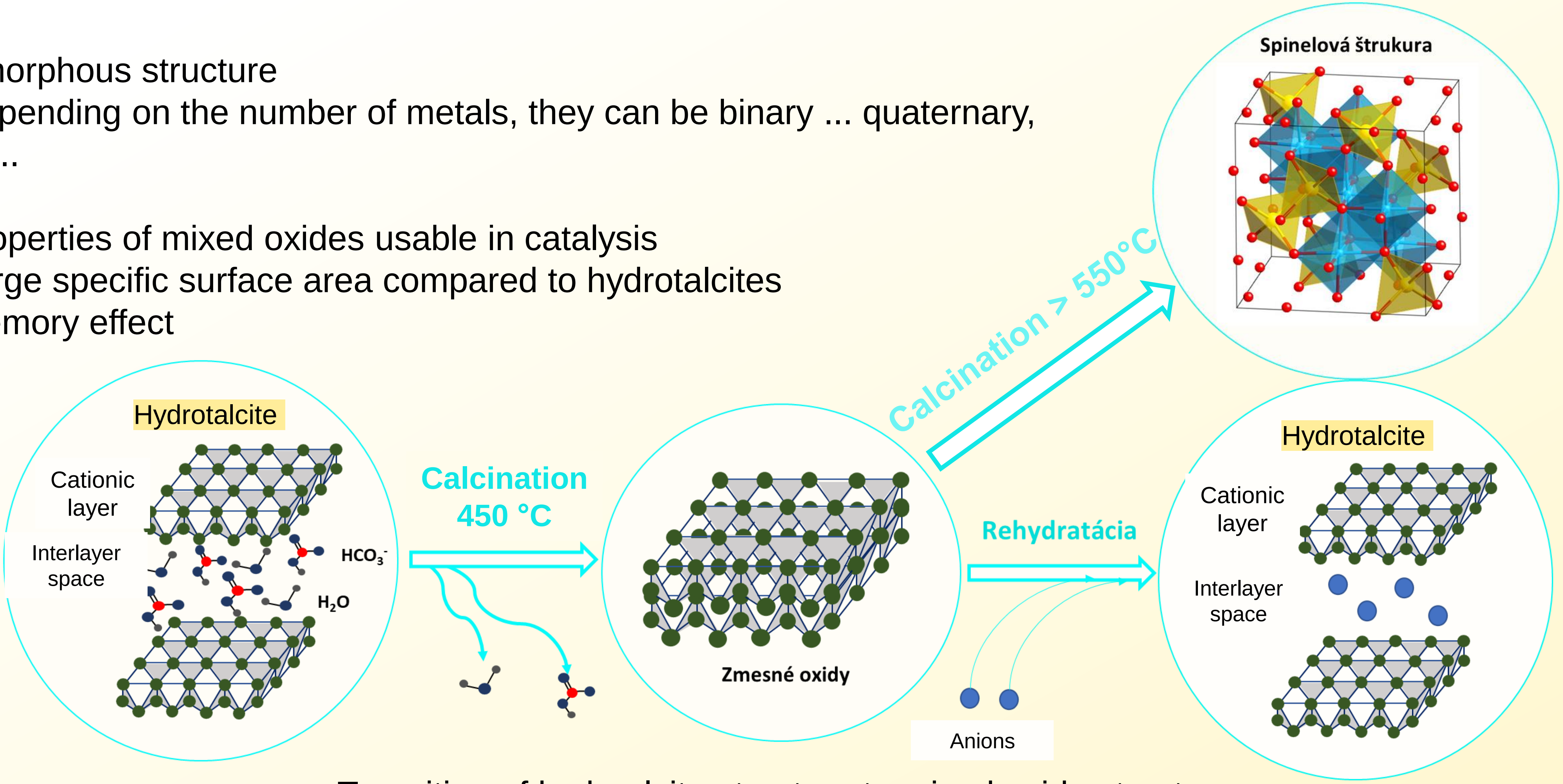
Rehydratation

- Reintroduction of anions into mixed oxides prepared by calcination

Mixed oxides

Amorphous structure
Depending on the number of metals, they can be binary ... quaternary, etc..

Properties of mixed oxides usable in catalysis
Large specific surface area compared to hydrotalcites
Memory effect

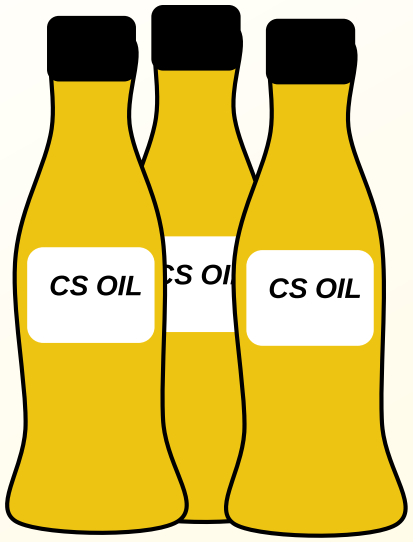


Transition of hydroalcite structure to mixed oxide structure

Materials and methods

Biodiesel preparation

- batch reactor with intense stirring



Heterogeneous Transesterification

140 ℃, 7 hours, 30:1 (Me/Oil)
3 wt.% of catalyst

Methyl esters (Biodiesel)

Catalyst and biodiesel characterisation

- Catalyst characterisation
  - ICP-EOS
  - FTIR (Infrared spectroscopy with fourier transformation)
  - TG/DTG (Termogravimetry / derivated termogravimetry)
  - TPD
    - TPD-CO_2 (Teperature programed desorption of CO_2)
    - TPDA (Teperature programed desorption of amonia)
  - XRD
  - Textural properties (specific surface area, pore volume, pore diameter)
- Determination of FAME content (EN14103 – GC)

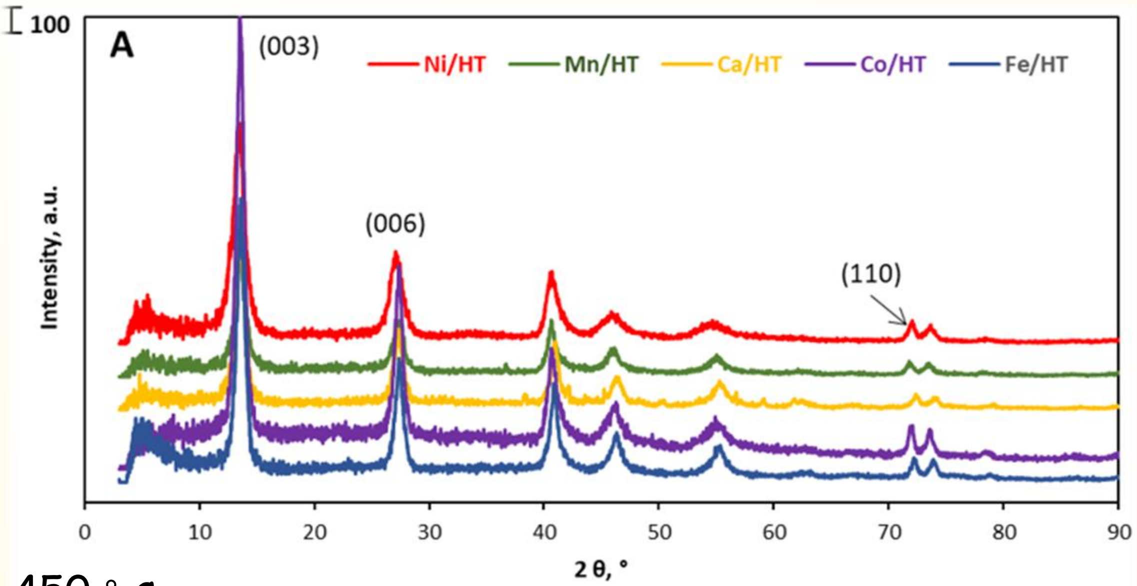
Obtained results

XRD

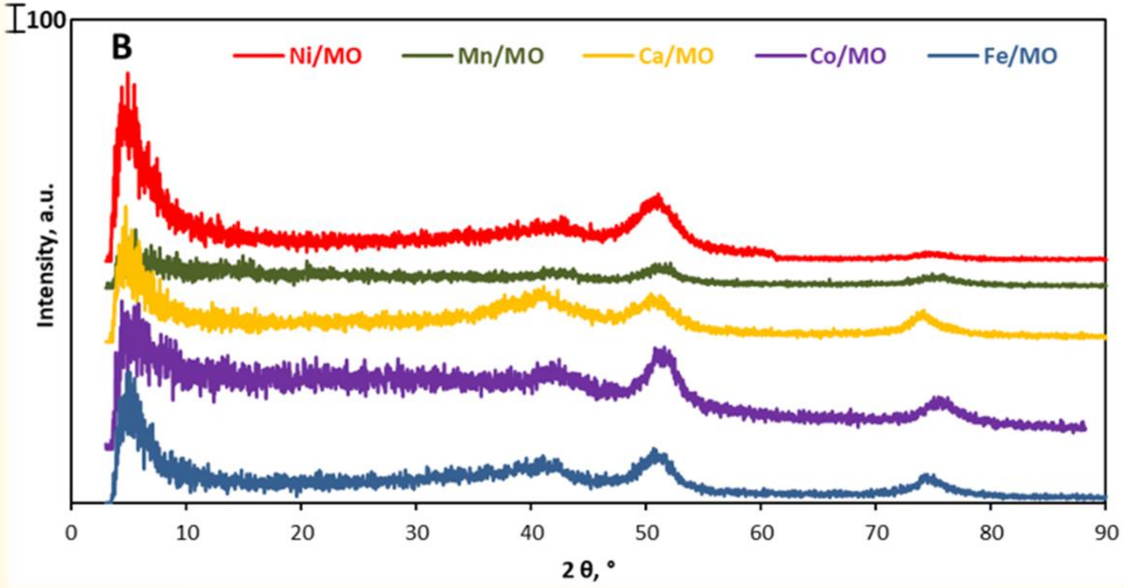
Characteristic XRD patterns for prepared five hydrotalcites and mixed oxides with diferent added metals

Mixed oxides	d_{003}, *A*	d_{110}, *A*	D, *nm*	a, A	c, A
Ni/MO	7.67	1.54	7.80	3.08	22.99
Mn/MO	7.56	1.53	11.42	3.06	22.69
Ca/MO	7.55	1.52	11.17	3.03	22.64
Co/MO	7.60	1.52	13.40	3.05	22.79
Fe/MO	7.56	1.52	11.81	3.03	22.69

(A) XRD Pattern of hydrotalcite structure



Calcination 450 ° C



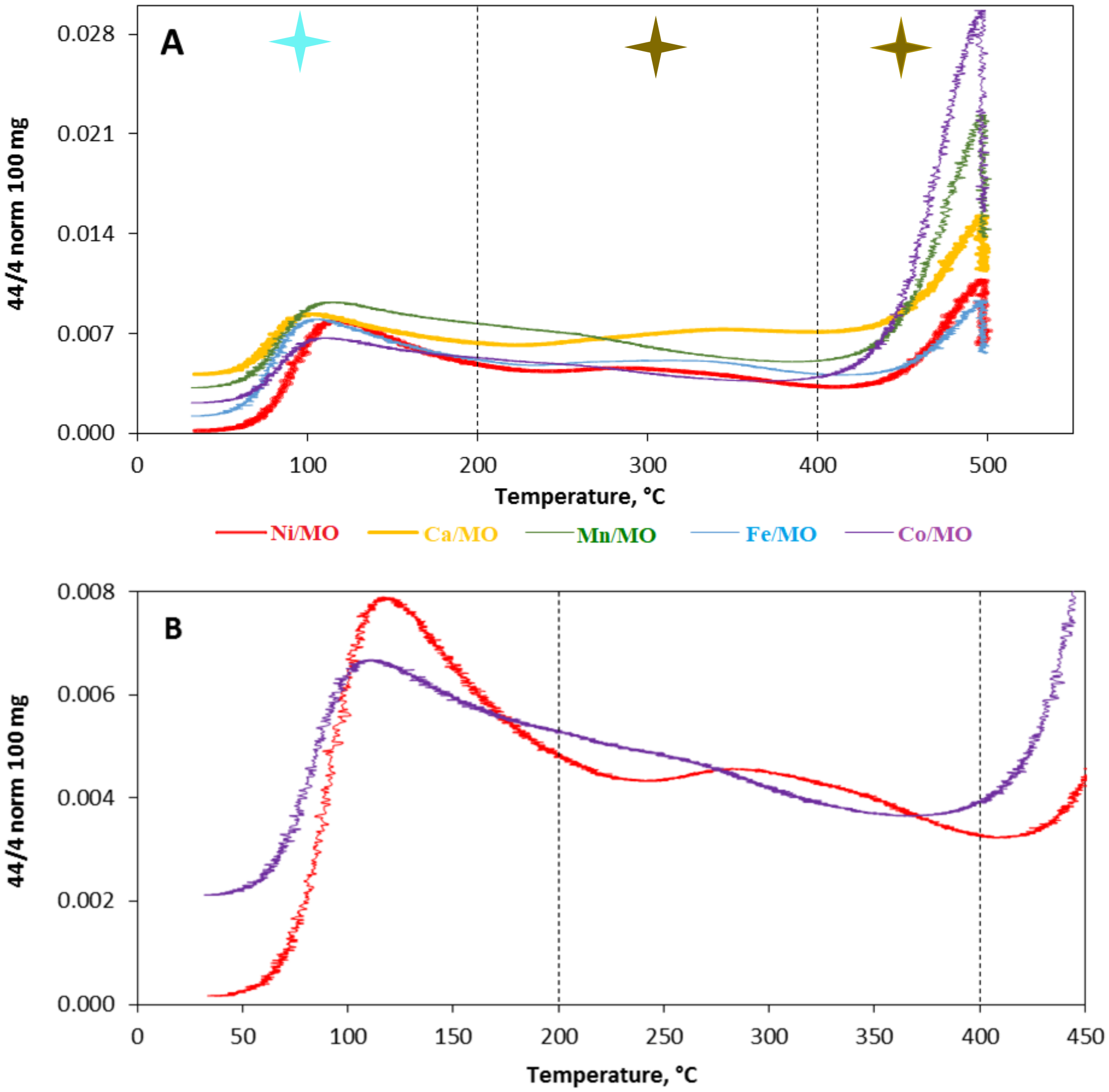
(B) XRD Pattern of mixed oxide structure

Specific surface area

- Differences between specific surface areas
- Significant impact of added metal into hydrotalcite / mixed metal oxides structure

Mixed oxides	S_{BET}, *m²/g*	V_p, *cm³/g*	D_p, *nm*
Ni/MO	262	0.632	5-19
Mn/MO	220	0.783	19-43
Ca/MO	147	0.428	13-47
Co/MO	180	0.710	16-39
Fe/MO	200	0.818	16-44

Basicity and Acidity



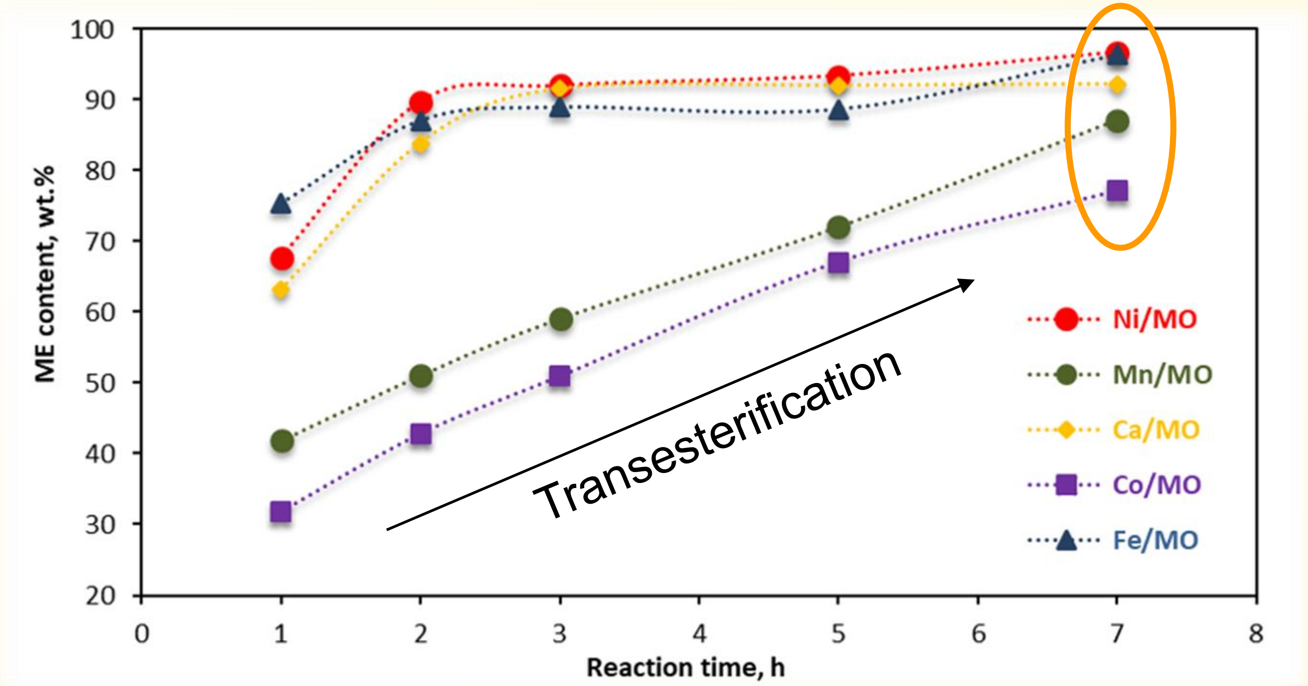
Mixed oxides	Low t.a.*, *area %*	Middle t.a.*, *area %*	High t.a.*, *area %*
Ni/MO	37	39	24
Mn/MO	35	33	31
Ca/MO	29	36	35
Co/MO	26	24	50
Fe/MO	39	39	23

Mixed oxides	Total basicity, *mmol CO_2/g*	Acidity, *mmol/g*
Ni/MO	0.541	0.56
Mn/MO	0.406	0.66
Ca/MO	0.317	0.62
Co/MO	0.292	0.75
Fe/MO	0.497	0.41

Transesterification

Mixed oxides	ME content, *wt.%*
Ni/MO	**96.7**
Mn/MO	**87.1**
Ca/MO	**92.2**
Co/MO	**77.1**
Fe/MO	**96.6**

Minimum FAME content in biodiesel according to EN 14214 is **96.5 wt.%**

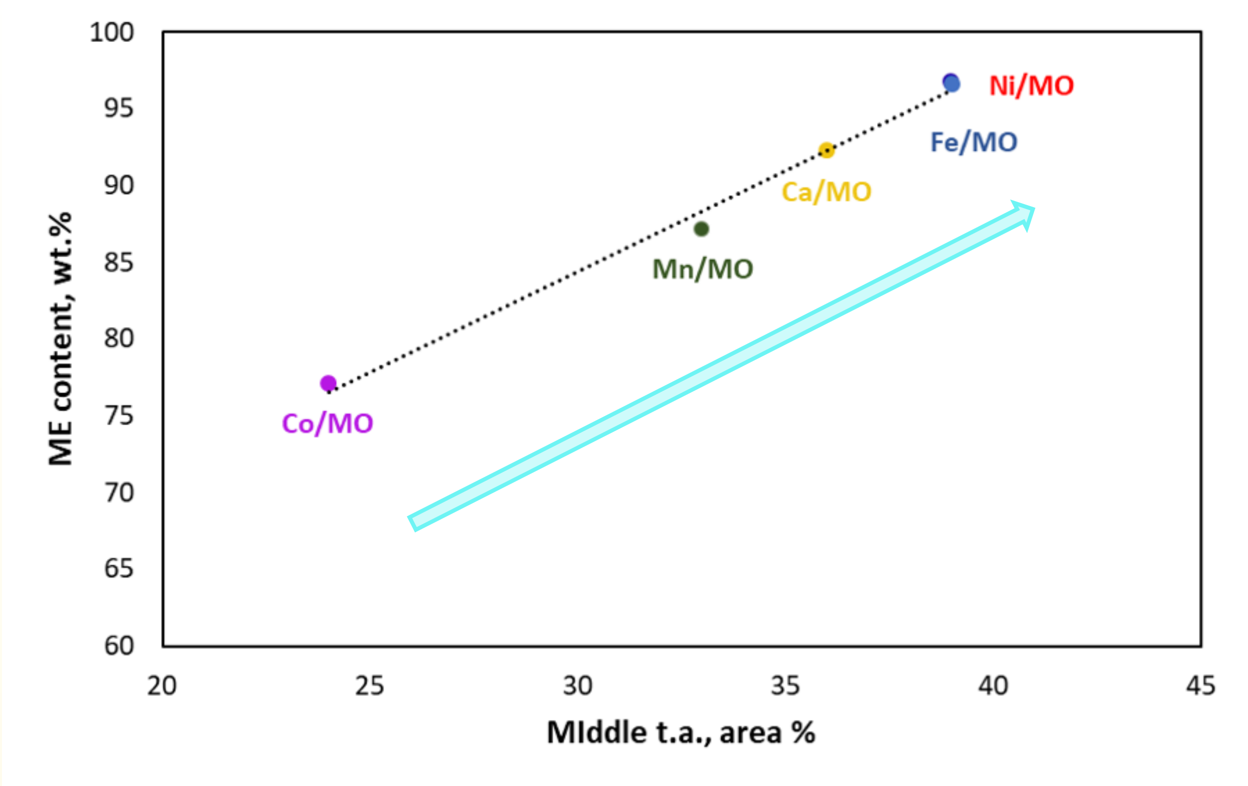


Discussion

Basicity ✓

✗ Acidity

Catalyst properties in relation with methyl ester content



Mixed oxides	Middle t.a.*, *area %*	ME content, *wt.%*	Acidity, *mmol/g*
Fe/MO	39	**96.6**	**0.41**
Ni/MO	39	**96.7**	**0.56**
Ca/MO	36	**92.2**	**0.62**
Mn/MO	33	**87.1**	**0.66**
Co/MO	24	**77.1**	**0.75**

Thank you for attention

Acknowledgement

European Regional Development Fund (Interreg, SKHU/1902/4.1/001/Bioeconomy)
www.skhu.eu

Interreg Slovakia-Hungary
European Union

Building Partnership