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FROM FUNDAMENTAL INSIGHTS TO ECONOMIC VIABILITY: RECOVERING NATURAL PRODUCTS FROM DEODORIZER DISTILLATES

A RICH SOURCE OF HEALTH BENEFICIAL COMPONENTS

The complex mixture includes major constituents such as FFA, glycerides, esters and high value "minor" components i.e. **tocopherols, sterols, squalene**, with applications in food, cosmetics and pharmaceuticals.

soybean

sunflower

oil deodorizer distillate

edible oil
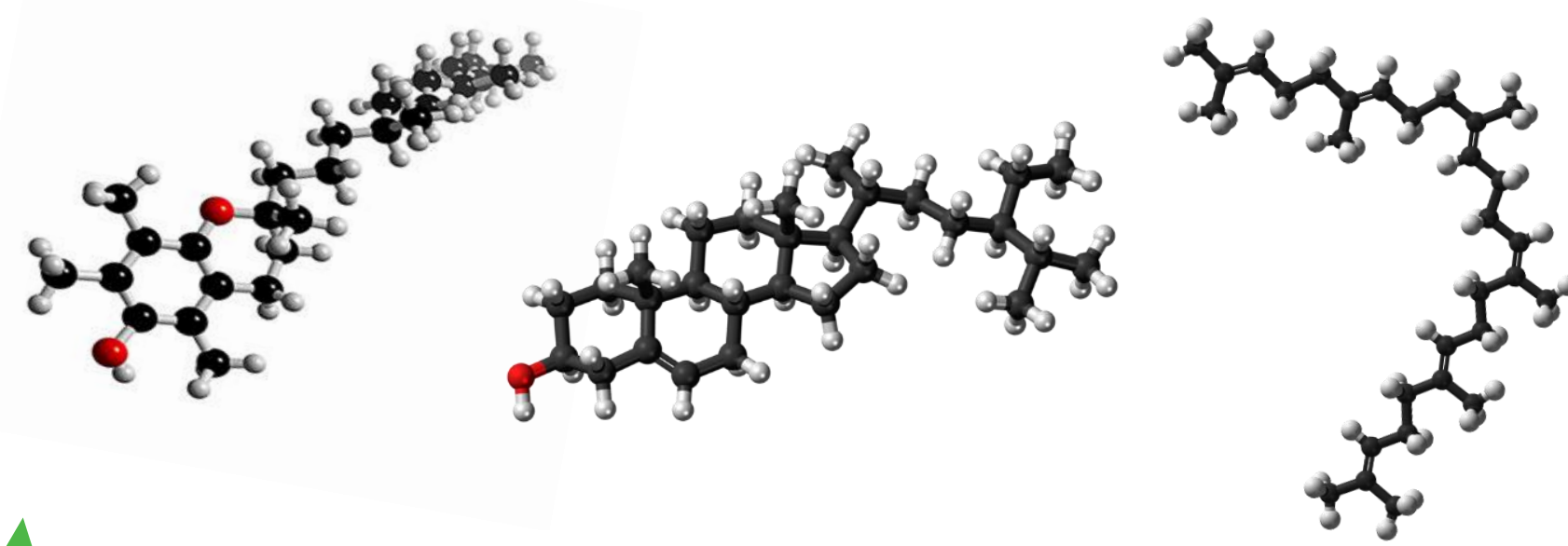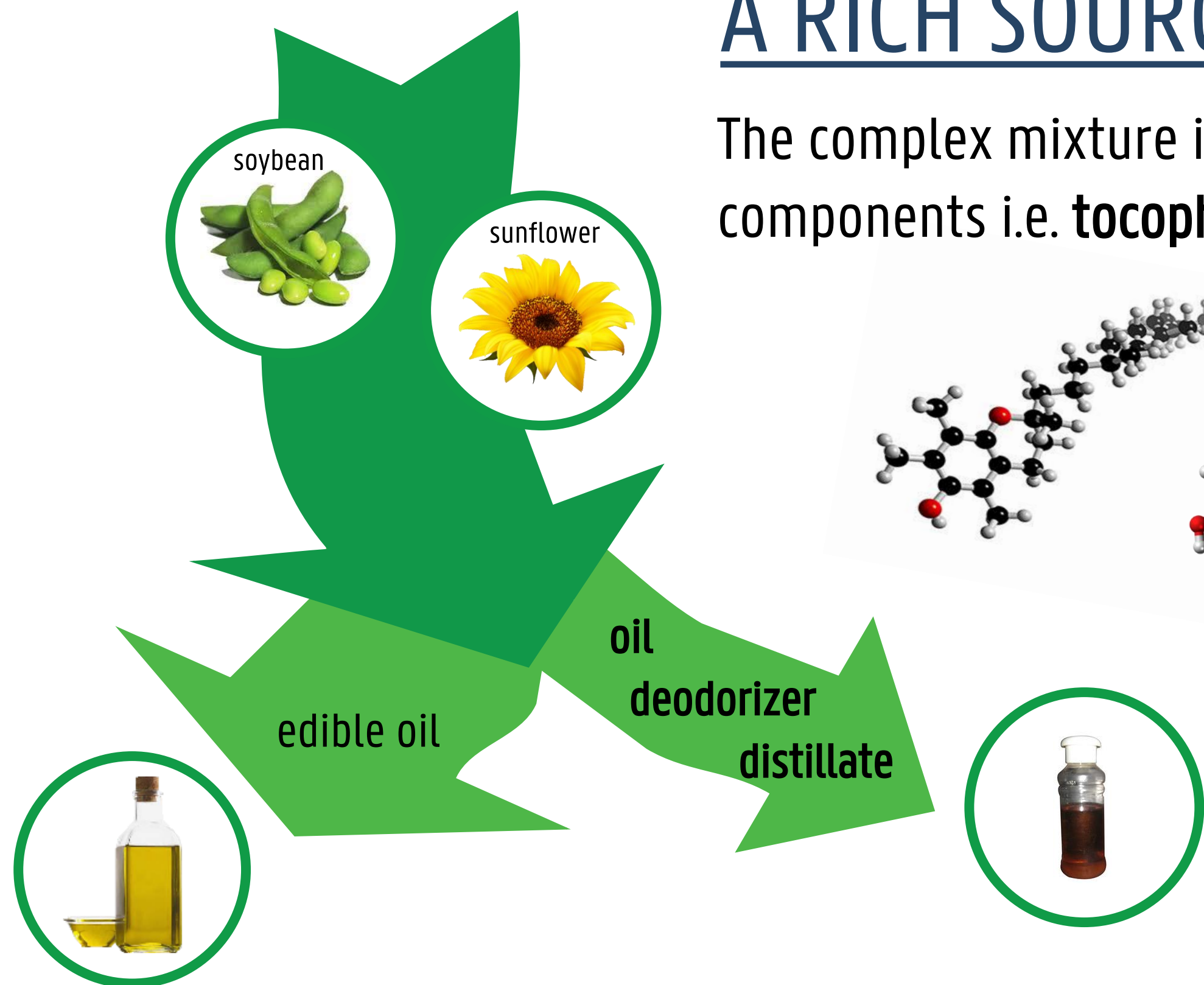
	🌻	🫘
minors	18.27 wt%	63.90 wt%
glycerides	24.16 wt%	13.60 wt%
FFA	56.02 wt%	20.44 wt%
FAME	1.55 wt%	2.06 wt%

GOAL

The enrichment of minor components by extraction of FAEE in supercritical CO_2 (sc-CO_2) after (trans)esterification of the glycerides/free fatty acids in the distillate.
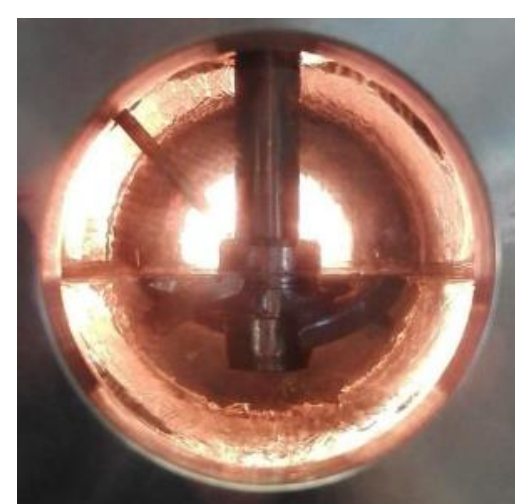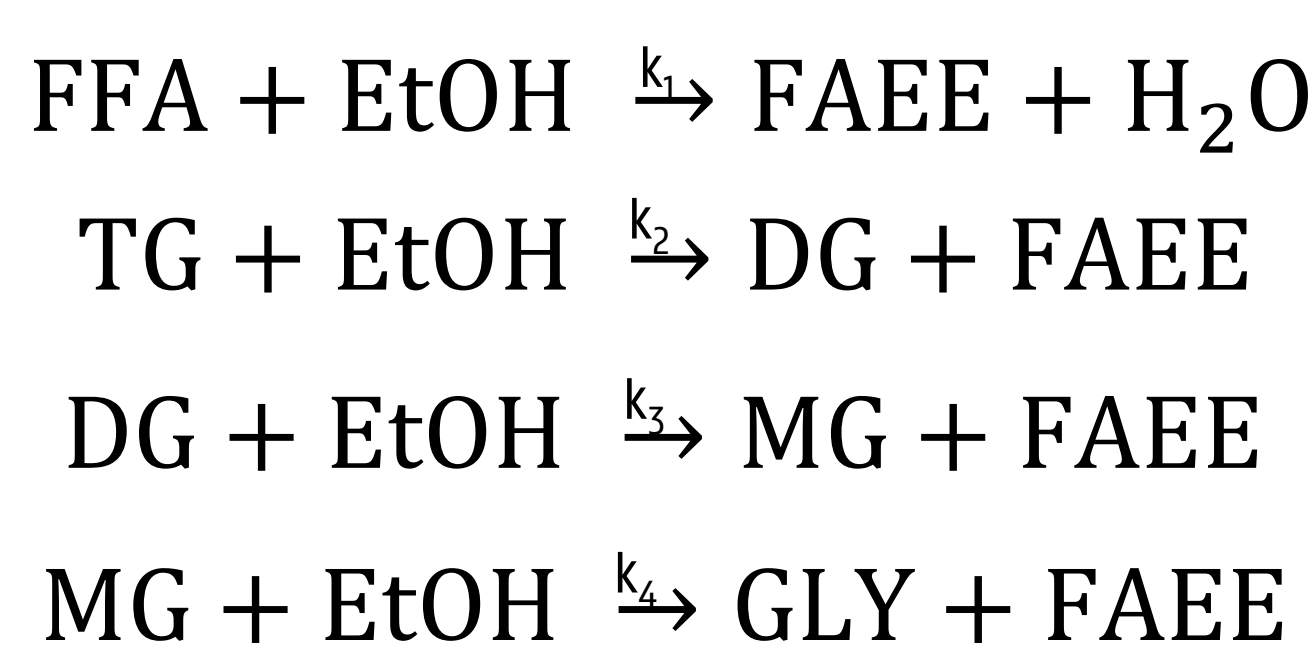
EXPERIMENTAL INVESTIGATION

sc-esterification

plug flow reactor
44 experiments with 🌻 ODD
τ = 7.5 – 60 min
T = 523 – 573 K
P = 7.5 – 15 MPa
EtOH/ODD = 0.3 – 1.5 g g^{-1}

sc-CO_2 extraction

T = 313 – 343 K
P = 10 – 15 MPa
CO_2/feed = 1 – 4 g g^{-1}

ESTERIFICATION MODELING

$$FFA + EtOH \xrightarrow{k_1} FAEE + H_2O$$

$$TG + EtOH \xrightarrow{k_2} DG + FAEE$$

$$DG + EtOH \xrightarrow{k_3} MG + FAEE$$

$$MG + EtOH \xrightarrow{k_4} GLY + FAEE$$

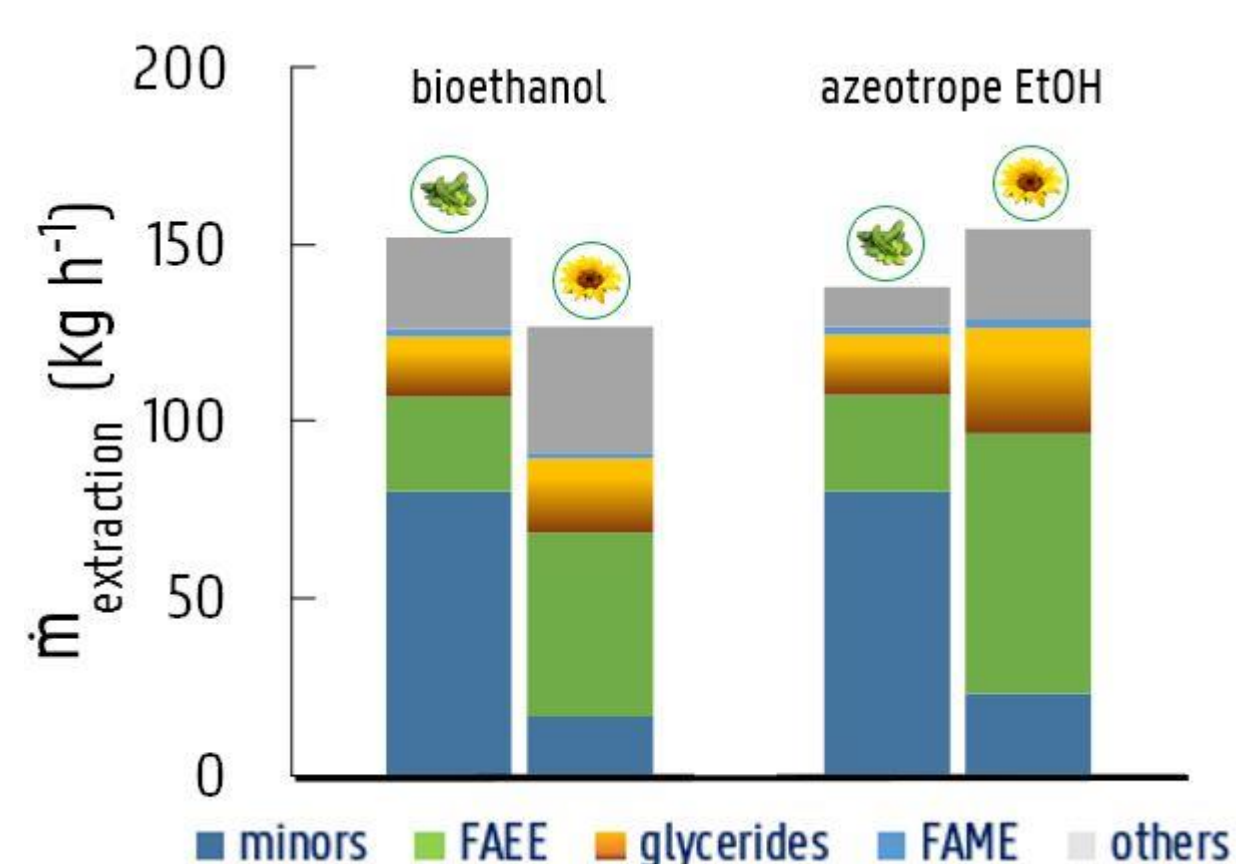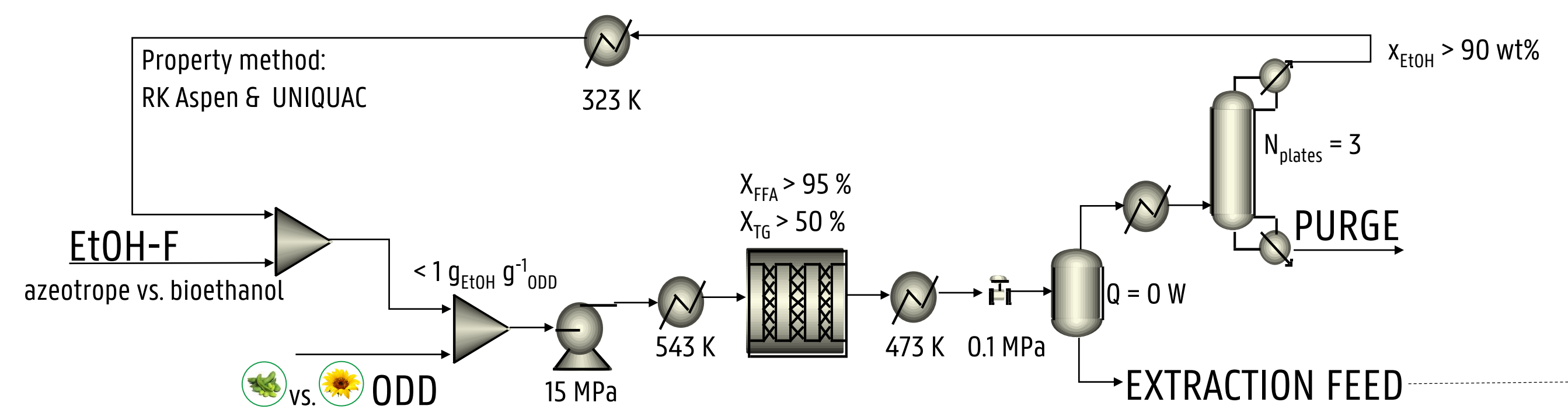|	A (10^{-8} m^3 mol^{-1} s^{-1})	E_a (kJ mol^{-1})
k_1	7.91± 1.51	35.6 ± 25.9
k_2	37.3 ± 4.50	24.7 ± 16.4
k_3	23.0 ± 5.99	61.6 ± 38.6
k_4	41.3 ± 21.1	160 ± 103

T = 548 K – P = 15 MPa
EtOH/ODD = 0.6 g g^{-1}

FAEE / FFA / TG / DG

Mass fraction (%) vs Residence time (min)

P = 15 MPa
EtOH/ODD = 0.6 g g^{-1}

Molar conversion (%) vs Residence time (min)
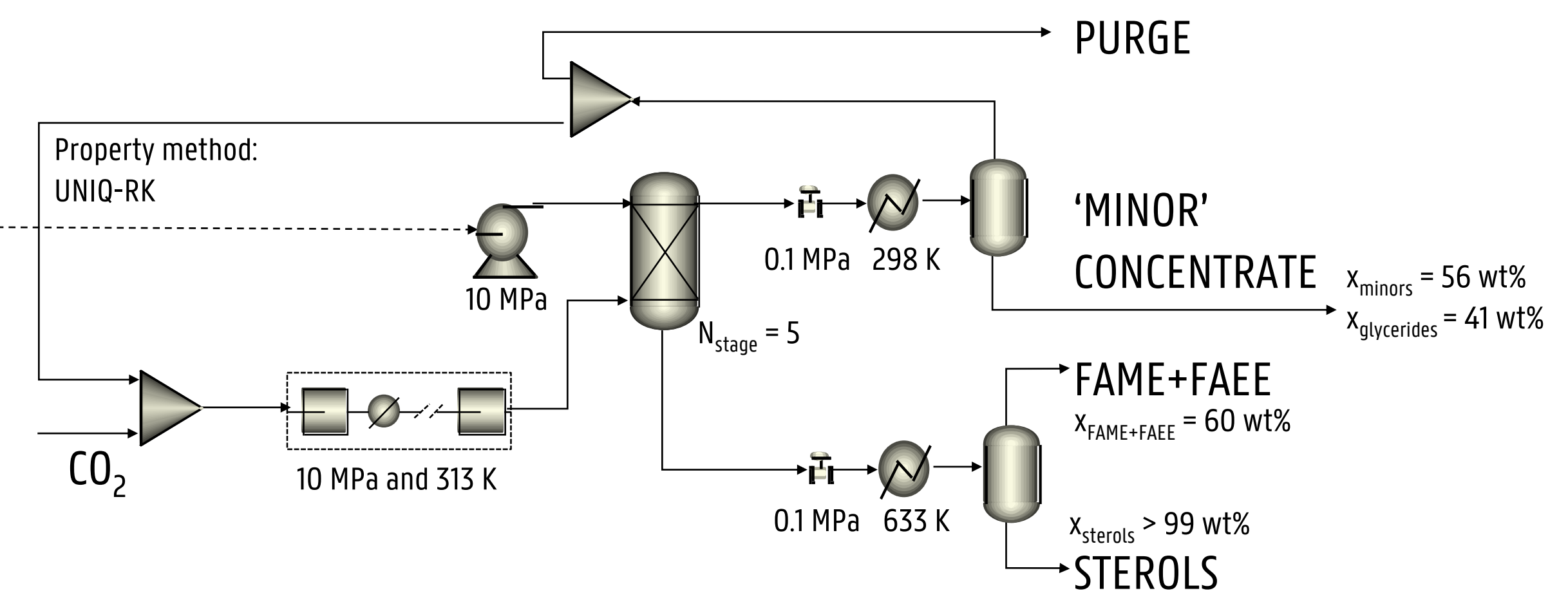
X_{FFA} at 523 K, 548 K, 573 K
X_{TG} at 523 K, 548 K, 573 K
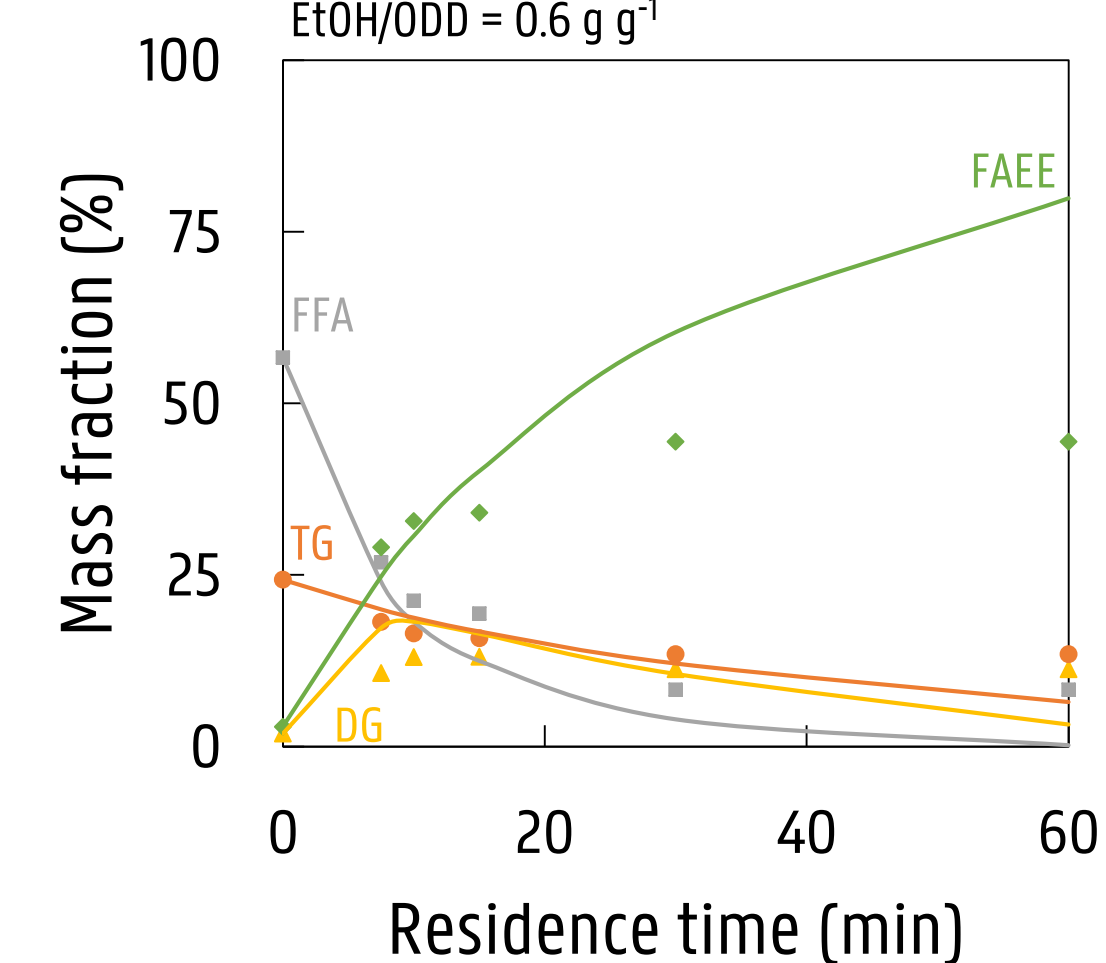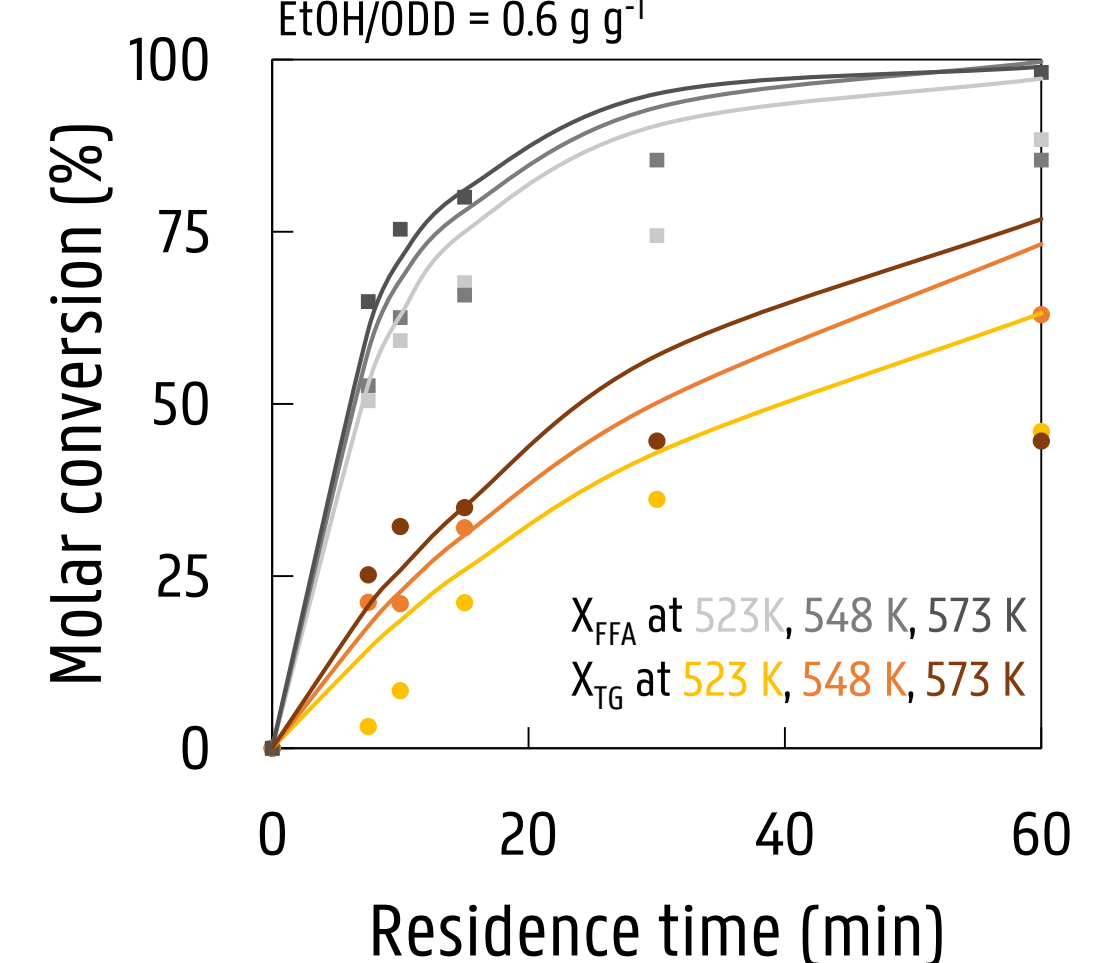
- statistically significant model
  - ✓ F_{test} = 5.38 10^4 > F_{tab} = 3.84
- statistically significant & physically relevant parameters
  - ✓ no correlations between parameters
  - ✓ $E_{a,TG \to DG}$ < $E_{a,DG \to MG}$ < $E_{a,MG \to GLY}$
    → consecutive transesterification is not favored
- model reproduces experimental trends

COMMERCIAL SCALE PROCESS DESIGN

Property method: RK Aspen & UNIQUAC

323 K

EtOH-F
azeotrope vs. bioethanol

< 1 g_{EtOH} g^{-1}_{ODD}

vs. 🌻 ODD

15 MPa

X_{FFA} > 95 %
X_{TG} > 50 %

543 K

473 K 0.1 MPa

N_{plates} = 3

x_{EtOH} > 90 wt%

PURGE

Q = 0 W

EXTRACTION FEED

Property method: UNIQ-RK

PURGE

10 MPa

N_{stage} = 5

0.1 MPa 298 K

'MINOR' CONCENTRATE x_{minors} = 56 wt% $x_{glycerides}$ = 41 wt%

CO_2 10 MPa and 313 K

0.1 MPa 633 K

FAME+FAEE $x_{FAME+FAEE}$ = 60 wt%

$x_{sterols}$ > 99 wt%

STEROLS

$\dot{m}_{extraction}$ [kg h^{-1}]
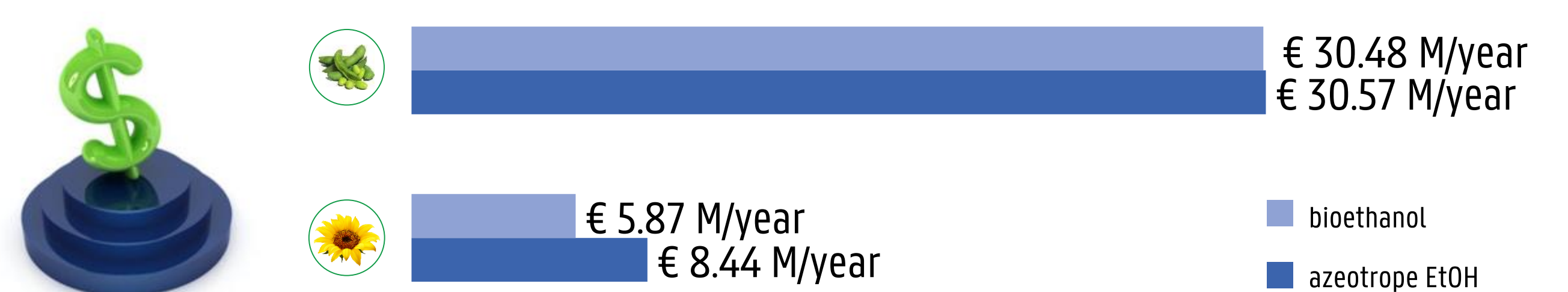
bioethanol azeotrope EtOH

minors / FAEE / glycerides / FAME / others

- higher FAEE formation with 🌻 ODD vs. higher minor content in 🫘 ODD
  - ✓ depending on which application is favored
- azeotrope EtOH has a lower waste products ("others")

maximum value added   after succesful extraction (x_{minor} > 99 wt%)

🫘 € 30.48 M/year (bioethanol)
€ 30.57 M/year (azeotrope EtOH)

🌻 € 5.87 M/year (bioethanol)
€ 8.44 M/year (azeotrope EtOH)

bioethanol
azeotrope EtOH

CONCLUSIONS

- The proposed bimolecular model is capable in predicting the experimental trends with statistically significant and physically relevant parameters.
- The same unit can be used for the esterification and extraction of different ODD or ethanol feedstock.
- Soybean ODD is economically more interesting due to the higher minor content.

FUTURE WORK

- Perform experiments with alternative alcohols (e.g. butanol) and investigate the influence on the model
- Optimization of sc-CO_2 extraction based on the experimental data acquired from a bench scale setup.