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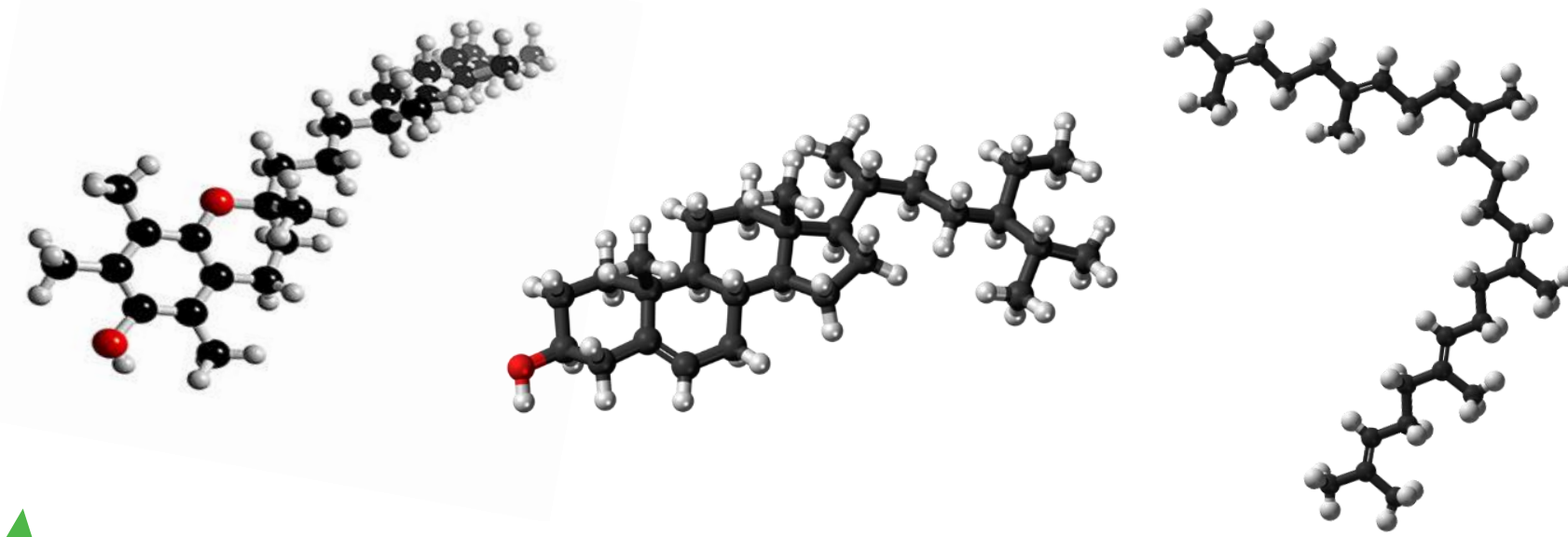
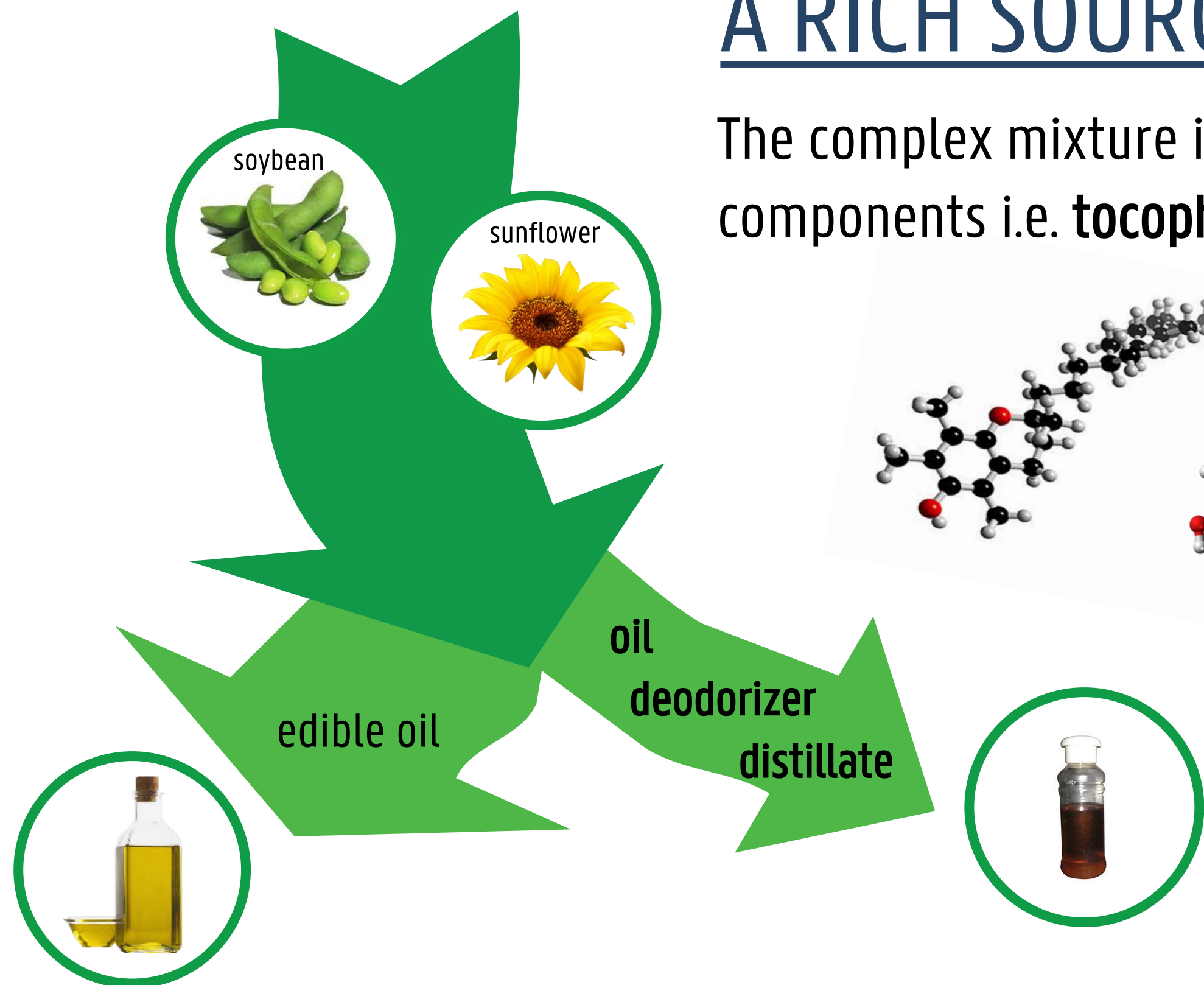
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4TH INTERNATIONAL CONGRESS ON CATALYSIS FOR BIREFINERIES
Lyon, France

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.



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 CO₂ (sc-CO₂) after (trans)esterification of the glycerides/free fatty acids in the distillate.

EXPERIMENTAL INVESTIGATION

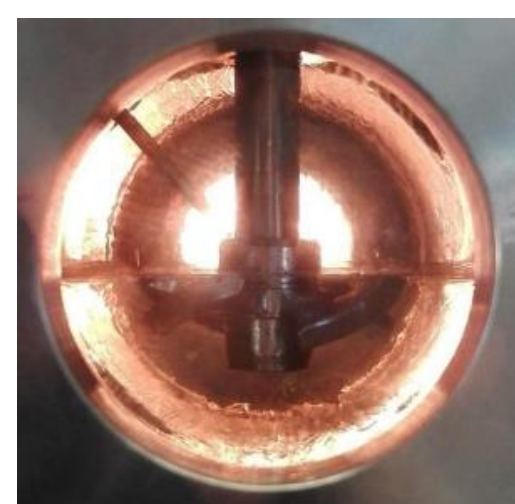
sc-esterification



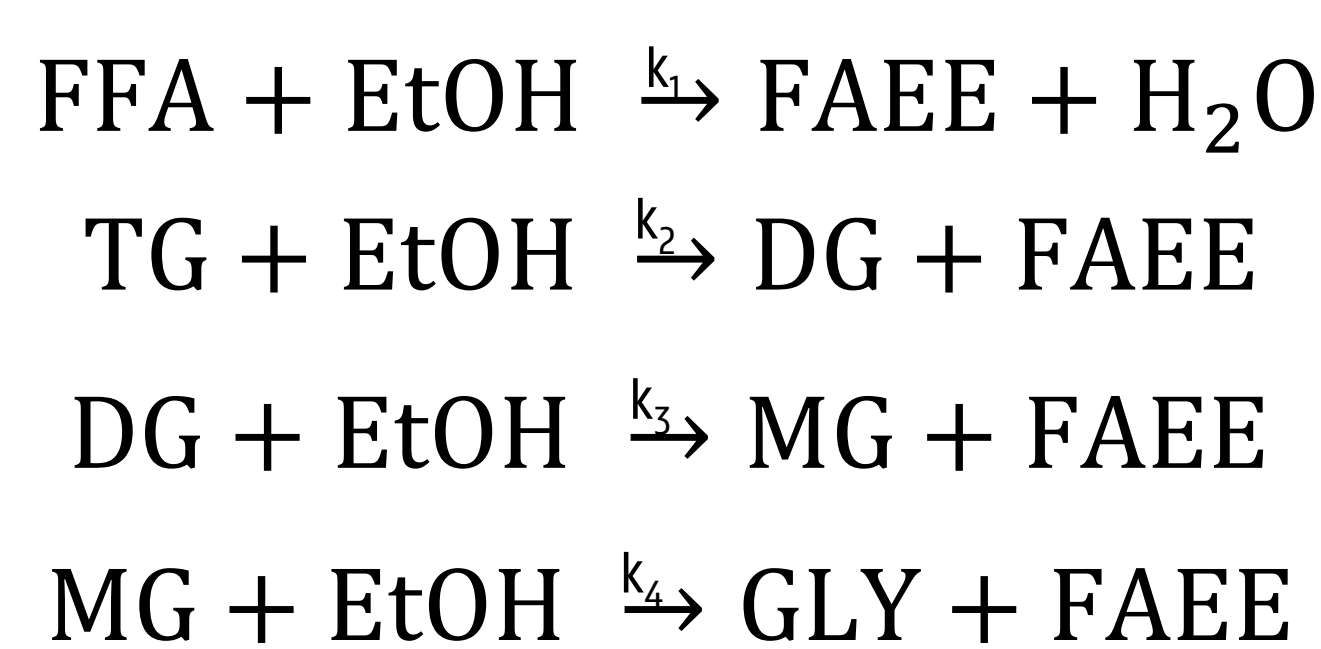
plug flow reactor
44 experiments with ODD
 $\tau = 7.5 - 60$ min
 $T = 523 - 573$ K
 $P = 7.5 - 15$ MPa
 $\text{EtOH/ODD} = 0.3 - 1.5$ g g⁻¹

sc-CO₂ extraction

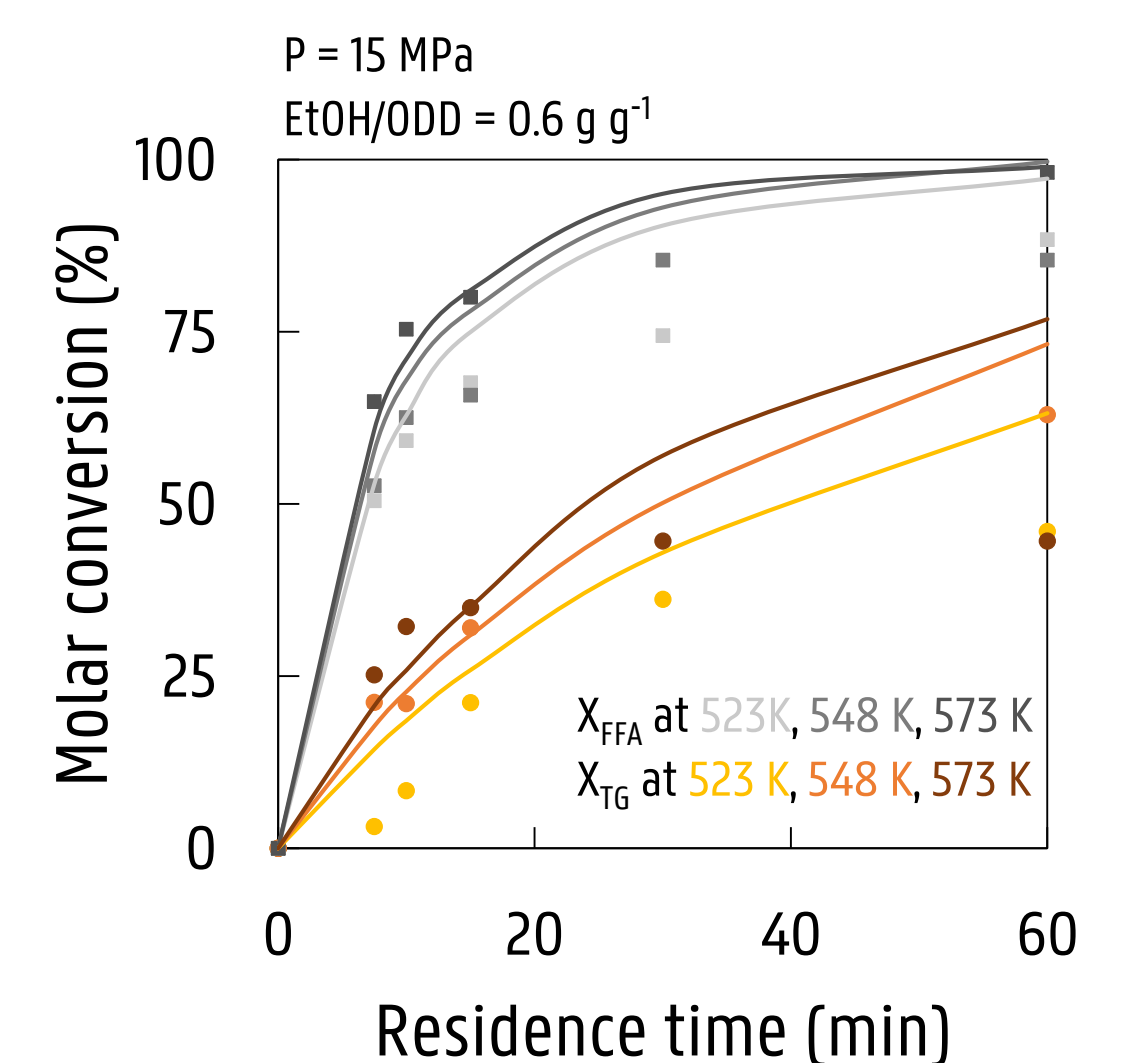
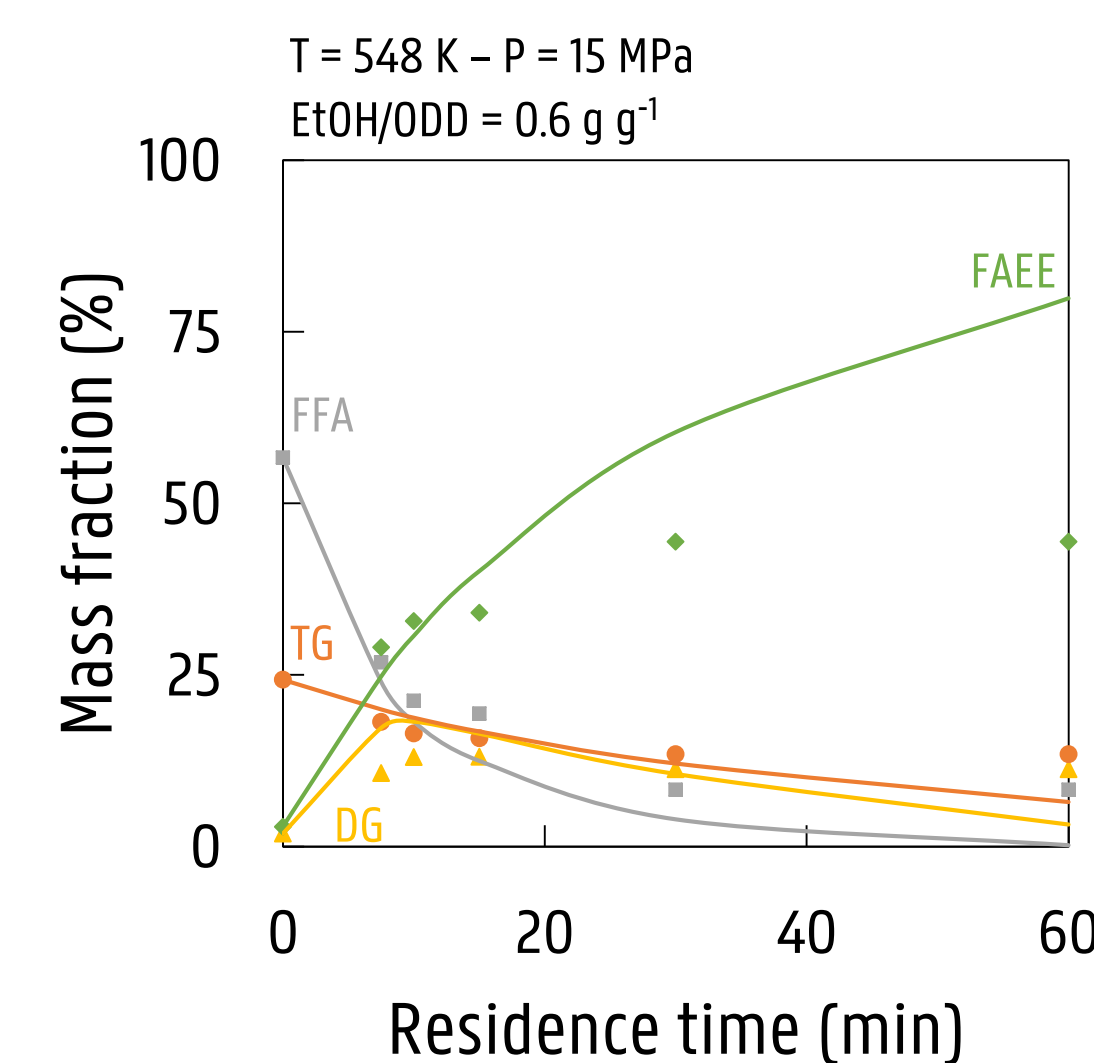
$T = 313 - 343$ K
 $P = 10 - 15$ MPa
 $\text{CO}_2/\text{feed} = 1 - 4$ g g⁻¹



ESTERIFICATION MODELING

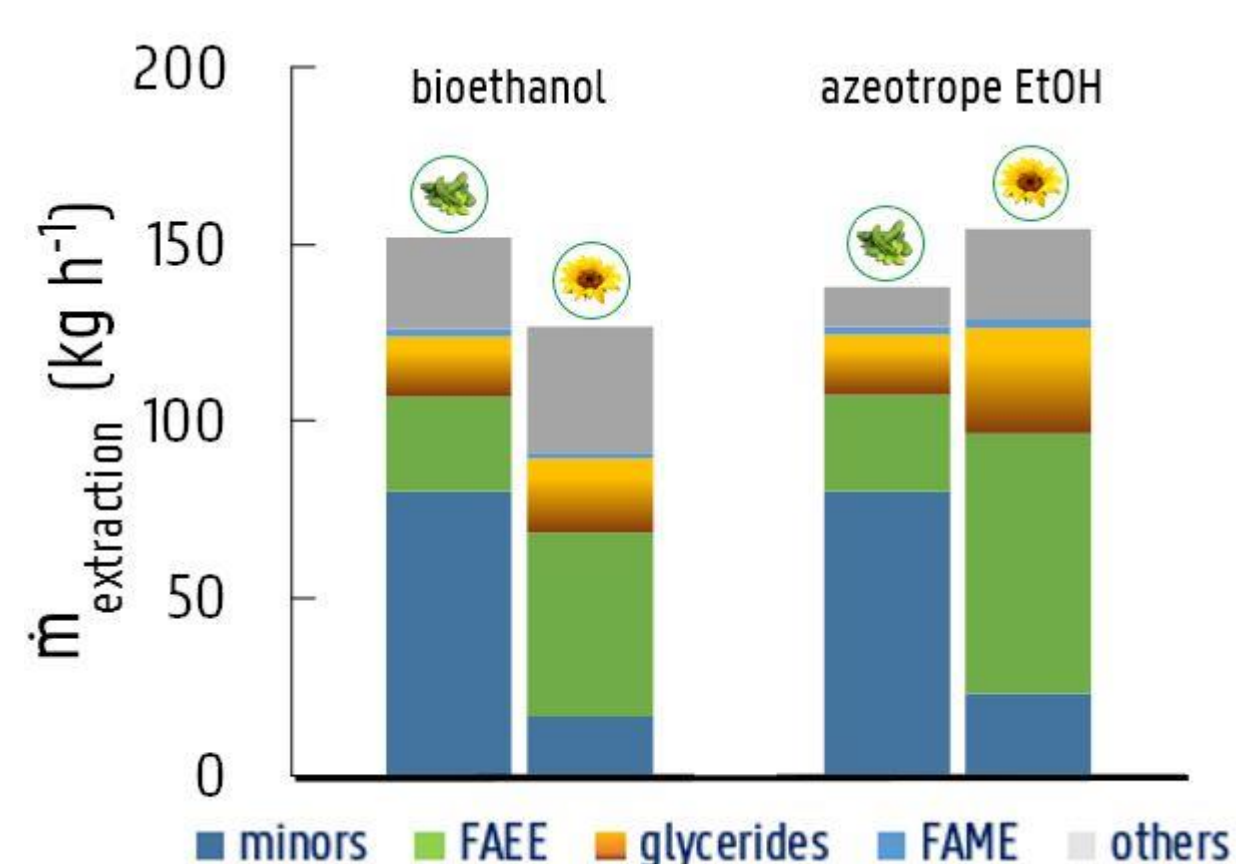
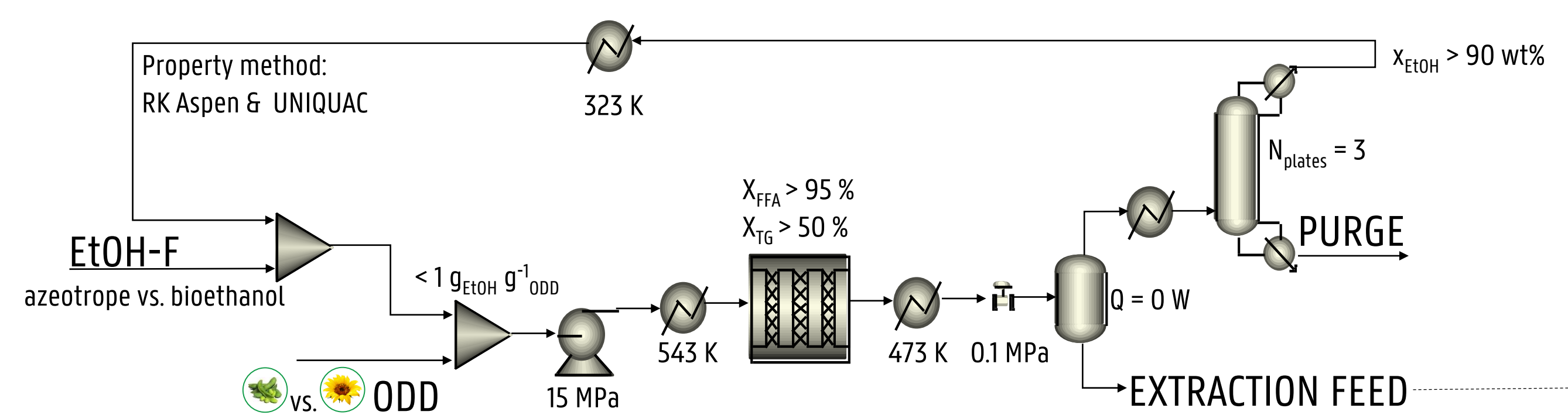


	A (10 ⁻⁸ m ³ mol ⁻¹ s ⁻¹)	E _a (kJ mol ⁻¹)
k ₁	7.91 ± 1.51	35.6 ± 25.9
k ₂	37.3 ± 4.50	24.7 ± 16.4
k ₃	23.0 ± 5.99	61.6 ± 38.6
k ₄	41.3 ± 21.1	160 ± 103

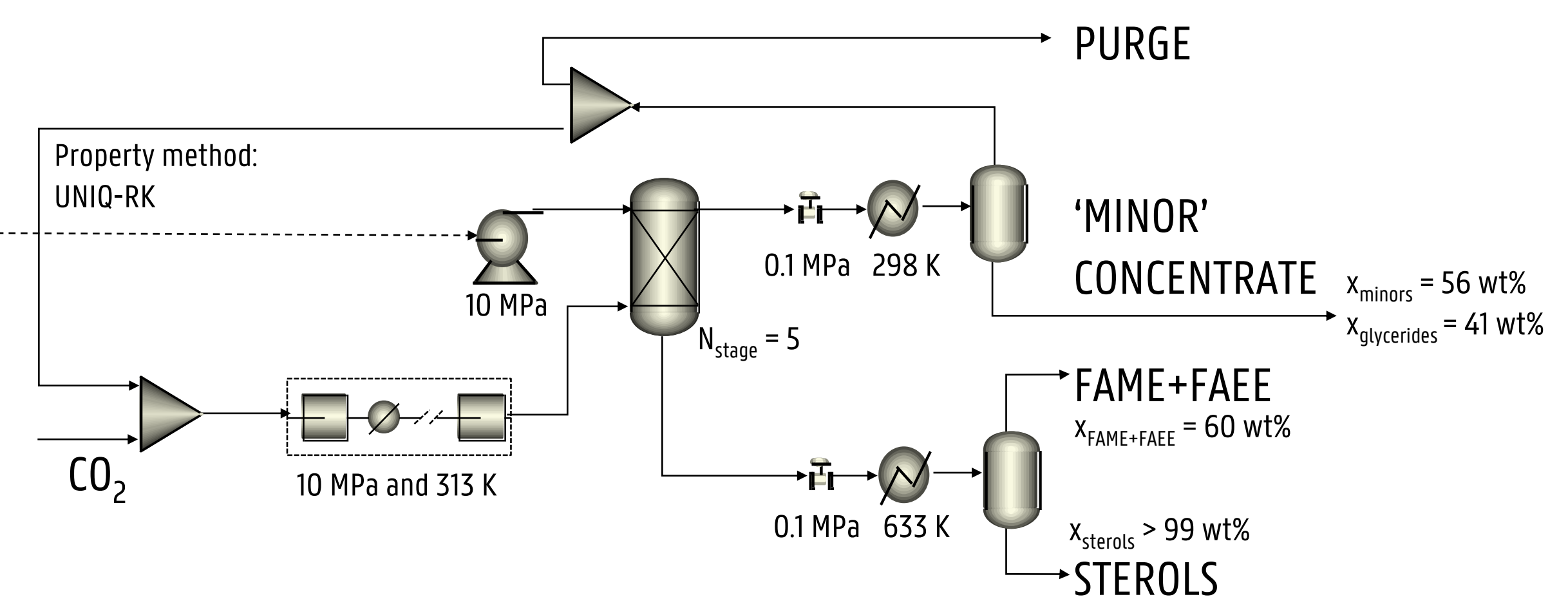


- statistically significant model
✓ $F_{\text{test}} = 5.38 \cdot 10^4 > F_{\text{tab}} = 3.84$
- statistically significant & physically relevant parameters
✓ no correlations between parameters
✓ $E_{a,\text{TG} \rightarrow \text{DG}} < E_{a,\text{DG} \rightarrow \text{MG}} < E_{a,\text{MG} \rightarrow \text{GLY}}$
→ consecutive transesterification is not favored
- model reproduces experimental trends

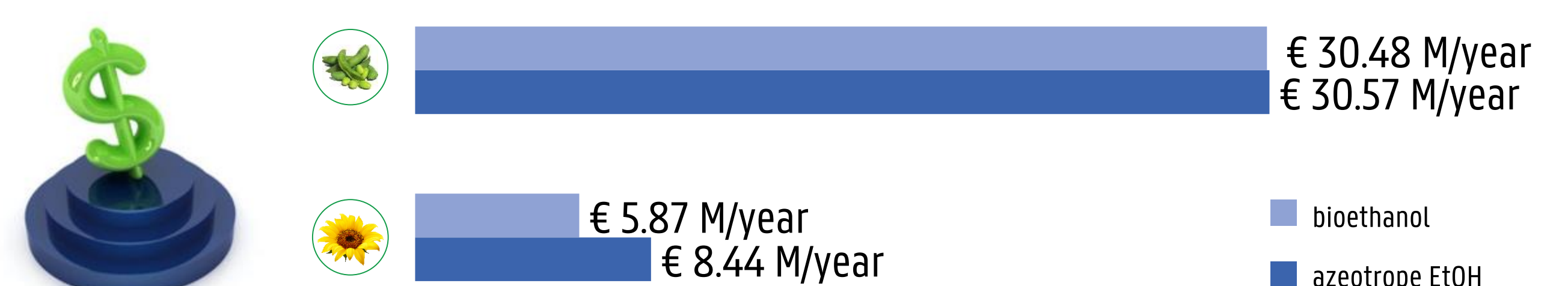
COMMERCIAL SCALE PROCESS DESIGN



- 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 successful extraction ($x_{\text{minor}} > 99$ wt%)



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-CO₂ extraction based on the experimental data acquired from a bench scale setup.