INFACT: FROM INSECT TO SURFACTANT

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RADIUS @ THOMAS MORE

RADIUS combines diverse expertise in relation to sustainability, with focus on insect breeding and microalgae cultivation (on waste streams) and extraction/implementation of biomaterials.

Insect breeding

Microalgae cultivation

Downstream processing

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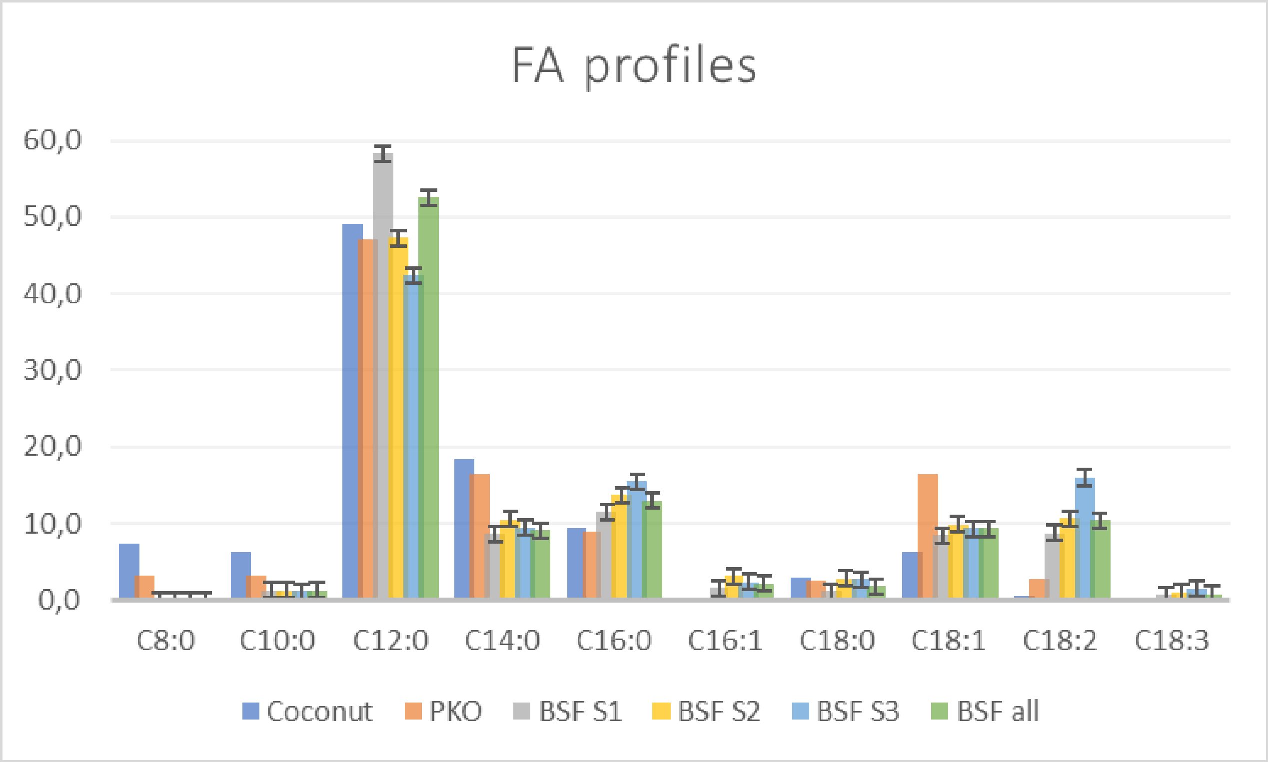
BLACK SOLDIER FLY

- Interesting species because:
  - Tropical species – not viable in our climate
  - Not a pest species
  - High food conversion rate
  - Reared on small surface at high density
  - Reared on many organic waste/sidestreams
  - Potential source for biomaterials:
    - Chitin/chitosan
    - Proteins
    - Fats

FATTY ACID PROFILE -> INFACT

Coconut and Palm Kernel Oil compared to BSF fats (3 sources):
- Very similar profiles
- High lauric acid content
- Similar applications possible?



- PKO and CCO: large impact on deforestation and biodiversity
- Case: surfactants using BSF instead of CCO (e.g. amilite)

➡ INFACT

The implementation of black soldier fly as a new high-value and sustainable source of fats for the production of green surfactants, making use of green and less polluting synthesis approaches

TETRA project – VLAIO: HBC.2017.0038

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INFACT - OVERVIEW

Amino-acyl based surfactants using BSF fatty acid coupled to:

- Case 1: Glycine
- Case 2: Lysine

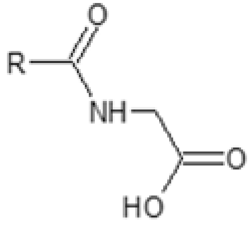
Synthesis approaches:

- Chemical approaches:
    - Schotten-Baumann (Case 1 and 2)
    - Coupling reagents (Case 2)
- Thermal amidation (Case 1 and 2)

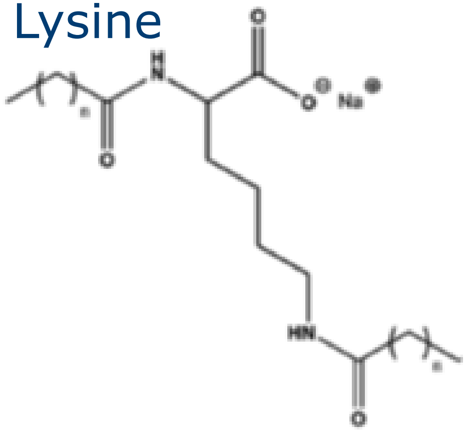
Characterisation of the surfactants

Implementation (cosmetics, crop protection, …)

Glycine



Lysine



INFACT - SYNTHESIS APPROACHES

Classical chemical syntheses:

1. Hydrolysation of fats to free fatty acids
2. Schotten-Baumann (Sreenu et al. 2014 Colloids and Surfaces A 449: 74-81)
   a) React fatty acids with thionylchloride
   b) React fatty acid chlorides to Gly (1 FA chain) or Lys (1 or 2 FA chains)
   c) Purify
3. Coupling reagents (Gomes et al., 2008 Synthetic Communications 38: 2013-2024)
   a) React Lys to thionychloride and methanol to generate methyl-protected Lys
   b) Couple M-Lys to fatty acid and deprotect the Lys group
   c) Purify

Alternative thermal amidation (Zhang et al 2013 AJAC 4: 445-450)

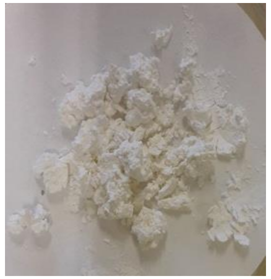
a) Incubate fat and Gly (or Lys) to reaction vessel with sodium methoxide at 160°C
b) Purify

INFACT - REACTION YIELDS

Reaction	N	Ave. Yield (%)	SD	Remarks
Fat hydrolysis	22	86,33	10,2	
Schotten Baumann				
FA-Cl formation		ND		expected 100%
FA-Cl Gly coupling	13	68,77	12,7	
FA-Cl to Lys coupling	4	70,82	8	
Gomes et al. 2008				
Lys-M formation	4	96,8	1,4	
Lys-M to FA coupling	2	>95%	nd	yield >100% for 1 reaction
Thermal amidation				
Gly-FA	14	36,53	24,4	Highly variable 10-80% - also due to purification step
Lys-FA	3	38	10,5	Variable 19-45% - brown/sticky product

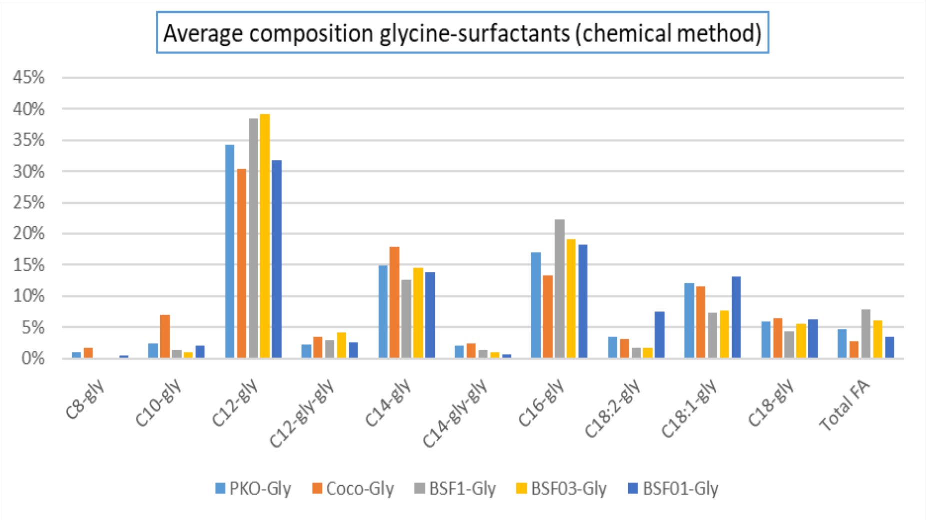
Yield>100% ? -> single bound surfactants, contaminants, use of average FA MW, LC-MS small peaks not taken into account

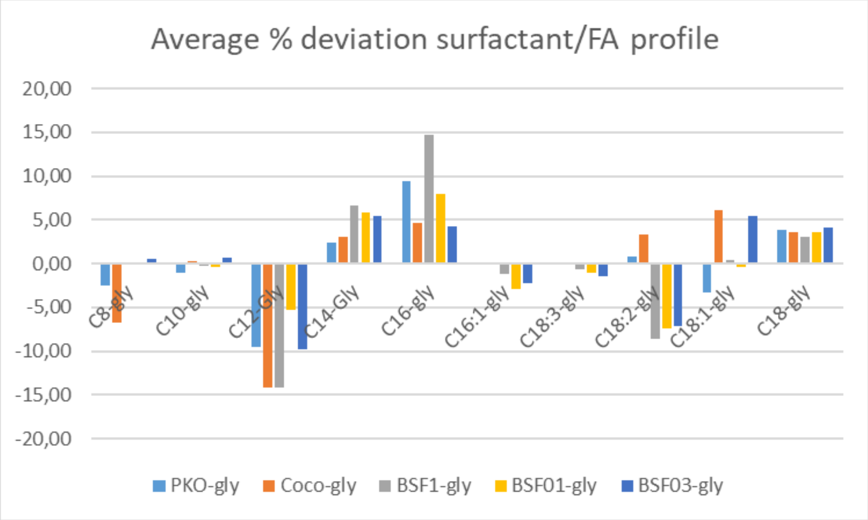
CASE 1: GLY-SURFACTANT



Profile determined by LC-MS – Schotten Baumann

- Gly-surfactants based on PKO, CCO and BSF from 3 sources (N=3)
- Profile of the different sources resemble each other closely
- Compared to initial fatty acid distribution, C12-surfactants are underrepresented and C16-surfactants overrepresented
- Small fraction 2 Gly coupled to C12 and C14
- Approx 5% FFA remaining





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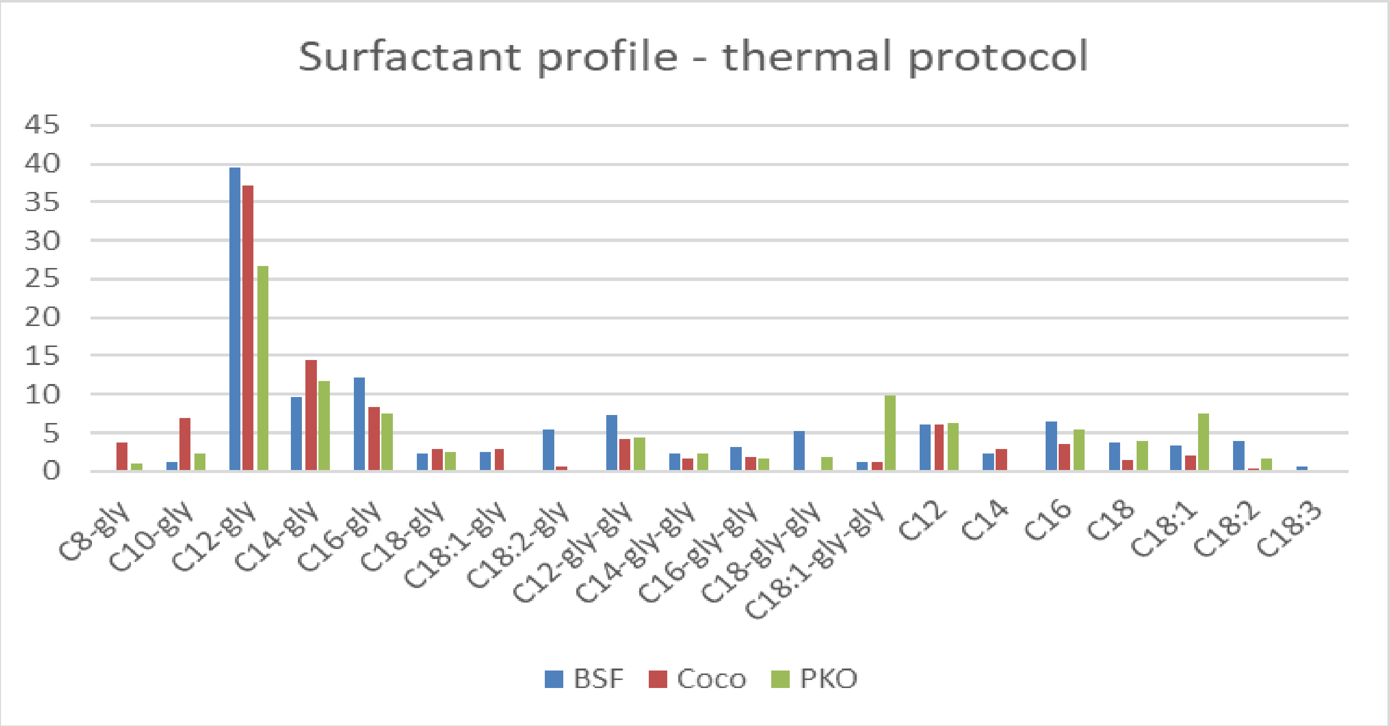
CASE 1: GLY-SURFACTANT

Thermal protocol: profile determined by LC-MS:

- C12, 14 and 16 are the main surfactant molecules formed
- 15% FFA remaining, but additional washing reduces FFA further
- Double-bound Gly surfactants are also observed



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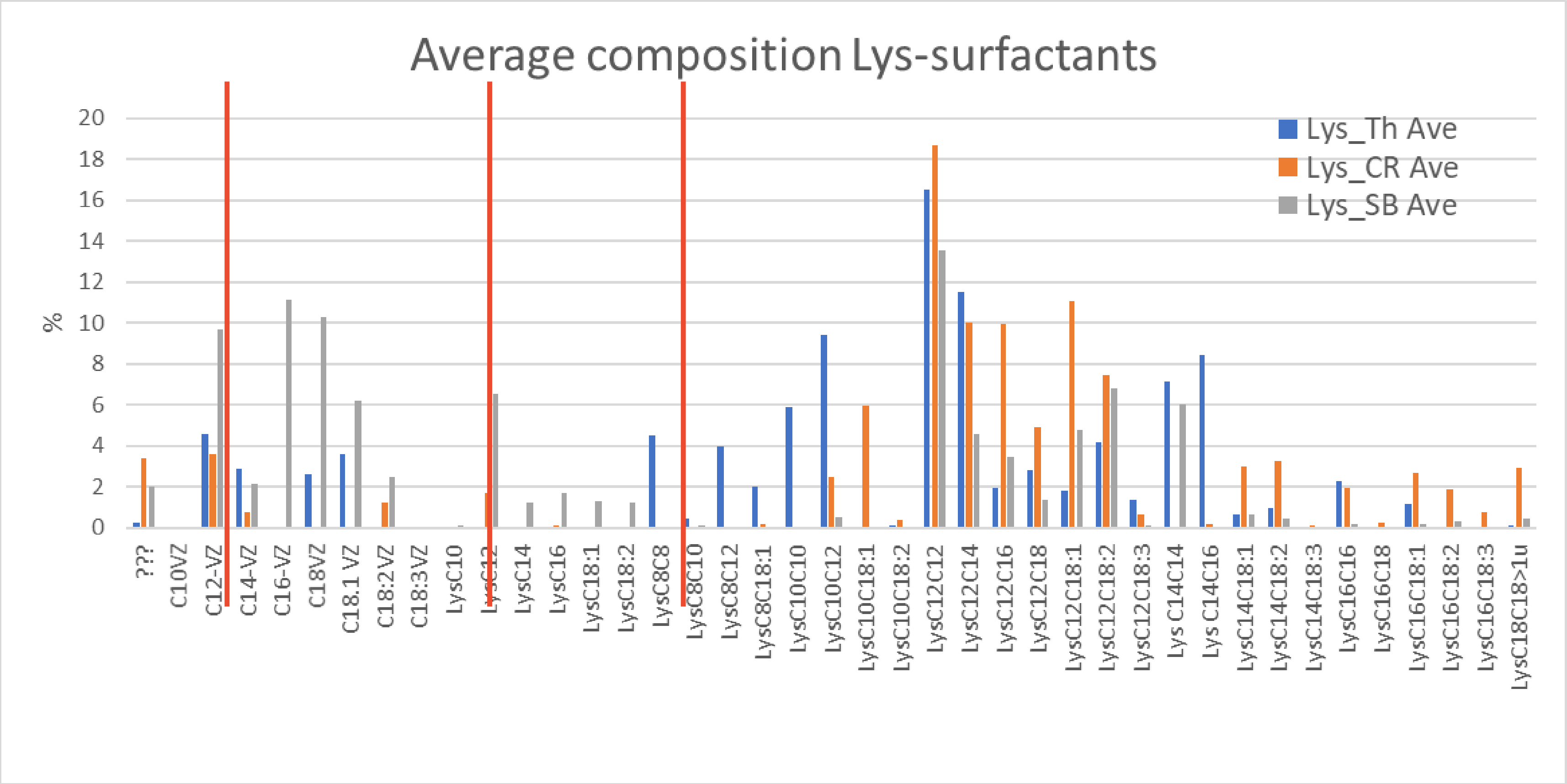
CASE 2: LYS SURFACTANT



Complex profile

Lys-C12C12 main product for all 3 synthesis methods

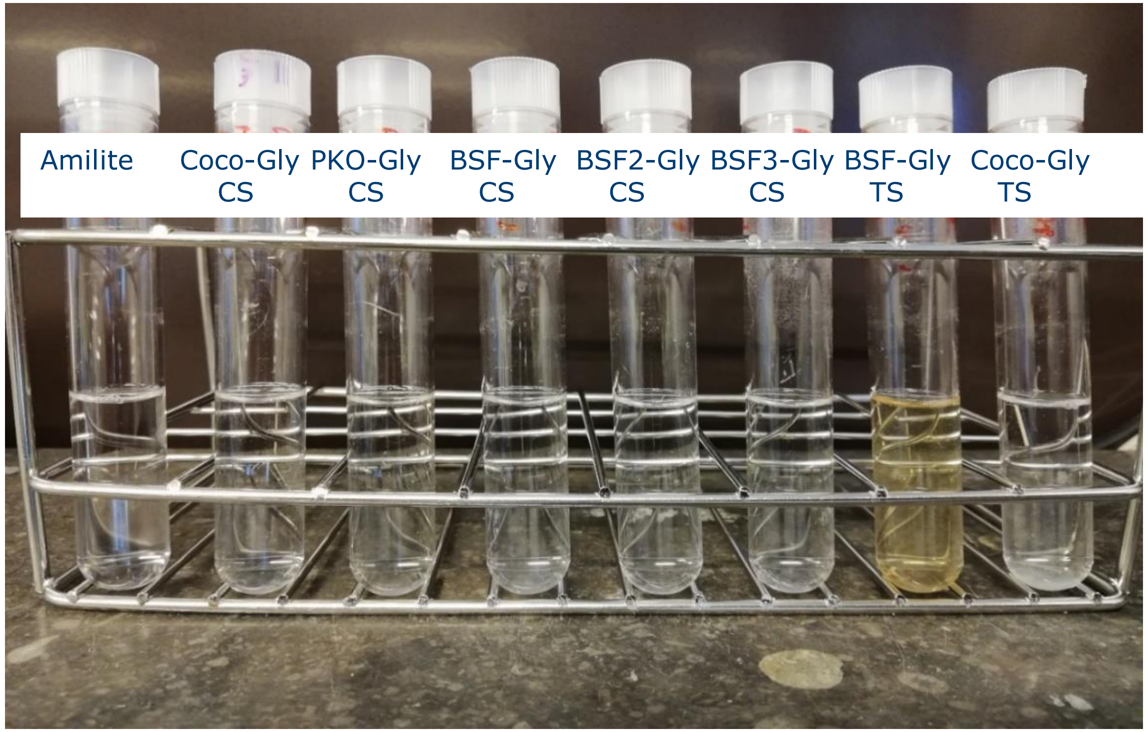
CASE 2: LYS-SURFACTANT

- Composition
  - Schotten Baumann: many FFA and single bound surfactant
  - Gomes (CR) mostly double bound surfactant
  - Thermal protocol: appr. 15% FFA but less yield compared to Gomes et al.

Product	Thermal	Gomes et al (CR)	Schotten Baumann
	N = 3	N = 6	N = 11
Double bound Lys (%)	87,3	89,0	43,7
Single bound Lys (%)	0,0	1,9	12,1
Free fatty acids (%)	13,6	5,6	42,1
Unknown (%)	0,2	3,4	2,1

SOLUBILITY

- Neutral pH:
  - Solubility is low for all Gly-and Lys-surfactants
  - < 1g/L
- Increasing pH
  - Solubility improves
  - Gly-surfactant > Lys-surfactant
  - 10 g/L confirmed at pH > 11
  - At 10 g/L lys-surfactant becomes a gel after a while



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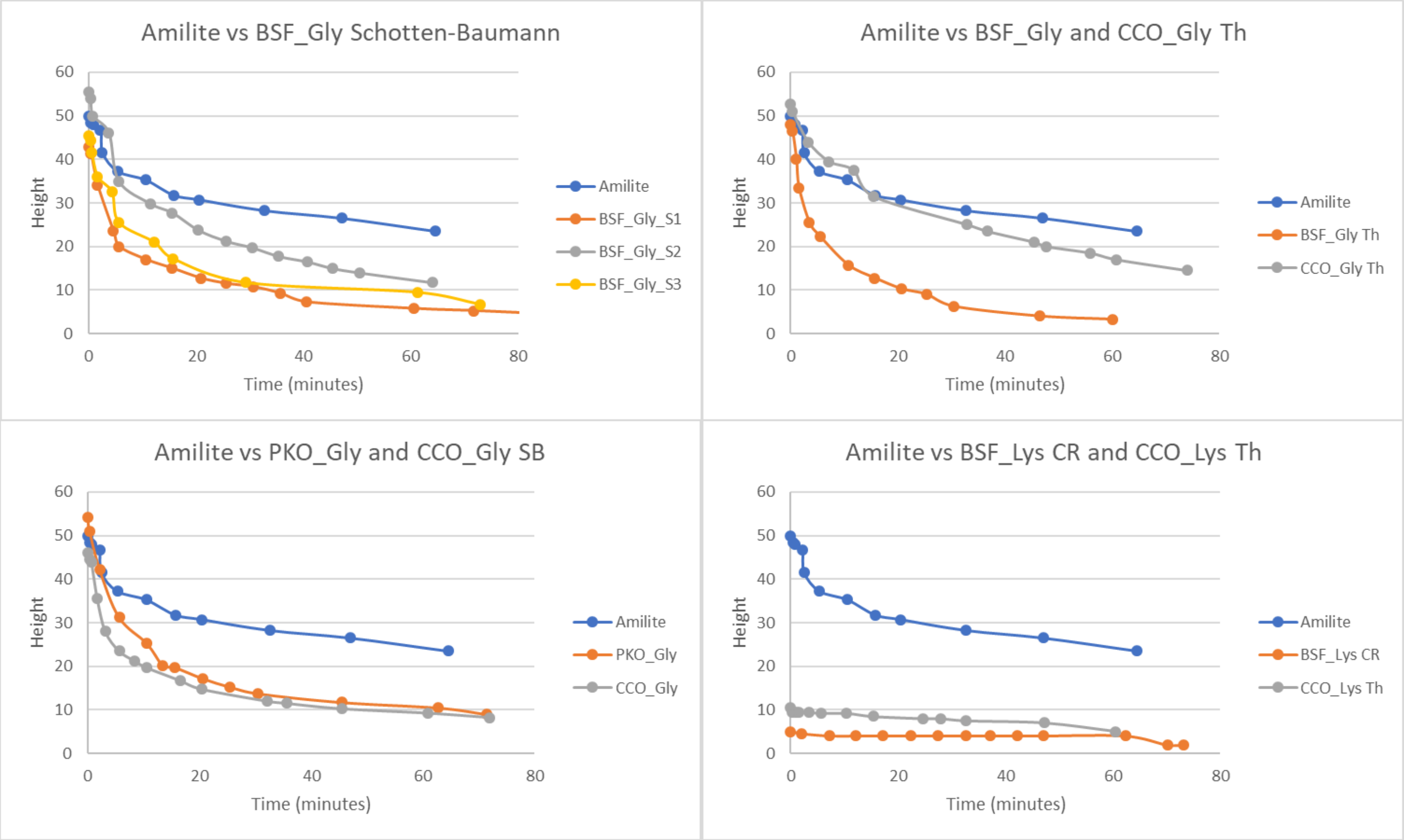
FOAMING

- 0,01 M solutions in water were prepared
- 30 mL solution was poured in a cilinder and rotated 5 times
- Foam height was determined at several timepoints
- Amilite largest foam height with gradual decay
- BSF, PKO and CCO_Gly (SB) same inital height but faster decay
- CCO_Th most similar to amilite
- Lys-based surfactants low foaming capacity



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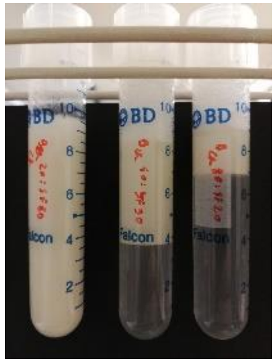
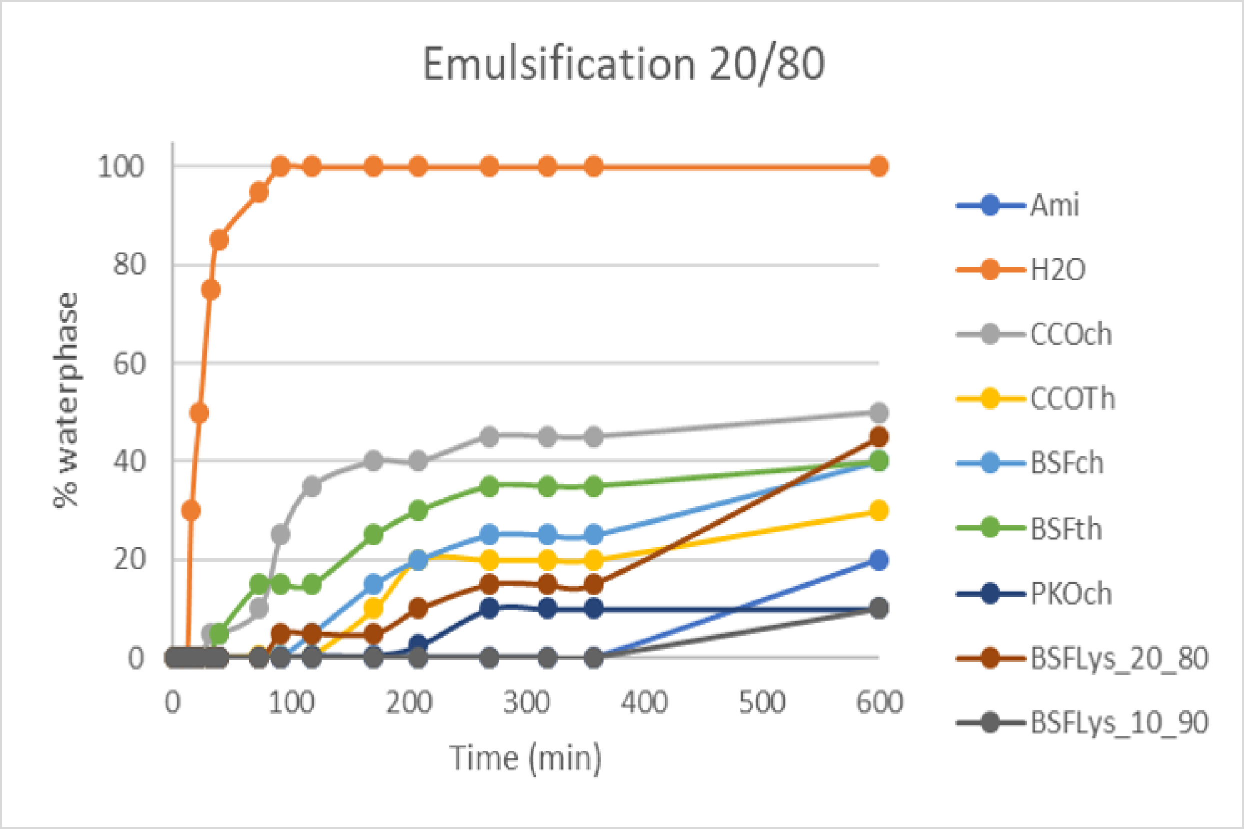
EMULSIFICATION

- Different proportions of water/surfactant (0,01M) and sunflower oil were prepared in tubes: 80:20, 50:50 and 20:80
- Tubes were shaken violently and the height of water was measured and set as percentage of the initial water volume
- Water dephases quickly
- Dephasing only overnight for amilite – 20%
- All other surfactants behave similar to each other, but all dephase
  - BSF_Lys (20/80) similar to Gly surfactants
  - BSF_Lys (10/90) stable up to overnight





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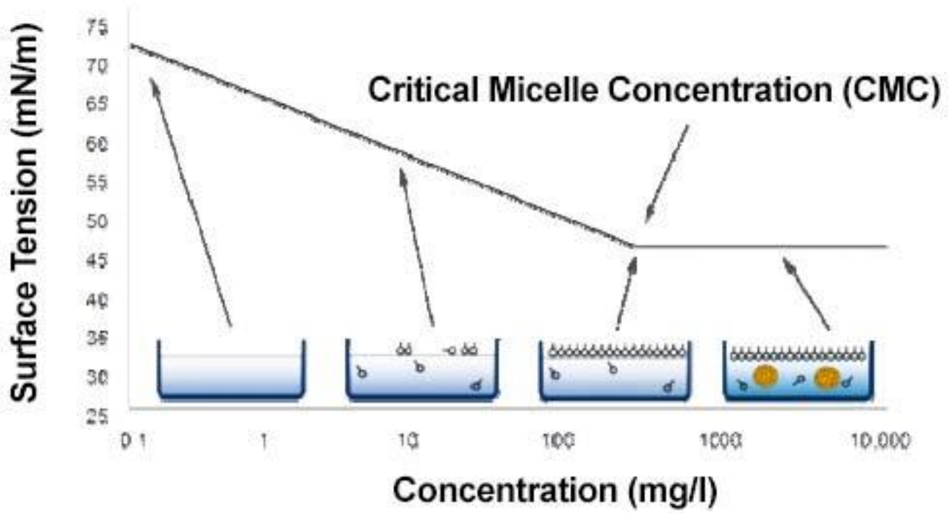
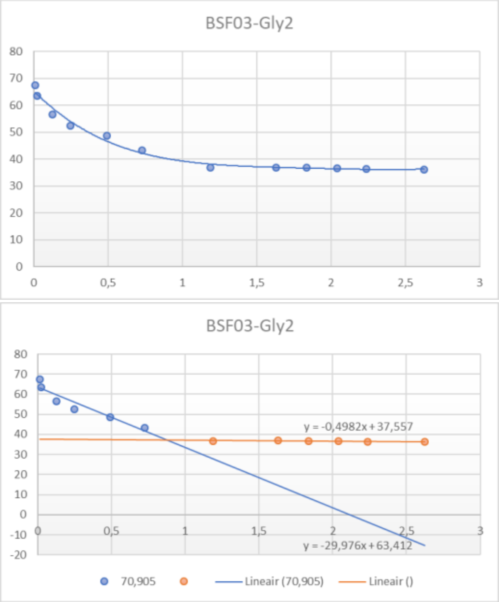
SURFACE TENSION AND CMC

Surface tension reduction and CMC

- Adding increasing amounts of surfactant to UP water
- Measure surface tension with Du Nouy ring method
- The surface tension reduction stops at the CMC, the concentration at which micelles start forming
- Biolin Attension Sigma 700





SURFACE TENSION AND CMC

Sample	N	Av. minimal surface tension (mN/m)	Av. CMC (mM)
Amilite	2	35,4 (0,1)	3,2 (0,4)
BSF01_Gly1	3	36,8 (0,5)	1,2 (0,2)
BSF03_Gly 1	3	36,6 (0,1)	0,8 (0,6)
BSF_FD_Gly	3	36,4 (0,2)	1,2 (0,3)
PKO_Gly1	3	35,9 (0,6)	0,8 (0,4)
Coco_Gly2	2	36,7 (0,1)	1,1 (0,1)
BSF_Gly_Th	1	36,9	1,1
Coco_Gly Th	1	36,7	1,2
BSF Lys Gomes	4	34,0 (1,0)	0,0152 (0,0004)
BSF Lys SB	1	32,3	0,1
Coco Lys Th	1	31,2	0,05

Min. ST of Gly-surfactants similar and comparable to amilite

CMC Gly-surfactants lower than amilite

Min. ST and CMC Lys-surfactants lower than Gly-surfactants and amilite

IMPLEMENTATION: COSMETICS

MYLÈNE

- Rinse-off products / showerfoam and showergel:
  - Use as secundary surfactant
  - Foam capacity is sufficient
  - Both solutions are not transparent, but is not an issue
  - Solubility is an issue for both glycinate and lysinate (old batch)

Amilite Gly Lys

- Leave-on product / hand cream:
  - Glycine surfactant
  - Initial Gly-surfactant phase separation
  - More pure Gly-surfactant: stable product
  - Further sensory, toxicity, irritation tests needed

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CONCLUSIONS

- BSF fats can be used as starting material for the synthesis of amino-acyl surfactant molecules
- Classical chemical synthesis routes have better yields compared to a more green thermal amidation
- The chemical composition of the surfactant molecule mixture resembles the initial fatty acid profile:
  - glycine-surfactant pure products can be obtained
  - lysine-surfactant Gomes approach gives pure but complex product
- Properties similar (solubility and CMC) or less (emulsification and foaming) than amilite (purity?)
- Cosmetics application:
  - optimisation is needed but the glycine-surfactant may be used in hand-cream formulations.
  - lysine-surfactant has not yet been tested with optimal product

QUESTIONS?

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