Palm oil dry fractionation: Impact of tri-saturated triacylglycerol content on process efficiency

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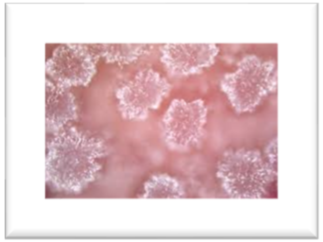
AOCS 2021 Virtual Meeting:
Edible Application Technology
Fundamentals of Fat Crystallization III –
From Liquid State to Structure

DRY FRACTIONATION – INDUSTRIAL PROCESS

- Process based on fractional crystallization by controlled cooling followed by separation of the crystals from the liquid by an efficient technology (stearin & olein).

- Drivers for fractionation: Quality improvement: better cold stability (ex. Fish Oil).
  Design of products with new specifications (ex. Palm Oil)

- **Quality requirements of a crystallizer:**
  Appropriate cooling surface and good heat exchange.
  Optimal mass transfer and no crystal fragmentation.



- **Crystallization modes:** High shear mixing (classical).
  Low shear mixing (innovative).
  Static (for some fats).
  Batch (classical).
  Continuous (innovative).

Crystallization selectivity ⬆
Crystallization cycle time ⬇

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Batch or Continuous Mode

"MOVING BUNDLE CRYSTALLIZER" MOBULIZER™ DESIGN

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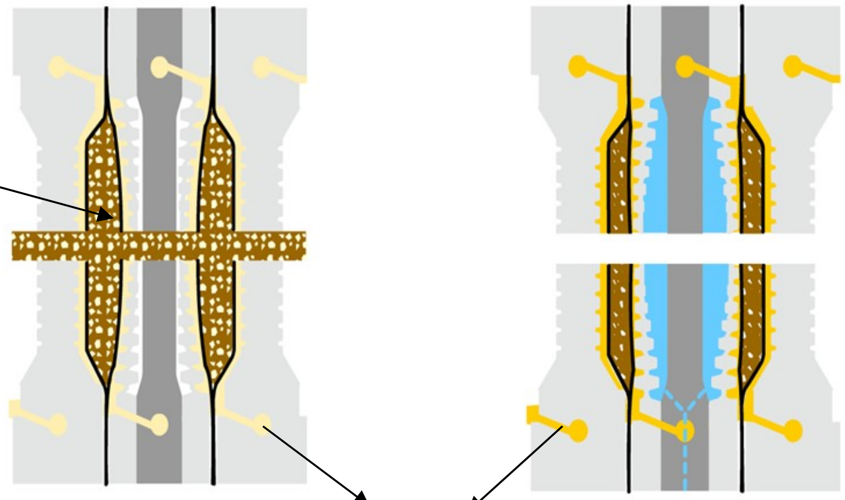
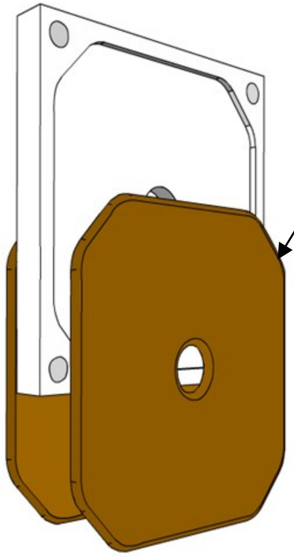
- **Separation of crystals** from the liquid (stearin & olein) requires an efficient technology.

Membrane press filter:

- Membrane plates, Chamber plates, Filter clothes.
- Squeezing pressure is applied on stearin cake.





Olein yield ⬆
Fraction quality ⬆

Squeezing pressure 6 bar to 30 bar

MEMBRANE PRESS FILTER

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Multi-step dry fractionation tree of Elaeis Guineensis palm oil

IV: Iodine Value

Refined Palm Oil
IV 51-53

Solid route

Step 1

Stearin
IV 30-32

Olein
IV 56-57

Step 2

Super Stearin
IV 9-14

Soft Stearin
IV 40-43

Soft PMF
IV 44-46

Super O
IV 64-65

Liquid route

- ❑ 3 fractionation steps
- ❑ 3 fractionation routes

Hard PMF
IV 32-34

Mid olein
IV 50-52

Mid Stearin
IV 56-58

Top O
IV 71-73

Step 3

Hard PMF route (CBE)

Science Behind

Technology

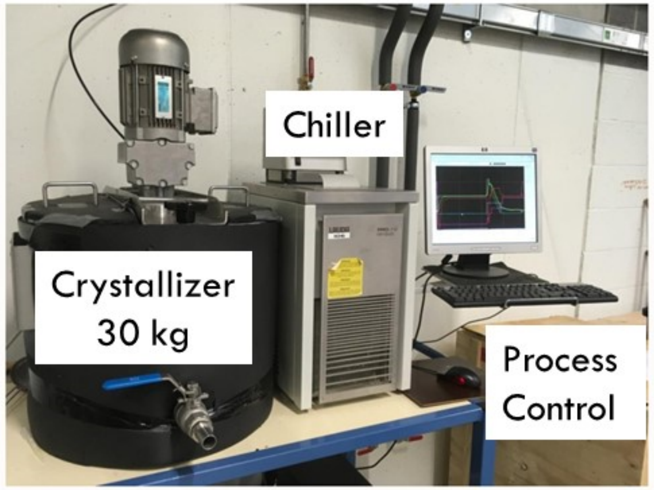
Refined Palm Oil
IV 51-53

Stearin
IV 30-32

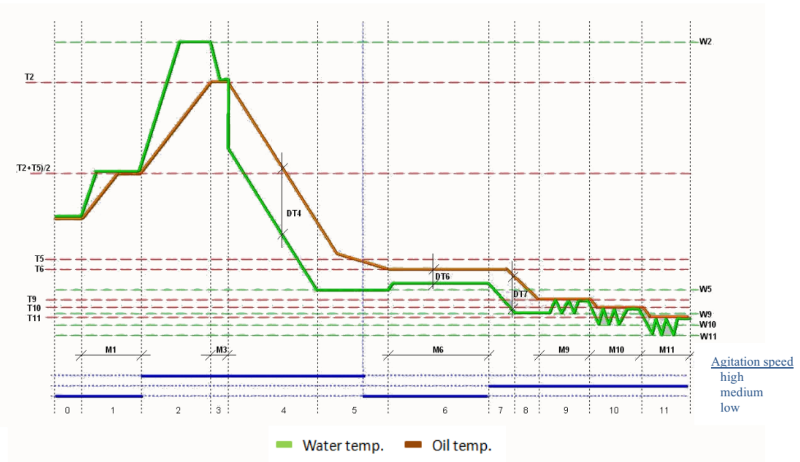
Step 1

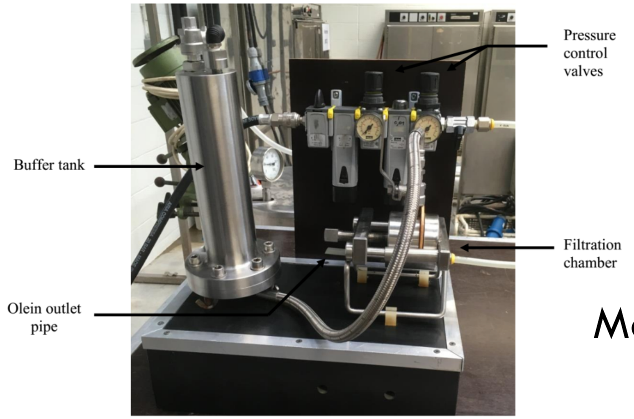
Olein
IV 56-57

Liquid route



Controlled crystallization curve





Membrane Press Filter
(6 bar squeezing)

Vacuum Filter

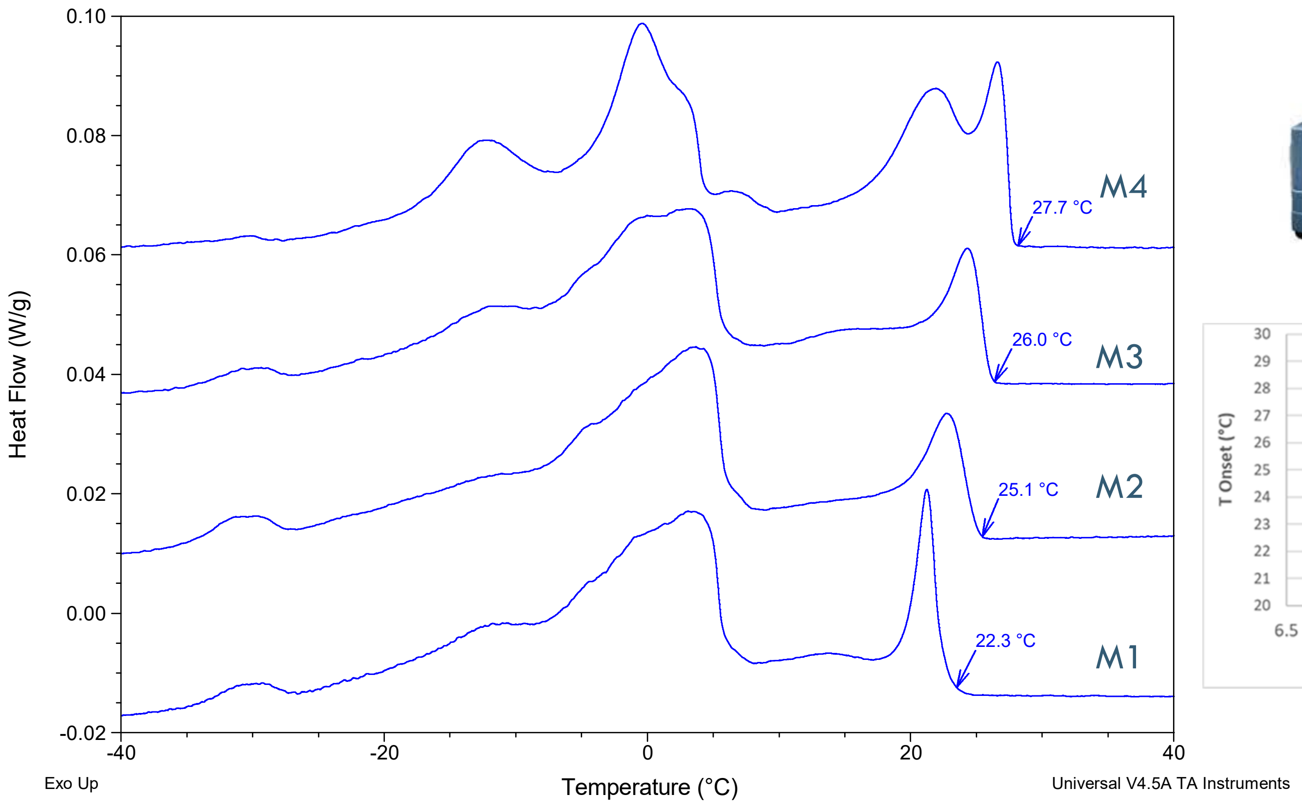
Palm oil and stearin blends to cover a range of StStSt content in the palm oil.

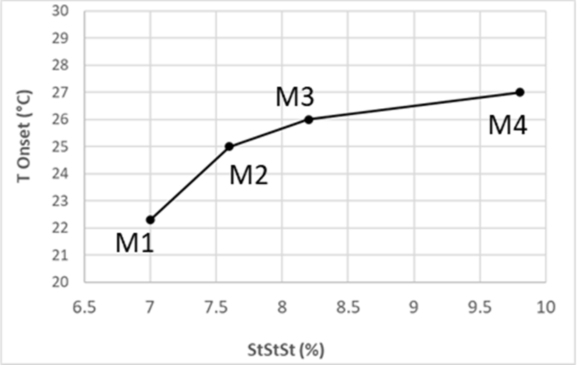
Matrix	M1	M2	M3	M4
StStSt (% HPLC)	**7.0** (+/- 0.1)	**7.6** (+/- 0.0)	**8.2** (+/- 0.0)	**9.8** (+/- 0.1)
TAG (% HPLC)				
MPP	0.5	0.5	0.5	0.5
PPP	**5.1** (+/- 0.1)	**5.6** (+/- 0.0)	**6.1** (+/- 0.0)	**7.5** (+/- 0.1)
P_2S	**1.2** (+/- 0.1)	**1.2** (+/- 0.1)	**1.3** (+/- 0.1)	**1.5** (+/- 0.1)
PS_2	0.1	0.2	0.2	0.2
SSS	0.1	0.1	0.1	0.1
DAG (% HPLC)	**9.3** (+/- 0.1)	**9.2** (+/- 0.1)	**9.1** (+/- 0.0)	**8.9** (+/- 0.1)
IV (Wijs)	**52.1**(+/- 0.2)	**51.6** (+/- 0.2)	**51.2** (+/- 0.2)	**49.9** (+/- 0.2)

TAG: triacylglycerol; M: myristic acid; P: palmitic acid; S: stearic acid; St: saturated fatty acids; DAG: diacylglycerol; IV: iodine value

DSC crystallization profiles (cooling rate 0.5°C/min.) of the different matrices: T onset (°C)

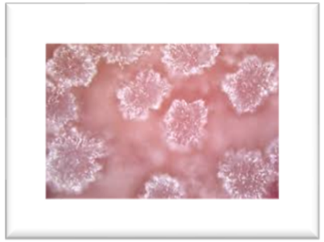
Matrix	M1	M2	M3	M4
T onset (°C DSC)	22.3 (+/- 0.1)	25.1 (+/- 0.1)	26.0 (+/- 0.1)	27.7 (+/- 0.1)

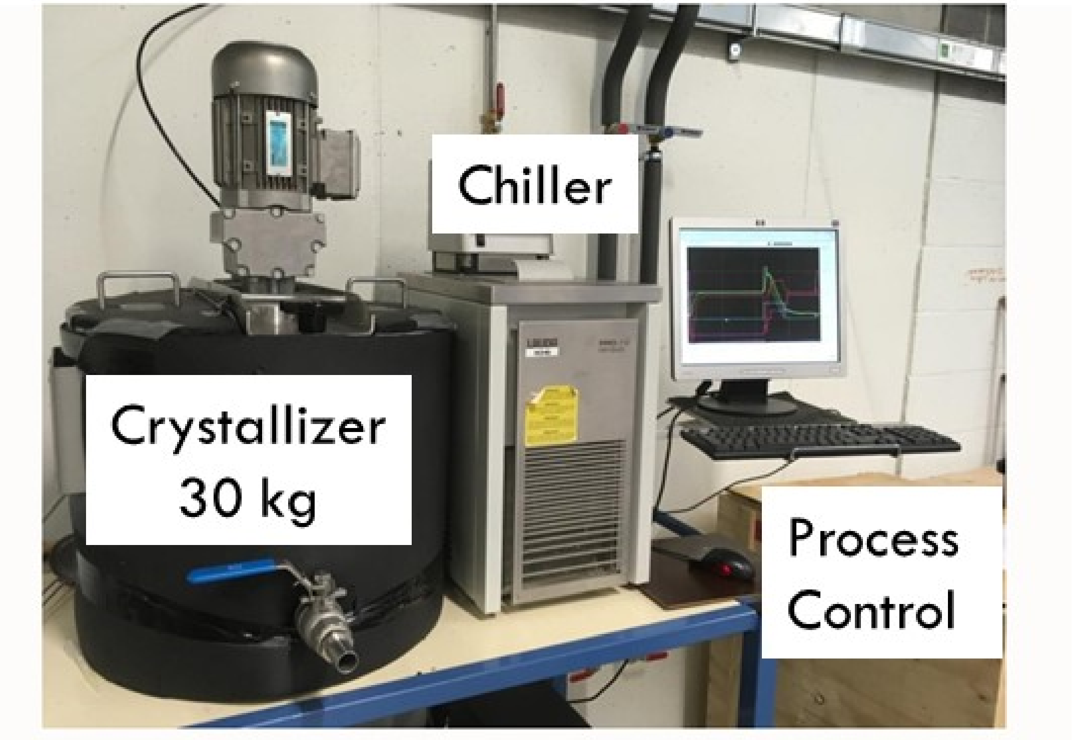




Science Behind

Crystallization selectivity ⬆
Crystallization cycle time ⬇





Technology

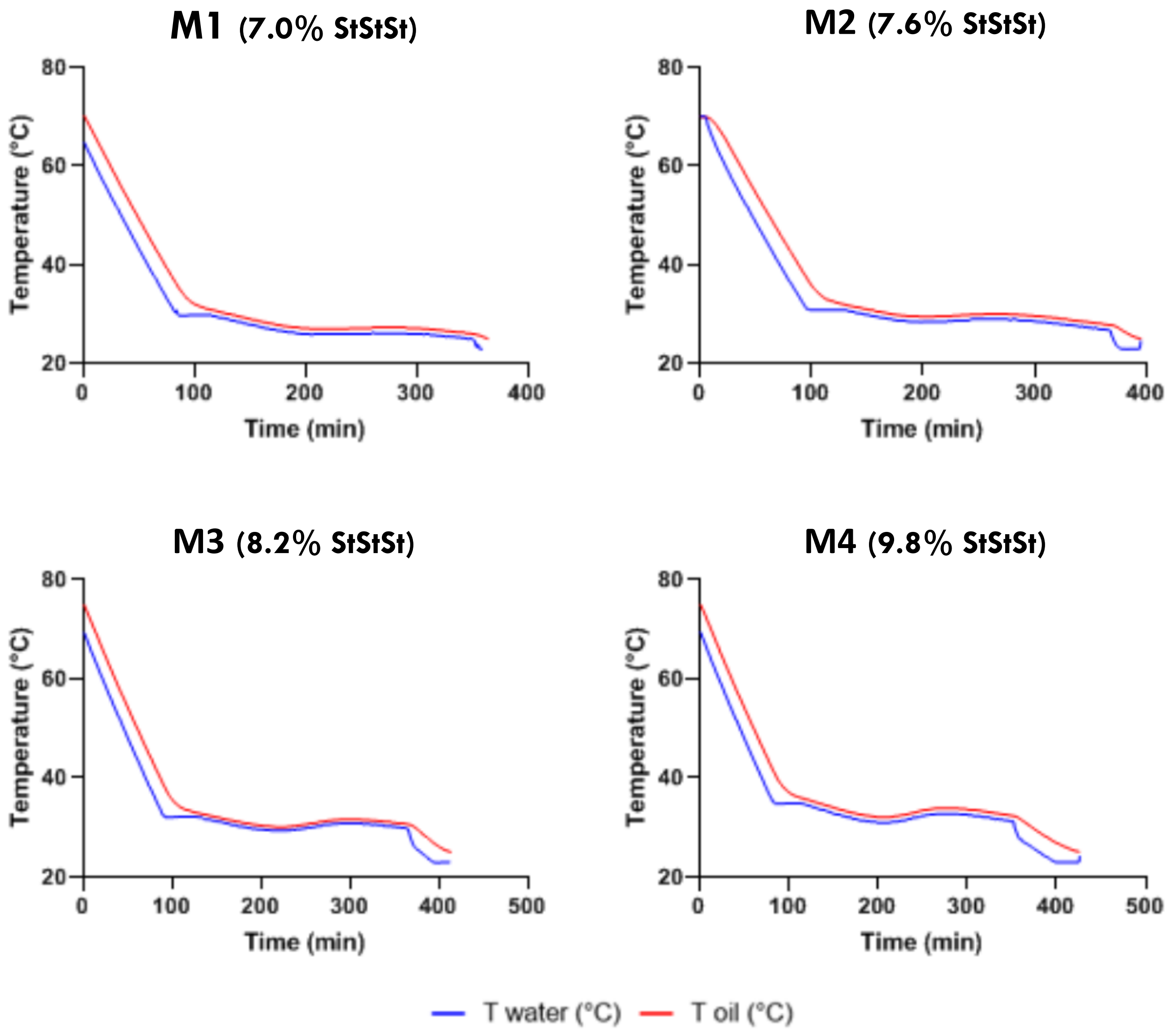
	Step	Parameter	M1 7.0 (+/- 0.1)	M2 7.6 (+/- 0.0)	M3 8.2 (+/- 0.0)	M4 9.8 (+/- 0.1)
FAST COOLING	2	Water temp. W2	75.0°C	75.0°C	80°C	80°C
		Oil temp. T2	70.0°C	70.0°C	75°C	75°C
	3	Mixing time M3	30 min	30 min	30 min	30 min
	4	Delta T 4 DT4	15.0 °C	15.0 °C	15.0 °C	15.0 °C
INITIATION CRYSTAL GROWTH	5	Water temp. W5	30.0°C	31.0°C	32.3°C	35°C
		Fast agitation end temp. T5	32.0°C	33.0°C	34°C	37°C
	6	Crystallization start temp. T6	31.0°C	32.0°C	33°C	36°C
		Delta T6 DT6	1.0°C	1.0°C	0.7°C	1.0°C
		Crystallization time M6	240 min	240 min	240 min	240 min
FINAL COOLING	7	Delta T 7 DT7	4.0°C	4.0°C	4.0°C	4.0°C
	8	Water control W9				
	9	Water temp. W9	23.0°C	23.0°C	23.0°C	23.0°C
		Oil temp. T9	25.0°C	25.0°C	25.0°C	25.0°C
		Maintain time M9	0 min	0 min	0 min	0 min

Olein
IV: 56-57

Science Behind

Technology

Crystallization cooling curves



In triplicate

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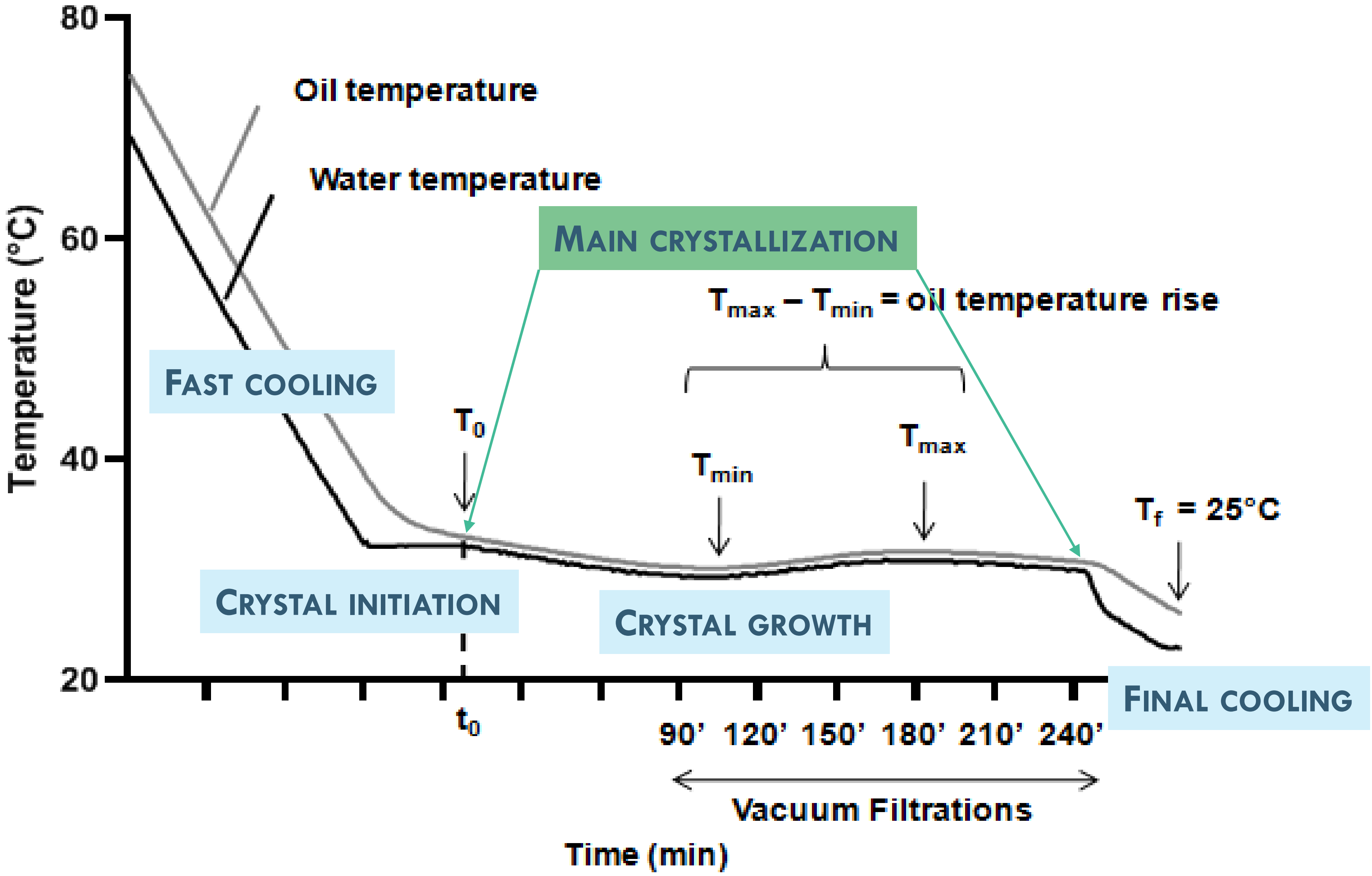
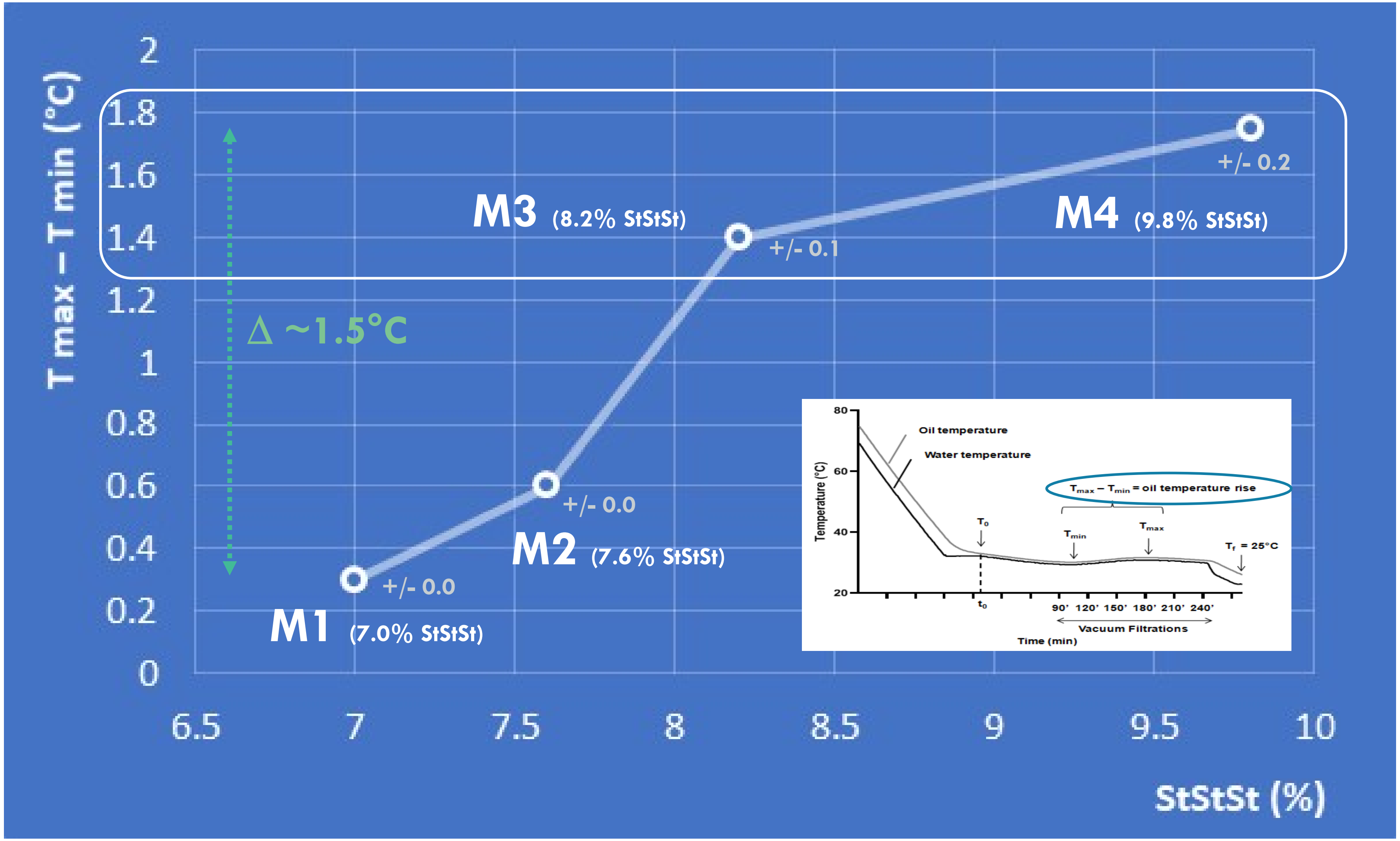
Science Behind

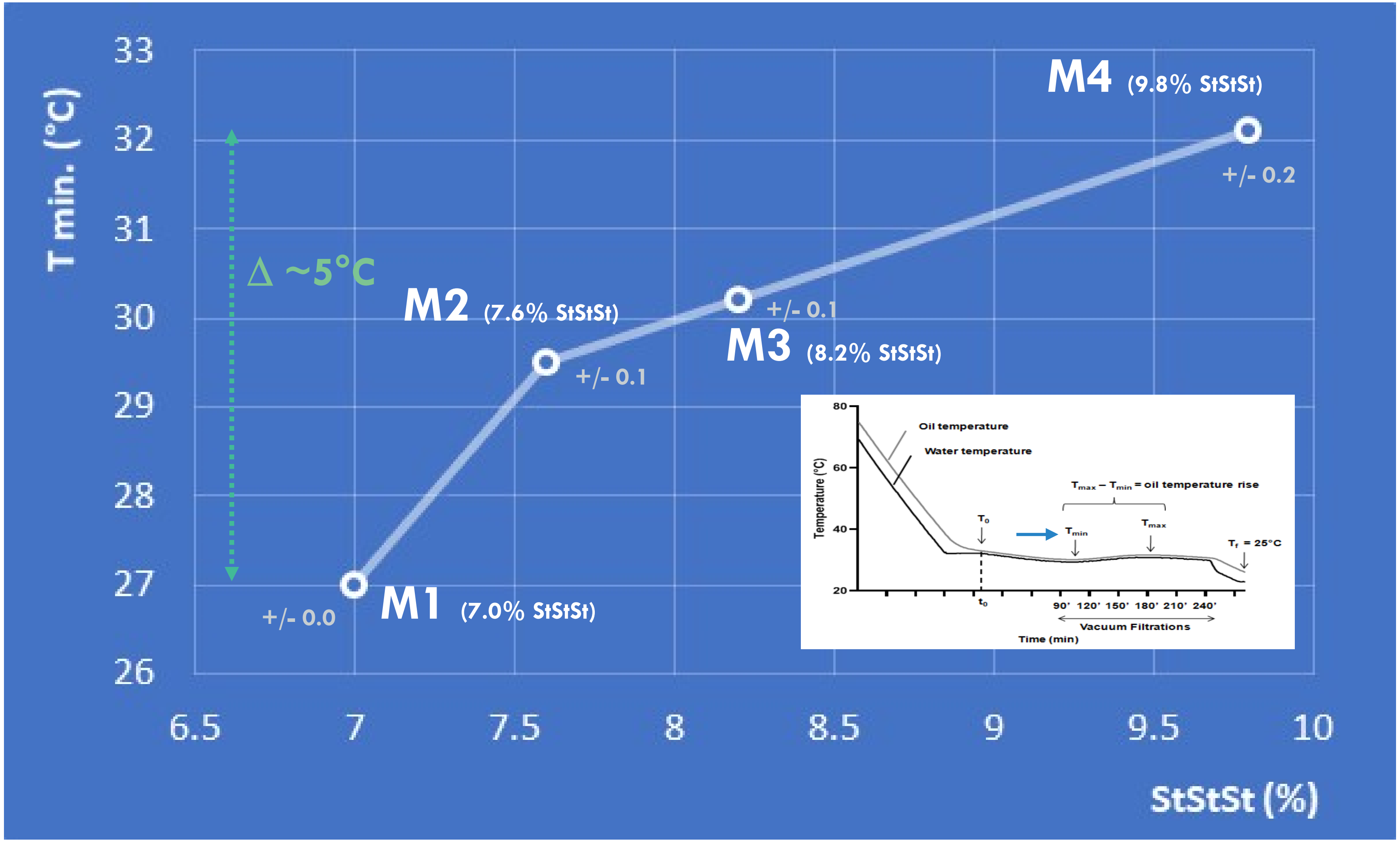


Technology

Oil temperature rise (T max. - T min.) during main crystallization



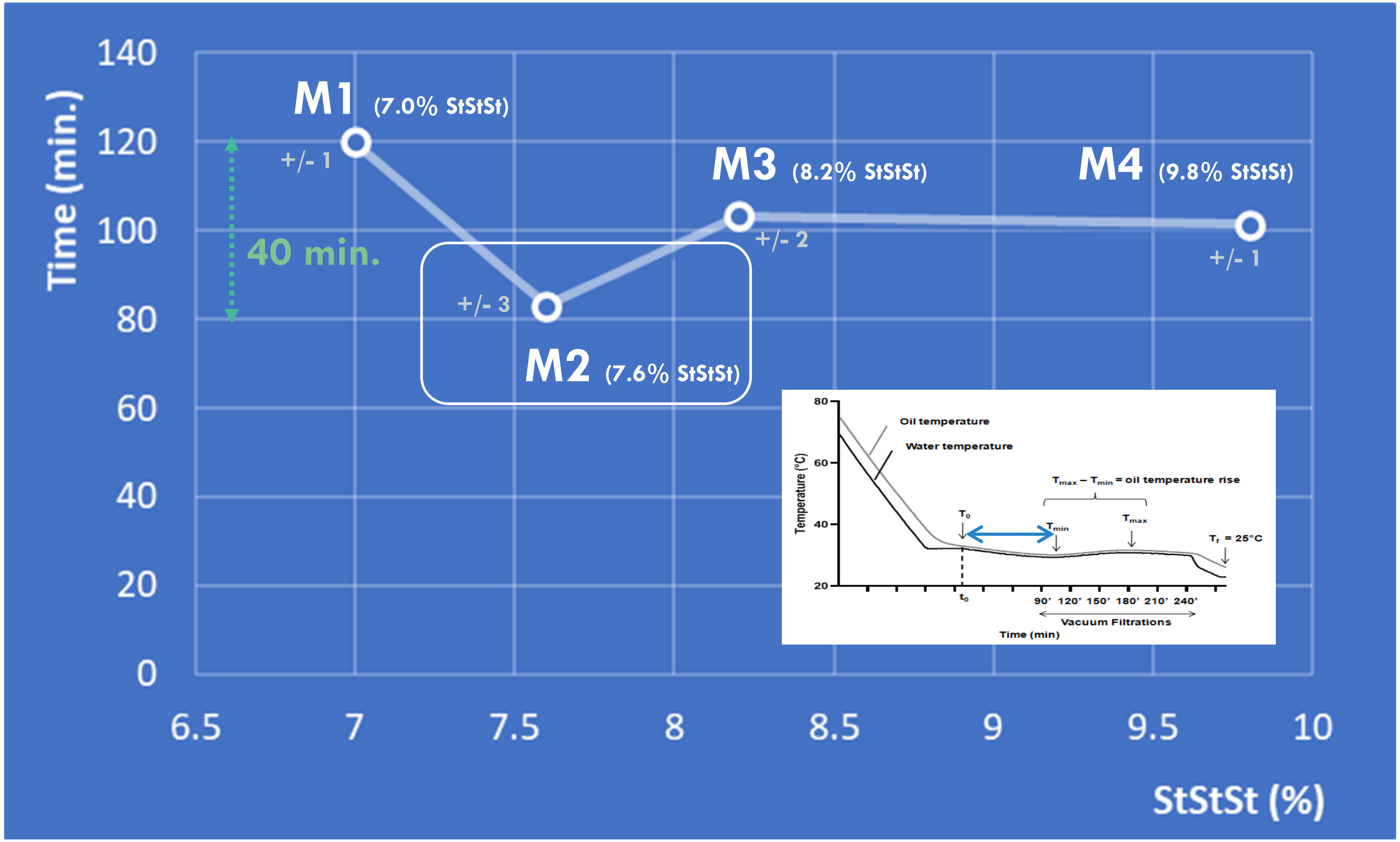
MINIMAL OIL TEMPERATURE (T min.) DURING MAIN CRYSTALLIZATION



Science Behind

Technology

Time before oil temperature rise during main crystallization



Science Behind

Technology

SUMMARY

- Crystallization is exothermic.
- This causes a rise in oil temperature during the main crystallization.
- This rise is more important at high StStSt contents: partial crystal melting for M4 & M5 (crystal quality↓).
- During the main crystallization, the oil temperature decreases before rising.
- This decrease is lower for higher StStSt contents.
- Time before the temperature rise is shorter for higher StStSt contents.
- Surprisingly, M2 shows the shortest time (faster initiation).

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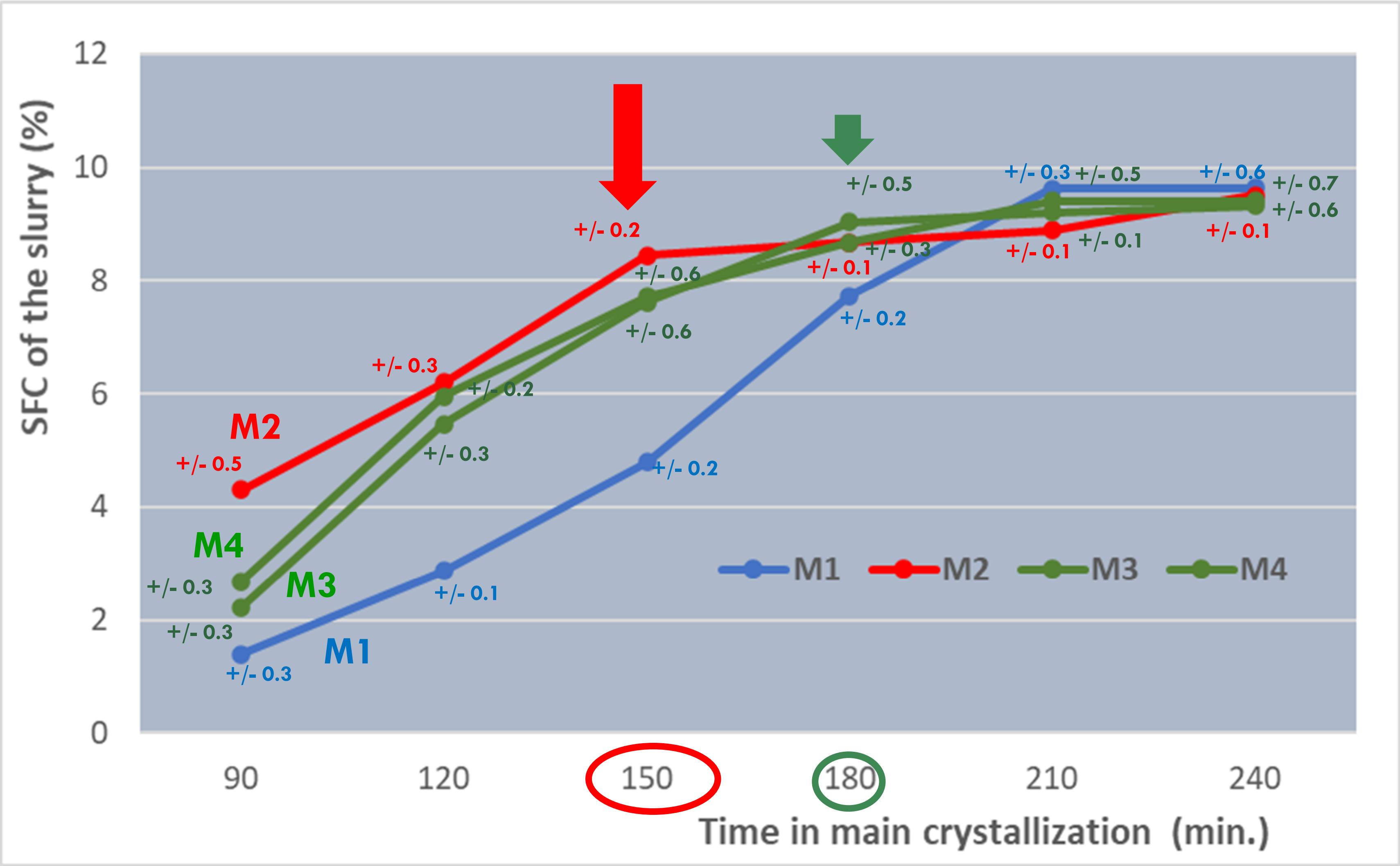
Science Behind

Technology

CRYSTALLIZATION KINETICS (SFC) DURING MAIN CRYSTALLIZATION



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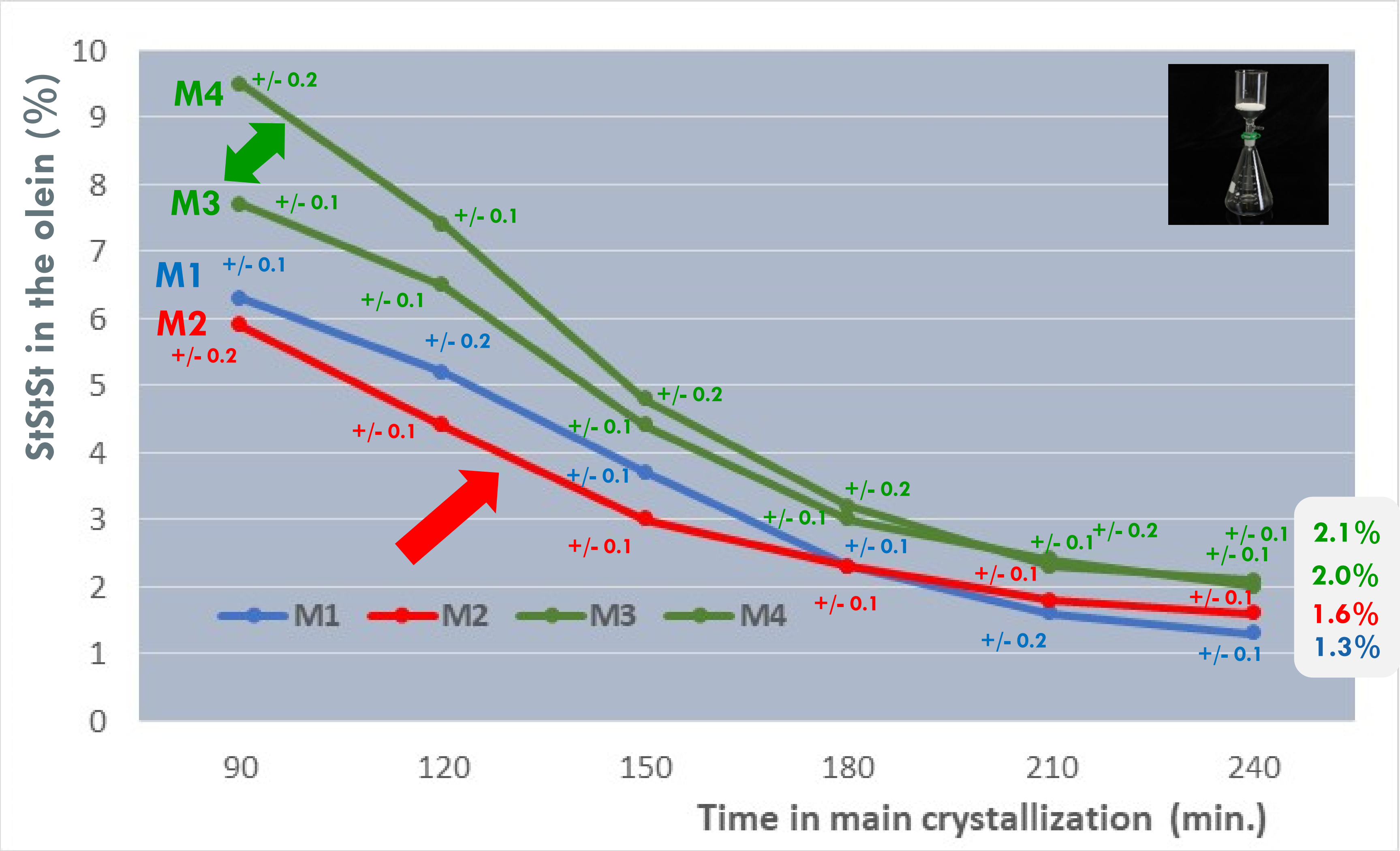
Science Behind

Technology

StStSt CONTENT (RP-HPLC) IN THE OLEIN FROM VACUUM FILTRATION



Science Behind

Technology

SUMMARY

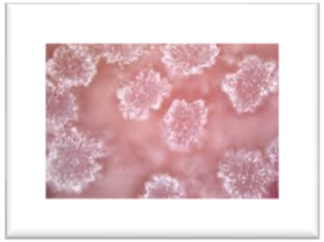
- StStSt accelerate the crystallization kinetics (M3 & M4).
- Surprisingly, the crystallization kinetics is the fastest for M2 (with a plateau after150 min.)
- Residual StStSt in the olein from vacuum filtrations is the highest in M3 & M4.
- Surprisingly, StStSt are more efficiently removed in M2 olein.

Science Behind

Technology

Crystal polymorphism
(powder XR diffraction)

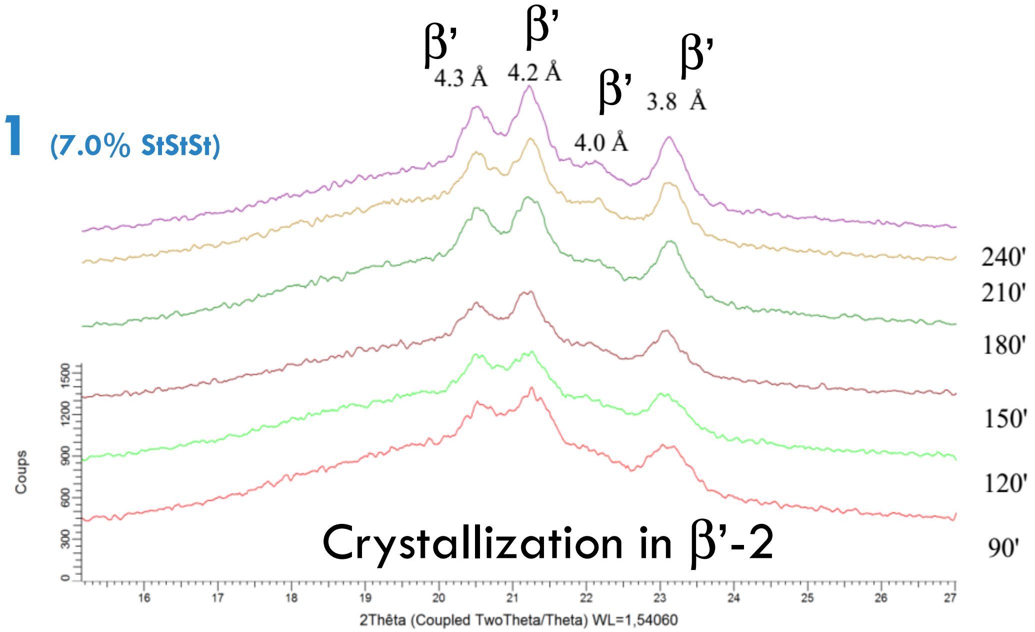
Crystal morphology



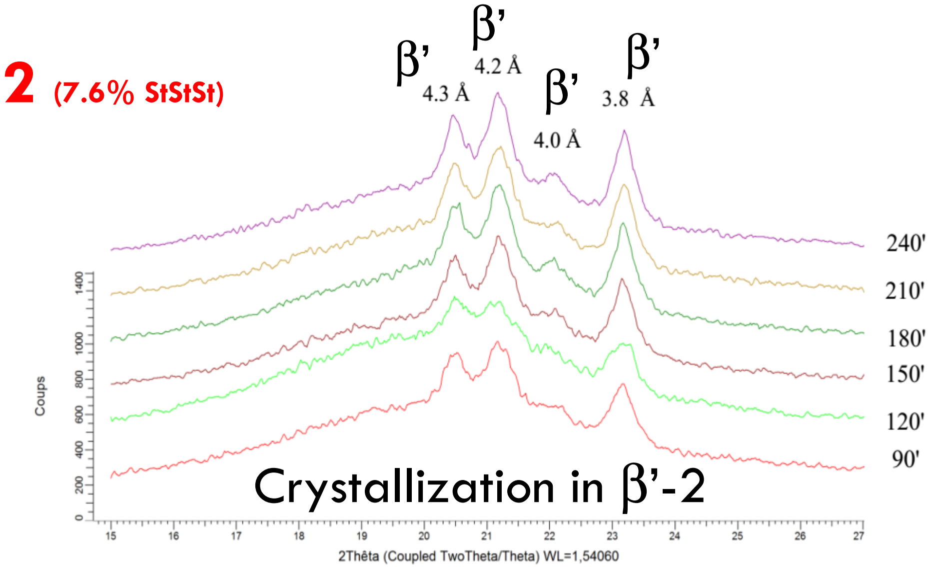
A SAMPLE WAS TAKEN EVERY 30 MIN. DURING MAIN CRYSTALLIZATION FOR POLYMORPHISM AND CRYSTAL MORPHOLOGY EVALUATION

M1; M2; M3; M4

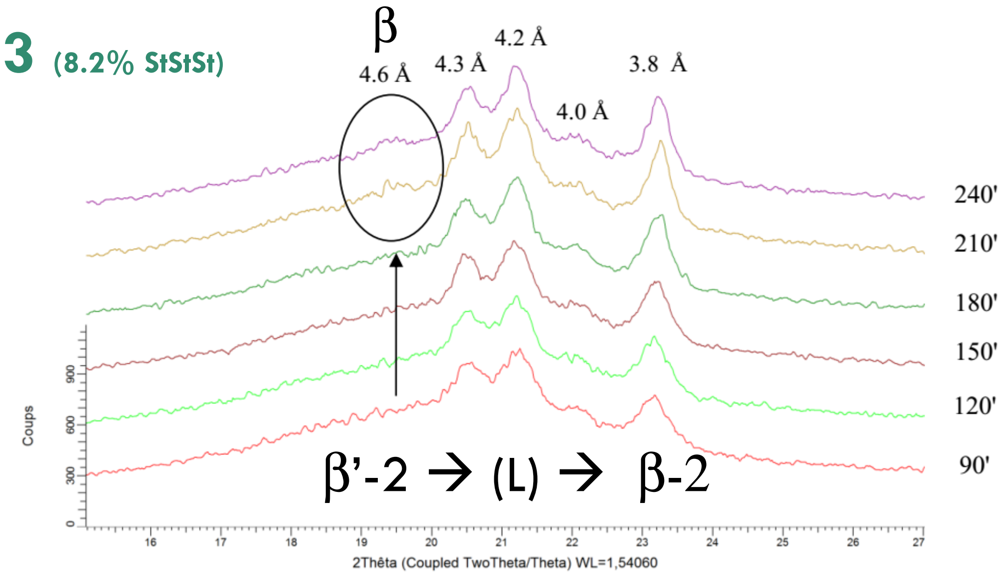
M1 (7.0% StStSt)



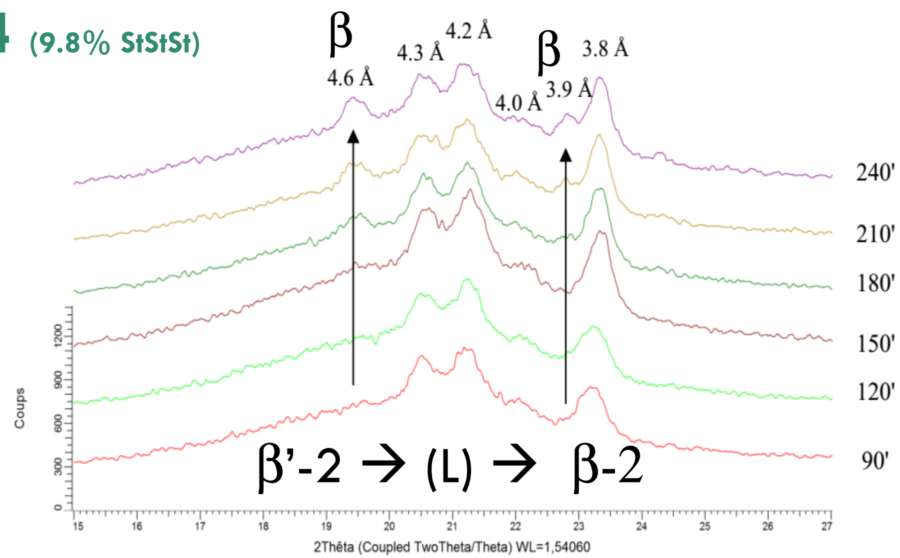
M2 (7.6% StStSt)



M3 (8.2% StStSt)

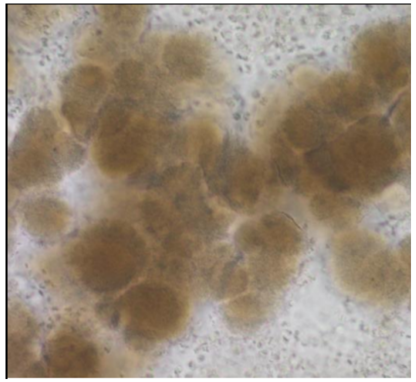


M4 (9.8% StStSt)



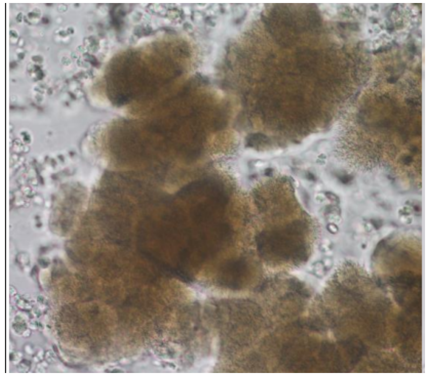
M1 | M2 | M3 | M4

Time: 90 min.



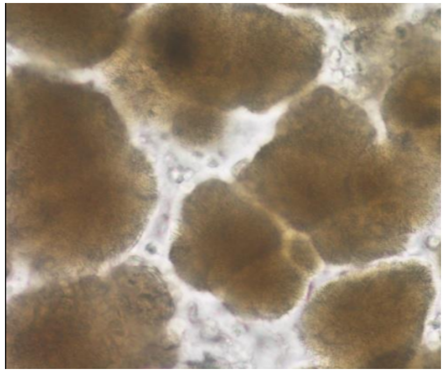
β’

Time: 90 min.



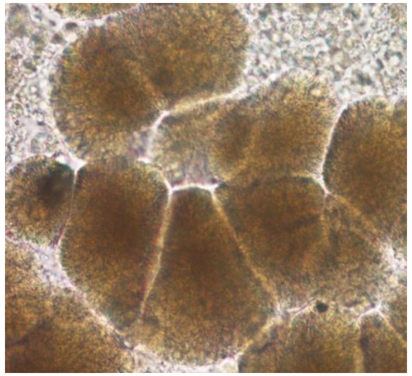
β’

Time: 90 min.



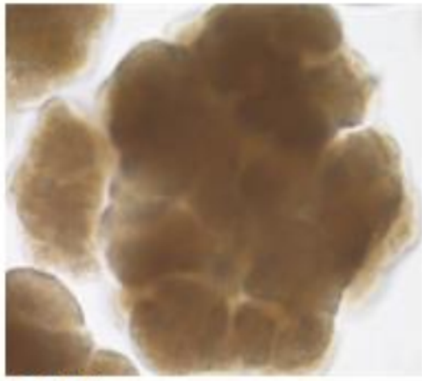
β’

Time: 90 min.



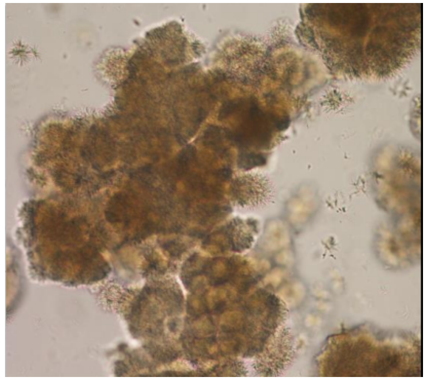
β’

Time: 240 min.



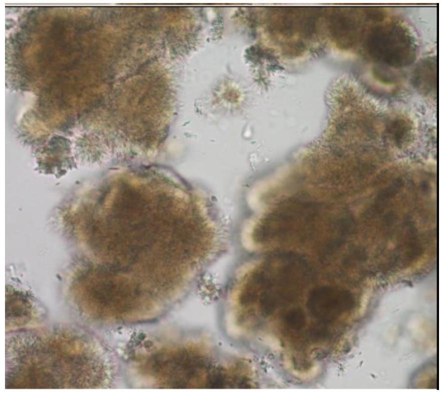
β’

Time: 240 min.



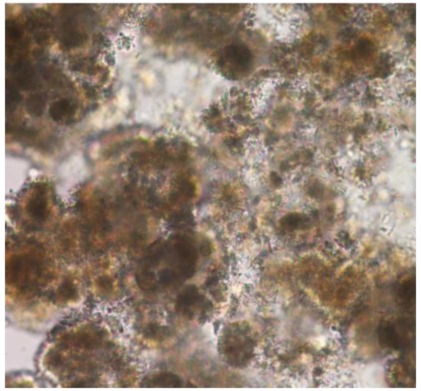
β’

Time: 240 min.



β’ → (L) → β

Time: 240 min.



β’ → (L) → β

100 µm

Science Behind

Technology

SUMMARY

- M1 and M2 crystallize in β' form (L-2).
- M3 and M4 crystallize in β' form (L-2):
  β form (L-2) is observed after ~210 min. for M3 and after ~180 min. for M4.
  → β form from re-crystallized liquid (melting of the slurry).
- Size of the crystals increases with StStSt content (90 min.).
- M2 presents a particular morphology especially visible after 240 min.
- M3 & M4 crystals are more dislocated (240 min.) due to partial melting; formation of a β layer on surface of the β' crystals.

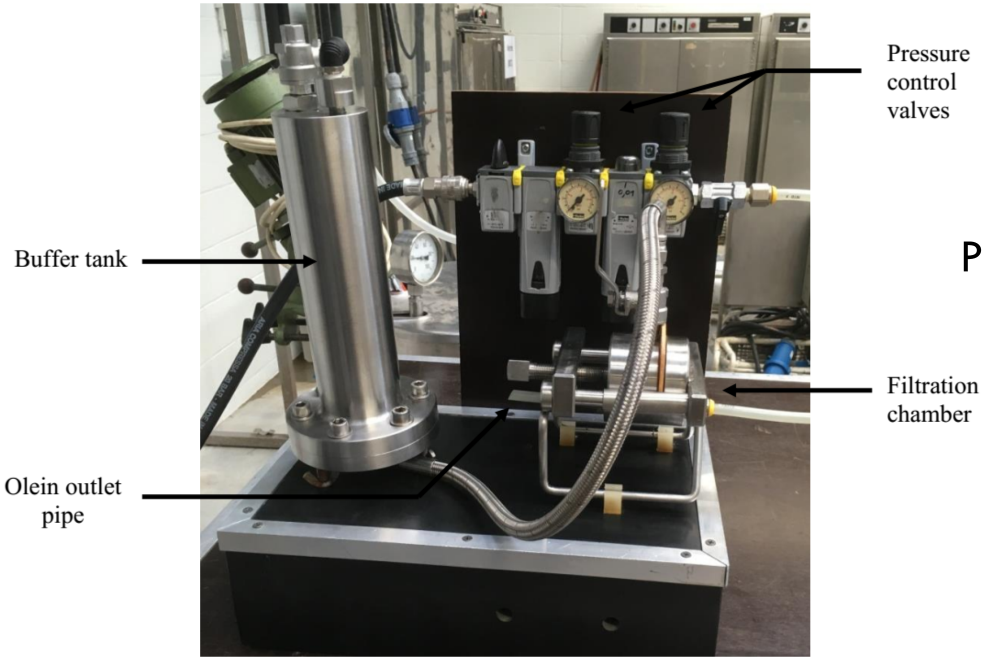
Science Behind

Technology

Olein yield ⬆
Fraction quality ⬆

Olein

Stearin



Press filtration after cooling at 25 °C

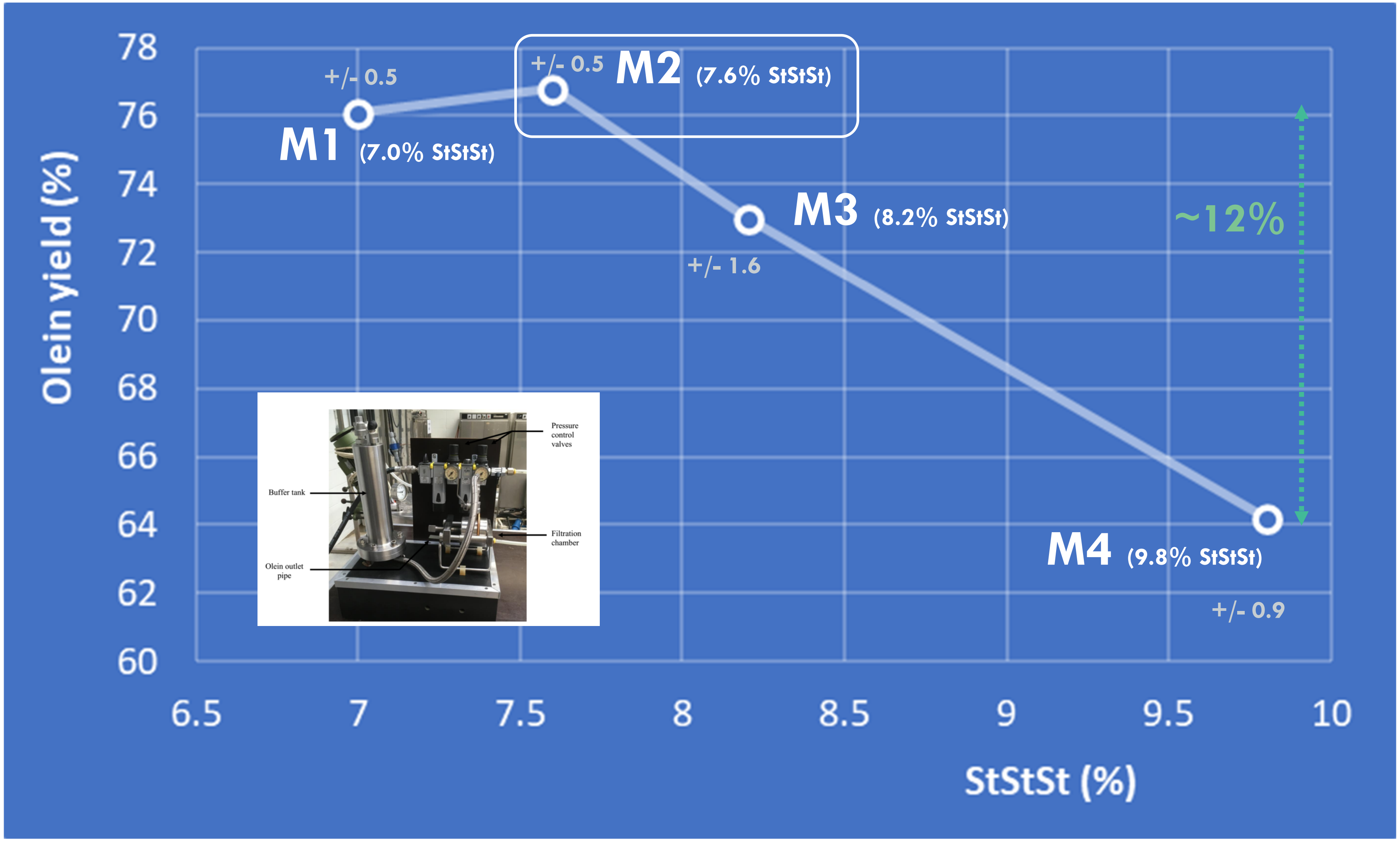
Olein
IV: 56-57

Membrane Press Filter
(6 bar squeezing)

Science Behind

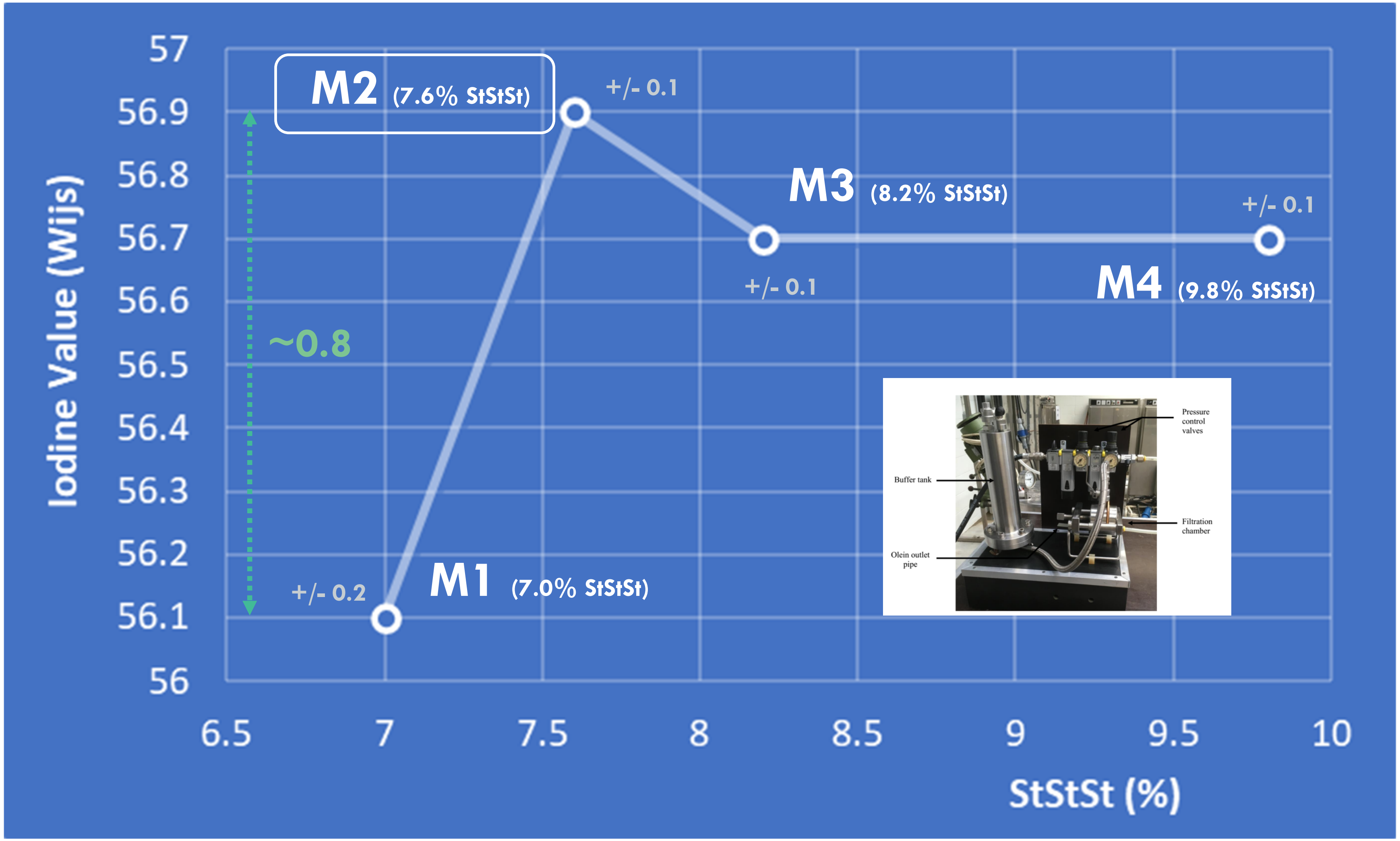
Technology

Olein yield after membrane press filtration at 25°C (6 bar)



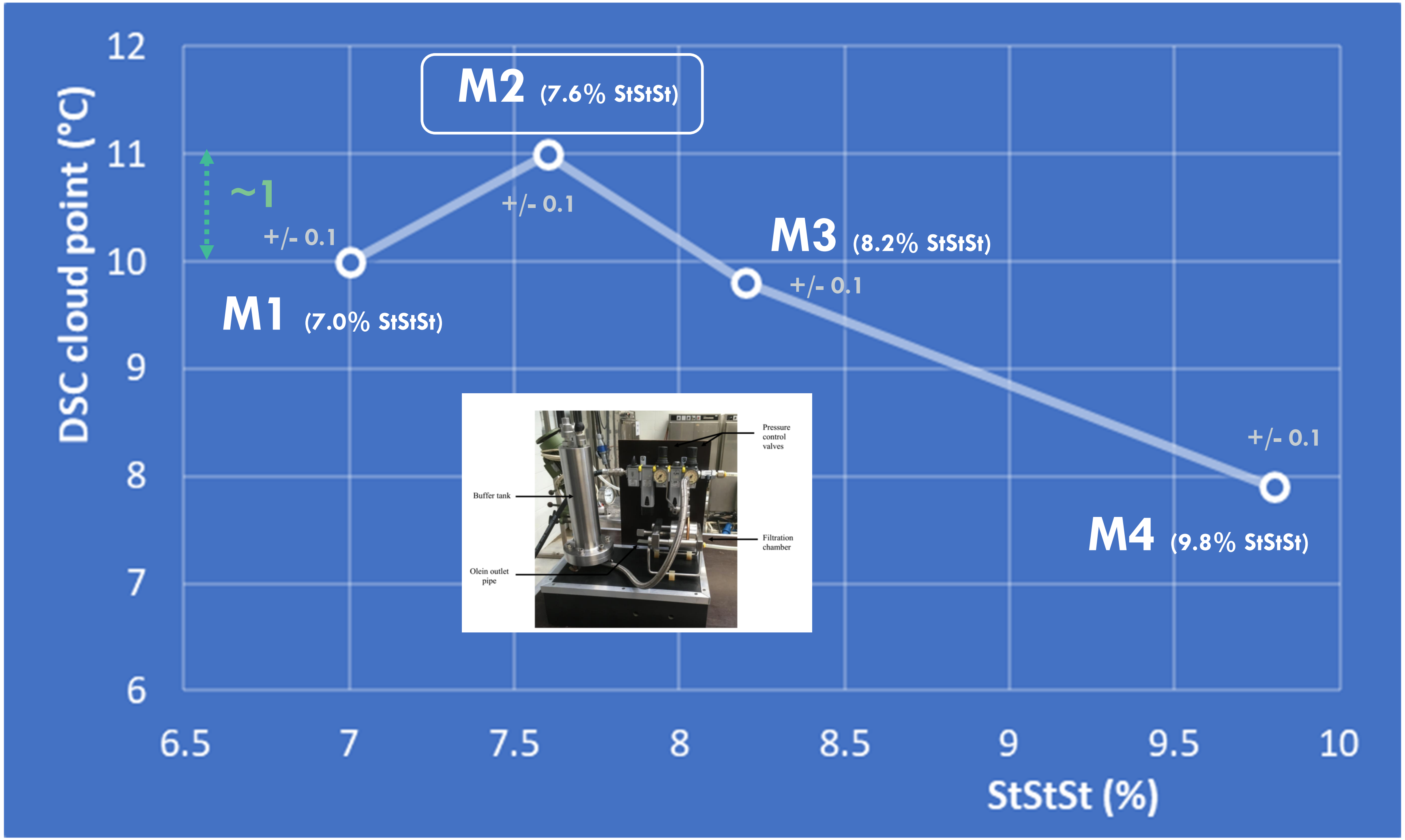
Science Behind

Olein iodine value (IV) after membrane press filtration at 25°C



Technology

Olein DSC cloud point (CP) after membrane press filtration at 25°C



Science Behind

Technology

Olein RP-HPLC composition after membrane press filtration at 25°C

Olein	From M1	From M2	From M3	From M4
TAG (% HPLC)				
StStSt	1.2 (+/- 0.0)	1.1 (+/- 0.1)	1.0 (+/- 0.0)	0.8 (+/- 0.0)
St_2U	44.3 (+/- 0.0)	44.7 (+/- 0.1)	44.8 (+/- 0.1)	44.8 (+/- 0.1)
StU_2	38.0 (+/- 0.3)	38.4 (+/- 0.1)	38.6 (+/- 0.0)	38.9 (+/- 0.1)
UUU	5.9 (+/- 0.1)	6.0 (+/- 0.0)	6.0 (+/- 0.1)	6.1 (+/- 0.0)
DAG (% HPLC)	10.6 (+/- 0.1)	9.7 (+/- 0.1)	9.5 (+/- 0.0)	9.4 (+/- 0.0)

TAG: triacylglycerol; St: saturated fatty acids; U: unsaturated fatty acids; DAG: diacylglycerol

- **Lowest StStSt content in Olein M4.**
  - **Unsaturated content increased from M1 to M4 Olein.**
  - **DAG content decreased from M1 to M4 Olein.**

→
  - In favor of higher Olein IV
  - In favor of lower Olein CP

No peculiar RP-HPLC composition associated to M2 Olein

Science Behind

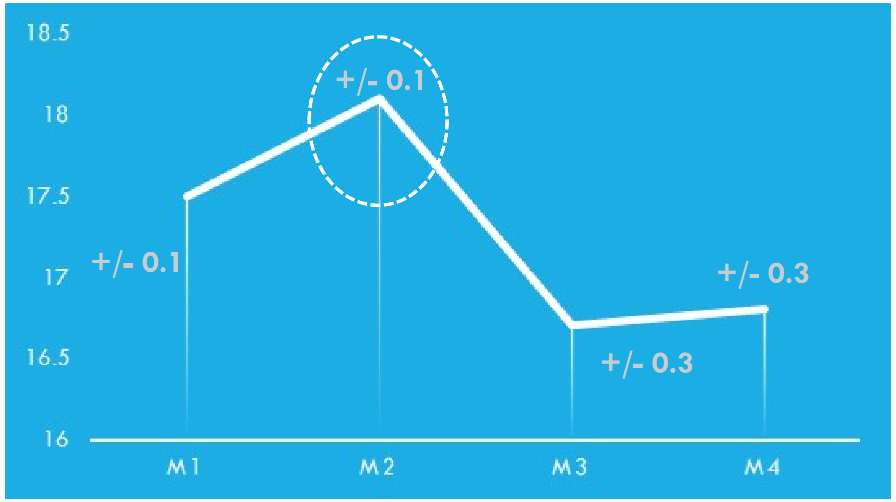
Technology

HPLC-SILVER ION MODIFIED-MS* OLEIN COMPOSITION AFTER MEMBRANE PRESS FILTRATION AT 25°C

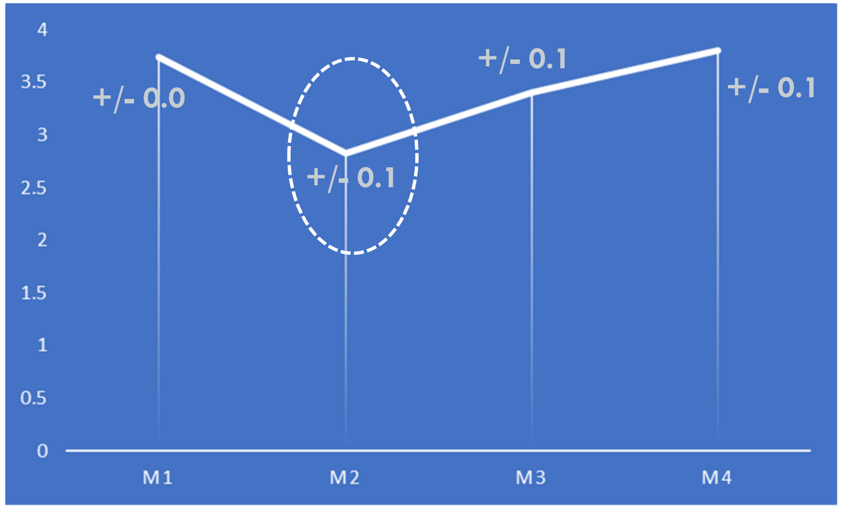
Most abundant TAG in Palm Olein from M1 to M4:

P_2O (POP+OPP) in the olein: ~22% (RP-HPLC)
PO_2 (POO+OPO) in the olein: ~28% (RP-HPLC)

% OPP versus POP (PEAK AREA)



% OPO versus POO (PEAK AREA)



* Method described in: Characterization and Determination of Interesterification Markers (Triacylglycerol Regioisomers) in Confectionery Oils by Liquid Chromatography-Mass Spectrometry; V. Santoro, F. Dal Bello, R. Aigotti, D. Gastaldi, F. Romaniello, E. Forte, M. Magni, C. Baiocchi and C. Medana; Foods, 2018.

SUMMARY

After press filtration at 25°C :

- Highest olein yield for M2.
- Olein yield decreases for M3 & M4 (highest StStSt contents).

- Olein from M2 has the highest iodine value.
- Olein from M2 has the highest DSC cloud point.

- M2 olein : No peculiar composition in RP-HPLC

- M2 olein (silver ion-HPLC) :
  Highest OPP versus POP
  Lowest OPO versus POO

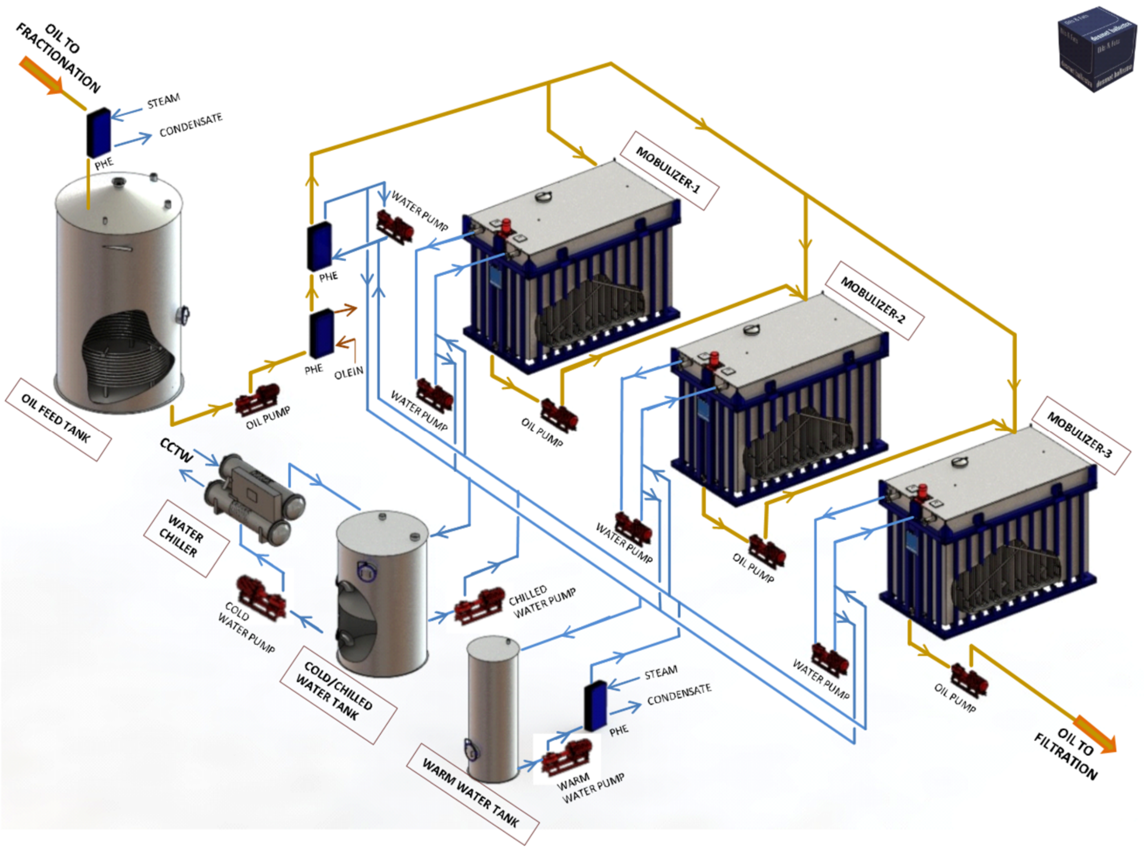
Science Behind

Technology

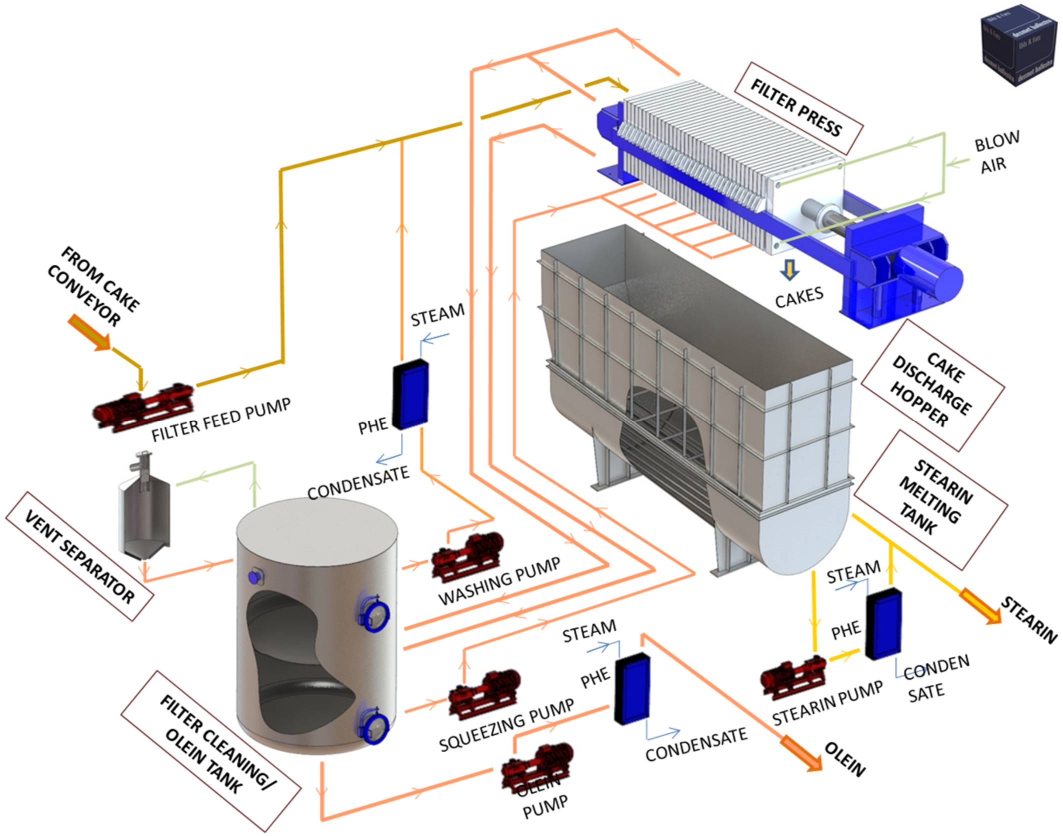
CONCLUSIONS

- Significant impact of StStSt on main crystallization with a difficult to control oil temperature increase at high contents. Partial melting of already formed β' crystals; re-crystallization in β (mix of β' and β) [M3&M4]
- Atypical behavior of M2 during main crystallization: faster crystallization and more efficient StStSt removal in the olein during vacuum filtrations.
- Crystal morphology of M2 is different although crystallizing in β' (like M1).
- Highest yield, highest iodine value, highest cloud point for M2 olein after press filtration at 25°C.
- More OPP (iso POP) and less OPO (iso POO) in M2 olein (silver-ion HPLC).
- **Particular PPP/P2O/PO2 co-crystallization behavior at M2 composition**

DRY FRACTIONATION PLANT



Crystallization section



Filtration section

THANK YOU

for your attention!

Science behind Technology

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