17. - 19. Februar 2008, DECHEMA-Haus, Frankfurt am Main

SULZER

Reinigung von Produkten aus nachwachsenden Rohstoffen mit fraktionierter Kristallisation

Manfred Stepanski, Sulzer Chemtech AG, Winterthur/CH

Photo: Huhtamaki

Matter of Biomass

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- Carbohydratres (Glucose, Starch, Cellulose, etc.)

- Fats and Oils

- Lignin

- Proteins
- Enzymes
- Vitamines
- Pigments
- Flavour and Odourous Substances

Crystallization used for Biomass Products

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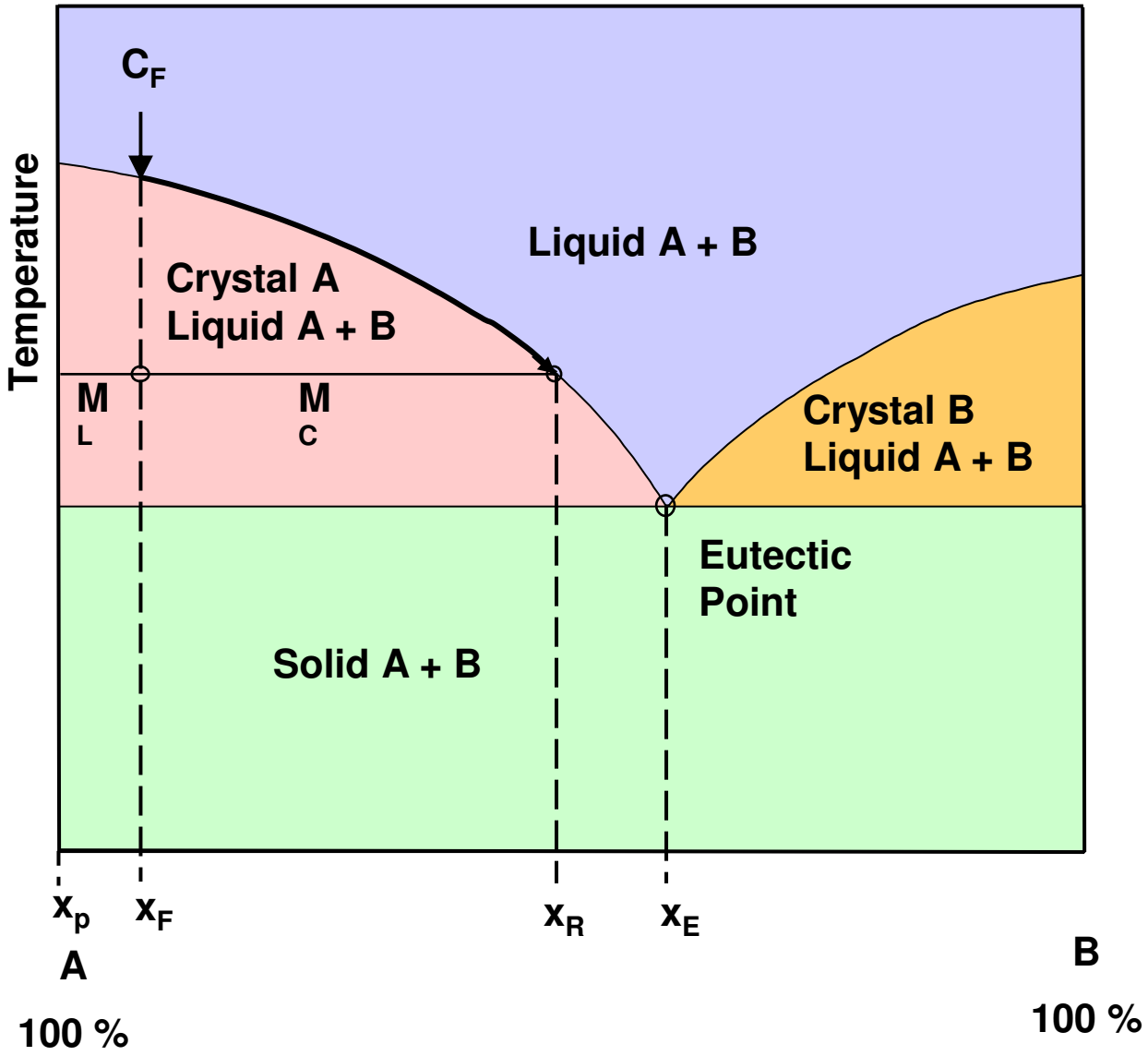
- Purification of lactide for Polylactic Acid (PLA)
- Winterization of oils
- Fractionation of higher and lower melting fat fractions
- Separation of essential fatty acids
- Purification of fatty acids
- Purification of minor components of fats (Phytosterol)

Binary Phase Diagram



Principle of Crystallization

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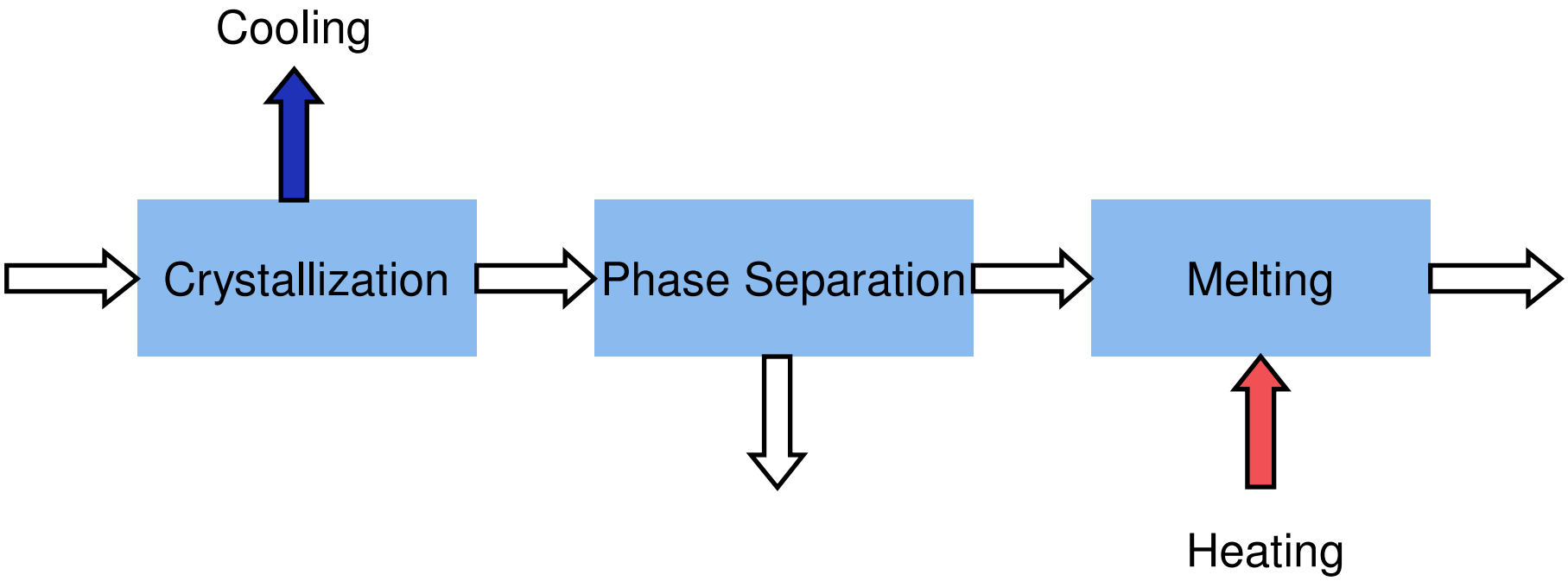
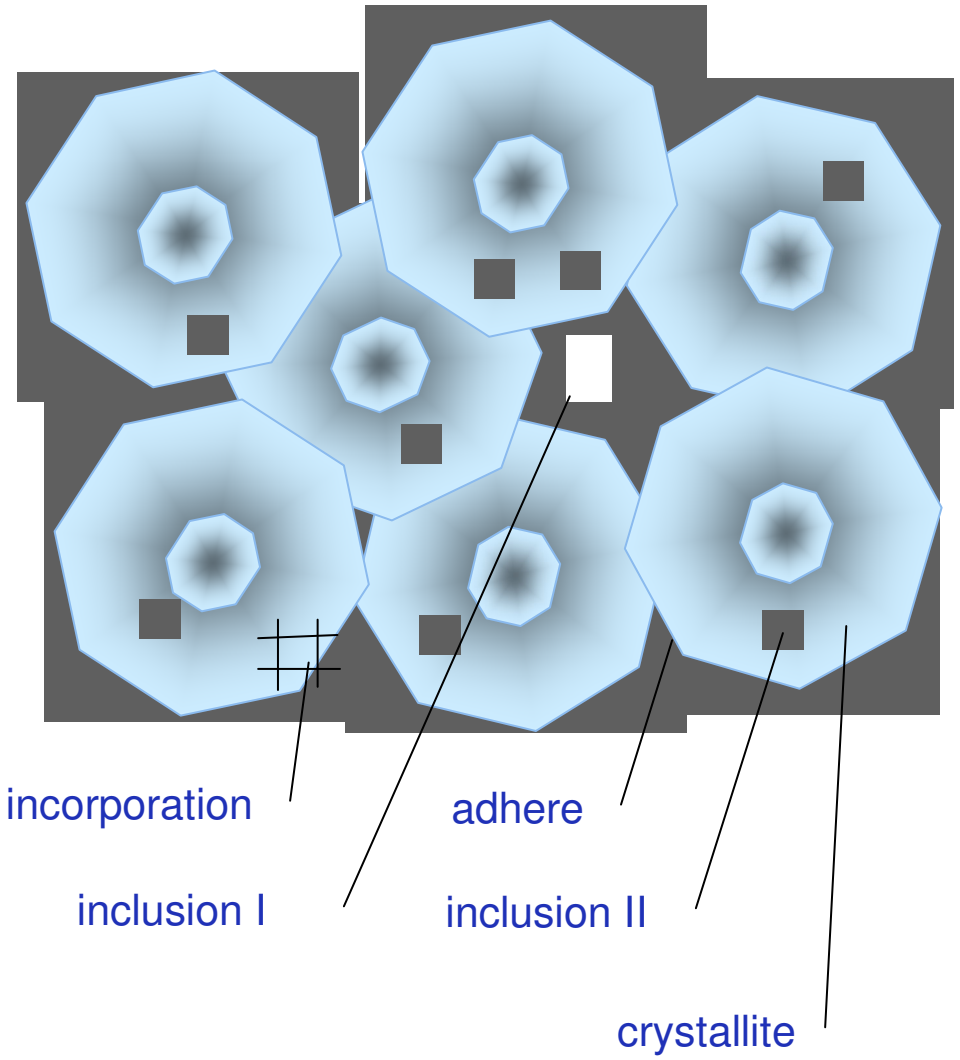
Mass and Energy Flow:



Phase Separation



Terms influencing the average composition of the solid state:

Adherence of liquid phase (adhere),

Inclusion of liquid phase inside the crystallites (inclusion I),

Inclusion of liquid phase between the crystallites (inclusion II),

Incorporation of other components In the crystal lattice (incorporation**).**

Source: König, University Erlangen

Features of Crystallization

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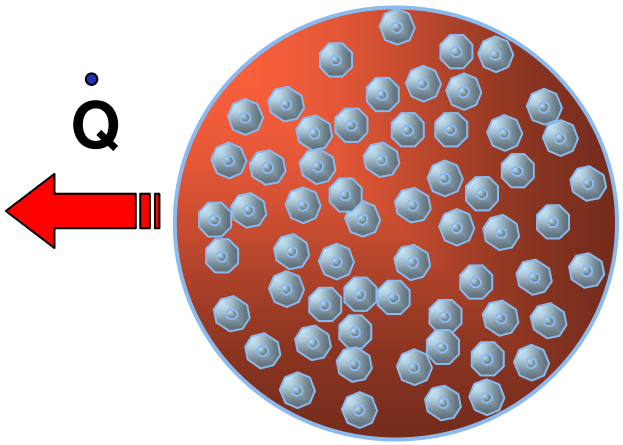
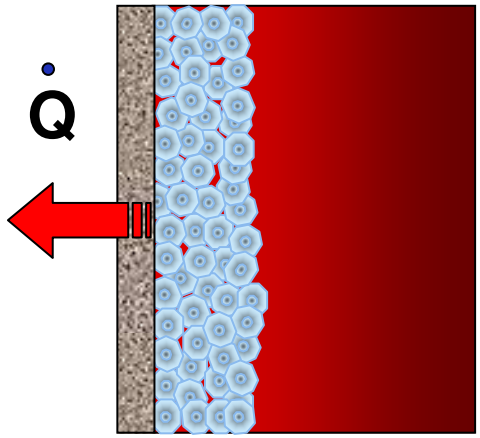
- Low temperature level
- Good selectivity
- Low energy consumption
- With or without solvent

  From solvent: Supersaturation (evaporation or cooling)

  From melt: „Simple“ cooling
- Suspension or layer crystallization



Suspension



Layer

Equipment for Suspension Crystallization

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Equipment for crystallization – batch or continuous operation:

- Agitated vessels with internal or external cooling
- Vessels with forced circulation and external cooling
- Scraped-wall crystallizers

Equipment for separation – batch or continuous operation:

- Drum or belt filters
- Filter presses
- Centrifuges
- Wash columns

Layer Crystallization

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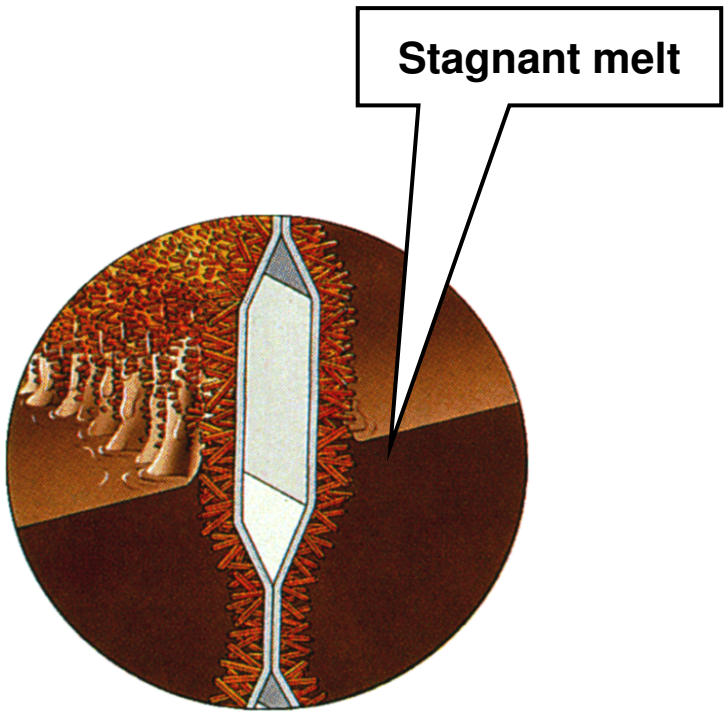
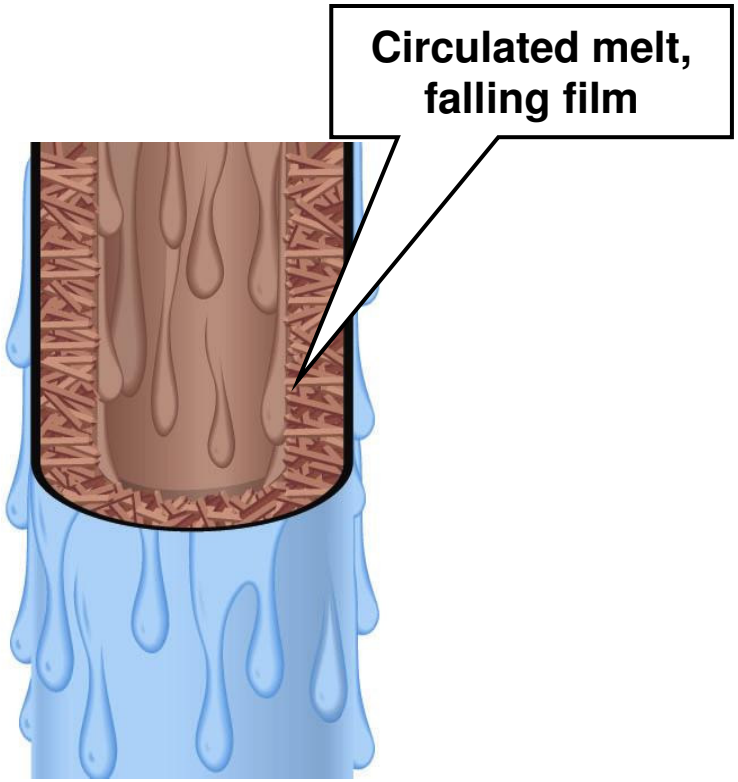
Static crystallization



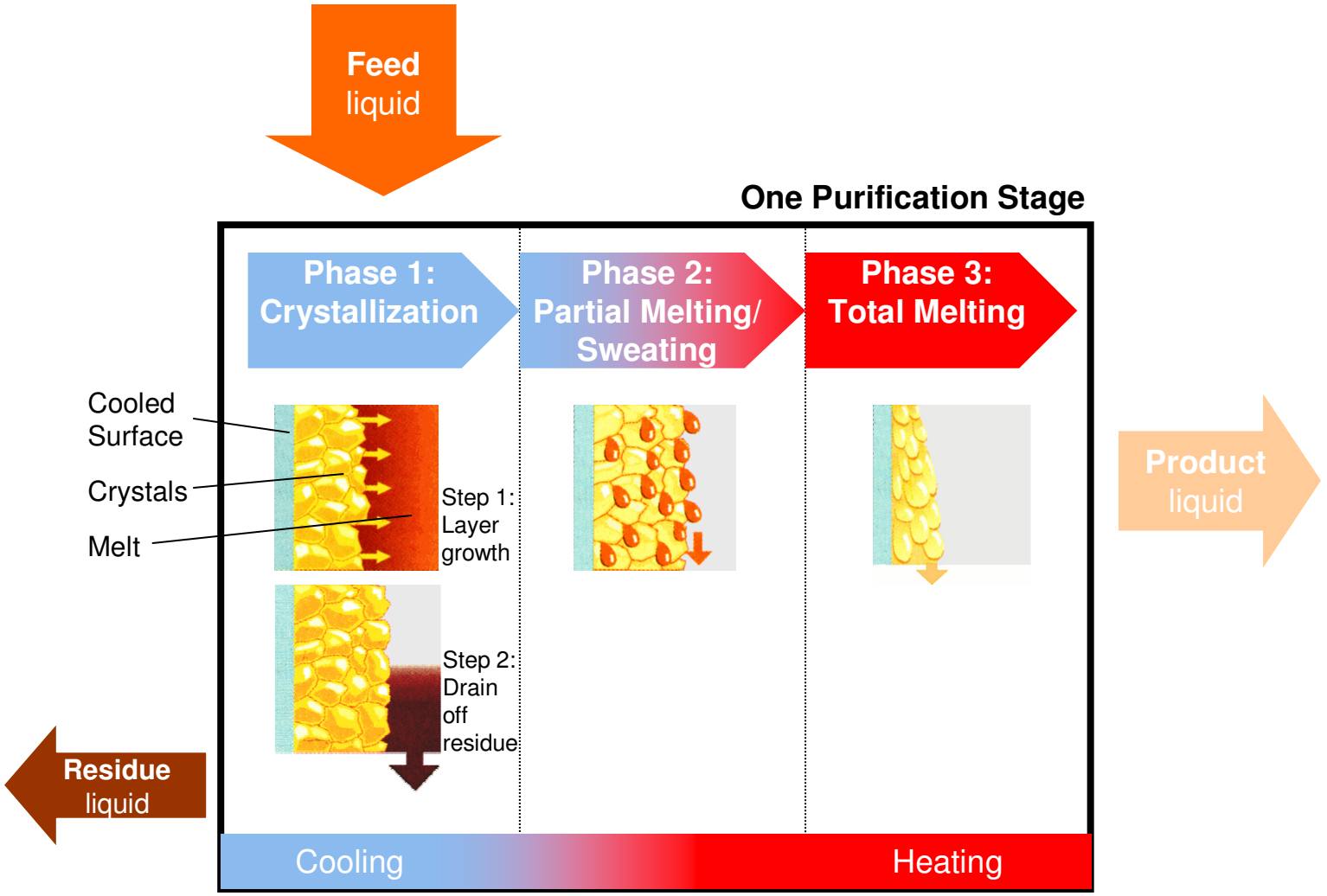
Plate

Falling film crystallization

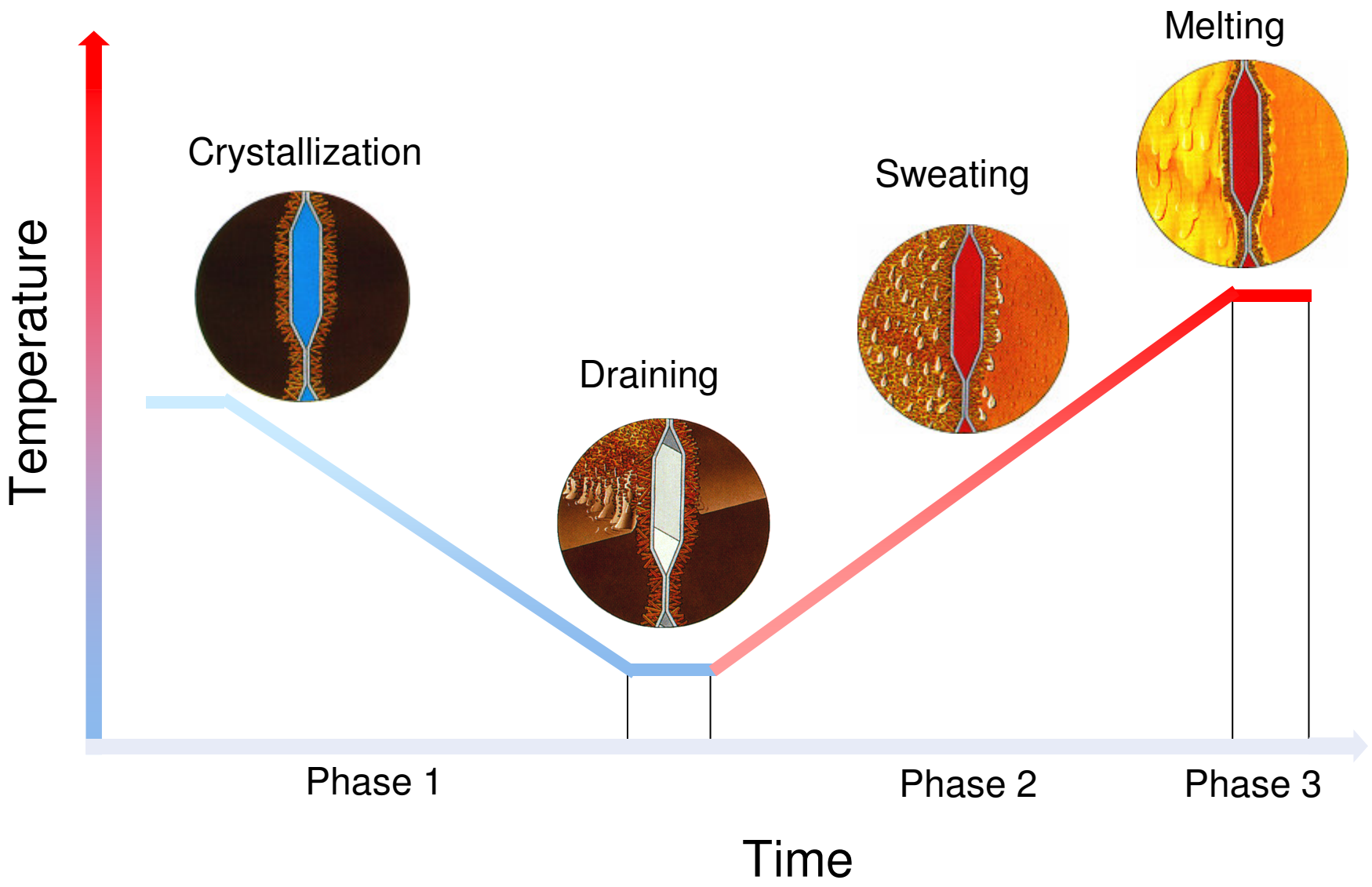


Tube

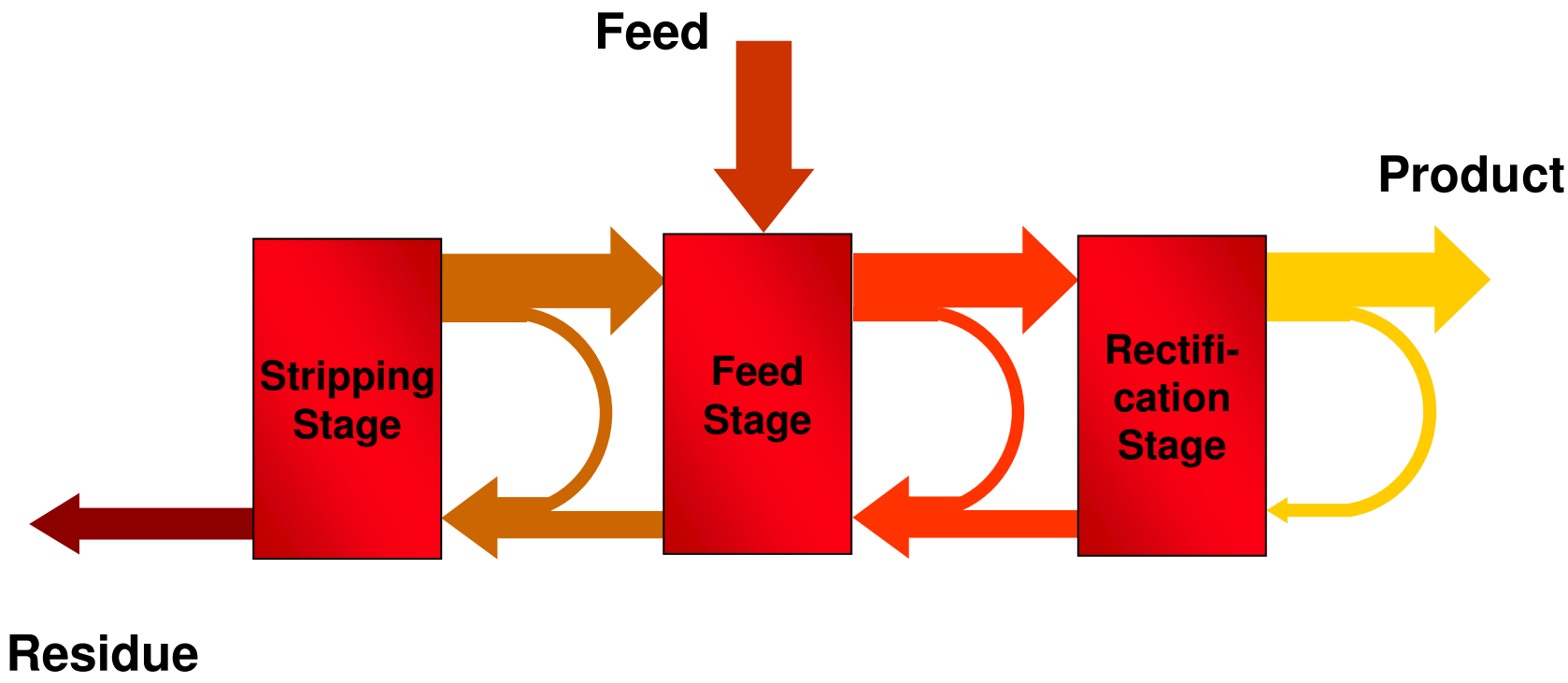
How does Fractional Crystallization work?



Temperature Cycle



Mass Flow Diagram



Static Crystallizer

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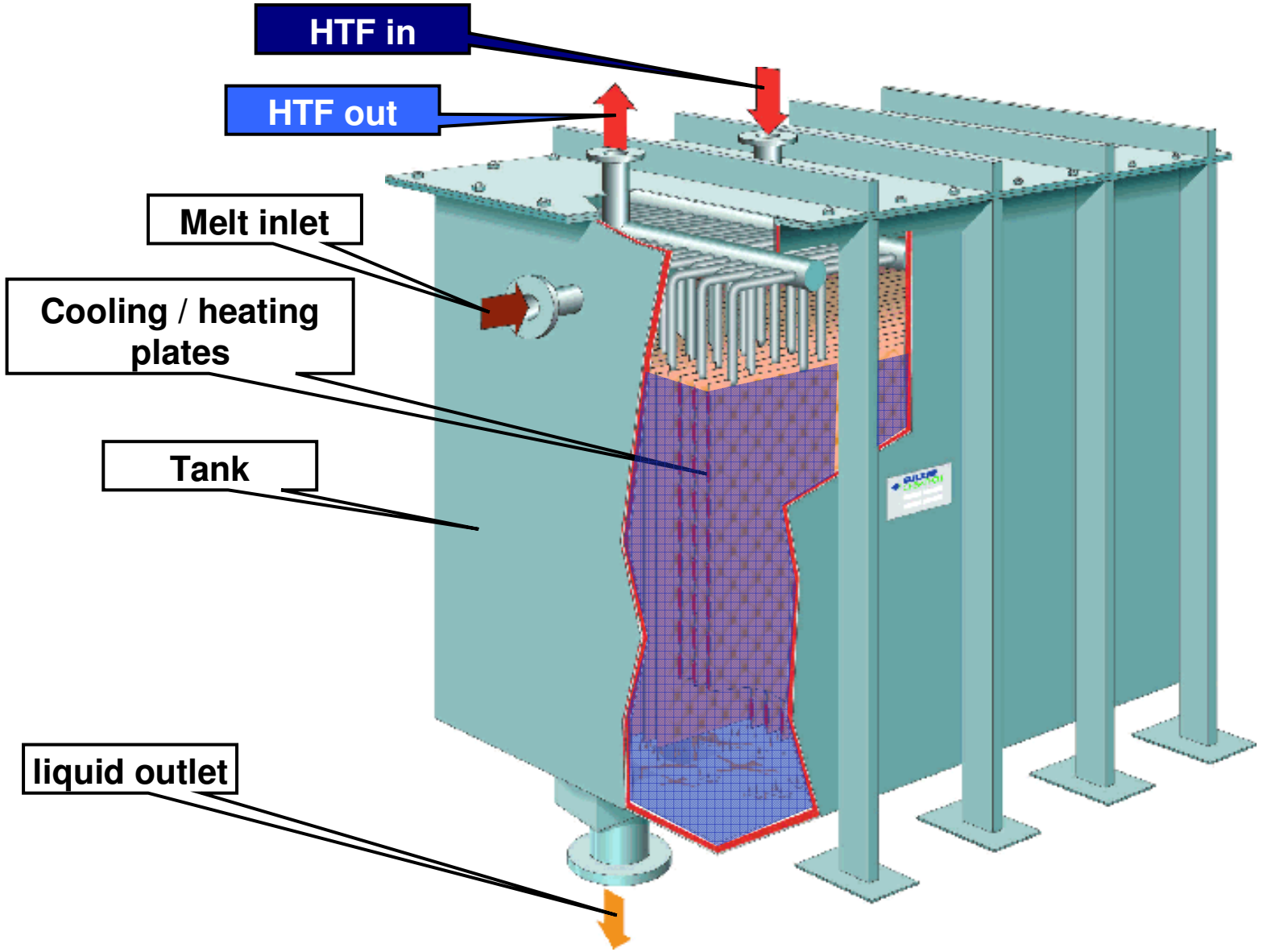
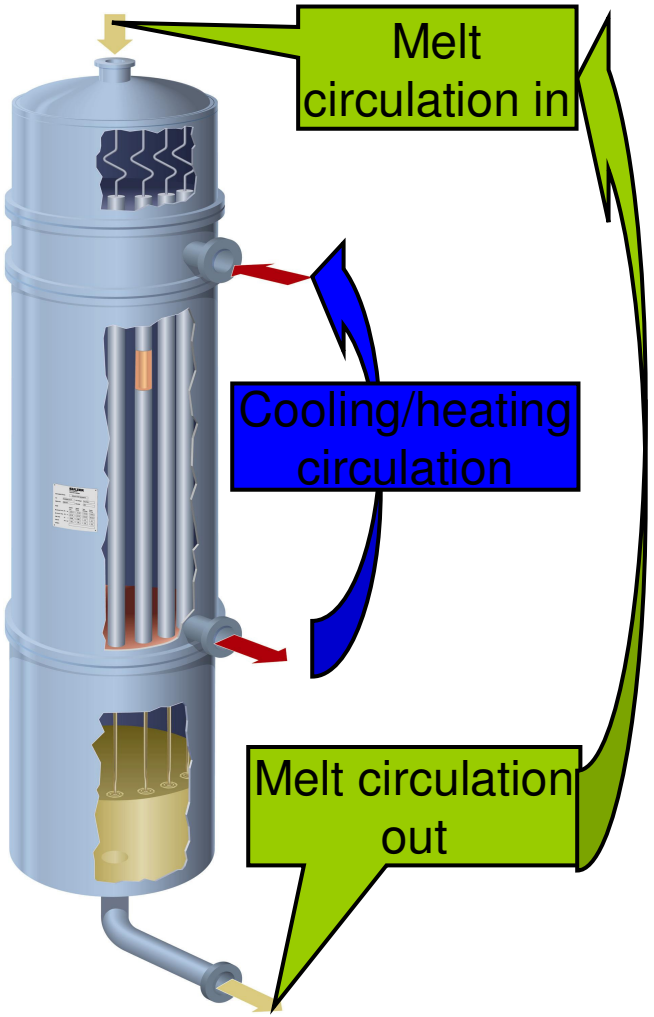
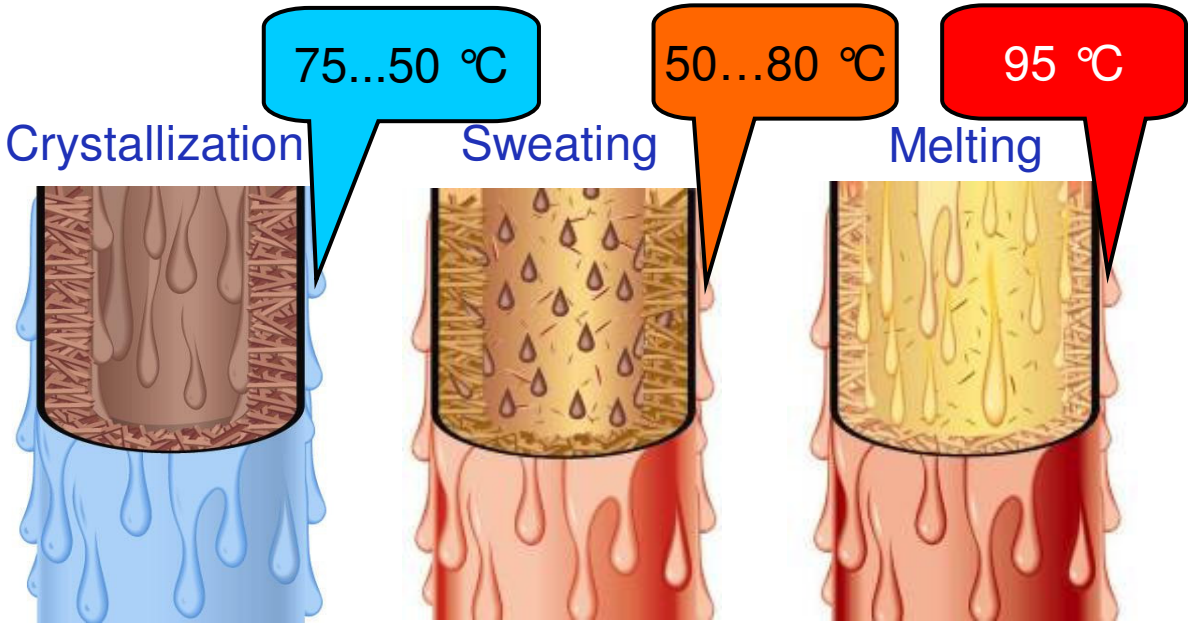


Falling Film Crystallizer, operation





- tubular crystallizer
- external heat transfer fluid, falling film
- internal melt circulation, falling film
- most efficient mass and heat transfer

Falling Film Crystallization

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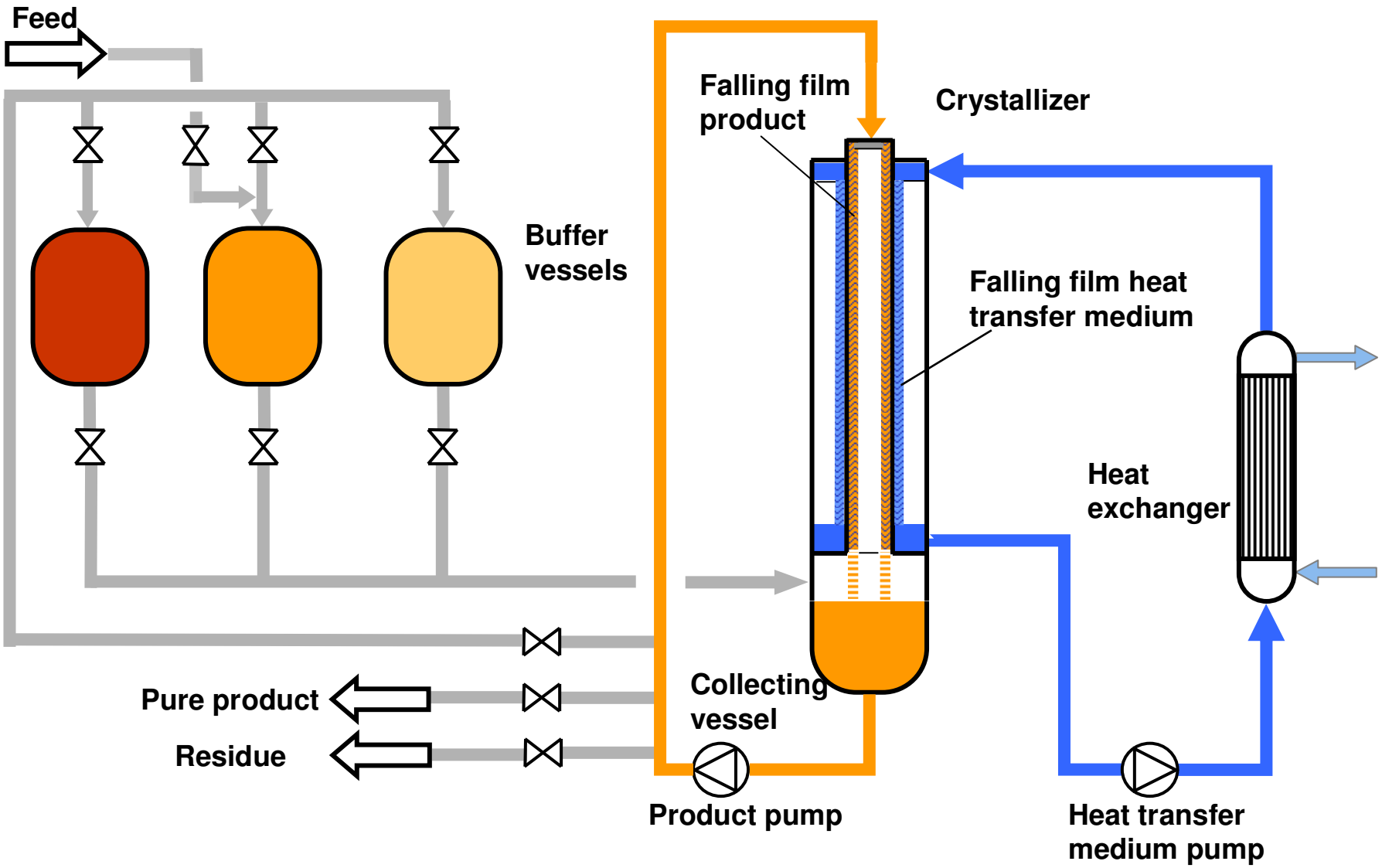

Falling Film Crystallizer

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Lactide Crystallization

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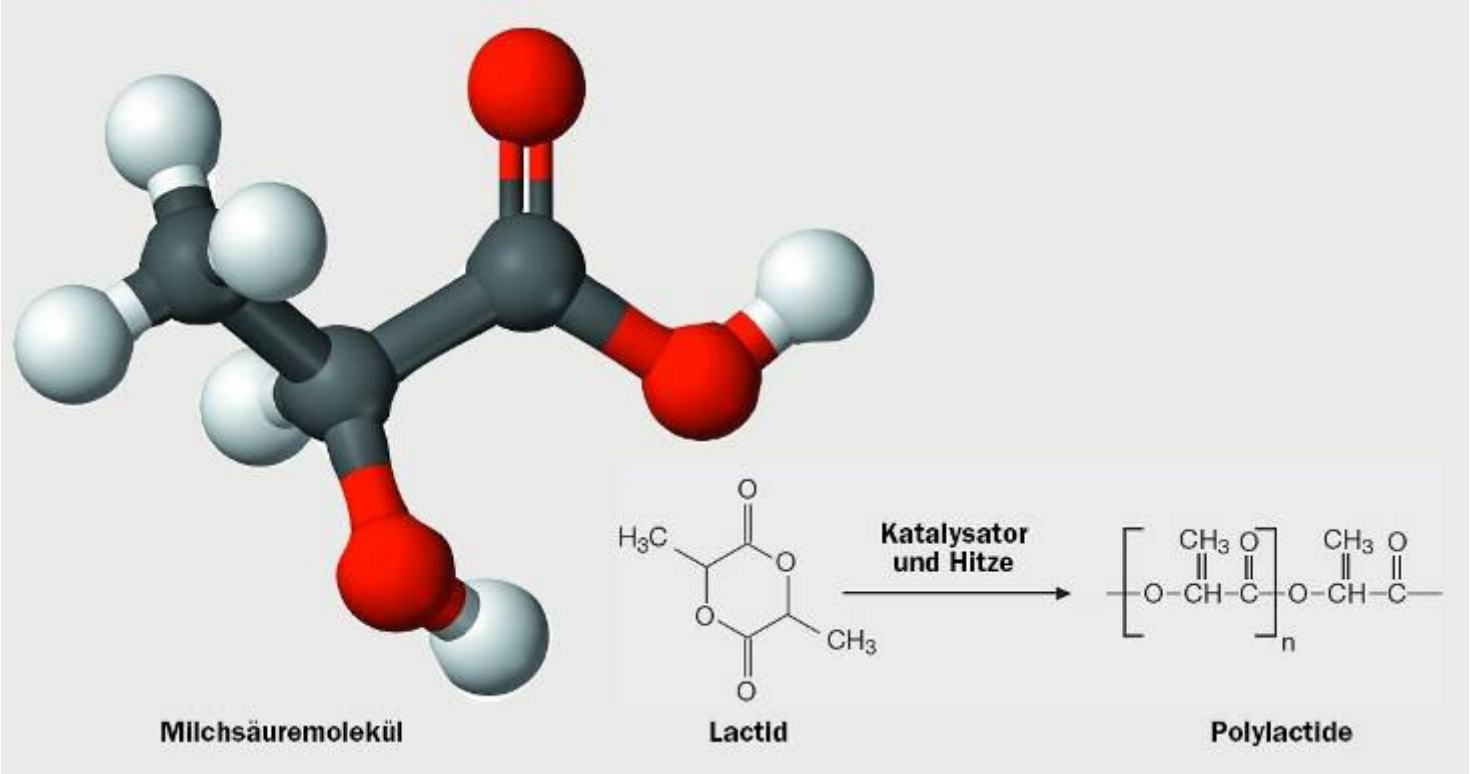
Crystallization of Lactide for Poly Lactic Acid



High purity lactide from melt crystallization
is the key for high quality PLA

PLA Market

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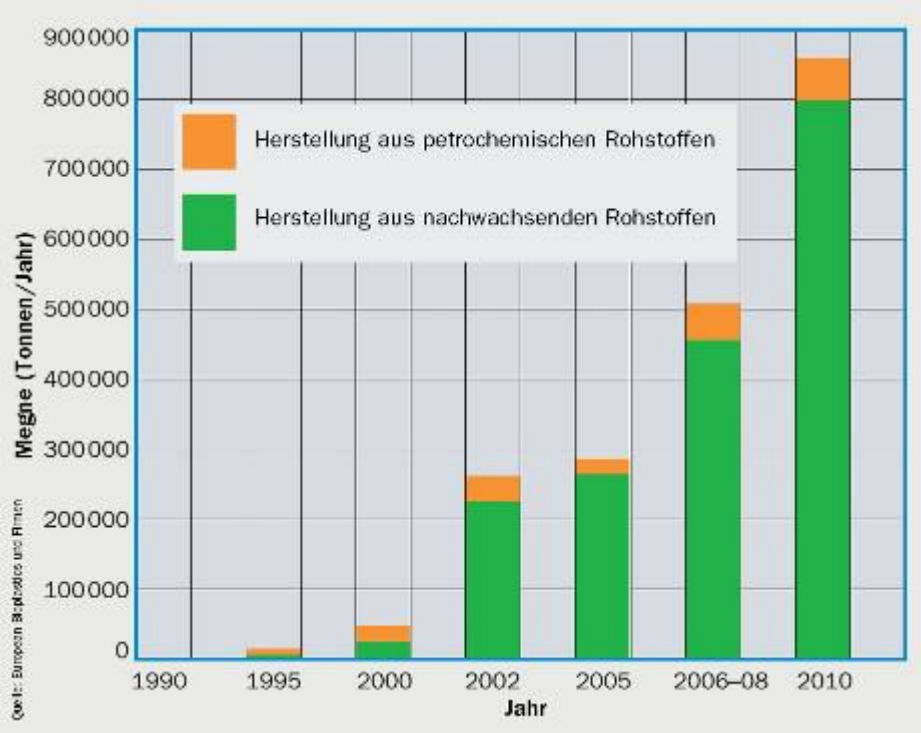
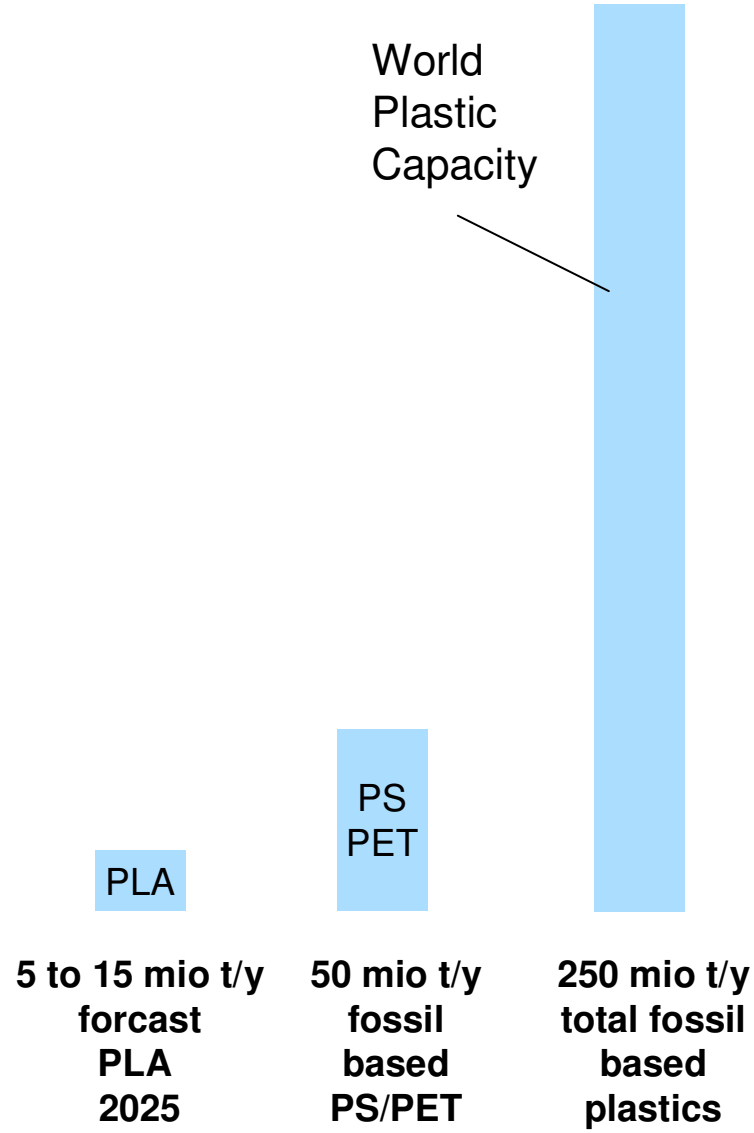
Key drivers of PLA demand:

- Positive regulatory and policy framework (Green Dot in Germany; Japanese directives)
- Stimulation of regional agricultural economies
- Innovation in chemical and plastics industries
- Consumer acceptance of bio-based polymers
- Green image of retailers and brand-owners



World capacity bio-plastics



Poly Lactic Acid Production Steps

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Sugars → Fermentation → Lactic acid → Lactide production

L-Lactide crystals

Lactide crystallization → Ring opening polymerization → PLA

Crystallization - Staging

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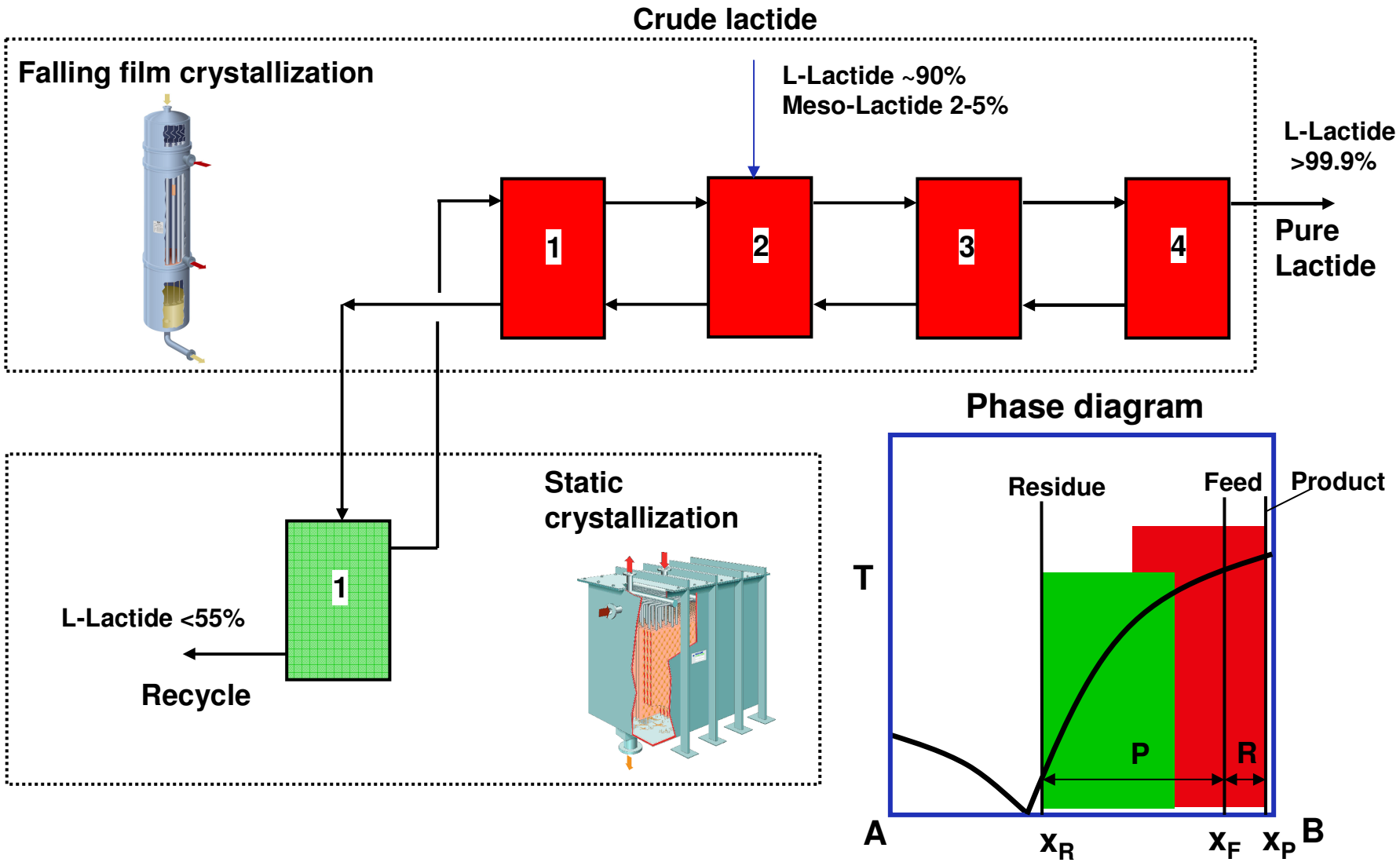

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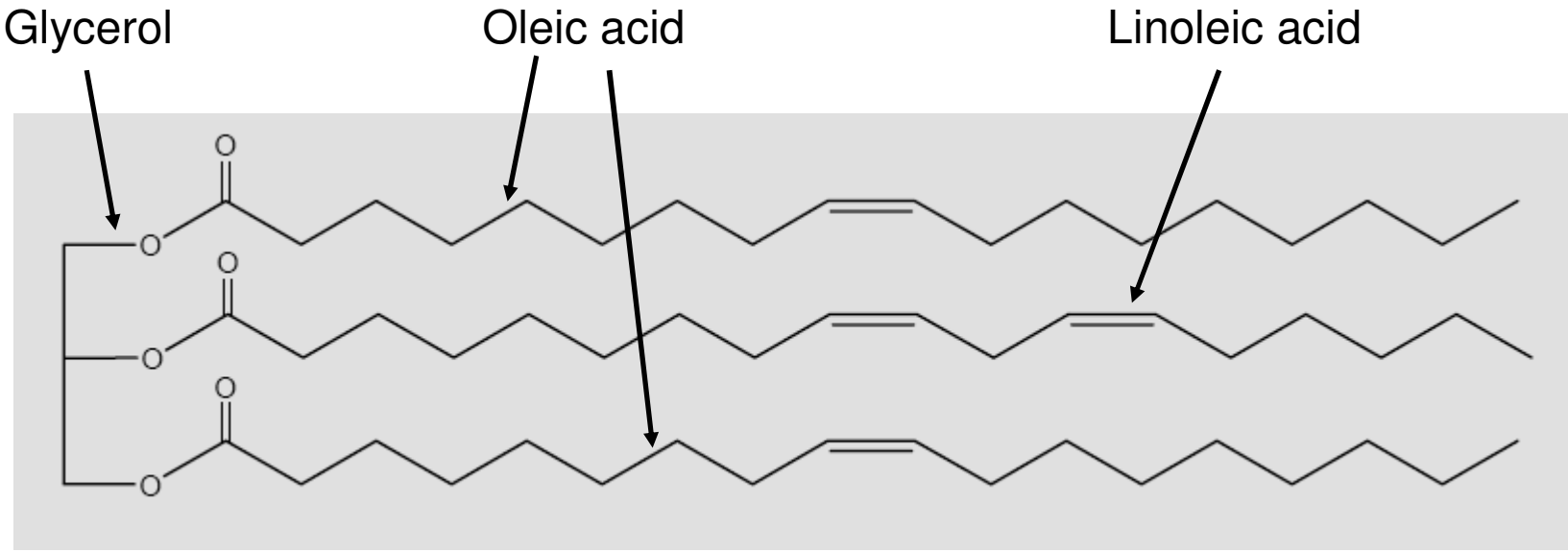
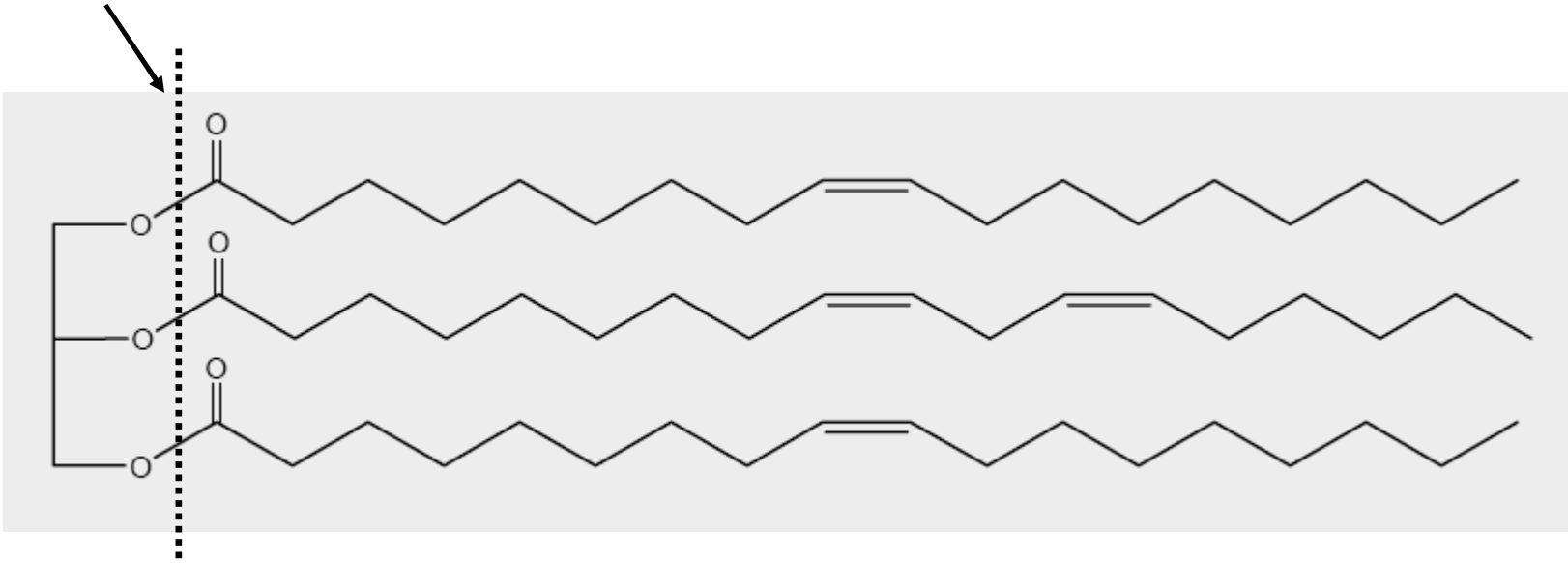
Natural esters (triglyceride)



Fractionation of Fat Fractions

These bonds breaks to produce
fatty acids and glycerol



Crystallization of
- Triglyceride or
- Fatty acids

Fatty Acid Sources

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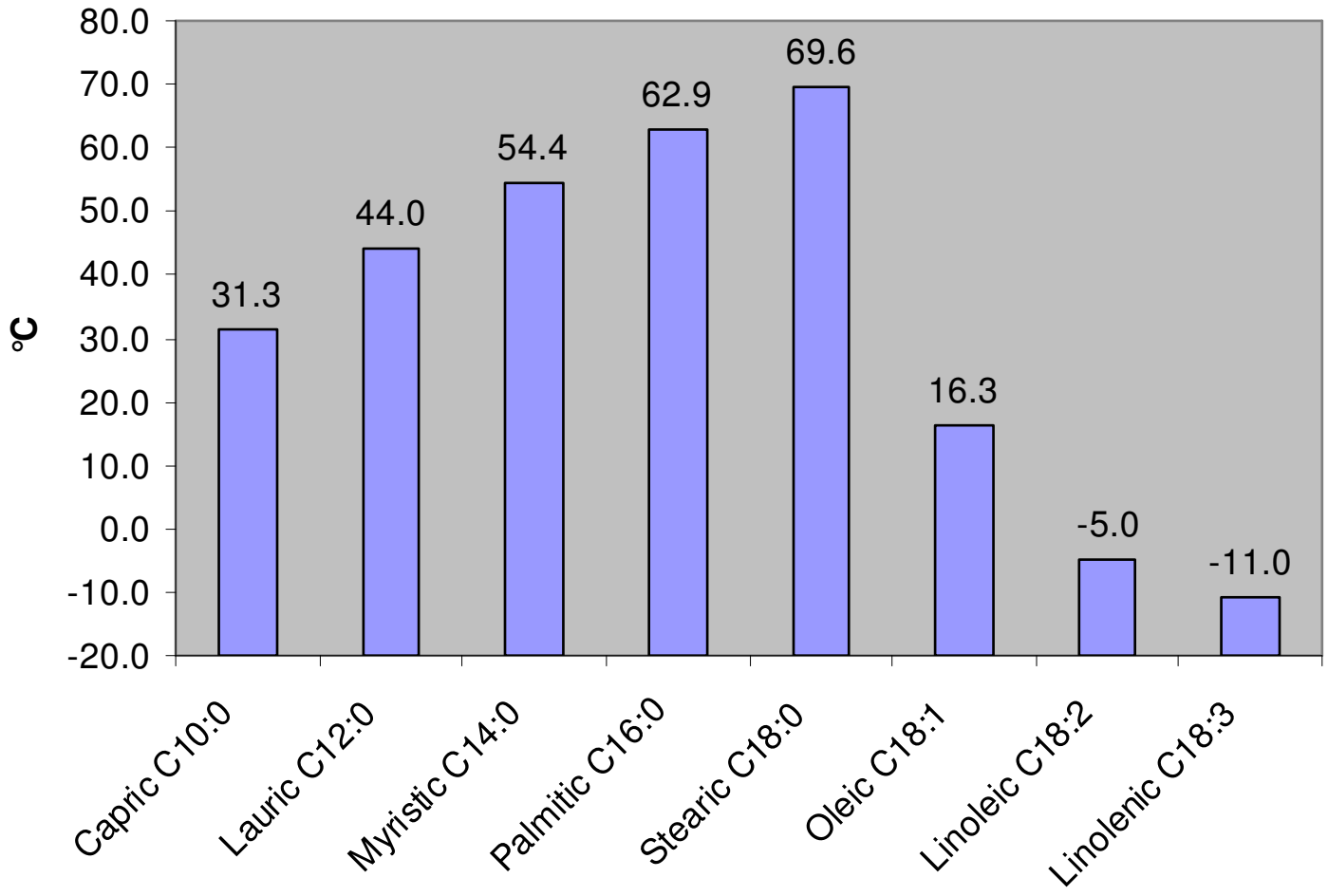
Typical Fatty Acid Composition of vegetabel and animal fats and oil

Oil or Fat	Unsat./Sat. ratio	Saturated					Mono unsaturated	Poly unsaturated	
		Capric Acid C10:0	Lauric Acid C12:0	Myristic Acid C14:0	Palmitic Acid C16:0	Stearic Acid C18:0	Oleic Acid C18:1	Linoleic Acid (ω6) C18:2	Alpha Linolenic Acid (ω3) C18:3
Almond Oil	9.7	-	-	-	7	2	69	17	-
Beef Tallow	0.9	-	-	3	24	19	43	3	1
Butterfat (cow)	0.5	3	3	11	27	12	29	2	1
Canola Oil	15.7	-	-	-	4	2	62	22	10
Cocoa Butter	0.6	-	-	-	25	38	32	3	-
Cod Liver Oil	2.9	-	-	8	17	-	22	5	-
Coconut Oil	0.1	6	47	18	9	3	6	2	-
Corn Oil	6.7	-	-	-	11	2	28	58	1
Cottonseed Oil	2.8	-	-	1	22	3	19	54	1
Flaxseed Oil	9.0	-	-	-	3	7	21	16	53
Grape seed Oil	7.3	-	-	-	8	4	15	73	-
Lard (Pork fat)	1.2	-	-	2	26	14	44	10	-
Olive Oil	4.6	-	-	-	13	3	71	10	1
Palm Oil	1.0	-	-	1	45	4	40	10	-
Palm Olein	1.3	-	-	1	37	4	46	11	-
Palm Kernel Oil	0.2	4	48	16	8	3	15	2	-
Peanut Oil	4.0	-	-	-	11	2	48	32	-
Safflower Oil	10.1	-	-	-	7	2	13	78	-
Sesame Oil	6.6	-	-	-	9	4	41	45	-
Soybean Oil	5.7	-	-	-	11	4	24	54	7
Sunflower Oil	7.3	-	-	-	7	5	19	68	1
Walnut Oil	5.3	-	-	-	11	5	28	51	5

Melting Point of Fatty Acids



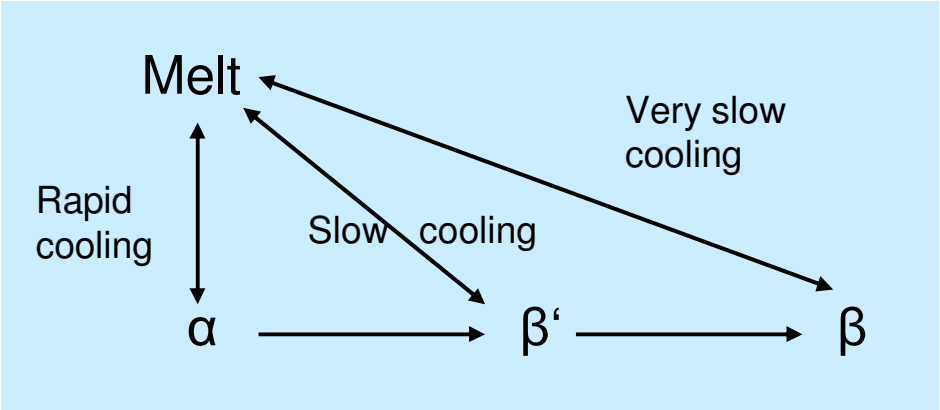
How to obtain crystals of fat?

From solvent:

- Supersaturation (evaporation or cooling)
- Crystallization in the most stable polymorphic form,
- Generally β

From melt:

- Cooling
- Cooling rate effect on the polymorphic forms: α, β‘ or β



Parameters Fat Crystallization

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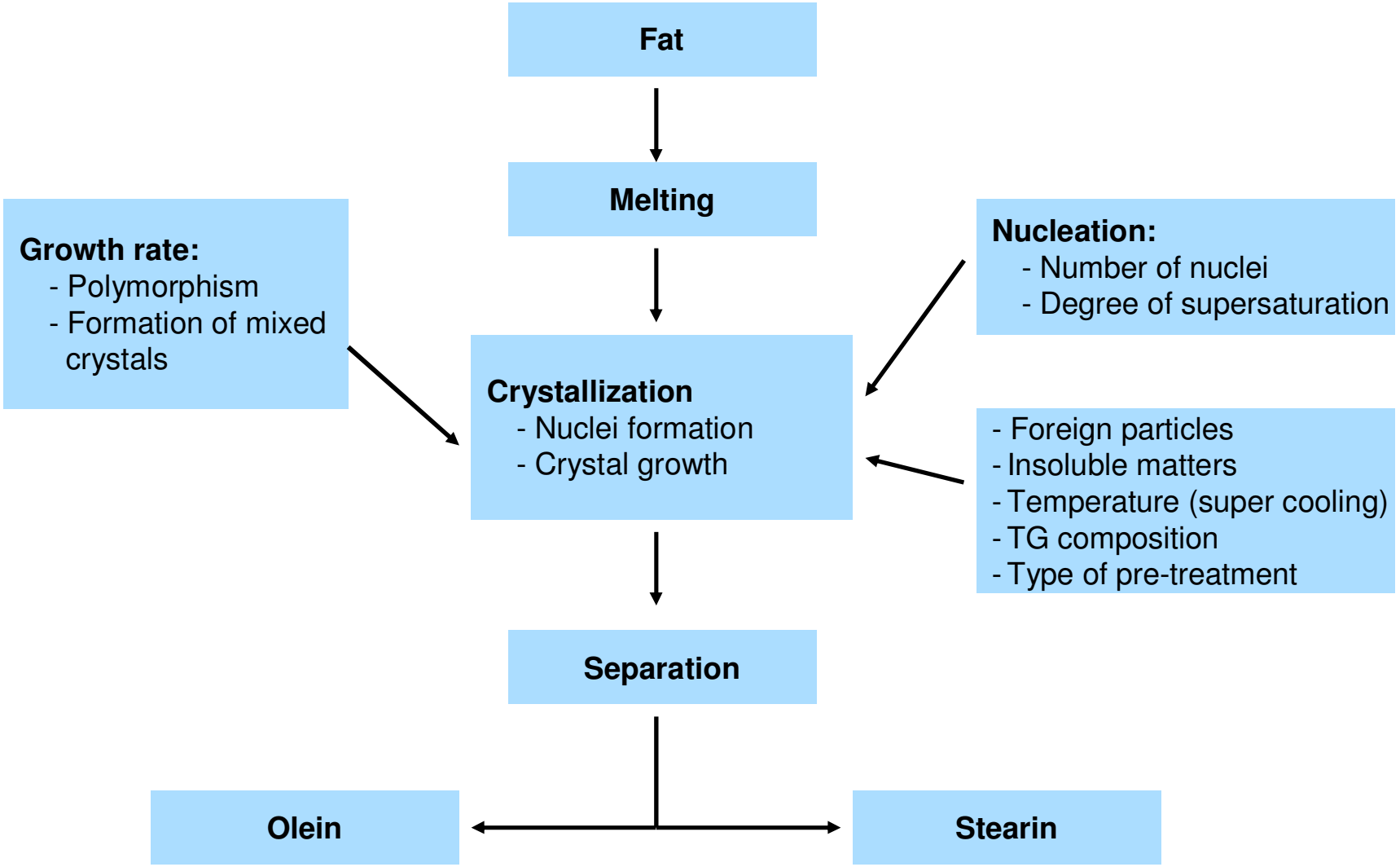

Fat Fractionation

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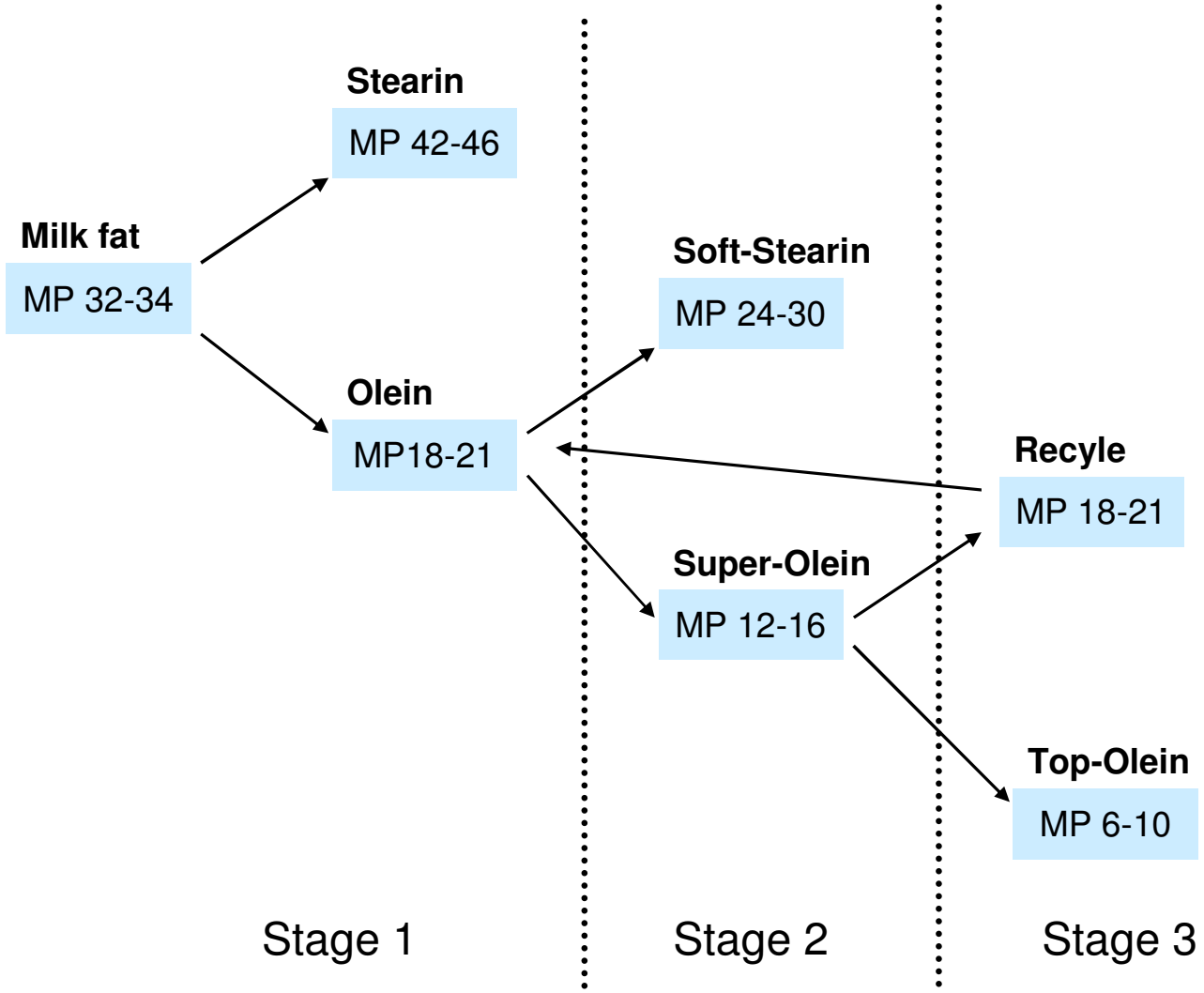
Fractionation of milk fat by staging:

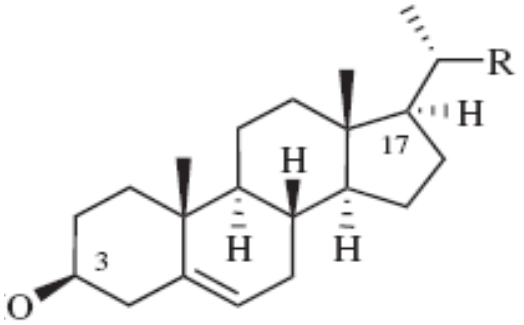


Phytosterol

- Phytosterols, also called plant sterols, are a group of steroid alcohol, naturally occurring in plants. (sitosterol, campesterol, stigmasterol)

- Nutritional Importance: Cholesterol-lowering effect

- Functional food (margarine, yoghurt, spreads, salad dressings, beverages etc.)



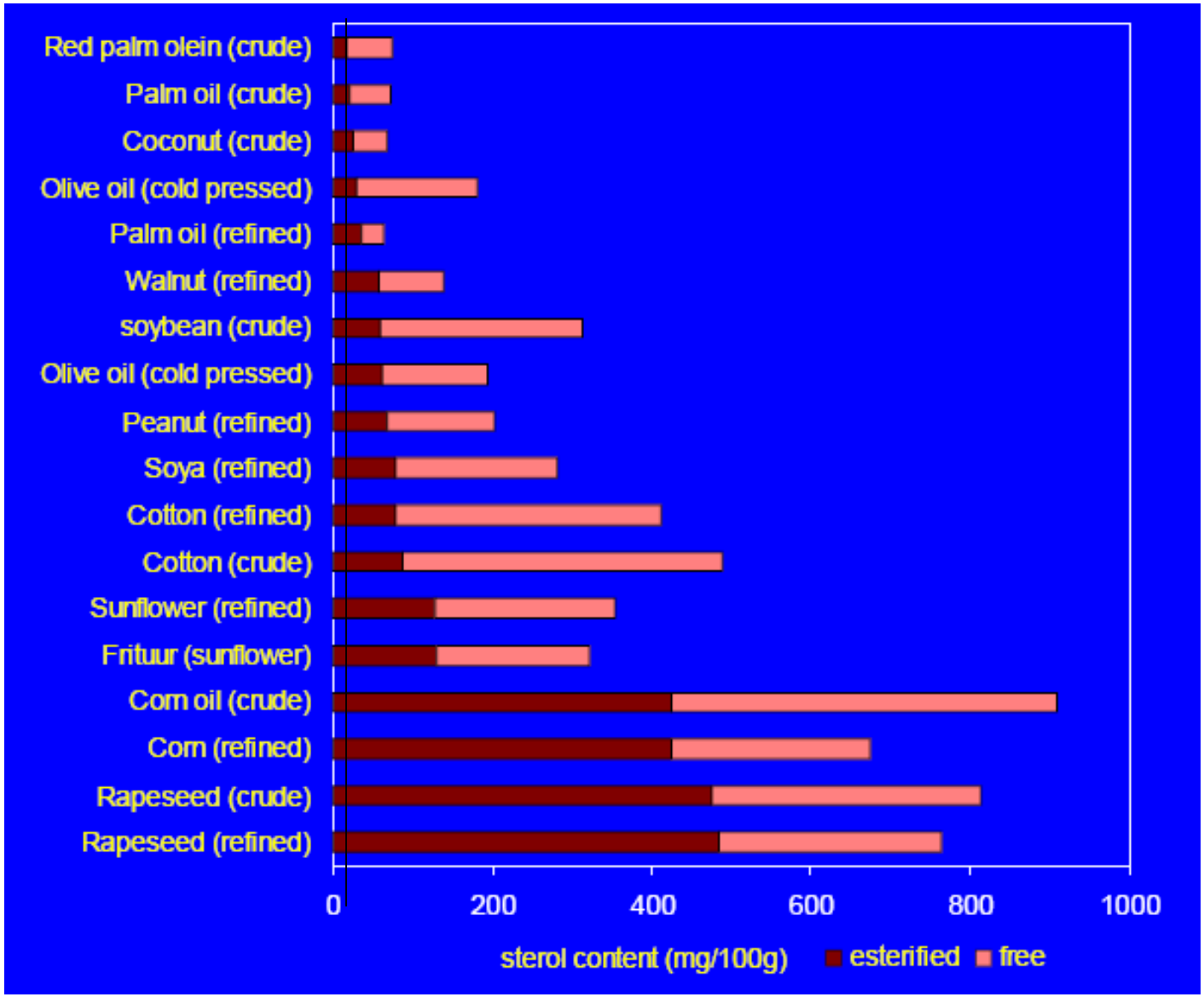
R =

beta-sitosterol

campesterol

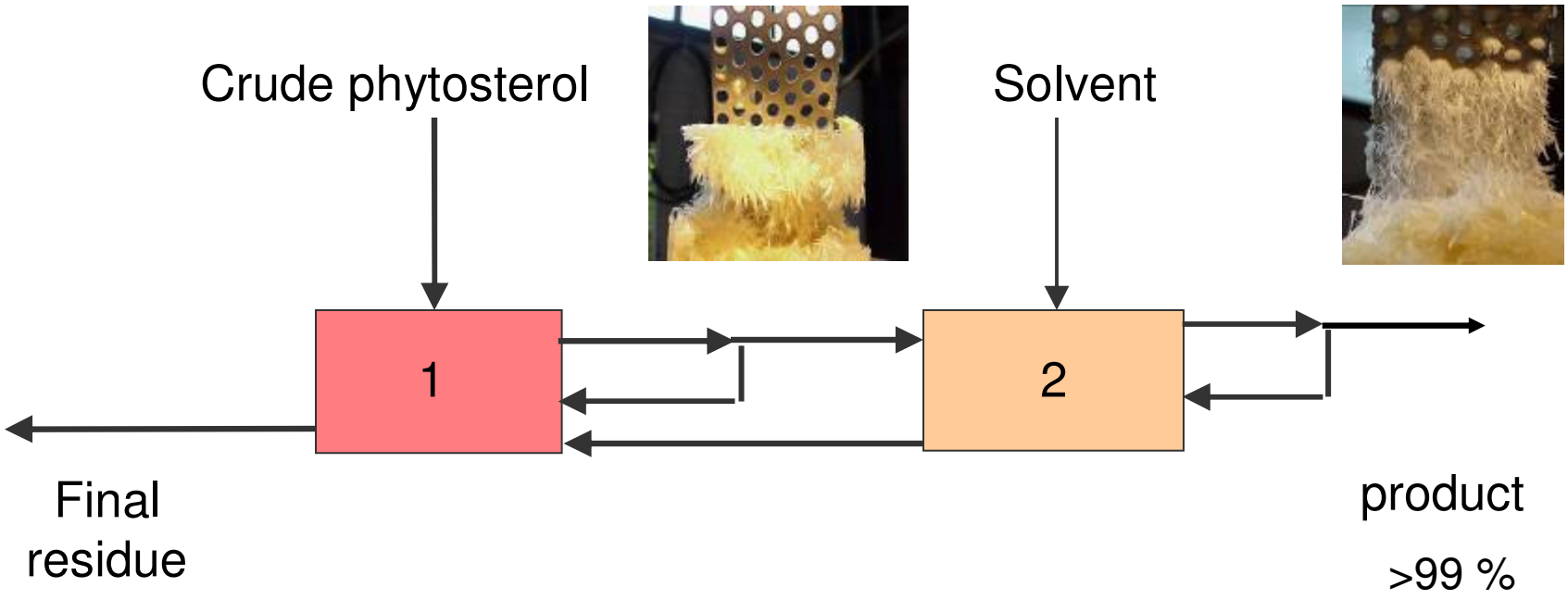
brassicasterol

Occurrence of Phytosterol in Vegetable Oil



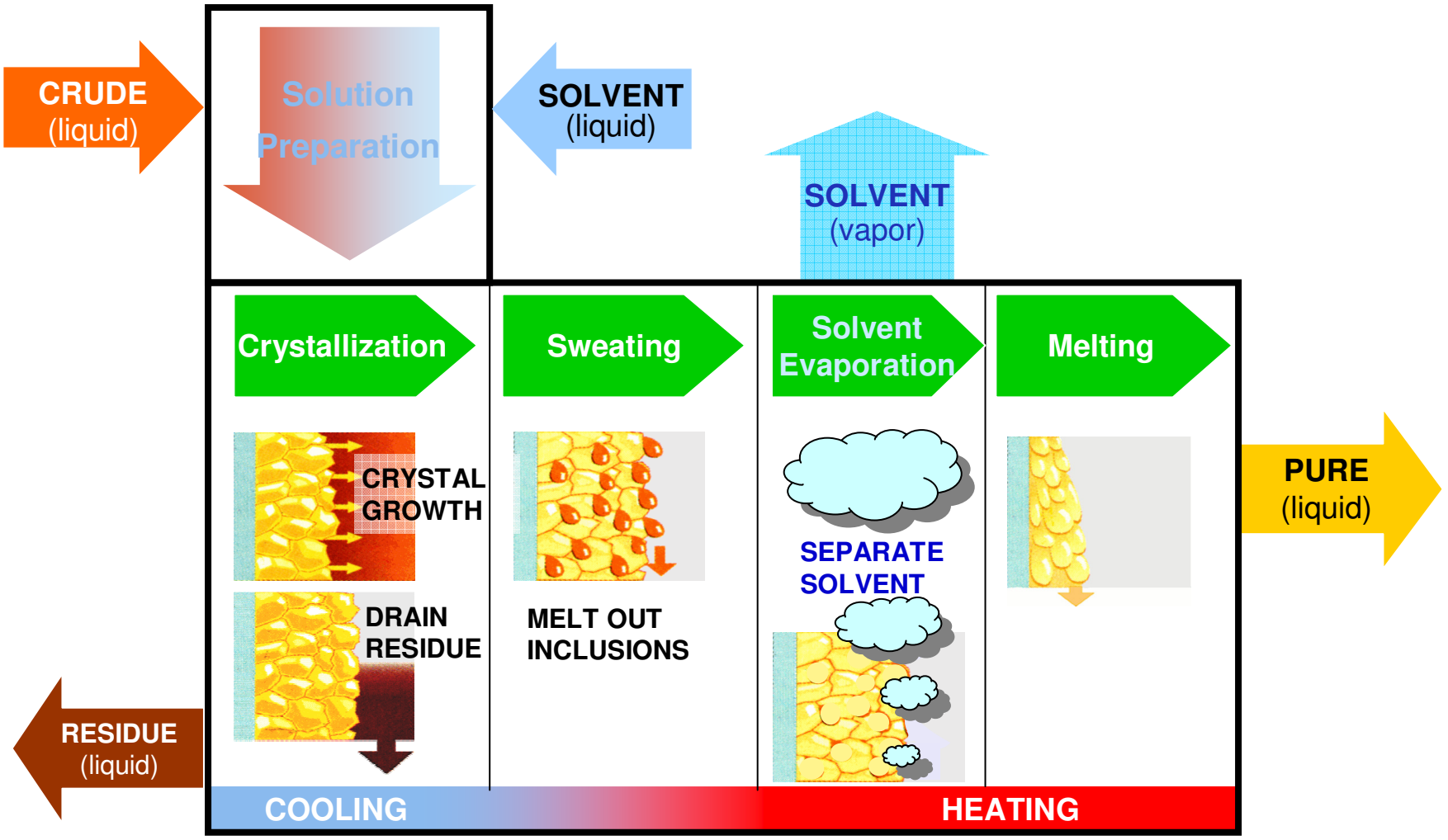
Mass Flow

A two stage crystallization

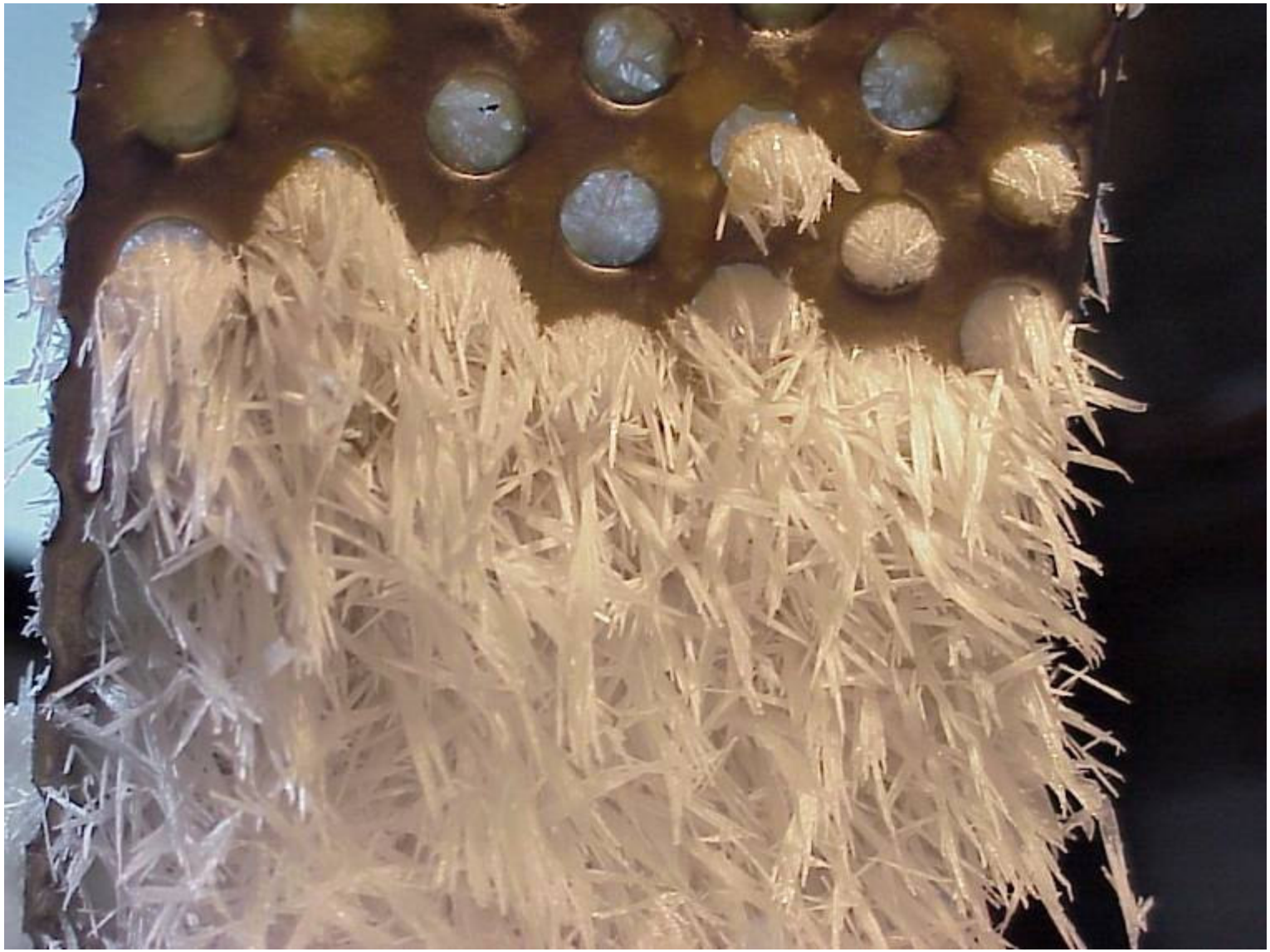


Yield = 90 %

Crystallization Stage



Final Product



Features of SULZER Process

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Fully automated control of the mass balance guarantees constant product quality.

Extremely flexible operation allows adaptation to changes in feed quality or product requirements

No addition equipment such as centrifuge or filter system is required for the phase separation.

No scale-up uncertainty; pilot plant results correlate 1:1 with the industrial plant

Very low maintenance costs since the plant has no moving parts except standard pumps and valves

Contact

Vielen Dank für Ihre Aufmerksamkeit

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