oils & fats

desmet ballestra

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Developments in Hydrogenation and Interesterification to Comply with New Nutritional and Health Standards for Edible Oils

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TRENDS IN EDIBLE OIL PROCESSING

Increased need for more efficient processes (commodity oils)

* More cost efficient processes (lower investment & operating costs)
* Valorisation and/or reduction of by-products
* Flexible plants able to process wide range of different oils
* Larger capacities (economics of scale)

Increased demand for higher quality food oils

* Low or no *trans* FA (formed during refining and hydrogenation)
* Balanced FA composition (optimal ratio satured/unsaturated FA)
* High concentration of natural anti-oxidants (tocopherols) and phytosterols
* No contaminants (pesticides, PAH, dioxins, PCB,....)

HIGH QUALITY FOOD OILS

OIL QUALITY

Organoleptic/stability

- Bland taste, no odor
- Light color (brilliant)
- High thermal stability
- High oxidative stability
- Long shelf life

Refining

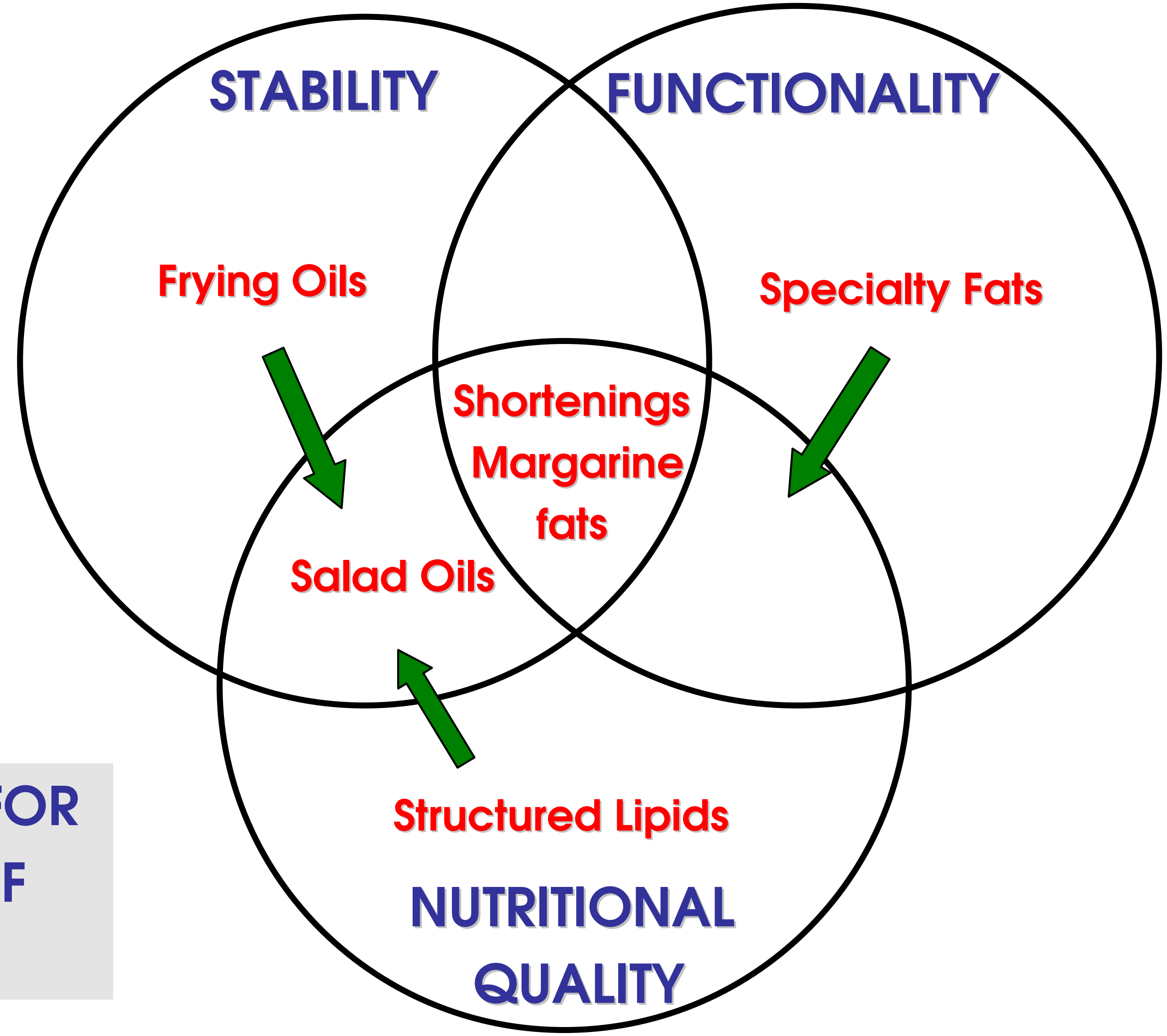
Functional Properties

- Good melting profile
- Desired Plasticity
- Crystallisation kinetics

Modification

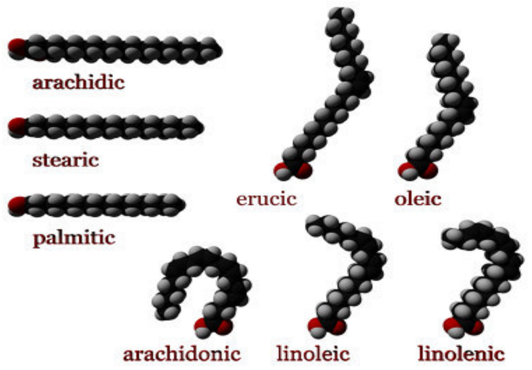
Nutritional Quality

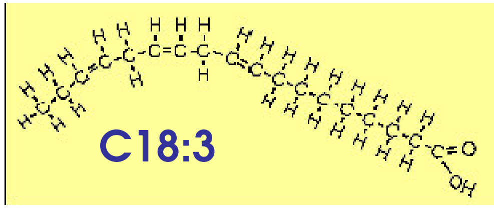
- Balanced FA composition (SFA/MUFA/PUSA)
- Low or no *trans* FA
- High natural antioxidants (tocopherols) and vitamins



INCREASED ATTENTION FOR NUTRITIONAL QUALITY OF FOOD OILS AND FATS

CURRENT NUTRITIONAL STANDARDS FOR FOOD OILS - I





FATTY ACIDS

ESSENTIAL FATTY ACIDS

Cannot be synthesized by the human body

w-6 FA : linoleic acid, arachidonic acid;

w-3 FA : linolenic acid, EPA, DHA

Optimal ratio w-6/w-3 < 10

EFFECTS ON RISK FOR CHD

C12:0, C14:0, C16:0 and C18:1*trans* are considered bad

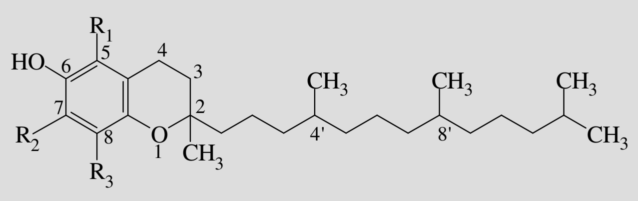
C18:0 and C18:1 are considered neutral

C18:2, C18:3 and CLA are considered good

CURRENT NUTRITIONAL STANDARDS FOR FOOD OILS - II

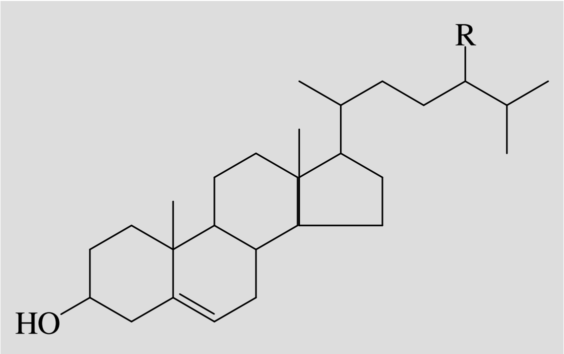
VALUABLE MINOR COMPONENTS

Tocopherols/Tocotrienols



Presence in oils desired
because of their Vitamin E activity

Phytosterols



- Reduction of Blood cholesterol levels
- Added to certain margarine fats (8-10%)

CONTAMINANTS

- Pesticides, PAH's, dioxins, PCB's
- Are only allowed in very low or non-detectable levels
- Removed during oil refining (adsorption or stripping)

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GENERAL COMPOSITION OF SOME FOOD OILS

Parameters	Soy	Palm	Rape	Sun	Olive	Fish[4]	Tallow
FAC (%)							
C16:0	8	42	4	6	10	12	25
C18:0	4	5	2	4	3	3	19
C18:1	28	41	60	28	75	15	35
C18:2	53	10	20	61	10	2	4
EPA/DHA	tr[1]	tr	tr	tr	tr	20	tr
Tocopherols[2]	1200	600	900	700	200	tr	tr
Sterols[2]	4000	2500	1000	4500	100	tr	3000[5]
Melting Point[3]	Liquid	35	Liquid	Liquid	Liquid	Liquid	25

[1]tr : traces; [2]expressed in ppm; [3] °C; [4]Cod Liver Oil; [5]cholesterol

Modification is required for use in food formulations

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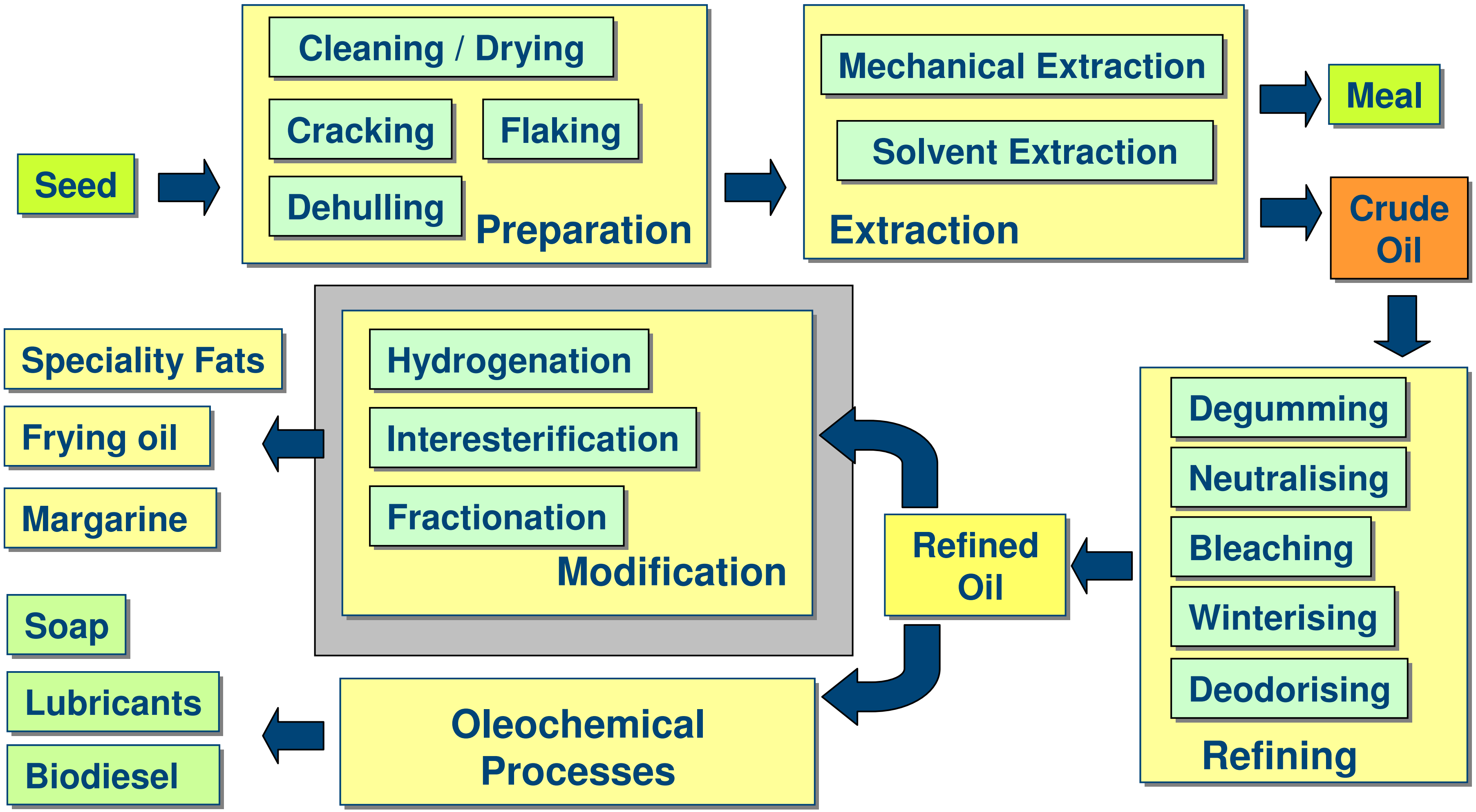

FAT REFINING

* Efficient adsorption processes
* Improved deodorization technology

FAT MODIFICATION

* Low trans hydrogenation
* Dry fractionation (multi-stage, new crystallisers)
* Interesterification (enzymatic *vs* chemical)

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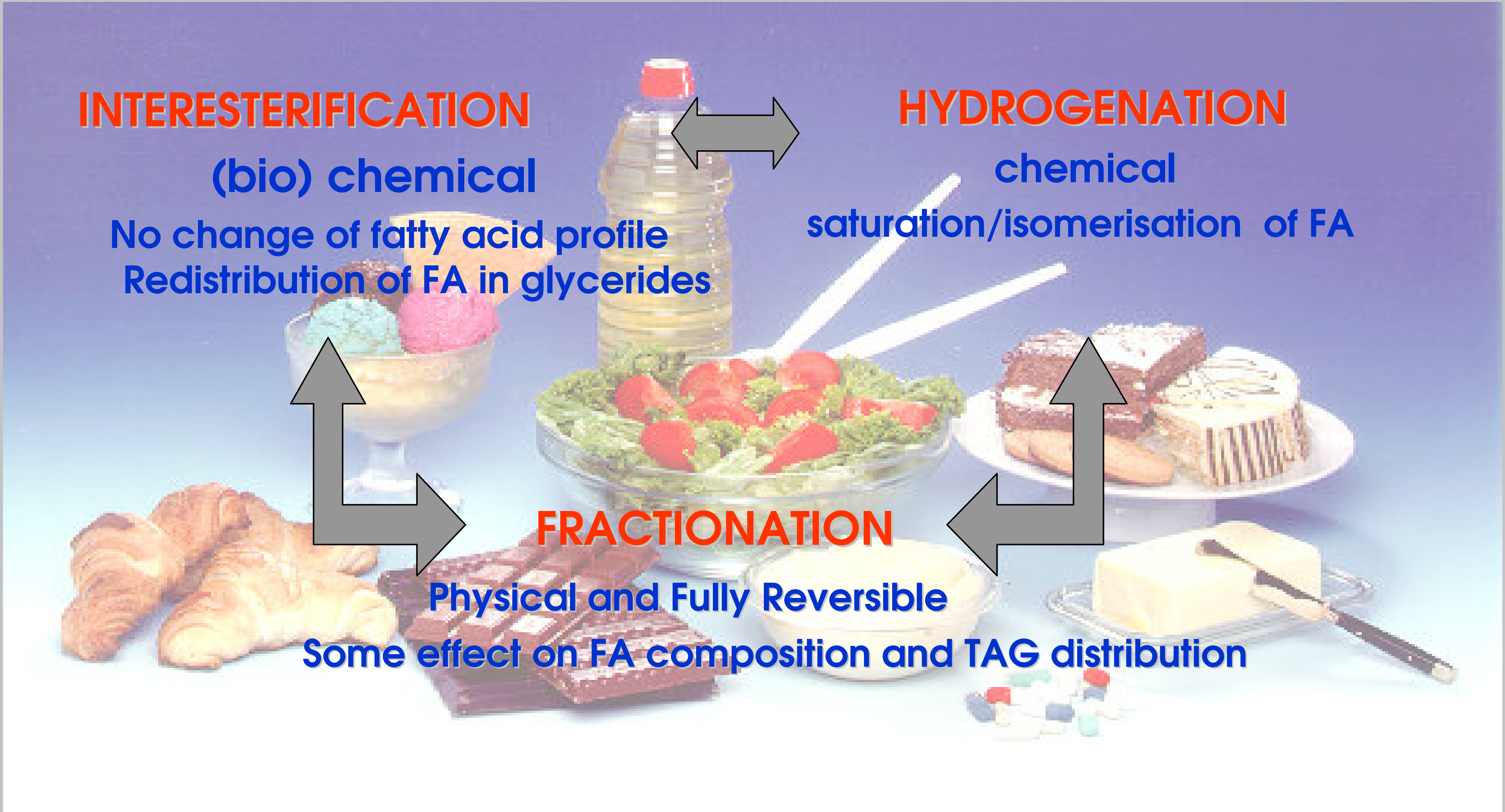

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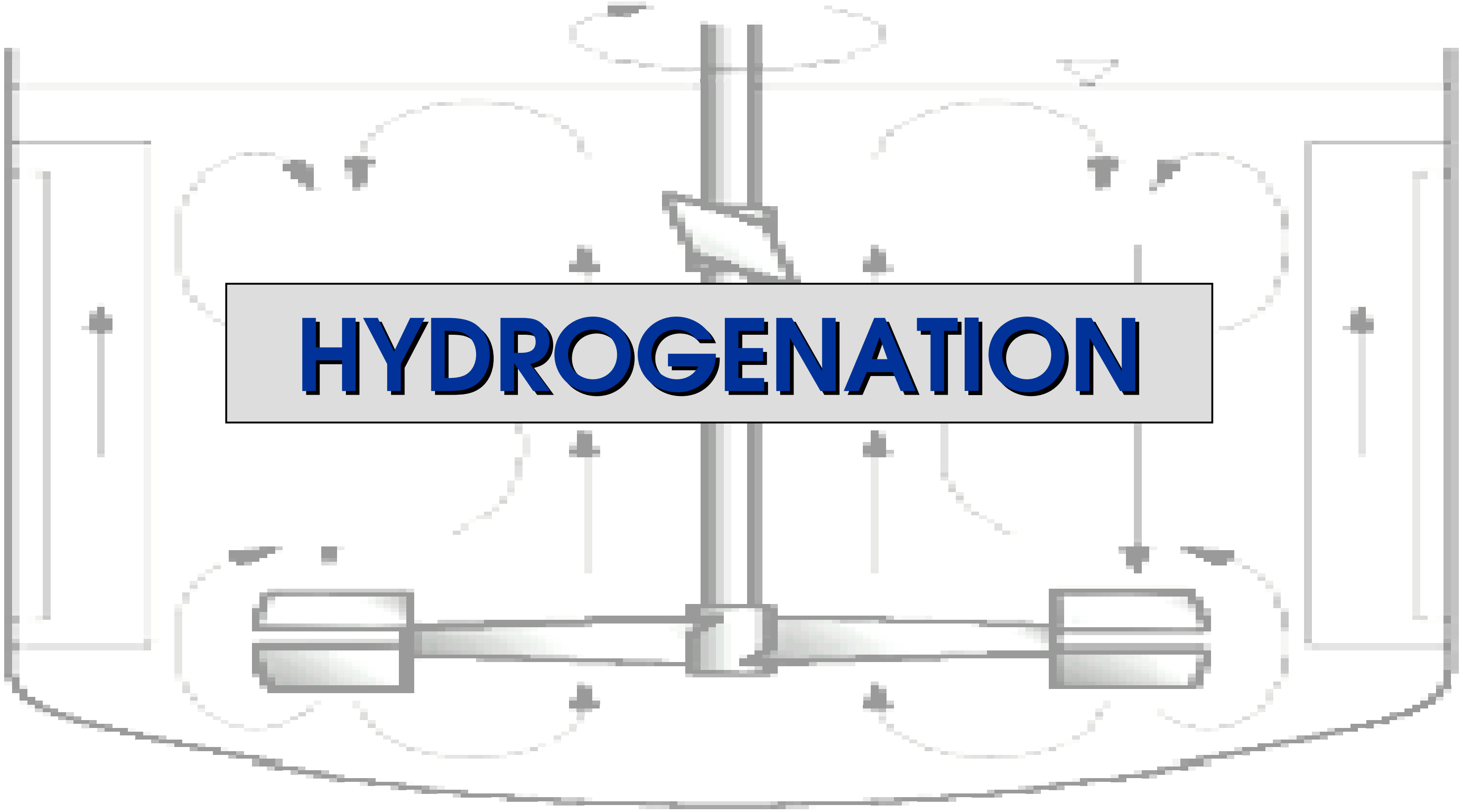
HYDROGENATION



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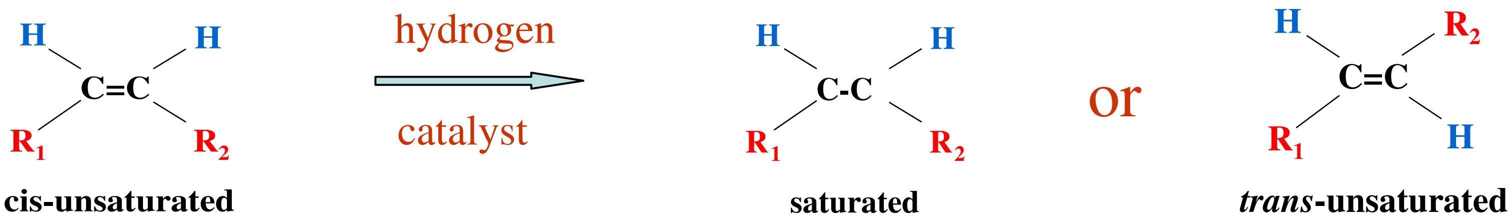
HYDROGENATION OF EDIBLE OILS



Selective Saturation of double bonds ⟷ Formation of *trans* fatty acids

Typical process conditions for partial hydrogenation

*Temperature : 150 - 180°C

* H_2 Pressure : 2- 20 bar

* Catalyst : Ni-catalyst (100 ppm Ni)

→

% *trans* = f (T, P, Ni)

Higher T gives more TFA

Higher P & more Ni gives less TFA

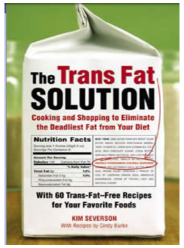
CURRENT STATUS OF HYDROGENATION

- ***Stricter labelling & legislation about trans fatty acids***
- ***Increase pressure from consumer organisations***

↓

Don't partially hydrogenate me
www.bantransfats.com

- ***Increase demand for :***



→ Low *trans* products : < 5% on fat basis
→ Zero *trans* products : < 0.5% on fat basis

↓

- ***Changing technology***
  - → **Dry fractionation/interesterification**
  - → **Full hydrogenation (no *trans*)**
  - → **Low *trans* hydrogenation**

LOW *TRANS* PARTIAL HYDROGENATION

- *Modified process conditions*

→ High Pressure hydrogenation (20 bar)
→ Low Temperature hydrogenation

- *Use of new catalysts*

→ Precious metal (Pd,Pt) catalysts
→ Zeolite based catalysts

- *New technologies (under development)*

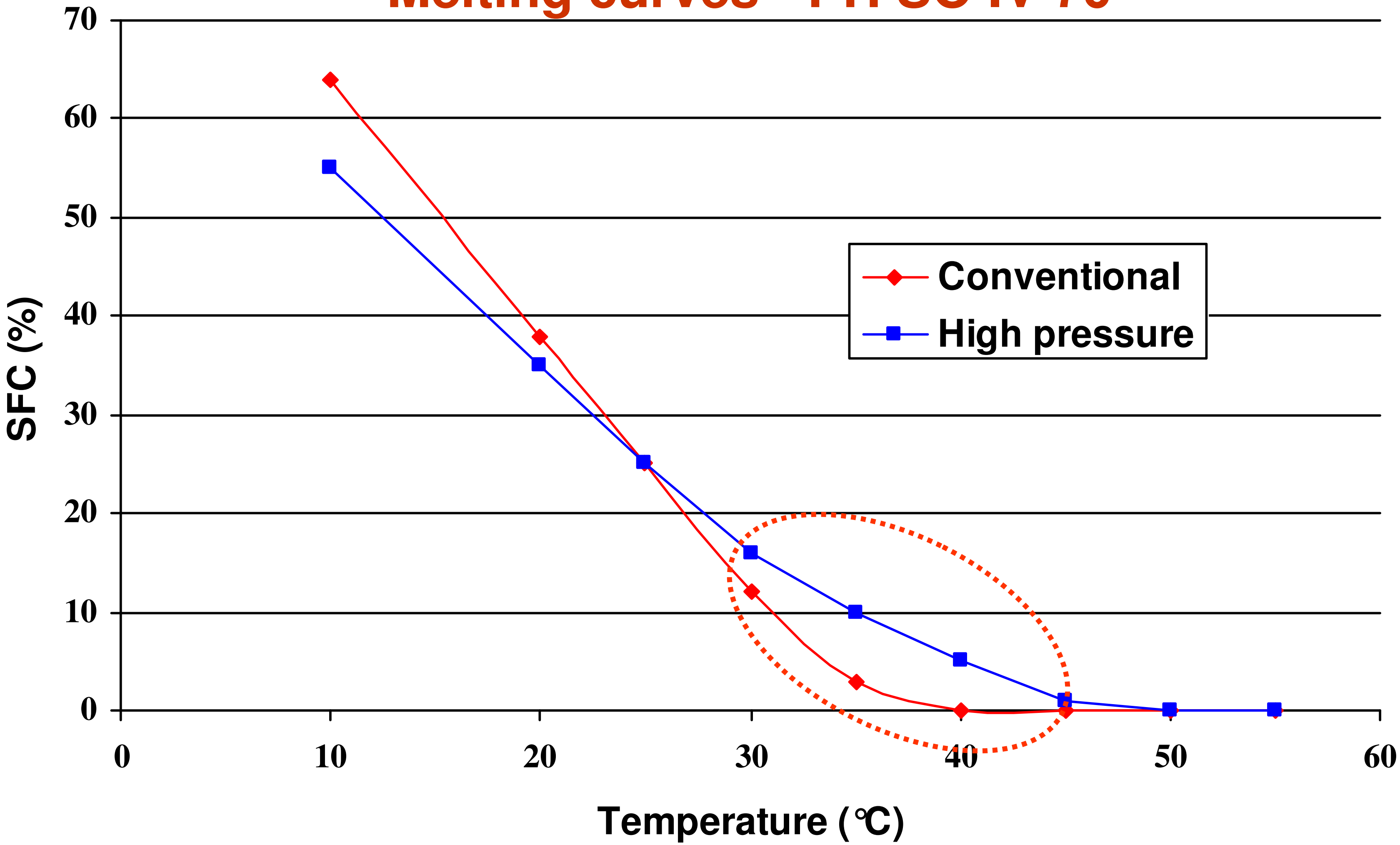
→ Supercritical hydrogenation
→ Continuous membrane hydrogenation

HIGH PRESSURE HYDROGENATION

Parameter	Reference	High pressure hydrogenation		
IV	70	100	70	60
FAC (%w:w)				
C18:0	10.3	8.0	20.7	27.6
C18:1t	*31.3*	*6.5*	*17.5*	*20.3*
C18:1c	43.5	38.2	40.8	35.5
C18:2t	*3.0*	*4.8*	*4.7*	*3.3*
C18:2c	0.5	27.9	4.6	1.7
C18:3t	*0.0*	*0.4*	*0.0*	*0.0*
C18:3c	0.0	1.3	0.0	0.0
Trans FA	***34.3***	***11.6***	***22.2***	***23.6***
SFC (% @ °C)				
10	63.6	9.1	54.6	73.5
20	38.0	2.4	35.7	57.0
30	11.8	0.5	16.4	33.3
35	3.0	0.0	9.5	21.9

Lab-scale trials : **110°C, 20 bar H_2, 100 ppm Ni (Nysosel 820)**

Melting curves - PH SO IV 70



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Parameter	Soybean oil	
	Feed	**Hydrogenated**	
Temp (°C)	-	40	50
Pressure (bar)	-	10-15	6.5
Cat (ppm Ni)	-	2200[1]	1980[2]
Time (min)	-	100	150
IV (calculated)	129.1	99.8	102.5
RS (ΔIV/min)	-	0.29	0.18
FAC (%w:w)			
C18:0	3.2	9.3	9.1
C18:1t	0.0	4.6	2.5
C18:1c	25.6	37.1	36.7
C18:2t	0.0	2.7	2.0
C18:2c	52.0	31.5	34.4
C18:3t	0.0	0.5	0.4
C18:3c	6.5	1.3	1.8
TFA	***0.9***	***7.8***	***4.9***
SFC (% @ °C)			
10	-	11.0	11.0
20	-	4.0	4.0

[1] 3500 g Oil + 35 g preheated Pricat 9920

[2] 15 tonnes Oil + 135 kg Pricat 9920

Losatra® Process

Cargill US patent application

Typical reaction conditions :

Temp : 30-50°C
Pressure : 1-25 bar
Catalyst : 2000-4000 ppm Ni

Characteristics

Low reaction rate : 0.1-0.5 ΔIV/min.
Low *trans*
Low SFC at 10°C : 11%

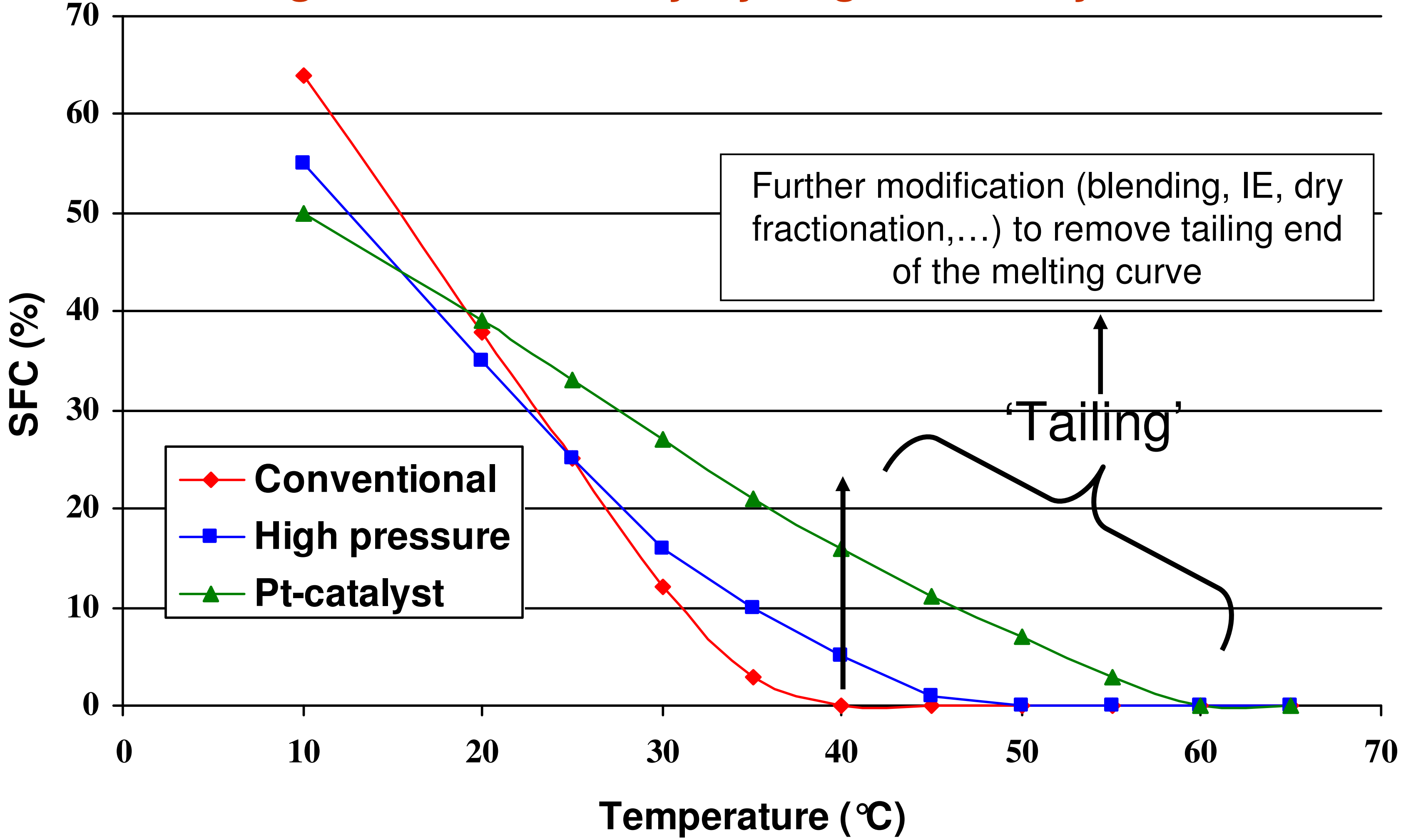
USE OF PRECIOUS METAL CATALYSTS

Parameter	**IV = 105**		**IV = 70**	
Catalyst	Ni	Pt	Ni	Pt
FAC (%w:w)				
C18:0	4.7	15.2	10.3	30.1
C18:1t	*12.6*	*1.5*	*31.3*	*3.0*
C18:1c	36.7	28.8	43.5	35.9
C18:2t	*5.3*	*0.8*	*3.0*	*1.0*
C18:2c	28.1	38.5	0.5	17.9
C18:3t	*0.1*	*0.4*	*0.0*	*0.1*
C18:3c	1.8	3.8	0.0	1.0
TFA	***18.0***	***2.6***	***34.3***	***4.2***
SFC (% @ °C)				
10	7.6	19.2	63.6	50.2
20	1.5	14.2	38.0	38.7
30	0.0	9.6	11.8	26.7
35	0.0	7.5	3.0	20.8

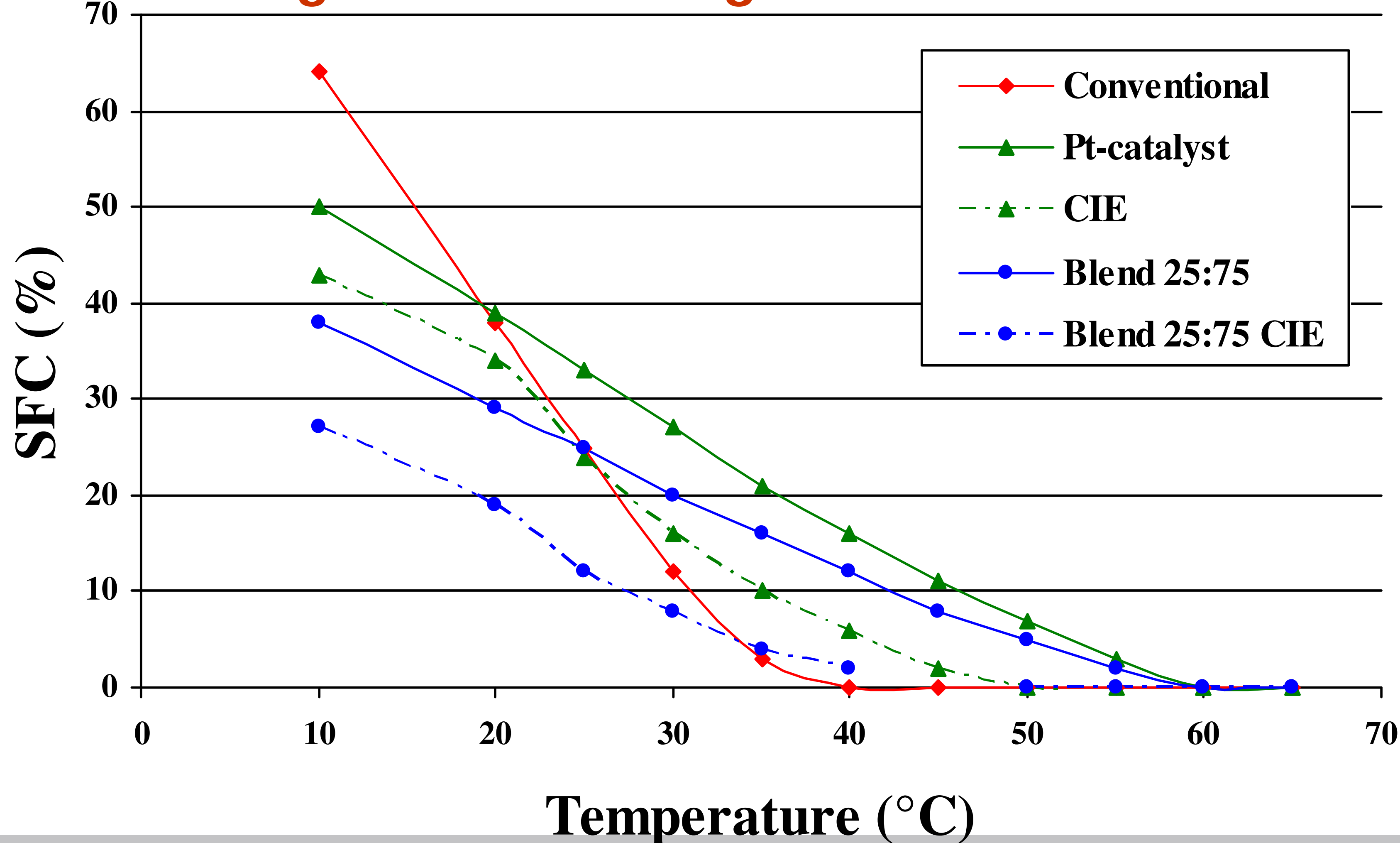
Lab-scale trials : 180-200°C, 3-4 bar H_2, 100 ppm Ni (Nysosel 820)

Soybean oil, 50°C, 4-5 bar H_2, 50 ppm Pt

Melting curves – Partially Hydrogenated Soybean oil IV 70



Straight CIE - Blending with SO – CIE of blend



LOW TRANS PARTIAL HYDROGENATION

Possible from technological point of view

Limited effect when applying high P/low T with traditional Ni-cat

Use of precious metal catalysts is still too expensive

Potential of membrane and supercritical hydrogenation doubtful

Is there a need/application for partially hydrogenated oils with low trans, but high saturated fatty acid content ?

More interesting/economical option

Production of hardstocks by full hydrogenation (no trans, no UFA)

Formulation of food fats with desired functional properties via combined **(enzymatic) interesterification**/dry fractionation

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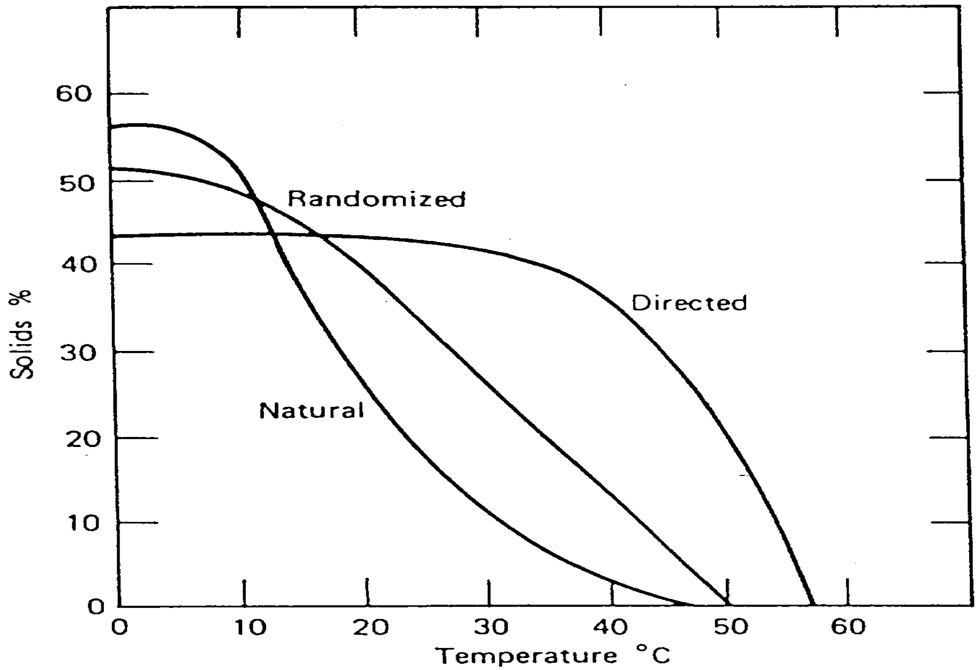
INTERESTERIFICATION

- Redistribution of FA on glycerol backbone
- With chemical or enzymatic catalysts
- Random or specific:

e.g. Palm Oil:



RANDOM INTERESTERIFICATION

$R_1R_1R_1 + R_2R_2R_2 \xrightarrow[\text{(random)}]{\text{CATALYST}}$

$R_1R_2R_1$

$R_1R_1R_2 \quad R_2R_1R_1$

$R_1R_1R_1 + R_2R_2R_2$

$R_2R_2R_1 \quad R_1R_2R_2$

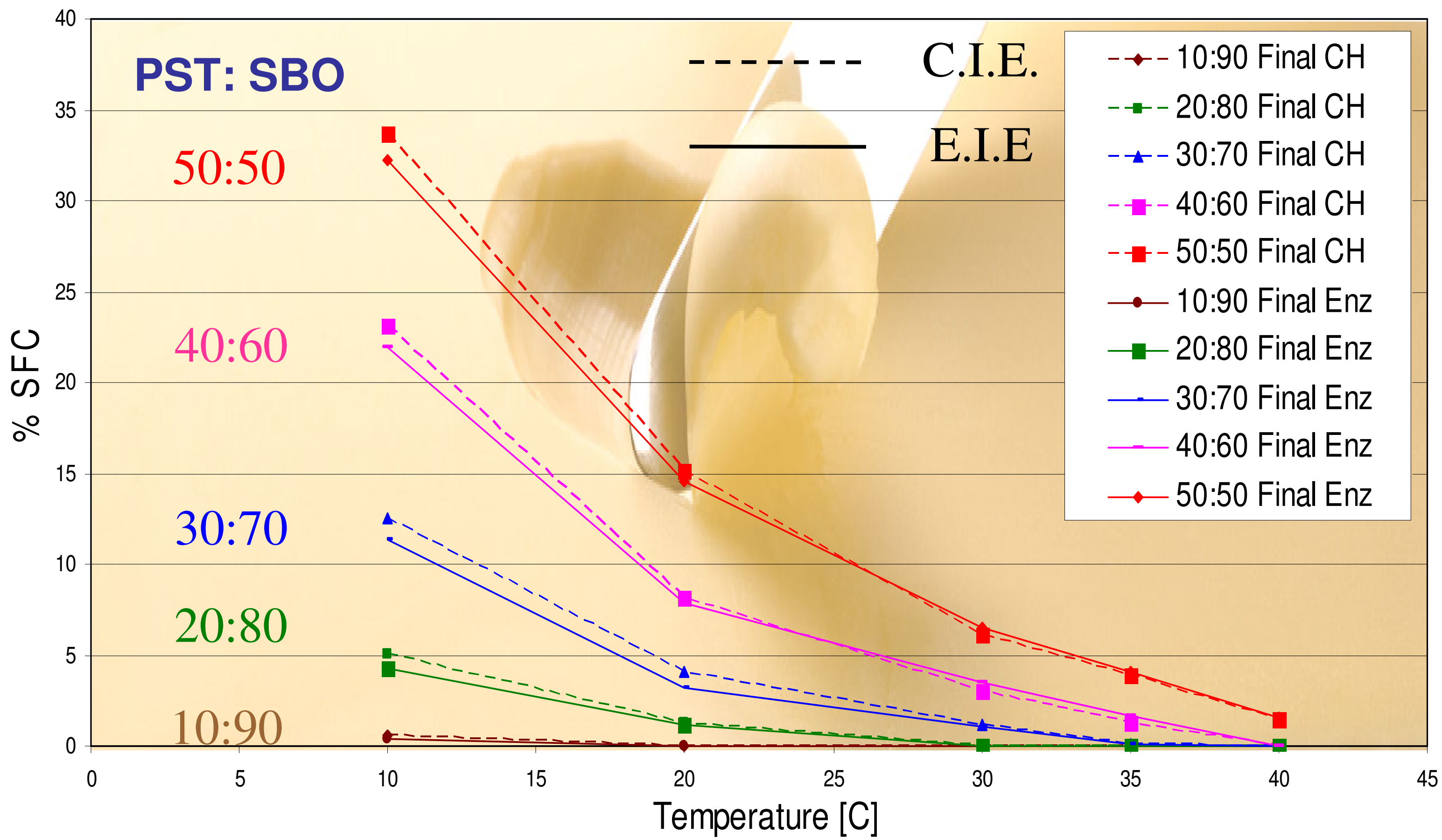
$R_2R_1R_2$

For 'Margarine fats'

- to improve overall melting profile
- to increase compatibility
- to enhance plasticity
  - ✓ margarines
  - ✓ shortenings

Chemical or Enzymatic

Margarine application: **little difference between CIE and EIE**



SPECIFIC INTERESTERIFICATION

$$R_1UR_1 + R_2UR_2 \xrightarrow[\text{(1,3 specific)}]{\text{CATALYST}} R_1UR_1 \quad R_1UR_2 + R_2UR_1 \quad R_2UR_2$$

For 'structured lipids':

Enzymatic

- Confectionery Fats (high SUS, CBE):
  - to increase compatibility with CB
  - to improve hardness and sharpness of the fat.
- Infant formulation (high OPO).
- East-to-digeste and low calory fats (MLM – medium chain type).

Production of POS/SOS-triacylglycerols:

- POS is main component in CB, also found in illipe oil
- POP is main SUS-component in palm oil (mid fractions)
- Strategy: `structuring' POP lipid in to POS/SOS lipid

POP + **Stearic acid** → (Specific EIE) → **POS/SOS** + **FFA**

FFA → removed by stripping

CHEMICAL INTERESTERIFICATION

- Low catalyst consumption (0.05-0.1%) due to better oil pre-treatment
- Lower oil losses
- Dry catalyst remains difficult to handle, induce unwanted side-reactions (e.g. degradation of tocopherols, color fixation…)

ENZYMATIC INTERESTERIFICATION

— ‘Random’ enzymatic interesterification: margarine fats

— ‘Specific’ enzymatic (inter)esterification: structured lipids

— Less expensive and more stable enzymes are commercially available

— Higher productivity resulting in an ‘economical’ operating cost

Chemical versus Enzymatic interesterification

Chemical interesterification

Pretreatment of oil → Reaction Catalyst: NaOCH3 → Deactivation water / acid → Postbleaching → Deodorization

Batch Process in stirred tank reactors – suitable for frequent stock changes

Enzymatic interesterification

Pretreatment of oil → Reaction Catalyst: Lipase → Deodorization

- No catalyst inactivation
- No postbleaching

⇩

Less Oil Losses

Continuous process through a series of fixed bed reactors –
Production of larger batches of 'bulk" EIE fat → Combined EIE-dry frac.

OIL PRETREATMENT FOR ENZYMATIC IE

Enzyme inactivation by following components :

Radicals (peroxides)

Polar Impurities (phosphatides, soaps,..)

Secondary oxidation products (ketons, aldehydes,..)

Trace elements (Nickel,…)

Acids (citric acid,…)

Oil quality prior to enzymatic interesterification is important

Chemical Refining : Neutralized-Bleached

Physical Refining : Preferably fully refined (bleached and deodorized)
Alternatively : silica treatment of bleached oil

Enzyme productivity for Lipozyme TL-IM (kg EIE oil/kg enzyme)

- Depends largely on feedstock quality
- Needs to be high because to keep operating cost competitive
- For 'random' EIE : min. productivity (valid for good feedstock) : 2.5 ton EIE oil/kg enz.
- Higher productivity up to 4 ton EIE oil/kg enzyme achieved in pilot trials

Enzyme activity (Flow rate – kg EIE oil/kg enzyme.hr)

- Enzymatic interesterification is a continuous process
- Constant but rather slow flow rate : typically 1-2 kg EIE oil/kg enzyme.hr
- Enzyme in use for 1250-2500 hr (50-100 days)

EIE Equipments

Lab scale unit

Pilot unit

Industrial unit

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Thank you for your attention

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