IUPAC-AOCS Workshop on Fats, Oils & Oilseeds Analyses & Production
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CHEMICAL *vs* ENZYMATIC INTERESTERIFICATION

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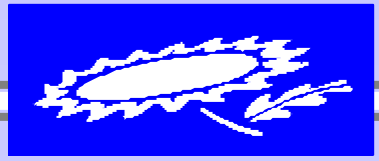
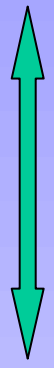


INTERESTERIFICATION : chemical vs enzymatic

- **CHEMICAL :** - 'Random' Interesterification
  (FA-distribution according to law of probability),
  - Preferred catalyst: CH_3ONa (powder)



- **ENZYMATIC :** - Lipase catalysed
  - Lipozyme TL IM (immobilised)
  - 'Selective' FA-interchange on sn-1,3 positions

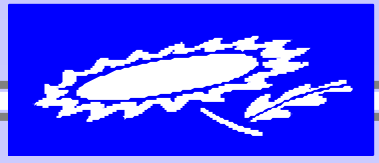
INTERESTERIFICATION : PAST SITUATION

- **CHEMICAL INTERESTERIFICATION**

- High oil losses (up to 5%, due to 'wet' catalyst inactivation)
- Risky operation (related to use of catalyst : e.g. Na/K alloys)
- Largely replaced by partial hydrogenation
  (UFA *vs* SFA, *Trans* Fatty acids was not an issue)

- **ENZYMATIC INTERESTERIFICATION**

- Expensive catalysts, low activity and stability, high operating cost
- Only used for high value-added products (CBE, structured lipids)



INTERESTERIFICATION : CURRENT SITUATION

Increasing trend to reduce / exclude *trans* fatty acids from food

→ because of stricter legislation

- ***trans*** **labelling in USA from 2006**
- **very strict Danish regulation : max. 2% in food fats**

→ increasing pressure from consumer organisations

Increasing trend to avoid chemicals in food processing

Major USA food producers (Mc Donalds, Fritolay, Nabisco,…) are replacing *trans* fats by low /zero TFA alternatives

INTERESTERIFICATION : CURRENT SITUATION

Increased demand for :

low *trans* products: < 5% on fat basis

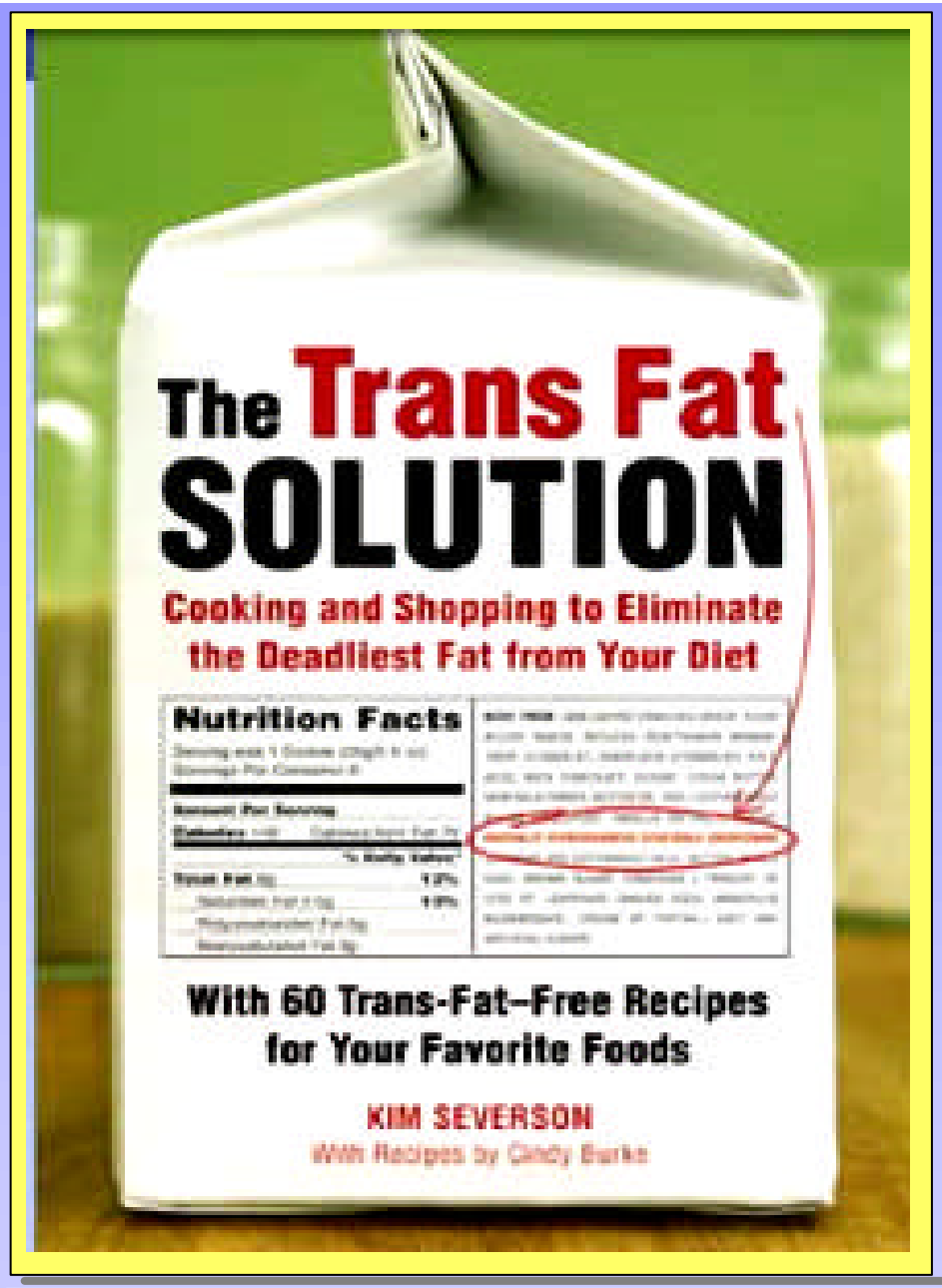
zero *trans* products: <0.5% on fat basis

INTERESTERIFICATION has become the alternative fat modification technology to PARTIAL HYDROGENATION

Past : Chemical interesterification for commodity fat blends

Enzymatic for 'specialty' fats (SUS fats)

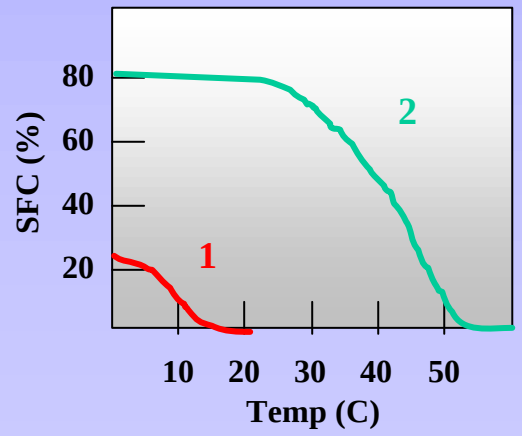
Today : Cost-effective enzymatic IE for commodity fats

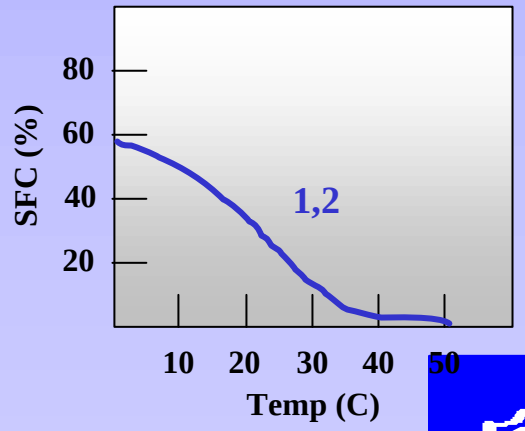


CHEMICAL INTERESTERIFICATION

CHEMICAL INTERESTERIFICATION: PRINCIPLE

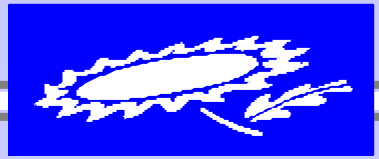
$R_1R_1R_1 + R_2R_2R_2$ —$NaOCH_3$ (random)→ R_1R_2R, $R_1R_1R_2$, $R_2R_1R_1$, $R_1R_1R_1 + R_2R_2R_2$, $R_2R_2R_1$, $R_1R_2R_2$, $R_2R_1R_2$





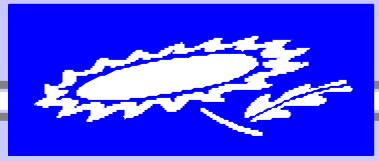
CHEMICAL INTERESTERIFICATION CATALYSTS

Type of catalyst	Concentration %	Temperature °C	Time min
Na, K, Na-K alloys	0.1-1	25-270	1-120
CH_3ONa, C_2H_5ONa	0.05-1	50-120	30-60
NaOH, KOH	0.5-2	150-250	90
NaOH + Glycerol	0.05-0.1	60-160	30-45
Sodium stearate	0.5-1	250	60
NaH, $NaNH_2$	0.2-2	170	3-120



CHEMICAL INTERESTERIFICATION CATALYST : $NaOCH_3$

- **Trivial names: Sodium methoxide; Sodium methylate**
- **Very alcaline catalyst (stronger than NaOH)**
- **Very reactive : exothermic decomposition into NaOH and CH_30H in presence of moisture**
- **Hazardous product, requiring carefull handling and controlled storage**
- **Available in powdered form for interesterification, *or* dissolved in MeOH (25%) for biodiesel production**
- **Supplied in plastic bags (10kg) sealed in drums**



CATALYST INACTIVATION

Poison		Catalyst inactivated (% on oil)		
Type	level	Na	CH_3ONa	NaOH
Water	0.01 %	0.013	0.03	
fatty acid	0.05 %	0.004	0.01	0.007
peroxide	1.0	0.0023	0.0054	0.004
total catalyst inactivated		0.0193	0.0454	0.0011

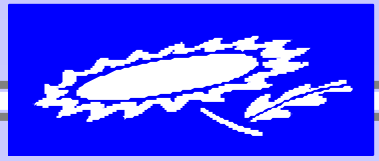
Feedstock Oil needs to be very dry and low in FFA

CHEMICAL INTERESTERIFICATION : OIL QUALITY

Chemical → **semi-refined (neutralized and bleached)**

Physical → **fully refined (bleached and steam refined)**

FFA :	**<**	**0.05 %**
Phosphorus :	**<**	**2 ppm**
Moisture :	**<**	**100 ppm**
Peroxide value :	**<**	**0.5 meq/kg**
p-Anisidine value :	**<**	**10**



CHEMICAL INTERESTERIFICATION : OIL DRYING

Physical equilibrium of water in oil (ppm)

Temp	5 mbar	10 mbar	25 mbar	50 mbar	75 mbar
75°C	31	63	156	310	469
100°C	17	34	85	171	256
125°C	10	21	53	105	158
150°C	7	14	36	72	108
175°C	6	12	30	60	90

In practice: equilibrium not reached

125°C - 25 mbar - 60 min gives 80 ppm water

INTERESTERIFICATION PROCESS

ADDITION OF THE CATALYST

-Addition of 0.05-0.1% $NaOCH_3$

-'Aggressive' catalyst

- Avoid direct contact

Automatic dosing

START OF THE REACTION

-Formation of deep red-brownish color

-Usually appears shortly after catalyst addition (few minutes)

INTERESTERIFICATION PROCESS

PROLONGATION OF THE RANDOMISATION

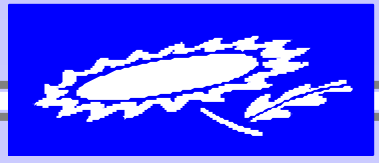
- Randomisation usually occurs quite fast (10-15 min.)

- Industrially reaction time is longer : 30-60 min.

- No quick on-line method to check completion/status of the reaction

- Once 'Randomization' is reached, reaction will continue (until destruction of catalyst), but with no 'net' effect

- Too long reaction will darken oil & give color fixation



CHEMICAL INTERESTERIFICATION : OIL LOSSES

- **Side reactions leading to oil losss (catalyst related)**

→ 1 mole $NaOCH_3$ gives 1 mole FAME & 1 mole Na-soap

1 mole FFA ↵ acid catalyst inactivation

→ % (FAME + FFA) = $^{+/-}$ 10 * % $NaOCH_3$ added

- **Oil loss during postbleaching = 0.3 * % bleaching earth**

- **Oil loss during deodorisation = +/- 1.3 * % (FFA+FAME)**

0.1% of $NaOCH_3$ catalyst

0.5% bleaching earth

→ Overall oil loss : min. 1.5%

CHEMICAL INTERESTERIFICATION : PROCESS STAGES

1. **Neutralisation:** FFA $\xrightarrow{NaOH}$ FA soaps (no removal)
2. **Drying:** H_20 < 100 ppm; preferably < 50 ppm
   120°C; < 20 mbar
3. **Reaction with catalyst:** 90-100 °C during 30 min. at 20 mbar
   max. 0.1 %; preferably 0.05% catalyst
4. **Reaction stop:** water / acid / acid activated silica
5. **Bleaching :** 0.2-0.5% Bleaching earth
6. **Deodorising:** 220-230°C (deodo) / 240-250°C (stripping)

CHEMICAL INTERESTERIFICATION : SIDE REACTIONS

$NaOCH_3$: strong 'alkaline' catalyst

→ will catalyze also unwanted side-reactions

-Degradation of tocopherols

-Formation of tocopherol esters

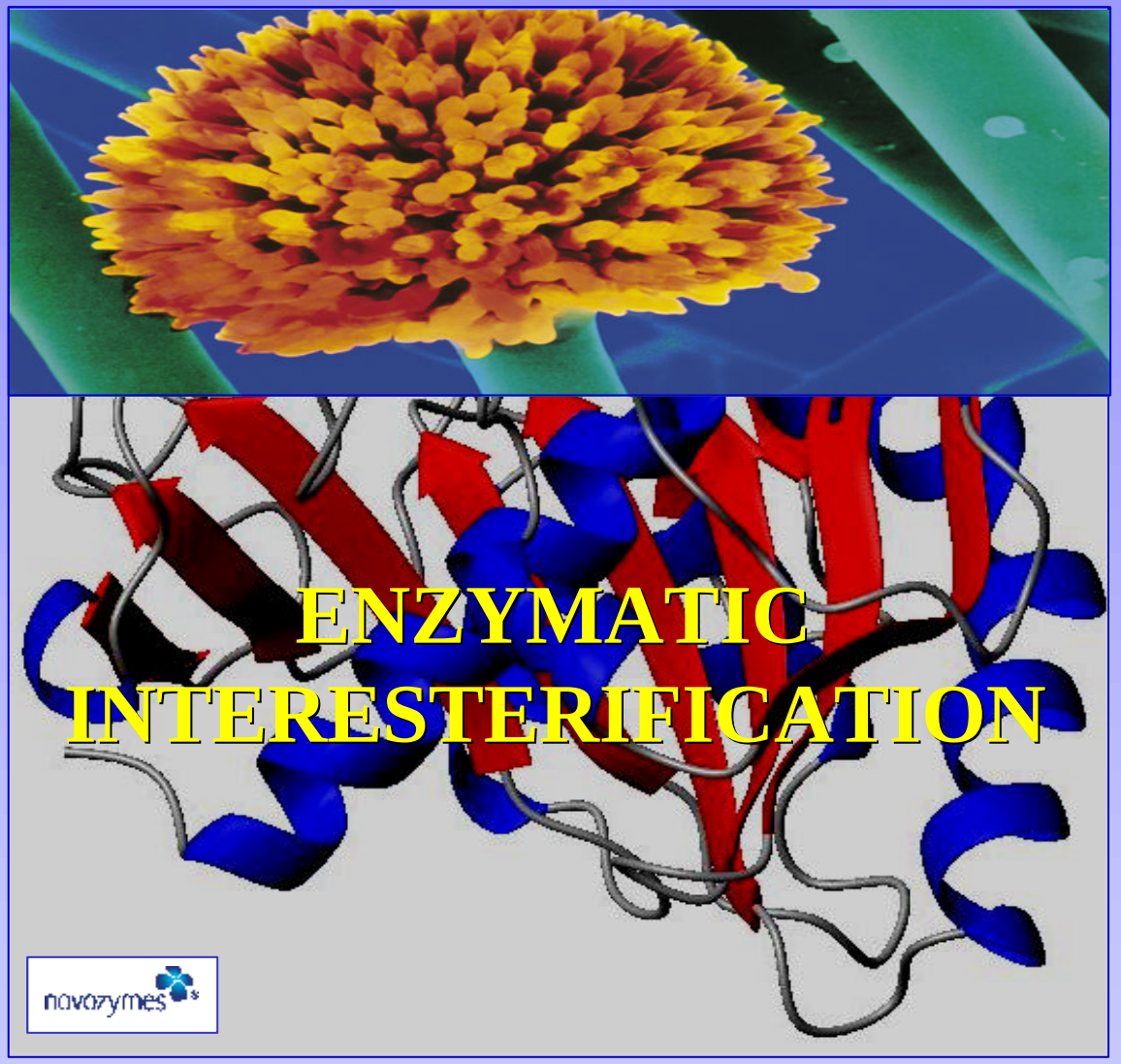
→ May affect oxidative stability

-Formation of di-alkylketones

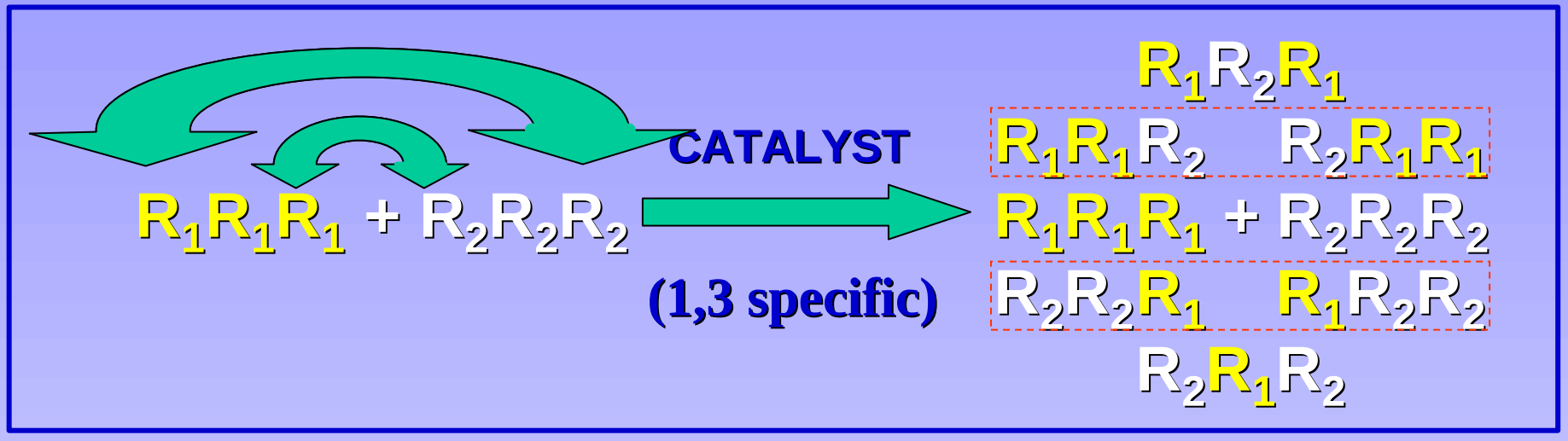
-Some formation of phytosterol esters

→ more side products at higher catalyst conc. & temperature

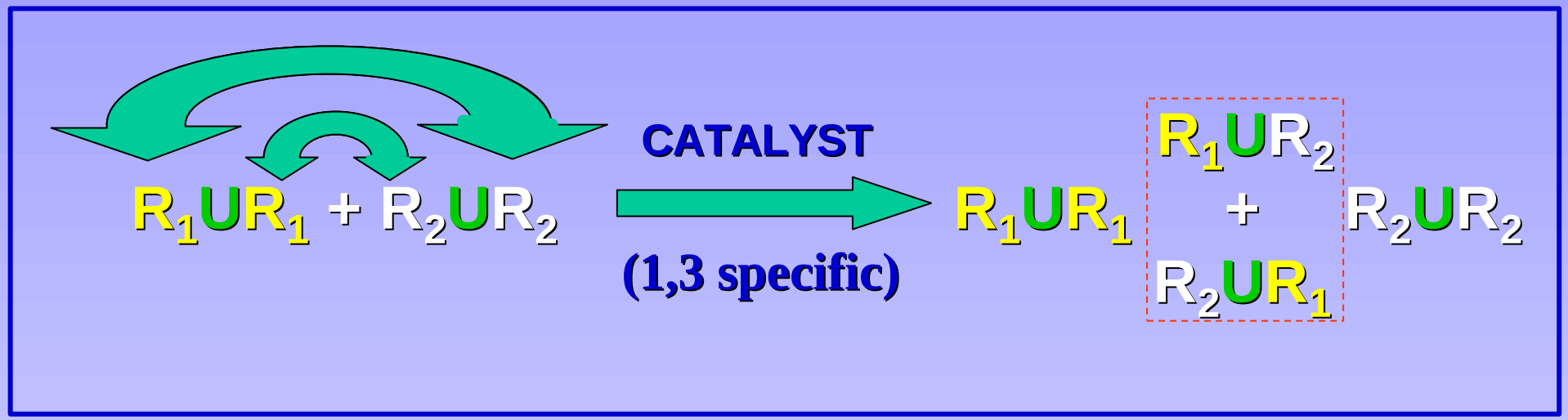
max. catalyst conc. : 0.1% - max. temperature : 120°C


ENZYMATIC
INTERESTERIFICATION
novozymes

ENZYMATIC INTERESTERIFICATION: PRINCIPLE



ENZYMATIC INTERESTERIFICATION OF SUS FATS : PRINCIPLE



ENZYMATIC INTERESTERIFICATION

Enzyme : LIPOZYME TL IM

- Triacylglycerolhydrolase (also named Lipase)
- Lipase from *Thermomyces lanuginosus. (in past from pancreas)*
- sn-1,3 specific and heat stable (max. temp. : 75°C)
- HALAL approved

Immobilized

- For use in fixed bed processes
- No enzyme in finished oil product
- Enables re-use of enzyme for better process economy
- Stabilizes the enzyme

ENZYMATIC INTERESTERIFICATION

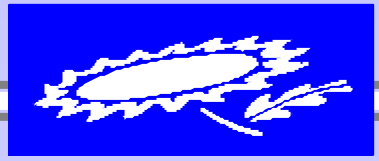
Enzyme : LIPOZYME TL IM

Enzyme inactivation due to : (stability)

Process temperature (max. 70°C)

Radicals (Peroxides)
Polar impurities (phosphatides, soaps
Secondary oxidation products : ketons, aldehydes…
Trace elements (e.g. Nickel)

Quality of Incoming oil is important : degummed – bleached-(deodorised)



ENZYMATIC INTERESTERIFICATION

Enzyme : LIPOZYME TL IM

Enzyme productivity : kg EIE oil/kg enzyme

Depending on incoming oil quality

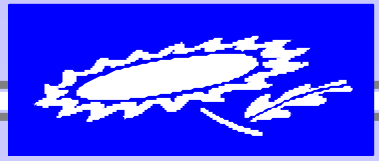
For good quality oil : min. 2500 kg EIE oil/kg enzyme

Productivity up to 4000 kg EIE oil/kg enzyme in pilot tests

Enzyme activity – Flow rate

Slow reaction : 1-2 kg IE oil/kg enzyme.hr

Enzyme in use for min. 2500 h (> 100 days)



ENZYMATIC INTERESTERIFICATION : PROCESS ISSUES

Batch *vs* Continuous (fixed bed) process

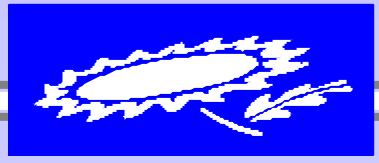
Single or Multiple fixed bed reactor

Multiple fixed bed reactor placed in series or in parallel

Flow rate : variable or constant

Process control – Control of enzymatic conversion

Cross-contamination



ENZYMATIC INTERESTERIFICATION : PROCESS ISSUES

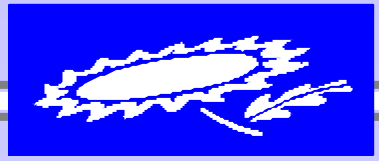
CHEMICAL INTERESTERIFICATION → BATCH

- Production of a large number of (small) batches
- Low degree of cross-contamination

ENZYMATIC INTERESTERIFICATION → CONTINUOUS

- Limited cross-contamination (plug flow)
- Less suitable in case of many stock changes
- More suitable for alternative approach :

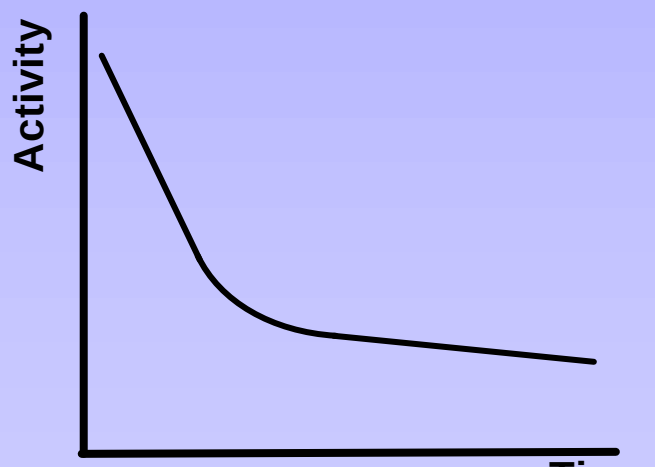
  Production of larger batches of 'bulk' EIE, followed by dry fractionation/blending to fine-tune properties

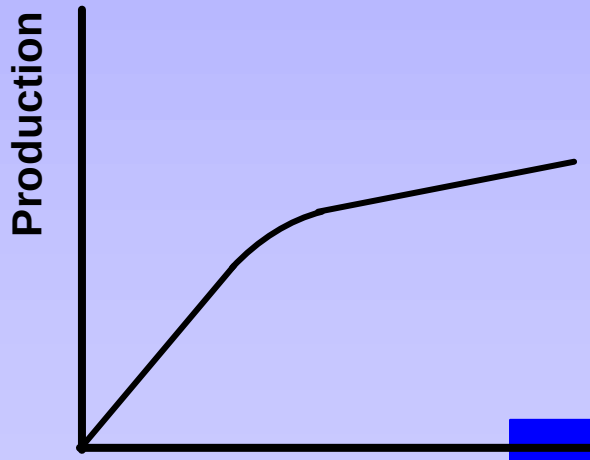


ENZYMATIC INTERESTERIFICATION : OPERATION

SINGLE FIXED BED REACTOR

- **Enzyme Activity decreases over time**
- **Flow to be adjusted to maintain conversion**
  - **Max. Initial flow :10 kg IE oil / kg catalyst.hr (blend dependent)**
  - **Regular analyses of the conversion required**
  - **Low production rate at the end of the enzyme's lifetime**

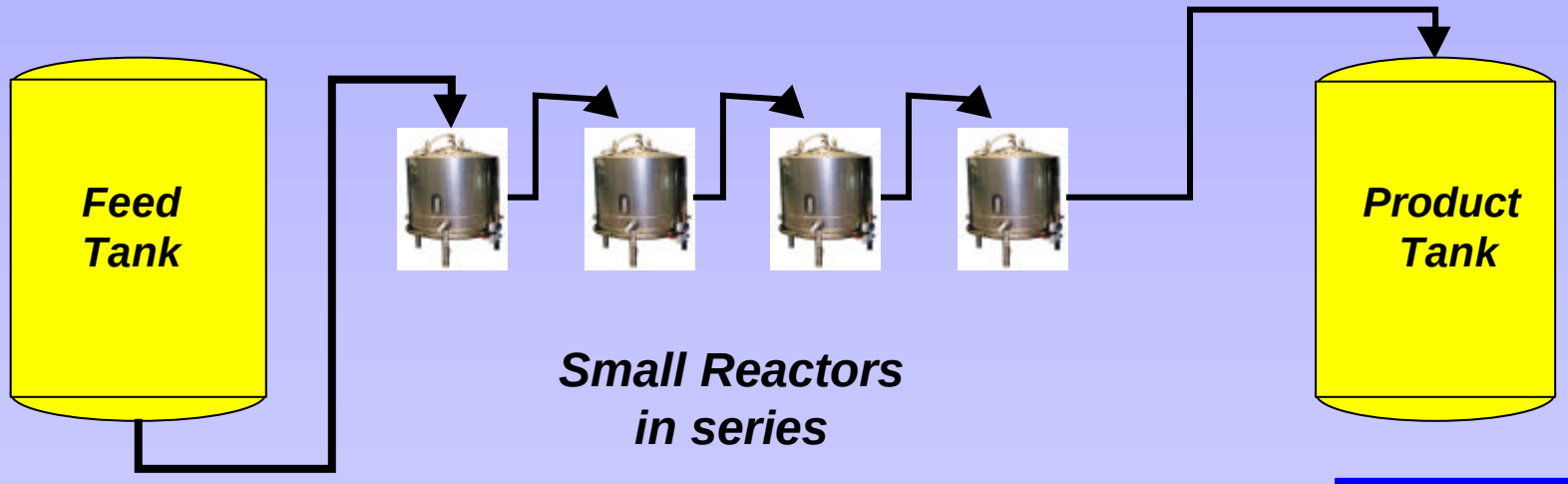




ENZYMATIC INTERESTERIFICATION : OPERATION

MULTIPLE FIXED BED REACTORS IN SERIES

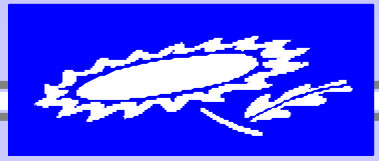
- **Different enzyme activity in each reactor**
  - **Lowest enzyme activity in first reactor : GUARD EFFECT**
  - **Highest enzyme activity in last reactor**
  - **Average production rate : 1-2 kg IE oil / kg enzyme.hr**



ENZYMATIC INTERESTERIFICATION : OPERATION

MULTIPLE FIXED BED REACTORS IN SERIES

- **GUARD EFFECT : only when reactors are in series**
  - **Absorption of 'harmful' components on (partially spent) enzyme (reactor 1)**
  - **Protection of more active enzyme in further reactors**
  - **Longer life time and higher productivity**
  - **Difficult to quantify**



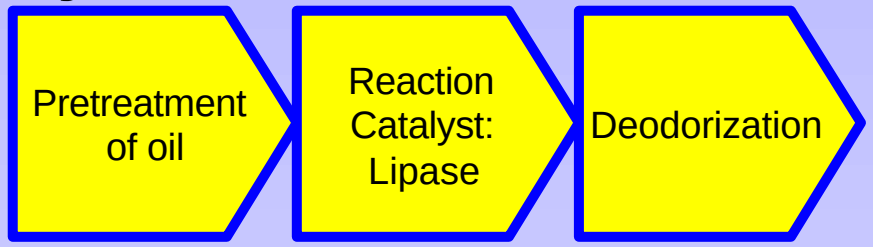
Process Comparison Chemical vs. Enzymatic Interesterification

Less steps with enzymatic process

Chemical interesterification

Pref. Batch Process

Enzymatic interesterification



Pref. Continuous process

Pilot enzymatic interesterification reactors with different enzyme capacities

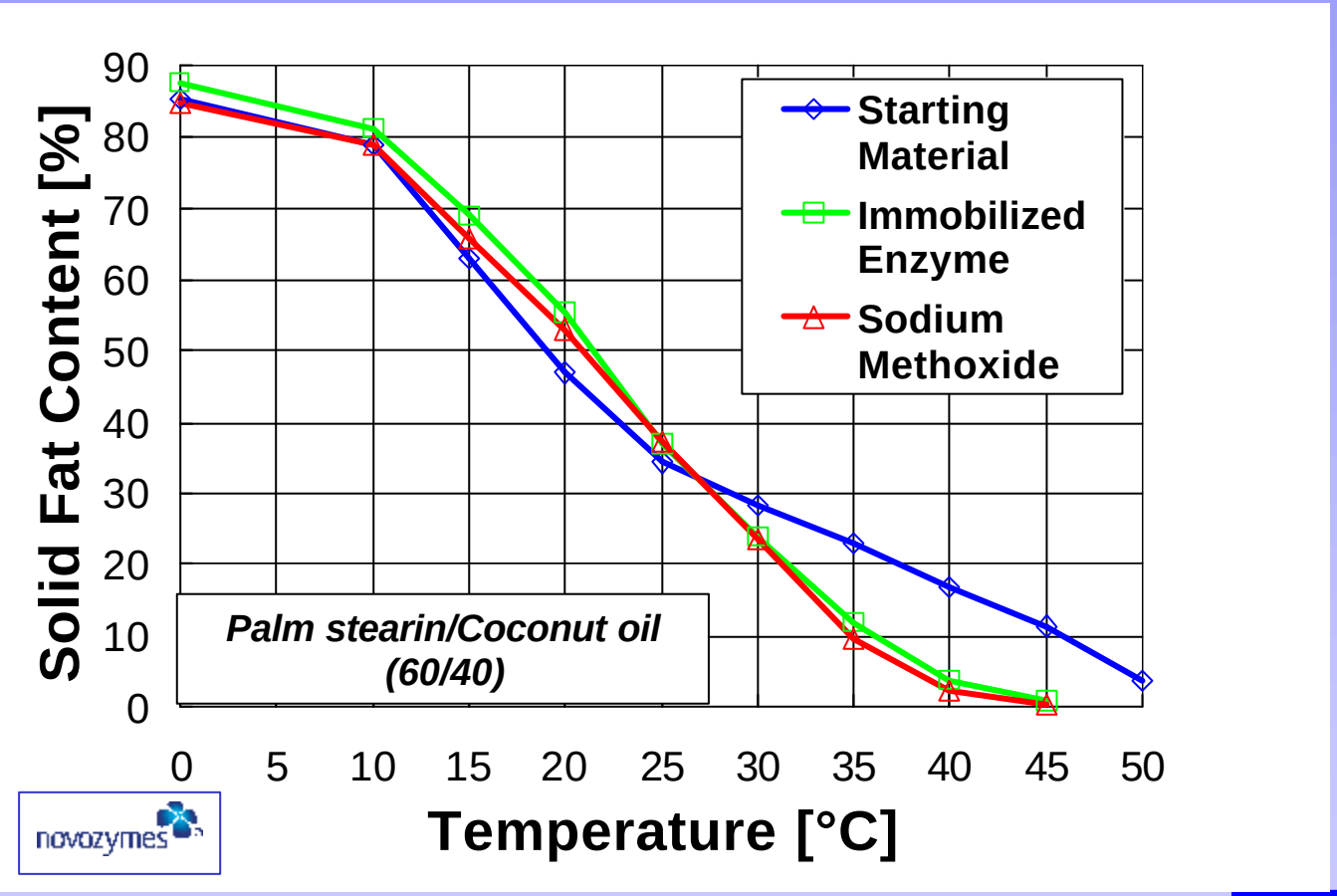
Single stage : 1 x 10 kg - 1 x 100 kg

Multiple stage :

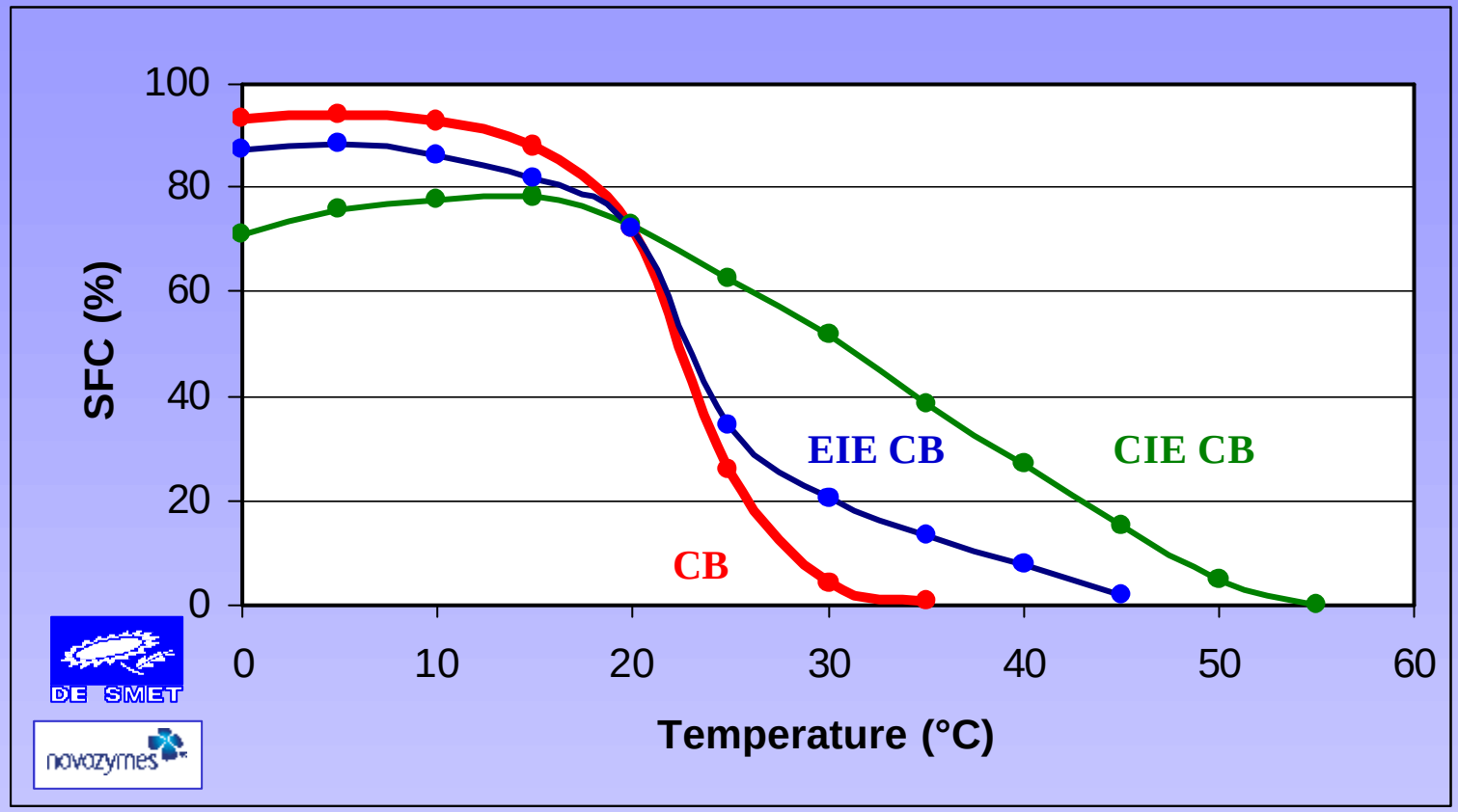
4 x 10 kg - 4 x 25 kg

Specific control of melting profile

Being able to control the melting characteristics, enzymatic interesterification can produce fat with physical properties similar to fat produced using chemical interesterification.



Interesterification of cocoabutter (high SUS fat)



Effect Chemical vs enzymatic I.E. on oil quality

PS / SFO	10/90			20/80			30/70			40/60			50/50		
	Feed	Chem	Enz	Feed	Chem	Enz	Feed	Chem	Enz	Feed	Chem	Enz	Feed	Chem	Enz
Color															
Yellow	11	15	10	15	10	9	16	11	8	19	16	8	19	18	10
Red 51/4	1.0	2.0	1.0	1.2	2.3	0.9	1.8	2.2	1.2	2	3	1.4	2.1	3.4	1.0
Tocopherol (ppm)	701	252	505	639	197	412	581	281	426	546	185	425	463	182	366
DAG (%)	1.5	3.9	2.0	1.7	3.7	3.0	1.9	4.5	3.5	2.14	4.2	3.0	2.4	4.9	3.5
Trans fats (%)	0.50	0.67	0.75	/	/	/	0.50	0.62	0.61	/	/	/	/	/	/

- EIE oil has a lighter colour than CIE oil (after pretreatment)
- EIE oil has a higher tocopherol content than CIE oil
- EIE oil has a lower diglyceride content than CIE oil

ENZYMATIC vs CHEMICAL INTERESTERIFICATION

+ CHEMICAL INTERESTERIFICATION

Fully random : final product determined by FA comp of blend, not by triglyceride composition

Highly reproducible and cost-effective

Easy Process (batch)

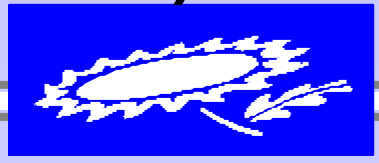
- CHEMICAL INTERESTERIFICATION

Hazardous catalyst: safe handling required

Side reactions can occur (at high catalyst conc./temp.)

Risk of flavor reversion & reduced stability

Loss of valuable minor-components (e.g. tocopherols)



ENZYMATIC vs CHEMICAL INTERESTERIFICATION

+ ENZYMATIC INTERESTERIFICATION

Cost-effective when running continuously on 'clean' bulk fat

Simple, clean & safe – 'Natural' process

No side reactions, no supplementary post-bleaching

Lower capital investment cost compared to chemical process

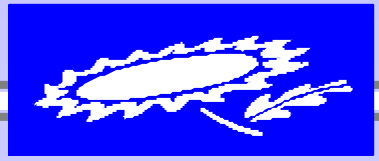
- ENZYMATIC INTERESTERIFICATION

Sensitive & costly catalyst (temp, moisture PV, gums, impurities)

Less easy stock-change (cross-contamination)

To certain extent triglyceride composition dependent

New & still rather unknown



Investment and operating cost – A comparison

Cost in US$/ton	Chemical IE	Enzymatic IE	Hydro
Investment cost	6.5	3.7	9.0
Operating cost	21.0	34.7	48.7
Oil losses	10.5	2.3	0.7
Total costs	**38.0**	**40.8**	**58.4**

De Smet Group

Worldwide Partnership