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Developments in Hydrogenation and Interesterification to comply with the New Nutritional Standards for Edible Oils

Dr. Ir. W. De Greyt and Dr.ir. M. Kellens

De Smet-Ballestra

Zaventem, Belgium

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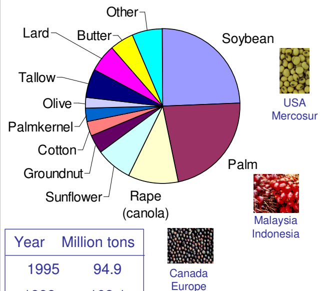

Year	Million tons
1995	94.9
1998	103.1
2002	120.9
2005	144.5

	•Oil type	•2004 •Mio tons	•2004 •%
76.6%	•Soybean	•31.4	•24.4
	•Palm	•28.4	•22.1
	•Rapeseed	•13.9	•10.8
	•Sunflower	•9.5	•7.4
	•Groundnut	•4.8	•3.7
	•Cotton	•4.1	•3.2
	•Palmkernel	•3.5	•2.7
	•Olive	•2.8	•2.2
17.0%	•Tallow	•8.1	•6.3
	•Lard	•7.3	•5.7
	•Butter	•6.5	•5.1
6.4%	•Other	•8.2	•6.4
	•Total	•128.5	•100

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CURRENT SITUATION

Overproduction / overconsumption in developed countries,
Shortage in less developed countries.

US / Europe ⇕ Bangladesh/India

45-55 kg oil/capita ⇕ 10-15 kg oil/capita ⇔ WHO target 20-25 kg p.p.

Year	Expected growth rate Consumption kg/capita	Population Billion	Demand Million tons
1980	12.8	4.4	56.8
1990	15.3	5.3	80.5
2000	18.3	6.1	110.5
2010	20.9	6.6	139
2020	23.8	7.4	175.3

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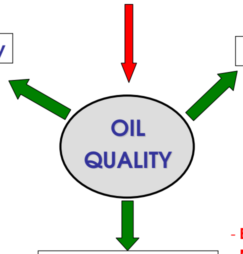
Food Oils & Fats

Composition
- (Tri-)acylglycerols
- Free Fatty Acids
- Phospholipids
- Minor components
- Contaminants

Quality
- Organoleptic/stability
- Functional properties
- Nutritional quality

Applications
- Salad oils, Frying Oils
- Margarine fats, Shortenings
- Specialty Fats
- Structured Lipids

OIL PROCESSING – MODIFICATION



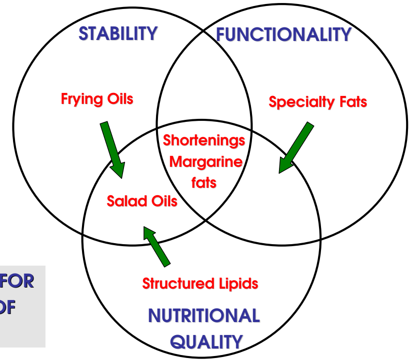
organoleptic/stability
- Bland taste, no odor
- Light color (brilliant)
- High thermal stability
- High oxidative stability
- Long shelf life

Functional Properties
- Good melting profile
- Desired Plasticity
- Crystallisation

Nutritional Quality
- Balanced FA composition
- No *trans* FA
- High tocopherol content
- Low fat degradation
- No contaminants,…..

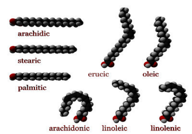
OILS AND FATS IN FOOD PRODUCTS

Application	Feedstock oil	Required quality
Frying oils	Refined vegetable oils Liquid olein fractions	High stability, Long shelf life
Salad oils	Refined vegetable oils (soy, rape, sun, olive,...)	High stability, Organoleptic quality
Margarine fats Shortenings	Modified vegetable oil blends Hard stearin fractions	High stability, High nutritional quality
Specialty fats	Refined vegetable butter (Hardened) fractions (CBS,CBR) Hard stearin fractions	Crystallisation behaviour Melting profile
Structured lipids	Refined vegetable oils	High nutritional quality



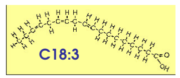
INCREASED ATTENTION FOR NUTRITIONAL QUALITY OF FOOD OILS AND FATS

CURRENT NUTRITIONAL STANDARDS FOR FOOD OILS - I



Nutritional aspects of Fatty Acids

ESSENTIAL FATTY ACIDS
- 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

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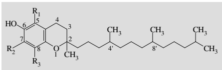
CURRENT NUTRITIONAL STANDARDS FOR FOOD OILS - II

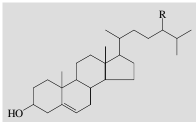
VALUABLE MINOR COMPONENTS

Tocopherols/Tocotrienols



Presence in oils desired because of their Vitamin E activity

Phytosterols



- Positive Nutritional Characteristics
- Reduction of blood cholesterol levels
- Added to margarine fats (8-10%)

CONTAMINANTS

- Pesticides, PAH's, dioxins, PCB's
- May only be present at 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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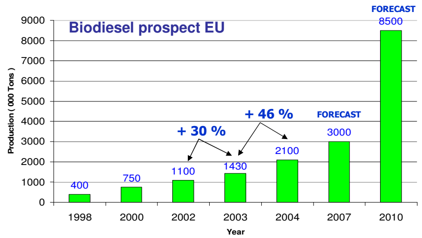
FOOD OILS AND FATS FOR THE FUTURE

Commodity Oils for Standard Applications

- Based on largely available feedstocks (soy, palm, rape, sun,...)
- Also potential feedstocks for technical applications (biodiesel)



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FOOD OILS AND FATS FOR THE FUTURE

High Quality Oils for niche applications

Novel Oils to which a specific minor ingredient is added such as natural tocopherol enriched oils or fats enriched with phytosterols (BENECOL)

Special **"diet" oils** (e.g. diglyceride oils) that aim at a weight reduction (ENOVA)

Organic oils that are only minimally processed to preserve maximally product quality (SOYA GOLD)

"balanced" oils that are oil blends with an optimum fatty acid composition (PUFA/MUFA/SAFA **1:1:0.4**)

➡ **IMPROVED REFINING AND MODIFICATION TECHNOLOGIES**

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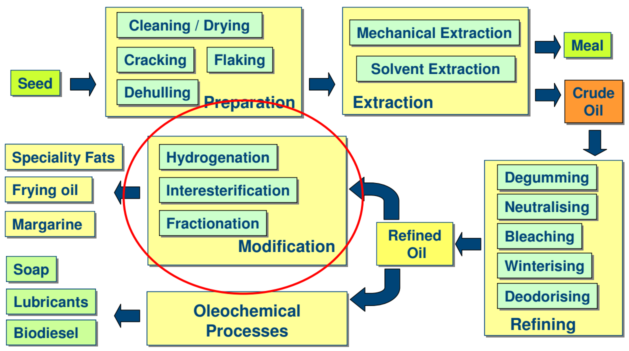

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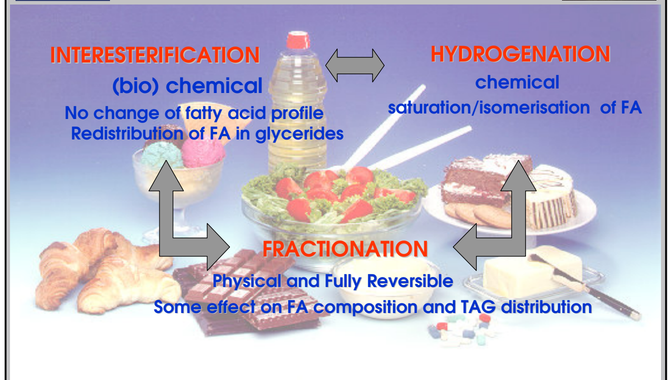

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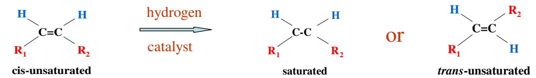
HYDROGENATION



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

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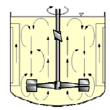
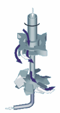
PARTIAL HYDROGENATION OF SOYBEAN OIL





Characteristics	Brush	Shortening	Margarine	Coating	Stearin
IV	115	75	70	75	<5
Trans-isomers (%)	15	30	50	65	-
C18:0 absolute (%) increase (%)	5 1	9 5	7 3	7 3	85 80
Temperature (°C)	170	150	210	210	220
Time (min)	30	60	60	60	300-150
H_2 pressure (bar)	1	2	1	2	max
Catalyst type	selective	selective/non select.	selective	Ni-S	high active
Amount (%) Ni (%)	0.02 0.005	0.04 0.01	0.04 0.01	0.2-0.4 0.05-0.1	0.2-0.6 0.05-0.15

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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*, no UFA)
  - → Low *trans* hydrogenation

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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*
  - → Supercritical hydrogenation
  - → Continuous membrane hydrogenation

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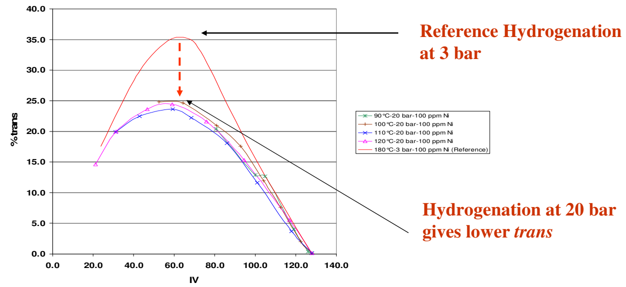
HIGH PRESSURE HYDROGENATION OF SOYBEAN OIL



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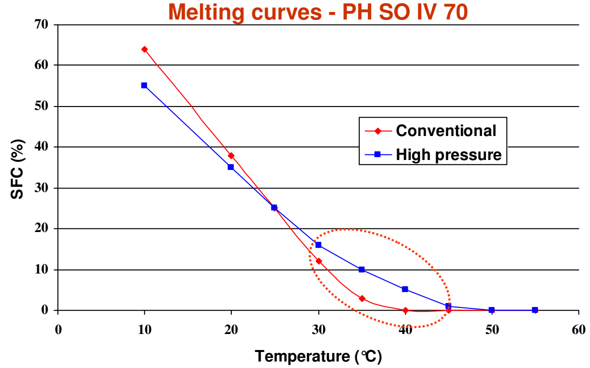
Melting curves - PH SO IV 70



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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%

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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

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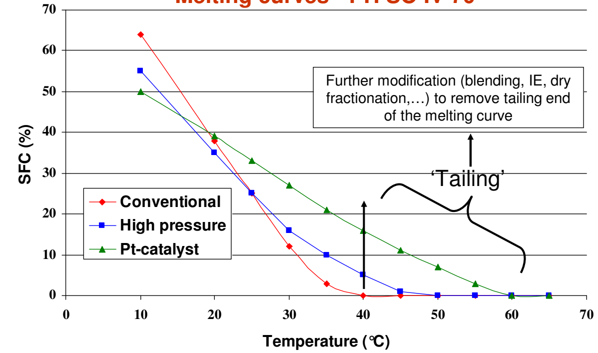
Melting curves - PH SO IV 70



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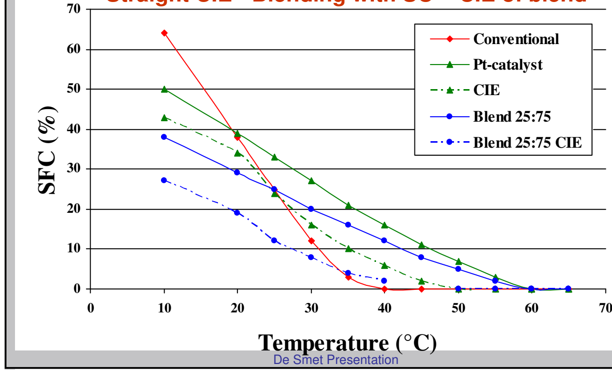
Straight CIE - Blending with SO – CIE of blend



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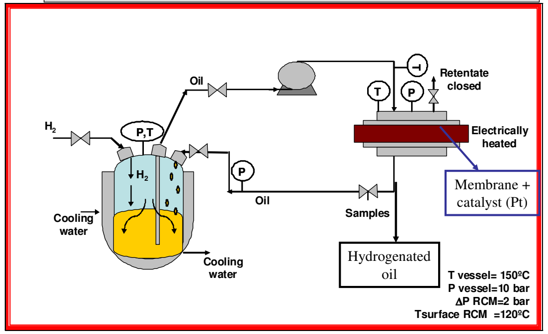
CONTINUOUS MEMBRANE HYDROGENATION



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Parameter	Feedstock	Membrane hydrogenated SFO		
Temperature (°C)	-	100	120	
Pressure (bar)	-	4	10	
Membrane catalyst	-	Pt	Pd	Pt
Time (min)	-	480	240	240
IV	126	89	53	60
Reaction rate (ΔIV/min)	-	0.08	0.30	0.28
FAC (%w:w)				
C18:0	3.0	-	32.2	25.6
C18:1	29.8	-	55.7	62.1
C18:2	59.0	-	2.5	0.9
TFA	-	***20.0***	***26.0***	***25.0***
SFC (% @ °C)				
20	-	-	86.0	76.4
25	-	-	77.4	65.5
30	-	-	66.5	52.8
35	-	-	53.1	38.4
40	-	-	36.7	23.9

Results obtained within the CAMERTOIL project (EU funded R&D project)

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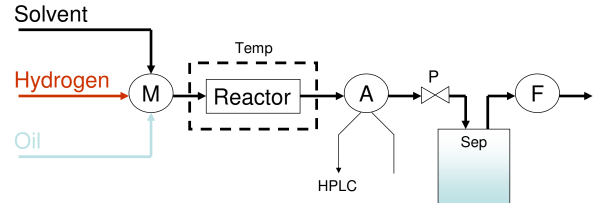
SUPERCRITICAL HYDROGENATION



Solvents : butane, propane,
Temperature : 50-120℃
Total pressure : up to 200 bar
Oil in solvent conc : 20-50 % (w/w)

→ Very fast reaction
40 ΔIV/min

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SUPERCRITICAL HYDROGENATION

Process claims

Extremely high reaction rates with low reaction volumes
Almost no formation of *trans* fatty acids
Very selective process : C18:3 → 0 with no increase of C18:0

Supercritical hydrogenation of soybean oil

IV 60 with total *trans* < 2.5% and C18:0 < 30%
Similar results as during hydrogenation with precious metal cat
Process seems more suitable for full hydrogenation

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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 : 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)

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INTERESTERIFICATION : CURRENT SITUATION

CHEMICAL INTERESTERIFICATION

- Low catalyst (NaOMe) consumption (0.05-0.1%) due to better oil pretreatment
- Lower oil losses due to lower catalyst consumption and dry catalyst inactivation
- Dry catalyst remains difficult to handle and can induce unwanted side-reactions
  (e.g. degradation of tocopherols, color fixation,….)

ENZYMATIC INTERESTERIFICATION

- Less expensive and more stable enzymes are commercially available
- Higher productivity resulting in an 'economical' operating cost
- 'Random' enzymatic interesterification for the production of margarine fats
- 'Specific' enzymatic (inter)esterification for production of structured lipids

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Chemical versus Enzymatic interesterification

Chemical interesterification

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

Batch Process in stirred tank reactors

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

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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

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PROCESS ASPECTS

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' IE : min. productivity (valid for good feedstock) : 2.5 ton EIE oil/kg
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 IE oil/kg enzyme.hr
Enzyme in use for 1250-2500 hr (50-100 days)

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Chemical versus Enzymatic interesterification

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

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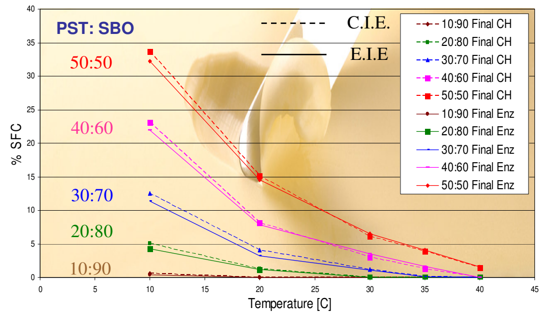
Enzymatic interesterification : examples



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 without bleaching has less colour than CIE after bleaching
- EIE oil conserves tocopherol
- EIE forms less DAG than chemical interesterification

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Chemical versus Enzymatic interesterification

IE of Soybean Oil (IV 130) with FH Soybean Oil (IV 2)

100 TPD – 330 DPY ⟶ 33000 TPY

	Chemical IE		Enzymatic IE	
Operating cost (US$/ton)	% $NaOCH_3$ 0.05	0.1	Ton oil/kg enzyme 2.5	4.0
Investment cost	9.09	9.09	5.15	5.15
Operating cost	19.51	21.01	34.71	25.71
Oil Losses	5.95	10.05	2.45	2.35
Total cost	**34.6**	**40.6**	**42.3**	**33.2**

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Thank you for your attention