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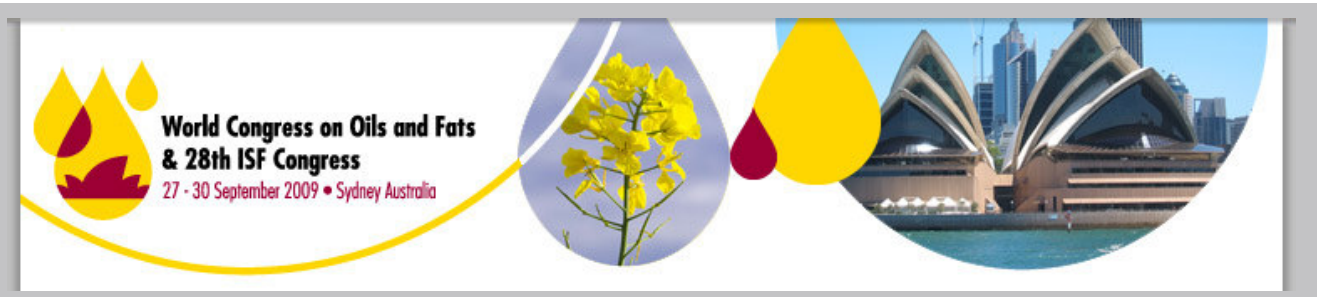
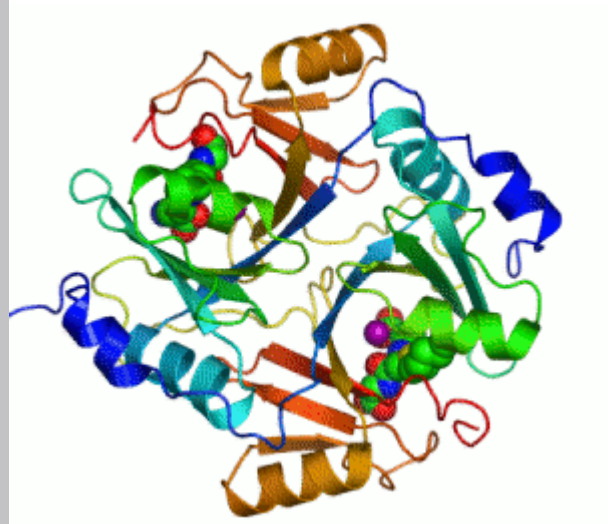


Oil Processing Challenges in the 21th Century:

Enzymes Key to Quality and Profitability



Marc Kellens
Desmet Ballestra Group,
Zaventem, Belgium

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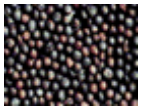
World Vegetable Oil Production

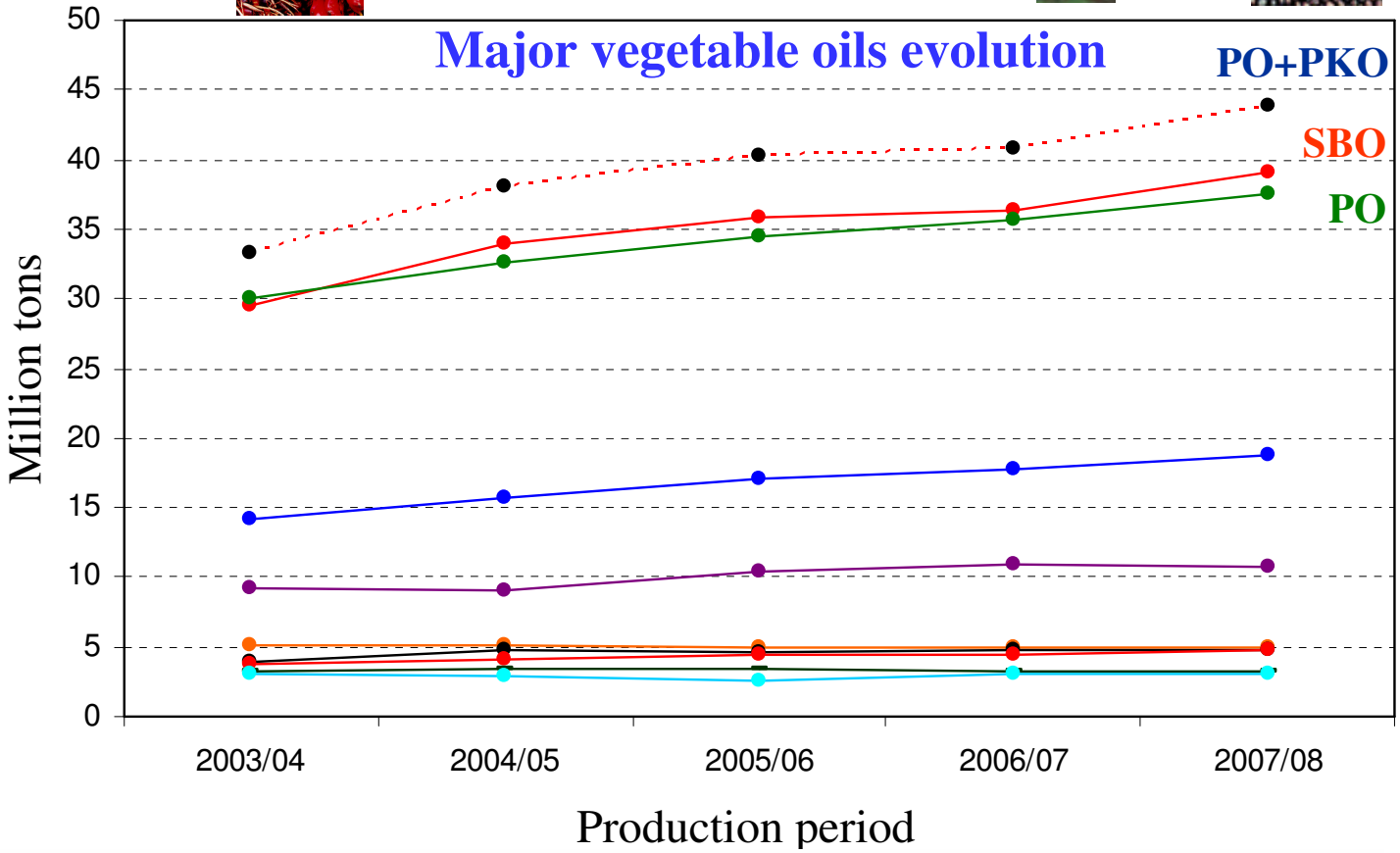
Malaysia
Indonesia

USA
Mercosur

Canada
Europe



> 85%



	%
Palm	30.1
Soybean	29.4
Rapeseed	14.4
Sunflower	8.7
Peanut	4.3
Cotton	4.0
Palm kernel	3.7
Coconut	2.9
Olive	2.5

USDA United States Department of Agriculture

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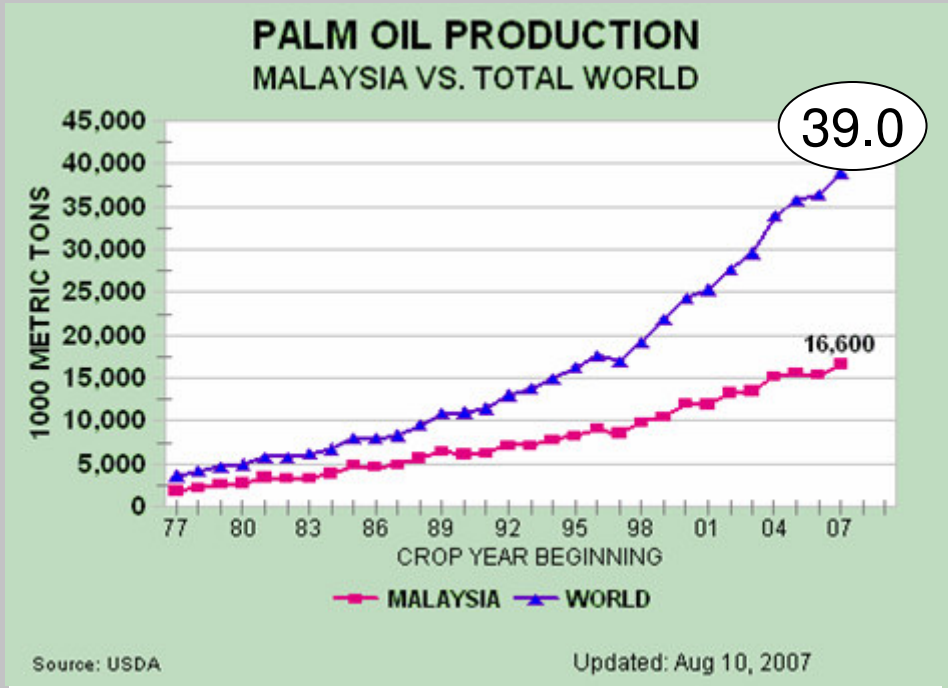
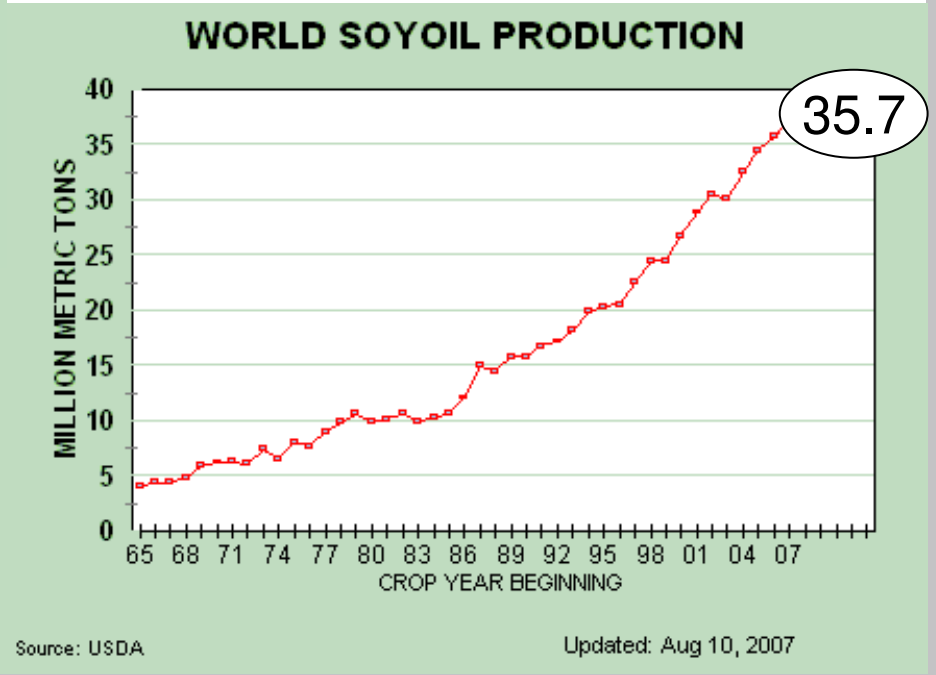
Palm & Soybean oil production evolution



PO = high sat oil

In 30 years a 10-fold increase



SBO = high unsat oil

In 40 years a 7-fold increase

Chicago Board of Trade

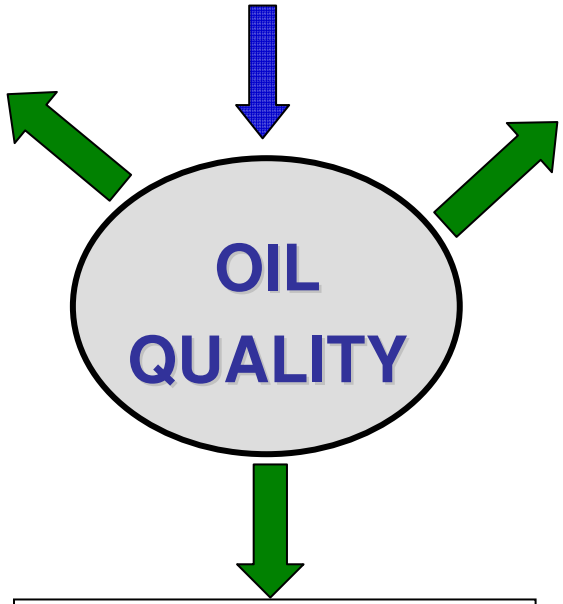
Trends in Oil Processing

Increased demand for high quality oils

Organoleptic/stability

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

Refining



Functional Properties

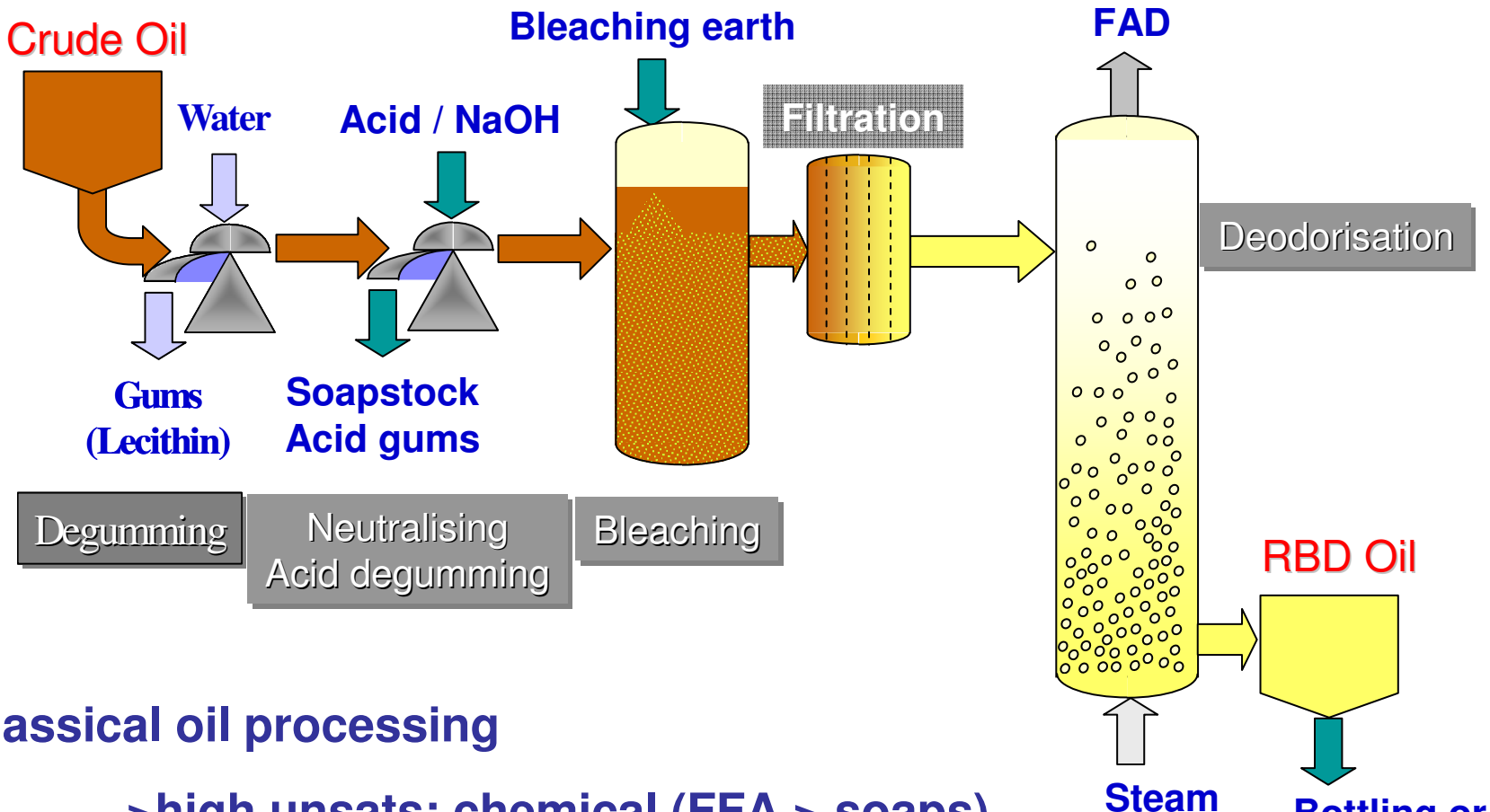
- Good melting profile
- Desired Plasticity
- Crystallisation kinetics

Modification

Nutritional Quality

- Balanced FA composition (SFA/MUFA/PUFA, ω3-6)
- Low or no *trans* FA (< 1%)
- High natural antioxidants (tocopherols) and vitamins

Trends in Oil refining



Classical oil processing

- >high unsats: chemical (FFA > soaps)
- >high sats: physical (FFA > FAD)

Trends in Oil refining

Strong demand for more efficient processes

* ***More cost efficient processes:***
  - Lower investment & processing costs,
  - Valorisation and/or reduction of by-products
* ***Flexible plants:***
  - Capable of processing multiple oils
* ***Fully automated plants:***
  - Higher consistency of operation, lower manpower cost
* ***Larger capacities (economics of scale):***

200-300 TPD ⟶ 1000 -> 2000 TPD

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Trends in Oil refining

Refineries need to reply to more and more stringent environmental rules and at same time need to improve their efficiency on both operational cost and delivery of highest quality

Trend: - less chemicals, more physical treatment

- more sustainable, less energy
- less environmental impact: zero effluent
- maximum retention of “nutritional” quality

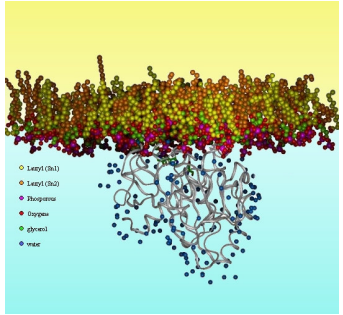
More bio, eco, green… enzymes a solution?

Enzymatic oil processing

Trends in edible oil processing

- More (energy) efficient & environmentally friendly processes
- Increased attention for the nutritional quality
- Milder processing giving more 'natural' products

→ ENZYMATIC PROCESSES



Enzymatic processing

Aspects of enzymatic process

PRO'S

- Mild , natural process
- Environmentally friendly
- Very specific, less random

CON'S

- Sensitive to heat and pH
- Sensitive to feedstock quality (impurities)
- Cost (mostly higher than conventional chemicals)

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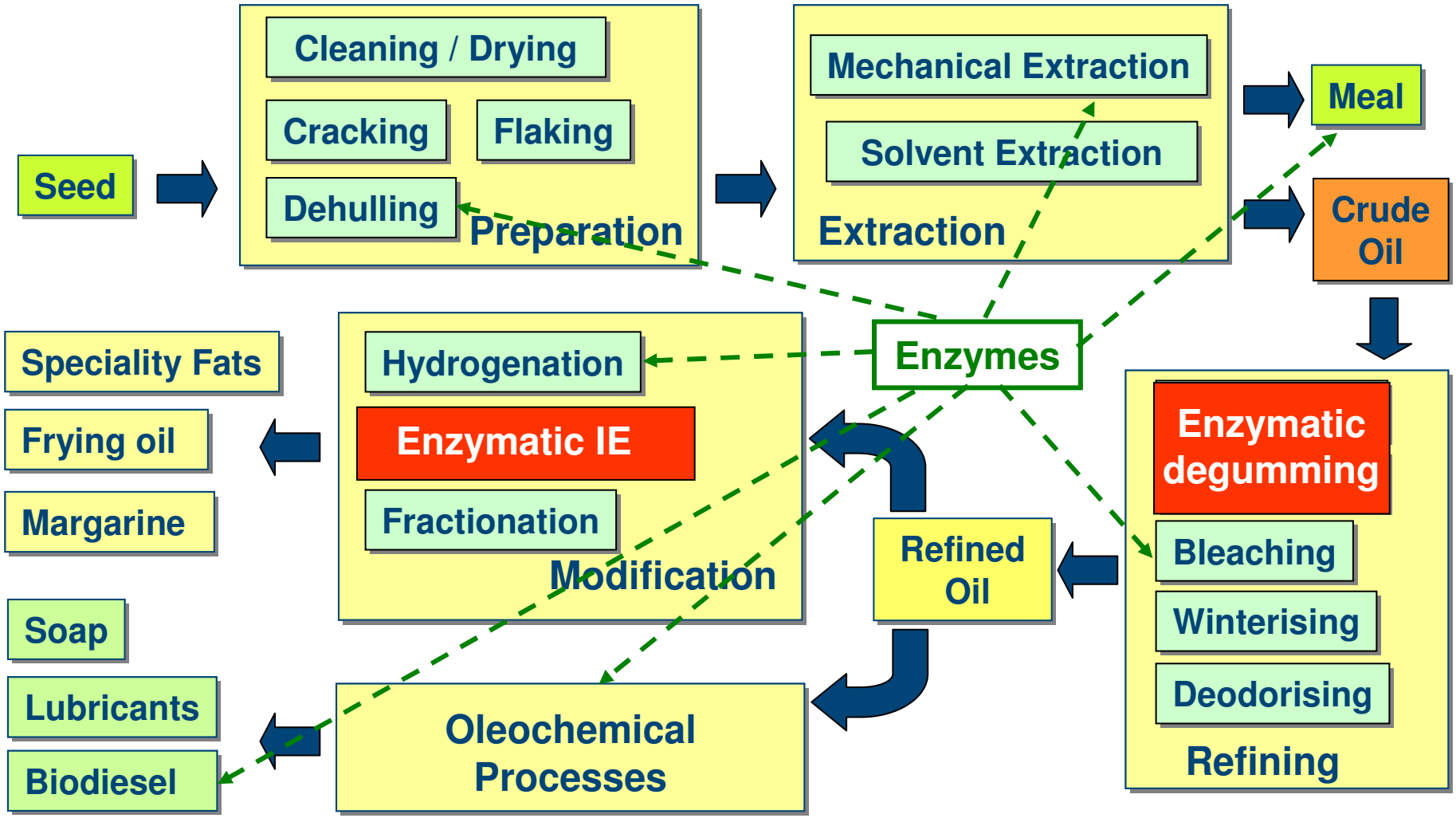
Enzyme processes in Oilseed/Oil processing



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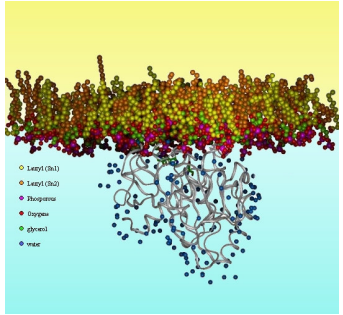
Enzymatic degumming

Main driver: oil quality or oil profitability?

° more selective than chemicals, thus attacking ONLY phospholipids

° treated gums contain less entrained oil, so higher yield

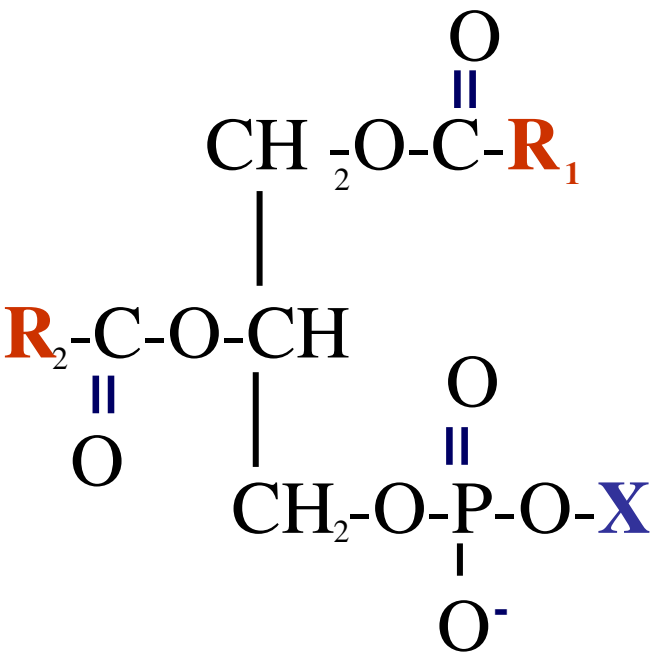
° with cost of enzymes << additional oil yield **: a winner**



Why does it take so long to convince industry?

Enzymatic degumming

PHOSPHOLIPIDS



R_1, R_2 : Fatty acids

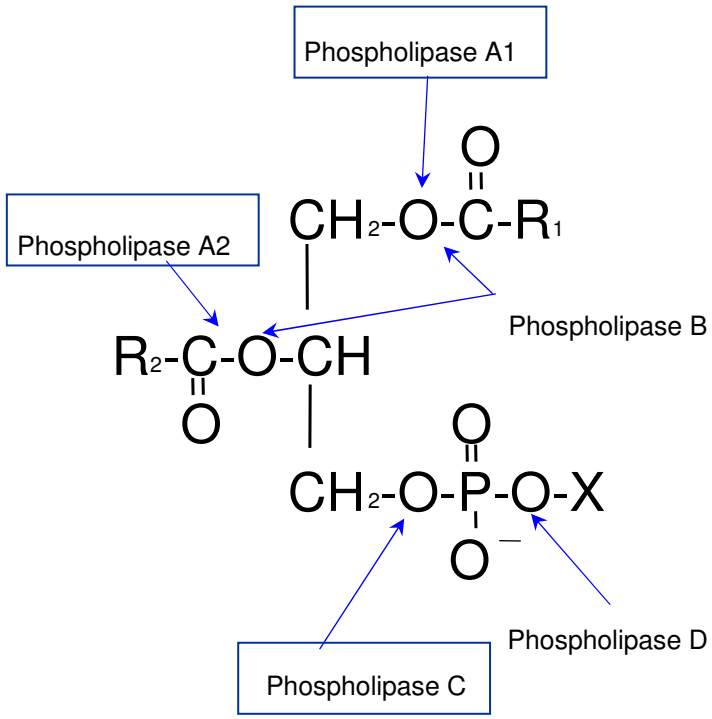
X : H (**PA**), choline (**PC**), ethanolamine (**PE**), serine (**PS**), inositol (**PI**),

⇓

Hydratable PL ⟷ Non-hydratable PL

Enzymatic degumming

PHOSPHOLIPASES



X = H, choline, ethanolamine, serine, inositol, etc.

5 subclasses of Phospholipases

A1, A2, B, C and D

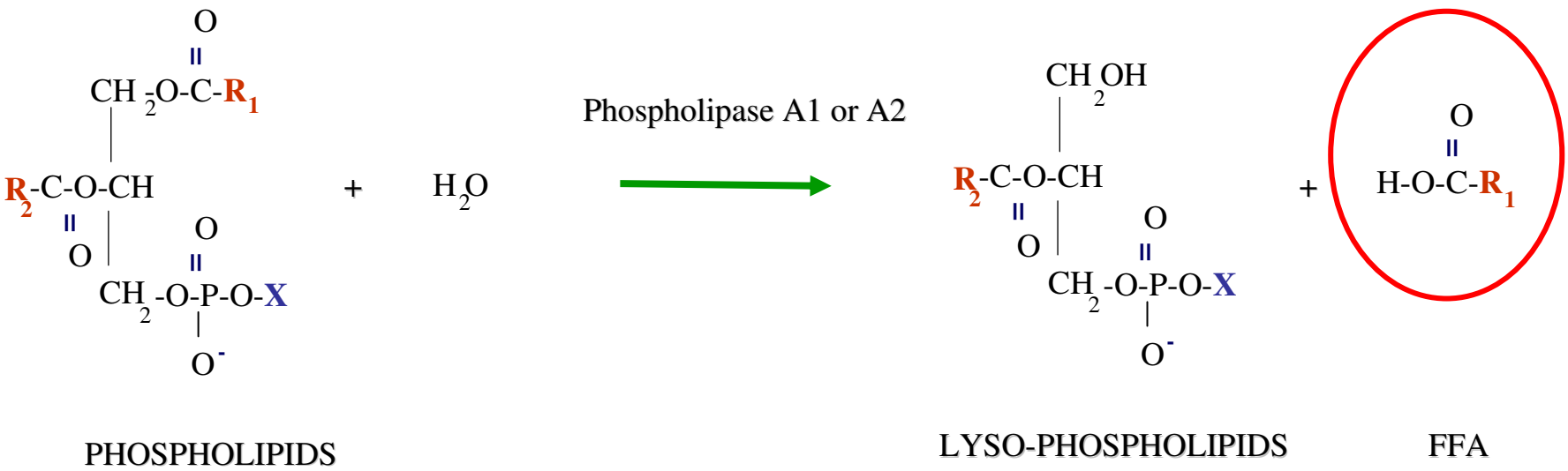
Phospholipases **A1, A2, C**

are commercially available

(Novozymes, Danisco, Verenium)

Enzymatic degumming

ENZYMATIC CONVERSION PLA1/PLA2



- Conversion of (non-hydratable) PL in hydratable Lyso-PL and FFA
- 0.036% FFA formed for each 0.1% PL converted

Enzymatic degumming

Past situation EDG

- **ENZYMAX® process by Lurgi**
  - **First industrial EDG process started early 90's**
  - **Use of heat stable phospholipase A2**
  - **Efficient if on high Q and fresh crude oil**
  - **High enzyme cost made enzyme recycling necessary**
  - **From porcine pancreas ⟶ problems with acceptability**
  - **limited sources and availability of enzyme**

Introduction of costefficient physical degumming alternatives (TOP, SOFT, IMPAC) blocked breakthrough of EDG

Enzymatic degumming

Re-introduction EDG

novozymes
Unlocking the magic of nature

- **Improved EDG by Novozymes (end 90's)**
  - Phospholipase A1 (Lecitase Ultra – Novozymes)
  - Stable and less expensive enzymes (third generation)
  - Temperature optimum : 55°C, pH optimum : 6
  - Residence: 3-6 hrs = f(catalyst consumption) ⟶ < 2 hr !
  - No enzyme recycling necessary , comsumption 50 ppm
  - Microbial origin ⟶ No problems with acceptability

Several industrial plants running today costcompetitive
Main negative point: what to do with high FFA ?

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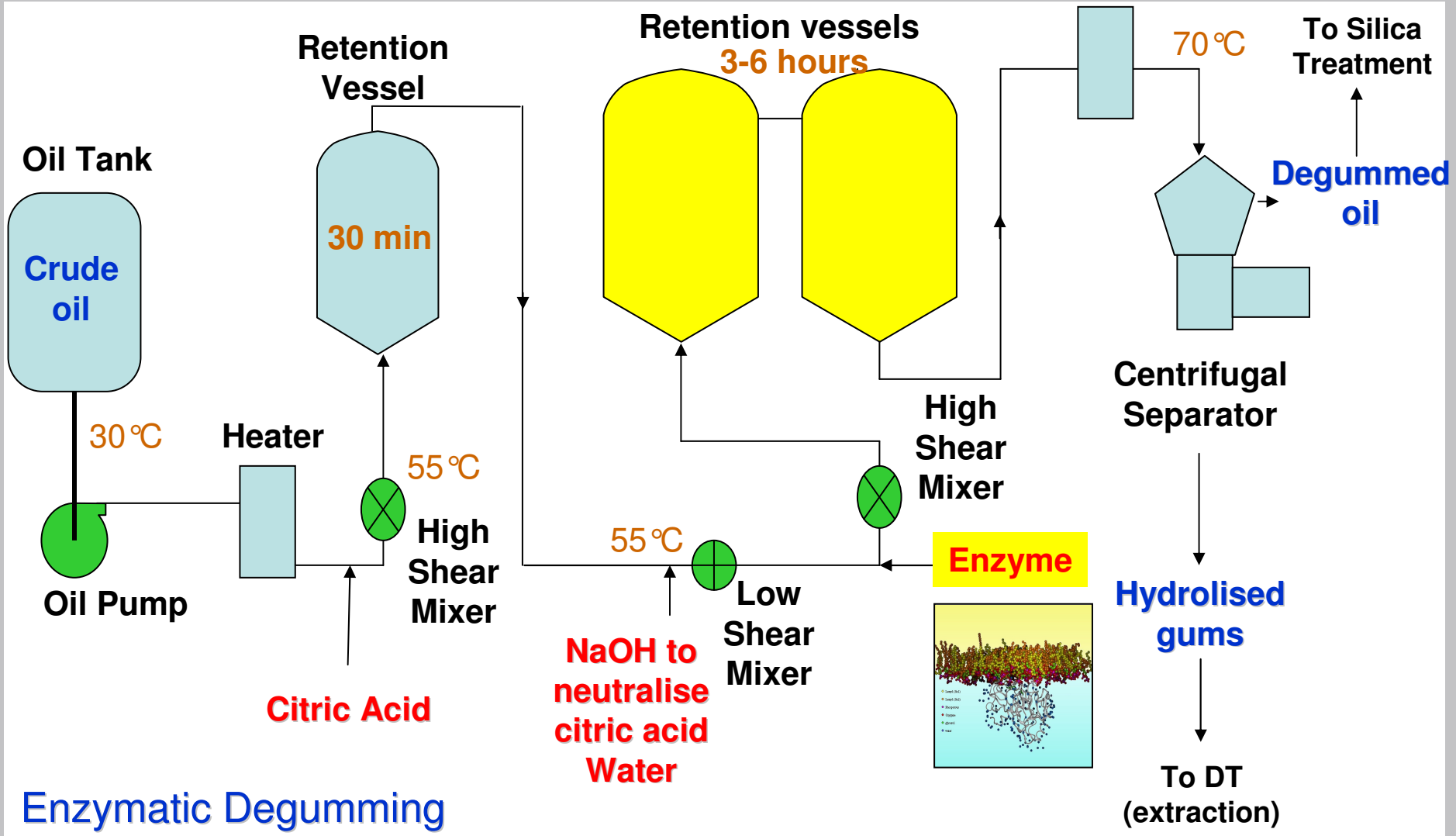
Enzymatic degumming PLA1 (Lecitase Ultra)



Enzymatic Degumming

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Case study
Conventional SBO water- followed by acid-degumming

PL: phospholipids

P: phosphorous

NO: neutral oil

LL: lysolecithin

WDG :waterdegumming

ADG: acid degumming

Crude soybean oil
100%
2,50% PL

Gums
2,80% yield
2,00% PL
0,80% NO

WDG
97,2%
0,50% PL

Acid gums
0,90% yield
0,45% PL
0,45% NO

ADG
96,30%
0,05% PL

total loss: 3,70%

1000 ppm P

200 ppm P

20 ppm P

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Case study
Crude SBO PLA1 degumming

70% conversion PL to LL+FFA

Partial EDG

Crude soybean oil
100%
2,50% PL

Gums
1,93% yield
1,68% PL
0,25% NO

PLA EDG
98,1%
0,25% PL
0,57% FFA ↗

Acid gums
0,40% yield
0,20% PL
0,20% NO

ADG
97,67%
0,05% PL

total loss: 2,33%

Full EDG

Crude soybean oil
100%
2,50% PL

Gums
2,10% yield
1,83% PL
0,27% NO

PLA EDG
97,9%
0,05% PL
0,62% FFA ↗

Acid gums
0,00% yield
0,00% PL
0,00% NO

ADG
97,90%
0,05% PL

total loss: 2,10%

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Enzymatic degumming PLA1

- **Case study crude SB0 2.5% PL (1000 ppm P)**
  - Full EDG vs (WDG & ADG)
  - P < 20 ppm
  - Gain in crude oil yield: about 1.3-1.6%
  - Gain in FFA: about 0.5-0.6%

  - Net gain in RBD oil yield after full refining: 0.8-1%
  - Net gain in FAD yield after full refining: 0.5-0.6%

    FAD ≠ loss !

  - No soaps, gums but also no lecithin !

Enzymatic degumming

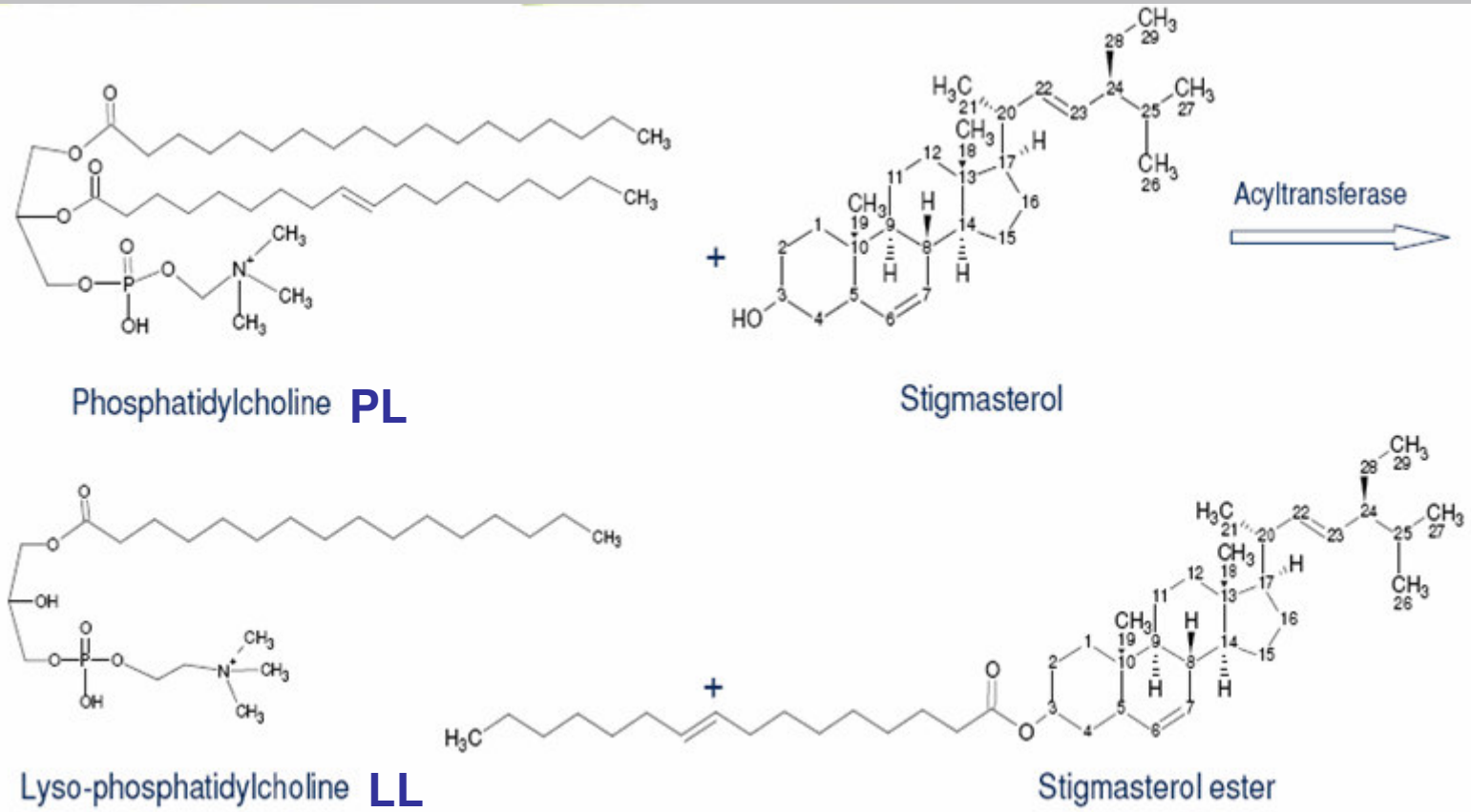
DANISCO

New enzymes (1)

- **EDG by Danisco**
  - Acyltransferase (~PLA2 type) (Lysomax Oil – Danisco)
  - Temperature 50-60°C and pH 5-7
  - Very short reaction (30 min!)
  - No enzyme recycling , comsumption 100 ppm
  - Microbial origin → No problems with acceptability
  - (Part of) FFA esterified with free sterols, giving less/no FFA

No industrial plants yet running, results to be confirmed

Enzymatic degumming using Acyltransferase (AT) (Danisco)



- Conversion of PL in LL and FFA (part) re-esterified with sterols
- 0.036% FFA formed for each 0.1% PL converted to LL
- 0.065% FFA re-esterified with each 0.1% free sterols,

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Case study
Crude SBO AT degumming

70% conversion PL to LL+FFA **Part FFA esterified with sterols**

No FFA increase

Crude soybean oil
100%
2,50% PL
0,30% free sterols

Gums
2,60% yield
2,27% PL
0,34% NO

AT EDG
97,4%
0,05% PL
0,00% FFA ↗
0,50% est. sterols

Acid gums
0,00% yield
0,00% PL
0,00% NO

ADG
97,40%
0,05% PL
0,50% est. Sterols

total loss: 2,60%

With FFA increase

Crude soybean oil
100%
2,50% PL
0,30% free sterols

Gums
2,10% yield
1,83% PL
0,27% NO

AT EDG
97,9%
0,05% PL
0,43% FFA ↗
0,50% est. sterols

Acid gums
0,00% yield
0,00% PL
0,00% NO

ADG
97,90%
0,05% PL
0,50% est. Sterols

total loss: 2,10%

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Enzymatic degumming AT

- **Case study crude SB0 2.5% PL, 0.3% Sterols**
  - Full EDG vs (WDG & ADG)
  - P < 20 ppm
  - Gain in crude oil yield: about 1.1-1.6%
  - Gain in FFA: about 0-0.4%

  - Net gain in RBD oil yield after full refining: 1.1-1.2%
  - Net gain in FAD yield after full refining: 0.0-0.4%

Any effect esterified vs free sterols on oil stability?

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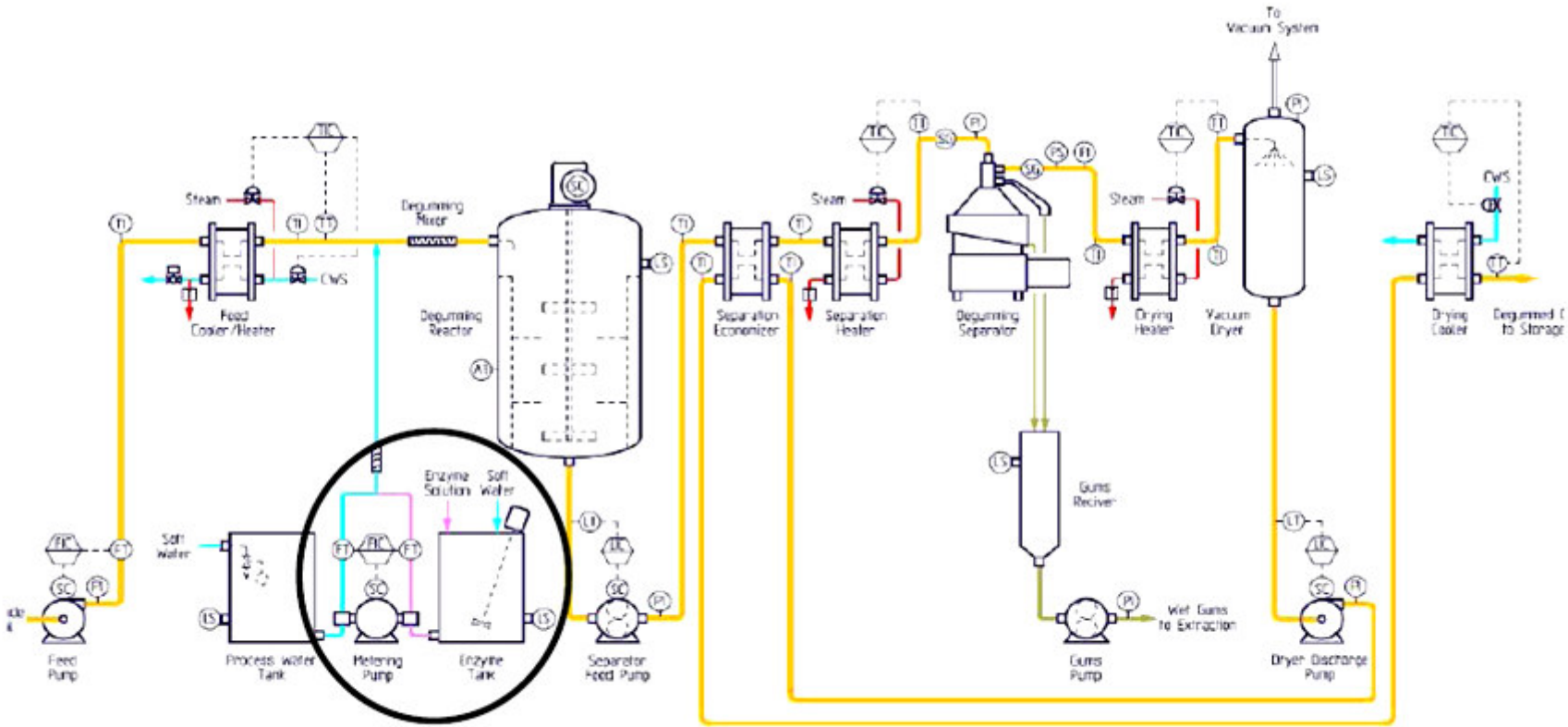
Enzymatic degumming using AT (Lysomax Oil)



Lysomax Oil degumming Process very similar to Lecitase Ultra (less residence)

Enzymatic degumming

Recent introduction of new enzymes (2)

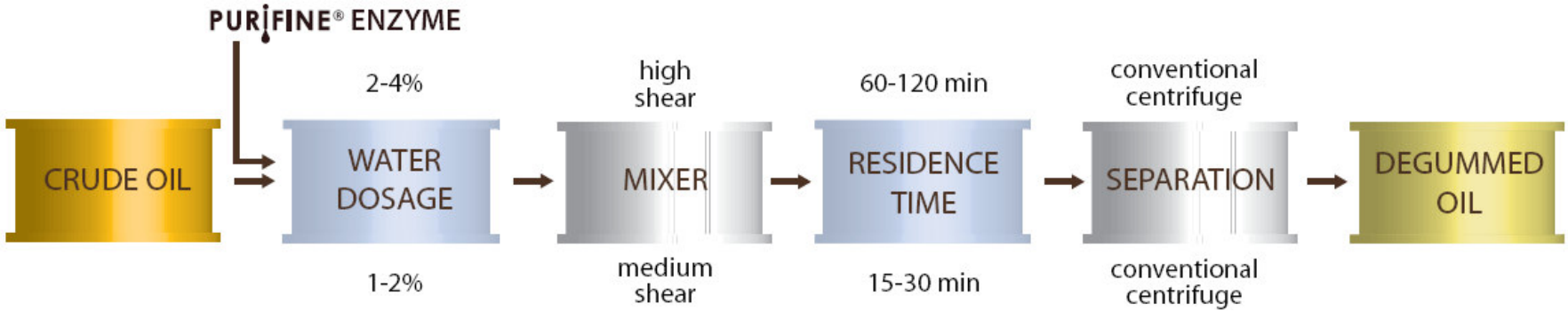
- **EDG by Verenium**

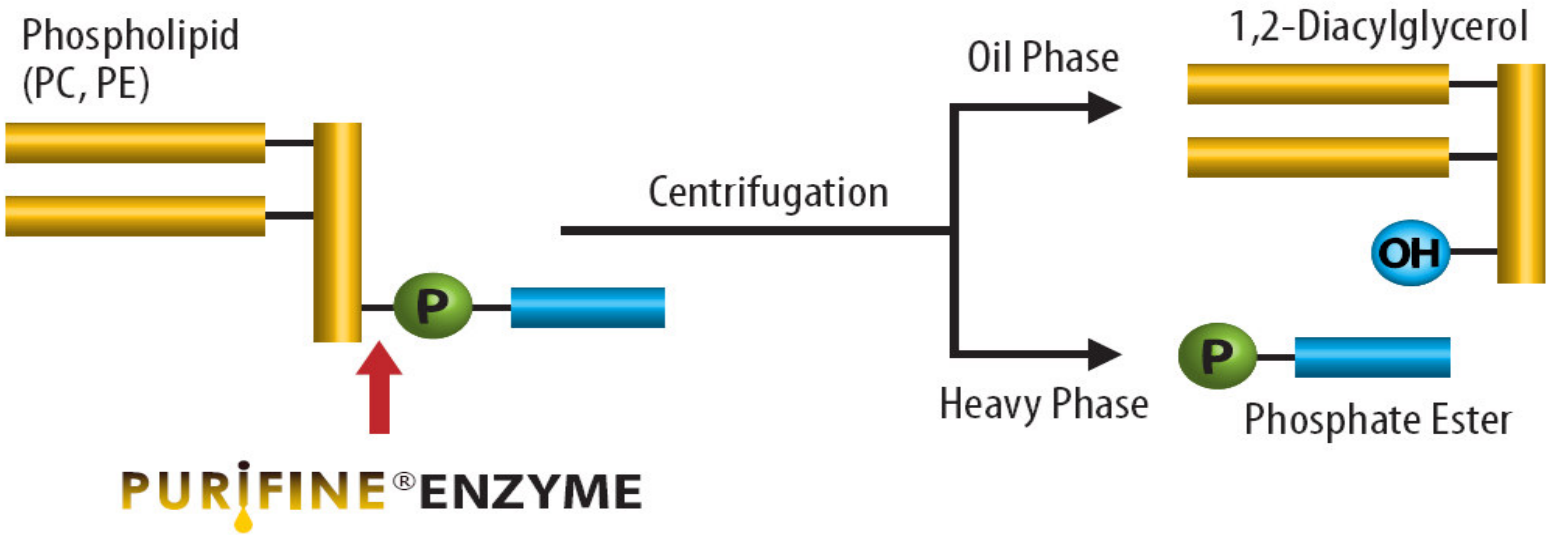
VERENIUM
THE NATURE OF ENERGY

- Phospholipase C (Purifine – Verenium)
- Temperature 60°C and pH 7
- Rather short reaction (1-2 hrs)
- No enzyme recycling , comsumption 200 ppm
- Microbial origin ⟶ No problems with acceptability
- Attacks only PE/PC, not PA/PI

First industrial plants under construction, no real industrial data available yet but highly promissing

Enzymatic degumming using PLC (Verenium)





0.84% DAG formed for each 0.1% PL (40 ppm P) converted

VERENIUM
THE NATURE OF ENERGY

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Case study
Crude SBO PLC degumming

70% conversion PL (PE/PC) to DAG+ Phosphate residue

Full EDG

Crude soybean oil
100%
2,50% PL

70%PE/PC

100% conversion + PE/PC

no free FFA

Gums
1,06% yield
0,92% PL
0,14% NO

PLC EDG
98,9%
0,25% PL
1,33% DAG

Acid gums
0,40% yield
0,20% PL
0,20% NO

ADG
98,54%
0,05% PL

total loss: 1,46%

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Enzymatic degumming PLC

- **Case study crude SB0 2.5% PL (70% PE/PC)**
  - EDG vs waterdegumming / ADG
  - P < 100 ppm, post-ADG needed (or PLA-EDG!)

  - Gain in crude oil yield: about 1.8 / 2.2%
  - No FFA, no extra loss in deodorising
  - Net gain in RBD oil yield after full refining: 1.8 / 2.2%

Best economics when combining PLC-WDG with PLA-EDG

Enzymatic degumming: key = yield

Main driving factor: yield

+ Less oil loss with gums, giving higher oil yields
+ Very suitable for high PL-oils (SBO, RSO) not for PO
+ Less effluent, less low value-added side products

+/- Not all processes yet industrially proven,
but high expectations
+/- Enzyme cost main factor in OPEX, low CAPEX

- No lecithin
- what enzyme to use? Now & in future?

Enzymatic deoiling of gums (EDO)

Alternative enzymatic processes for oil recovery:

Recovery of oil from lecithin

- Most oils are shipped and traded in a crude form
- Wateredegumming applied mainly to prevent settling of gums in storage tanks
- Gums contribute to shelf life of crude oils
- Part of gums converted to lecithin

Q: can entrained oil be recovered from the gums?

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Lecithin deoiling

Process principle

Enzymatic Treatment of Lecithin Fraction (from WDG)

LECITHIN → **LYSO-LECITHIN** + **RECOVERED OIL**

35-50% oil

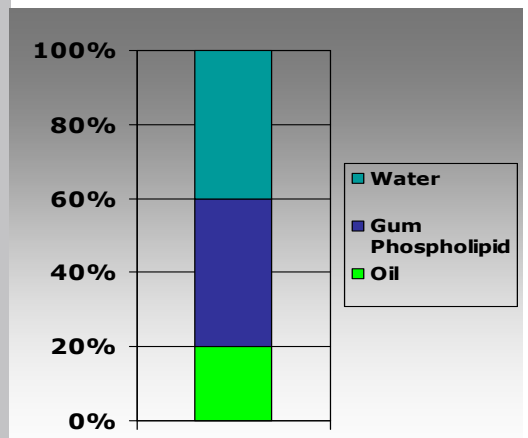
50-65% A.I.

Eg. Lecitase Ultra
250-500 ppm on dry lecithin

Less than half as compared to EDG

Extracted Meal in DT

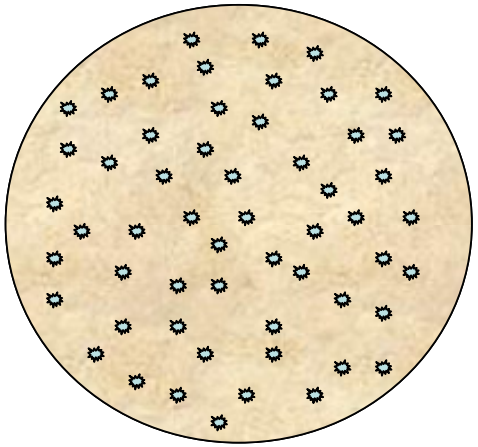
Back to main Oil stream



Wet gums

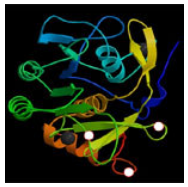
Lecithin deoiling

Wet Gums

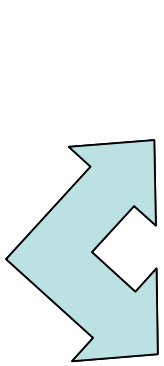


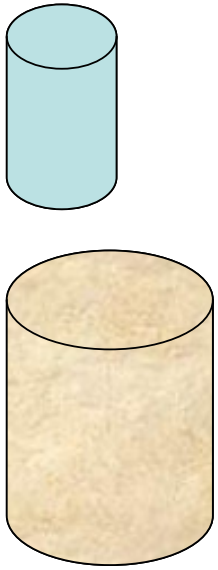
+

Lecitase Ultra



PLA2





Oil

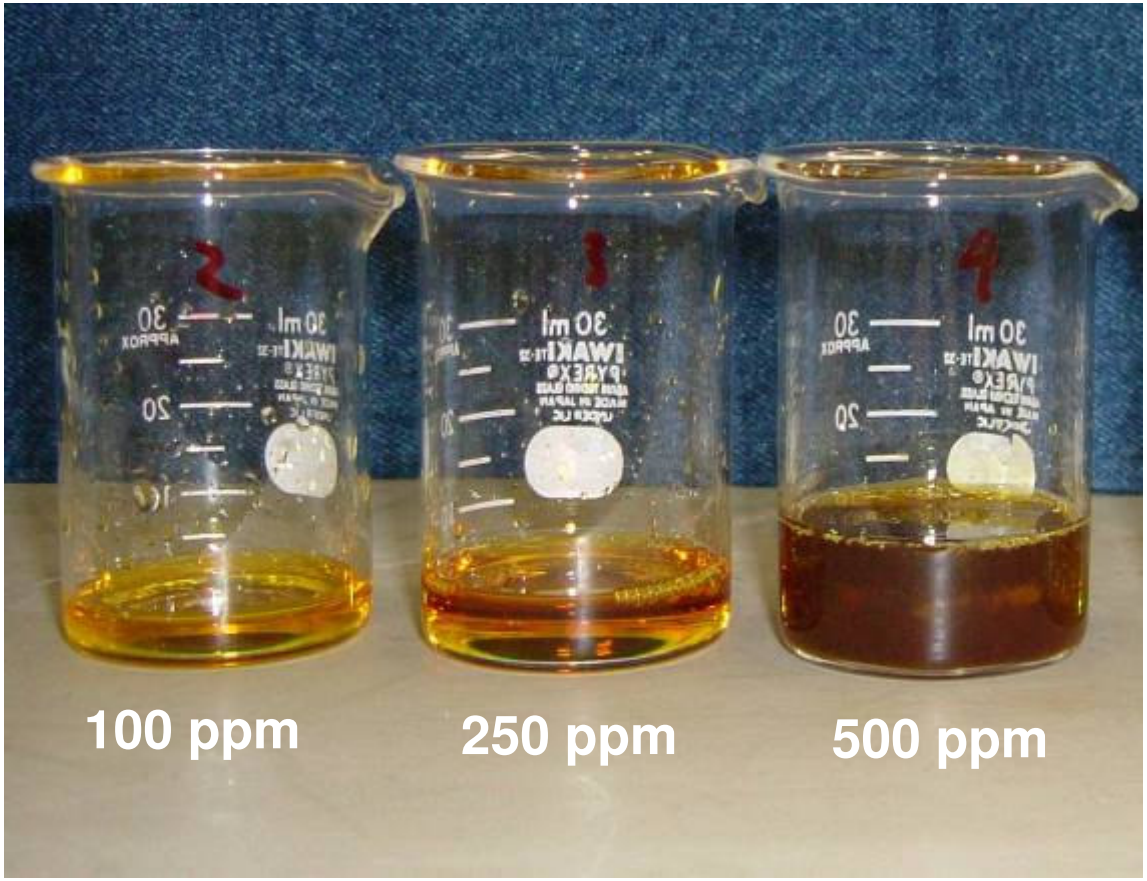
De-oiled Gums

2-4 hrs

Wet Gums + Enzyme

Deoiled gums + Oil

Lecithin deoiling



More enzyme gives :

- Faster Oil Recovery
- More recovered oil

-Darker oil with higher FFA content

Lab trials conducted by novozymes®
Unlocking the magic of nature

Lecithin deoiling

Enzymaric deoiling of soy lecithin

1. Cooling Soy Lecithin to 55℃
2. Addition of Lecitase Ultra (250 – 500 ppm)
3. Enzymatic reaction (2-4 hr at 55℃)
4. Heating treated soy lecithin to min. 70℃
5. Separation recovered oil from lyso-lecithin

Lecithin deoiling potential with PLA

70% conversion PL to LL+FFA

RECOVERED OIL FROM SOY LECITHIN USING PLA2

- Recovery : 80-90% of oil usually entrained in gums
- Calculation example for 1 ton crude soybean oil

LECITHIN → (PLA2) RECOVERED OIL + LYSO-LECITHIN

28 kg dry gums
from which 8 kg oil

10 kg recovered oil
FFA : 35-40%

18 kg dry gums
part= lysolecithin

WDG → 982 kg WDG SBO
with 200 ppm P

?

Meal

1000 kg crude SBO
with 1000 ppm P

Lecithin deoiling potential with PLC

70% conversion PL (PE/PC) to DAG+ Phosphate residue

RECOVERED OIL FROM SOY LECITHIN IF USING PLC

- Recovery : 80-90% of oil usually entrained in gums+ DAG
- Calculation example for 1 ton crude soybean oil

LECITHIN —PLC→ RECOVERED OIL + LYSO-LECITHIN

28 kg dry gums
from which 8 kg oil

18 kg recovered oil
DAG : 55-60%

10 kg dry gums

WDG → 990 kg WDG SBO
with 200 ppm P

?

Meal

1000 kg crude SBO
with 1000 ppm P

oils & fats

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Enzymatic oil degumming (EDG) or Enzymatic lecithin deoiling (EDO)

EDG:

- When applied on crude oil, recovered oil directly blended into main oil stream (PLA: FFA ↗, PLC: DAG ↗)
- Gums not useable to produce functional lecithins
- Larger volumes to be treated (full crude oil stream)

EDO:

- Phospholipids more concentrated and hence more accessible (?)
- But much higher viscosity (dilution with oil = solution)
- Gums not useable to produce functional lecithins
- Recovered oil kept separate from main oil stream (eg. Biodiesel)
- Much smaller streams to be treated (30-40 times less volume)

Trends in Enzymatic Oil Modification

Application of vegetable oil: determined by physical state

37.4 Mill. tons

- Soybean oil
- Rapeseed oil
- Sunflower oil
- Peanut oil
- Cotton oil
- Olive oil

Liquid oil

Interesterification
Hydrogenation → chemical

Fractionation → physical

(semi) Solid oil

42.6 Mill. tons

- Palm oil
- Palm Kernel oil

- Coconut oil
- (Animal fats)

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Trends in Enzymatic Oil Modification

Hydrogenation improves the physical properties but reduces nutritional value

Main drawback: formation of TFA

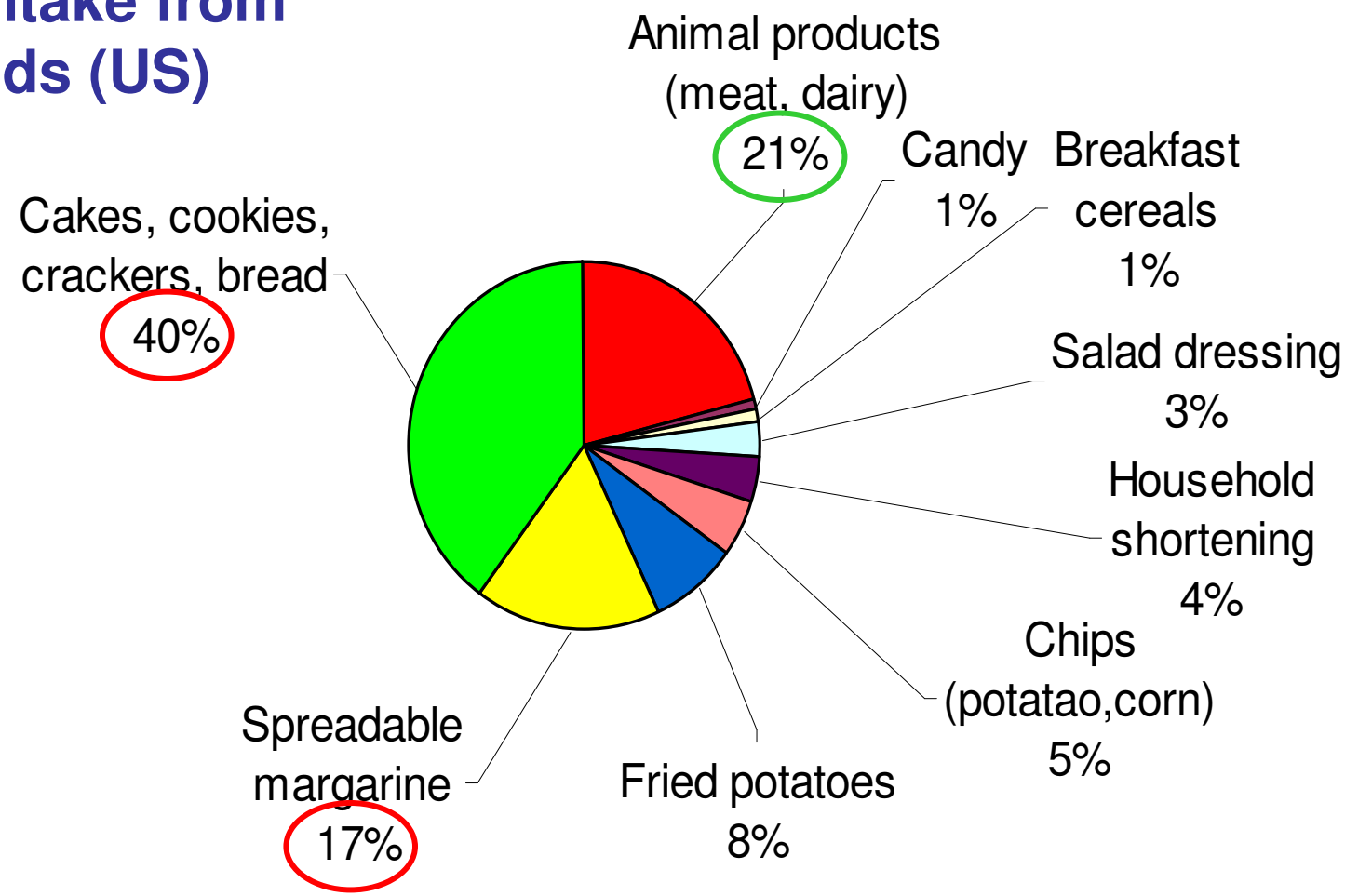
Negative impact on health (Cholestreol)

⇩

Today clear tendency to avoid, and even ban TFA out of Foods

Trends in Enzymatic Oil Modification

TFA intake from foods (US)



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Trends in Enzymatic Oil Modification

PH Soybean oil fractionation

	Salad oil			Frying oil		
	Feed 1	Olein	Stearin	Feed 2	Olein	Stearin
IV	109	112.5	92	87	94	74
Yield %	/	85	15	/	65	35
TFA %	11	9	20	20	18	23
MP °C	19	/	27	25	/	32
SFC						
10°C	7	0	33	28	0	65
20°C	2	/	16	9	/	40
30°C	/	/	2	0	/	7
CT 0°C hr	/	>36	/	/	>10	/

Trends in Enzymatic Oil Modification

What alternative do we have then to avoid TFA when modifying oils?

Chemical Interesterification = first answer to low/zero TFA chemical modification

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Trends in Enzymatic Oil Modification

Ban on TFA and hence partial hydrogenation, has increased demand for interesterification

But chemical interesterification also under pressure:

"Early scientific reports -- one of which was released in mid-January 2007 by joint-researchers from Malaysia and the UK -- suggest that interesterified fat is far more harmful than trans fats.

Interesterified fat was found to depress the level of HDL (good cholesterol) more than trans fat.

In addition, interesterified fat raised blood glucose levels and depressed the level of insulin. This strongly suggests that interesterified fat could lead to diabetes"

Solution: enzymatic interesterification & MORE USE OF PALM OIL

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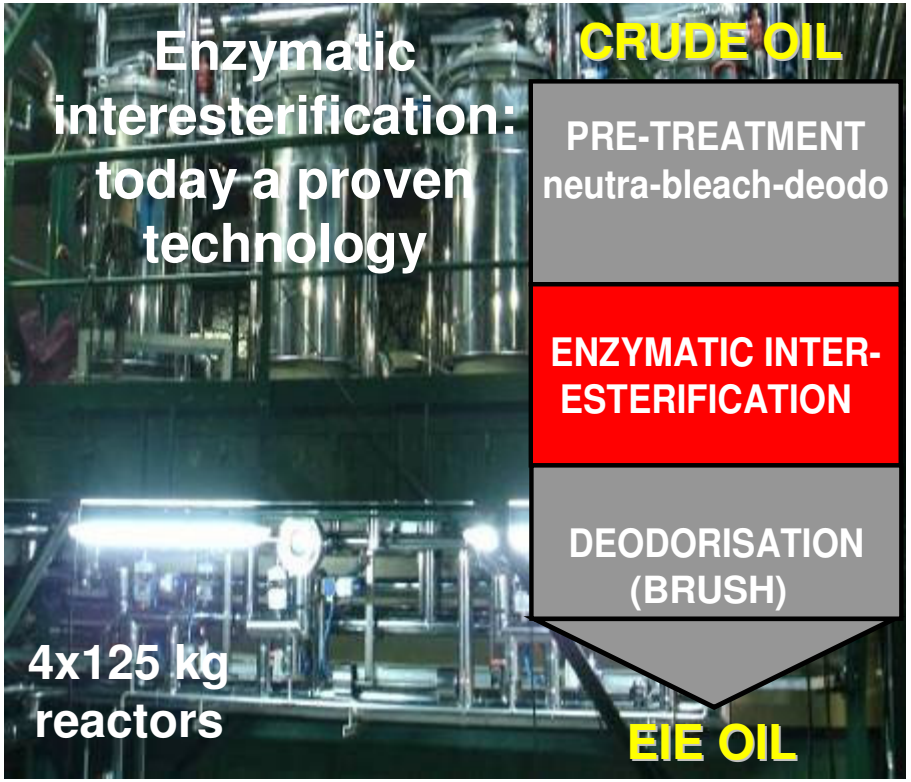
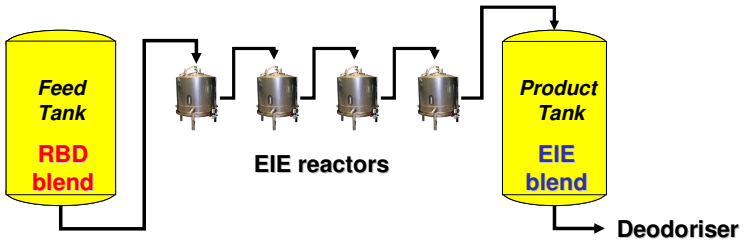
Enzymatic Oil Interesterification: Proven principle





By-products

- **No contaminants** (Soaps-FAME) (Dialkylketones)
- ~~FFA~~
- Diglycerides
- None

EIE >> Oil quality >> CIE

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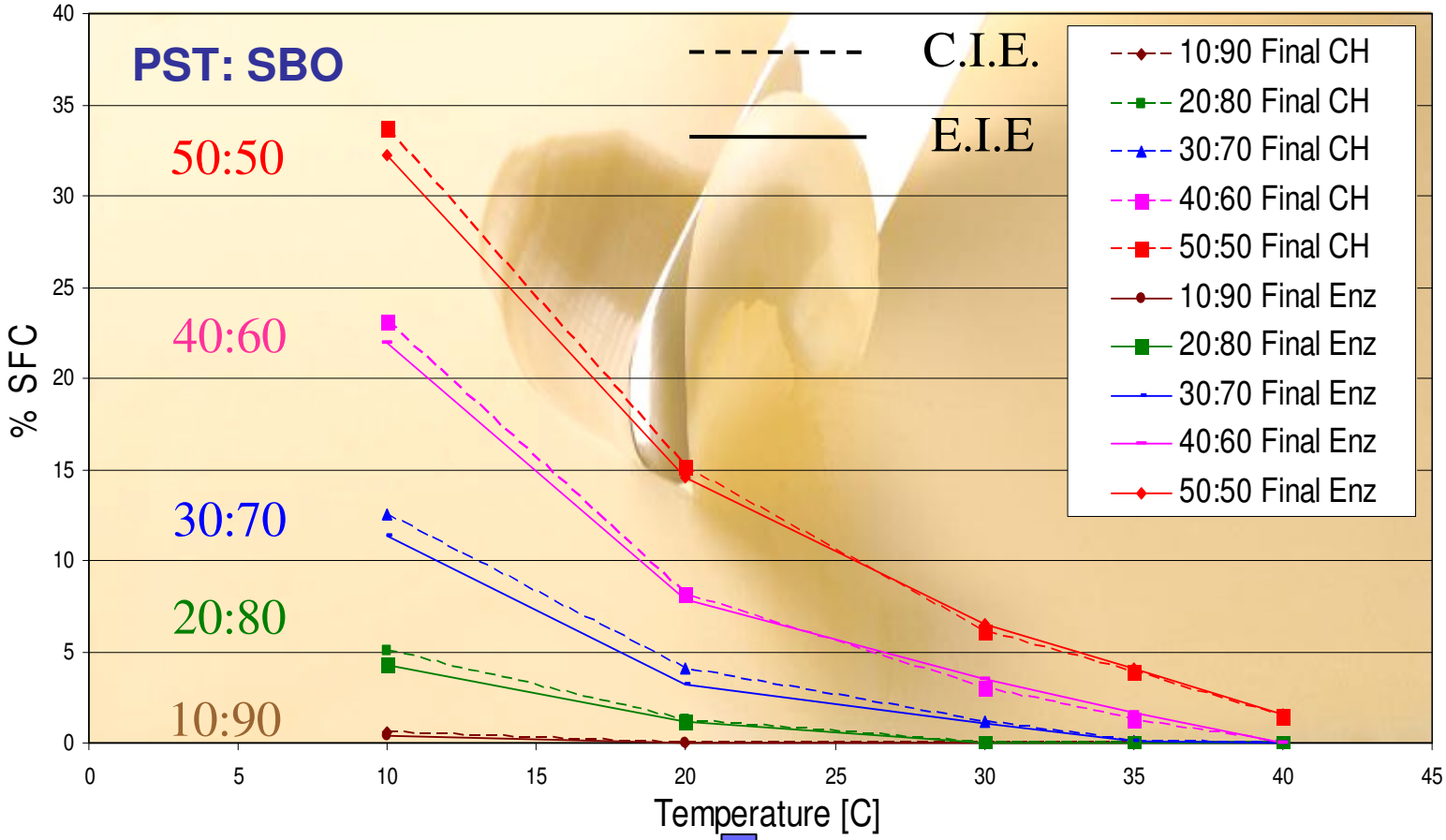
Enzymatic Oil Interesterification: Proven process



novozymes

CIE full random = EIE 1,3 selective (for commodity blends)

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Enzymatic Oil Interesterification: Proven technology

EIE plant

4 x 500 kg

(50-80 tpd)

Plant-Design

- **Feedstock quality**
- **Feedstock composition**
- **Feedstock changes**

Enzymatic oil processing

What may bring the future?

Enzymatic hydrogenation:	**Any potential in future ?**
Enzymes in oleochemistry:	**Enzymatically produced biodiesel**
Enzymes in bleaching:	**Selective destruction of carotene/chlorophyl?**
Enzyme assisted expelling:	**release of oil under mild conditions (cfr. Algae)**

And what about GM of oil composition inside the crop to ease oil refining & increase nutritional value

Anything possible... Where will we be in 10 years?

Enzymes play an important role in our foodproducts

Why not in processing of one of its major ingredients:

OILS and FATS

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