Oil Processing Challenges in the 21st Century:

Enzymes Key to Quality and Profitability

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Major vegetable oils evolution

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

Production period

- Malaysia
- Indonesia
- USA
- Mercosur
- Canada
- Europe
- Malaysia
- Indonesia
- USA
- Mercosur
- Canada
- Europe

> 85%
Palm & Soybean oil production evolution

**Palm Oil Production**
- **PO** = high sat oil
- **In 30 years a 10-fold increase**

**Soybean Oil Production**
- **SBO** = high unsat oil
- **In 40 years a 7-fold increase**

Source: USDA
Updated: Aug 10, 2007
Increased demand for high quality oils

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 kinetics

Refining

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  \( \rightarrow \) 1000 -> 2000 TPD
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)
Enzyme processes in Oilseed/Oil processing

Seed → Preparation
- Cleaning / Drying
- Cracking
- Dehulling

Speciality Fats
- Frying oil
- Margarine

Oleochemical Processes
- Hydrogenation
- Enzymatic IE
- Fractionation

Enzymes
- Refined Oil

Modification
- Enzymatic degumming
- Refining
- Bleaching
- Winterising
- Deodorising

Extraction
- Mechanical Extraction
- Solvent Extraction

Preparation
- Meal
- Crude Oil

Mechanical Extraction
- Solvent Extraction
- Extraction

Cracking
- Flaking
- Cleaning / Drying

Enzyme processes in Oilseed/Oil processing
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**

\[
\begin{align*}
R_1, R_2 &: \text{Fatty acids} \\
X &: \text{H (PA), choline (PC), ethanolamine (PE), serine (PS), inositol (PI),} \\
\text{Hydratable PL} &\leftrightarrow \text{Non-hydratable PL}
\end{align*}
\]
Enzymatic degumming

**PHOSPHOLIPASES**

5 subclasses of Phospholipases
A1, A2, B, C and D

- Phospholipase A1
- Phospholipase A2
- Phospholipase B
- Phospholipase C
- Phospholipase D

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

Phospholipases A1, A2, C are commercially available (Novozymes, Danisco, Verenium)
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
**Re-introduction EDG**

- **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, consumption 50 ppm
  - Microbial origin → No problems with acceptability

**Several industrial plants running today cost competitive**

**Main negative point: what to do with high FFA ?**
Enzymatic degumming PLA1 (Lecitase Ultra)

- Oil Tank
- Crude oil
- Oil Pump
- 30°C
- Heater
- 55°C
- High Shear Mixer
- 30 min
- Retention Vessel
- Retention vessels
- 3-6 hours
- Enzyme
- High Shear Mixer
- Low Shear Mixer
- NaOH to neutralise citric acid
- Water
- Citric Acid
- Centrifugal Separator
- Hydrolised gums
- To DT (extraction)
- To Silica Treatment
- Degummed oil
- 70°C
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
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

ADG
- 0,40% yield
- 0,20% PL
- 0,20% NO

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

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

ADG
- 0,00% yield
- 0,00% PL
- 0,00% NO

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

total loss: 2,10%
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%

- No soaps, gums but also no lecithin!
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, consumption 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,
De Smet Presentation 23

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

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

total loss:
2,60%

total loss:
2,10%
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?
Enzymatic degumming using AT (Lysomax Oil)

Lysomax Oil degumming Process very similar to Lecitase Ultra (less residence)
Recent introduction of new enzymes (2)

° **EDG by Verenium**

- Phospholipase C (Purifine – Verenium)
- Temperature 60 °C and pH 7
- Rather short reaction (1-2 hrs)
- No enzyme recycling, consumption 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 promising
Enzymatic degumming using PLC (Verenium)

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

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%

100% conversion + no free FFA
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?
Lecithin deoiling

Process principle

Enzymatic Treatment of Lecithin Fraction (from WDG)

LECITHIN

35-50% oil
50-65% A.I.

→

LYSO-LECITHIN + RECOVERED OIL

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
De Smet Presentation 33

Wet Gums + Enzyme

Lecitase Ultra

PLA2

2-4 hrs

De-oiled Gums + Oil

Wet Gums

Oil

Deoiled gums + Oil

Lecithin deoiling
Lecithin deoiling

More enzyme gives:
- Faster Oil Recovery
- More recovered oil
- Darker oil with higher FFA content

Lab trials conducted by

De Smet Presentation
Enzymaric deoiling of soy lecithin

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

1000 kg crude SBO with 1000 ppm P

982 kg WDG SBO with 200 ppm P

18 kg dry gums part = lysolecithin

10 kg recovered oil FFA: 35-40%

Meal

70% conversion PL to LL+FFA
Lecithin deoiling potential with PLC

**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**
- **990 kg WDG SBO** with 200 ppm P
- **1000 kg crude SBO** with 1000 ppm P
- **18 kg recovered oil** DAG: 55-60%
- **10 kg dry gums**

**WDG**

**Meal**

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

Interesterification → chemical
Hydrogenation

Liquid oil

(semi) Solid oil

Fractionation → physical

37.4 Mill. tons
Soybean oil
Rapeseed oil
Sunflower oil
Peanut oil
Cotton oil
Olive oil

42.6 Mill. tons
Palm oil
Palm Kernel oil
Coconut oil
(Animal fats)
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)

- Cakes, cookies, crackers, bread: 40%
- Fried potatoes: 8%
- Animal products (meat, dairy): 21%
- Candy: 1%
- Breakfast cereals: 1%
- Salad dressing: 3%
- Household shortening: 4%
- Chips (potato, corn): 5%
- Spreadable margarine: 17%
Trends in Enzymatic Oil Modification

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

Chemical Interesterification = first answer to low/zero TFA chemical 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*
Enzymatic Oil Interesterification: Proven principle

CRUDE OIL

PRE-TREATMENT
neutra-bleach-deodo

ENZYMATIC INTER-
ESTERIFICATION

DEODORISATION
(BRUSH)

EIE OIL

4x125 kg
reactors

No contaminants
(Soaps-FAME)
(Dialkylketones)

By-products

FFA
Diglycerides
None

EIE >> Oil quality >> CIE

No contaminants
(Soaps-FAME)
(Dialkylketones)

4x125 kg
reactors

Enzymatic interesterification: today a proven technology
Enzymatic Oil Interesterification: Proven process

CIE full random = EIE 1,3 selective (for commodity blends)
Enzymatic Oil Interesterification: Proven technology

EIE plant
4 x 500 kg
(50-80 tpd)

• 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 food products. Why not in processing of one of its major ingredients: OILS and FATS

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