Biochemistry, nutrition and technology of lipids. Partie II
Claire Bourlieu-Lacanal

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4. TECHNOLOGY OF VEGETABLE OILS
TECHNOLOGY OF VEGETABLE LIPIDS

Seeds, Grains, Fruits
Control, Cleaning, Dehulling
 Grinding, heating, pressing, separation

Pressure raw oil → Refining → Food oil → Hydrogenation
 Interesterification → Fractionning

Meal
Extraction
Hexane, CO₂ supercritical

De-oiled meal → Animal feed

Extraction oil

Margarines, ...

Food oil
Seeds, Fruits
100 kg (42% fat)

Cleaning

Grinding
Heating

Pressure

Liquid Fraction
34 kg

Solid residues elimination
Filtration, centrifugation

Cleaned solid material

Extraction

Meals
65 kg

De-oiled meals
57 kg (1-2% MG)

Liquid fraction
34 kg

Physical extraction with screw press

Refining

41 kg
EXTRACTION

Miscella Oil (40%) - Hexane

Meal (10-15% oil)

Hexane

Distillation

Chemical extraction by solvant

Extraction by percolation

Solvanted Meal (hexane: 30%)

Solvant extractor

Desolvanted meal

Desolvanted oil

vacuum

Raw oil of extraction

Refining
Hexane extraction plant

SAIPOL Le Mériot Pant (photo C. Helsly)

Solid supply

Miscella towards distillation

Hexane

Vapors evacuation

Cooled meals

Extracteur

Désolvantiseur
## Unwanted Constituents

<table>
<thead>
<tr>
<th>NATURE</th>
<th>TENEUR</th>
<th>ORIGINE</th>
<th>EFFET</th>
</tr>
</thead>
<tbody>
<tr>
<td>AG libres</td>
<td>0,5 – 5%</td>
<td>Hydrolyse (naturel)</td>
<td>Goût, Fumée</td>
</tr>
<tr>
<td>P.lipides</td>
<td>0,2 – 1,5%</td>
<td>Naturel</td>
<td>Trouble, instabilité, Organoleptique</td>
</tr>
<tr>
<td>Produits d’ox.</td>
<td>f(Mat lère)</td>
<td>Auto-ox.</td>
<td>Instabilité, Organoleptique, Nutrition</td>
</tr>
<tr>
<td>Flaveurs</td>
<td>&lt; 0,1%</td>
<td>Naturel, Auto-ox.</td>
<td>Odeur, Goût</td>
</tr>
<tr>
<td>Cires</td>
<td>≈ 100 mg/kg</td>
<td>Naturel</td>
<td>Trouble</td>
</tr>
<tr>
<td>Pigments</td>
<td>≈ 10 mg/kg</td>
<td>Naturel</td>
<td>Goût, Couleur</td>
</tr>
<tr>
<td>Métaux</td>
<td>≈ 1 mg/kg</td>
<td>Naturel</td>
<td></td>
</tr>
<tr>
<td>Contamin.</td>
<td>≈ 10 mg/t</td>
<td></td>
<td>santé</td>
</tr>
</tbody>
</table>
REFINING OF FOOD FATS

Rapeseed oil
Raw oil
Meal
Refined oil
Diester
Raw Glycerine
REFINING

Objectives

- Get rid of undesirable const.
- Respect food grade application
  → strict reglementation

Principles:

- insolubilisation (1)
- adsorption (2)
- distillation (3)

Technology

degumming (1)

P. lip.

Neutralization (1)

AGL

Washing - drying

Bleaching (2)

Pigments

(Dewaxing) (1)

Waxes

Deodorisation (3)

Flavors

Refined oil
Degumming oil

Washing

Drying

Refined and dry oil

vide

Dryer

Washing water

Neutralised oil

Deacidification

NaOH

Neutralised oil

Soaps

Gums

Raw oil

H₃PO₄

H₂O

1- mixer
2- contactor
3- centrifuge separator
4- heat exchanger
5- feed pump
Collection Preservation
Collect, sort
Dry, parboil

Processing 1
(Frying), boiling,
crushing, milling, mixing,
heating, collection

Processing 2
Bulking,
storing,
transporting,
selling

Intermediate trade
Buy
sheabutter
Filtering
sheabutter
Conditioning,
Packing,
labelling,
cooling,
storing,
(cooled)
transport to
Lagos

Processing bulk SB
Cooling,
Paletting
Storing,
Formalities,
Loading,
Transport to
US, EU
Sales

Export
Sheanuts → Sheabutter → Chocolate Cosmetics
degumming
**phospholipases**: phospholipase A2 hydrolyses for instance fatty acid in position sn-2, releasing R2 FFA and a lysophospholipid. This lysophospholipid is a powerful detergent able to break cellular membranes. Snake and bee venoms are very rich in PLA2.
ENZYMATIC DEGUMMING

Phospholipids

- In the conventional degumming and chemical refining process, gums work as emulsifiers and are responsible for the major part of the oil losses.

Triglycerides

- In enzymatic degumming, the enzyme action eliminates the emulsification properties of the gums. The oil savings are proportional to the phosphorus (gums) in a ratio of 1 (oil) to 2 (gums).
ENZYMATIC DEGUMMING
ENZYMATIC DEGUMMING

Global Innovation

Crude Vegetable Oil

Refined Oil

Heavy Phase

DDO

Yield

96.5

97.4

98.3

Caustic

PLA₁

PLA + PLC

TAG

gum

DAG

Phosphatidic Group

Fatty acid
Commercial enzymes

AB Enzymes’ PLA₂, Rohalase® MPL
Dansico’s PLA₂, FoodPro™ LysoMax
Novozymes’ PLA₁, Lecitase® Ultra
Verenium’s PLC, Purifine™
DSM’s PLA₂, GumZyme™

From left to right: sediment of soybean oil from lab tests. Left (2% water) and right (2% water with Lecitase® Ultra)

Physical Refining


### Neutralization

→ Get rid of FFA under the form of soap or «neutralization pastes»: crucial unitary operation of refining. Pastes: soaps of sodium, soda, water, salts, sodium phosphates, mucilages, neutral oil can be retained, coloring constituents, oxydation products and diverse contaminants.

→ Reactions taking place during this process are:
  ✓ neutralization of excess of phosphoric acid added to degum oils (1)
  ✓ neutralization of FFA under the form of sodic soaps:

\[
R-\text{COOH} + \text{NaOH} \rightarrow R-\text{COONa} + \text{H}_2\text{O} \quad (2)
\]

→ As weak acids, reaction in excess of alkali displaces equilibrium towards soaps formation, ↓ residual acidity. Excess ~ 0.01 et 0.05 % for degummed soya oil

→ AVOID «side saponification» (3), *i.e.* partial saponification of triglycerides => glycerol and sodium soaps. ↑ losses.

→ Kinetics (1) & (2) >> (3)
Washing and drying

→ **Get rid of alkalines substances** (soaps and soda in excess) present at the outlet of neutralization turbine, + last traces of metals, phospholipids and other impurities. Objectives: < 30 ppm of soap.

→ **Good separation of raw oil/degumming** otherwise → important emulsions are being formed, difficult elimination of soaps.

→ Washing more effective if done in two steps, water washing must be as hot as possible (90°C).

→ **Post-stream Drying: humidity removal** if still present in washed oil before decoloring operation → risk of filter clogging specially in the presence of soaps.
BLEACHING

NEUTRALIZED OIL (100°C)

Dewaxing / filtration

vacuum

Adsorbing clays

Filters

vaccum

desodorizing

Dry vapor

heater

(cooler)

Filters

N Saturation

REFINED OIL

DESODORIZATION

NEUTRAL BLEACHED OIL
23

Vertical Filter

Inlet bleached oil

Inlet blend oil/clays

elimination of clays
DESODORISATION

Effect of desodorisation parameters (couple temperature/length) on isomerisation degree of unsaturated acids (ex: linolenic acid C18:3)

Content in *trans* FA in refined oils (colza oils, combined oils) - Source ITERG

<table>
<thead>
<tr>
<th>Teneur en AGT</th>
<th>Moyenne</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>En % des AG Totaux</td>
<td>0.8</td>
<td>0.3</td>
<td>1.9</td>
</tr>
</tbody>
</table>
# Refined Fats

## Results

<table>
<thead>
<tr>
<th>OIL</th>
<th>RAW</th>
<th>Refined</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAG</td>
<td>85 – 89%</td>
<td>98 – 99%</td>
</tr>
<tr>
<td>P. Lipids</td>
<td>0.1 – 1.5%</td>
<td>&lt; 50 mg/kg</td>
</tr>
<tr>
<td>FFA</td>
<td>0.5 – 5%</td>
<td>&lt; 0.1%</td>
</tr>
<tr>
<td>Trans FA</td>
<td>&lt; 0.1%</td>
<td>0.3 – 1.9%</td>
</tr>
<tr>
<td>Sterols</td>
<td>0 – 2% (soja)</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>tocopherol</td>
<td>0.15%</td>
<td>0.1%</td>
</tr>
<tr>
<td>Pr. Ox</td>
<td>Variable</td>
<td>Variable</td>
</tr>
<tr>
<td>Waxes</td>
<td>≈ 100 mg/kg</td>
<td>&lt; 5 mg/kg</td>
</tr>
<tr>
<td>Pigments</td>
<td>≈ 10 mg/kg</td>
<td>&lt; 0.02 mg/kg</td>
</tr>
<tr>
<td>Metals</td>
<td>≈ 1 mg/kg</td>
<td>≈ 1 mg/t</td>
</tr>
<tr>
<td>Contaminants</td>
<td>≈ 10 mg/t</td>
<td>≈ 1 mg/t</td>
</tr>
</tbody>
</table>
ADAPTATION OF FATS to FOOD APPLICATIONS

Objectives:
- stability
- technological, organoleptic and nutritionnal properties

Physical Levers:
- Kinetics control of cooling (size and nature of fat crystals)
- Fractionation (increase in FA with high or low melting points)

Chemical Levers:
- Hydrogenation (melting profile modif. [nature of FA] + stability)
- Interesterification (modif. Of melting profile [position of FA])

Enzymatic levers:
- Interesterification => structuration of TAG
- Glycerolysis => emulsifying power

Authorized treatments (arrêté du 12/02/73)
FRACTIONATION

FAT

Controlled cooling

Melting

Composition

Equipment:
- Cooling system

Parameters:
- Cooling speed
- Overcooling
- Agitation speed
- Cristallisation time
- Temperature

HIGH melting point Fraction

LOW melting point Fraction

decanting
centrifugation
filtration
FRACTIONATION OF FATS

- Continuous Filtration -
FRACTIONATION OF FATS

- Press Filter -

Inlet (partially cristallized fat)

Olein (permeate)

Press Filter

Stearin cake

vapor

Stearin (retentate)
FRACTIONATION OF PALM OIL

**PALM**

<table>
<thead>
<tr>
<th>Composition moyenne</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Trisaturés (PPP)</td>
<td>6%</td>
</tr>
<tr>
<td>Disaturés monoinsaturés (PPO, POP)</td>
<td>50%</td>
</tr>
<tr>
<td>Monosaturés diinsaturés (POO, OPO)</td>
<td>40%</td>
</tr>
<tr>
<td>Triinsaturés (OOO)</td>
<td>4%</td>
</tr>
</tbody>
</table>

![Diagram](image)

<table>
<thead>
<tr>
<th>Cristallisation (28°)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtration</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Stéarine (20%)</th>
<th>Oléine (80%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPP</td>
<td>30%</td>
</tr>
<tr>
<td>PPO, POP</td>
<td>26%</td>
</tr>
<tr>
<td>OOP, OPO</td>
<td>44%</td>
</tr>
<tr>
<td>OOO</td>
<td>0%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oléine</th>
<th>Palme</th>
<th>Stéarine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indice d’iode</td>
<td>56/58</td>
<td>50/55</td>
</tr>
<tr>
<td>Pt fusion</td>
<td>19/21</td>
<td>36/38</td>
</tr>
<tr>
<td>%S à 15°</td>
<td>18/22</td>
<td>38/42</td>
</tr>
<tr>
<td>%S à 20°</td>
<td>5/7</td>
<td>28/32</td>
</tr>
<tr>
<td>%S à 25°</td>
<td>2</td>
<td>23/27</td>
</tr>
</tbody>
</table>
HYDROGENATION

\[ \text{CH} = \text{CH} - + \text{H}_2 \rightarrow \text{CH}_2 - \text{CH}_2 - \]

+ catalysts  
[Ni, Cr, Cu, Mn]

- \( \uparrow \) melting point
- \( \uparrow \) stability (rapeseed - soya)

TOTAL or PARTIAL Hydrogenation, selective or not:
selectivity = \( f([\text{catalysts}], \text{temperature} : k_3 / k_2; k_2 / k_1) \)

\[
\begin{align*}
\text{C18:3} & \xrightarrow{k_3} \text{C18:2} & \xrightarrow{k_2} \text{C18:1} & \xrightarrow{k_1} \text{C18:0} \\
(\text{linolenic}) & \quad (\text{linoleic}) & \quad (\text{oleic}) & \quad (\text{stearic})
\end{align*}
\]

→ Apparition of trans forms (15 - 40% depending on conditions)  ex: elaïdic acid (trans-\( \Delta^9 \) 18:1)

→ Apparition position isomers (~ 40%), conjugaison (~ 2%)

Applications: raw matter for margarine, pastry, frying oils, ….
PRINCIPE SCHÉMATIQUE DE L’HYDROGÉNATION

Huiles brutes → Huiles neutres sèches

Paramètres :
- Température
- Pression
- Agitation
- Catalyseur (%, type, activité)

Huiles hydrogénées brutes → Catalyseur usagé

Post raffinage → Recyclage

Catalyseur neuf (Ni, Cu)
Influence of temperature and quality of catalyst on AG trans formation

- Elevated T°
  - Used catalyst

- Low T°
  - New Catalyst

Hydrogenation degree

- Partial
- Total
## Trans FA content in several food products

<table>
<thead>
<tr>
<th>AG Trans</th>
<th>Teneur Mini (% AG Totaux)</th>
<th>Teneur Maxi (% AG Totaux)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandwich bread</td>
<td>3.7</td>
<td>21.2</td>
</tr>
<tr>
<td>Pastry</td>
<td>24.5</td>
<td>34.8</td>
</tr>
<tr>
<td>Puff pastry, pizza</td>
<td>16.6</td>
<td>61</td>
</tr>
<tr>
<td>Dehydrated soups</td>
<td>4.3</td>
<td>27</td>
</tr>
<tr>
<td>Bovine meat</td>
<td>1.0</td>
<td>2.8</td>
</tr>
<tr>
<td>Lamb</td>
<td>3.6</td>
<td>5.4</td>
</tr>
<tr>
<td>Butter</td>
<td>4</td>
<td>11</td>
</tr>
<tr>
<td>Milk (cow/goat/ewe)</td>
<td>1.8</td>
<td>5.6</td>
</tr>
</tbody>
</table>
TRANS FA

- Negative health effects of industrial trans: effect on plasmatic lipoproteines and prostaglandines synthesis
- Compulsory labelling of trans FA

Increase / optimizing of fat processing

- New definition of process parameters (desodorisation, desacidification)
  - lower temperature, shorter time, intense vacuum
- Alternatives to partial hydrogenation:
  - physical fractionation, IE (chemical or enzymatic) …
Trans Fat

This page contains links to all of the content on the Food section of FDA.gov about trans fat. There are links for consumer information, guidance documents, other industry information, science and research reports, and resources from other sites.

*Trans fat* is a specific type of fat that is formed when liquid oils are turned into solid fats, such as shortening or stick margarine. During this process — called hydrogenation — hydrogen is added to vegetable oil to increase the shelf life and flavor stability of foods. The result of the process is *trans fat*.

- Consumer Materials
- Guidance and Regulations
- Additional Information for Industry
- Science and Research
- Resources from Other Sites
**PRINCIPLE** : rearrangement of FA on glycerol

→ modif. Of melting behavior of oil without modification of the oil global FA composition

- Non directed : $T > T_{\text{melting of FA}}$
  → Modification of melting profile

- Directed : $T_{\text{intermediate}}$
  → Cristallisation of high melting point TAG
    (displacement of equilibriums)
Example: Soy Salad Oil + Palm Stearine
CHEMICAL INTERESTERIFICATION
CHEMICAL INTERESTERIFICATION

The Catalyst

Catalyst dry storage tank

Rotary dosing valve

Catalyst dosing tank

Sodium methyleate is a hazardous catalyst

Special catalyst dosing systems are important for safe chemical catalyst handling
**Principle**: rearrangement of FA on glycerol
→ specificity of biocatalyst to direct modification

**Use of sn-1,3 lipases**

![Chemical reaction diagram showing the rearrangement of fatty acids (FAs) on glycerol using lipase.](image)

\[\text{O} \quad \text{S} \quad \text{O} \quad \text{Lipase} \quad \text{O} \quad \text{S} \quad \text{O} \]

- \(O = \) Oleic acid
- \(S = \) Stearic acid

=> Cocoa butter analogues – texture control

=> Analogue human milk fat in Betapol®, with palmitoyl in sn-2 and PUFA in sn-1,3
Proven results
The better fat ingredient

Numerous studies with Betapol® conducted in both premature and full-term infants have proven the nutritional superiority of formula blends that have a similar fatty acid composition to human breast milk.

Fat absorption

One leading study compared infant absorption of saturated fatty acids in various control formulas and those that contained Betapol®. All blends had a similar percentage of palmitic acid (C16:0) of 20-25%. In order to mimic human milk fat as closely as possible, the Betapol® formulas were comprised of fats with 66-76% of the C16:0 in the beta position. The control formulas contained 12.5% of the C16:0 in the beta position. Infants that were fed formulas containing Betapol® showed a significant improvement in C16:0 absorption of 22% (pre-term) and 18% (full-term) compared to infants on the control formulas. This clearly established that the more palmitic acid there is at the sn-2 position, the better.

EFFECT OF LOW AND HIGH C16:0 IN THE SN-2 POSITION ON BONE MINERAL CONTENT IN TERM INFANTS

Enzymatic IE (Batch)

Continuous EIE

Heater

Water bath system (aquarium)

Columns with enzyme (+/- 90 g in both)

Pump

Desmet Ballestra
ENZYMATIC INTERESTERIFICATION

Use of non selective lipases is also possible => randomization

NON-SELECTIVE ENZYME: Lipozyme TL IM, a lipase from *Thermomyces lanuginosus* (Novozymes)

Re-arrangement of FA over the glycerol backbone according to law of probability

Solid fat Content Profile (SFC) by p-NMR
ENZYMATIC INTERESTERIFICATION

Ex application palm oil

Palm oil

- Increase SFC – eeding with cristals (IV)
ENZYMATIC INTERESTERIFICATION

Ex application palm oil

DSC (differential scanning calorimetry) melting profiles of Palm Oil an EIE Palm Oil
ENZYMATIC INTERESTERIFICATION

Ex application palm oil

SFC profiles of Palm Oil and EIE Palm Oil

Composition of Palm Oil and EIE Palm Oil
[St: saturated FA; U: unsaturated FA on TAGs]

Palm Oil
- StStSt: 7%
- StUST: 46%
- StUU: 40%
- UUU: 7%

EIE Palm Oil
- StStSt: 12% (+++)
- StUST: 38% (- -)
- StUU: 37% (-)
- UUU: 12% (+++)
**PROCESSES COMPARISON**

**Chemical Interestorification**

- Pretreatment of oil
- Catalyst: $\text{NAOCH}_3$
- Bleaching
- Desodorisation

**Enzymatic interesterification**

- Pretreatment of oil
- Catalyst: lipase
- Desodorisation

Simpler process but precaution have to be taken to prolonge life of biocatalyst
Random Enzymatic Interesterification

Quality parameters of the feed oil in order to ensure a sufficient lifetime to the enzyme

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>FFA</td>
<td>&lt;0.1%</td>
</tr>
<tr>
<td>Moisture</td>
<td>&gt;0.02% min.</td>
</tr>
<tr>
<td>Moisture &amp; impurities</td>
<td>0.1% max.</td>
</tr>
<tr>
<td>Soaps</td>
<td>1 ppm max.</td>
</tr>
<tr>
<td>P</td>
<td>&lt;3 ppm</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;0.1 ppm</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt;0.02 ppm</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;0.01 ppm</td>
</tr>
<tr>
<td>AnV</td>
<td>&lt;5</td>
</tr>
<tr>
<td>PV</td>
<td>&lt;1 meqO₂/kg</td>
</tr>
<tr>
<td>pH of water extract</td>
<td>6-9</td>
</tr>
<tr>
<td>Citric acid</td>
<td>&lt;25 ppm</td>
</tr>
</tbody>
</table>

For high, long and consistent enzyme activity, **fully refined** (RBD) oils are preferred.

High attention with respect to:
- **Oxidation parameters**, that must be kept as low as possible.
- **Acidity of the oil in terms of pH of water extract**: > 6 and < 9.
**PROCESSES COMPARISON**

Soya and palm oils

![Graph showing temperature vs. % SFC for various oil mixtures](image)

**Result:** Enzymatic process without bleaching makes lighter oil than chemical process after post-bleaching

<table>
<thead>
<tr>
<th>PS / SFO</th>
<th>10:90</th>
<th>20:80</th>
<th>30:70</th>
<th>40:60</th>
<th>50:50</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Chem</td>
<td>Enz</td>
<td>Feed</td>
<td>Chem</td>
</tr>
<tr>
<td>Color</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yellow</td>
<td>11</td>
<td>15</td>
<td>10</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>Red 514</td>
<td>1.0</td>
<td>2.0</td>
<td>1.0</td>
<td>1.2</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>2.1</td>
<td>3.4</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Result:** Enzymatic process retains more tocopherol

<table>
<thead>
<tr>
<th>Tocopherol (ppm)</th>
<th>701</th>
<th>252</th>
<th>505</th>
<th>639</th>
<th>197</th>
<th>412</th>
<th>581</th>
<th>281</th>
<th>426</th>
<th>546</th>
<th>185</th>
<th>425</th>
<th>463</th>
<th>182</th>
<th>366</th>
</tr>
</thead>
</table>

Sunflower and palm oils
Capital and Operating Cost: A Comparison

- 0.5 kg NaOCH₃ randomises 1 ton of oil within a few minutes
- 600 kg enzymes require 1 hour to randomise 1 ton of oil
- NaOCH₃ costs some 4 $/kg; enzyme costs about 40 $/kg
## PROCESSES COMPARISON

<table>
<thead>
<tr>
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<th>Chemical IE</th>
<th>Enzymatic IE</th>
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<tbody>
<tr>
<td><strong>advantages</strong></td>
<td>- Reproductive and efficient</td>
<td>- Reproductive and efficient if no inlet change occurs</td>
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<td></td>
<td>- batch operation</td>
<td>- simple, clean and safe process</td>
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<tr>
<td></td>
<td></td>
<td>- less post-treatment</td>
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<td></td>
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<td>- better nutritionnal quality of fat</td>
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<td></td>
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<td>- lower initial investment</td>
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<td><strong>Drawbacks</strong></td>
<td>- Toxic catalyst</td>
<td>- biocatalyst affected by initial purity of oil</td>
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<td></td>
<td>- highTemp</td>
<td>- hydrolysis</td>
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<td></td>
<td>- side reactions</td>
<td>- acyls moieties migration</td>
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<td></td>
<td>- off flavours and oxidation</td>
<td>- less flexibility</td>
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<td></td>
<td>- important loss of oil</td>
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MARGARINE: principle of processing

**Fat Phase:**

Neutral /bleached oils:
- Fractionated
- Hydrogenated
- Interesterified

Liposoluble Ingredients:
- Lecithine
- Monoglycerides
- dyes

**Aqueous Phase:**

Additives:
- Salt
- Sugar
- preservative
- Citric acid

Without trans FA

Refined oil

\[ X \]

Fraction

\[ 1-X \]

Fully hydrogenated

Saturated oil

Interesterified

Dosing pump

Emulsion, cooling

Cristallisation, blending

Packaging

Cold

Agitation
PARTIAL GLYCERIDES PRODUCTION BY GLYCEROLYSIS

- Used to rearrange FA and produce blends of partial glycerides (MAG, DAG, TAG). Enzyme sn-1, 3 or not specific

- Preferred immobilized Enzyme/ elevated content in glycerol
PARTIAL GLYCERIDES PRODUCTION BY GLYCEROLYSIS

- Glycerolysis with Lipozyme 435 (2%) and various glycerol addition rates at 80°C/24 hours

Glycerolysis with Lipozyme 435 (2%) and glycerol (3.4M) at 80°C, 0-24 hours
PARTIAL GLYCERIDES PRODUCTION DE
BY GLYCEROLYSIS

Alternative routes

- MAG and DAG can also be synthesised by combining glycerol and fatty acids
- Using liquid enzymes reduces the conversion to DAG but does not eliminate it.
- Presence or absence of a solvent alters the relative proportions of MAG and DAG

Yang, Rebsdorf, Engelrud, and Xu, Monoacylglycerol synthesis via enzymatic glycerolysis in an efficient reaction system, *J. Food Lipids* 12, 299-312, 2005.
4. Few oils monographies
Huiles courantes en alimentation

• Huile de Colza, Brassica napus, Brassicacées

Plante herbacée bisannuelle à tiges ramifiées, fleurs jaunes.

Partie utilisée : graines dont on extrait l’huile

Composition : AG oléique, linoléique, palmitique, stéarique. L’insaponifiable est riche en stérols et tocophérols. Certains sont plus riches en acide érucique que d’autres.
• Huile de Tournesol, *Helianthus annuus*, Asteraceae


Partie utilisée : graines dont on extrait l’huile

Composition de l’huile : AG linoléique, oléique, palmitique, stéarique. L’insaponifiable contient de nombreux stérols.
**Huile de soja**

Source : huile grasse raffinée obtenue à partir de graines de *Glycine soja* et *Glycine max*.
Appartient à la famille des Fabaceae. Culture aux EU, Brésil, Chine, Argentine...

Composition chimique : glucides, protéines contenant les 9 acides aminés essentiels en bonnes proportions, lipides. Composition en acides gras : linoléique, oléique, linolénique, palmitique…
Essai :
- détermination des indices habituels
- L’insaponifiable : <1.5%
- CPG pour déterminer la teneur en brassicастérols.

Emploi de l’huile :
- l’huile de soja raffinée est utilisée pour l’alimentation par voie parentérale (apport calorique et d’acides gras essentiels).
- Alimentation.
**Huile d’olive**

Source : l’huile d’olive est obtenue à partir de drupes mûres par pression à froid ou par tout autre moyen mécanique approprié.

L’huile raffinée est préparée à partir du fruit par pression à froid, par centrifugation ou par tout autre procédé mécanique reconnu.

Production en zone méditerranéenne.
Drogue :
Fruits (drupe) : alimentation
Feuilles : phytothérapie

Composition chimique : fruit frais riche en eau, en glucides et surtout en lipides.

Composition en AG de l’huile : oléique, linoléique, palmitique,…

L’insaponifiable de l’huile vierge : <1.5%. renferme des stérols, des tocophérols, des triterpènes, des pigments…
Huile de Lin, *Linum usitatissimum*, Linacées

 Parties utilisées : Les graines et l'huile tirée des graines.

Habitat et origine : Probablement issue du bassin méditerranéen, cette plante annuelle est aujourd'hui cultivée un peu partout sous les climats tempérés et tropicaux. Elle préfère un sol sablonneux et argileux, voire limoneux, profond et bien irrigué. On récolte la plante après la floraison, avant que les graines ne soient entièrement mûres et ne tombent au sol.
FEW CONCLUSIONS

- 95-98% lipids = TAG, triester of FA and glycérol

- Hydrolyzed partially before being absorbed by enterocytes, resynthétized under the form of TAG and transported by lipoproteines until target tissues (adipose, liver, muscles…)

- Mutiplr part and essential: energy carrier, structure, signalization, gene expression modulation

- FA: carbon chain with carboxyle moities at one extremity. Chain can be devoid of double bond => saturated FA or present double bonds:

Then FA are said:
- monounsaturated (most frequent in nature oleic acid, MUFA)
- Polyunsaturated (PUFA)
2 series or PUFA very important: n-6 serie (or omega 6) and n-3 serie (or omega 3) with first double bond located respectively at 6 or 3 carbons from the methul extremity of the molecule. Precursor of omega 6 and omega 3 series are linoleic acid (LA, 18:2 n-6) and alpha-linolenic acid (ALA, 18:3 n-3). These two acids are said « essential » because they can not be synthesized by animal organism and must be brought by diet.

FA Profile very specific and determine with FA position on TAG => oil properties

Chemical and enzymatic process help refig oil and modulated their functionnal properties

Development of enzymatic method for biomodifications

Complex socio economical context: competition for ressources (biofuels), high pressure on agricultural lands linked to emergents markets and increasing demand of ois, complexity of some supply chain (palm), strong image of lipids/fat in collective conscience and complex relationship with health.
Corps gras

- Triglycérides
  - Acides gras
  - Glycérol
  - Insaponifiable
    - Aliphatique
      - Alcools gras
      - Hydrocarbures
      - Cires...
    - Terpénique
      - Stérols
      - Tocophéros
      - Squalène
      - Alcools terpéniques
      - Carotènes...
  - Naturels
    - 0,1 à 3 %
    - Lipides polaires
      - Phospholipides
      - Sphingolipides
      - Glycolipides...

Constituants mineurs

- ppt, ppb, ppm

Indésirables

Contaminants

Composés d’altération

Composés maintenus à l’état de traces (qualité, sécurité sanitaire) par bonnes pratiques de fabrication et contrôles qualité
Cire de carnauba

La carnaúba est une cire issue des feuilles d'un palmier du nord-est du Brésil, le Copernicia prunifera. Elle se trouve généralement sous la forme de copeaux jaunes-bruns, cassants, très odorants.

Merci pour votre attention.
High TG Levels Impact Other Lipids

- Metabolism creates lipid remnants
- Creates small, dense LDL
* L. Bellows, Colorado State University Extension food and nutrition specialist and assistant professor; and R. Moore, graduate student. 3/02. Revised 11/12.