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

To cite this version:
Claire Bourlieu-Lacanal. Biochemistry, nutrition and technology of lipids. Partie II. Master. Postgraduate Food and Nutrition Program (PPGAN) - Unirio (Biochemistry, nutrition and technology of lipids. Partie II), 2017. hal-02786344

HAL Id: hal-02786344
https://hal.inrae.fr/hal-02786344
Submitted on 4 Jun 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
4. TECHNOLOGY OF VEGETABLE OILS
TECHNOLOGY OF VEGETABLE LIPIDS

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

Pressure raw oil → Meal

Refining
Food oil

Extraction
Hexane, CO₂ supercritical

Extraction oil

De-oiled meal → Animal feed

Hydrogenation
Interesterification
Fractionning

Margarines,...
Seeds, Fruits
100 kg (42% fat)

Cleaning

Grinding
Heating

Pressure

Liquid Fraction
34 kg

Solid residues elimination
Filtration, centrifugation

Extraction

Meals
65 kg

65 kg

FR 
AL 
OIL OBTAINED
BY PRESSURE

41 kg

Refining

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

Physical extraction with screw press
EXTRACTION

Miscella Oil (40%) - Hexane

Meal (10-15% oil)

Hexane

Desolvanted Meal (hexane: 30%)

Solvant extractor

Distillation

Chemical extraction by solvant

Extraction by percolation

Desolvanted oil

vacuum

Raw oil of extraction

Refining

Desolvanted meal
Hexane extraction plant

SAIPOL Le Mériot Pant (photo C. Helsly)

Solid supply

Miscella towards distillation

Hexane

Extracteur

Vapors evacuation

Cooled meals

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 Ière)</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
Objectives

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

Principles:

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

Technology

- degumming (1)
- Neutralization (1)
- Washing - drying
- Bleaching (2)
- (Dewaxing) (1)
- Deodorisation (3)
- Refined oil

P. lip.
AGL
Waxing
Pigments
Waxes
Deodorisation
Refined oil

Flavors
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

Triglycerides

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

- 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

The diagram illustrates the enzymatic degumming process involving enzymes PLA₁ and PLA₂, as well as phospholipase C (PLC). The process starts with the breakdown of glycerol into fatty acids and is catalyzed by PLA₁ and PLA₂. PLC further processes the fatty acids and glycerol to release phospholipids.
ENZYMATIC DEGUMMING

Global Innovation

- Crude Vegetable Oil
- PLA + PLC
- PLA₁
- Caustic

Refined Oil  Heavy Phase  DDO  Yield

96.5

97.4

98.3
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

<table>
<thead>
<tr>
<th>Generation 1</th>
<th>Generation 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>PLA / PLC</td>
</tr>
<tr>
<td>Physical</td>
<td>Physical</td>
</tr>
<tr>
<td>97.4%</td>
<td>98.3%</td>
</tr>
</tbody>
</table>
Global Innovation

Crude Oil → Citric Acid

Mixer

Acid Retention

Caustic → Water → Enzymes → Cooler

Mixer

Economizer

High Shear Mixer

Enzyme Retention

Citric Acid

US 7,713,727

Refined oil Surge

Centrifuge

Preheater

Heavy Phase gums
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, oxdation products and diverse contaminants.

→ Reactions taking place during this process are:
  ✓ neutralization of exces of phosphoric acid added to degum oils (1)
  ✓ neutralization of FFA under the form of sodic soaps:
    \[ \text{R-COOH} + \text{NaOH} \rightarrow \text{R-COONa} + \text{H}_2\text{O} \] (2)

→ As weak acids, reaction in exces 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)

Filters

N Saturation

REFINED OIL

DESODORIZATION

Adsorbing clays

Filters

vacuum

desodorizing

Dry vapor

heater

cooler

(Dewaxing/filtration)
Vertical Filter

Inlet bleached oil
Inlet blend oil/clays
Elimination of clays
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></th>
<th>Raw</th>
<th>Refined</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAG (85 – 89%)</td>
<td>85 – 89%</td>
<td>98 – 99%</td>
</tr>
<tr>
<td>P. Lipids (0.1 – 1.5%)</td>
<td>0.1 – 1.5%</td>
<td>&lt; 50 mg/kg</td>
</tr>
<tr>
<td>FFA (0.5 – 5%)</td>
<td>0.5 – 5%</td>
<td>&lt; 0.1%</td>
</tr>
<tr>
<td>Trans FA (&lt; 0.1%)</td>
<td>&lt; 0.1%</td>
<td>0.3 – 1.9%</td>
</tr>
<tr>
<td>Sterols (0 – 2%)</td>
<td>0 – 2% (soja)</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>Tocopherol (0.15%)</td>
<td>0.15%</td>
<td>0.1%</td>
</tr>
<tr>
<td>Pr. Ox (Variable)</td>
<td>Variable</td>
<td>Variable</td>
</tr>
<tr>
<td>Waxes (≈ 100 mg/kg)</td>
<td>≈ 100 mg/kg</td>
<td>&lt; 5 mg/kg</td>
</tr>
<tr>
<td>Pigments (≈ 10 mg/kg)</td>
<td>≈ 10 mg/kg</td>
<td>&lt; 0.02 mg/kg</td>
</tr>
<tr>
<td>Metals (≈ 1 mg/kg)</td>
<td>≈ 1 mg/kg</td>
<td>≈ 1 mg/t</td>
</tr>
<tr>
<td>Contaminants (≈ 10 mg/t)</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

Equipments:
- Cooling system
- decanting
- centrifugation
- filtration

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

HIGH melting point Fraction

LOW melting point Fraction
FRACTIONATION OF FATS

- Continuous Filtration -

Inlet

Recycling pump

Recycling

Aspiration

Vacuum

Olein

Stearin

Vapor

stearin cake
FRACTIONATION OF FATS

- Press Filter -

Inlet (partially crystallized fat)

Olein (permeate)

Stearin (retentate)

Press Filter

press

Stearin cake

vapor
# Fractionation of Palm Oil

## Palm

### Composition moyenne

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</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>

### Cristallisation (28°C)

### Filtration

<table>
<thead>
<tr>
<th>Component</th>
<th>Oléine (20%)</th>
<th>Oléine (80%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPP</td>
<td>30%</td>
<td>0%</td>
</tr>
<tr>
<td>PPO, POP</td>
<td>26%</td>
<td>51%</td>
</tr>
<tr>
<td>OOP, OPO</td>
<td>44%</td>
<td>44%</td>
</tr>
<tr>
<td>OOO</td>
<td>0%</td>
<td>5%</td>
</tr>
</tbody>
</table>

## Indice d’iode

<table>
<thead>
<tr>
<th>Component</th>
<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>
<td>32/36</td>
</tr>
<tr>
<td>Pt fusion</td>
<td>19/21</td>
<td>36/38</td>
<td>50/55</td>
</tr>
<tr>
<td>%S à 15°C</td>
<td>18/22</td>
<td>38/42</td>
<td>76/82</td>
</tr>
<tr>
<td>%S à 20°C</td>
<td>5/7</td>
<td>28/32</td>
<td>67/73</td>
</tr>
<tr>
<td>%S à 25°C</td>
<td>2</td>
<td>23/27</td>
<td>58/62</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 = \(f([\text{catalysts}], \text{temperature}: k_3/k_2; k_2/k_1)\)

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

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

\(\rightarrow\) 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)

REACTEUR

H₂

Filtration

Huiles hydrogénées brutes → Post raffinage

Catalyseur neuf (Ni, Cu)

Recyclage

Catalyseur usagé
Influence of temperature and quality of catalyst on AG trans formation
## 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 (chimical ou 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
INTERESTERIFICATION

*Principle:* rearrangement of FA on glycerol

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

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

- Directed: $T$ 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
ENZYMATIC INTERESTERIFICATION

*Principle*: rearrangement of FA on glycerol

→ specificity of biocatalyst to direct modification

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

![Chemical reaction diagram]

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 12.6% 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.

http://europe.croklaan.com/ProductGroups/Betapol/
Enzymatic IE (Batch)

Continuous EIE

Heater

Water bath system
(aquarium)

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

Pump

Desmet Ballestra
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

![Graph showing the solid fat content profile](image-url)
ENZYMATIC INTERESTERIFICATION

Ex application palm oil

- Increase SFC – seeding with crystals (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 Interesterification**

- Pretreatment of oil
- Catalyst: 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>Specification</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

---

Sunflower and palm oils

**Graph:**

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>15</td>
<td>10</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>
</tbody>
</table>

**Result:** Enzymatic process retains more tocopherol

**Table:**

| Tocopherol (ppm) | 701 | 252 | 505 | 639 | 197 | 412 | 581 | 81 | 281 | 426 | 546 | 185 | 425 | 463 | 182 | 366 |

---
Capital and Operating Cost: A Comparison

- 0.5 kg NaOCH$_3$ randomises 1 ton of oil within a few minutes
- 600 kg enzymes require 1 hour to randomise 1 ton of oil
- NaOCH$_3$ costs some 4 $/kg; enzyme costs about 40 $/kg
## PROCESSES COMPARISON

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

Fraction

1-X

Fully hydrogenated

Saturated oil

Interesterified

Emulsion, cooling
Cristallisation, blending
Packaging

Dosing pump

cold

Agitation

Milk

Water
PARTIAL GLYCERIDES PRODUCTION DE
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 DE
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 extraît 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 brassicastérols.

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, resynthétéetized 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 reltionship with health.
Corps gras

- Triglycérides
  - Acides gras
    - Alcools gras
    - Hydrocarbures
    - Cires...
  - Glycérol
    - Insaponifiable
      - Aliphatique
        - Stérols
        - Tocophérols
        - Squalène
        - Alcools terpéniques
        - Carotènes...
      - Terpénique
  - Naturels
    - Lipides polaires
      - Phospholipides
      - Sphyngolipides
      - Glycolipides...

Constituants mineurs

- 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

Liver

Insulin Resistance

↑ FFA

DGAT

Glycerol

VLDL

ApoB-100

ApoA-I

HDL

Small, dense HDL

CETP

TG

CE

HTGL

ApoB-100

LDL

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.