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

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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
→ 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

Physical extraction with screw press

Filtration, centrifugation

Cleaning

Grinding

Heating

Pressure

Liquid Fraction
34 kg

Extraction

Meals
65 kg

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

Refining

Solid residues elimination

Filtration, centrifugation

41 kg

7 kg
Hexane extraction plant

SAIPOL Le Mériot Pant (photo C. Helsly)

Solid supply

Miscella towards distillation

Hexane

Extracteur

Vapors evacuation

Désolvantiseur

Cooled meals
## 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 Organolementique</td>
</tr>
<tr>
<td>Produits d’ox.</td>
<td>f(Mat lère)</td>
<td>Auto-ox.</td>
<td>Instabilité Organolementique Nutrition</td>
</tr>
<tr>
<td>Flaveurs</td>
<td>&lt; 0,1%</td>
<td>Naturel</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)

Refined oil

Waxes

Flavors

Refined oil
Transformation des graines oléagineuses

1. Nettoyage - Tri
2. Aplatissage
3. Cuisson - Séchage
4. Pression
5. Tamisage - Séchage
6. Huile de pression
7. Extraction
8. Désolvantisation - Toastage
9. Pelletisation
10. Distillation
11. Huile d'extraction
12. Démucilaginations / Neutralisation
13. Décoloration
14. Déodorisation
15. Refroidissement sous vide

A. Fabrication d'aliments pour animaux
B. Stockage huiles à usage industriel
   (Diester, lipochimie, solvants, bio-lubrifiants)
C. Huile alimentaire
Degumming

1- mixer
2- contactor
3- centrifuge separator
4- heat exchanger
5- feed pump

Raw oil

H₂PO₄

H₂O

Degumming oil

Gums

Refined and dry oil

Washing

Washing water

H₂O

Neutralised oil

Soaps

NaOH

Drying

Deacidification
The flowchart illustrates the processing stages of sheanuts to sheabutter:

**Collection Preservation**
- Collect, sort
- Dry, parboil

**Processing 1**
- Frying
- Boiling
- Crushing
- Milling
- Mixing
- Heating
- Collection

**Processing 2**
- Bulking
- Storing
- Transporting
- Selling

**Intermed. trade**
- Buy sheabutter
  - Filtering
- Conditioning
- Packing
- Labelling
- Cooling
- Storing
- (cooled) transport to Lagos

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

The final products are Sheabutter and 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

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
ENZYMATIC DEGUMMING

Global Innovation

Crude Vegetable Oil → Refined Oil + Heavy Phase + DDO

Caustic
PLA₁
PLA + PLC

Yield
96.5
97.4
98.3

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 exces of phosphoric acid added to degum oils (1)
  ✓ neutralization of FFA under the form of sodic soaps:
    \[ R-COOH + NaOH \rightarrow R-COONa + H_2O \] (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)

BLEACHING

Filters

N Saturation

cooler

Dry vapor

heater

DEODORIZATION

vacuum

Adsorbing clays

Filters

(Dewaxing/filtration)

REFINED OIL

DESODORIZATION

NEUTRAL BLEACHED OIL
Inlet bleached oil

Inlet blend oil/clays

elimination of clays

Vertical Filter
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 cristals)
- 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

Composition

Melting

Controlled cooling

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

Equipments:
- Cooling system
- Decanting
- Centrifugation
- Filtration

HIGH melting point Fraction

LOW melting point Fraction
FRACTIONATION OF FATS

- Continuous Filtration -
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

<p>| | |</p>
<table>
<thead>
<tr>
<th></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>

Stéarine (20%) Oléine (80%)

<table>
<thead>
<tr>
<th></th>
<th>Stéarine (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>
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</tbody>
</table>

Indice d’iode

<table>
<thead>
<tr>
<th>Oléine</th>
<th>Palme</th>
<th>Stéarine</th>
</tr>
</thead>
<tbody>
<tr>
<td>56/58</td>
<td>50/55</td>
<td>32/36</td>
</tr>
<tr>
<td>19/21</td>
<td>36/38</td>
<td>50/55</td>
</tr>
<tr>
<td>18/22</td>
<td>38/42</td>
<td>76/82</td>
</tr>
<tr>
<td>5/7</td>
<td>28/32</td>
<td>67/73</td>
</tr>
<tr>
<td>2</td>
<td>23/27</td>
<td>58/62</td>
</tr>
</tbody>
</table>

Pt fusion

<table>
<thead>
<tr>
<th>Oléine</th>
<th>Palme</th>
<th>Stéarine</th>
</tr>
</thead>
<tbody>
<tr>
<td>19/21</td>
<td>36/38</td>
<td>50/55</td>
</tr>
<tr>
<td>18/22</td>
<td>38/42</td>
<td>76/82</td>
</tr>
<tr>
<td>5/7</td>
<td>28/32</td>
<td>67/73</td>
</tr>
<tr>
<td>2</td>
<td>23/27</td>
<td>58/62</td>
</tr>
</tbody>
</table>

%S à 15°

<table>
<thead>
<tr>
<th>Oléine</th>
<th>Palme</th>
<th>Stéarine</th>
</tr>
</thead>
<tbody>
<tr>
<td>18/22</td>
<td>38/42</td>
<td>76/82</td>
</tr>
<tr>
<td>5/7</td>
<td>28/32</td>
<td>67/73</td>
</tr>
<tr>
<td>2</td>
<td>23/27</td>
<td>58/62</td>
</tr>
</tbody>
</table>

%S à 20°

<table>
<thead>
<tr>
<th>Oléine</th>
<th>Palme</th>
<th>Stéarine</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/7</td>
<td>28/32</td>
<td>67/73</td>
</tr>
<tr>
<td>2</td>
<td>23/27</td>
<td>58/62</td>
</tr>
</tbody>
</table>

%S à 25°

<table>
<thead>
<tr>
<th>Oléine</th>
<th>Palme</th>
<th>Stéarine</th>
</tr>
</thead>
<tbody>
<tr>
<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]

- ⇒ melting point
- ⇒ stability (rapeseed - soya)

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

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

→ 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 → Raffinage → Huiles neutres sèches

Catalyseur usagé

Huiles neutres sèches → Filtration → Catalyseur usagé

Catalyseur neuf (Ni, Cu)

Huiles hydrogénées brutes → Post raffinage

Filtration

H₂

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

Recyclage
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
**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**: \( T \) intermediate
  → Cristallisation of high melting point TAG
  (displacement of equilibriums)
Example: Soy Salad Oil + Palm Stearine
CHEMICAL INTERESTERIFICATION

The Catalyst

Sodium methyleate is a hazardous catalyst

Catalyst dry storage tank

Rotary dosing valve

Catalyst dosing tank

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**

\[
\begin{array}{c}
\text{O} \\
\text{O} \quad \text{S} \quad \text{O} \\
\end{array}
\xrightarrow{\text{Lipase}}
\begin{array}{c}
\text{S} \\
\text{O} \quad \text{O} \\
\end{array}
\begin{array}{c}
\text{O} \\
\text{S} \\
\end{array}

O = \text{Oleic acid} \quad S = \text{Stearic acid}

\rightarrow \text{Cocoa butter analogues – texture control}

\rightarrow \text{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.
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
ENZYMATIC INTERESTERIFICATION

Ex application palm oil

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

Ex application palm oil

DSC (differential scanning calorimetry) melting profiles of Palm Oil and EIE Palm Oil

Palm Oil

EIE Palm Oil

5°C/min.
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% (++)
Chemical Interestereification

Pretreatment of oil → Catalyst: NAOCH$_3$ → Bleaching → Desodourisation

Enzymatic interestereification

Pretreatment of oil → Catalyst: lipase → Desodourisation

Simpler process but precaution have to be taken to prolong 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

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

Result: Enzymatic process retains more tocopherol
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>- Reproductible and efficient</td>
<td>- Reproductible and efficient if no inlet change occurs</td>
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<tr>
<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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<tr>
<td></td>
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<td>- lower initial investment</td>
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<tr>
<td><strong>Drawbacks</strong></td>
<td>- Toxic catalyst</td>
<td>- biocatlyst affected by initial purity of oil</td>
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<td></td>
<td>- highTemp</td>
<td>- hydrolysis</td>
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<tr>
<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>- 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
  - Fraction
    - Fully hydrogenated
  - Saturated oil
    - Interesterified

**Process Flow:**
- Dosing pump
- Emulsion, cooling
- Cristallisation, blending
- Packaging
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 Lipzyme 435 (2%) and various glycerol addition rates at 80°C/24 hours

Glycerolysis with Lipzyme 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 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, 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 carboxylic 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

95-99 %

Triglycérides

90-95 %

Acides gras

3-5 %

Glycérol

1-5 %

Naturels

0,1 à 3 %

Insaponifiable

0,1-0,2 %

Lipides polaires

- Stérols
- Tocophérols
- Squalène
- Alcools terpéniques
- Carotènes...

- 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.