Developments in Hydrogenation and Interesterification to Comply with New Nutritional and Health Standards for Edible Oils

W. De Greyt, V. Gibon and M. Kellens

Desmet Ballestra Group
Zaventem, Belgium
TRENDS IN EDIBLE OIL PROCESSING

Increased need for more efficient processes (commodity oils)

* More cost efficient processes (lower investment & operating costs)
* Valorisation and/or reduction of by-products
* Flexible plants able to process wide range of different oils
* Larger capacities (economics of scale)

Increased demand for higher quality food oils

* Low or no trans FA (formed during refining and hydrogenation)
* Balanced FA composition (optimal ratio saturated/unsaturated FA)
* High concentration of natural anti-oxidants (tocopherols) and phytosterols
* No contaminants (pesticides, PAH, dioxins, PCB,...)
HIGH QUALITY FOOD OILS

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

Refining

OIL QUALITY

Functional Properties
- Good melting profile
- Desired Plasticity
- Crystallisation kinetics

Modification

Nutritional Quality
- Balanced FA composition (SFA/MUFA/PUSA)
- Low or no trans FA
- High natural antioxidants (tocopherols) and vitamins
INCREASED ATTENTION FOR NUTRITIONAL QUALITY OF FOOD OILS AND FATS
CURRENT NUTRITIONAL STANDARDS FOR FOOD OILS - 1

FATTY ACIDS

ESSENTIAL FATTY ACIDS
Cannot be synthesized by the human body
- w-6 FA: linoleic acid, arachidonic acid;
- w-3 FA: linolenic acid, EPA, DHA
Optimal ratio w-6/w-3 < 10

EFFECTS ON RISK FOR CHD
- C12:0, C14:0, C16:0 and C18:1 trans are considered bad
- C18:0 and C18:1 are considered neutral
- C18:2, C18:3 and CLA are considered good
CURRENT NUTRITIONAL STANDARDS FOR FOOD OILS - II

VALUABLE MINOR COMPONENTS

**Tocopherols/Tocotrienols**

Presence in oils desired because of their Vitamin E activity

**Phytosterols**

- Reduction of Blood cholesterol levels
- Added to certain margarine fats (8-10%)

CONTAMINANTS

- Pesticides, PAH’s, dioxins, PCB’s
- Are only allowed in very low or non-detectable levels
- Removed during oil refining (adsorption or stripping)
### GENERAL COMPOSITION OF SOME FOOD OILS

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Soy</th>
<th>Palm</th>
<th>Rape</th>
<th>Sun</th>
<th>Olive</th>
<th>Fish&lt;sup&gt;4&lt;/sup&gt;</th>
<th>Tallow</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAC (%)</td>
<td>8</td>
<td>42</td>
<td>4</td>
<td>6</td>
<td>10</td>
<td>12</td>
<td>25</td>
</tr>
<tr>
<td>C16:0</td>
<td>4</td>
<td>5</td>
<td>2</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>19</td>
</tr>
<tr>
<td>C18:0</td>
<td>28</td>
<td>41</td>
<td>60</td>
<td>28</td>
<td>75</td>
<td>15</td>
<td>35</td>
</tr>
<tr>
<td>C18:1</td>
<td>53</td>
<td>10</td>
<td>20</td>
<td>61</td>
<td>10</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>C18:2</td>
<td>tr&lt;sup&gt;1&lt;/sup&gt;</td>
<td>tr</td>
<td>tr</td>
<td>tr</td>
<td>tr</td>
<td>20</td>
<td>tr</td>
</tr>
<tr>
<td>EPA/DHA</td>
<td>1200</td>
<td>600</td>
<td>900</td>
<td>700</td>
<td>200</td>
<td>tr</td>
<td>tr</td>
</tr>
<tr>
<td>Tocopherols&lt;sup&gt;2&lt;/sup&gt;</td>
<td>4000</td>
<td>2500</td>
<td>1000</td>
<td>4500</td>
<td>100</td>
<td>tr</td>
<td>3000&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td>Sterols&lt;sup&gt;2&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melting Point&lt;sup&gt;3&lt;/sup&gt;</td>
<td>Liquid</td>
<td>35</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Liquid</td>
<td>25</td>
</tr>
</tbody>
</table>

<sup>1</sup>tr : traces;  <sup>2</sup>expressed in ppm;  <sup>3</sup>°C;  <sup>4</sup>Cod Liver Oil;  <sup>5</sup>cholesterol

Modification is required for use in food formulations
FAT REFINING

* Efficient adsorption processes
* Improved deodorization technology

FAT MODIFICATION

* Low trans hydrogenation
* Dry fractionation (multi-stage, new crystallisers)
* Interesterification (enzymatic vs chemical)
**INTERESTERIFICATION**
(bio) chemical
- No change of fatty acid profile
- Redistribution of FA in glycerides

**HYDROGENATION**
chemical
- Saturation/isomerisation of FA

**FRACTIONATION**
Physical and Fully Reversible
- Some effect on FA composition and TAG distribution
HYDROGENATION
HYDROGENATION OF EDIBLE OILS

Selective Saturation of double bonds ⇐⇒ Formation of trans fatty acids

Typical process conditions for partial hydrogenation

* Temperature: 150 - 180°C
* H₂ Pressure: 2 - 20 bar
* Catalyst: Ni-catalyst (100 ppm Ni)

% trans = f (T, P, Ni)

Higher T gives more TFA
Higher P & more Ni gives less TFA
CURRENT STATUS OF HYDROGENATION

- Stricter labelling & legislation about trans fatty acids
- Increase pressure from consumer organisations

- Increase demand for:
  - Low trans products: < 5% on fat basis
  - Zero trans products: < 0.5% on fat basis

- Changing technology
  - Dry fractionation/interesterification
  - Full hydrogenation (no trans)
  - Low trans hydrogenation
LOW TRANS PARTIAL HYDROGENATION

- **Modified process conditions**
  - High Pressure hydrogenation (20 bar)
  - Low Temperature hydrogenation

- **Use of new catalysts**
  - Precious metal (Pd,Pt) catalysts
  - Zeolite based catalysts

- **New technologies (under development)**
  - Supercritical hydrogenation
  - Continuous membrane hydrogenation
## HIGH PRESSURE HYDROGENATION

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reference</th>
<th>High pressure hydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IV</td>
<td>70</td>
</tr>
<tr>
<td>FAC (% w:w)</td>
<td>C18:0</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td>C18:1t</td>
<td>31.3</td>
</tr>
<tr>
<td></td>
<td>C18:1c</td>
<td>43.5</td>
</tr>
<tr>
<td></td>
<td>C18:2t</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>C18:2c</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>C18:3t</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>C18:3c</td>
<td>0.0</td>
</tr>
<tr>
<td>Trans FA</td>
<td></td>
<td>34.3</td>
</tr>
<tr>
<td>SFC (% @ °C)</td>
<td>10</td>
<td>63.6</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>38.0</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>11.8</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Lab-scale trials: 110°C, 20 bar H₂, 100 ppm Ni (Nysosel 820)
Melting curves - PH SO IV 70

SFC (%) vs Temperature (°C)

- Conventional
- High pressure
## Losatra® Process

Cargill US patent application

### Typical reaction conditions:

- **Temp**: 30-50°C
- **Pressure**: 1-25 bar
- **Catalyst**: 2000-4000 ppm Ni

### Characteristics

- Low reaction rate: 0.1-0.5 ΔIV/min.
- Low *trans*
- Low SFC at 10°C: 11%

### Table: Soybean oil transformation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Feed</th>
<th>Hydrogenated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp (°C)</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>-</td>
<td>10-15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.5</td>
</tr>
<tr>
<td>Cat (ppm Ni)</td>
<td>-</td>
<td>2200&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1980&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Time (min)</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150</td>
</tr>
<tr>
<td>IV (calculated)</td>
<td>129.1</td>
<td>99.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>102.5</td>
</tr>
<tr>
<td>RS (ΔIV/min)</td>
<td>-</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.18</td>
</tr>
<tr>
<td>FAC (% w:w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C18:0</td>
<td>3.2</td>
<td>9.3</td>
</tr>
<tr>
<td>C18:1t</td>
<td>0.0</td>
<td>4.6</td>
</tr>
<tr>
<td>C18:1c</td>
<td>25.6</td>
<td>37.1</td>
</tr>
<tr>
<td>C18:2t</td>
<td>0.0</td>
<td>2.7</td>
</tr>
<tr>
<td>C18:2c</td>
<td>52.0</td>
<td>31.5</td>
</tr>
<tr>
<td>C18:3t</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>C18:3c</td>
<td>6.5</td>
<td>1.3</td>
</tr>
<tr>
<td><em>TFA</em></td>
<td>0.9</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.9</td>
</tr>
<tr>
<td>SFC (% @ °C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>11.0</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>4.0</td>
</tr>
</tbody>
</table>

<sup>1</sup> 3500 g Oil + 35 g preheated Pricat 9920

<sup>2</sup> 15 tonnes Oil + 135 kg Pricat 9920
## USE OF PRECIOUS METAL CATALYSTS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>IV = 105</th>
<th></th>
<th>IV = 70</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>Ni</td>
<td>Pt</td>
<td>Ni</td>
<td>Pt</td>
</tr>
<tr>
<td>FAC (%w:w)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C18:0</td>
<td>4.7</td>
<td>15.2</td>
<td>10.3</td>
<td>30.1</td>
</tr>
<tr>
<td>C18:1t</td>
<td>12.6</td>
<td>1.5</td>
<td>31.3</td>
<td>3.0</td>
</tr>
<tr>
<td>C18:1c</td>
<td>36.7</td>
<td>28.8</td>
<td>43.5</td>
<td>35.9</td>
</tr>
<tr>
<td>C18:2t</td>
<td>5.3</td>
<td>0.8</td>
<td>3.0</td>
<td>1.0</td>
</tr>
<tr>
<td>C18:2c</td>
<td>28.1</td>
<td>38.5</td>
<td>0.5</td>
<td>17.9</td>
</tr>
<tr>
<td>C18:3t</td>
<td>0.1</td>
<td>0.4</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>C18:3c</td>
<td>1.8</td>
<td>3.8</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>TFA</td>
<td>18.0</td>
<td>2.6</td>
<td>34.3</td>
<td>4.2</td>
</tr>
<tr>
<td>SFC (% @ °C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>7.6</td>
<td>19.2</td>
<td>63.6</td>
<td>50.2</td>
</tr>
<tr>
<td>20</td>
<td>1.5</td>
<td>14.2</td>
<td>38.0</td>
<td>38.7</td>
</tr>
<tr>
<td>30</td>
<td>0.0</td>
<td>9.6</td>
<td>11.8</td>
<td>26.7</td>
</tr>
<tr>
<td>35</td>
<td>0.0</td>
<td>7.5</td>
<td>3.0</td>
<td>20.8</td>
</tr>
</tbody>
</table>

Lab-scale trials: 180-200°C, 3-4 bar H₂, 100 ppm Ni (Nysosel 820)
Soybean oil, 50°C, 4-5 bar H₂, 50 ppm Pt
Further modification (blending, IE, dry fractionation,…) to remove tailing end of the melting curve.

Melting curves – Partially Hydrogenated Soybean oil IV 70

- Conventional
- High pressure
- Pt-catalyst

‘Tailing’
Straight CIE - Blending with SO – CIE of blend

- Conventional
- Pt-catalyst
- CIE
- Blend 25:75
- Blend 25:75 CIE
Limited effect when applying high P/low T with traditional Ni-cat
Use of precious metal catalysts is still too expensive
Potential of membrane and supercritical hydrogenation doubtful

*Is there a need/application for partially hydrogenated oils with low trans, but high saturated fatty acid content?*

**More interesting/economical option**
Production of hardstocks by full hydrogenation (no trans, no UFA)
Formulation of food fats with desired functional properties via combined *(enzymatic) interesterification/dry fractionation*
INTERESTERIFICATION
• Redistribution of FA on glycerol backbone
• With chemical or enzymatic catalysts
• Random or specific:
  
  e.g. Palm Oil:
RANDOM INTERESTERIFICATION

\[ R_1R_1R_1 + R_2R_2R_2 \rightarrow (\text{random}) \]

For ‘Margarine fats’
- to improve overall melting profile
- to increase compatibility
- to enhance plasticity
  - margarines
  - shortenings

Chemical or Enzymatic
Margarine application: little difference between CIE and EIE

PST: SBO

C.I.E.

E.I.E

Temperature [°C]

% SFC

OFI Middle East 2008
Technical and Commercial Conference
Hilton Hotel
Abu Dhabi, UAE, April 15-16, 2008
For ‘structured lipids’:

- Confectionery Fats (high SUS, CBE):
  - to increase compatibility with CB
  - to improve hardness and sharpness of the fat.
- Infant formulation (high OPO).
- East-to-digeste and low calory fats (MLM – medium chain type).
Production of POS/SOS-triacylglycerols:

- POS is main component in CB, also found in illipe oil
- POP is main SUS-component in palm oil (mid fractions)
- Strategy: ‘structuring’ POP lipid in to POS/SOS lipid

\[
\text{POP} + \text{Stearic acid} \rightarrow \text{Specific EIE} \rightarrow \text{POS/SOS} + \text{FFA}
\]

removed by stripping
CHEMICAL INTERESTERIFICATION

- Low catalyst consumption (0.05-0.1%) due to better oil pre-treatment
- Lower oil losses
- Dry catalyst remains difficult to handle, induce unwanted side-reactions (e.g. degradation of tocopherols, color fixation…)

ENZYMATIC INTERESTERIFICATION

- ‘Random’ enzymatic interesterification: margarine fats
- ‘Specific’ enzymatic (inter)esterification: structured lipids
- Less expensive and more stable enzymes are commercially available
- Higher productivity resulting in an ‘economical’ operating cost
Chemical versus Enzymatic interesterification

**Chemical interesterification**
- Pretreatment of oil
- Reaction Catalyst: NaOCH3
- Deactivation water / acid
- Postbleaching
- Deodorization

Batch Process in stirred tank reactors – suitable for frequent stock changes

**Enzymatic interesterification**
- Pretreatment of oil
- Reaction Catalyst: Lipase
- Deodorization

Continuous process through a series of fixed bed reactors – Production of larger batches of ‘bulk” EIE fat

- No catalyst inactivation
- No postbleaching

Less Oil Losses

Combined EIE-dry frac.
OIL PRETREATMENT FOR ENZYMATIC IE

Enzyme inactivation by following components:
- Radicals (peroxides)
- Polar Impurities (phosphatides, soaps, ..)
- Secondary oxidation products (ketons, aldehydes, ..)
- Trace elements (Nickel, ..)
- Acids (citric acid, ..)

Oil quality prior to enzymatic interesterification is important
- Chemical Refining: Neutralized-Bleached
- Physical Refining: Preferably fully refined (bleached and deodorized)
  Alternatively: silica treatment of bleached oil
Enzyme productivity for Lipozyme TL-IM (kg EIE oil/kg enzyme)

- Depends largely on feedstock quality
- Needs to be high because to keep operating cost competitive
- For ‘random’ EIE: min. productivity (valid for good feedstock): 2.5 ton EIE oil/kg enz.
- Higher productivity up to 4 ton EIE oil/kg enzyme achieved in pilot trials

Enzyme activity (Flow rate – kg EIE oil/kg enzyme.hr)

- Enzymatic interesterification is a continuous process
- Constant but rather slow flow rate: typically 1-2 kg EIE oil/kg enzyme.hr
- Enzyme in use for 1250-2500 hr (50-100 days)
EIE Equipments

Pilot unit

Lab scale unit

Industrial unit
Thank you for your attention