Developments in Edible Oil Refining for the Production of High Quality Food Oils

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WORLD VEGETABLE OIL PRODUCTION - 2008

Total: 140 Mio Ton

- Palm
- Soybean
- Rapeseed
- Sunflower
- Palm Kernel
- Cottonseed
- Coconut
- Olive
- Corn
- Others

Total vegetable oil production in 2008 was 140 million tons, with Palm and Soybean being the most significant contributors.
VEGETABLE OILS : GENERAL COMPOSITION

Acylglycerols (92-95%)
- Mainly Triacylglycerols
- Some Di- and Monoacylglycerols

FFA (0.3-5%)

Phospholipids (<3%)
- Hydratable PL
- Non-hydratable PL

Minor components (0.3-2%)
- Tocopherols, Sterols, Pigments,…
- Contaminants, Impurities,…
VEGETABLE OILS: MINOR COMPONENTS

Valuable Minor Components

- Tocopherols, Sterols, …
- Desired in the refined oil
- Good nutritional properties
- To be retained during refining

Side Reaction Products

- Trans FA, polymers, (3-MCPD esters), …
- Formed during refining
- Bad nutritional properties
- Unwanted

Contaminants

- Pesticides, PAH, Dioxins, …
- Present in crude oils
- Carcinogenic/Toxic
- To be removed during refining
REFINED OIL QUALITY PARAMETERS

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

**Nutritional Quality**
- High tocopherol content
- No trans FA
- No contaminants
- No side-reaction products
- (Fatty acid composition)

**‘Standard’ Quality Parameters**

**‘New’ Quality Parameters**

Optimized Edible Oil Processing required to meet new oil Quality Parameters
REFINERS CHALLENGE

EFFICIENCY

REFINING PROCESS CONDITIONS

SUSTAINABILITY

QUALITY
EDIBLE OIL REFINING: PROCESS OPTIONS

101st AOCS Annual Meeting
May 16-19, 2010
Phoenix, Arizona, USA

Crude Oil

Water degumming

WDG Oil

Soapstock

Acid degumming

Acid Gums

Spent bleaching earth

Bleaching

Deodorization

Deodorizer Distillate

Fully Refined Oil

Chemical refining

Physical refining

Gums

Physical deacidification Deodorization
CONTAMINANT REMOVAL DURING OIL PROCESSING

- Adsorption on specific adsorbents (active carbon)
  - Heavy Polycyclic Aromatic Hydrocarbons (PAH)
  - Dioxins and furans from Fish Oils
  - Dioxin-like PCB (non-ortho PCB)

- Deodorization/Steam Stripping
  - Pesticides (herbicides, insecticides, fungicides,....)
  - Light PAH (e.g. from coconut oil)
  - Ortho-PCB (non dioxin-like PCB)
Combiclean process meets refiners challenge

Removal of contaminants

1. Silica + Prebleaching
2. Pre filtration
3. Bleaching
4. Final filtration

Vacuum unit
Active carbon
Filter press
Polish filters
Spent carbon
To deodorisation
TFA formation during soybean oil deodorization

TFA max. 1.0%

%TFA

Time (minutes)

270°C
260°C
250°C
230°C

REDUCING HEAT LOAD AND KEEPING STRIPPING EFFICIENCY HIGH
LOW HEAT LOAD – DUAL TEMPERATURE

Scrubber

Stripper

Deaerator

Deodorizer

Low pressure short pack

Single or Dual Temp

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IMPROVED VACUUM SYSTEMS

CHILLED BAROMETRIC WATER

ICE CONDENSING

* Lower pressure in the deodorizer - Lower motive steam consumption
* Less odor emissions
NEW CHALLENGE: 3-MCPD / GLYCIDOL ESTERS

MCPD ESTERS

<table>
<thead>
<tr>
<th>Structure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>3-MCPD mono-(sn1) ester</td>
</tr>
<tr>
<td>OR</td>
<td>Cl</td>
</tr>
<tr>
<td>OR'</td>
<td>Cl</td>
</tr>
</tbody>
</table>

GLYCIDOL ESTERS

<table>
<thead>
<tr>
<th>Structure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH H2C C CH2</td>
<td>Free glycidol</td>
</tr>
<tr>
<td>OCOR H2C C CH2</td>
<td>Glycidol-ester</td>
</tr>
</tbody>
</table>
### OCCURRENCE IN REFINED FOOD OILS

MCPD-ester content in various vegetable oils (source: FEDIOL)

<table>
<thead>
<tr>
<th>OIL</th>
<th>N° Samples</th>
<th>Average content 3-MCPD ester</th>
<th>Max. level of 3-MCPD ester</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rapeseed Oil</td>
<td>31</td>
<td>0.3 mg/kg</td>
<td>1.5 mg/kg</td>
</tr>
<tr>
<td>Sunflower Oil</td>
<td>49</td>
<td>1.0 mg/kg</td>
<td>5.7 mg/kg</td>
</tr>
<tr>
<td>Corn Oil</td>
<td>15</td>
<td>2.8 mg/kg</td>
<td>7.0 mg/kg</td>
</tr>
<tr>
<td>Palm Oil</td>
<td>37</td>
<td>4.5 mg/kg</td>
<td>13 mg/kg</td>
</tr>
</tbody>
</table>

* Reported data vary widely (due to applied method?)
* Most used (DGF) method not generally accepted
* Mechanism of formation not fully understood
* Very difficult to develop an efficient mitigation strategy
MECHANISM OF FORMATION : HYPOTHESIS

MONOGLYCERIDES AS PRECURSOR

MAG

Glycidol ester

Nucleophilic substitution

3-MCPD mono-ester

MECHANISM OF FORMATION: HYPOTHESIS

DIGLYCERIDES AS PRECURSOR

DAG

Nucleophilic substitution

3-MCPD di-ester

Radical mechanism

Glycidol-esters

Mono- and diglycerides and 3-MCPD ester formation

* Low DAG content will result in low 3-MCPD/glycidol-ester content
* If DAG > 4%, then 3-MCPD/glycidol ester content is mostly > 5 ppm
* No apparent correlation between MAG and 3-MCPD/glycidol ester formation

Source: Karel Hrncirik (Unilever, 2009) and Bertrand Matthaus (MRI, 2009)
EFFECT OF TEMPERATURE

Temperature more important parameter than time
At t > 240°C, mainly glycidol-esters are formed (exponential increase)
Formation of 3-MCPD esters is relatively independent of temperature (2-4 ppm)

Source: Bertrand Matthaus (MRI, 2009)
MITIGATION STRATEGY

Current statement of BfR (German Federal Institute for Risk Assessment)

*Alternative techniques have to be developed that guarantee the production of refined food oils with reduced or no 3-MCPD esters (and related compounds)*

Today’s *informal* position of FEDIOL

*Information so far obtained is insufficient to optimize the refining process for the mitigation (reduction/removal) of 3-MCPD esters and related compounds while maintaining the quality and food safety of the refined oil/fat*
### MITIGATION STRATEGY

**3-MCPD esters**
- Require acidic conditions and presence of chloride
- Can be formed during acid degumming and bleaching
- Washing may remove chlorides from crude oil
- Systematic monitoring of chlorides in all processing aids

**Glycidol esters**
- Can be formed from MAG via nucleophilic substitution (in absence of Cl⁻)
- Formation from DAG possible via radicalair reaction at $T > 240°C$
- Most likely to be formed during deodorization at high temp. (physical refining)
- Dual temperature deodorization concept may give lower levels
CONCLUSION

Vegetable Oil Refining can be optimized to meet new oil quality standards

- Activated carbon process for removal of ‘heavy’ contaminants
- Optimized steam distillation/deodorization for removal of ‘light’ contaminants
  minimal trans formation
- Other refiners challenges (efficiency, environmental impact) are also met

3-MCPD and glycidiol esters

- Still some knowledge gaps makes good mitigation strategy difficult
- Need for a more reliable and accurate analytical methodology
- Better understanding of mechanisms of formation during food processing
  in general and oil refining in particular required