Mitigation of 3-monochloropropane-1,2-diol and glycidol esters in refined palm oil via modified refining process

Chin Ping TAN
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• Recent scientific opinion on MCPDE and GE issues (2016 EFSA’s report)
• Malaysian scenario: 3-MCPDE and GE in palm olein
• Mitigation of 3-MCPDE and GE in palm oil
Introduction

• 3-monochloropropane-1,2-diol (MCPD)- and 2-Monochloropropane-1,3-diol (2-MCPD) and their esters and glycidyl esters are food contaminants found highest in refined vegetable oils.

• In refined vegetable oils, especially palm oil, these contaminant are formed during physical refining process.

• However, the exact mechanism of formation is still unclear.
Acyloxonium ion pathway vs. Glycerolphosphates pathway
EFSA Report

• According to the EFSA report “Risks for human health related to the presence of 3- and 2-mono(chloro)propanediol (MCPD), and their fatty acid esters, and glycidyl fatty acid esters in food”, the panel on Contaminants in the Food Chain (CONTAM panel) has evaluated a total of 7,175 data.

• The report found that 3- and 2-MCPD and glycidyl esters are constantly highest in palm oil/fat while other vegetables oils containing substantially low levels of these process contaminants.

• Across the data, average content of these contaminants are:
  – 3-MCPDE : 2.91 ppm
  – 2-MCPDE : 1.56 ppm
  – GE : 3.99 ppm
Hazard characterization of MCPDE and GE

• The CONTAM panel suggested the tolerable daily intake (TDI) for 3-MCPD is 0.8 μg/kg body weight (bw) per day.

• For glycidol, the Panel selected a T25 value of 10.2 mg/kg bw per day for neoplastic effects in rats. *(T25 is the chronic daily dose in mg per kg bodyweight which will give 25% of the animals tumours at a specific tissue site)*

• However, no TDI could be established for 2-MCPD and its ester because of lacking of reliable data.
Level of MCPD esters in palm olein

3-MCPDE level in commercial RBD palm olein in Malaysia market

3-MCPDE levels:
0.34 – 4.45 mg/kg
Level of GE in palm olein

GE level in commercial RBD palm olein in Malaysia market

GE levels: 0.34 – 10.98 mg/kg
However, palm oil has its uniqueness and functional properties to the food industry.
The Oil Palm – most productive oil crop

<table>
<thead>
<tr>
<th>Oil Crops</th>
<th>Production (Mn T)</th>
<th>% of total production</th>
<th>Total area (Mn Ha)</th>
<th>% of total area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil palm*</td>
<td>59.39</td>
<td>42.3</td>
<td>14.8</td>
<td>8.3</td>
</tr>
<tr>
<td>Soybean</td>
<td>41.8</td>
<td>29.8</td>
<td>103.8</td>
<td>58.4</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>24.4</td>
<td>17.4</td>
<td>33.3</td>
<td>18.7</td>
</tr>
<tr>
<td>Sunflower</td>
<td>14.8</td>
<td>10.5</td>
<td>25.9</td>
<td>14.6</td>
</tr>
</tbody>
</table>

Source: Oil World Annual 2013
* Combined tonnage of palm oil and palm kernel oil
Refining process and the factors influencing formation of 3-MCPD & glycidyl esters
3-MCPD & glycidyl esters in palm oil

Factors influencing formation of 3-MCPD & glycidyl esters

- CPO quality
- Acid degumming dosage
- Bleaching adsorbent used
- Deodorization temperature
Reduction of 3-MCPD & glycidyl esters in palm oil

CPO ➔ Washing ➔ Degumming ➔ Washing ➔ Bleaching ➔ Deodorization

- [50 °C, 15 min]
- [20 min, phosphoric acid 97%]
- [50 °C, 15 min, 1% water]
- [90 °C, 30 min, 1% Magnesol R60 & activated clay]
- [90 min]

DESIGN-EXPERT Plot

3-MCPD (mg/kg)

Actual Factors
A: % Water = 2.5
B: % Acid = 0.05
C: Degum T = 60
D: Activated clay = 0.5
E: Deodorize T = 250

Perturbation

Deviation from Reference Point

Zulkurnian et al., Food Chem., 2012
## Effects of degumming and bleaching on the reduction of ME and GE

**Design of experiment:** **D-optimal design**
16 experimental runs - 3 factorial and 4 center points

<table>
<thead>
<tr>
<th>Process variables:</th>
<th>Response:</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) Phosphoric acid dosages (20%)   (0 – 2.5 % w/w)</td>
<td>i) 3-MCPD ester</td>
</tr>
<tr>
<td>ii) Types of bleaching earths (1% w/w)</td>
<td>ii) Glycidyl esters</td>
</tr>
<tr>
<td>- Acid activated bleaching earth (acidic pH) (AAA)</td>
<td>iii) Carotene</td>
</tr>
<tr>
<td>- Acid activated bleaching earth (neutral pH) (AAN)</td>
<td></td>
</tr>
<tr>
<td>- Natural bleaching earth (NBE)</td>
<td></td>
</tr>
</tbody>
</table>
3-MCPD esters

- AAA exerted a significant effect on ME reduction compared with NBE and AAN
- Precursors responsible for ME formation were removed from PO prior to deodorization
- Properties and the adsorption capacities of the bleaching earth were the predominant factors in ME removal rather than its acidity.

Table: Properties of three types of bleaching earths

<table>
<thead>
<tr>
<th>Types of bleaching earth</th>
<th>pH</th>
<th>Total Pore volume (cm³/g)</th>
<th>Total Pore area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Activated (Acidic)</td>
<td>3.18 ± 0.01</td>
<td>0.380138</td>
<td>340.363</td>
</tr>
<tr>
<td>Acid Activated (Neutral)</td>
<td>7.27 ± 0.06</td>
<td>0.296388</td>
<td>177.953</td>
</tr>
<tr>
<td>Natural</td>
<td>8.61 ± 0.01</td>
<td>0.286729</td>
<td>120.564</td>
</tr>
</tbody>
</table>

*The total pore volume and area reported refers to pores with a diameter of 13.0 to 210.0 Å.*
Glycidyl esters

- GE was largely removed when AAA + degumming process with high dosage phosphoric acid
- Possible mechanisms: Epoxide ring opening of GE to form glycerol monoester by a reaction with water under acidic conditions
## Optimization of the physical refining process

### Design of experiment: **Face-centered small central composite design**

29 experimental runs - 16 factorial, 8 axial and 5 center points

### Process variables:

1. Phosphoric acid dosages (25%)
2. Degumming temperature
3. Bleaching earth dosage
4. Deodorization temperature

### Response:

1. 3-MCPD ester
2. Glycidyl esters
3. FFA levels
4. Colour

<table>
<thead>
<tr>
<th>Factors</th>
<th>Symbol</th>
<th>Levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>+1</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td><strong>Phosphoric acid dosage (%)</strong></td>
<td><strong>a</strong></td>
<td><strong>0</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>1.5</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>3</strong></td>
</tr>
<tr>
<td><strong>Degumming temperature (ºC)</strong></td>
<td><strong>T</strong></td>
<td><strong>50</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>70</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>90</strong></td>
</tr>
<tr>
<td><strong>Bleaching earth dosage (%)</strong></td>
<td><strong>b</strong></td>
<td><strong>1</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>2</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>3</strong></td>
</tr>
<tr>
<td><strong>Deodorization temperature (ºC)</strong></td>
<td><strong>T_d</strong></td>
<td><strong>240</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>250</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>260</strong></td>
</tr>
</tbody>
</table>
Major outcomes from the modification of refining process

Optimized conditions:

- 0.31% phosphoric acid dosage
- 50 °C degumming temperature
- 3% bleaching earth dosage
- 240 °C deodorization temperature

3-MCPD esters:
- 1.10 mg/kg → 0.18 mg/kg
- Up to 90% reduction

Glycidyl esters:
- 0.85 mg/kg → 0.17 mg/kg
- 80% reduction