Surfactant Impact on Inhibition of Fat Nucleation and Crystal Growth in Palm Olein Based Cooking Oil

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Agenda

- DuPont Nutrition & Health
- Palm olein based cooking oil
  - Commercial needs
  - Palm olein types
  - Impact of olein quality
- Effect of sorbitan tristearate
- Effect of alkanoates
- Thoughts on mechanism
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What we do

We use renewable raw materials to create food ingredients…

- Emulsifiers
- Hydrocolloids
- Antioxidants
- Antimicrobials
- Enzymes
- Cultures
- Probiotics
- Proteins
- Sweeteners
- Fibers …

…that food manufacturers use to create safe, nutritious and healthy products

Diagnostics and services help increase food safety and reduce food waste
Supermarket samples – palm olein cooking oil
How clear does the oil need to be ......
Background

The challenge ...........

- In air-con supermarkets and temperate zones, ambient conditions compatible with *palm olein oil partially crystallizing in days*.

- *Need to hold back nature for several months*: resist the oil’s progress to more favoured, lower energy (crystalline) state.

Current approaches problematic and/or expensive

- Multiple fractionation of olein or use of soft oils.

- Polyglycerol esters of fatty aids.

- Sorbitan tristearate (STS).

- Lecithin.
Fractionation is used to produce olein for cooking oil

- palm oil is tempered under controlled conditions
- partial crystallisation occurs - crystals removed by filtration
- palm oil separated into a solid fraction (stearin) and a liquid fraction (olein).
- stearin enriched in high-melting triglycerides
- cold stability of olein superior to starting material
Untreated control:

- First signs of crystallisation: 25 days.
- Extensive crystallisation: 38 days

Treated oil

- First signs of crystallisation: 123 days

60 IV Palm Olein

- Free fatty acid (% as palmitic): 0.05
- Moisture & Impurities (%): 0.05
- Lovibond Red (5 1/4” cell): 3.0R
- Iodine Value: 60.5
Not all palm oleins are equal: diacylglycerol effect on cloud point

Mettler cloud point of palm oleins IV 56 with increasing diacylglycerol contents

<table>
<thead>
<tr>
<th>Palm olein IV 56 Sample #</th>
<th>DAG Content (%)</th>
<th>Mettler Cloud Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>6.1</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>6.5</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>7.9</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>9.1</td>
</tr>
<tr>
<td>5</td>
<td>9</td>
<td>10.8</td>
</tr>
<tr>
<td>6</td>
<td>11</td>
<td>12.0</td>
</tr>
</tbody>
</table>

Source: Gibon et al., OCL 16(4), 193-200 (2009)
Impact of quality on treatability of olein

<table>
<thead>
<tr>
<th>Olein % DAG</th>
<th>Iodine Value</th>
<th>Days clear Untreated</th>
<th>Days Clear +0.08% STS</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.2</td>
<td>61.3</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>8.7</td>
<td>62.8</td>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>8.1</td>
<td>62.1</td>
<td>1</td>
<td>23</td>
</tr>
<tr>
<td>7.7</td>
<td>61.7</td>
<td>3</td>
<td>31</td>
</tr>
</tbody>
</table>

Storage temperature = 20°C
Synergy found between STS and alkali metal stearates

- Studies found that Na. stearate affects lipid crystallisation under certain conditions
- Testing in cooking oil: significant extension of oil shelf life over STS alone

Olein CP 5°C, IV60 tested at 15°C: image recorded after 47 days.

Useful result; complex in practise
Might SSL also interfere with fat crystallization?

SSL soluble in room temperature vegetable oil up to around 0.025%
Readily soluble in other surfactants such as STS
Structural variants: % lactic acid; fatty acid moiety
SSL can delay crystallisation onset: Potentiates action of STS

Days elapsed until visible initiation of crystallization of 60IV palm olein (Cloud Point 5°C).

<table>
<thead>
<tr>
<th>Lactic acid content (%)</th>
<th>Days Clear 18°C – SSL* alone</th>
<th>Days Clear 18°C SSL + STS</th>
<th>Days Clear 18°C – STS* alone</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSL #1: 25±2%</td>
<td>27</td>
<td>175</td>
<td>38</td>
</tr>
<tr>
<td>SSL #2: 32.5±1.5%</td>
<td>20</td>
<td>110</td>
<td>28</td>
</tr>
</tbody>
</table>

*SSL was used at 0.01% and STS was used at 0.04%. Control olein lasted 14 days (SSL#1) and 9 days (SSL#2) respectively.
Impact of fatty acid chain length on inhibition of crystallization in palm olein based oil at 12°C

<table>
<thead>
<tr>
<th>Na. A2L type</th>
<th>Days clear: control*</th>
<th>Days clear: + A2L*</th>
</tr>
</thead>
<tbody>
<tr>
<td>lauroyl</td>
<td>3</td>
<td>9</td>
</tr>
<tr>
<td>palmitoyl</td>
<td>3</td>
<td>9</td>
</tr>
<tr>
<td>stearoyl</td>
<td>3</td>
<td>15</td>
</tr>
<tr>
<td>behenoyl</td>
<td>3</td>
<td>9</td>
</tr>
</tbody>
</table>

- A2L = alkanoyl-2-lactylate. Oils tested at 12°C in a 50/50 blend of Cloud Point 5°C palm olein and canola oil. Na. A2L was added at 0.01%.

- In all cases synergy was seen with STS
Oil samples monitored isothermally at 10°C for 30 hours
Possible mechanisms

1. Surface free energy of crystals and interfacial tension between crystal surface and bulk oil

- Anticrystalliser increases the energy barrier for fat crystal nucleation.
- Nuclei must be larger to grow into crystals.
- Overall fat crystallisation is thereby delayed.
**Possible mechanisms**

1: Surface free energy of crystals and interfacial tension between crystal surface and bulk oil

SAXS measurements at 10°C during initial crystallisation of palm olein IV60 with and without 0.05% commercial anticrystalliser blend (includes SSL)

Apparent changes to initial crystallisation pattern and timing thereof

Nuclei formed and seemingly disappear again prior to the main crystallisation event when anticrystalliser present

Neat palm olein

with 0.05% anticrystalliser
Possible mechanisms

2: Blocking effect

- Co-crystallisation of the emulsifiers together with the first nuclei hinders further growth.
- Perhaps sorption to surface of the nuclei is sufficient?

Positive effect

a) Retardation

(De-clustering)

Negative effect

b) Promotion

(Templating)

kink

(blocking)
Conclusions

- Extending timeframe of oil clarity is a desirable goal RE: saleability of cooking oils.
  - Becomes more acute as growth of sales volume through air-con stores increases

- Several surfactant types have been demonstrated to have a delaying effect on crystallisation onset

- Alkanoyl-2-lactylates demonstrated to have effect in own right, and moreso, potentiate action of other agents

- Some evidence for increase in crystal surface energy as cause, but mechanism(s) not yet elucidated
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