Real Time and In Situ Monitoring of the Crystallization of Palm Oil-based Products using Focused Beam Reflectance Measurement (FBRM)

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OVERVIEW

Introduction
- Palm oil
- Palm oil fractionation
- Focused beam reflectance measurement (FBRM)

Materials and Methods
- Crystallization experiments
- Compositional analyses

Results and Discussion
- Palm Oil Crystallization - Crystals population
- Palm Oil Melting – Melting mechanisms
- Palm Olein Crystallization - Crystal size distribution & Crystallisation mechanisms
- Palm Olein Blend with Legume Seed Oil – effect of blending on crystallization mechanism

Conclusions
Palm oil – largest produced vegetable oil in the world, >59.5 million tonnes in 2014. (Source: Oil World Annual 2014)

Palm oil mainly consists of a multicomponent mixture of:
- Triacylglycerols (TAGs): 94%
- Diacylglycerols, monoacylglycerols and free fatty acids: 6%.

Serves as feedstock for a variety of industries, i.e. food, oleochemicals, biofuels etc.

Palm-based food products range from cooking oils, salad oils to margarines and shortenings and confectionery fats.
PALM OIL FRACTIONATION

- **Dry fractionation**: controlled *partial crystallisation* of oil from the melt and *filtration* of crystallized slurry

- **Crystallisation**: driven by differences in the melting points of the TAGs & operating temperature

- Quality of subproducts depend on the operating conditions during the crystallization stage and crystal characteristics such as size, numbers and shape have a profound effect on the filtration stage.
MOTIVATION

- Most crystallization studies are performed on static systems – Differential Scanning Calorimetry (DSC), polarized light microscopy (PLM), X-ray diffraction (XRD) etc.

- Static systems do not accurately reflect the actual industrial process. Dynamic systems are less studied due to fewer available monitoring devices.

- Particle characteristic studies – image analysis, laser particle counters, particle size analyzers.

- Most require sampling the material and in some cases dilution -> changes material in study

- **Focused beam reflectance measurement (FBRM)** – non-destructive technique capable of monitoring particle characteristics on-line in real time.
FOCUSED BEAM REFLECTANCE MEASUREMENT (FBRM)

- *In-situ* measuring device
- **Real time** tracking of particle size, population and events.
- No sampling or dilution required
- Particle size range: 0.8 – 1000 µm
- Particle size in chord length
- Measurement depends on crystal orientation

Source: Mettler Toledo
CRYSTALLIZATION METHODS

- Material: 700 mL oil
- 1 L Mettler Toledo LabMax Automatic Lab Reactor with LASENTEC FBRM Model D600L
- Agitation speed: 50 rpm
- Isothermal Crystallization time:
  - Palm oil: 2 hours
  - Palm olein: 6 hours
  - Blended oil: 5 hours
- Morphological analysis by polarised light microscope
COMPOSITIONAL ANALYSES

Fatty acids composition
• ISO 5508:1990
• GC-FID Conditions
  – Column: DB-23, 60m L x 0.25 mm i.d., film thickness 0.25 µm
  – Oven T: 185 °C
  – Injector & detector T: 240 °C
  – Carrier gas: He @ 0.8 mL/min
  – Split ratio 1:100

Triacylglycerols composition
• AOCS Method Ce 5c-89
• HPLC-RID Conditions
  – Column: Purospher RP-18, 4.6 mm i.d. x 250 mm L, 5 µm particles, 2 connected in series
  – Column & detector T: 35 °C
  – Acetone:Acetonitrile = 63.5:36.5
  – Flowrate: 1 mL/min
PALM OIL CRYSTALLIZATION
Crystal population of palm oil crystallized at 32 °C

Melting mechanism of pre-crystallized palm oil from 24 to 46 °C

PALM OLEIN CRYSTALLIZATION
Crystal population of palm olein crystallized at 9, 13 and 15 °C

Crystal size distribution of palm olein crystallized at 9, 13 and 15 °C

Palm Olein Crystallization

Fatty acid composition of palm olein crystallized at 9, 13 and 15 °C

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>SFA (%)</th>
<th>MUFA (%)</th>
<th>PUFA (%)</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>13.3</td>
<td>47.2</td>
<td>39.4</td>
<td>61.5</td>
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<tr>
<td>11</td>
<td>12.1</td>
<td>45.3</td>
<td>42.5</td>
<td>58.9</td>
</tr>
<tr>
<td>13</td>
<td>11.8</td>
<td>44.9</td>
<td>43.3</td>
<td>57.5</td>
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</tbody>
</table>

IV: Iodine value
PUFA: polyunsaturated fatty acids
SFA: saturated fatty acids
MUFA: monounsaturated fatty acids
Major triacylglycerol groups of palm olein crystallized at 9, 13 and 15 °C

- **SUS**: monounsaturated
- **SUU**: diunsaturated
- **UUU**: triunsaturated
OIL BLEND CRYSTALLIZATION
Crystals population of palm olein blended with winged bean seed oil at 13 °C

- Primary nucleation
- Secondary nucleation

- Palm Olein
- 2.5% WBSO
- 5% WBSO
Crystal size distribution of palm olein blended with winged bean seed oil at 13 °C
<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Palm Olein</th>
<th>WBSO</th>
<th>2.5% WBSO in palm olein</th>
<th>5% WBSO in palm olein</th>
</tr>
</thead>
<tbody>
<tr>
<td>C16:0</td>
<td>39.74</td>
<td>5.59</td>
<td>31.77</td>
<td>31.21</td>
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<tr>
<td>C18:0</td>
<td>4.30</td>
<td>3.90</td>
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<tr>
<td>C18:1</td>
<td>42.53</td>
<td>31.88</td>
<td>45.60</td>
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<td>C18:2</td>
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<td>15.74</td>
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<td>1.37</td>
<td>0.48</td>
<td>0.51</td>
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<tr>
<td>C20:0</td>
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<td>0.34</td>
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<td>C20:1</td>
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<td>0.32</td>
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<tr>
<td>C22:0</td>
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<td>11.90</td>
<td><strong>0.35</strong></td>
<td><strong>0.61</strong></td>
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<tr>
<td>C24:0</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>Iodine value</td>
<td>56.63</td>
<td>95.05</td>
<td>67.72</td>
<td>68.42</td>
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</table>
CONCLUSIONS

- FBRM is a useful tool to characterize crystallization of palm oil-based products and oils and fats systems, in general.

- FBRM provides valuable information such as population, size distribution and mechanisms of particle formation/disappearance.

- *In situ* and real time data – representative of actual process conditions.

- By complementing FBRM data with an imaging technique and compositional analysis, more information on crystallization behavior can be deciphered.

- Utilization of FBRM enables proper control and optimization of crystallization conditions to ensure production of optimum crystal characteristics.
See You at PIPOC 2015

6 - 8 October 2015
Kuala Lumpur Convention Centre,
Kuala Lumpur, Malaysia
Thank you