Fast and Straightforward Determination of the Oxidation Stability of Fats and Oils

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Introduction

- RapidOxy: Determining the oxidation stability of products under accelerated conditions
  - Increased temperature
  - Exposure to excess of pure oxygen

- Originates from PetroOxy: Determining oxidation stability of fuels according to ASTM D7525 (gasoline) and ASTM D7545 (diesel, diesel and FAME, biodiesel)

- RSSOT = Rapid Small Scale Oxidation Test
Introduction

- RapidOxy: Determining the oxidation stability of products under accelerated conditions
  - Increased temperature
  - Exposure to excess of pure oxygen

- Stainless steel test chamber: Sample is set under pressure (up to 700 kPa) with pure oxygen and heated (up to 200 °C)

- The temperature is kept constant and the pressure is continuously traced

- Due to oxygen consumption the pressure drops
Measuring Principle of the Instrument

- Induction period (IP)
  - Time elapsed between starting the heating procedure of the test chamber and the moment when the formation of oxidation products rapidly increases, which is indicated by a defined pressure drop (break point)
Measuring Principle of the Instrument

- **Induction period (IP)**
  - Time elapsed between starting the heating procedure of the test chamber and the moment when the formation of oxidation products rapidly increases, which is indicated by a defined pressure drop (break point)
  - **Standard IP at 10 % pressure drop**

- **Break point**
  - Point at which a defined pressure drop is detected (i.e. p max - 10 %) indicating the consumption of oxygen

![Diagram showing pressure over time with Induction period and Break point highlighted]
Measuring Principle of the Instrument: Options

- Stop measurement at customized pressure drop
  - Relative or absolute pressure drop
  - Value can be chosen

- Stop measurement after certain time
  - Duration of measurement can be chosen
  - Useful for very stable samples, record pressure drop after certain time and compare stabilities

- Stop measurement after certain measurement time or pressure drop
Measuring Principle of the Instrument: Options

- Temperature up to 200 °C:
  - Optimum temperature depending on sample (sensitivity, reactivity, oxidation stability); stable plateau of maximum pressure is important for repeatability (IP ≥ 20 min)
  - The higher the temperature, the faster the oxidation process, the shorter the IP
  - For many samples Arrhenius dependency of IP can be found

- Initial oxygen pressure up to 700 kPa:
  - Purging of line system prior to filling: Including or excluding sample chamber
  - Standard filling pressure for non volatile samples 700 kPa
  - Standard filling pressure for volatile samples 300 – 500 kPa, no purging of sample chamber prior to measurement

- For solid or semi-solid samples a glass dish is provided for simple sample handling, convenient removal of samples and cleaning afterwards
Induction period (IP) of different basic edible oils

RapidOxy parameters for measurement:
- $T = 140 \, ^\circ C$
- Initial oxygen pressure 700 kPa
- Stop criterion
  - $\Delta p = 10 \%$
  - $\Delta p = 60 \%$ (gray)

Clear and simple distinction between samples with 10 % pressure drop as stop criterion
Investigation of Repeatability: Edible Oil Sample

- Measurement of sunflower oil repeated ten times
  - Pressure and stop criterion was kept constant ($p = 700$ kPa, $\Delta p = 10\%$)
  - $T = 110\, ^\circ C$ and $T = 140\, ^\circ C$

- Very good repeatability demonstrated at both temperatures

<table>
<thead>
<tr>
<th>Date</th>
<th>Result at 110 °C (minutes)</th>
<th>Date</th>
<th>Result at 140 °C (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>08.09.2016</td>
<td>123.10</td>
<td>05.09.2016</td>
<td>21.55</td>
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<td>08.09.2016</td>
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<td>08.09.2016</td>
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<td>21.65</td>
</tr>
<tr>
<td>08.09.2016</td>
<td>123.06</td>
<td>06.09.2016</td>
<td>21.60</td>
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<td>09.09.2016</td>
<td>123.03</td>
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<td>21.61</td>
</tr>
<tr>
<td>09.09.2016</td>
<td>123.11</td>
<td>06.09.2016</td>
<td>21.80</td>
</tr>
<tr>
<td>15.09.2016</td>
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<td>07.09.2016</td>
<td>21.43</td>
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<tr>
<td>15.09.2016</td>
<td>121.78</td>
<td>07.09.2016</td>
<td>21.51</td>
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<tr>
<td>19.09.2016</td>
<td>120.88</td>
<td>07.09.2016</td>
<td>21.51</td>
</tr>
</tbody>
</table>

| Maximum    | 123.23                      | Maximum    | 21.80                       |
| Minimum    | 120.88                      | Minimum    | 21.43                       |
| Max-Min    | 2.35                        | Max-Min    | 0.37                        |
Investigation of Repeatability and Reproducibility

- Round robin (ILS#1383) for developing an ASTM method for determining the oxidation stability of lubricating greases with the RapidOxy (RSSOT = Rapid Small Scale Oxidation Test, ASTM WK 55271)

- 9 lubricating grease samples, RapidOxy parameters:
  - 4 g sample in glass dish
  - p = 700 kPa
  - Stop criteria: 10 % pressure drop
  - T = 140 °C and T = 160 °C

- Statistical evaluation of round robin at 140 °C:
  - Repeatability = 0.094 * (x) min
  - Reproducibility = 0.164 * (x) min

Range: 199.3 min – 2354.73 min
Number of laboratories: 10 (11)
Investigation of Repeatability and Reproducibility

- Round robin (ILS#1383) for developing an ASTM method for determining the oxidation stability of lubricating greases with the RapidOxy (RSSOT = Rapid Small Scale Oxidation Test, ASTM WK 55271)

- 9 lubricating grease samples, RapidOxy parameters:
  - 4 g sample in glass dish
  - p = 700 kPa
  - Stop criteria: 10 % pressure drop
  - T = 140 °C and T = 160 °C

- Statistical evaluation of round robin at 160 °C:
  - Repeatability = 0.093 * (x) min
  - Reproducibility = 0.154 * (x) min

Range: 53.16 min – 1461.65 min
Number of laboratories: 11 (11)
Investigation of Correlation to Other Test Methods

- In-house study: Measurement of 17 different vegetable oil samples

- RapidOxy parameters
  - $T = 120 \degree C$ and $T = 140 \degree C$
  - $p = 700 \text{kPa}$, stop at $\Delta p = 10 \%$

- Cd12b_92_13 (Rancimat) parameters
  - $T = 100 \degree C$
  - Air stream 20 l/hour

- Good correlation between methods, RapidOxy measurement with by far shorter measurement time
Investigation of Correlation to Other Test Methods

- Study of external customer: Correlation to pressure vessel method (ASTM D942) for 8 lubricating grease samples
  - RapidOxy parameters
    - $T = 160 \, ^\circ C$
    - $p = 700 \, kPa$, stop at $\Delta p = 10 \%$
  - ASTM D942 parameters
    - $T = 100 \, ^\circ C$
    - $p = 700 \, kPa$
    - Result is recorded pressure drop after certain time (100 h and 400 h)
- Good correlation between methods, RapidOxy measurement with by far shorter measurement time
Investigation of Fresh and Aged Macadamia Nut Oil

- Macadamia nut oil 1: Fresh sample; Macadamia nut oil 2: Aged (5 months) sample
- RapidOxy parameters: Initial oxygen pressure 700 kPa; Stop criterion 10 % pressure drop, temperatures 80 °C, 110 °C and 140 °C

Results are in accordance with expectation of the customer, oven storage (3 months, 40 °C, sensory analysis)
Induction period significantly decreases by increasing the temperature.

Logarithm of test result (IP) plotted against inverse temperature.

Arrhenius plot shows linear temperature dependency of test results (IP) in both cases.

Activation energy of oxidation reaction can be determined via slope of graph.
Investigation of Oil-in-Water Mixture

- Determining oxidation stability of oil-in-water mixture, pure and with different natural antioxidants:
  - Ascorbyl palmitate (E 304, also emulsifier)
  - Vitamin D
  - Vitamin E

- Parameter for RapidOxy measurement:
  - $T = 140 \, ^\circ C$
  - $p = 700 \, kPa$, stop at $\Delta p = 10 \%$

- RapidOxy oxidation stability order:
  Vit. E > Vit. D > Ascorbyl palmitate
Investigation of Storage Stability of Edible Fat

- Storage conditions for margarine:
  - Refrigerator (8 °C)
  - Room temperature (approx. 23 °C)
  - Drying oven (40 °C)

- Parameters for RapidOxy measurement:
  - T = 140 °C
  - p = 700 kPa, stop at Δp = 10 %

- Oxidation Stability (IP) decreases with storage time

- Influence of storage condition can be demonstrated
Investigation of Food Emulsifier

- Sorbitan Tristearate classified as E492
  - Measurement of pure E492 (sample 1)
  - Measurement of E492 with antioxidant (sample 2)

- Parameters for RapidOxy measurement:
  - $T = 140 \, ^{\circ}C$
  - $p = 700 \, \text{kPa}$, stop at $\Delta p = 10 \%$

- Addition of antioxidant increases oxidation stability of food emulsifier

- Good repeatability demonstrated in both cases

<table>
<thead>
<tr>
<th>Sample 1 (min)</th>
<th>1. Test</th>
<th>2. Test</th>
<th>Mean value</th>
<th>Max-Min/Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>188.13</td>
<td>178.13</td>
<td>183.13</td>
<td>0.05</td>
</tr>
<tr>
<td>Sample 2 (min)</td>
<td>219.48</td>
<td>212.50</td>
<td>215.99</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Investigation of Cocoa Mass

- 4 different cocoa liquor samples (sample A – D) were tested with the RapidOxy

- Parameters for RapidOxy measurement:
  - $T = 120 \, ^\circ C$
  - $p = 700 \, kPa$, stop at $\Delta p = 10\%$

- Oxidation stability order determined:
  - Sample A > Sample B > Sample C > Sample D

- The determined order for oxidation stability was confirmed by the customer

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>356.32</td>
</tr>
<tr>
<td>B</td>
<td>343.78</td>
</tr>
<tr>
<td>C</td>
<td>318.49</td>
</tr>
<tr>
<td>D</td>
<td>303.27</td>
</tr>
</tbody>
</table>
Summary

- **RSSOT = Rapid Small Scale Oxidation Test**

- Fast measurement due to accelerated oxidation conditions, parameters can be chosen for optimum conditions:
  - Temperature up to 200 °C
  - Pressure (O₂) up to 700 kPa
  - Stop criterion pressure drop, time, or both

- Very good precision of test results

- Fluid, semi-solid and solid samples can be measured without any prior sample preparation

- No tedious cleaning procedure after measurement
Thank you for your attention!
Appendix
Benefits at a glance

- Measuring temperature up to 200 °C
- Small amount of sample: 5 mL or 4 g
- Fast measurement due to accelerated oxidation conditions
- No sample preparation and therefore no additional chemicals/reagent waste (ecological)
- Standalone instrument
- Pressure curve monitoring on display of the instrument during measurement
- Live temperature, time and pressure display in real time
- OxyLogger software for live data transfer to PC during measurement
- Small, compact instrument with dimensions 24 cm x 40 cm x 26 cm
- Low weight of only about 11 kg
- Safety approved by the BAM (German Federal Institute for Materials Research and Testing)
- Glass dishes for very simple solid and semi-solid sample handling and cleaning process