The use of PAT Tools in Biodiesel Production

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Outline

- Introduction
- PAT in Raw-Materials – i.e., Oils Qualification
- PAT in Production – i.e., Process Supervision
- PAT in Final Product – i.e., Biodiesel QC
- Conclusions

PAT Building Blocks

Monitoring  Supervision

PAT  Control  Diagnosis

PAT Based Biofuel Production

- Assessing Raw-Materials’ Variability
  - Complex raw-materials (RM): fast qualification schemes (QC)
  - Opportunity for RM supervision systems (QA)
  - Formulating mixed lots of RMs for targeted specifications

- Handling RM Variability During Processing
  - Monitoring quality attributes in-process (IPCs) at-line or on-line
  - Process supervision (e.g., multivariate trajectories)
  - Controlling critical to quality parameters

- End Product Quality Control
  - Biofuels multiparametric QC (e.g., conformity index)
  - Blending operations for targeted specifications
How can PAT be important?

- Investment costs (storage) & profit margins (QC)

```
<table>
<thead>
<tr>
<th>raw-mat</th>
<th>process</th>
<th>product</th>
</tr>
</thead>
<tbody>
<tr>
<td>vegetable (soybean, palm, jatropha etc)</td>
<td>catalytic &amp; reactive phase separation, washing &amp; drying biodiesel</td>
<td>biodiesel</td>
</tr>
</tbody>
</table>
```

A batch process likely to become continuous prone to process spectroscopy monitoring.

Monitoring with a Lab Instrument

Interfaced with the Process

- Process Finger-printing
- Process Tagging
- Process Supervision, Fault Detection
- End-Point Determination
- Conformity Index (Multiparametric QC)

PAT Tools - Portable NIR Analyzers

- Application in several industrial fields
- Fast, accurate and non-destructive analysis
- Opportunity to data analysis
- Need calibrations development
- Incoming raw-material inspection
- Quality control and assurance
- Portable field use
- At-Line process monitoring
- Counterfeit products ID

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Raw Materials Qualification

Type of Oil
PCA of Pure oils

<table>
<thead>
<tr>
<th>Type of Oil</th>
<th>Iodine number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palm</td>
<td>0.5</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>-0.5</td>
</tr>
<tr>
<td>Soybean</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Raw Materials Monitoring

Raw Materials Monitoring

QC of Oil Properties
NIR PLS Calibrations

<table>
<thead>
<tr>
<th>Property</th>
<th>Error of the reference method</th>
<th>Error of NIR models (RMSEP)</th>
<th>Calibration Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water content (mg/kg)</td>
<td>50</td>
<td>68</td>
<td>478 – 1776</td>
</tr>
<tr>
<td>Iodine Value (g I₂/100 g)</td>
<td>3</td>
<td>1.0</td>
<td>60 – 126</td>
</tr>
<tr>
<td>Acid Value (mg KOH/g)</td>
<td>0.1</td>
<td>0.41</td>
<td>0.13 – 6.56</td>
</tr>
<tr>
<td>Dynamic Viscosity (cP)</td>
<td>2</td>
<td>1.9</td>
<td>5 – 74</td>
</tr>
<tr>
<td>Density at 15°C (kg/m³)</td>
<td>0.5</td>
<td>0.9</td>
<td>875 – 925</td>
</tr>
</tbody>
</table>

Note: oils mixtures were laboratory prepared by weighing and mixing the oils in the desired proportions.

EN14214 imposes Iodine Number < 120

QC of Oil Blending (%)
NIR PLS Calibrations

<table>
<thead>
<tr>
<th>Property</th>
<th>Error of NIR models (RMSEP in %)</th>
<th>Calibration Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Soybean Oil (SO)</td>
<td>2.4</td>
<td>0 - 100%</td>
</tr>
<tr>
<td>% Rapeseed Oil (RO)</td>
<td>3.2</td>
<td>0 - 100%</td>
</tr>
<tr>
<td>% Palm Oil (PO)</td>
<td>1.2</td>
<td>0 - 100%</td>
</tr>
</tbody>
</table>

Note: oils mixtures were laboratory prepared by weighing and mixing the oils in the desired proportions.
Raw Materials Formulation

Oil Mixtures Compositions (% of SO in SO/RO/PO mixtures)

NIR PLS Calibrations

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Production Process Monitoring

Following the transesterification reaction

Production Process Monitoring

Following Biodiesel/Glycerol Separation

Batch Process

NIR Probe in Biodiesel Phase
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Final Product Quality Control

Accurate calibrations developed for 15 quality biodiesel quality specs (EN 14214  25 parameters

<table>
<thead>
<tr>
<th>Property</th>
<th>EN 14214 Limit</th>
<th>Calibration Range</th>
<th>Error of NIR models (RMSEP)</th>
<th>Error of the reference method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl esters composition (%)</td>
<td>Not specified</td>
<td>Depends on the ester</td>
<td>Depends on the ester</td>
<td>Depends on the ester</td>
</tr>
<tr>
<td>Iodine value (g I₂/100 g)</td>
<td>&lt; 120</td>
<td>62 – 135</td>
<td>0.7</td>
<td>3</td>
</tr>
<tr>
<td>Density at 15°C (kg/m³)</td>
<td>850 – 900</td>
<td>875 – 925</td>
<td>0.9</td>
<td>0.5</td>
</tr>
<tr>
<td>Kinematic viscosity at 40°C (mm²/s)</td>
<td>3.5 – 5.0</td>
<td>3.47 – 4.41</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>Water content (mg/kg)</td>
<td>&lt; 500</td>
<td>218 – 1859</td>
<td>72</td>
<td>50</td>
</tr>
<tr>
<td>Acid value (mg KOH/g)</td>
<td>&lt; 0.5</td>
<td>0.09 – 0.40</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Oxidative Stability (%)</td>
<td>&gt; 6</td>
<td>4.32 – 16.8</td>
<td>0.28</td>
<td>0.12</td>
</tr>
<tr>
<td>CFPP (ºC)</td>
<td>Varies</td>
<td>-13 to 5</td>
<td>1.0</td>
<td>1</td>
</tr>
<tr>
<td>OP (ºC)</td>
<td>Not specified</td>
<td>-9 to 9</td>
<td>0.6</td>
<td>1</td>
</tr>
</tbody>
</table>
### Final Product Quality Control

**EN 14214 vs ASTM**

<table>
<thead>
<tr>
<th>Property</th>
<th>EN 14214 Limit</th>
<th>ASTM 6751 Limit</th>
<th>NIRS Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol Content (%)</td>
<td>&lt; 0.2</td>
<td>&lt; 0.2</td>
<td>√</td>
</tr>
<tr>
<td>Water &amp; Sediment (%) Vol</td>
<td>-</td>
<td>&lt; 0.05</td>
<td>-</td>
</tr>
<tr>
<td>Water Content (mg/kg)</td>
<td>&lt; 0.05</td>
<td>-</td>
<td>√</td>
</tr>
<tr>
<td>Sulfur (mg/kg)</td>
<td>&lt; 10</td>
<td>15 or 500</td>
<td>X</td>
</tr>
<tr>
<td>Free Glycerol (%)</td>
<td>&lt; 0.02</td>
<td>&lt; 0.02</td>
<td>√</td>
</tr>
<tr>
<td>Total Glycerol (%)</td>
<td>&lt; 0.25</td>
<td>&lt; 0.24</td>
<td>√</td>
</tr>
<tr>
<td>Acid number (mg KOH/g)</td>
<td>&lt; 0.5</td>
<td>&lt; 0.5</td>
<td>√</td>
</tr>
<tr>
<td>Oxidation Stability (h)</td>
<td>&gt; 6</td>
<td>&gt; 3</td>
<td>√</td>
</tr>
<tr>
<td>Cloud Point (º C)</td>
<td>Contract</td>
<td>Contract</td>
<td>√</td>
</tr>
</tbody>
</table>

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### Biodiesel Quality Control

Biodiesel analyses are very expensive and time consuming. It can take +2 days to perform the reference methods that analyze the 15 quality parameters calibrated with NIRS. To perform the simultaneous analyses of the calibrated properties by NIRS, it is only necessary to acquire the NIR spectrum of the sample, a procedure that takes less than 2 minutes. The prediction errors of NIRS models are comparable to the reference methods errors.

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### Good Chemometric Practices

Robust long-term accurate calibrations established using industrial and lab-scale samples. Example: methanol and FAME in biodiesel.

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### End-Product QA: Blending & Counterfeit

Mixtures of oil, biodiesel and fossil diesel.
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Conclusions

NIR Spectroscopy is a very powerful analytical technique in biodiesel production specially if used as process analytical technology
fingerprinting, multiparametric and whole-process-based

NIRS is accepted as analytical technique for parametric release of
food products (that we eat – when healthy)
pharmaceuticals (that we take – when ill)
why not for Biodiesel? (oh no, not in my car!)
### Different Processing Industries: a similar PAT Approach

<table>
<thead>
<tr>
<th>Industry</th>
<th>Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brewing &amp; Dairy</td>
<td><img src="brewing_dairy.png" alt="Image" /></td>
</tr>
<tr>
<td>Biomanufacturing</td>
<td><img src="biomanufacturing.png" alt="Image" /></td>
</tr>
<tr>
<td>Pharma</td>
<td><img src="pharma.png" alt="Image" /></td>
</tr>
<tr>
<td>Petrochemical</td>
<td><img src="petrochemical.png" alt="Image" /></td>
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- Chemical (CPI)
- Pharma (API)
- Petrochemical
- Biofuels
- Food

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High Resolution vs. Low Resolution Analyzers

Wavelength ranges: 715-1630 nm
Optical resolution: 0.5 nm
Wavelength range: 400-1800 nm
Optical resolution: 100 nm
Measurement time: 5-2 seconds