Chemical methods in the development of eco-efficient pellet production and utilization of wood ash

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DEVELOPMENT OF WOOD-BASED PELLET PRODUCTION AND TECHNOLOGY

MAIN FIELDS OF OUR PELLET RESEARCH

1. Developing new materials for pellet production
2. Effective harnessing of industrial secondary flows
3. Binding material applications
4. Biodegradation of pellets and materials used; BOD OxiTop
5. Cross-linking mechanisms of wood-based pellets; optical microscopic staining method
6. Drying processes of pellet raw materials, also new technologies
7. Properties of wood ash in terms of its eco-efficient utilization
Pelletizing – Background

- Patented 1976 (USA), after oil crisis
- Sweden as pioneer country
  - Use over 1M tn/year, small scale use common
- Use of pellets became common only just in 21st century, reasons:
  - Increase in oil price and oil reserve exhaustion
  - Climate political reasons
  - Emission trade in EU, pellets CO₂ neutral
  - Increase of profitability for alternative energy forms
Pelletizing - Background

Europe:
- DEN significant user
- RUS second largest producer (ca. 650 000 tn/year -05)
- AUT expansion in use, especially in one-family houses
- Baltic Countries significant exporters along with FIN
Pelletizing - Background

- **USA and Canada:**
  - Pellet fireplace became common in mid-1980s
  - Mainly used in one-family house and vacation home heating
  - Over million pellet fireplaces
Pelletizing - Background

- Trend of pellet production capacity in Finland:
  - 1998: 10,000 tonnes
  - 2001: 80,000 tonnes
  - 2003: 170,000 tonnes
  - 2005: 400,000 tonnes
  - 2009 estimated 1M tonnes

- Rapid growth
  - Production capacity limit has already been reached with traditional raw materials (shavings and dry cutter chips)

- Aim to expand raw material basis
  - In Finland ca. 15-20M tn/year biomass is left unused in forests during forestry operations
  - Utilization of new raw materials (bark, thinning and logging residues, branches, stocks, “trash tree species”)

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Pelletizing - Background

- Pellet production has been undeveloped
  - Need for research and development work in pellet production and technology
    - Increased information for consumers
    - Along with pellets also pellet know-how will be export product
Pelletizing - Background

- Raw material is pressed through matrix
  - Friction increase
  - Temperature increase
  - Pressure increase
  - Lignin solidification during cooling period
    - Forming of compact structure
Pelletizing - Background
Problems of pellet production

1. Dust problem
   - Exposure health risk
     - Occupational safety instructions must be observed in pellet plants
   - Danger of explosion and fire in combustion
   - Sieving of disadvantageous particle size
   - Use of binding materials
Problems of pellet production

2. Quality and compactness
   - Logistic problems – it is not profitable to transport fines
   - Important for small scale users
     - Increase of domestic consumption in Finland
     - Small scale burners are sensitive for quality changes
   - Can be affected with binding materials and pretreatment techniques
Problems of pellet production

Ash and slagging problem in combustion

Pulpwood

Undelimbed mixed wood
Problems of pellet production

3. Underdevelopment of equipment
   - Energy efficiency
     - BAT must be introduced
   - Research and development work as solution
### Table 1. Useful research methods for pellet production and development.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Equipment</th>
<th>Purpose of determination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>Heat oven and scales</td>
<td>Amount of water content</td>
</tr>
<tr>
<td>Density</td>
<td>Volume and weight determinations</td>
<td>Compactness of materials</td>
</tr>
<tr>
<td>Calorific heat</td>
<td>Bomb calorimeter</td>
<td>Energy content</td>
</tr>
<tr>
<td>BOD tests</td>
<td>BOD Oxitop® equipments</td>
<td>Biodegradation / loss of materials</td>
</tr>
<tr>
<td>Dust content, strength</td>
<td>Vibrator, sieve analysis</td>
<td>Mechanical stability of the pellet</td>
</tr>
<tr>
<td>properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Structure analysis</td>
<td>Staining reagents and optical microscope</td>
<td>Information about pellet structure and cross-linking mechanism</td>
</tr>
<tr>
<td>TG analysis</td>
<td>Thermogravimeter</td>
<td>Volatilization of water and VOC`s, ash content</td>
</tr>
<tr>
<td>Elementary analysis</td>
<td>ICP/OES</td>
<td>Heavy metals and/or nutrients</td>
</tr>
<tr>
<td>Particle size distribution</td>
<td>Laser diffraction particle size analyzer,</td>
<td>Information about particle size distribution in wood materials</td>
</tr>
<tr>
<td></td>
<td>image analysis</td>
<td></td>
</tr>
</tbody>
</table>
BOD measurements

- BOD OxiTop system used for biodegradability studies in solid (left) and liquid (right) phase
BOD measurements

- Biodegradation of pellets

- Biodegradation of raw materials and binding agents
  - Information of material loss
  - Information of storage and transport effect
  - Information of binding agent effect for pellet biodegradation
Microscopic staining method

1. Epoxy molding of pellet samples
   - Two orientations in every mold sample
Microscopic staining method

2. Polishing of pellet sample surfaces
   - Cross section cut
   - Axial cross section cut

3. Staining of pellet samples
   - Staining with selective reagents to functional groups of the binding agent; starch -> KI (potassium iodide)
   - Flushing of extra reagents (ethanol or water)
   - Drying of the samples
4. Microscopic examination

- Reference sample comparison; no binding material used

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Microscopic staining method

Visual analysis of starch containing pellet samples

Unstained

Stained with KI

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Microscopic staining method

5. Conclusions of results

- In the microscope pictures starch compounds appear as dark spots (KI staining)
- Microscope pictures enable to analyze the binding structure of the pellet and binding material penetration
- Our characterization method can be used for the control and development of pellet production (optimization of correct feed point and mixing of binding materials)
Microscopic staining method

- Publication in progress:

Utilization of wood pellet ash

Table 2. The physical-chemical properties and the easily soluble nutrient concentrations in the wood pellet ash

<table>
<thead>
<tr>
<th>Parameter / nutrient</th>
<th>Unit</th>
<th>Wood pellet ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (1:5)</td>
<td>---</td>
<td>13.3</td>
</tr>
<tr>
<td>Electrical conductivity (EC)</td>
<td>mS cm⁻¹</td>
<td>58</td>
</tr>
<tr>
<td>Dry matter content (105 °C)</td>
<td>%</td>
<td>99.7</td>
</tr>
<tr>
<td>Loss on ignition (LOI, 550 °C)</td>
<td>% (d.w.)</td>
<td>5.3</td>
</tr>
<tr>
<td>Total organic carbon (TOC)</td>
<td>g kg⁻¹ (d.w.)</td>
<td>57</td>
</tr>
<tr>
<td>Neutralizing value (NV)</td>
<td>% (Ca; d.w.)</td>
<td>34</td>
</tr>
<tr>
<td><strong>Liming capacity</strong></td>
<td>t / t</td>
<td>1.1*</td>
</tr>
<tr>
<td>Ca</td>
<td>g kg⁻¹ (d.w.)</td>
<td>100</td>
</tr>
<tr>
<td>Mg</td>
<td>g kg⁻¹ (d.w.)</td>
<td>16.5</td>
</tr>
<tr>
<td>Na</td>
<td>g kg⁻¹ (d.w.)</td>
<td>5.0</td>
</tr>
<tr>
<td>K</td>
<td>g kg⁻¹ (d.w.)</td>
<td>70</td>
</tr>
<tr>
<td>S</td>
<td>g kg⁻¹ (d.w.)</td>
<td>6.7</td>
</tr>
<tr>
<td>P</td>
<td>g kg⁻¹ (d.w.)</td>
<td>0.08</td>
</tr>
<tr>
<td>Mn</td>
<td>mg kg⁻¹ (d.w.)</td>
<td>1370</td>
</tr>
<tr>
<td>Cu</td>
<td>mg kg⁻¹ (d.w.)</td>
<td>23</td>
</tr>
<tr>
<td>Zn</td>
<td>mg kg⁻¹ (d.w.)</td>
<td>350</td>
</tr>
</tbody>
</table>

* Correspondence between commercial limestone
Utilization of wood pellet ash

Table 3. Total heavy metal concentrations (mg kg\(^{-1}\); d.w.) in the wood pellet ash and the current Finnish limit values (mg kg\(^{-1}\); d.w.) for wood-, peat- and biomass-derived ashes used as forest and agricultural fertilizer

<table>
<thead>
<tr>
<th>Metal</th>
<th>Wood pellet ash</th>
<th>Limit value Forest fertilizer</th>
<th>Limit value Agricultural fertilizer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>16</td>
<td>17.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Cu</td>
<td>160</td>
<td>700</td>
<td>600</td>
</tr>
<tr>
<td>Pb</td>
<td>12</td>
<td>150</td>
<td>100</td>
</tr>
<tr>
<td>Cr</td>
<td>180</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Zn</td>
<td>640</td>
<td>4500</td>
<td>1500</td>
</tr>
<tr>
<td>As</td>
<td>&lt; 3.0</td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td>Ni</td>
<td>110</td>
<td>150</td>
<td>100</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt; 0.03</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Utilization of wood pellet ash

The results indicate:

- The wood pellet ash is a potential forest fertilizer and neutralizing agent (to substitute commercial CaCO$_3$)
- All total heavy metal concentrations were lower than the current Finnish limit values for forest fertilizer (see Table 3)
- Only Cd value was higher than limit value for agricultural fertilizer (see Table 3)

- Utilization of ash and other industrial residues always need prior approval by the competent authority

Publications: