Utilisation of *Miscanthus x giganteus* Grown on Heavy Metal Contaminated Land

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Aims:
- Cultivation of Energy Crops
- Utilisation of arable land not fit for food production
- Determine suitability crops for thermochemical conversion

Biomass studied:
Standard clone *Miscanthus x giganteus* and seed-based Miscanthus hybrids: GNT41, GNT 34.
The plants were cultivated on contaminated arable land in Bytom (Upper Silesia), Poland. This is a test site of the Institute for Ecology of Industrial Areas. The soil has been contaminated over the last century with zinc, cadmium and lead as a result of nearby Pb/Zn smelting.

These genotypes of Miscanthus tend to have high yields even when grown on contaminated soil.
Heavy metal uptake in the three genotypes of Miscanthus, grown on heavy metal contaminated soils, according to three plant height regions (0 to 100, 100-200 and 200-300 cm regions with the leaves were retained along with the main stems).

TGA studies used to examine influence of contamination on thermal degradation rates/behaviour.

Table 1. Soil analysis of plots used to the grow biomass crops used in this work.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total</th>
<th>Bioavailable</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb [mg/kg]</td>
<td>Cd [mg/kg]</td>
<td>Zn [mg/kg]</td>
</tr>
<tr>
<td>GNT34</td>
<td>747.9</td>
<td>27.3</td>
<td>3740.4</td>
</tr>
<tr>
<td>GNT41</td>
<td>630.0</td>
<td>22.1</td>
<td>2508.4</td>
</tr>
<tr>
<td>Mxg</td>
<td>746.3</td>
<td>31.0</td>
<td>3474.1</td>
</tr>
</tbody>
</table>

Extraction with: aqua regia + heat  
CaCl2 metal conc.

Metals determined in extracts using a flame atomic absorption spectrometer (FAAS)
Some Observations

- The last section (200-300 cm) presents the highest concentration for all metals, for both ICP and XRF. This behavior is likely due to the inclusion of leaves in the sample, present at much higher quantities at the top of the plants.

**Fig. 1.** Metal analysis (ICP top line and XRF second line) in biomass samples according to plant height.
Fig. 2. Pyrolysis weight loss curves for the three biomass samples at different plant heights.
Apparent first-order reaction kinetic data obtained from the pyrolysis results indicate low activation energies for all the biomass samples (on the order of $E_a \equiv 65$ kJ/mol and $\ln A \equiv 8$ s$^{-1}$), as can be expected of biomass samples with a high metal content.

**Fig. 3.** Kinetic parameters for biomass samples at different plant heights.
For the limited 40 minute duration of the CO$_2$ gasification experiment, the reactions progressed to different extents for the different fuels. Conversion ($\alpha$) was always highest for Mxg, followed by GNT34 and GNT41. The conversion progress seems independent of specific metal content, though could again be influenced by the total metals present.

**Fig. 4.** Gasification conversion according to biomass type and plant height.
There is variation in the initial rates that appears independent of K, Zn, and Pb content and plant type. This could be due to differences in char morphology etc.

Fig. 5. Linear trends of gasification rates and conversion.
Preliminary conclusions

- Novel seed-based Miscanthus hybrids: GNT41, GNT 34 and standard clone *Miscanthus x giganteus*, grown on heavy metal contaminated land have been analysed for metal uptake with XRF and ICP according to plant height sections.
- All samples exhibited a high efficacy of metal uptake.
- A gradient in the concentration of metals with the highest values toward the top of the plants was observed.
- Apparent first-order reaction kinetic data derived from TGA pyrolysis results showed low and yet similar activation energies for all the samples ranging between 60-70 kJ/mol and lnAs between 5.8 and 8.6 s\(^{-1}\), indicating a strong catalytic effect of the metal content and also implying that beyond a certain additive metal content, no further changes in reactivities is observed.
- Preliminary gasification studies in CO\(_2\) show little dependence of reactivity on the presence of K, Zn and Pb. Total metal concentrations are likely to play a role on gasification rates, along with char morphology.
Ongoing/Future work

- Analysis of total metals in crops from several plots with varying levels of contamination.
- Seasonal accumulation of meals in different plant parts (portable XRF)
- Influence of metals on char and char formation
- Gasification studies (TGA and bench scale) including rates, and analysis of gas and solids
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