Phytoremediation for heavy metal contaminated soils and combined bio-energy production

A. Peene (OWS)
L. Van Ginneken and W. Dejonghe (VITO)
Aim MIP-project

- Use of phytoremediation for two purposes:
  - Remediate soils that are diffusely polluted with heavy metals
  - Production of bio-energy

- Used plants:
  - Rapeseed
  - Maize
  - Wheat

- Plants will be grown on Kempen area mainly polluted with Zn, Cd and Pb
### Partners: 8

<table>
<thead>
<tr>
<th>Company</th>
<th>Task</th>
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</thead>
<tbody>
<tr>
<td>OWS (A. Peene, J. Smis)</td>
<td>Anaerobic digestion</td>
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<tr>
<td>Vyncke (H. Fastenaekels)</td>
<td>Incineration</td>
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<tr>
<td>EnviTech NV (E. Beeckman)</td>
<td>Plasmagasification</td>
</tr>
<tr>
<td>INDINOX (S. De Schepper)</td>
<td>Biodiesel production</td>
</tr>
<tr>
<td>Umicore (J. Kegels)</td>
<td>Energy and metal reduction in a melter</td>
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</tbody>
</table>
| UHasselt (J. Vangronsveld, A. Ruttens) (T. Thewys, N. Witters) | • Biological stimulation phyto-extraction  
• Economical analysis industrial application phytoremediation – production bio-fuels |
| UG (E. Meers, S. Vanslycken, F. Tack) | • Physico-chemical stimulation phytoextraction  
• Massbalances heavy metals in soil, plant, energy production processes |
| VITO (W. Dejonghe, L. Van Ginneken, R. Guisson) | • Biodiesel production  
• Massbalances heavy metals and energy in energy production processes  
• Coordination |
Task 1: Optimalisation phytoextraction

• UHasselt (J. Vangronsveld, A. Ruttens):
  – Stimulation of uptake of heavy metals by plants by microbial factors
• UGent (E. Meers, S. Vanslycken, F. Tack):
  – Stimulation of uptake of heavy metals by plants by physico-chemical factors (pH, micronutrients, manure, ...)

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Task 2: Recuperation bio-energy

WOOD (studied in BeNeKempen project + by Umicore)

OIL CROPS (Rapeseed)

Maize

Wheat

Growth- + heavy metal uptake optimalisation + balances heavy metals in plants and soils (UGent, UHasselt)

YEARNING HARVEST

TWO YEARLY HARVEST

PLANTS

SEEDS

ENERGY AND METAL REDUCTION (Umicore)

INCINERATION (Vyncke)

GASIFICATION (EnviTech)

ANAEROBIC DIGESTION (OWS)

HEAT

SLAG

HEAT

SLAG

SYNTHETIC GAS

biogas + COMPOST

Biodiesel

OIL (Indinox, VITO)
Task 3: Economical feasibility

- **VITO (R. Guisson, L. Van Ginneken, W. Dejonghe):**
  - Compare massbalances heavy metals and energy in different energy production processes

- **UHasselt (T. Thewys, N. Witters):**
  - Compare different crops for remediation performance and energy production
  - Compare Economical aspects of soils remediated by traditional techniques and phytoremediation
Effect heavy metals on performance two energy-production processes

• Biodiesel production from heavy metal polluted rapeseed: Luc Van Ginneken (VITO)

• Biogas production from heavy metal polluted maize: Andy Peene (OWS)
Effect heavy metals on performance two energy-production processes

- Biodiesel production from heavy metal polluted rapeseed: Luc Van Ginneken (VITO)

- Biogas production from heavy metal polluted maize: Andy Peene (OWS)
Biodiesel = FAME

Transesterification of TRIGLYCERIDES

<table>
<thead>
<tr>
<th>MeOH</th>
<th>Me-Ester</th>
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<th>Me-Ester</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triglyceride</td>
<td>Diglyceride</td>
<td>Monoglyceride</td>
<td>Glycerol</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\text{CH}_2\text{COOR}^1 \\
\text{CHCOOR}^2 + 3 \text{CH}_3\text{OH} \\
\text{CH}_2\text{COOR}^3 \\
(\text{Triglycerides}) & \quad (\text{Methanol}) & \quad (\text{Glycerol}) & \quad (\text{Methyl esters}) \\
\text{CH}_2\text{OH} & \quad \text{R}^1\text{COOCH}_3 \\
\text{CHOH} & \quad \text{R}^2\text{COOCH}_3 \\
\text{CH}_2\text{OH} & \quad \text{R}^3\text{COOCH}_3 \\
= \text{biodiesel} & \quad & \quad \end{align*}
\]
High Temperature Pressurized Methanol (HTPM) Process

HTPM ↔ Conventional process

- Continuous reactor ↔ batch
- 15 min ↔ 1-4 h
- Heterogeneous catalyst ↔ base or acid
- No side reactions ↔ purification (soaps)
- Higher yield of biodiesel

Smaller amounts methanol but higher T and pressure
HTPM Process: Lab-scale

\[ V_{\text{reactor}} = 20 \, \text{mL} \]
Optimal conditions HTPM Process
Rapeseed oil – 0,6 g/g MeOH/oil – 15 min – 150 bar

280 °C
HTPM Process: Cd-containing feedstock

- Mimicking the processing of Cd-contaminated rapeseed oil
  - Spiking of methanol with CdNO$_3$
  - Adding commercially available rapeseed oil
  - $[\text{Cd}^{2+}]_{\text{oil}} = 265$ ppm; $[\text{NO}_3^-]_{\text{oil}} = 166$ ppm
  - Determination of presence of Cd on conversion rate at « optimal » process conditions
Effect of CdNO$_3$ on conversion rate
Rapeseed oil – 0,6 g/g MeOH/oil – 15 min – 150 bar

Shift to lower temperatures!!
Effect of HNO₃ on conversion rate
Rapeseed oil – 0.6 g/g MeOH/oil – 15 min – 150 bar

Effect due to Cd, not HNO₃!!
Work in progress

- Spiking of methanol with different forms of Cd-salts (Cl⁻, NO₃⁻, SO₄²⁻,..)
  - Effect on conversion rate
  - Metal mass balance (FAMEs, glycerol, methanol)
- Other metals (Zn, Cu)
- Mixes of metals (Cd/Zn, Cd/Cu, Cu/Zn)
- Different concentrations of different heavy metals
- Conventional process versus HTPM
- Determine heavy metal concentrations in different parts rapeseed (UHasselt and UGent)
Effect heavy metals on performance
two energy-production processes

• Biodiesel production from heavy metal polluted rapeseed: Luc Van Ginneken (VITO)

• Biogas production from heavy metal polluted maize: Andy Peene (OWS)
Digestion

• OWS:
  – Engineering department
  – Lab department

• DRANCO - proces
  – Dry, thermophilic
  – Inputs: waste, energy crops \(\rightarrow\) phytoremediation crops?
  – More than 20 full-scale DRANCO-plants worldwide

• Digestability tests:
  – Phase 1: Batch tests: Determination of substrate
  – Phase 2: Semi-continuous: Long-term effects?
Batch tests

- Contaminated versus clean maize:
  - Difference in biogas production
    - Dependant on species
    - No influence of heavy metals
  - Heavy metal analyses by UGent

- Influence of harvesting time
  - Total plant: optimal harvesting time?
  - Grains: the later, the better
  - Rest of plant? Different parts of plant?
Batch tests

- Parts of maize plant
  - Weight fraction
  - Biogas production
  - Further split-up:
    - Grain
    - Corncob
    - Flyleafs
    - Stalk and leaves
    - 0-30 cm, just above soil level
  - Heavy metal analyses: UGent
Batch tests

• Preliminary results:
  – Very low concentration of heavy metals in grain (UGent)
  – Influence of harvesting time:
    • Grain: Biogas productivity increases
    • 0-30 cm: Biogas productivity decreases

• Future research:
  – Digestion of maize without grain: interesting?
Continuous tests

- Digestion of maize silage
- Contaminated maize versus Clean maize
- Questions:
  - Heavy metal concentration?
  - Influence at long term?
  - Post-treatment of digestate:
    - Heavy metals in press liquid or press cake?
    - Press cake: next phase? Incineration, pyrolysis, …?
Continuous tests

• Preliminary results:
  – No influence of heavy metals on digestion process
  – Definitive evaluation:
    • Dependant on retention time (RT)
    • Test duration = minimum 3 or 4 times the RT
  – UGent: preliminary heavy metal analysis

Maize silage

Digestate
Continuous tests

% Total Solids (TS)

Contaminated  Clean

Silage  Digestate
Continuous tests

<table>
<thead>
<tr>
<th></th>
<th>Contaminated</th>
<th>Clean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silage</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>Digestate</td>
<td>25</td>
<td>30</td>
</tr>
</tbody>
</table>

Total N (g/kg TS)
Continuous tests

Zinc (mg/kg TS)

- **Silage**
  - Contaminated: 267 mg/kg TS
  - Clean: 19 mg/kg TS

- **Digestate**
  - Contaminated: 458 mg/kg TS
  - Clean: 116 mg/kg TS
Continuous tests

![Graph showing cadmium levels in contaminated and clean silage and digestate.]

Cadmium (mg/kg TS)

- Silage
- Digestate

Contaminated: 1.07 mg/kg TS
Clean: 0.08 mg/kg TS for silage, 0.29 mg/kg TS for digestate.
Conclusions

• Presence of heavy metals in plants
  – Stimulates HTPM biodiesel production process
  – Seems to have no influence on the digestion process

• Evaluate the effect of the plant material and heavy metals in the plasmagasification and incineration processes

• Compare the energy performance of the 5 studied energy production processes