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

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L. Van Ginneken and W. Dejonghe (VITO)

Aim MIP-project

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

- Used plants:
  - Rapeseed
  - Maize
  - Wheat

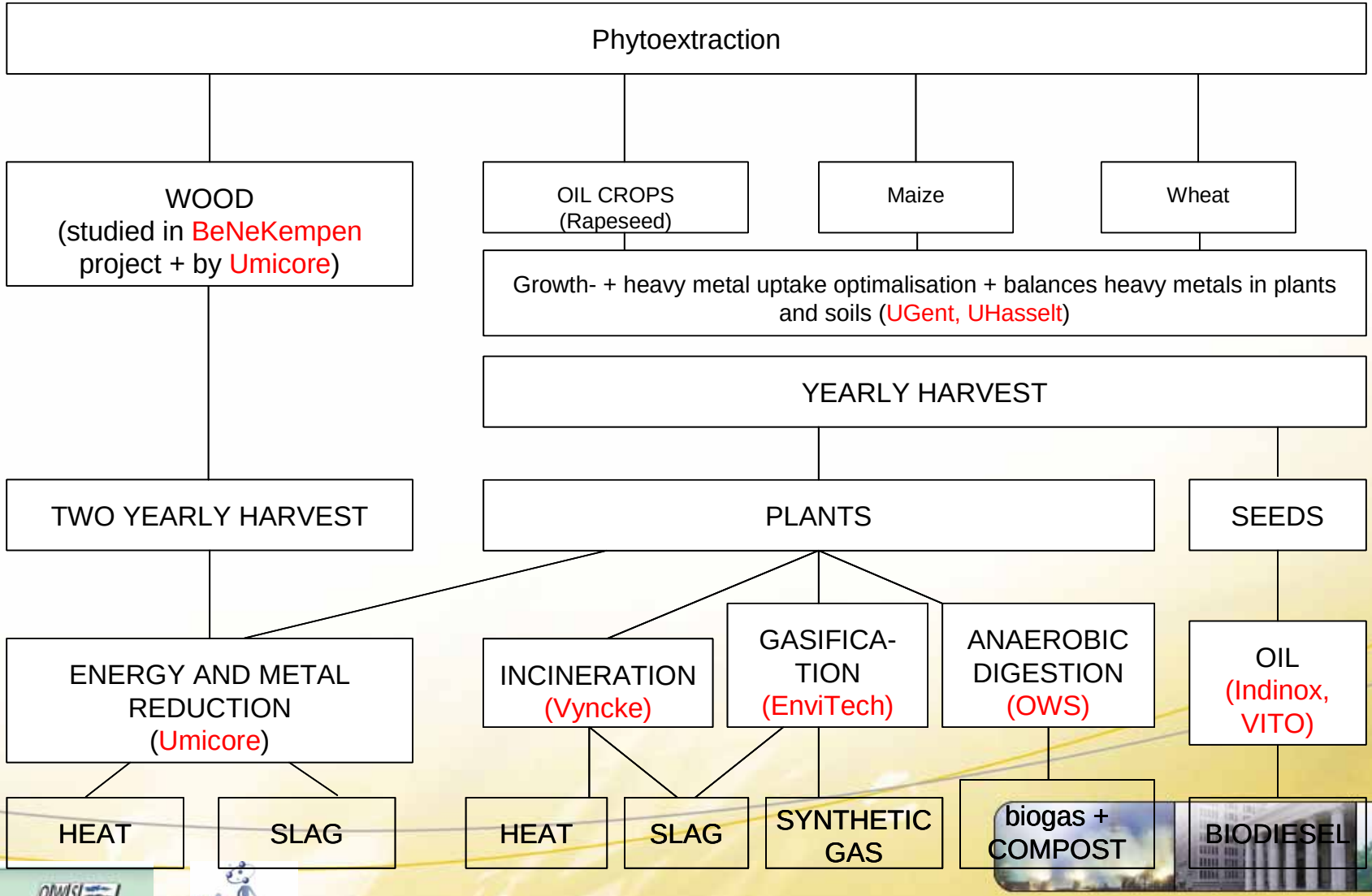
Partners: 9

Company	Task
OWS (A. Peene, J. Smis)	Anaerobic digection
Vyncke (H. Fastenaekels)	Incineration
EnviTech NV (E. Beeckman)	Plasmagasification
INDINOX (S. De Schepper)	Biodiesel production
Umicore (J. Kegels)	Energy and metal reduction in a melter
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, …)

Task 2: Recuperation bio-energy



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)

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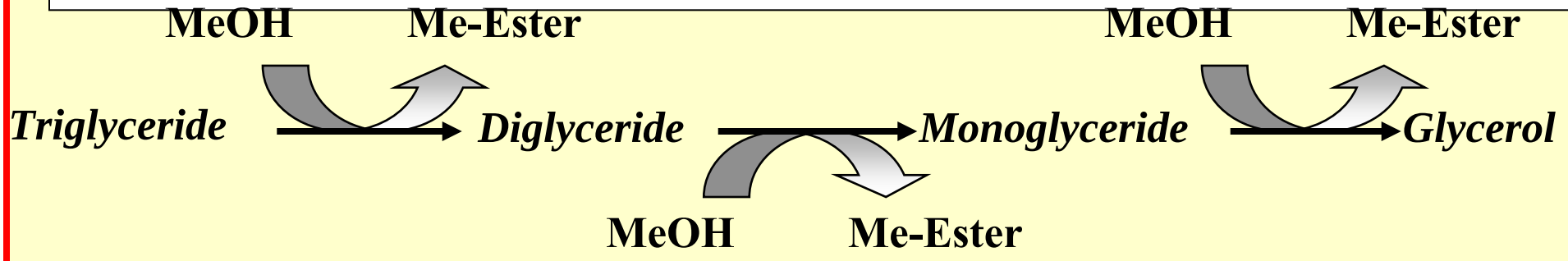
Biodiesel = FAME

Transesterification of TRIGLYCERIDES

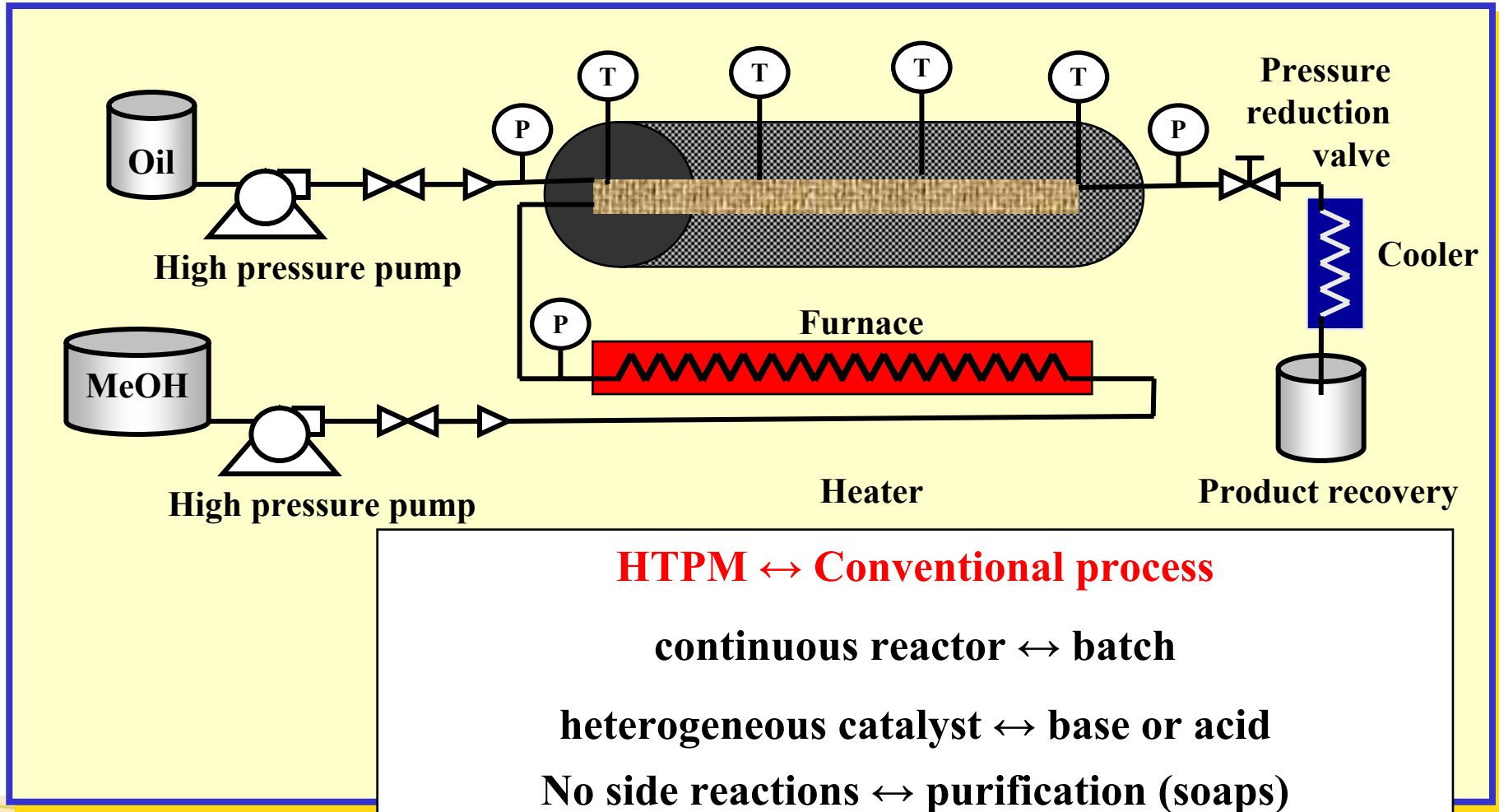


$$\begin{array}{l} CH_2COOR^1 \\ CHCOOR^2 \\ CH_2COOR^3 \end{array} + 3\ CH_3OH \rightleftharpoons \begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \end{array} + \begin{array}{l} R^1COOCH_3 \\ R^2COOCH_3 \\ R^3COOCH_3 \end{array}$$

(Triglycerides) *(Methanol)* *(Glycerol)* *(Methyl esters)*

= *biodiesel*

High Temperature Pressurized Methanol (HTPM) Process



HTPM ↔ Conventional process

continuous reactor ↔ batch

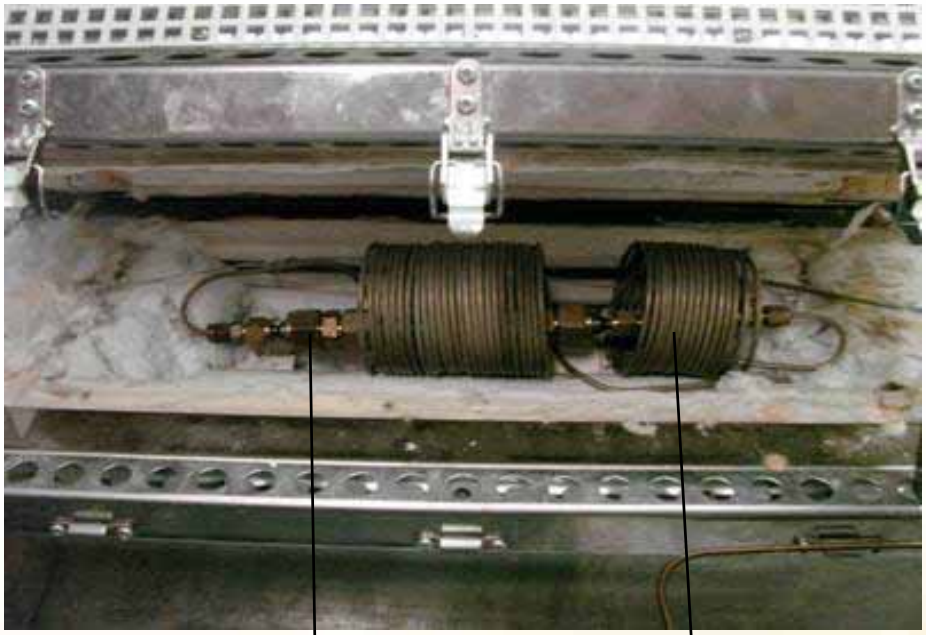
heterogeneous catalyst ↔ base or acid

No side reactions ↔ purification (soaps)

Higher yield of biodiesel

HTPM Process: Lab-scale

$V_{reactor} = 20\ mL$



Tube with catalyst

heating

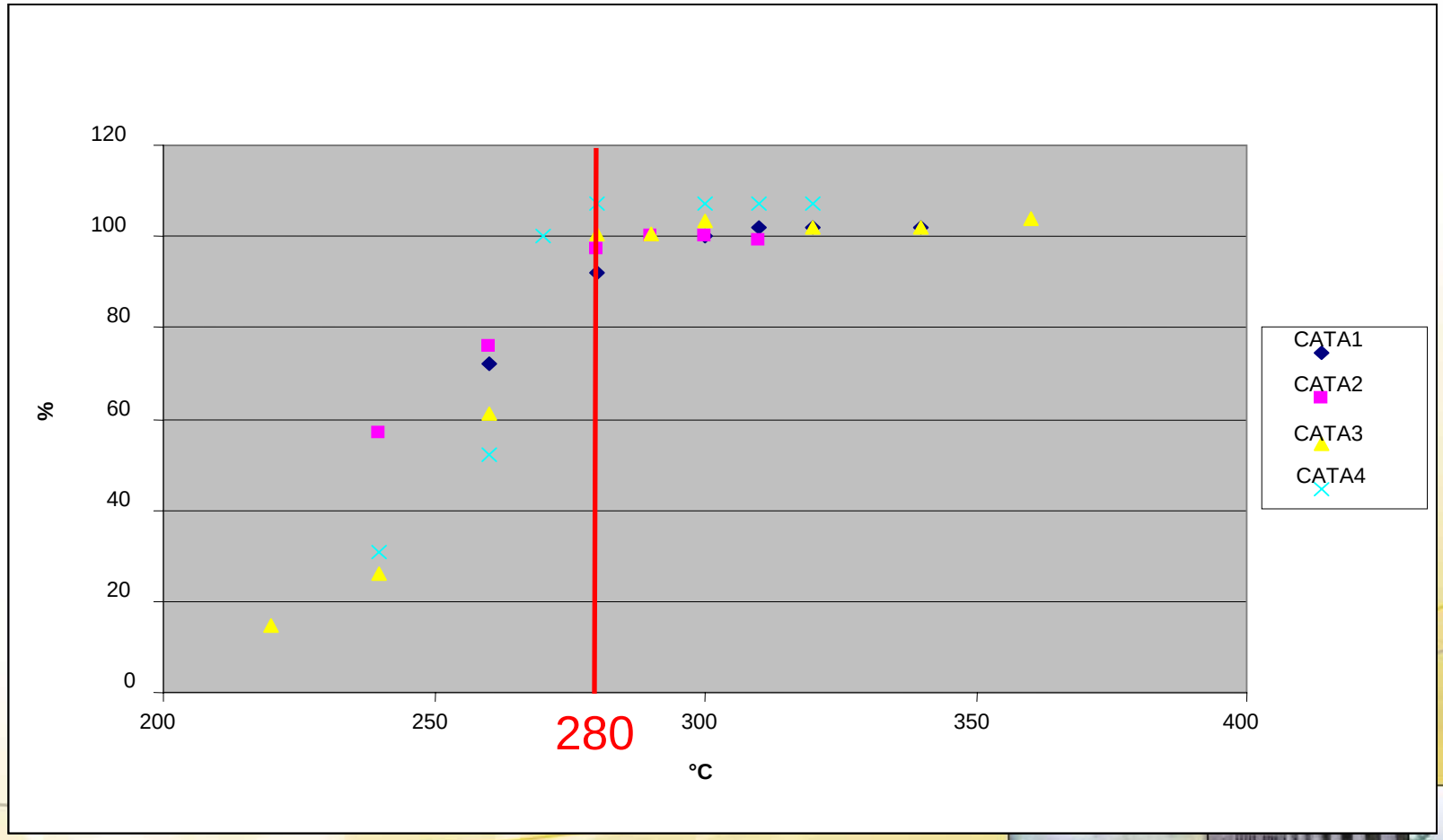
HTPM reactor

Methanol

Oil

Optimal conditions HTPM Process

Rapeseed oil – 0,6 g/g MeOH/oil – 15 min – 150 bar

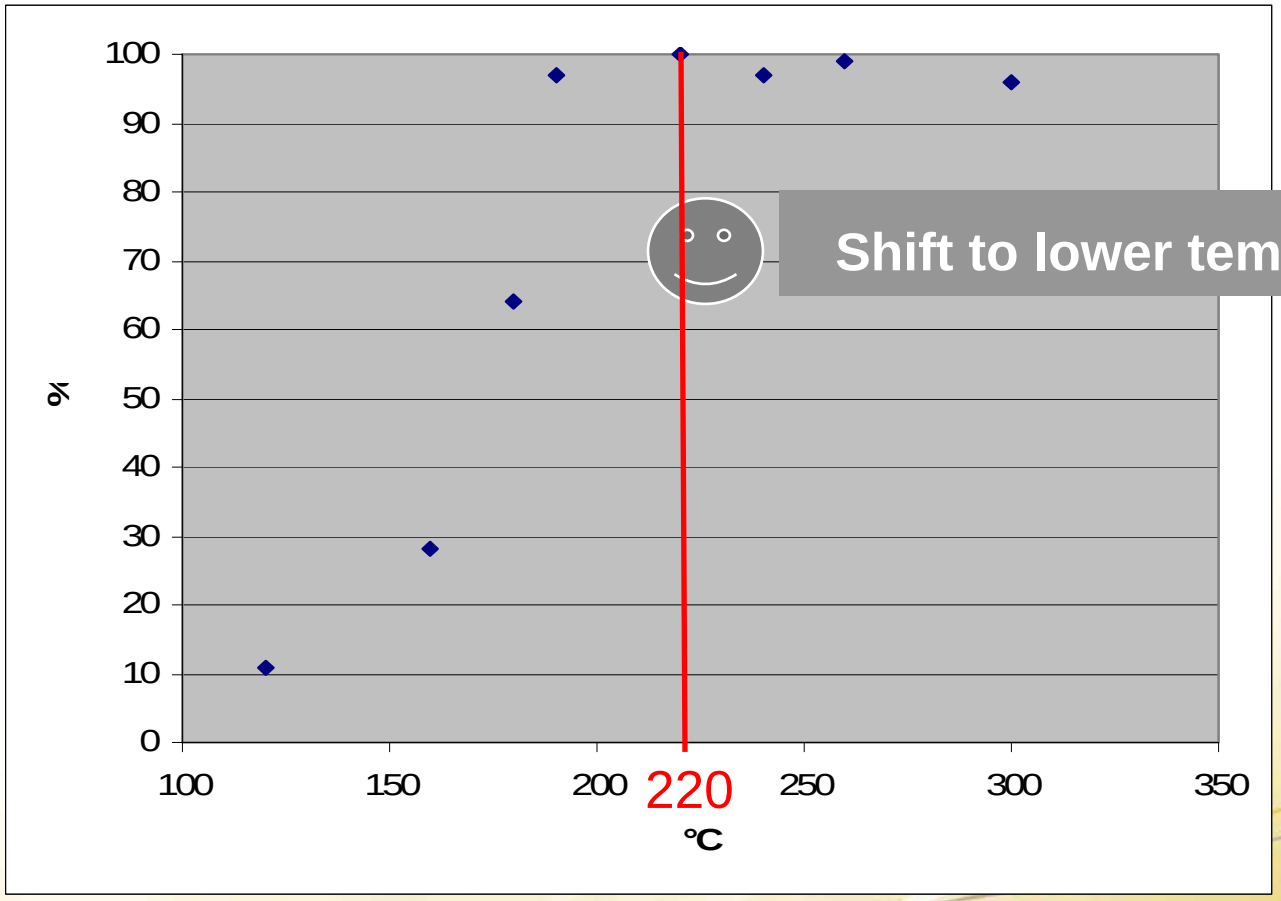


HTPM Process: Cd-containing feedstock

- **Mimicking the processing of Cd-contaminated rapeseed oil**
  - Spiking of methanol with $CdNO_3$
  - Adding commercially available rapeseed oil
  - $[Cd^{2+}]_{oil}$ = 265 ppm; $[NO_3^-]_{oil}$ = 166 ppm
  - Determination of presence of Cd on conversion rate at « optimal » process conditions

Effect of $CdNO_3$ on conversion rate

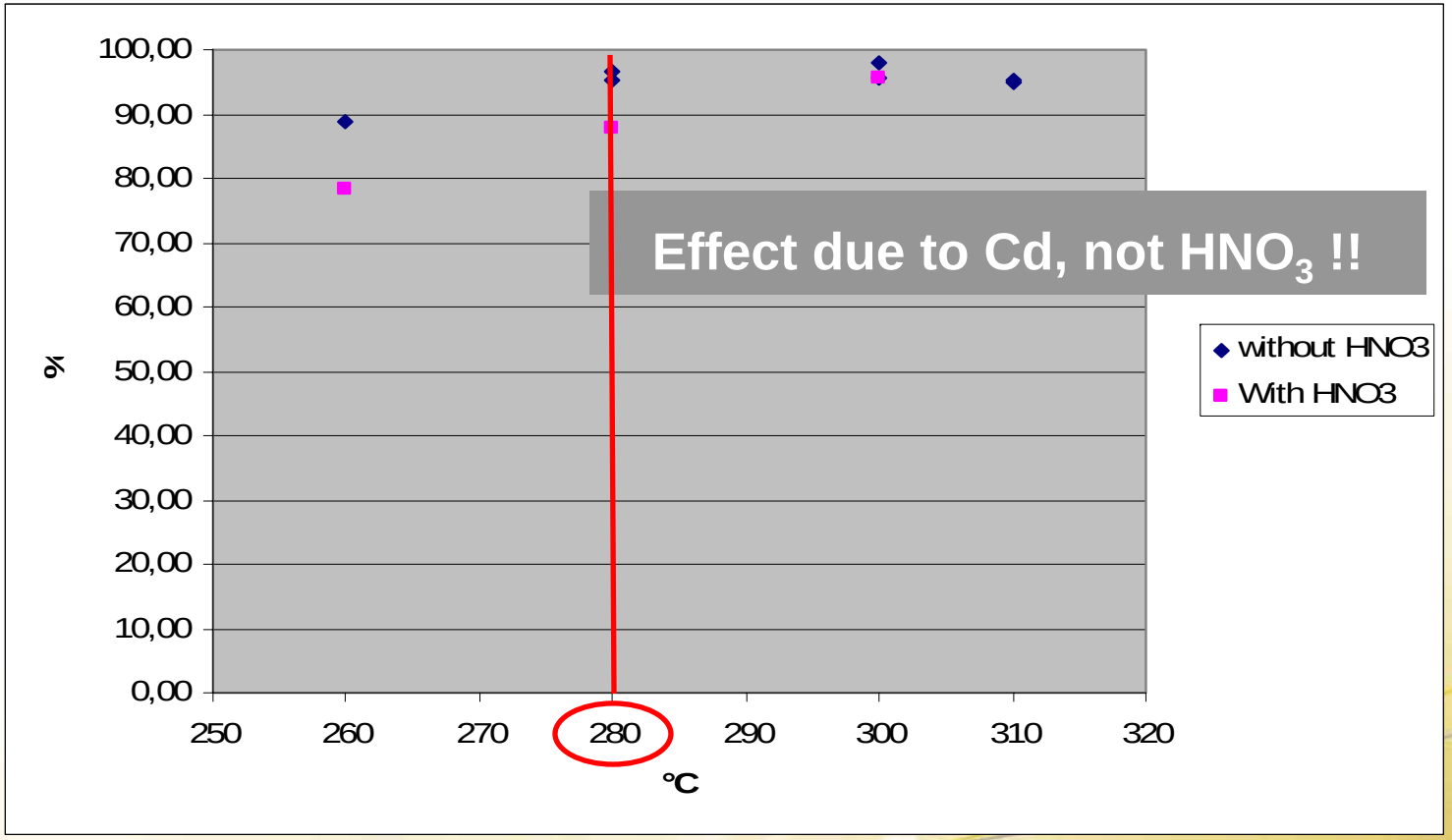
Rapeseed oil – 0,6 g/g MeOH/oil – 15 min – 150 bar



Shift to lower temperatures !!

Effect of HNO_3 on conversion rate

Rapeseed oil – 0,6 g/g MeOH/oil – 15 min – 150 bar



Work in progress

- **Spiking of methanol with different forms of Cd-salts (Cl^-, NO_3^-, SO_4^{2-},..)**
  - Effect on conversion rate
  - Metal mass balance (FAMEs, glycerol, methanol)
- **Other metals (Zn, Cu)**
- **Mixes of metals (Cd/Zn, Cd/Cu, Cu/Zn)**
- **Conventional process versus HTPM**

Effect heavy metals on performance two energy-production processes

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Digestion

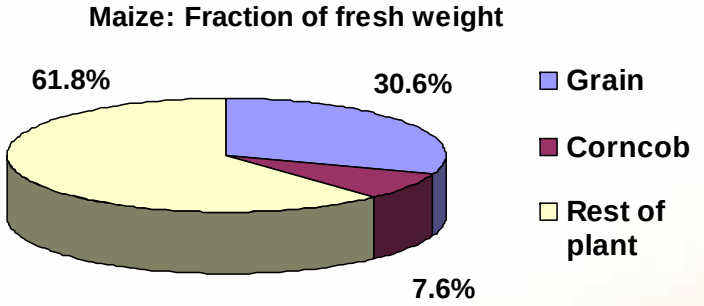
- OWS:
  - Engineering department
  - Lab department
- DRANCO - proces
  - Dry, thermophilic
  - Inputs: waste, energy crops → phytoremediation crops?
  - More than 20 full-scale DRANCO-plants worldwide
- Digestability tests:
  - Phase 1: Batch tests: Determination of substrate
  - Phase 2: Semi-continuous: Long-term effects?

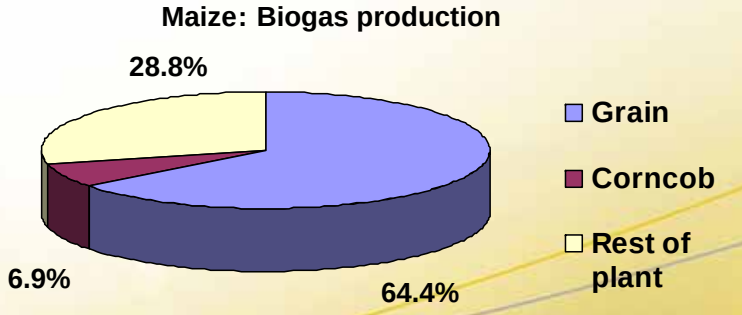
Batch tests

- 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 leafs
    - 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, …?

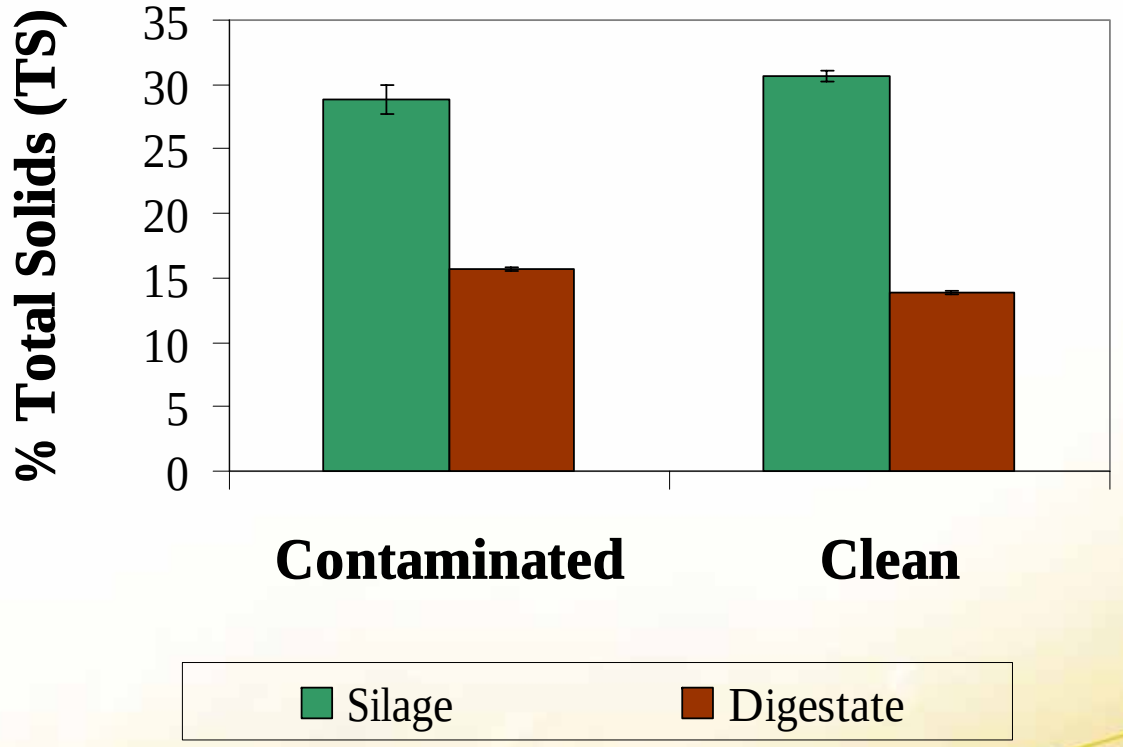
Continuous tests

- 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

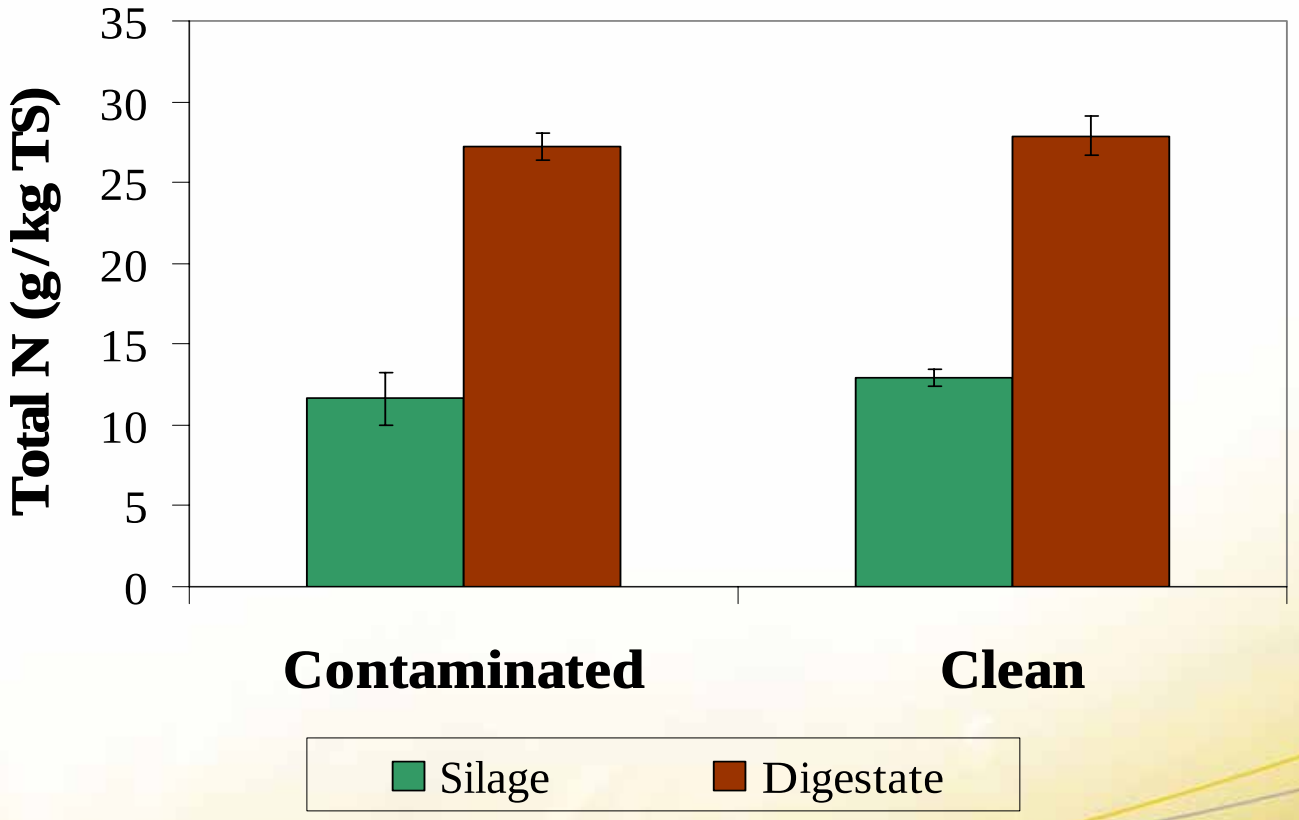
Maize silage

Digestate

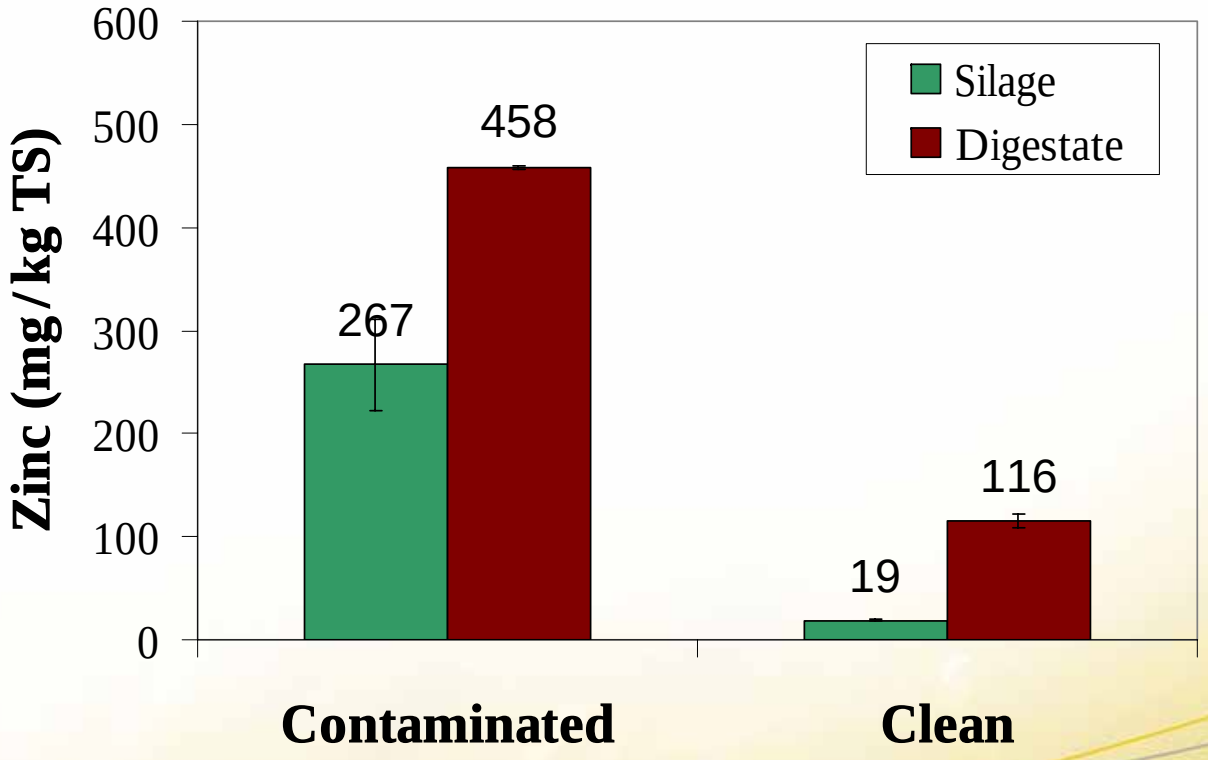
Continuous tests



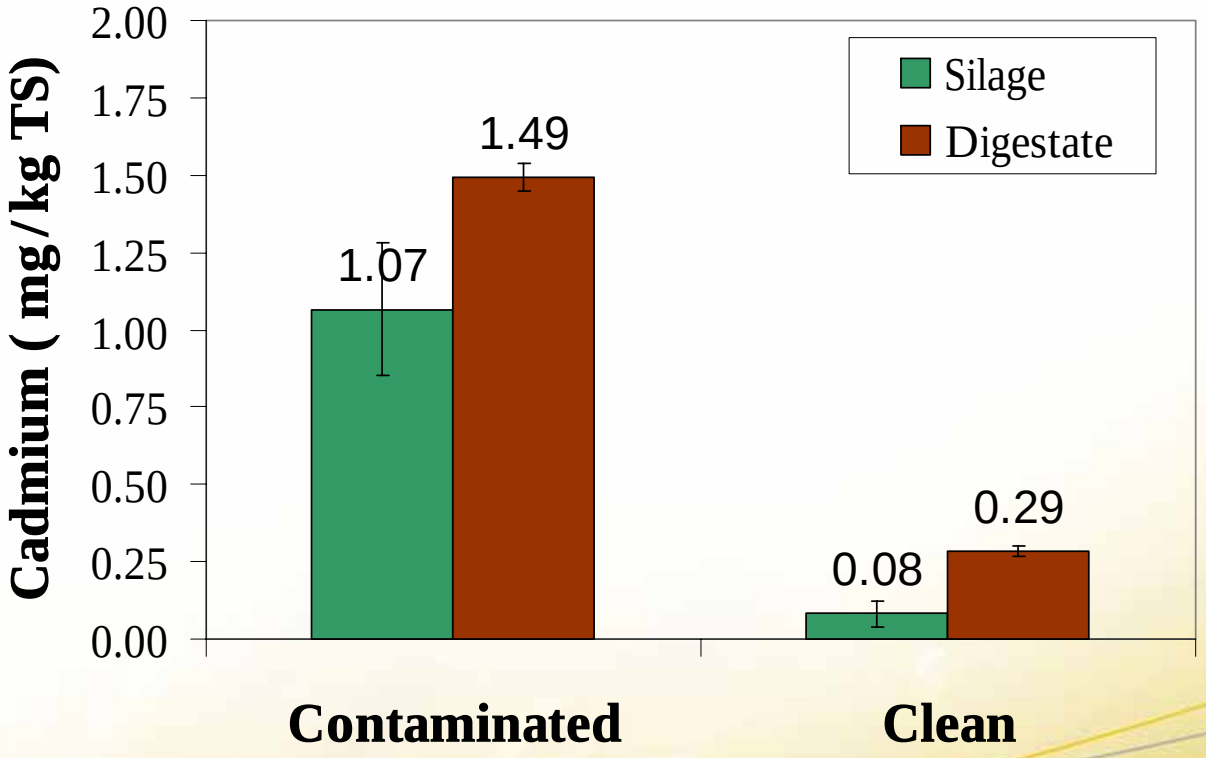
Continuous tests



Continuous tests



Continuous tests



Conclusions

- Presence of heavy metals in plants
  - Stimulates HTPM biodiesel production process
  - Does not influence the digestion process

- Evaluate the effect of the plant maetrial and heavy metals in the plasmagasification and incineration process
- Compare the energy performance of the 5 studied energy production process