Development of selective catalytic oxidation (SCO) technology and other high temperature NH_3 removal processes for gasification power plants

AMMONIA REMOVAL

Dr. Pekka Simell

VTT Processes

BIO-ENERGY
ENLARGED PERSPECTIVES

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Project Consortium

- VTT, Technical Research Centre of Finland (*Dr. Pekka Simell*)
- Åbo Akademi University, Finland (*Dr. Pia Kilpinen*)
- Universidad Complutense de Madrid, Spain (*Prof. J. Corella*)
- University of Leeds, UK (*Dr. Jenny Jones*)
- Foster Wheeler Energia Oy, Finland (*Dr. Matti Hiltunen*)
- Energie E2, Denmark (*Erik Winter*)

Duration 36 moths

1.4.2000 - 31.3.2003

NOx reduction methods in gasification applications

NOx REDUCTION METHODS

Gasification

GASIFICATION PROCESS

- MINIMIZING FORMATION OF NITROGEN SPECIES (NH3, HCN) IN GASIFIER
- GAS SCRUBBING
- CATALYTICAL GAS TREATMENT
  – DECOMPOSITION > 800 °C
  – DECOMPOSITION AT 400 - 700 °C

COMBUSTION CONTROL

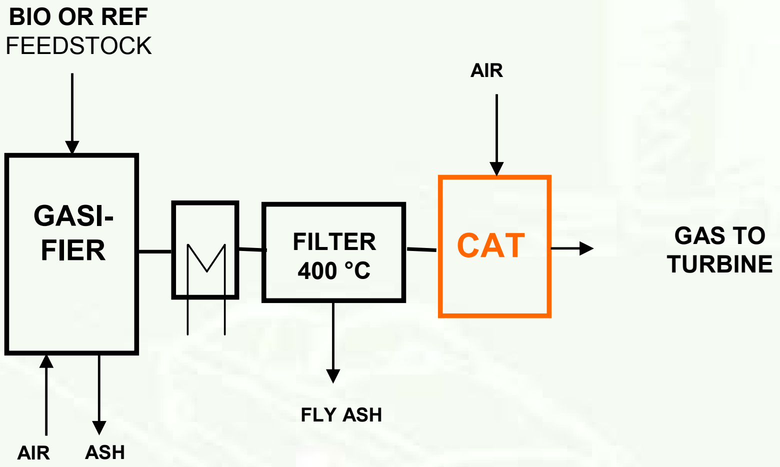
LOW-NOx BURNERS

FLUE GAS TREATMENT

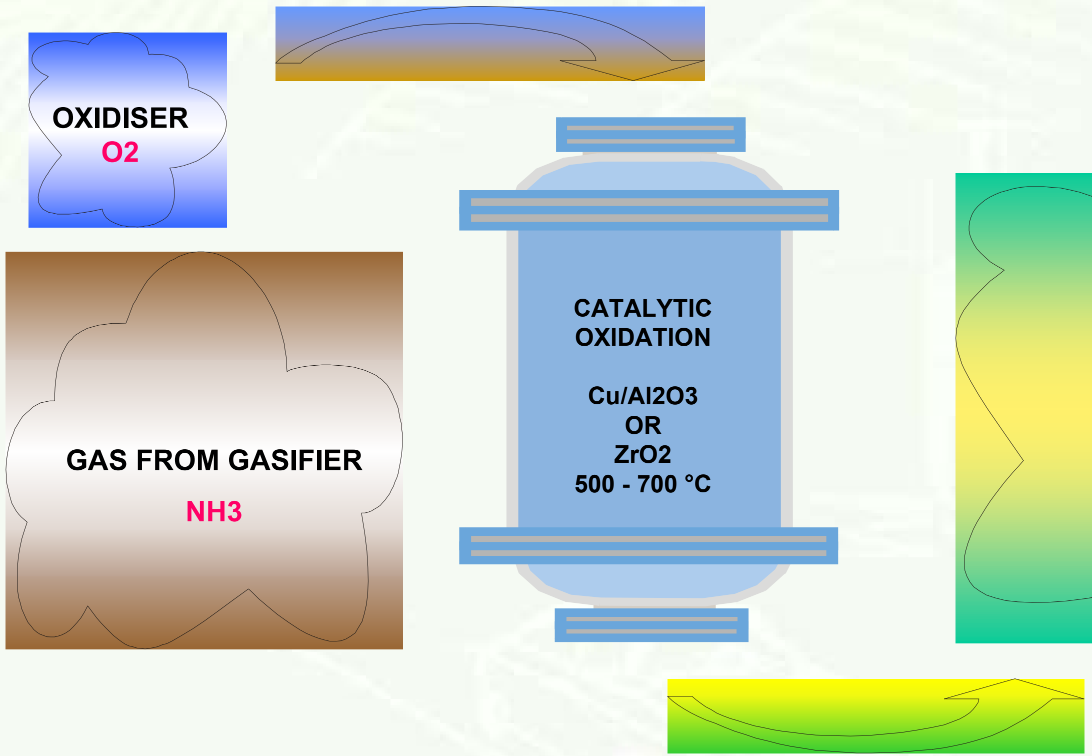
- SCR
- OTHERS

Challenges

- NO_x emissions can be reduced or almost totally eliminated by reducing the amount of nitrogen compounds in the gas
- Solution 1: Catalytic decomposition (SCO = selective catalytic oxidation) at LOW temperature (400 - 700 °C)



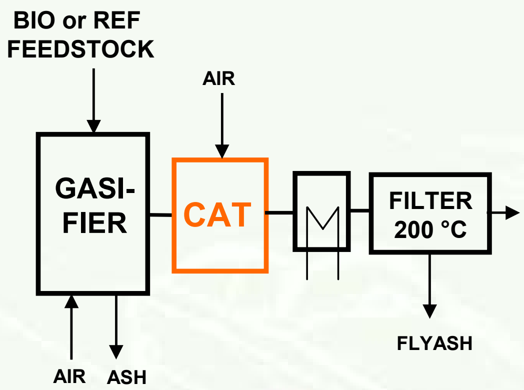
Selective catalytic oxidation (SCO)



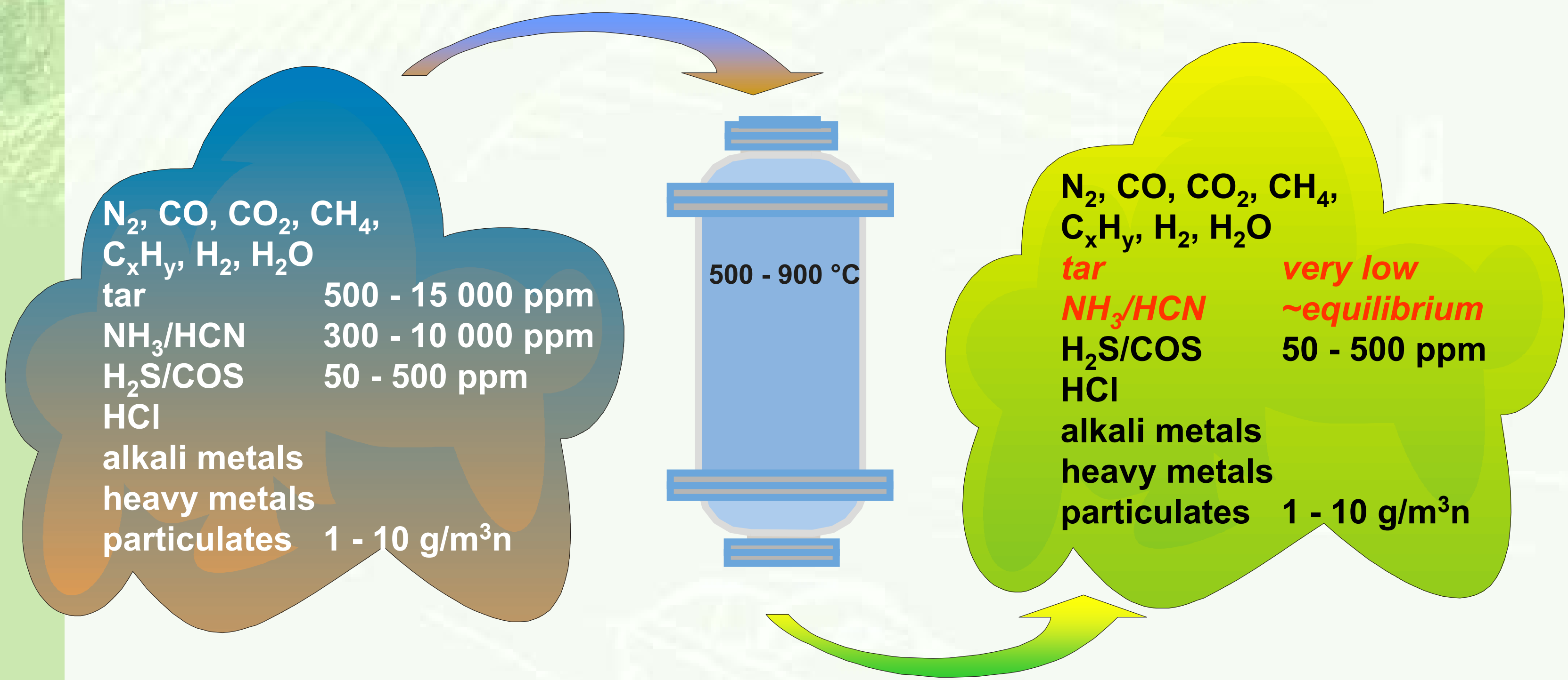
Challenges

- NO_x emission can be reduced or almost totally eliminated by reducing the amount of nitrogen compounds in the gas

- Solution 2: Catalytic decomposition at HIGH temperature (>800 °C) with Ni-catalysts



OPERATION CONDITIONS FOR CATALYTIC GAS CLEANING IN BIOMASS GASIFICATION



Key questions
SCO catalysts

- **Can the SCO catalyst activity be improved?**

⇒ catalyst screening tests in lab-scale, 500 - 900 °C

⇒ alumina activation was not successful

⇒ metal/alumina catalysts tested

⇒ very high activity observed with Cu/Al_2O_3

⇒ **no sulfur deactivation**

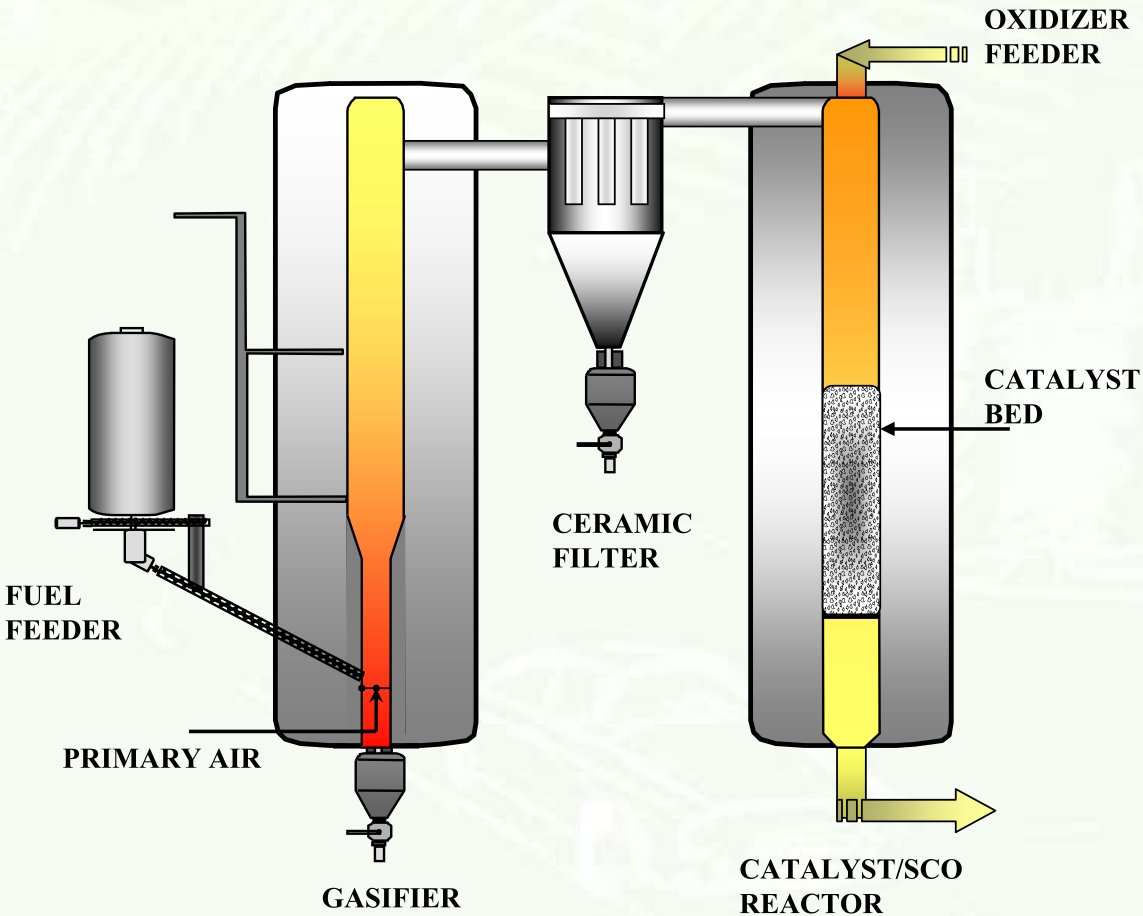
⇒ **no activity decrease within 48 h with lab gases**

Key questions
SCO catalysts

- **Are the SCO catalysts active with real gases?**

  ⇒ tests with bench-scale fluid-bed gasifier
  ⇒ tests in slip-stream
  ⇒ ZrO2-catalyst gave promising results
    ⇒ **ammonia & tar decomposition**
    ⇒ **no coke**
    ⇒ **deactivated slightly within 200 h**
  ⇒ Cu/Al2O3 catalyst not yet tested with real gas

Atmospheric fluidised-bed gasifier and SCO-reactor of VTT



Key questions
SCO catalysts

- **How is the SCO catalyst working?**

⇒ homogeneous (gas-phase) ammonia decomposition at gasification conditions modelled

⇒ heterogeneous chemistry of the H2/NH3/O2 system on Cu/Al2O3 modelled

⇒ kinetic experiments with lab scale reactor

⇒ very good fit to the experimental data

$2NH_3 + 1.5O_2 + Cu(S) \Rightarrow Cu(S) + N_2 + 3H_2O$ (1) NH_3 oxidation reaction

$H_2 + 0.5O_2 + Cu(S) \Rightarrow Cu(S) + H_2O$ (2) H_2 oxidation reaction

$CO + H_2O + Cu(S) \Rightarrow Cu(S) + CO_2 + H_2$ (3) WGS (water gas shift) reaction

$CO_2 + H_2 + Cu(S) \Rightarrow Cu(S) + CO + H_2O$ (4) Reverse WGS reaction

Key questions
nickel catalysts

- **Activity & operation of different nickel catalysts?**
- **Reactor model?**

⇒ commercial steam-reforming catalysts active for NH3 and tar

⇒ catalysts for naphtha are much better than those for natural gas

⇒ narrow operating window identified

⇒ **high temp., low inlet tar, high H2O/*C**

⇒ filter necessary if ring-shaped catalysts applied

⇒ modelling gave insight into the operation of a monolith reactor

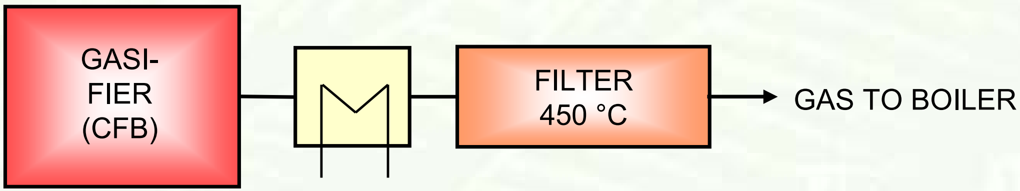
Key questions
both solutions

- **What is the technical & economical feasibility of the both catalytic gas cleaning systems developed in the project**?

⇒ 6 case studies
  - **CFB**
  - **fuel input 90 MW**
  - **feedstock: SRF**

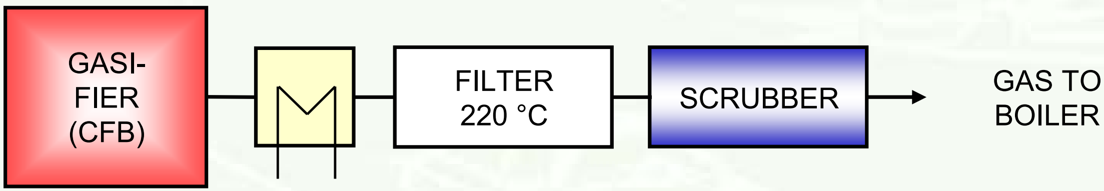
⇒ price comparison of the produced energy in the various cases

Case 1. Basic



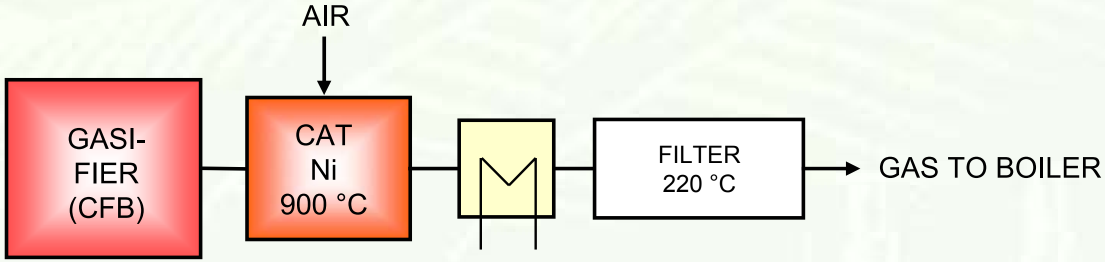
$\eta = 93$ %

Case 2. Amer wood gasification plant (old)

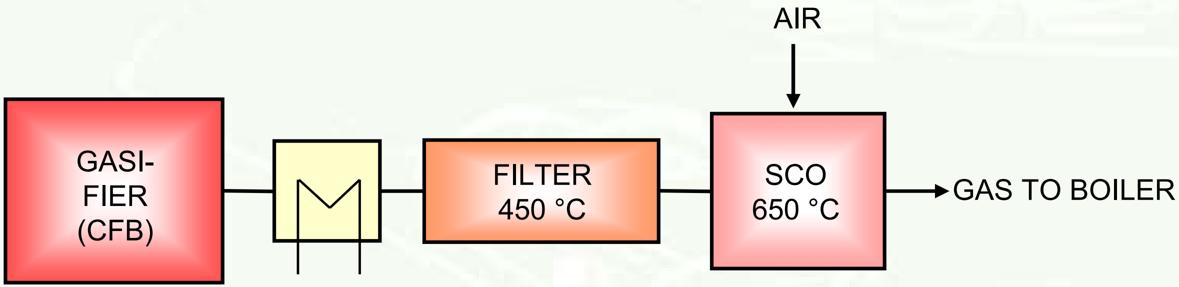


$\eta = 85$ %

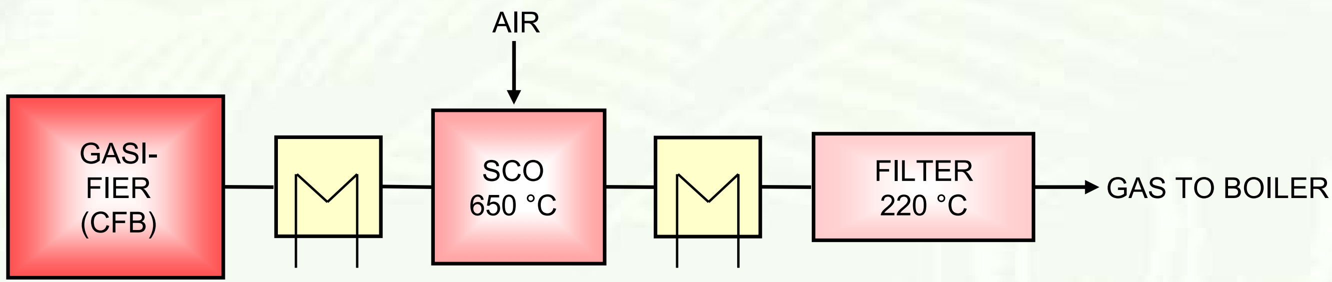
Case 3. Nickel Monolith



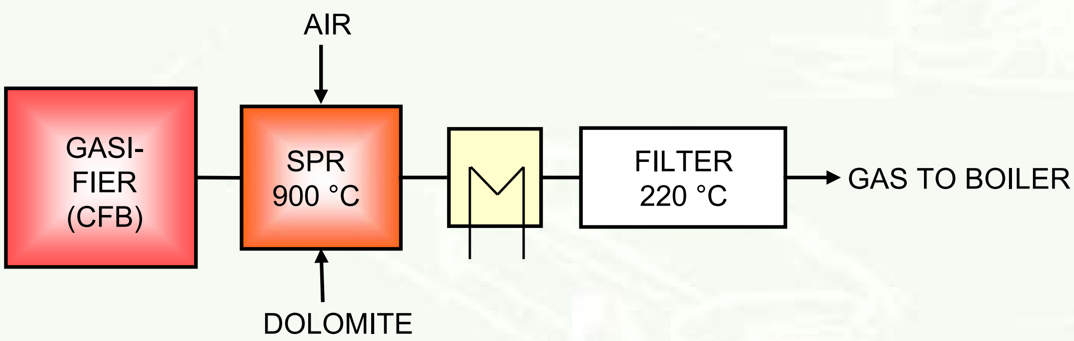
Case 4. SCO with Filter



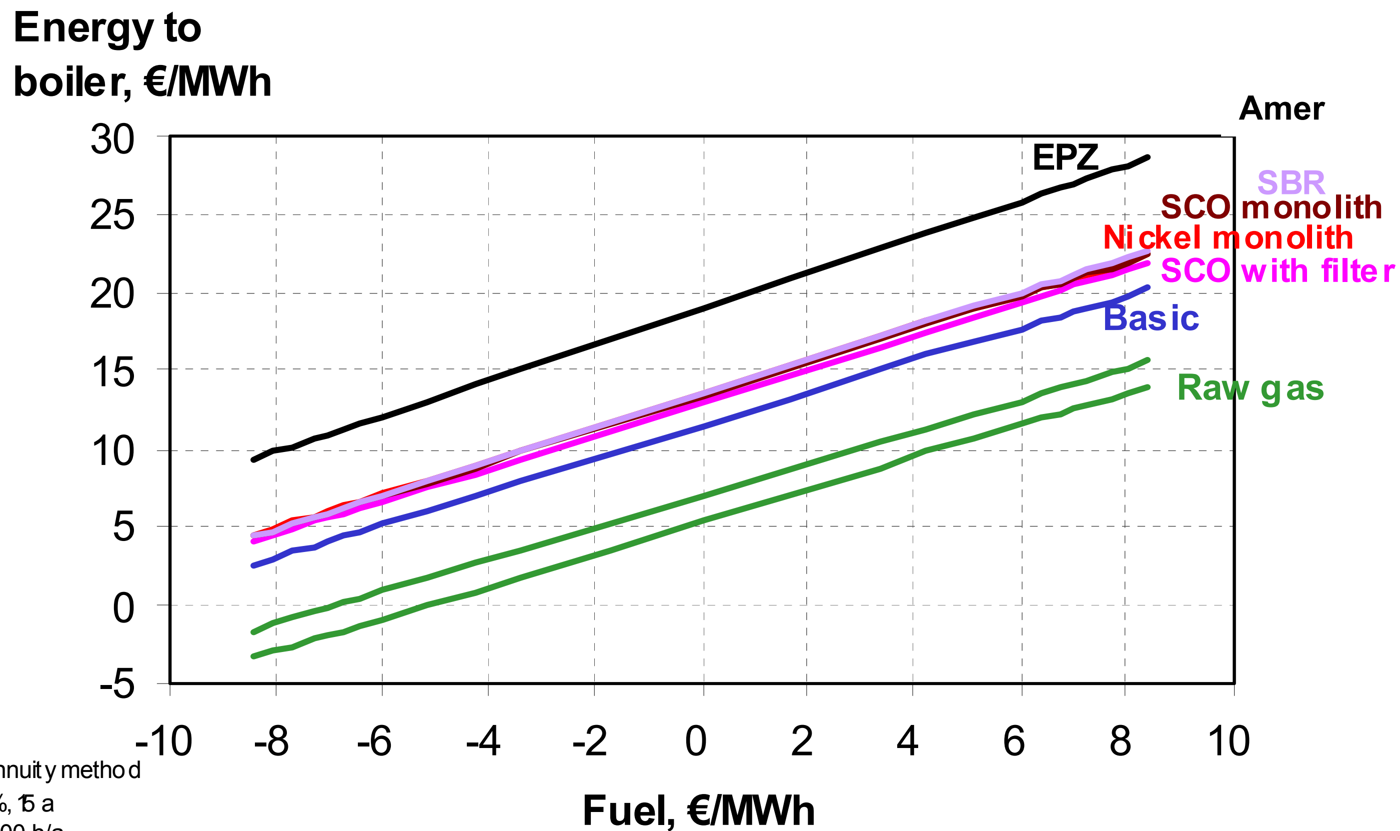
Case 5. SCO Monolith



Case 6. Spouted Bed Reformer



The price of energy delivered to the boiler (as product gas and steam)



Annuity method
5%, 15 a
5500 h/a
Flyash disposal 120 EUR/t

Key questions
both solutions

- **What is the technical & economical feasibility of the both catalytic gas cleaning systems developed in the project**?

⇒ 6 case studies
- **CFB**
- **fuel input 90 MW**
- **feedstock: SRF**

⇒ price comparison of the produced energy in the various cases

⇒ all studied catalytic gas cleaning concepts are very close to each other economically

⇒ election can be fully based on technical feasibility and on the required level of gas cleaning

⇒ all catalytic gas cleaning concepts are more expensive than the reference case based on filtration only

Conclusions

- **Project primary objective achieved**
  - highly selective and active SCO catalyst identified = Cu
  - also Zr-based catalysts seem promising
  - mechanistic understanding gained

- **Economical evaluation made**
  - no marked difference between the studied catalytic processes

⇒ ***New catalysts on market within 2 - 4 years?***