RE2 – Optimization of Bioenergy Use GASIFICATION, research

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Jukka Konttinen
University of Jyväskylä
Renewable Energy Programme

Gasification research - CONTENTS

- Future challenges → to give guidelines to R&D

- Gasification process / modelling
  - Gasification reactivity & behaviour of biomass ash
  - Formation of impurities
  - Combustion of product gas

- Gas cleaning
  - tars, particulates, heavy metals, chlorine, sulfur, nitrogen,…
  - THE MOST CRUCIAL ISSUE FOR ADVANCED APPLICATIONS

- R & D on the catalytic production of liquid biofuels will not be presented here

GASIFICATION

FUTURE CHALLENGES

→ Guidelines to R&D

Future challenges, gasification of biomass

- Gasification
  - "difficult" fuels (agro biomasses: ash melting/bed material sintering)
  - Formation mechanisms of impurities, such as: Waste-type fuels → heavy metals
  - Conversion of unconverted char

  Biomass combustion processes have the same challenges, but gasification can offer ways to get rid of the problems easier (for example metals can be separated by filtration before the processing of product gas to end products)

- Gas cleaning
  - Fly ash
  - Tar formation and cracking (catalysts)
  - Waste-type biomasses and wastes → heavy metals and halogenes
  - Fuel-N to NH_3 – staged combustion is required
  - **BIGGEST CHALLENGE: Ultra-cleaning required for advanced applications (IGCC, fuel cells, catalytic synthesis processes)**
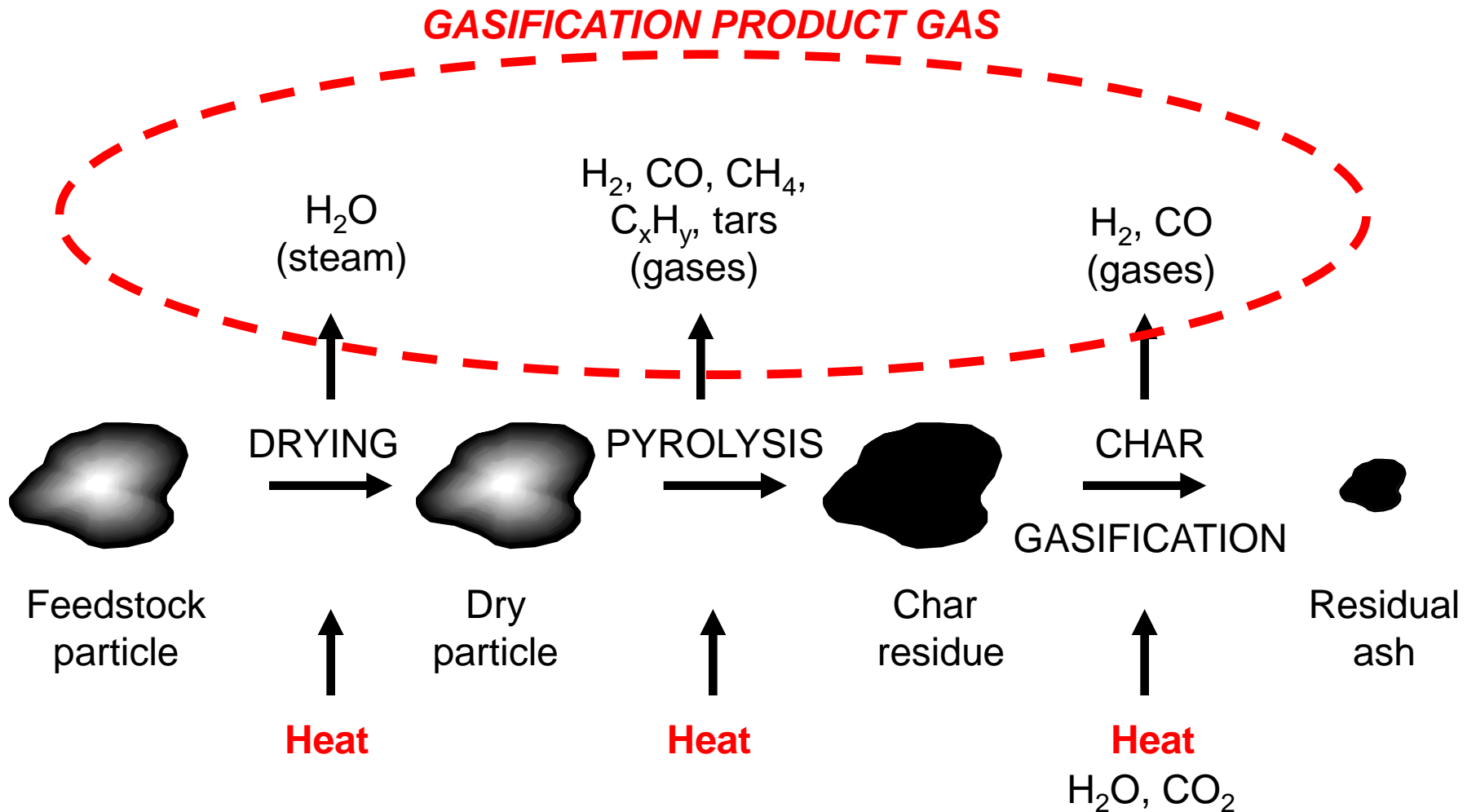
- Process integration/optimization
  - Long-term availability needs to be proven
  - Operation as a stand-alone plant, fuel availability
  - Integration in a pulp mill
  - High pressure operation (treatment of solids) and materials

- Economics
  - Price of electricity, price of heat (steam)
  - Price of liquid biofuels produced

What happens in gasification?

GASIFICATION PRODUCT GAS

H_2O
(steam)

H_2, CO, CH_4,
C_xH_y, tars
(gases)

H_2, CO
(gases)

DRYING → PYROLYSIS → CHAR

GASIFICATION

| Feedstock particle | Dry particle | Char residue | Residual ash |

Heat　　　　**Heat**　　　　**Heat**
H_2O, CO_2

Partial combustion of fuel with oxygen brings in the **heat**

Why modelling?

- Design

- Simulation

- Minimization&understanding of pollutant formation

- Plant economics / sustainability

Gasification phenomena & modelling

- External and internal heat transfer
- External and internal mass transfer
- Volume and porosity development
- Drying is controlled by heating rate
- Devolatilization rate correlations need validation by measurements
- Tar formation is based on measurements (little understood)
- Water-gasification reaction $C + H_2O \rightarrow CO + H_2$
- Boudouard reaction $C + CO_2 \rightarrow 2CO$
- Oxygen-gasification $C + \frac{1}{2}O_2 \rightarrow CO$ (normally negligible)
- Shift conversion $CO + H_2O \leftrightarrow CO_2 + H_2$

Järvinen, M. P., 2002, Numerical modeling of the drying, devolatilization and char conversion processes of black liquor droplets. Doctoral Dissertation, Acta Polytechnica Scandinavica, Mechanical Engineering Series No. 163, Espoo 2002, 77 p.

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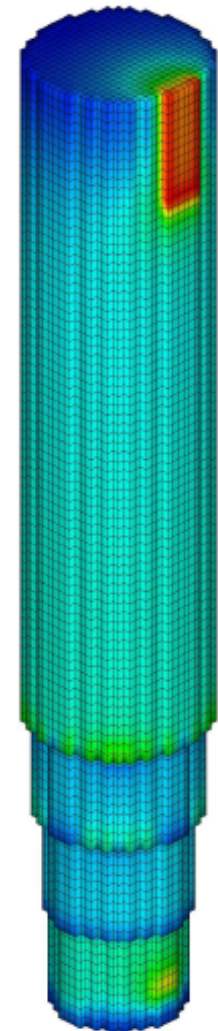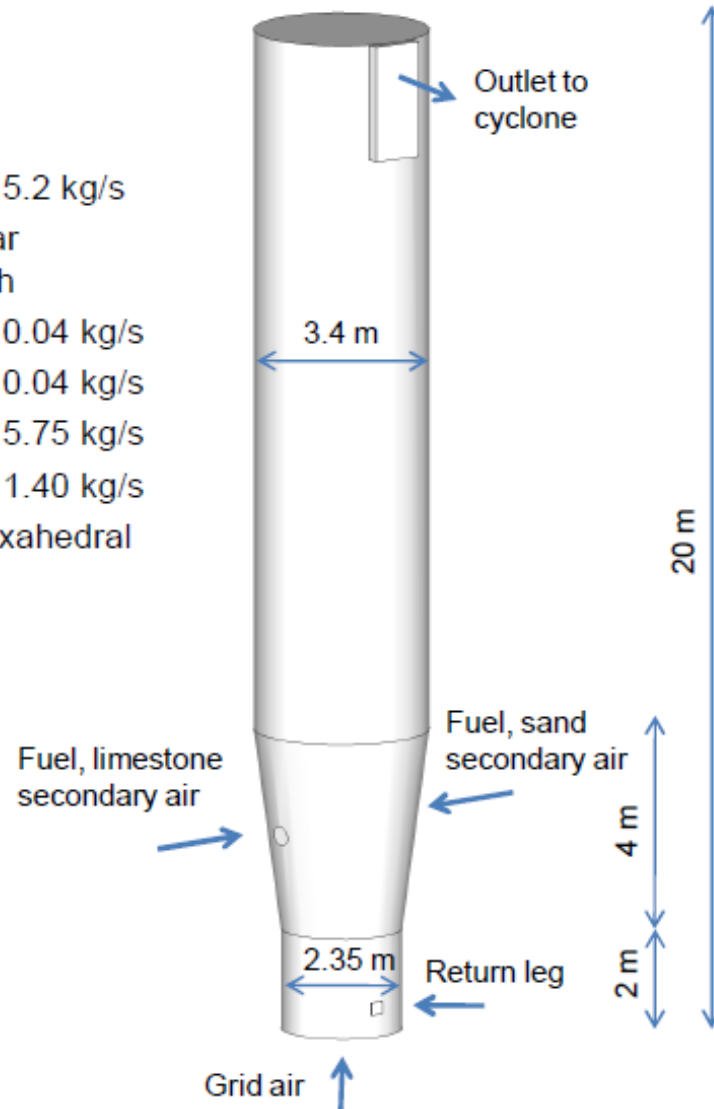# GASIFICATION MODELLING - EXAMPLES OF RESEARCH

Processes in FB gasifiers
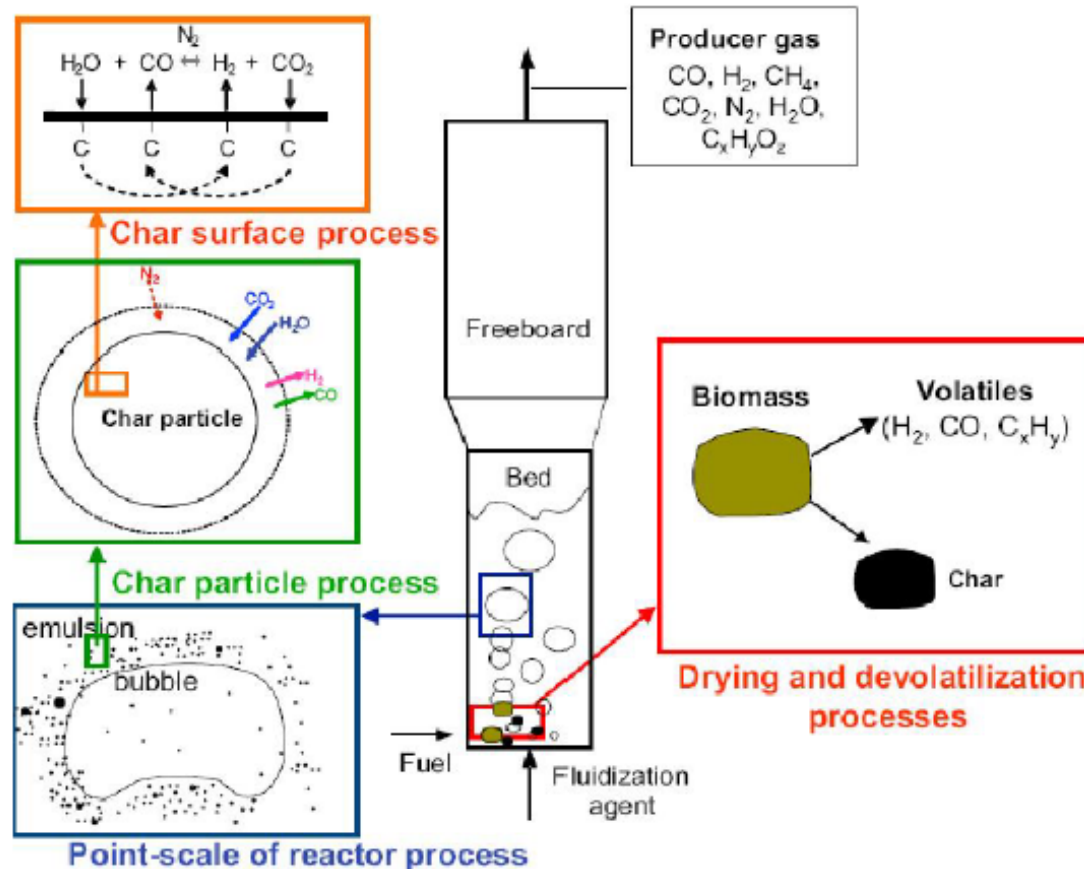
Gómez-Barea, A. and Leckner, Bo, 2010, Modeling of biomass gasification in fluidized bed. Progress in Energy and Combustion Science, Vol. 36, No. 4, August 2010, pp. 444 - 509.

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Calculation case: Air blown 50 MWth

- Thermal capacity: 50 MWth
- Fuel: wood based biomass   5.2 kg/s
  - 49.8% volatiles, 9.0% char
    40.0% moisture, 1.2% ash
- Sorbent: calcitic limestone   0.04 kg/s
- Make up sand   0.04 kg/s
- Grid air   5.75 kg/s
- Secondary air to fuel inlets   1.40 kg/s
- Geometry approximated by hexahedral control volumes.

Outlet to cyclone

3.4 m

Fuel, limestone secondary air

Fuel, sand secondary air

2.35 m   Return leg

Grid air

20 m

4 m

2 m

Surface mesh colored by solid velocity magnitude

Water-gas reaction [kg/m3s]
C + H2O -> CO + H2
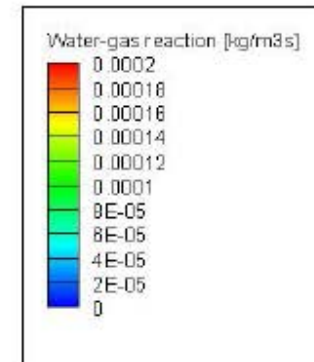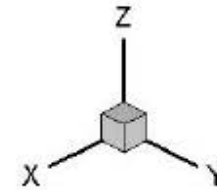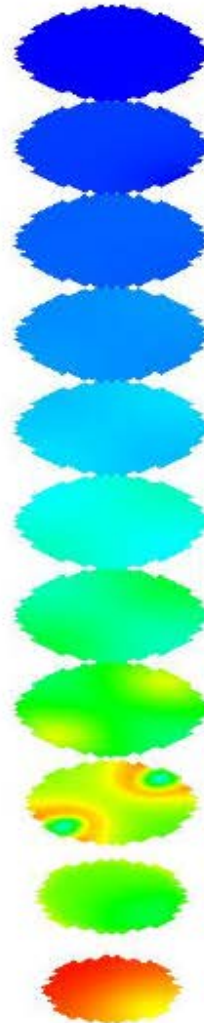
Profile of the Average Gas Composition
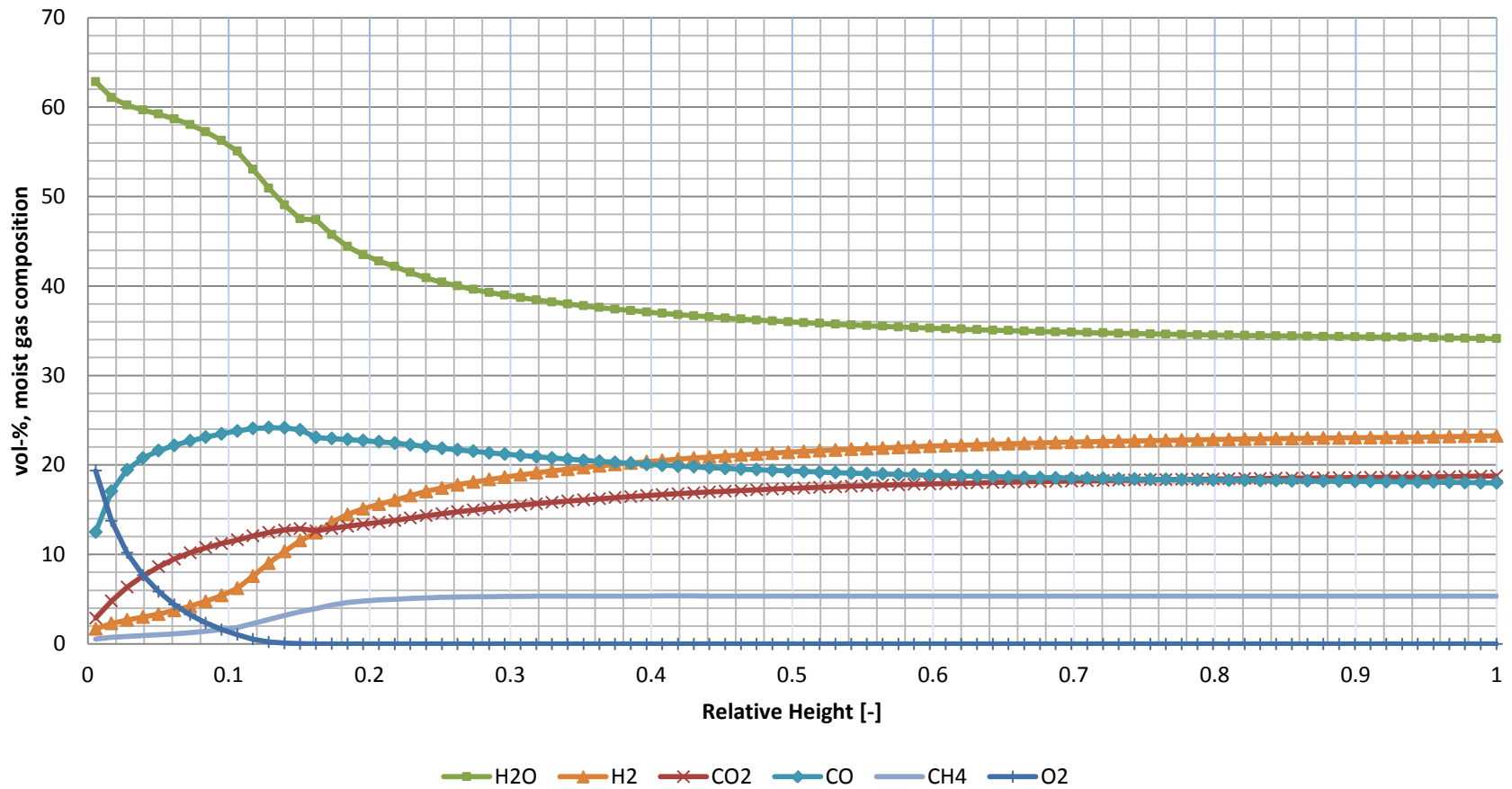
Gasifier simulations at LUT

Summary

- First demonstration calculation of a CFB gasifier was performed by three-dimensional furnace model CFB3D.

- The results are promising: visualization of the process helps to understand the different phenomena and can be used to support the development of gasifier designs.

- The applied reaction rate correlations are based on literature and thus the results are only indicative.

- Many other empirical model parameters are rough estimates as well.

- Validation studies are necessary for improving the prediction capability of the model.

BIOFUEL GASIFIER FEEDSTOCK REACTIVITY –
EXPLAINING THE DIFFERENCES AND CREATING PREDICTION MODELS

- In the project, a method is generated to predict the gasification behavior of biomass fuels in a gasification reactor
  - The method should be based on reasonable cost and effort

- The results of the project will help to understand the differences in the gasification behavior of biomass fuels.
  - An essential hypothesis in the project is that the decrease of the catalysis properties of biomass ash will decrease biomass char gasification reactivity and thus the final carbon conversion

- Partners University of Jyväskylä, VTT and Åbo Akademi University
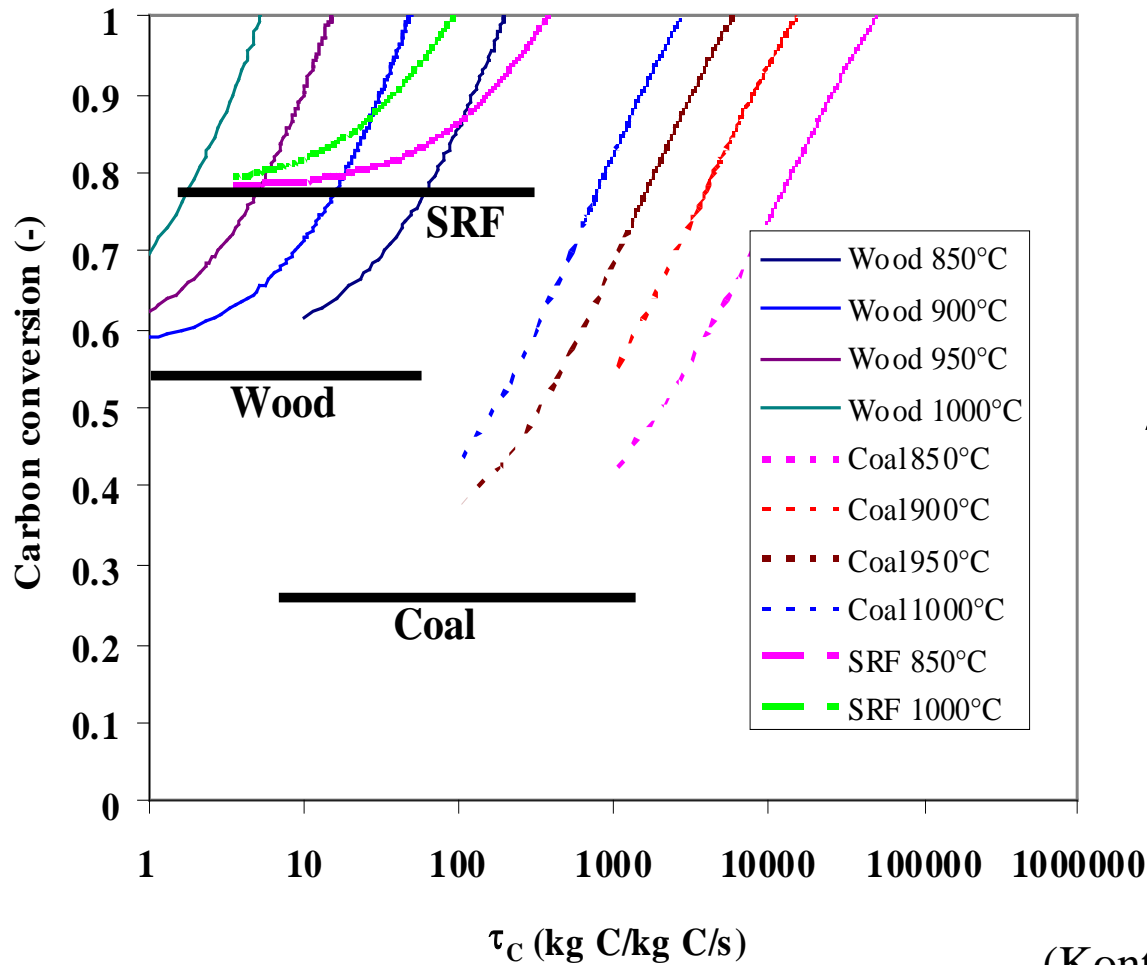
Research in gasification
"CARBON CONVERSION PREDICTOR"
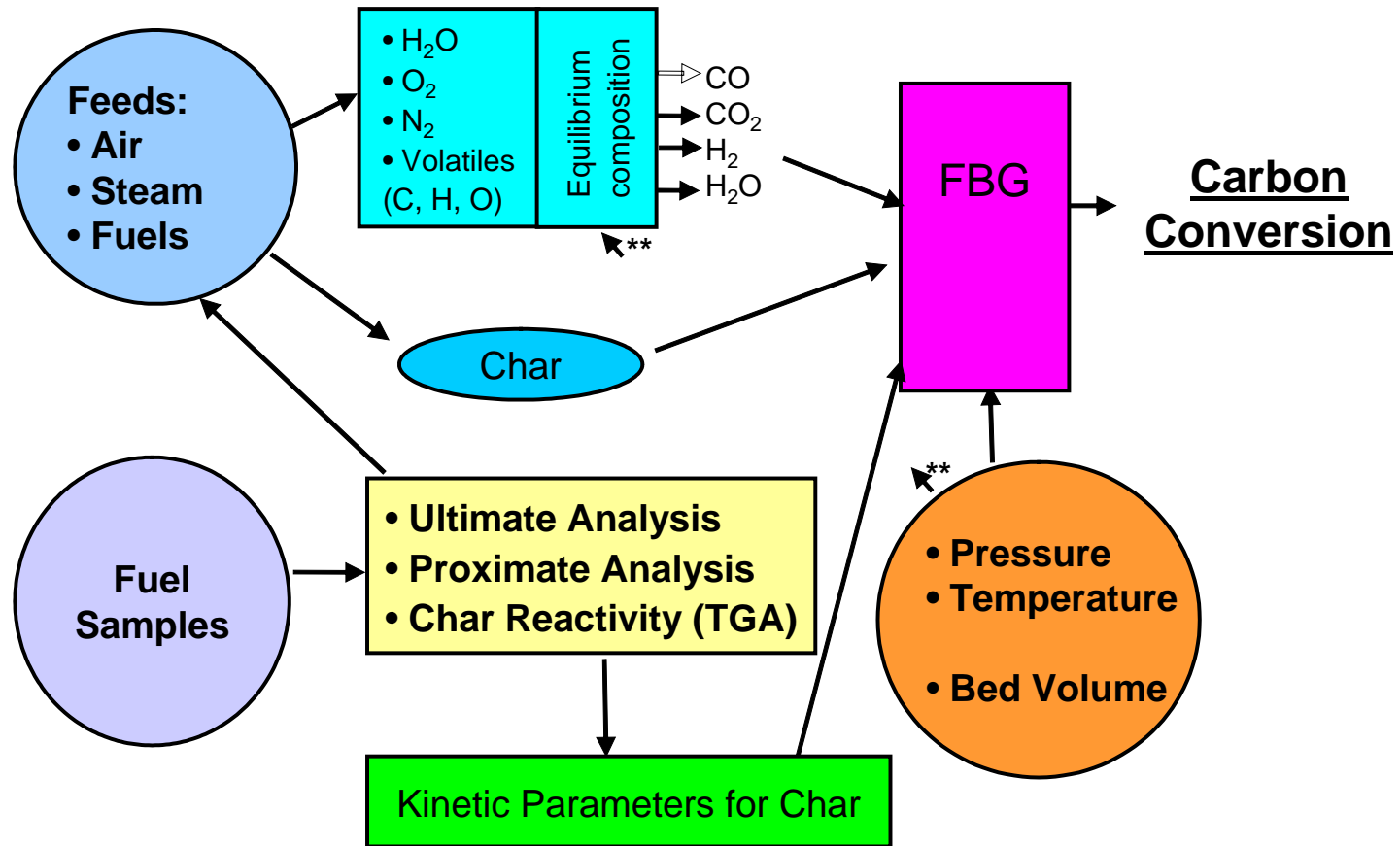
$$R_{C-H_2O} = \frac{k_{1f}\ P_{H2O}}{1 + \dfrac{k_{1f}}{k_3}P_{H2O} + \dfrac{k_{1b}}{k_3}P_{H2}}$$

$$R_{C-CO_2} = \frac{k_{1f}\ P_{CO2}}{1 + \dfrac{k_{1f}}{k_3}P_{CO2} + \dfrac{k_{1b}}{k_3}P_{CO}}$$

Carbon conversion predictor results

$$\tau_C = \frac{M_{Cbed}}{m_{Cf}}$$

(Konttinen et al., STCBC
Victoria, Canada, 2004)

BIOFUEL GASIFIER FEEDSTOCK REACTIVITY – EXPLAINING THE DIFFERENCES AND CREATING PREDICTION MODELS

There are several subprojects with different objectives:

a) Tests with thermogravimetric analyzer to generate the experimental data.
- Several biomass fuels with industrial interest will be selected
- Samples will be taken during testing from the original fuels and from their leftovers after testing.
- Also some tests will be interrupted to take samples from partly reacted materials

b) SEM analysis and chemical fractionation of the samples taken in subproject a)

c) Determination of kinetic parameters

d) The addition of kinetic parameters as parts of the Carbon Conversion Predictor. Modeling efforts with the predictor to simulate the behavior of the fuels in a large-scale fluidized bed gasifier

e) Gasification experiments (2-4 h) with 3 selected fuels in a bench-scale gasifier. The comparison of results with the lab-scale results and with the prections of the Carbon Conversion Predictor.

Ash related problems

- Ash-related problems including sintering, agglomeration, deposition, erosion and corrosion are the main obstacles to economical and viable applications of biomass gasification technologies.

- Alkali metals, such as potassium, react readily with silica, even at temperatures far below 900 ^oC, by breaking the Si–O–Si bond and forming silicates or reacting with sulfur to produce alkali sulfates.

- The alkali silicates and sulfates have melting points even lower than 700 1C and tend to deposit on the reactor walls and leave a sticky deposit on

- the surface of the bed particles, causing bed sintering and defluidization.

- The presence of ash such as alkali in syngas can cause problems of deposition, corrosion and erosion for equipment that utilizes syngas such as a gas turbine.

Wang, Lijun ; Weller, Curtis L. ; Jones, David D. and Hanna, Milford A., 2008, Contemporary issues in thermal gasification of biomass and its application to electricity and fuel production. Biomass and bioenergy, Vol. 32, No. 8, November 2008, pp. 573 – 581.

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Syngas cleaning and processing

Contaminant	Examples	Problems	Cleanup method
Particulates	Ash, char, bed material	Erosion, plugging	Filtering, scrubbing
Alkali metals	Sodium (Na) and potassium (K) compounds	Hot corrosion, catalyst poisons	Cooling, absorbtion, condensation, filtering
Heavy metals and trace elements	Mercury (Hg), Arsenic (As), Cadmium (Cd), Lead (Pb), Tellurium (Te),…	Catalyst poisons	Condensation, filtering, guard beds, scrubbing ("ultra-cleaning")
Fuel-bound nitrogen	Mainly NH_3 and HCN	NO_x formation in gas combustion	Scrubbing, selective catalytic reduction
Tars	Reactive aromatics	Filter plugging, internal condensation and deposition	Tar cracking/reforming, scrubbing
Sulphur, chlorine	HCl and H_2S (and some COS)	Catalyst poisons, corrosion, gaseous sulphur emissions	Limestone or dolomite, zinc-based guard beds, scrubbing, absorption

Modified from the source: Bridgwater, A. et al.: An Assessment of the Possibilities for Transfer of European Biomass Gasification Technology to China. Part 1. Report of Mission to China. 1998, 65 p.

Hot ash removal and gas cleaning

- Ash can be removed by cyclones, bag filters, baffle filters, ceramic filters, fabric filters, rotating particle separators, wet electrostatic precipitators and water scrubbers.

- Water scrubbing and wet electrostatic precipitation are unattractive due to their economics and the environmental pollution of residue water.

- Most mechanical methods; fabric filters, rotating particle separators and water scrubbers, can operate only at low temperatures (i.e., <200 °C).

- Hot gas cleaning improves energy efficiency

- Char and other particles in hot syngas can be removed using ceramic filters, which can be operated up to a temperature of 600 °C.

- However, ceramic filters are used mainly for particle removal from high-pressure gas because the pressure drop through ceramic filters is high.

Wang, Lijun ; Weller, Curtis L. ; Jones, David D. and Hanna, Milford A., 2008, Contemporary issues in thermal gasification of biomass and its application to electricity and fuel production. Biomass and bioenergy, Vol. 32, No. 8, November 2008, pp. 573 – 581.

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FORMATION OF TARS - EXAMPLES OF RESULTS

Typical ranges of producer gas composition for selected gasifiers

		Low temperature atm. steam blown dual fluidized bed gasifier [1]	Low temperature press. oxygen blown fluidized bed gasifier[2]	High temperature press. oxygen blown entrained flow gasifier[3]
H_2	%	35 - 40	23 - 28	29 - 35
CO	%	25 - 30	16 - 19	35 - 44
CO_2	%	20 - 25	33 - 38	17 - 22
CH_4	%	9 - 11	10 - 13	<1
N_2	%	<1	<5	<5

Biomass tar formation temperature

	Range (°C)	Products	
Primary	400 – 600	Acids, phenols, ketones, guaialcols, furans, furfurals	
Secondary	600 – 800	Phenols, heterocyclic ethers monoaromatic hydrocarbons	
Tertiary	800 - 1000	Non-substituted polyaromatic hydrocarbons	

Brown, David ; Gassner, Martin ; Fuchino, Tetsuo and Maréchal, François, 2009, Thermo-economic analysis for the optimal conceptual design of biomass gasification energy conversion systems.
Applied Thermal Engineering, Vol. 29, No. 11-12, August 2009, pp 2137 - 2152.

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Elimination of tars from gasification gas

- Tars are formed in the thermochemical processing of fuel, due to incomplete conversion of fuel carbon and hydrogen

- If not reduced, tars can go downstream the gasification/syngas processing line and condense → blockages of valves, filters or catalysts

- Tars can be reduced using catalytic metal oxide materials, via the hydrocarbon reforming reaction:

$$C_nH_{2n+2} + nH_2O \rightarrow nCO + (2n+1)H_2$$

Product gas from the gasifier → **REFORMER** → Treated product gas

Steam   Air / oxygen   Heat
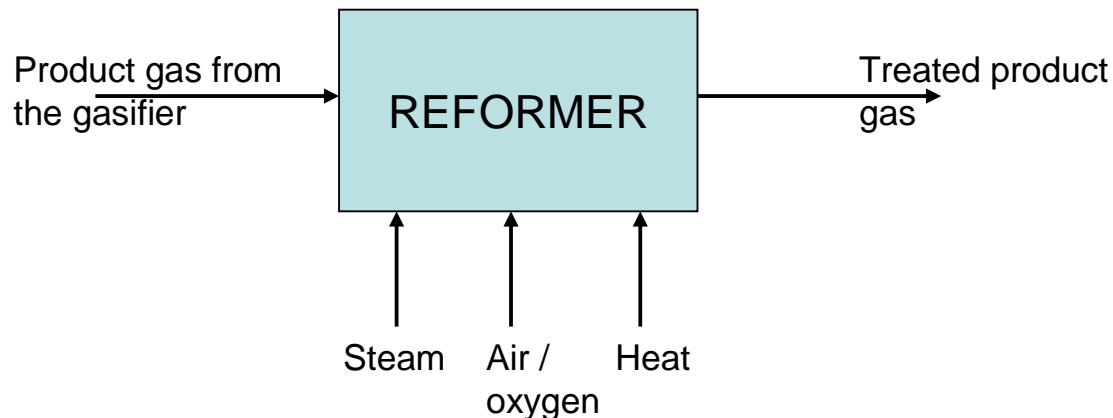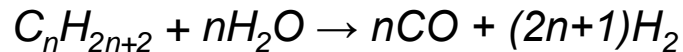
Tar removal processes

- Air or steam can be used to reduce tar
- High temperature reduces tar
- Filtering with ceramic filters
- Scubbing with water or solvents
- Packed bed filtering
- Thermal cracking (>1000 °C)
- Catalytic conversion

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FORMATION OF HEAVY METALS -
EXAMPLES OF RESULTS

Sources:

-Konttinen, J.; Backman, R.; Hupa, M.; Moilanen, and Kurkela E.: Trace element behaviour in the fluidized bed gasification of solid recovered fuels A thermodynamic study. Åbo Akademi University, Process Chemistry Centre, Combustion and Materials Chemistry, Report 05-02, Åbo Akademi University, 2005. ISBN 952-12-1510-0.

-Konttinen et al. 19th International Conference on Fluidised Bed Combustion, Vienna, Austria, 2006

EU Council directive on incineration of waste containing fuels

Emission limits:

Cd +Tl total twice	0.05 mg/m³n (measurement a year)
Hg twice	0.05 mg/m³n (measurement a year)
Sb + As + Co + Cr + Cu Pb + Mn + Ni + V total twice	0.5 mg/m³n (measurement a year)

0.5 mg/m³n in flue gases ≈ 4.2 mg/kg dry fuel

Heavy metals in woody biomass

Trace element and heavy metal contents (mg/kg dry matter) of timber (heartwood) collected from various parts of Finland, compared with the contents in whole wood.

Element	Timberwood City of				Wood (Phyllis 2000)		
	Iisalmi	Riihimäki	Tornio	Harjavalta	Min	Max	Average
Cl	20	10	10	20	10	11890	590
Hg	< 0.1	< 0.1	< 0.1	< 0.1	0	2	0.1
Cd	<0.05	0.07	0.17	0.12	0	3	0.7
Sb	< 2	< 2	< 2	< 2	0	4	0.8
As	< 1	< 1	< 1	< 1	0	6.8	1.4
Co	< 4	< 4	< 4	< 3	0.1	6	1.9
Cr	< 4	< 4	< 4	< 3	0.4	130	24
Cu	< 4	< 4	< 4	< 3	0.3	400	22
Pb	< 1	< 1	< 1	< 1	0.2	340	30
Mn	102	54	97	55	7.9	840	181
Ni	< 4	< 4	< 4	< 3	0.4	540	29
Zn	8,9	7.0	11	9.6	2.2	130	50
Tl	< 2	< 2	< 2	< 1	-	-	-
Sn	< 2	< 2	< 2	< 1	0.3	10	1.7
V	< 4	< 4	< 4	< 3	0.2	23	4.3
Fe	66	9	270	437	6	3600	227

Source: Moilanen, A., Academic Dissertation, Åbo Akademi University, 2006

Heavy metals in solid recovered fuel (SRF)

Elemental analysis and fuel characteristics of SRFs produced in plants ET, F and Ew from source separated wastes from the cities of Jyväskylä, Pietarsaari and Lahti. Dry and energy wastes are included for comparison (Juvonen & Moilanen 2002, Moilanen et al. 2005, LHV = Lower heating value, % = weight %, d = dry matter, ar = as received).

SRF/Waste	Cl	S	N	Na + K*	Metallic Al	Hg	Cd	Sb	As	Co	Cr	Cu	Pb	Mn	Ni	Zn	Tl	Sn	V	P	Fe	Moisture	Ash	LHV	C	H
				%, d								mg/kg, d										%, ar	%, d	MJ/kg, ar	%, d	
ET/Jyväskylä	0.63	0.16	0.7	0.43	0.18	0.23	2.5	54	29	370	77	1400	530	210	260	250	<5	140	18	880	11500	26.2	43.4	9.47	29.5	3.8
ET/Pietarsaari	1.04	0.12	0.9	0.47	0.58	0.11	5.0	18	4.0	20	65	650	220	120	82	440	<5	110	<6	940	2400	35.2	14.5	13.15	51.1	7.1
ET/Lahti	0.49	0.10	0.5	0.16	0.19	0.15	2.3	13	8.1	77	35	210	50	60	250	230	<5	12	<70	430	1400	15.7	8.6	18.73	54.0	7.4
F/Jyväskylä	0.76	0.10	0.5	0.38	0.63	0.6	1.3	19	5.6	2.0	120	192	80	103	21	937	<1	96	4	437	2227	23.0	9.7	16.68	52.3	7.2
F/Pietarsaari	0.82	0.08	0.6	0.37	0.87	0.29	0.43	25	3.7	1.6	67	451	287	71	5.0	180	<1	183	4	453	857	24.2	9.4	16.44	52.2	7.3
F/Lahti	0.34	0.06	0.4	0.17	0.16	0	0.33	19	3.0	1.1	16	153	250	27	4.0	88	<1	247	<4	187	873	11.8	7.3	19.92	53.7	7.4
Ew/Jyväskylä	1.04	0.24	0.5	0.40	0.84	0.31	9.4	48	5.9	3.9	96	987	150	113	14	377	<1	32	6	633	2900	2.2	12.8	21.49	51.6	7.1
Ew/Pietarsaari	0.96	0.13	0.5	0.35	0.83	0	1.6	16	5.5	4.2	70	753	62	88	20	683	<1	13	5	620	1363	2.7	9.4	22.45	53.8	7.6
Ew/Lahti	0.85	0.08	0.3	7.5	0.18	0.3	2.1	19	3.6	2.0	50	163	34	59	15	127	<1	12	5	280	2270	1.7	8.6	22.64	54.0	7.5
Waste from stores	1.04	0.06	0.3	0.21	0.07	<0.09	3.0	3.4	<4	0.8	48	60	18	15	<7	110	<1	43	<4	180	550	18.1	2.6	26.39	71.8	10.2
Dry waste from Jyväskylä	1.03	0.18	1.5	0.65	0.48	0.5	5.2	16	<4	3.0	340	32	54	37	5.7	240	<2	15	<6	460	840	31.5	7.6	15.24	56.7	7.4
Dry waste from Pietarsaari	1.04	0.12	0.9	0.47	0.58	0.11	5.0	na.	na.	na.	na.	na.	na.	na.	na.	na.	na.	na.	na.	na.	na.	35.2	14.5	13.15	51.1	7.1
Energy waste from Lahti	0.65	0.06	0.7	0.19	0.23	<0.1	5.3	<10	<10	5	20	30	20	25	<10	95	<1	10	<4	220	685	33.9	6.6	15.11	56.2	7.8

Source: Moilanen, A., Academic Dissertation, Åbo Akademi University, 2006

Gasifier and gas cooling equilibium modelling

Case A
Cooling   Filtering

CFB tai B/CFB gasifier

Fuel feed

Bed material feed

Air   Bottom ash   Ca(OH)$_2$ Fly ash/ filter ash

300... 500°C   Case B

Coal fired boiler District heating/ CHP-plant Industrial boiler

Case A: Gasifier reactor
Case B: Product gas cooling
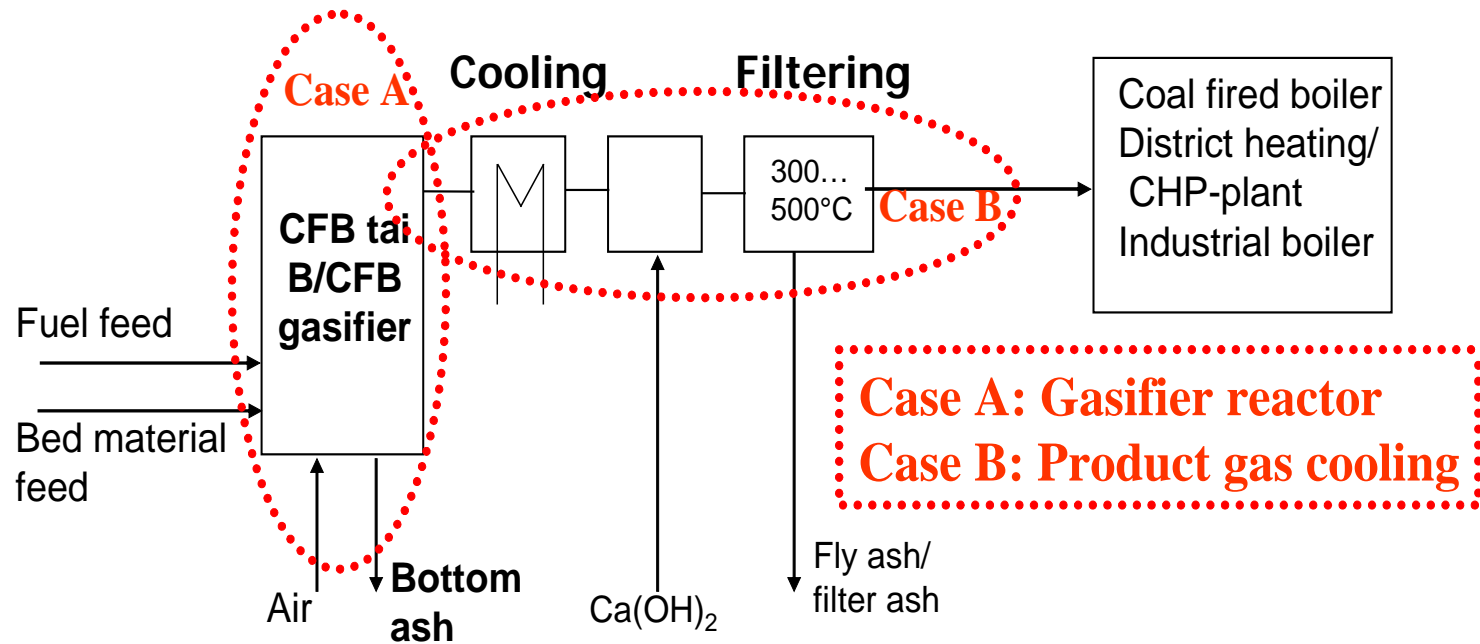
The ÅAU thermodynamic database "Basgas" for gasification conditions

oxidizing **and** reducing conditions

- **35 elements**
  - C, H, O, N *(inert)*, S, Cl, *Br**, F, P
  - Ca, Mg, K, Na, Al, Si, Fe............................main ash components
  - As, Cd, Cr, Cu, Co, Hg, Mn, Ni, Pb, Sb, *Tl**, V...................EDD
    Ba*, *Be**, Mo, *Se**, Sn, Ti, Zn......................other trace elements
    *Element not included in this calculation

- **200 heavy metal gaseous species**

- **250 heavy metal stoichiometric compounds**

- **17 solutions** incl. SiO_2 melt with
  - CaO, MgO, K_2O, Na_2O, Al_2O_3, Fe_2O_3
  + As_2O_3, Cr_2O_3, Cu_2O, MnO, NiO, PbO, ZnO, S, Cl

Source: Konttinen et al. 19th Int. Conf. on FBC, Vienna, Austria, 2006

Some of the stoichiometric heavy metal compounds

Cr5S6(s)	FeCr2O4(s)	NiS(s)	CuCl(s)	Ca3(AsO4)2(s)	CdCl2(s)	O3PbS(s)
Cr6S7(s)	(MnO)(Fe2O3)(s)	NiS2(s)	CuCl2(s)	Co3(AsO4)2(s)	Cd(OH)Cl(s)	PbSO4(s)
Cr2(SO4)3(s)	CoO(s)	Ni3S2(s)	CuFeO2(s)	Ni3(AsO4)2(s)	Cd3(AsO4)2(s)	PbOPbSO4(s)
Mn2SiO4(s)	Ni2SiO4(s)	CuFeS2(s)	MoS2(s)	Sb2O5(s)	Pb2S2(s)	HgS(s)
Mn2Al4Si5O18(s)	Ni2P2O7(s)	Cu5FeS4(s)	MoS3(s)	Sb2S3(s)	(PbO)2(PbSO4)(s)	HgSO4(s)
Mn3Al2Si3O12(s)	Ni3(PO4)2(s)	ZnO(s)	Mo2S3(s)	Sb2(SO4)3(s)	(PbO)3(PbSO4)(s)	Hg2SO4(s)
MnHPO4(s)	Ni3S4(s)	Zn(OH)2(s)	(FeO)(MoO3)(s)	SbCl3(s)	(PbO)4(PbSO4)(s)	Sn(s)
MnS(s)	Ni6S5(s)	ZnCO3(s)	CdO(s)	SbOCl(s)	PbCl2(s)	Sb(s)
MnS2(s)	NiSO4(s)	Na2O2Zn(s)	Cd(OH)2(s)	HgO(s)	PbClOH(s)	As(s)
MnSO4(s)	NiCl2(s)	ZnAl2O4(s)	CdCO3(s)	Hg2CO3(s)	Pb4(OH)6Cl2(s)	Cd(s)
MnCl2(s)	(NiO)(Cr2O3)(s)	Zn2SiO4(s)	(CdO)(Al2O3)(s)	HgCl2(s)	PbCl2(PbCO3)(s)	Pb(s)
Co3O4(s)	(NiO)(Fe2O3)(s)	ZnSO4(s)	(CdO)(SiO2)(s)	Hg2Cl2(s)	Ca2PbO4(s)	V(s)
Co(OH)2(s)	CuO(s)	ZnO(ZnSO4)2(s)	Cd3(PO4)2(s)	PbO(s)	PbCa2Si3O9(s)	Mn(s)
CoCO3(s)	Cu2O(s)	ZnCl2(s)	CdS(s)	PbO2(s)	Pb3Ca2Si3O11(s)	Co(s)
(CoO)2(SiO2)(s)	Cu(OH)2(s)	Ca2ZnSi2O7(s)	CdSO4(s)	Pb3O4(s)	Pb8CaSi6O21(s)	Ni(s)
CoS2(s)	CuCO3(s)	ZnFe2O4(s)	SnO(s)	Pb(OH)2(s)	Pb(MnO4)2(PbO)3(s)	Cu(s)
Co3S4(s)	CuP2(s)	As2O3(s)	SnO2(s)	PbCO3(s)	PbFe4O7(s)	Zn(s)
CoSO4(s)	Cu3P(s)	As2O5(s)	SnS(s)	(PbO)(PbCO3)(s)	PbFe10O16(s)	Mo(s)
CoCl2(s)	Cu2P2O7(s)	As2S2(s)	SnS2(s)	Na2O2Pb(s)	Pb2Fe2O5(s)	Cr(s)
CoCl2(H2O)2(s)	Cu3(PO4)2(s)	As2S3(s)	Sn2S3(s)	(PbO)(Al2O3)(s)	Pb2FeSi2O7(s)	Cr2S3(s)
CoCl2(H2O)6(s)	CuS(s)	Cu3(AsO4)2(s)	Sn3S4(s)	(PbO)(Al2O3)6(s)	Pb2Fe2Si2O9(s)	Cr3S4(s)
(CoO)(Cr2O3)(s)	Cu2S(s)	Zn3(AsO4)2(s)	SnSO4(s)	(PbO)2(Al2O3)(s)	Pb10Fe2Si2O17(s)	CrCl2(s)
(CoO)(Fe2O3)(s)	CuSO4(s)	MoO2(s)	Sn(SO4)2(s)	PbSiO3(s)	PbZnSiO4(s)	CrCl3(s)
NiO(s)	Cu2SO4(s)	MoO3(s)	SnCl2(s)	Pb2SiO4(s)	Pb2ZnSi2O7(s)	K2CrO4(s)
Ni(OH)2(s)	(CuO)(CuSO4)(s)	Mo(CO)6(s)	SbO2(s)	(PbO)4(SiO2)(s)	Pb8ZnSi6O21(s)	CaCr2O4(s)
NiCO3(s)	(CuO)(Fe2O3)(s)	(Na2O)(MoO3)(s)	Sb2O3(s)	PbHPO4(s)	(PbO)(MoO3)(s)	MnO(s)
(NiO)(Al2O3)(s)	(Cu2O)(Fe2O3)(s)	(MgO)(MoO3)(s)	Sb2O4(s)	PbS(s)	Hg(liq)	MnO2(s)
Ti(s)	TiAl(s)	V4O7(s)	VCl3(s)	VS(s)	Cr5O12(s)	Mn2O3(s)
TiH2(s)	TiAl3(s)	(Na2O)(V2O5)(s)	(CaO)(V2O5)(s)	VS4(s)	Cr8O21(s)	VCl2(s)
TiC(s)	VO(s)	(Na2O)2(V2O5)(s)	(CaO)2(V2O5)(s)	V2S3(s)	Cr(CO)6(s)	MnSiO3(s)
TiO(s)	VO2(s)	(Na2O)3(V2O5)(s)	(CaO)3(V2O5)(s)	CrO2(s)	Na2CrO4(s)	V2O5(s)
TiO2(s)	VO2(s2)	(MgO)(V2O5)(s)	Mn3O4(s)	CrO3(s)	(Na2O)(Cr2O3)(s)	
Ti2O3(s)	V2O3(s)	(MgO)2(V2O5)(s)	MnCO3(s)	Cr2O3(s)	(MgO)(Cr2O3)(s)	
V3O5(s)	V2O4(s)	VOSO4(s)	Al2MnO4(s)	Cr3O4(s)	CrS(s)	

Measured cases (VTT) for comparison

	CFB 1997/38A	CFB 2000/38A2	BFB 2002/10B	BFB 2002/10C2
Fuels	wood waste	REF pellets wood pellets	REF	REF
Bed	limestone	sand limestone	sand limestone	sand limestone
Sorbent	no	$Ca(OH)_2$	no	$Ca(OH)_2$
T_{bed} [°C]	940	890	840	850
P [bar]	1.1	1.1	1.1	1.1
λ	0.34	0.25	0.40	0.40

Source: Konttinen et al. 19th Int. Conf. on FBC, Vienna, Austria, 2006

Summary of heavy metal species

Vaporization degree of different inorganic elements as function temperature at cooling and cleaning section conditions of waste fuel gasification (Modelling results of CASE B conditions). (Konttinen et al., 2005).

Temperature of the gasification gas
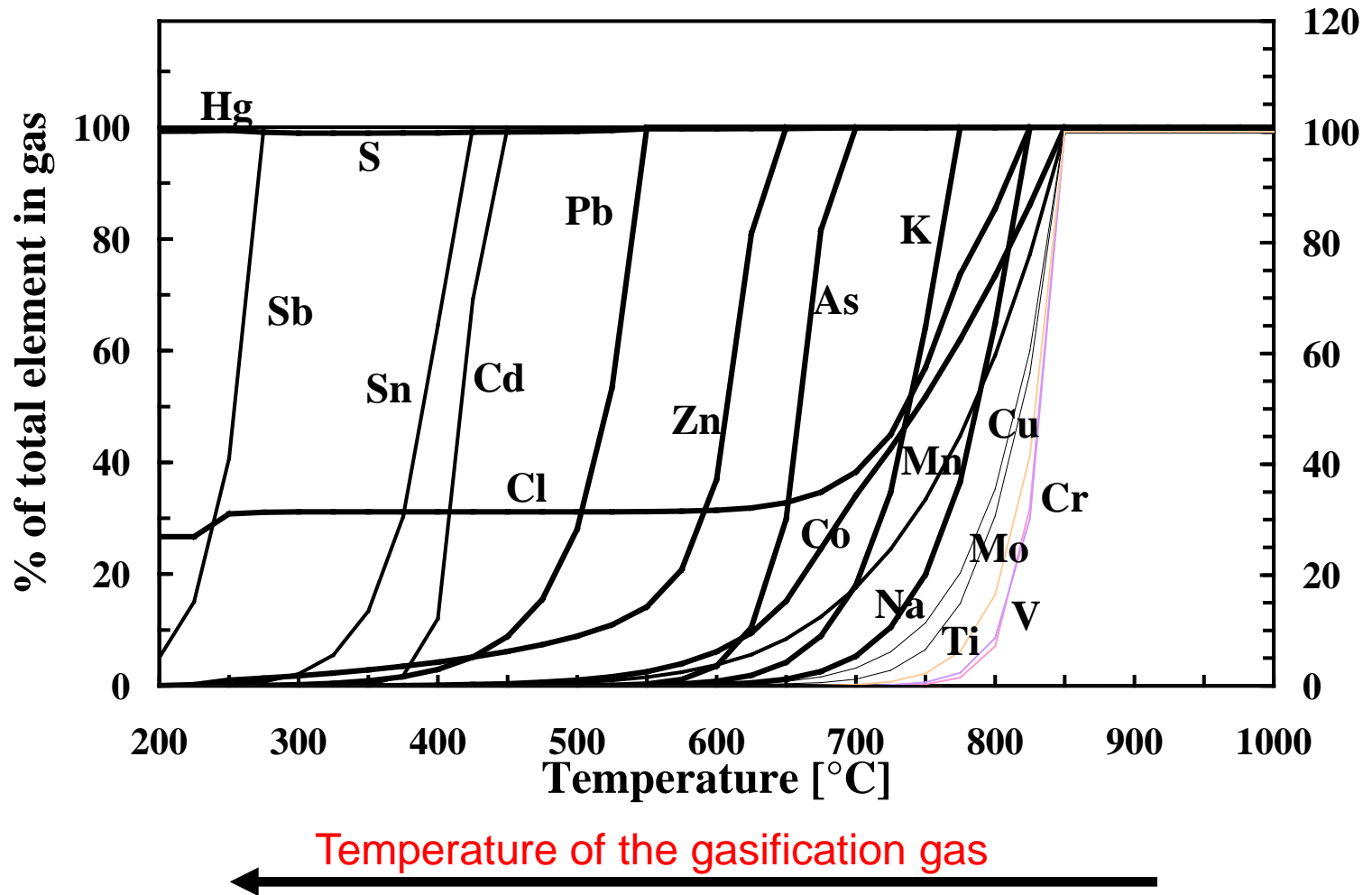
Comparison with pilot-scale data
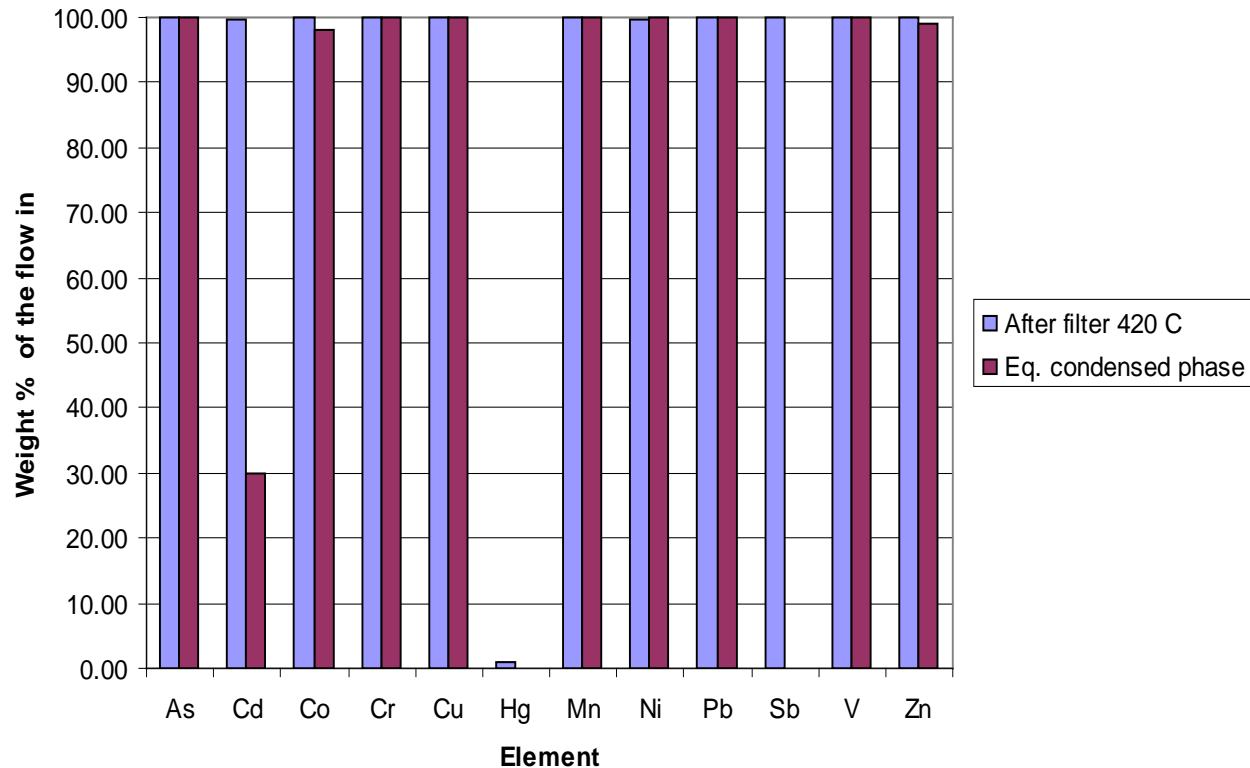
Weight percentages of condensed metals (EDD-elements and zinc) after cooled product gas (420˚C) conditions of the pilot plant balance BFB2002/10C2. Comparison between filter ash contents and equilibrium calculation result (Case B)

# Sulfur removal from gasification gas

- Fuel sulfur forms mainly gaseous H_2S and some traces of COS and CS_2

- Solid sorbent materials can be added in fluidized-bed gasification
  - Calcium-based sorbents (limestone, dolomite) can be used, but their sulfur removal efficiency (thermodynamic properties) are not good for biomass applications

- More effective metal oxide sorbents have been developed (Fe, Zn, Ni, Cu,…)

- Regenerable sulfur removal processes
  - The once sulfided sorbent can be oxidised to release sulfur as SO_2 in a separate reactor
  - Durability of sorbent materials in continuous cycling is still a challenge

- For advanced gasification applications (fuel cells, catalytic synthesis processes) a separate sulfur guard ultra-cleaning step is required

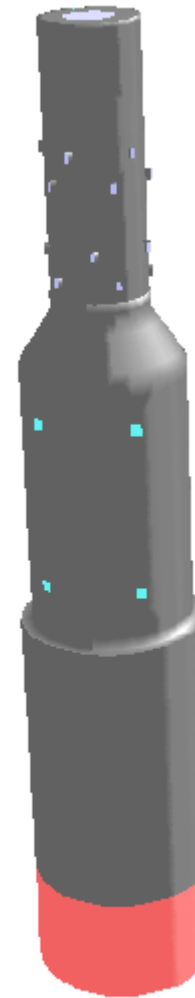# Elimination of nitrogen species from gasification gas

- Fuel nitrogen forms mainly gaseous NH_3 and some traces of HCN
  - Conversion of fuel-N to NH3 and HCN can be as high as 90 %
  - Some biomass fuels relatively rich in nitrogen (agro biomasses, such as alfalfa)

- If not reduced, and the gasification product gas is combusted, will form considerable amounts of nitrogen oxides NO_x
  - NOx emissions can be reduced with staged combustion
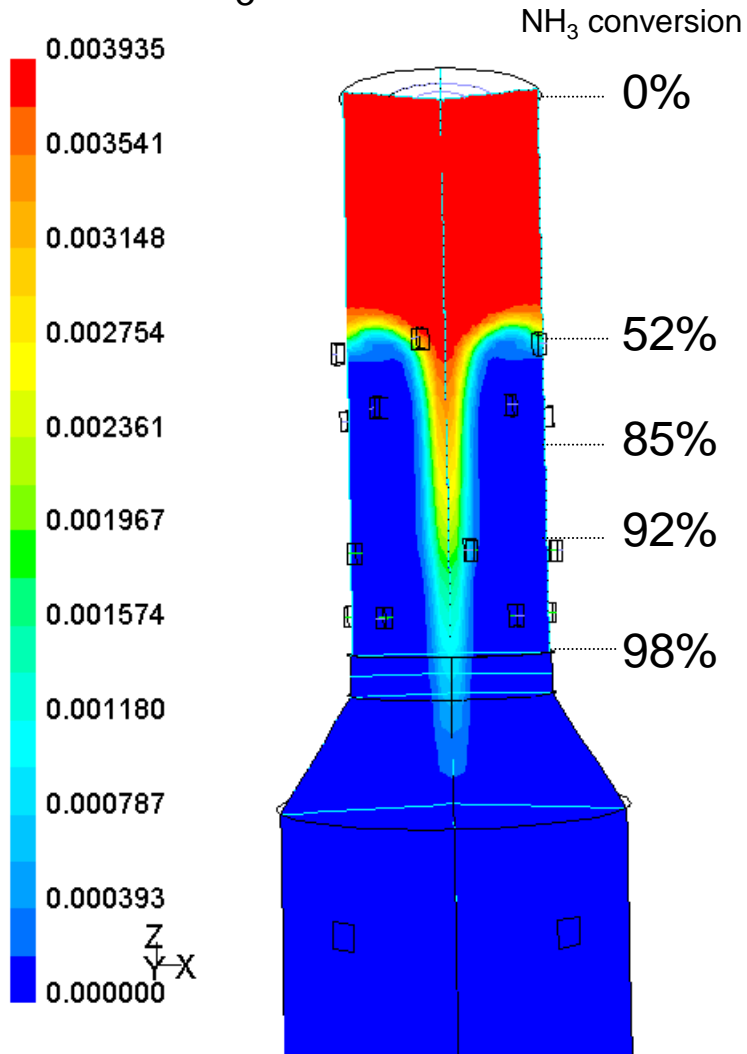
Gasifier gas combustor
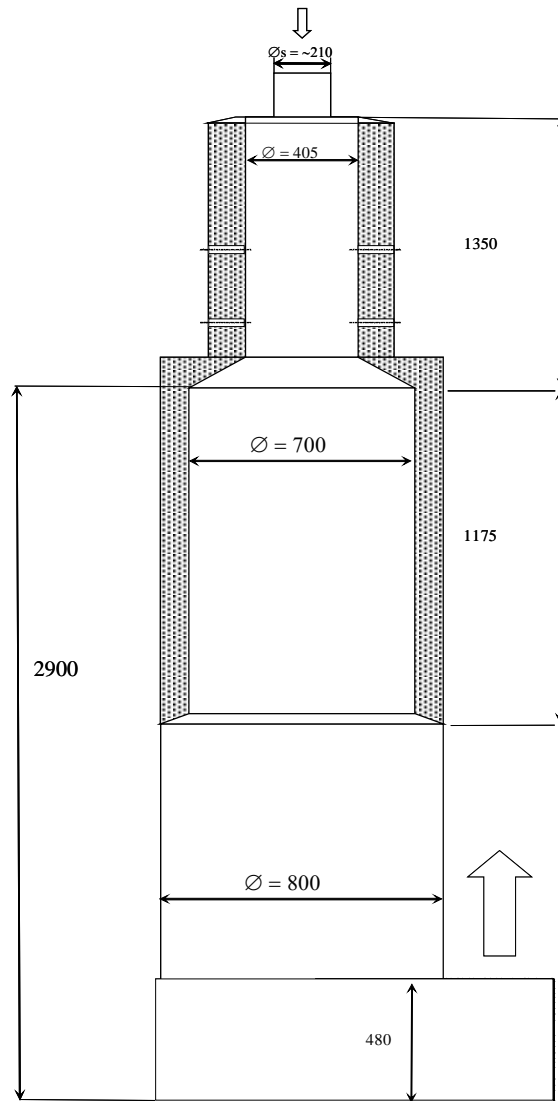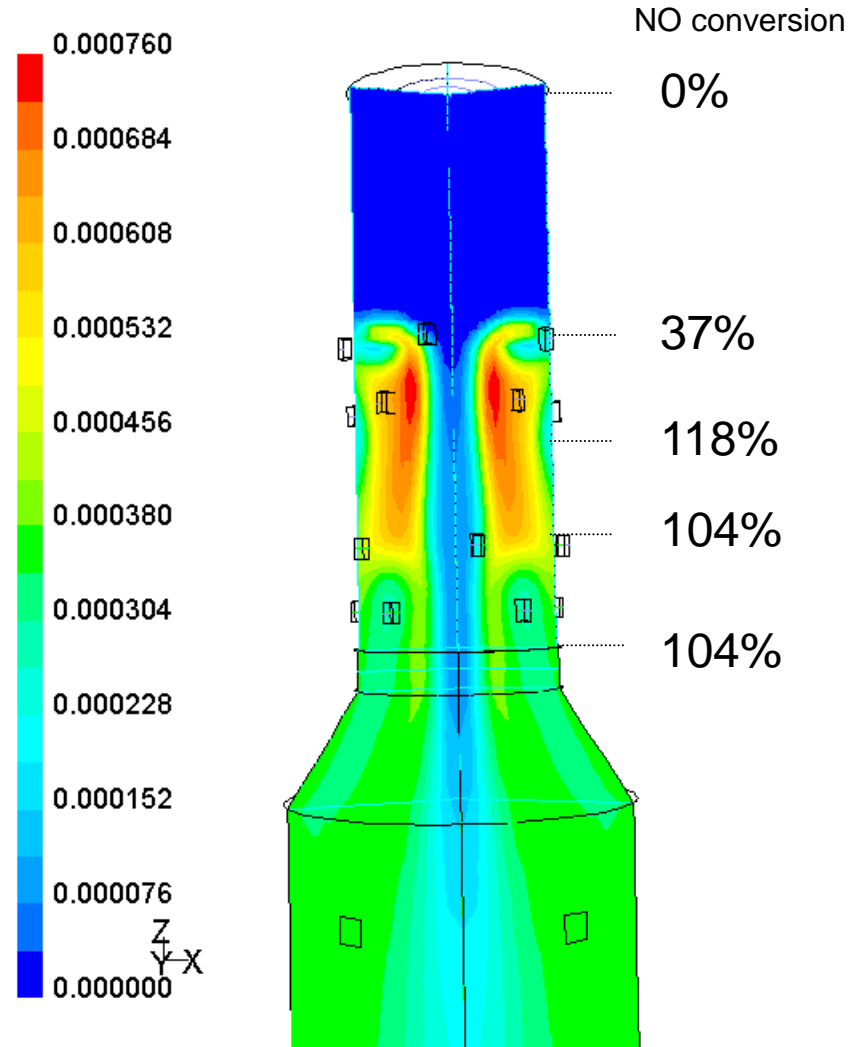

Schematic drawing

CFD representation

Brink et al.
Åbo Akademi 2004

Nitrogen chemistry in combustion

Coda Zabetta et al.
Åbo Akademi 2000

Results

NH₃ mole fraction

NH₃ conversion

- 0%
- 52%
- 85%
- 92%
- 98%

NO mole fraction

NO conversion

- 0%
- 37%
- 118%
- 104%
- 104%

Brink et al.
Åbo Akademi 2004

Results

Measurements			Calculations		
O_2 vol-%	NO_x ppm$_v$	Nf > NO yield %	O_2 vol-%	NO ppm$_v$	Nf > NO yield %
4.8	362	21	4.5	406	22
2.2	343	18	2.1	399	19

Brink et al.
Åbo Akademi 2004

Future challenges, gasification, CHECKLIST

- **Gasification**
  - "difficult" fuels (agro biomasses: ash melting/bed material sintering)
  - Formation mechanisms of impurities, such as: Waste-type fuels → heavy metals
  - Conversion of unconverted char
  - Elevated pressures, oxygen gasification of solid fuels

  Biomass combustion processes have the same challenges, but gasification can offer ways to get rid of the problems easier (for example metals can be separated by filtration before the processing of product gas to end products)

- **Gas cleaning**
  - Fly ash
  - Tar formation and cracking (catalysts)
  - Waste-type biomasses and wastes → heavy metals and halogenes
  - Fuel-N to NH_3 – staged combustion is required
  - **BIGGEST CHALLENGE: Ultra-cleaning required for advanced applications (IGCC, fuel cells, catalytic synthesis processes)**

- **Process integration/optimization**
  - Long-term availability needs to be proven
  - Operation as a stand-alone plant, fuel availability
  - Integration in a pulp mill
  - High pressure operation (treatment of solids) and materials

- **Economics**
  - Price of electricity, price of heat (steam)
  - Price of liquid biofuels produced

One (wild) idea?!

Nuclear power → electricity → H_2O separation → $H_2 + 0.5\ O_2$

→ O_2 to gasification → syngas production ($CO + H_2$)

→ H_2 and syngas combined ($H_2/CO = 2$)→ producing liquid biofuels

-Advantages (According to Idaho National Laboratory, USA, 2009)
- 2.5 times more liquid biofuels yield than with gasification alone
- replacing fossil raw oil TOTALLY in producing liquid transport fuels!?