Business from technology

Fluidised-bed gasification R&D at VTT to support industrial development of BTL, SNG or bio-H2

IEA Task 33 Meeting - 18.10.2011 Piteå
Workshop: Biomass gasification opportunities in the forest industry

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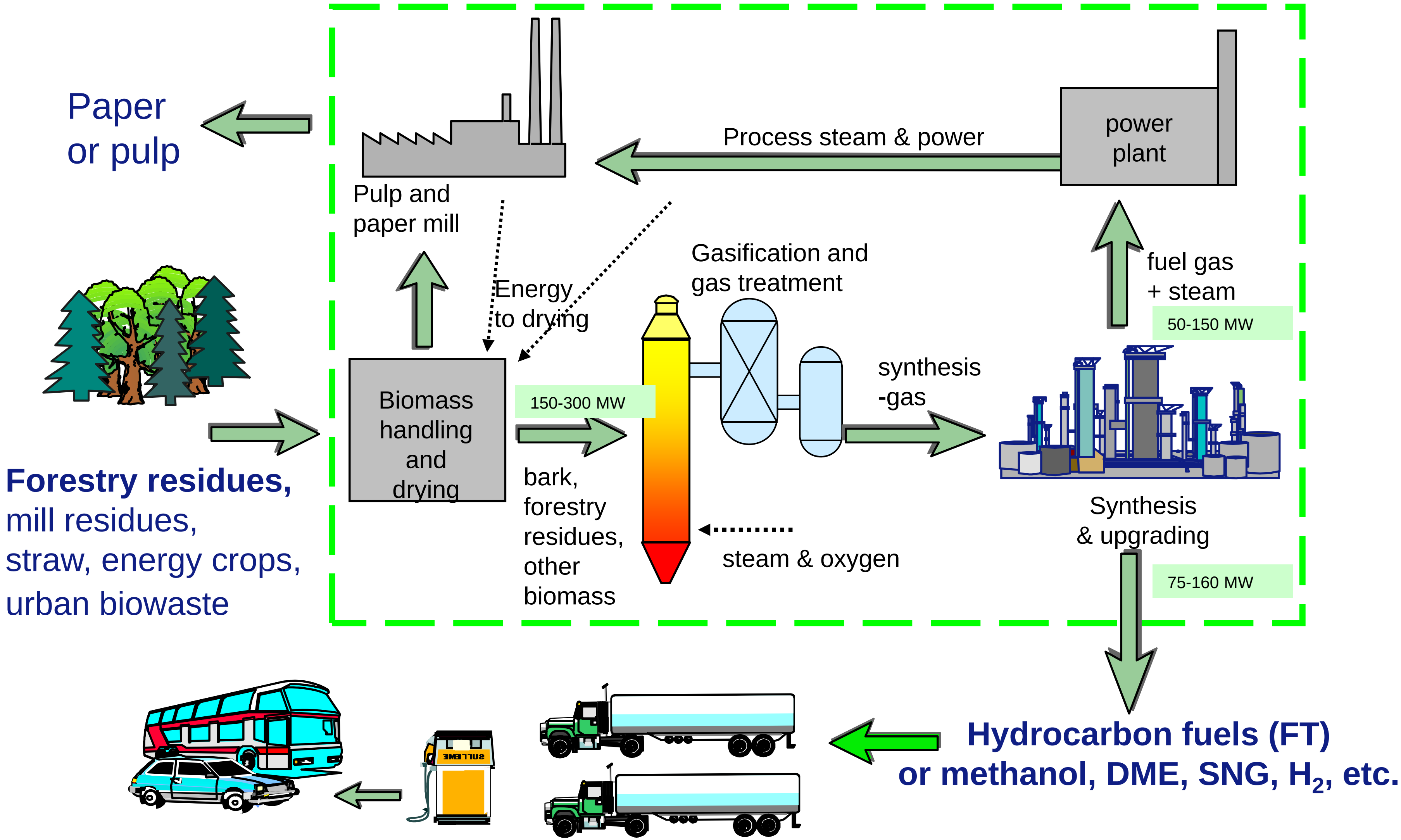
Syngas Route to Biofuels – Integrated Concept Studied at VTT's UCG-project in 2004-07

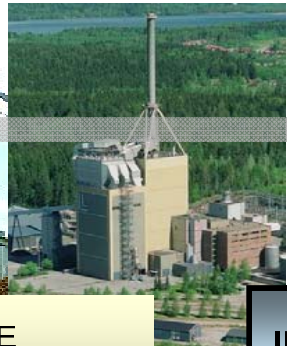


SYNTHESIS GAS FROM BIOMASS

FROM R&D TO INDUSTRIAL SUCCESS

(road map generated in VTT:s UCG project in 2006)

PEAT
AMMONIA
PLANT
OULU/FINLAND



BIOMASS/WASTE
GASIFICATION FOR POWER
(LAHTI, CORENSO,
VÄRNAMO)

INDUSTRIAL R&D & DEMONSTRATION
- REPLACEMENT OF OIL
- START-UP IN 2009

BIOREFINERIES AT PULP AND PAPER MILLS AND AT LARGE CHP PLANTS
- FUEL PRODUCTION: 70-150 000 tons/plants
- BY-PRODUCT HEAT FOR PROCESS STEAM OR DISTRICT HEATING
- HIGH OVERALL EFFICIENCY

FIRST SYNFUEL PRODUCTION PLANT
- 200-250 MW FEED CAPACITY
- 105 000 tons/a DIESEL FUEL
- 2-3 % FINNISH TRANSPORT FUEL
- START-UP IN 2012-14

NEW APPLICATIONS
- FUEL CELLS, 2nd GEN. IGCC
- HYDROGEN OR METHANE
- RENEWABLE CHEMICALS

1985	1995	2000	2005	2010	2015	2020	2025	2030

SYNTHESIS GAS
R&D IN EUROPE
AND USA IN 1980's

R & D ON HOT
FILTRATION AND
CATALYTIC
GAS CLEANING

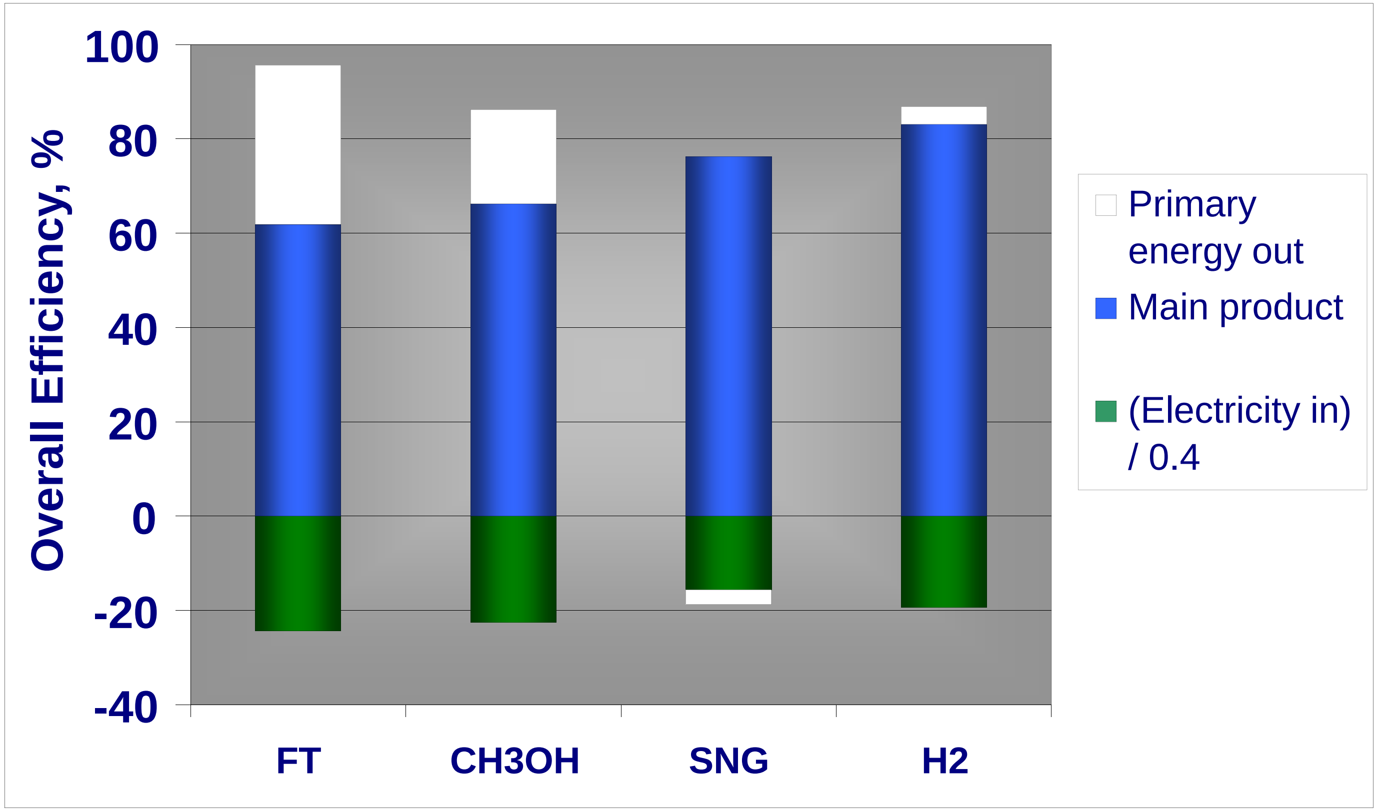
VTT-UCG
OPTIMISED
SYNGAS R&D
& PDU-SCALE
TESTING

FURTHER R&D
- PROCESS OPTIMISATION
- WASTE GASIFICATION
- HYDROGEN TECHNOLOGIES

Efficiencies with Industrial-Heat Production

Efficiency = 100 x [LHV-energy of main product + high-grade byproduct energy – {electricity / 0.4}] / [LHV-energy of as-received feedstock]

Previous studies carried out in VTT's UCG project in 2004-07



Feedstock drying: from 50 % moisture to 30 % with secondary heat; from 30 % to 15 % with by-product steam

From: McKeough & Kurkela, NWBC, Stockholm 2008.

Gasification and Gas Cleaning Process

- Developed and tested at VTT on 1 MW scale

NEW INNOVATIVE TECHNOLOGY

FUEL-FLEXIBLE FLUID-BED GASIFICATION
- STEAM/OXYGEN
- PRESSURISED

→

GAS CLEANING
- TAR & METHANE REFORMING
- FILTRATION
- DIRTY SHIFT

→

ULTRA CLEANUP

→

FT-DIESEL
CH_3OH

HYDROGEN
SNG

GASOLINE
JET FUEL

Typical pressures: 1 - 10 bar | 20 - 30 bar | 20 - 200 bar

GASIFIER TARGETS
- NO ASH-RELATED PROBLEMS
- SIMPLE DESIGN AND HIGH RELIABILITY
- HIGH C-CONVERSION TO GAS+TARS
- LOW OXYGEN CONSUMPTION

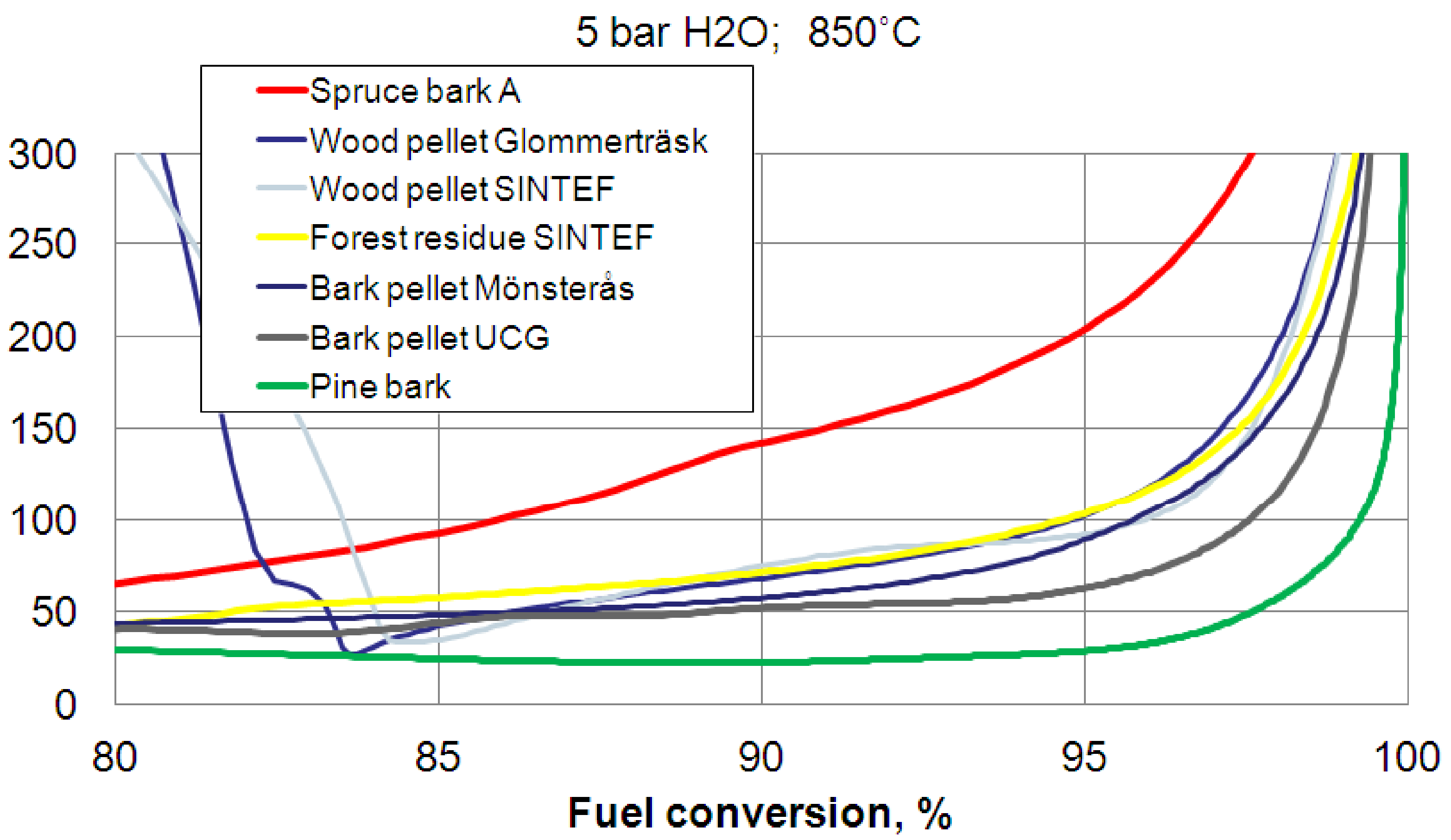
GAS CLEANING TARGETS
- COMPLETE TAR DECOMPOSITION
- 60-80% METHANE REFORMING
- H_2/CO RATIO SUITABLE TO FT-SYNTHESIS

Biomass-to-Syngas projects at VTT in 2011

- **NEXTUCG: 2007 – 2011**
  - Industrial project funded by NSE Biofuels (Neste Oil ja Stora Enso), co-operation also with Foster Wheeler
  - Resulted in NER300 proposal – large FT-production unit
- **NORDSYNGAS: 2010-14**
  - Nordic co-operation: Luleå, Piteå, Sinteff, VTT
  - Fundamental aspects of pressurised gasification
  - System studies related to integrated plants to pulp and paper industries
- **GASIFICATION REACTIVITY 2011 – 2014**
  - Fundamental research with Åbo Akademi and Jyväskylä Univ.
  - Funded by Finnish Akademi
- **US-CO-OPERATION PROJECT ON EVALUATION OF GASIFICATION-BASED SYSTEMS 2011-12**
  - Ilkka Hannula as visiting scientist at Princeton University
  - Co-utilisation of biomass and coal for liquids and electricity and combinations of biotechnical and thermochemical routes
  - Evaluation of US development projects
  - Aspen modelling of selected concepts and technologies
- **PRODUCTION OF SNG OR H_2 FROM BIOMASS 2011 - 2014**
  - Evaluation of process alternatives – less capital intensive and suitable to smaller size that BtL plants
  - Pre-competitive R&D on gasification and gas cleaning

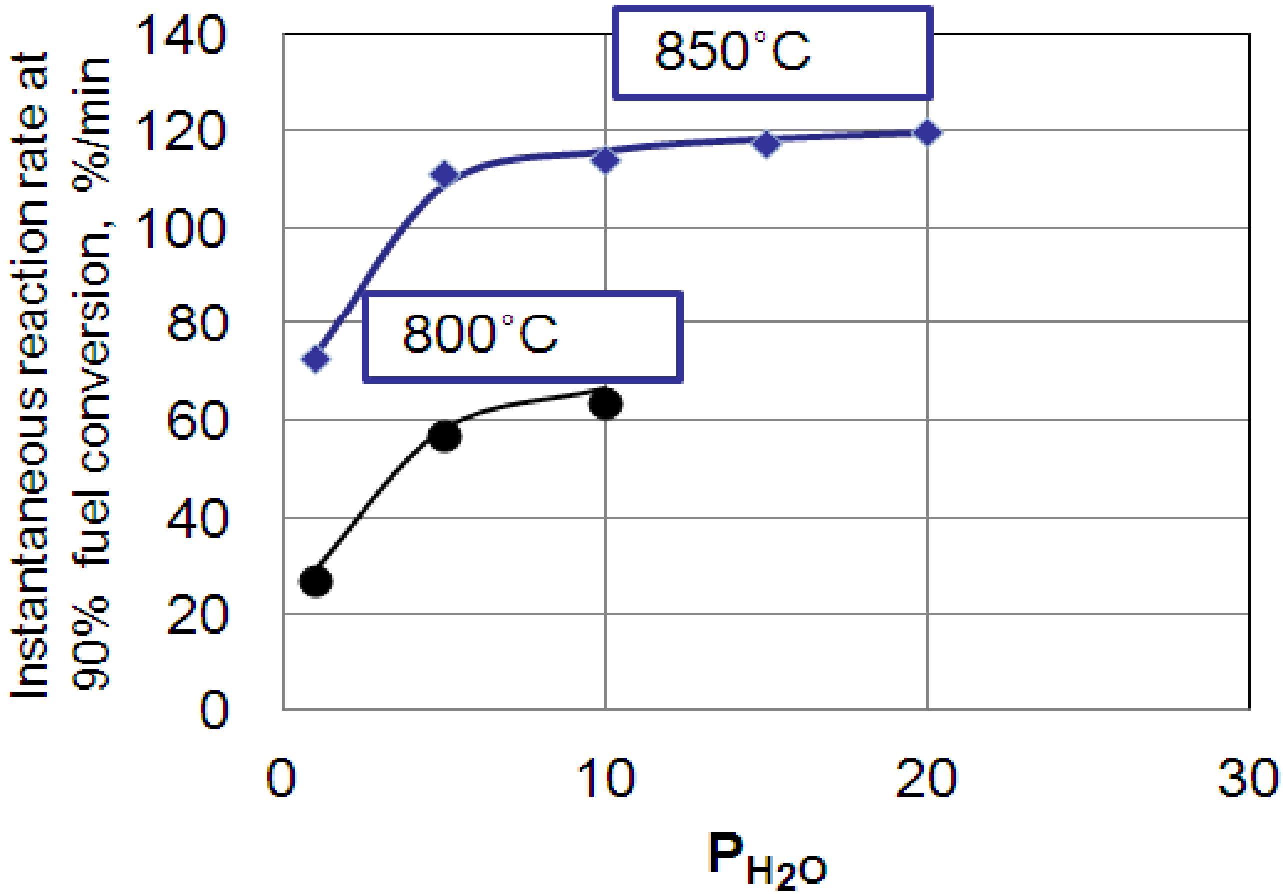
Biomass comparison

Instantenous reaction rate, %/min



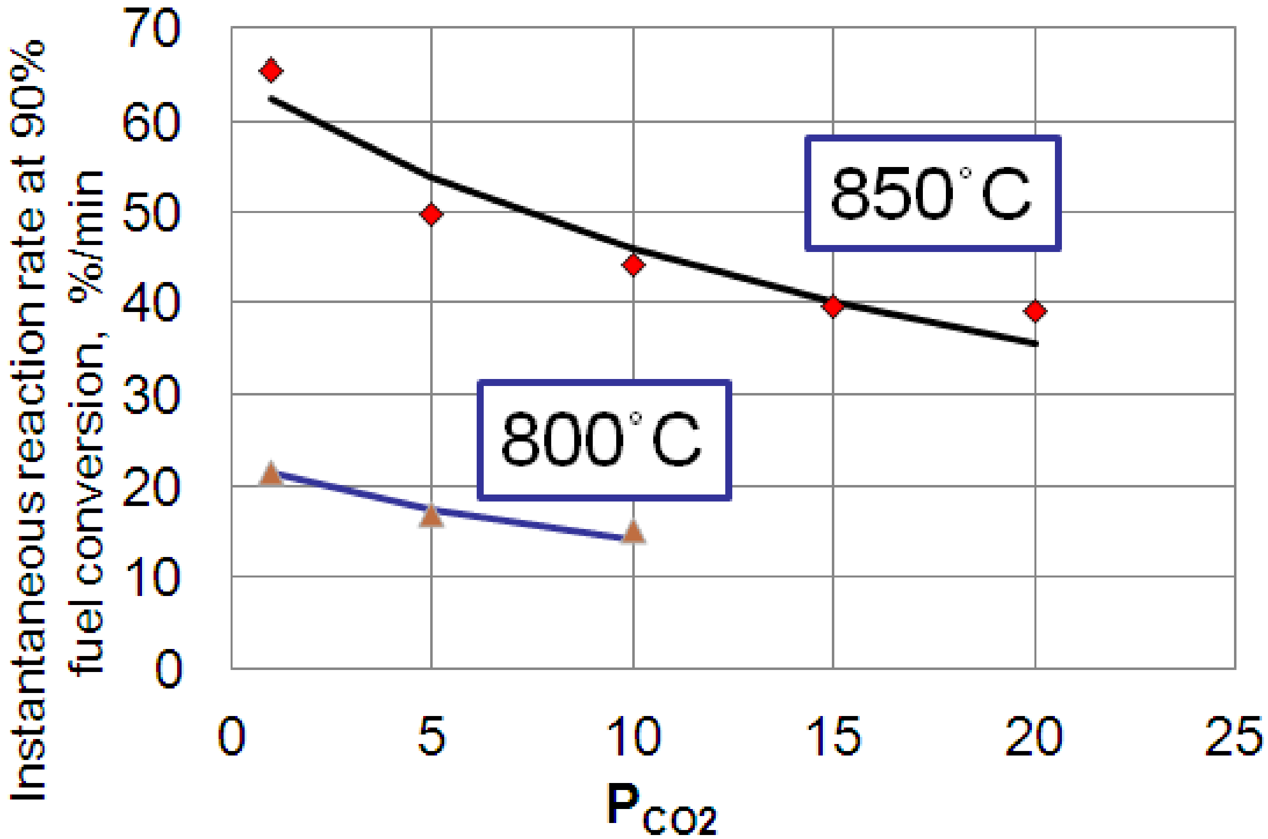
Preliminary results from NORDSYNGAS
Moilanen A. & Kurkela M, 2011

Reaction rate *vs.* steam pressure
Spruce bark



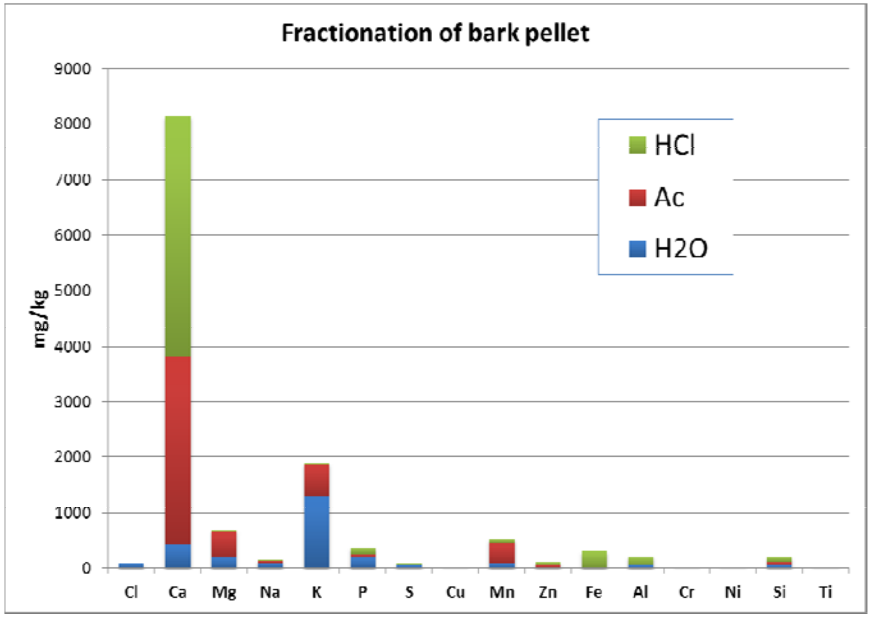
Preliminary results from NORDSYNGAS
Moilanen A.,2011

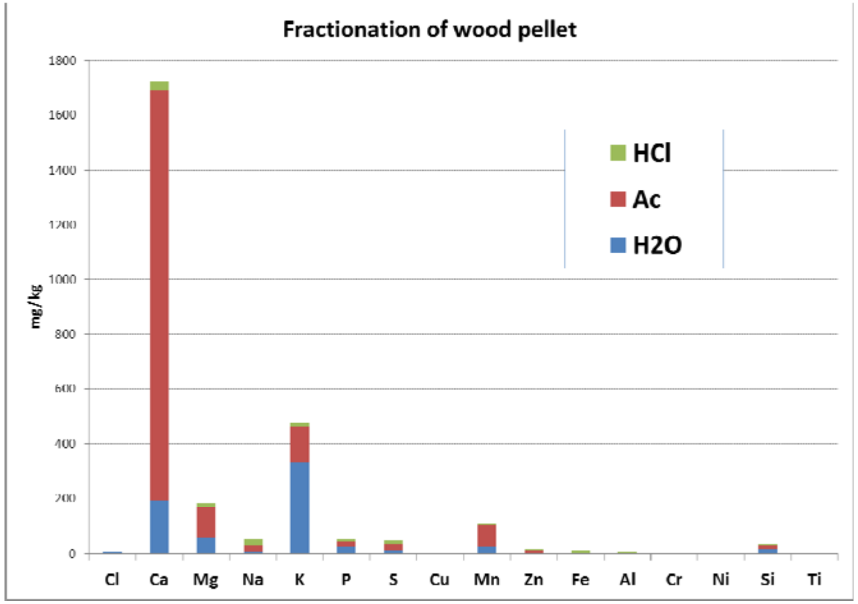
Reaction rate vs. CO_2 pressure Spruce bark

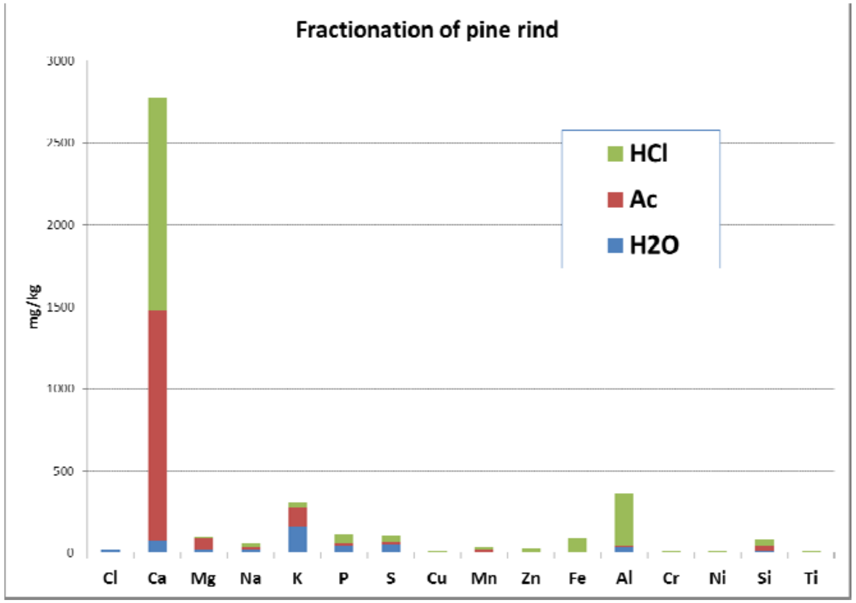


Preliminary results from NORDSYNGAS
Moilanen A.,2011

Chemical fractionation







Preliminary results from NORDSYNGAS
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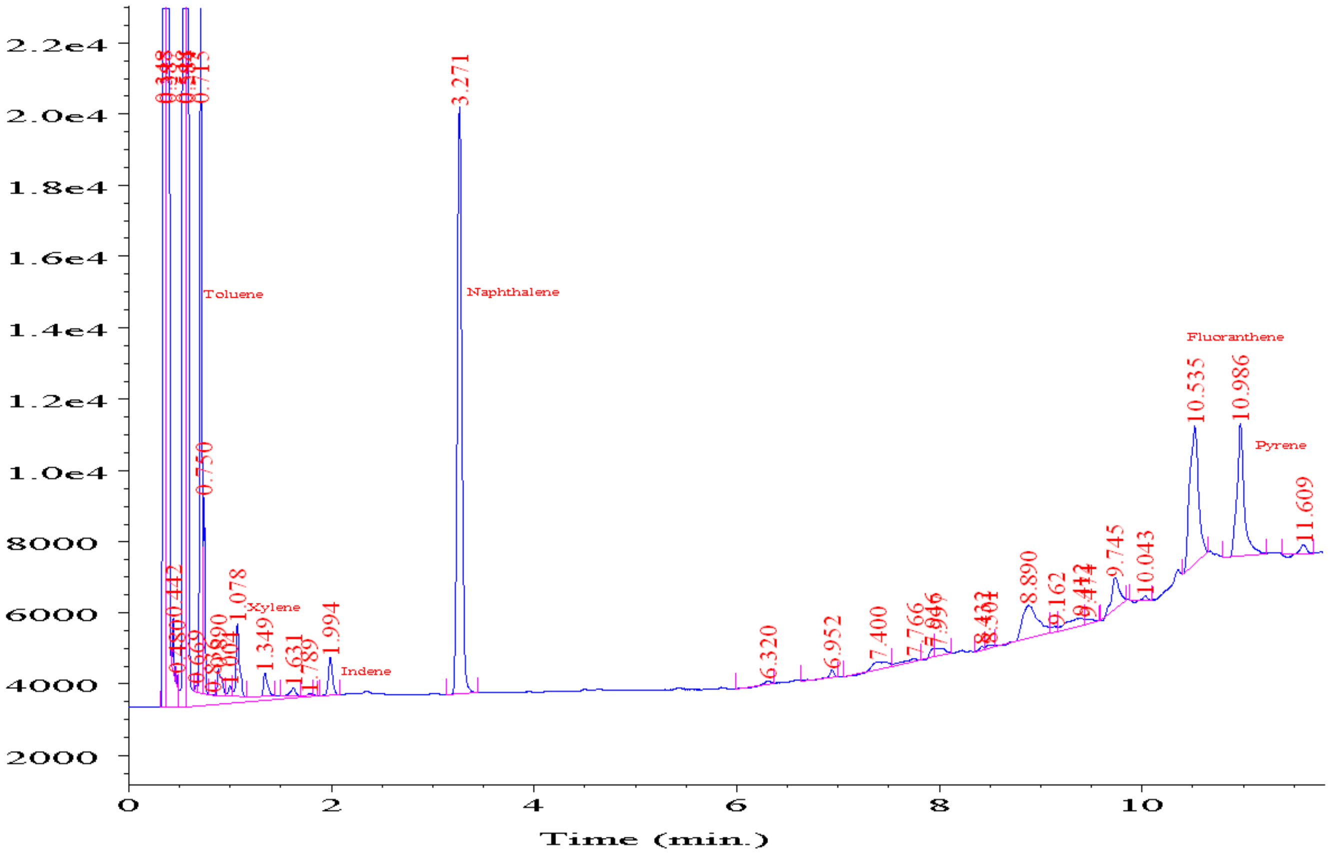
Advanced analysis techniques for gasification gas

- The aim has been to develop better analysis methods for the impurities in biomass gasification gas
  - Shorten the analysis time, improve accuracy and reduce labor intensity
  - From off-line to on-line
- Research subjects:
  - Analysis of small concentrations of sulphur in the gasification gas
  - Improved analysis method for alkalimetals
  - Establish on-line-tar analysis for light tars
  - Improved NH_3- and HCN-measurement methods
- Development work in a projects with Carbona, Neste, Stora-Enso, Foster Wheeler , Metso, VAPO, UPM and Gasum

'Rapid' on-line tar analysis of reformed gasification gas

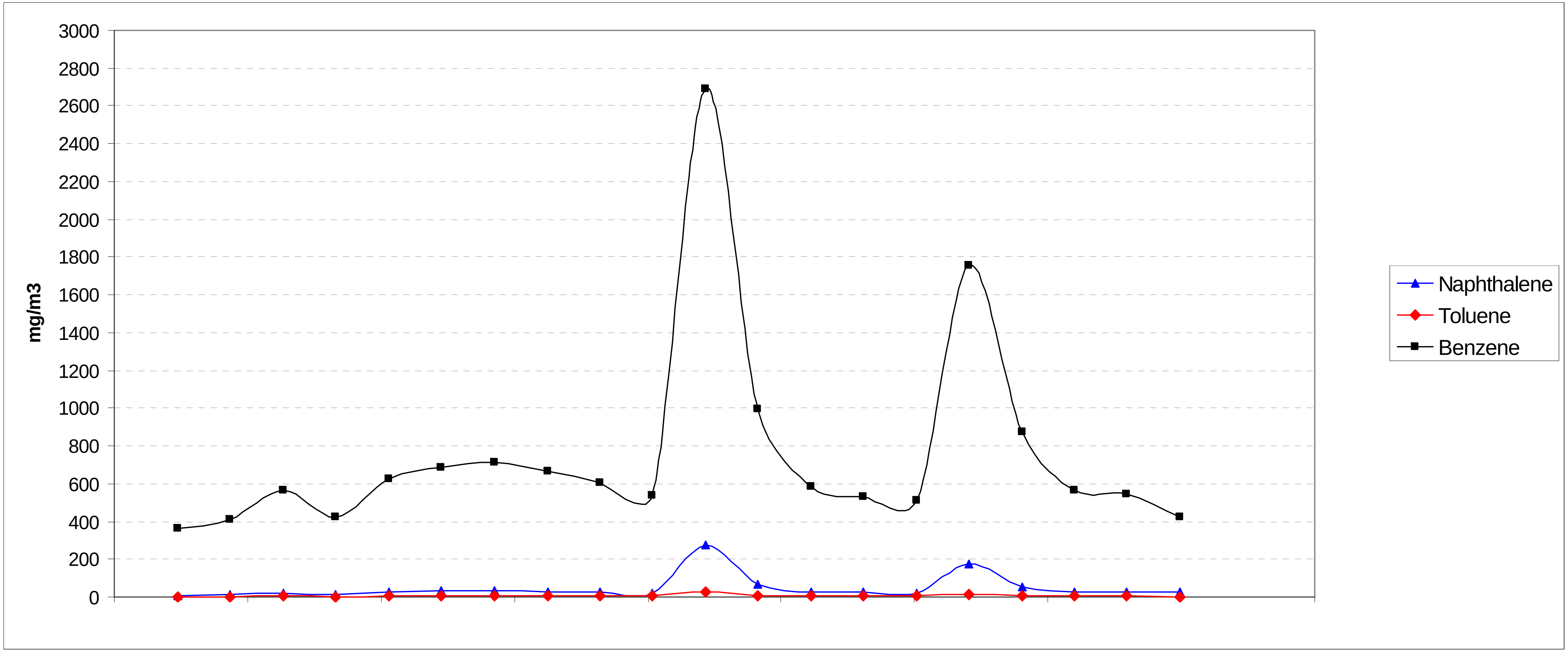
- Analysis time 5-20 min (several possible operation modes)
- Calibrated compounds:
  - Benzene
  - Toluene
  - Naphthalene
  - Phenanthrene
  - Anthracene
  - Fluoranthene
  - Pyrene
  - (if desired, 30 additional compounds)
- HP-1 (10 m x 0.53 mm x 0.26 µm) or HP Ultra 2 –column (25 m x 0.32 mm x 0.52 µm)
- Gas phase samples online
- Can be connected to the reactor automation system
- Has been in use at VTT for more than three Years



Validation of the on-line tar measurement method

- More than 500 tar measurements were carried out and compared
- Under carefully controlled conditions both the Tar Protocol and the on-line method give consistent results

Example of rapid tar measurement by on-line-GC



Air-blown CFB gasification followed by tar reformer – interruption in the process conditions could be seen in the tar data

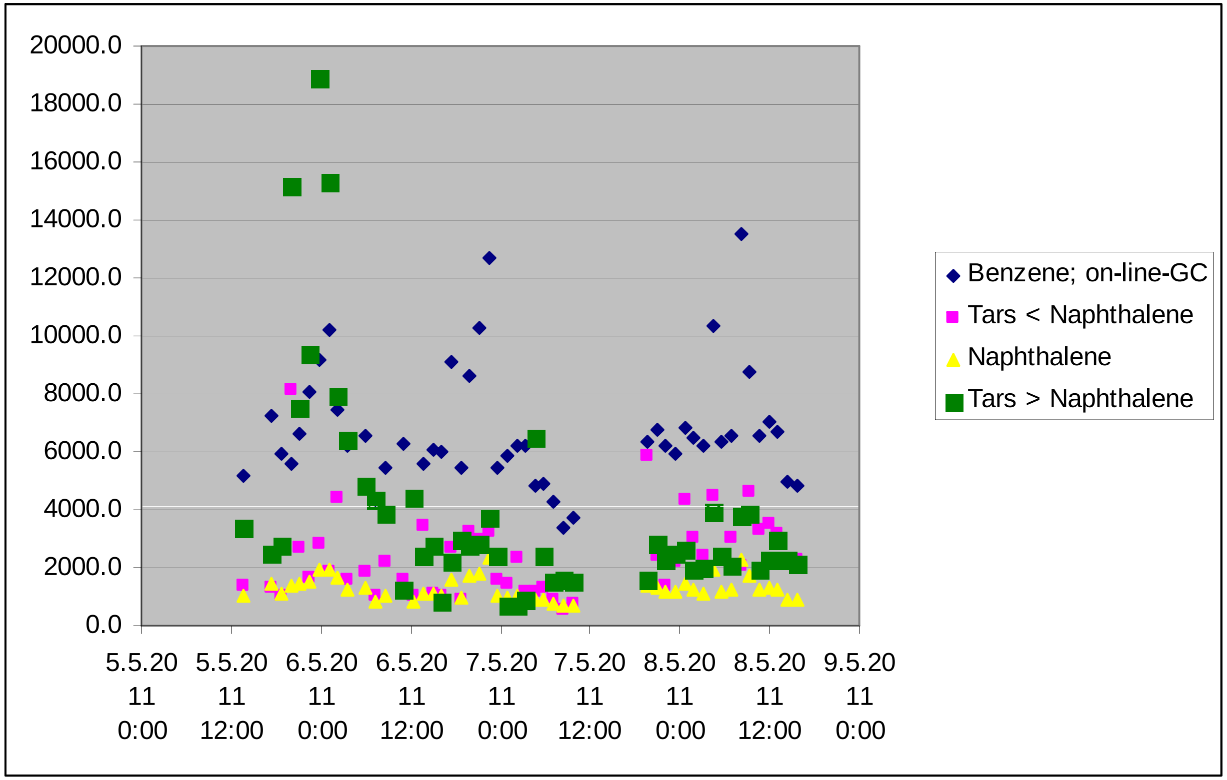
Dilution sampling

- Based on technology patented by VTT (e.g. WO/2007/080221)
- Can be applied to both atmospheric and pressurised systems
- Temperature range 280-800°C
- Dilution ratio typically 0-100
- Can be used for instance with a GC, ICP or FT-IR

- Results with very tarry raw gas have been promising
    - Results consistent with controlled off-line sampling
    - No problem with condensation of tars in the sampling lines
    - Good repeatability

Dilution sampling: tar measurement of tarry gas

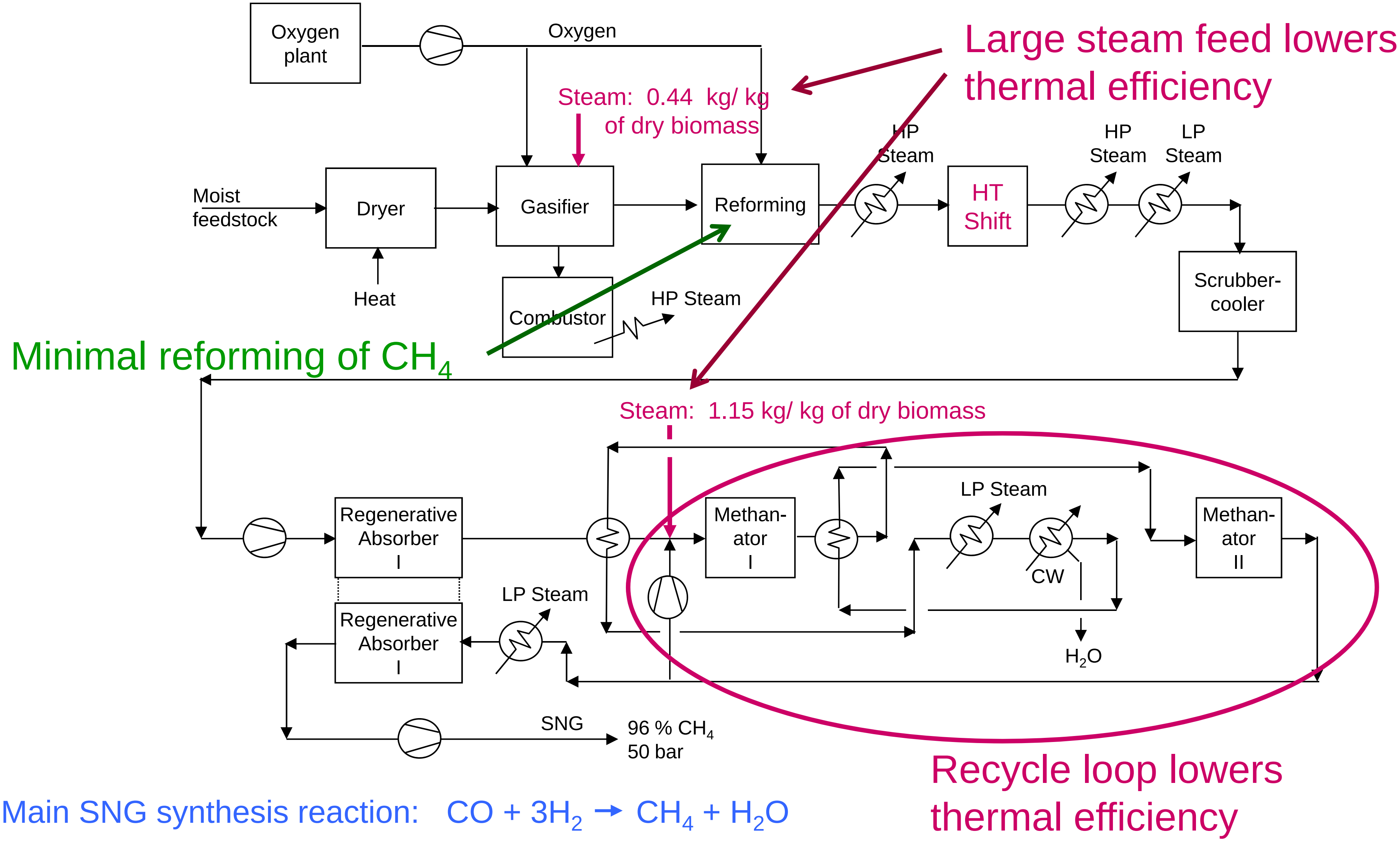
Benzene	Acenaphtylene
Pyridine	Acenaphthene
Toluene	Dibenzofurane
Ethenylbenzene	Bibenzyl
m-Xylene	Fluorene
Ethynylbenzene	Phenanthere
Styrene	Anthracene
o-Xylene	Carbazole
Benzaldehyde	1-Phenylnaphthalene
Phenol	2-Methylanthracene
Benzonitrile	4H-Cyclopenta(def)Phenantherene
4-Methylstyrene	Fluoranthene
Indene	Benz(e)acenaphthylene
o-Cresol	Pyrene
m+p-Cresol	Chrysene
Naphthalene	1,2 Benzanthracene
Quinoline	2,3 Benzanthracene
Isoquinoline	Benzo(b)fluorant
Quinatsoline	Benzo(e)pyrene
1H-Indole	Benzo(a)pyrene
2-Methylnaphthalene	Perylene
1-Methylnaphthalene	Benzo(ghi)peryle
Biphenyl	Anthanthrene
2-Ethylnaphthalene	Coronene
1.6 Dimethylnaphtalene	



Woody biomass based gasification process development for hydrogen or SNG production (VETAANI)

- Tekes/Biorefine project 1.6.2011 – 31.12.2013
- Total budget 1,5 M€, TEKES 60 %, VTT 30 %, companies 10 % (GASUM, HELEN, Metso, NesteOil, HVK, Outotec)
- Applications:
  - SNG, suitable for pipeline distribution
  - Bio-Hydrogen or hydrogen-methane gas mixture, e.g.for refineries
  - Clean fuel gas for SOFC power plants or NG based IGCC
  - Clean medium-Btu gas for industrial process kilns
- R&D methods
  - **System studies using Aspen Plus modeling tools**
  - **Selective tar reformer and hot filtration R&D**
  - Indirectly heated gasification and reforming
  - Overall process optimization: Higher efficiency and/or lower costs

Process Scheme for Production of SNG



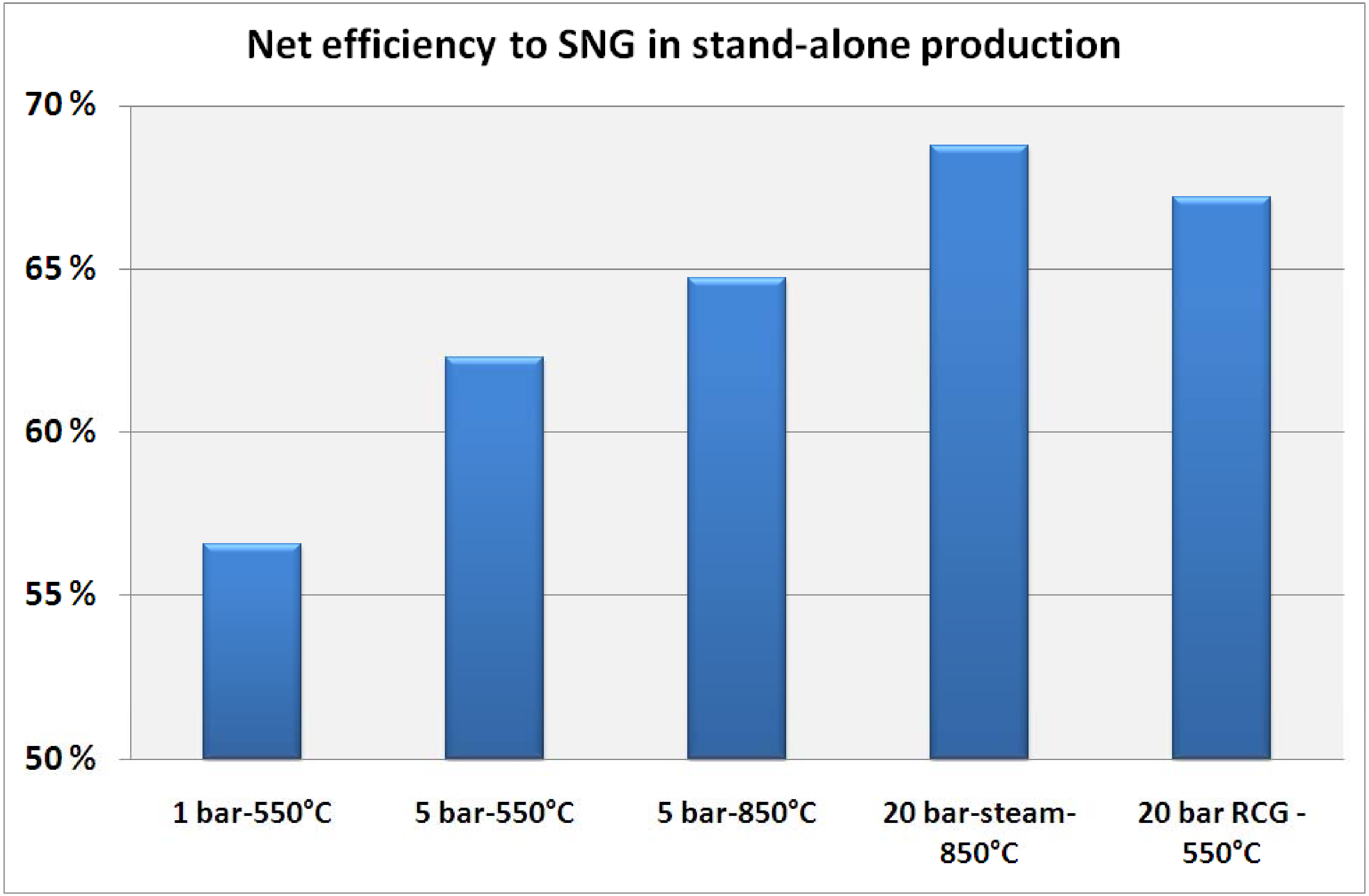
Main SNG synthesis reaction: $CO + 3H_2 \rightarrow CH_4 + H_2O$

From: McKeough & Kurkela, 2007

Preliminary results of new system studies carried out in Vetaani-project

Case	Pressure bar	Gasifier Temp. °C	Steam/O2 feed ratio	Recycle gas	Filter Temp. °C	CH4 conv. reformer	reformer Temp. °C
1 bar basic	1	870	1,0	No	550	30 %	820
5 bar basic	5	870	1,0	No	550	30 %	850
5 bar opt	5	850	1,0	No	850	0 %	820
20 bar high steam opt	20	850	1,5	No	850	0 %	850
20 bar RCG basic	20	870	0,8	Yes	550	0 %	850

- Steam-oxygen gasification
- Hot Gas Filtration and Gas Reforming
- Final gas cleaning and SNG synthesis according to previous VTT studies
- The effect of pressure on gasifier and reformer performance estimated
  - gasification reactivity limits => more steam or use of recycle gas needed at 20 bar
  - reforming easier at low pressure, higher temperature and steam feed needed at high pressure

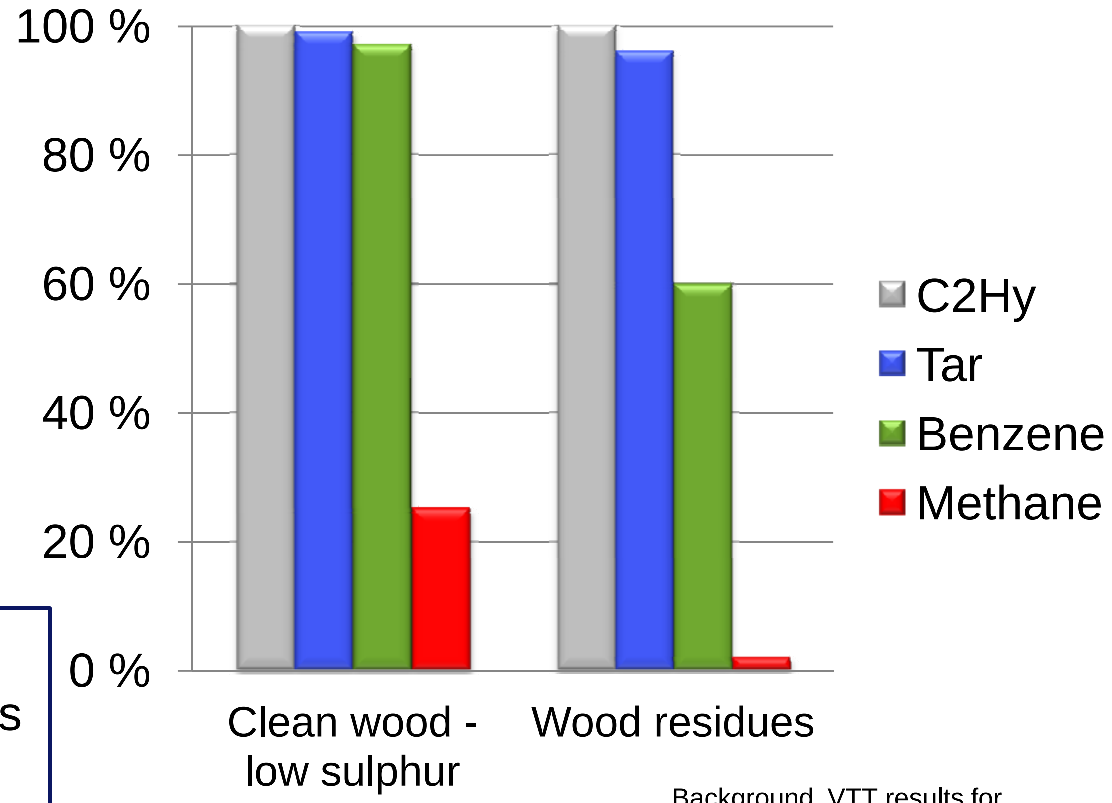


Input: wood at 50 % moisture, electricity produced from by product steam and additional wood combustion at 42 % efficiency, wood drying by low temperature heat streams

Targets for catalytic reforming and shift conversion in SNG applications

- Complete conversion of C_2-hydrocarbon gases
- Low conversion of CH_4
- Tar conversion > 99 %
- As high benzene conversion as possible
- Shift conversion before gas cooling in order to minimize total steam consumption

Conversions achieved in VTT's reformer



<u>Followed by</u>

- oil scrubbing of benzene & residual tars
- replacement of Rectisol by cheaper desulphurisation and CO_2 removal?

Background VTT results for Vetaani-project
Zr/noble metal catalysts

Possible ways to improve the synthesis gas route

- preliminary plans for a new national R&D project 2012- 14

- Optimised high-pressure steam-oxygen gasification process aiming to improved fuel-to-syngas conversion efficiency and to wider feedstock basis (above 200 MW scale)
- Indirectly heated or air-blown gasification processes for smaller size range (50 - 200 MW)
- Simplified final gas cleaning to replace Rectisol
- Syntheses/catalysts with less stringent gas purity requirements compared with present processes
  - Higher inert concentration (N_2)
  - Lower requirements for CO_2 removal
  - Higher tolerance for sulphur
- Co-production of fuels, heat and electricity – integration to forest industries and district heating

VTT creates business from technology