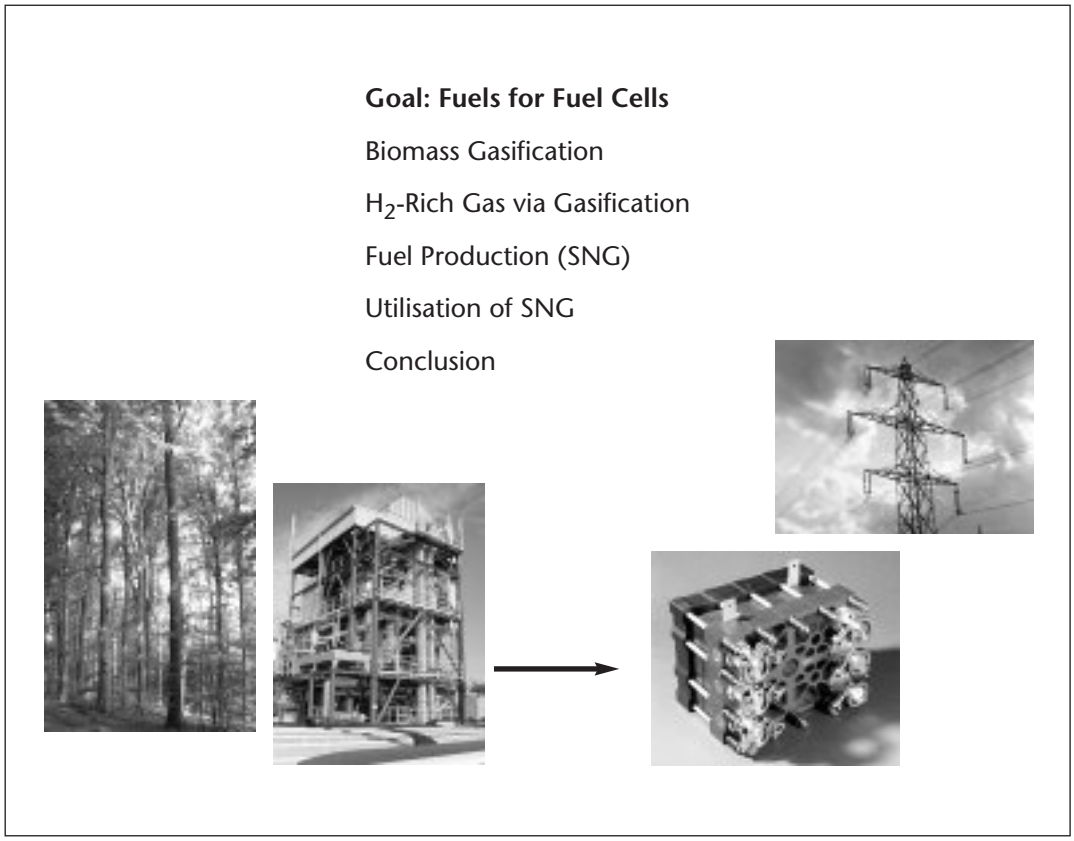
Regenerativer Wasserstoff durch thermochemische Konversion biogener Brennstoffe

Michael Specht
ZSW
michael.specht@zsw-bw.de

Contents: Hydrogen (Fuel Cell Fuels) via Biomass Gasification



Why Hydrogen?
➔ Fuel for Fuel Cells
Resources?
Where From?
➔ Biomass Option

What is the best coupling

Biomass Gasification / Fuel Cell ?

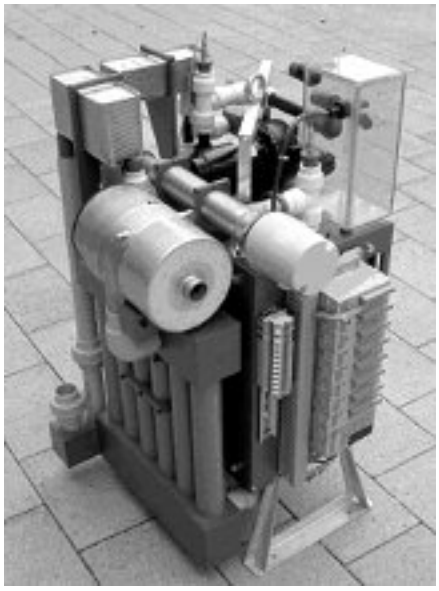



Statement

Fuel cells have a high potential for electricity generation, but they do not solve the problems:

- Dependency on fossile resources
- CO_2-emissions

➔ These problems can only be solved in combination with renewable fuels.



Promising Renewable Fuels for Stationary and Automotive Applications

Neat Fuels:

- Plant Oil
- Fatty Acid Methyl Ester (FAME)
- **Ethanol (EtOH)**
- **Methanol (MeOH)**
- **Substitute Natural Gas (SNG)**
- Fischer-Tropsch Hydrocarbons (FT-HC)
- **Dimethyl Ether (DME)**
- **Hydrogen**

Blends with Conventional Fuels:

- EtOH in Gasoline
- MeOH in Gasoline
- MTBE (Methyl Tertiary Butyl Ether) in Gasoline
- ETBE (Ethyl Tertiary Butyl Ether) in Gasoline
- FT-HC in Gasoline
- Plant Oil in Diesel
- FAME in Diesel
- MeOH in Diesel
- EtOH in Diesel
- FT-HC in Diesel
- **H_2 in NG (Natural Gas)**
- **SNG in NG**

Grey: Usability for Fuel Cells

What are the best Renewable Fuels for Fuel Cells?

What are the best Renewable Fuels for Fuel Cells ?

- Road Transport

  ➔ **Hydrogen**

- Gas Grid-Bounded Stationary Fuel Cells

  ➔ **SNG**

- Non Gas Grid-Bounded Stationary Fuel Cells

  ➔ **MeOH, DME, EtOH ????**

- „4C"-Market (Cordless Tools: Computer, Camcorder ….)

  ➔ **Hydrogen, Methanol**

Goal: Fuels for Fuel Cells

Biomass Gasification

H_2-Rich Gas via Gasification

Fuel Production (SNG)

Utilisation of SNG

Conclusion




Contents: Hydrogen (Fuel Cell Fuels) via Biomass Gasification

Thermo-chemical Conversion

Synthesis

Biomass ➔ Synthesis Gas ➔ FC, SynFuel

$(CH_{1.52}O_{0.65})$

CO, H_2, CO_2


Goal: Electricity/SynFuel from Biomass

Gasification of Biomass: Main (Homogeneous) Gas-Phase Reactions

Steam Reforming of Biomass Decomposition Products

$CH_xO_y + (1 - y)\ H_2O \rightarrow CO + (0.5\ x + 1 - y)\ H_2$ $\quad \Delta H_R > 0$

Homogeneous Water Gas Shift Reaction

$CO + H_2O(g) \rightarrow H_2 + CO_2$ $\quad \Delta H_{298K} = -41$ kJ/mol

Homogeneous Methanation

$CO + 3\ H_2 \rightarrow CH_4 + H_2O\ (g)$ $\quad \Delta H_{298K} = -206$ kJ/mol

Oxidation Reactions

$CO + ½\ O_2 \rightarrow CO_2$ $\quad \Delta H_{298K} = -283$ kJ/mol

$H_2 + ½\ O_2 \rightarrow H_2O(g)$ $\quad \Delta H_{298K} = -242$ kJ/mol

Gasification of Carbon: Main (Heterogenous) Reactions

Heterogeneous Water Gas Shift Reaction

$C + H_2O(g) \rightarrow CO + H_2$ $\quad \Delta H_{298K} = 131.3$ kJ/mol

Boudouard-Reaction

$C + CO_2 \rightarrow 2\,CO$ $\quad \Delta H_{298K} = 159.9$ kJ/mol

(Partial) Oxidation

$C + O_2 \rightarrow CO_2$ $\quad \Delta H_{298K} = -393.1$ kJ/mol

$C + ½\ O_2 \rightarrow CO$ $\quad \Delta H_{298K} = -110.5$ kJ/mol

Heterogeneous Methanation

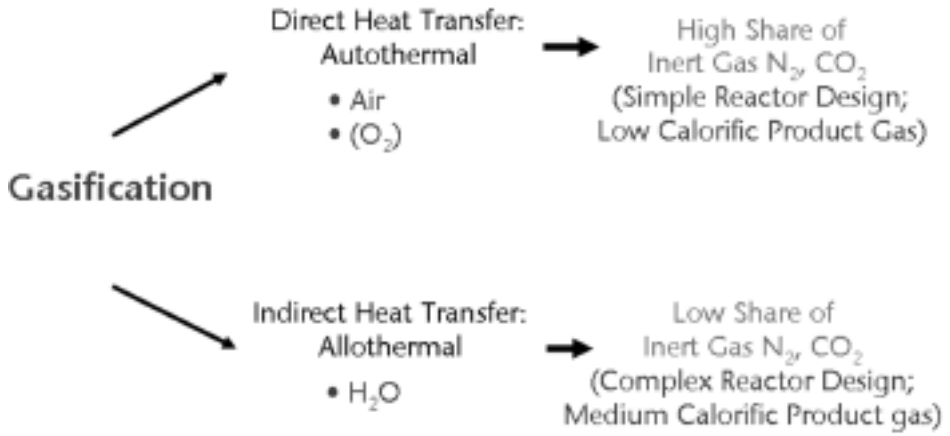
$C + 2\ H_2 \rightarrow CH_4$ $\quad \Delta H_{298K} = -74.9$ kJ/mol

Classification of Gasification Processes

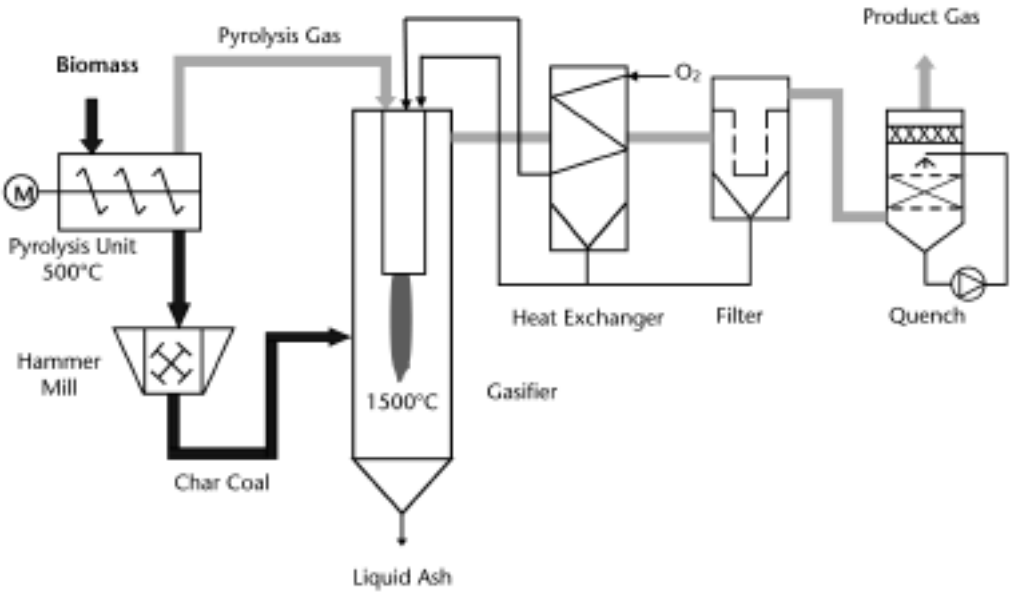
- **Operation Mode**
  - ➔ Autothermal (Partial Oxidation of Biomass)
  - ➔ Allothermal (Indirect Heating)

- **Gasifier Type**
  - ➔ Fixed Bed Gasifier 0.2 - 5 (25) MW_{th}
  - ➔ Fluidised Bed Gasifier 5 - 100 MW_{th}
    - – Bubbling Fluidised Bed (BFB)
    - – Circulating Fluidised Bed (CFB)
  - ➔ Entrained Flow Gasifier 50 - 500 MW_{th}

Heat Transfer: Autothermal and Allothermal

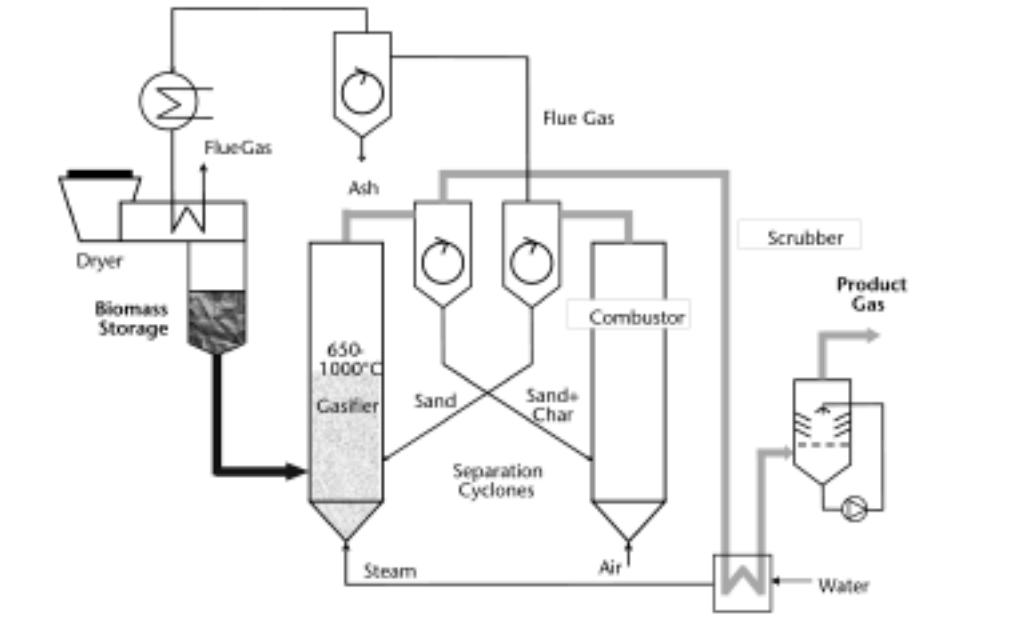


Carbo-V / CHOREN – Process: Entrained Flow Gasifier – Autothermal (T > 1000 °C)



Source: Rudloff 2004

Battelle/FERCO (SilvaGas) Process: Twin Fluidised Bed Gasifier – Allothermal (T < 1000 °C)



Source: Paisley 2000

Goal: Fuels for Fuel Cells

Biomass Gasification

H_2-Rich Gas via Gasification

Fuel Production (SNG)

Utilisation of SNG

Conclusion

Contents: Hydrogen (Fuel Cell Fuels) via Biomass Gasification

Steam Reforming / Gasification of Biomass

$CH_xO_y + (1-y)\ H_2O \rightarrow CO + (0.5x + 1 - y)\ H_2 \qquad \Delta H_R >> 0$

CO Shift Reaction

$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H_R < 0$

Combined with a HT-CO_2 Absorption

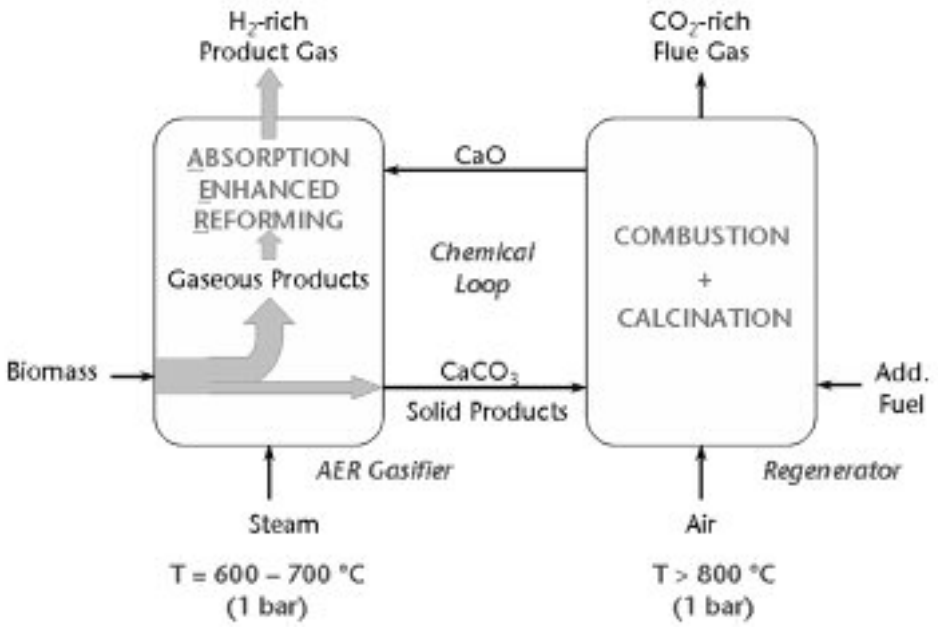
$CO_2 + CaO \rightarrow CaCO_3 \qquad \Delta H_R << 0$

Overall (600 – 700 °C, 1 bar)

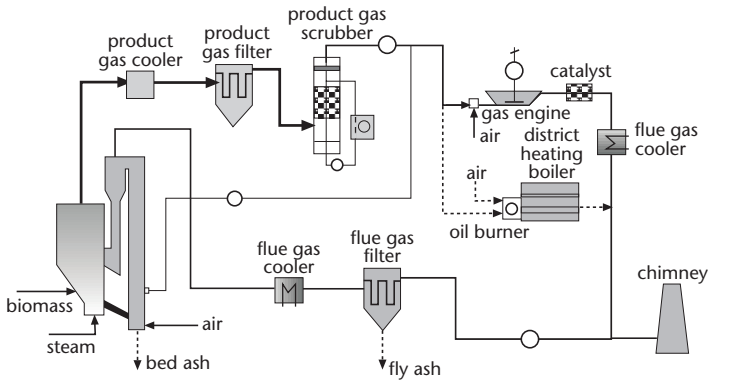
$CH_xO_y + (2 - y)\ H_2O + CaO \rightarrow CaCO_3 + (0.5\ x + 2 - y)\ H_2 \qquad \Delta H_R \approx 0$

AER - Reactions (Absorption Enhanced Reforming)

AER-Process: Twin Fluidised Bed Gasifier - Allothermal - in situ CO_2 Removal



Test of AER-Process in Biomass 8 MW_{th} FICFB Power Plant Güssing / Austria

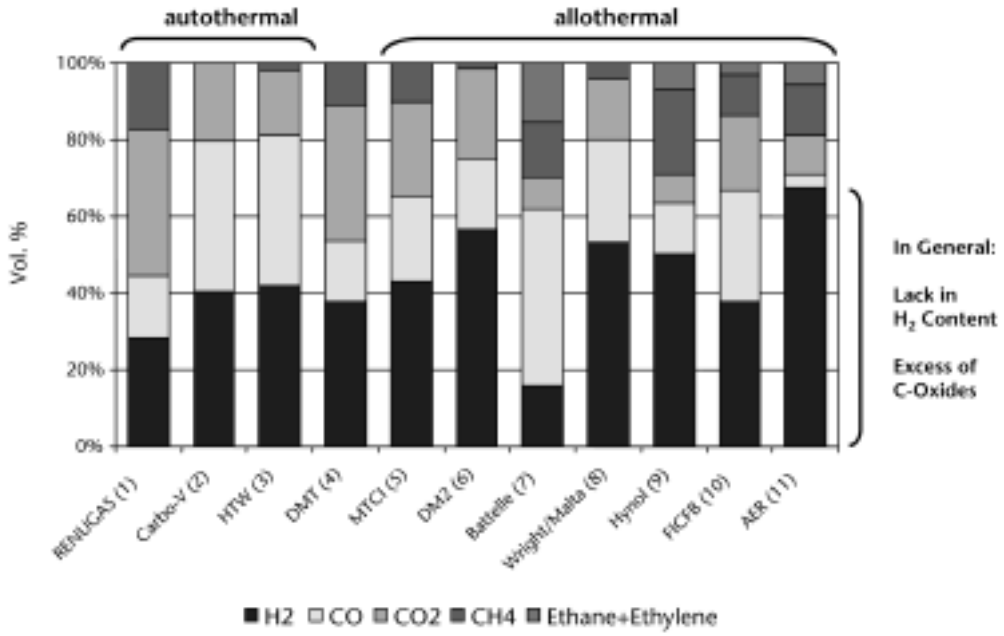


Source: TUV

AER Advantages:

- High Efficiency
- **High H_2 Content (70 Vol.%)**
- Low Rank Biomass
- Adapted Gas

2007: First AER Test Campaign in Güssing!



Producer Gas from Different Biomass Gasifiers – Are they Suitable for Fuel Cells and SynFuels ?

Goal: Fuels for Fuel Cells

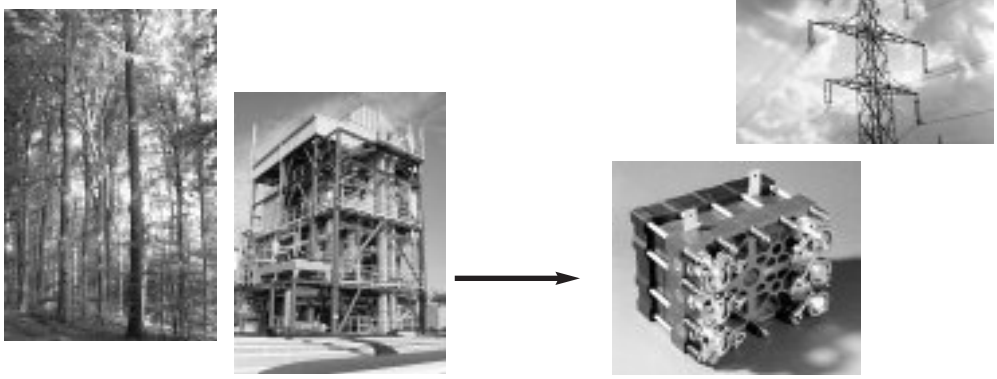
Biomass Gasification

H_2-Rich Gas via Gasification

Fuel Production (SNG)

Utilisation of SNG

Conclusion



Contents: Hydrogen (Fuel Cell Fuels) via Biomass Gasification

Substitute Natural Gas (SNG) from Thermo-Chemical Biomass Conversion

Which Thermo-Chemical Energy Conversion?

„Low-Temperature" Gasification in Fluidised Bed:

Main Products: H_2, CO, CO_2, **CH_4**

➔ **Electricity Production (HT Fuel Cell) / SNG**

„High-Temperature" Gasification in Entrained Flow Gasifier:

Main Products: H_2, CO, CO_2

➔ **Electricity Production / Liquid Synfuels**

Process Realisation with AER-Process:

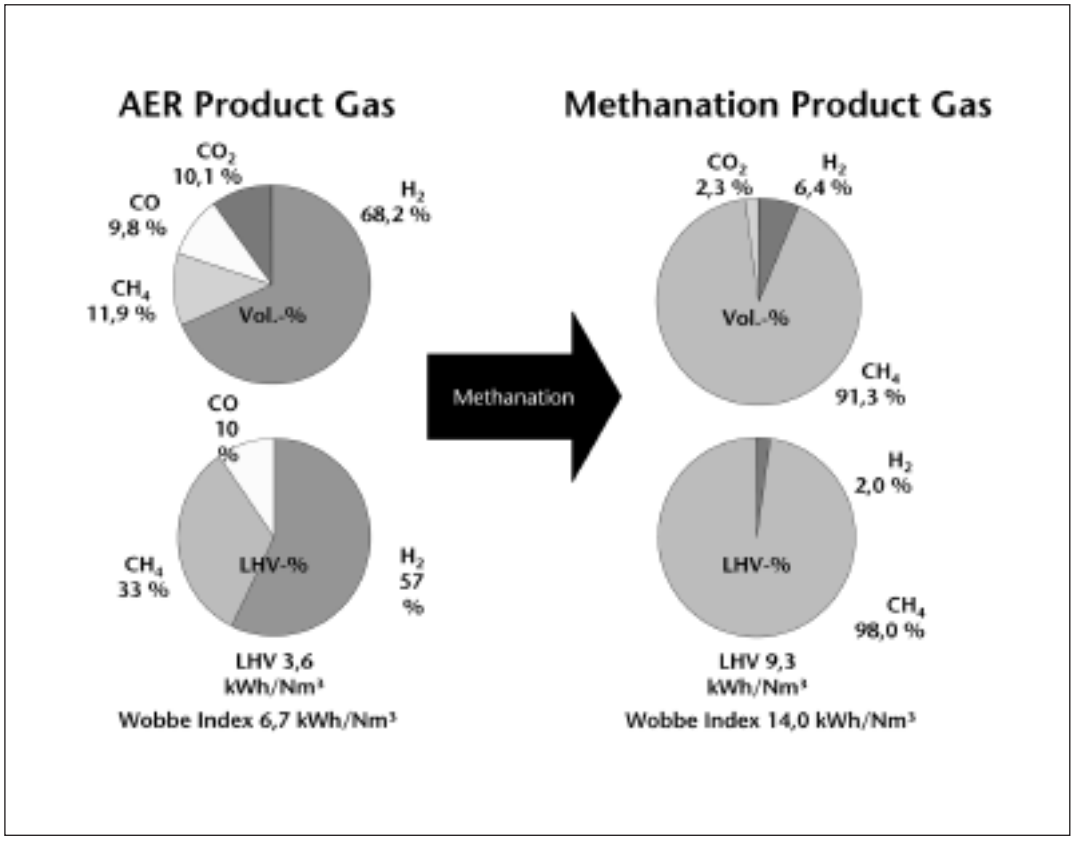
1. Step: Biomass Gasification with
   - High H_2 and High CH_4 Content
   - Low CO_x-Content
2. Step: Methanation of Rest-CO_x

Methanation of CO_x in Bio-Syngas

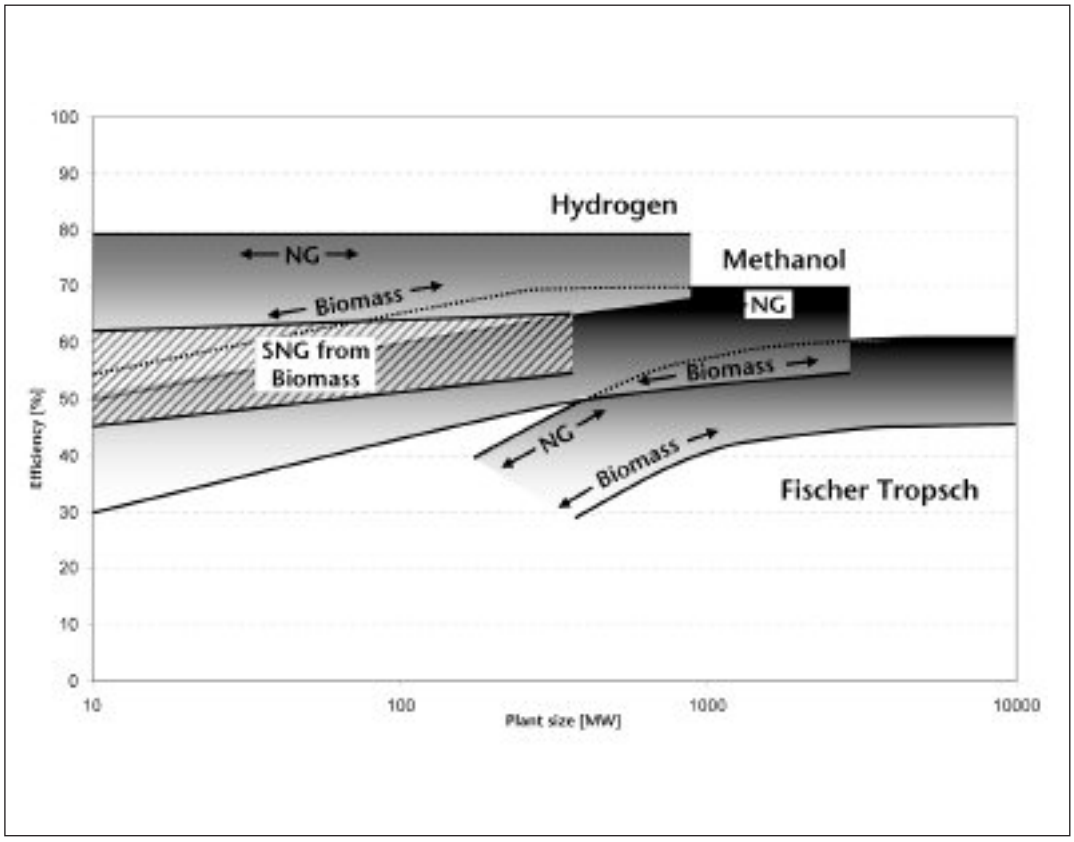
$$CO + 3\,H_2 \longrightarrow CH_4 + H_2O(g) \qquad \Delta H_{298K} = -206.158\ kJ/mol_{CH4}$$

$$CO_2 + 4\,H_2 \longrightarrow CH_4 + 2\,H_2O(g) \qquad \Delta H_{298K} = -165.475\ kJ/mol_{CH4}$$

$$2\,CO + 2\,H_2 \longrightarrow CH_4 + CO_2 \qquad \Delta H_{298K} = -246.841\ kJ/mol_{CH4}$$



Experimental Result: SNG from AER Product Gas



Efficiency Range of Biomass-to-Synfuel/ Hydrogen and Natural Gas-to-Synfuel/ Hydrogen Conversion

Contents: Hydrogen (Fuel Cell Fuels) via Biomass Gasification

Goal: Fuels for Fuel Cells

Biomass Gasification

H_2-Rich Gas via Gasification

Fuel Production (SNG)

Utilisation of SNG

Conclusion

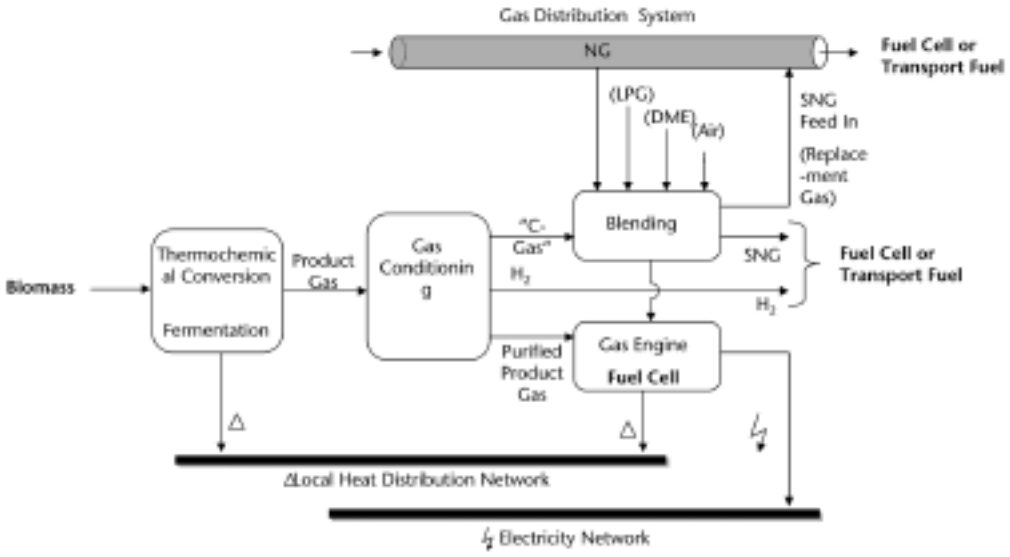



Substitute Natural Gas (SNG) - Why?

➔ **Today:** The existing NG infrastructure can be used for SNG


Source: Mahler, Stuttgart

➔ **Future Option:** NG (SNG) infrastructure can be used for decentralised H_2 production at fuel stations



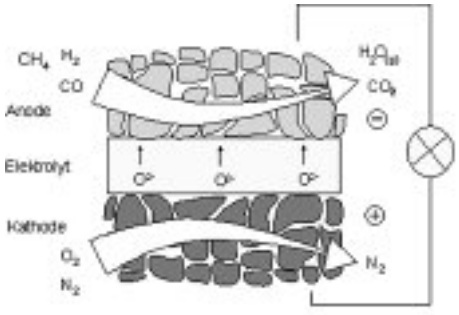
Electricity, Heat and Transport Fuel from Biomass: „Vectorisation" of Renewable Energy

Advantages

- Utilisation of the Existing Gas Distribution System
- Higher Electric Efficiency of High Temperature-FCs compared to H_2
- CO_2 Removal Option is an Integrated Component of an NG / SOFC-System

➔ **(S)NG is an Excellent Energy Carrier for Stationary Fuel Cell Systems**

➔ **A H_2 Pipeline Infrastructure is not Essential for Stationary Fuel Cell Systems**

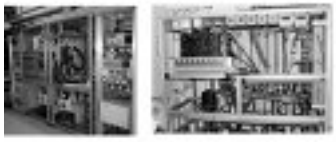


Utilisation of (Substitute) Natural Gas for Stationary High Temperature Fuel Cell Systems

ZSW – Technology Platform Stationary PEM Fuel Cell Systems

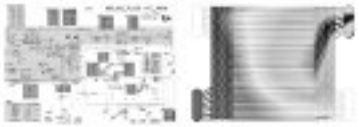
System Integration

Test Equipment



- Evaluation of Main Components
- Pre-Qualification of BOP Components
- Characterisation of Catalyst Materials

Modelling & Simulation



- Modelling/Simulation of Stacks
- Modelling/Simulation of Components
- Process Simulation & Engineering

➔ **Goal: Utilisation of SNG as renewable fuel !**

Contents: Hydrogen (Fuel Cell Fuels) via Biomass Gasification

R&D Demand: SNG/H2 Production via Biomass Gasification / SNG/H2 Utilisation in Fuel Cells

Technology

- Biomass gasification
- SNG production / CO/CO_2 methanation
- SNG feed-in into NG grid
- H_2 production / H_2 separation
- Utilisation of H_2/SNG in Fuel Cells

R&D Demands

- Thermochemical gasification to produce adapted Syngas/Fuel Gas or Hydrogen for downstream processes
- System complexity
- System costs

R&D Demand: Stationary Fuel Cell Systems for Home Energy Supply

Technology

- 1 – 5 kW_e Based on Natural Gas (SNG)
- Mainly NT-PEM and HT-PEM
- SOFC

R&D Demands

- Lifetime (e.g. stack > 25.000h in 2012)
- Efficiency (η_e = 33-35 %)
- System complexity
- System costs

(Details: National Development Plan 2007)

Conclusions

- **Indirect coupling Biomass Gasification / Fuel Cell:**

  „Low temperature gasification" with high CH_4/C_nH_m-content, SNG production and SNG feed-in into NG-grid

  – Utilisation of SNG:

    · In stationary fuel cell systems for home energy supply

    · SNG-reforming at fuel stations for H_2-generation for fuel cell propulsion in road transport

    · In central Combined Cycle/SOFC/MCFC power stations, in NG vehicles, etc.

- **Direct coupling Biomass Gasification / Fuel Cell:**

  „Low temperature gasification" with high CH_4/C_nH_m-content and „High temperature fuel cell": MCFC or SOFC

  ➔ No need of a H_2 infrastructure!