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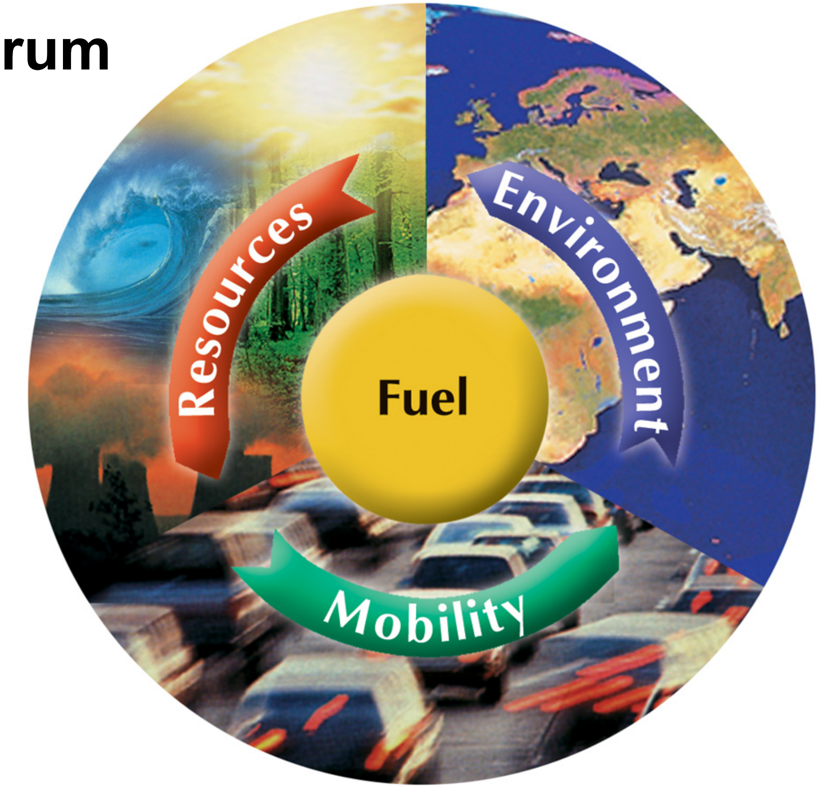
Kompetenz + Innovationszentrum Brennstoffzelle (KIBZ)

Kompetenzzentrum Umwelttechnik (KURS)

Stuttgart

28.11.2005



Regenerative Brennstoffe für Brennstoffzellen

Michael Specht

Centre for Solar Energy and Hydrogen Research (ZSW) – Stuttgart, Germany

Department: Renewable Fuels and Processes (REG)

ZSW Locations

- **Management, Central Office**
- **Photovoltaics Division**
- **Systems Analysis**
- **Renewable Fuels and Processes**

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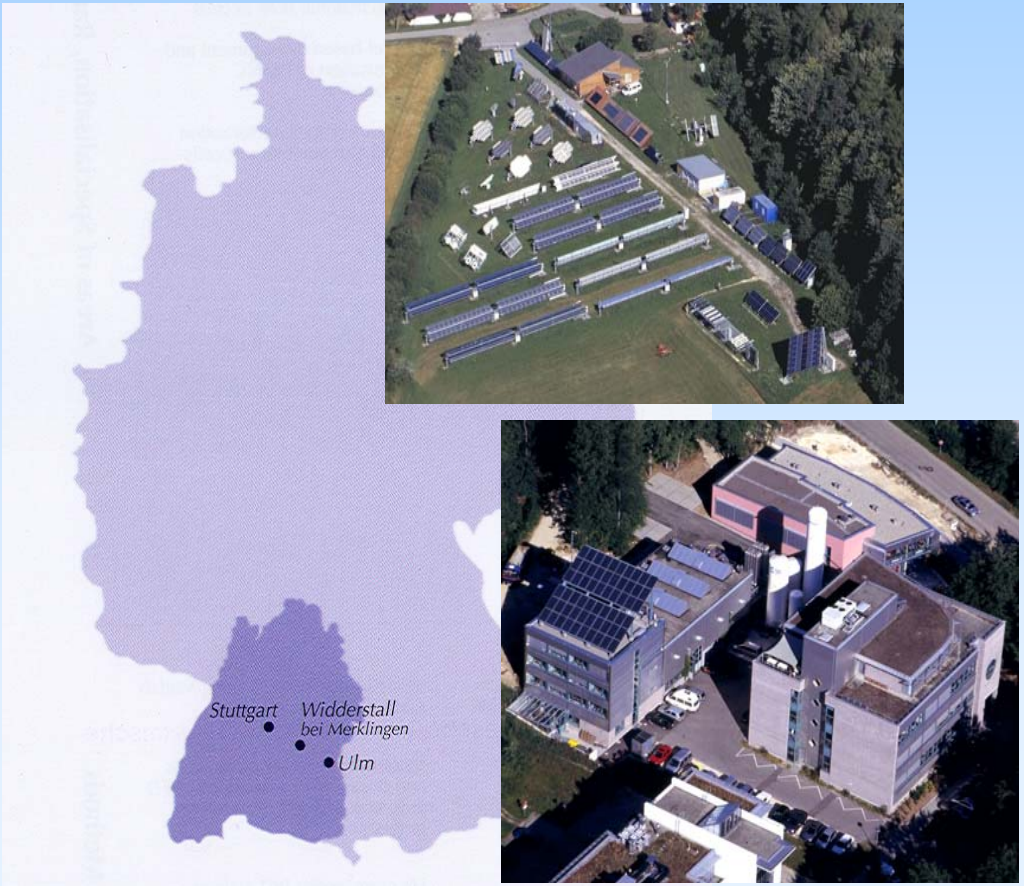

- **Solar Test Field Widderstall**

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Tel.: +49 (0)7337 – 9 23 94 0
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- **Electrochemical Energy Conversion and Storage Division**

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Tel.: +49 (0)731 – 95 30-0
Fax: +49 (0)731 – 95 30-666

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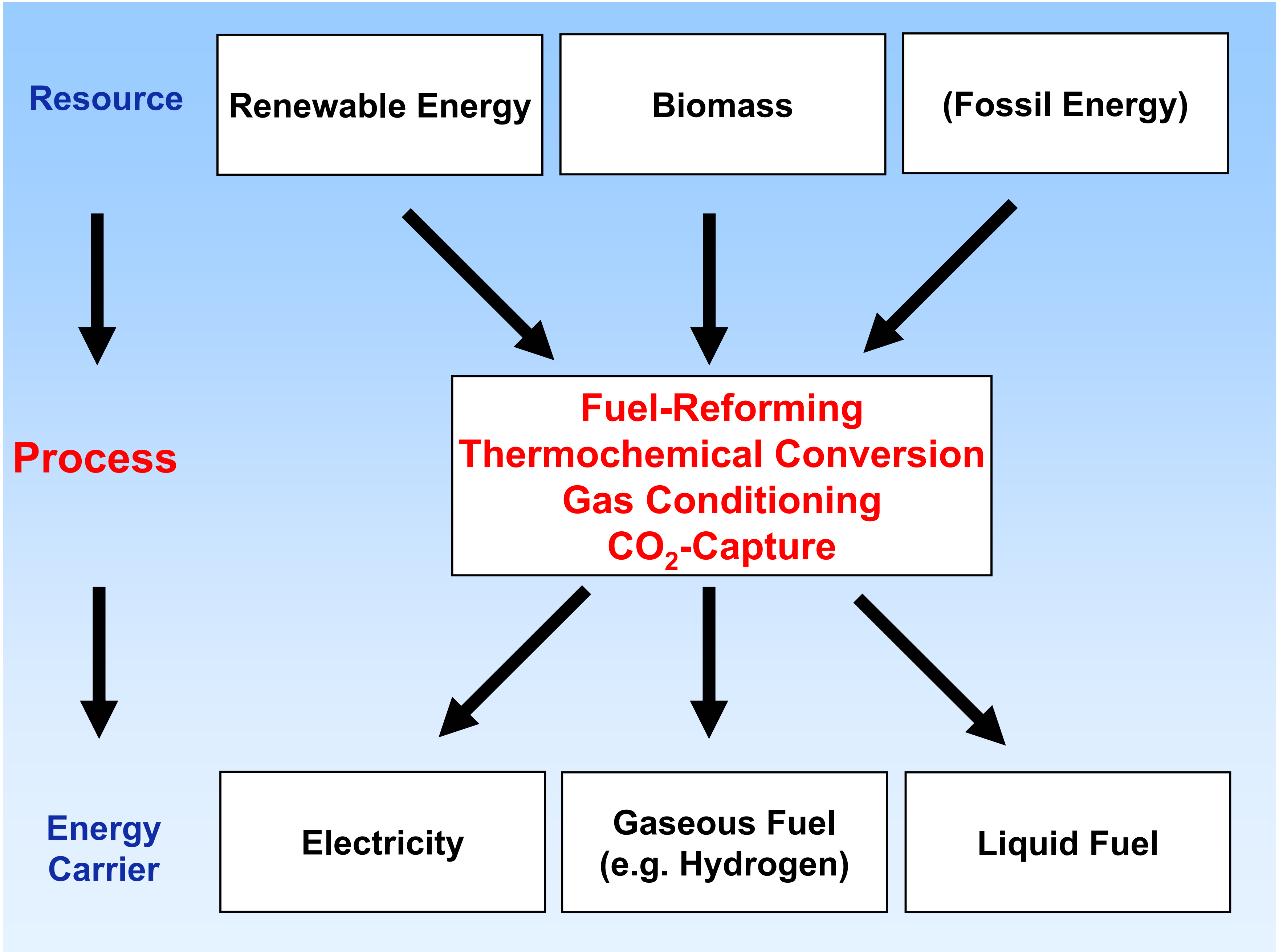
ZSW-Department: Renewable Fuels and Processes



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ReFuels 4 FCs

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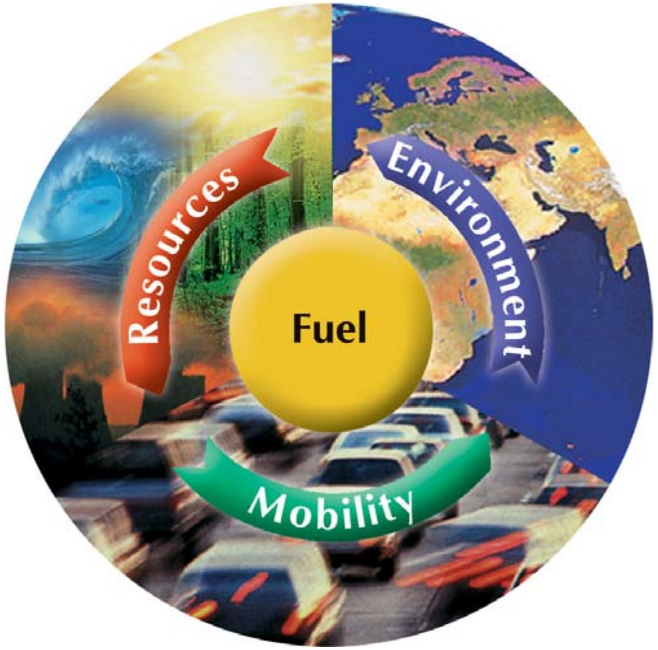

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Motivation
Biomass Resources for ReFuels
Promising ReFuels
Utilisation of (Re)Fuels in FCs (“bw-cell”)
ReFuel Production
Outlook

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Why Renewable Fuels?

- Reduction of GHG Emissions
- Finiteness of Fossil Resources
- Security of Supply
- Reduction of Local Pollutants
- Agriculture Policy
- Employment Effects

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Motivation: Vehicle CO_2 Emissions

Vehicle with a Gasoline Consumption of 8 l Gasoline /100 km

→ **18664 g_{CO2}/100km** [1)]

187 g_{CO2}/km

→ **100 l_{CO2}/km** [2)]

at 120 km/h and 8 $l_{Gasoline}$/100 km:

→ **3.2 l_{CO2}/sec**

1) 2333 $g_{CO2}/l_{Gasoline}$

2) M_{CO2} = 44.009 g/mol
Mole Volume = 22.414 l/mol (273.15 K, 101.325 kPa)

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ReFuels 4 FCs

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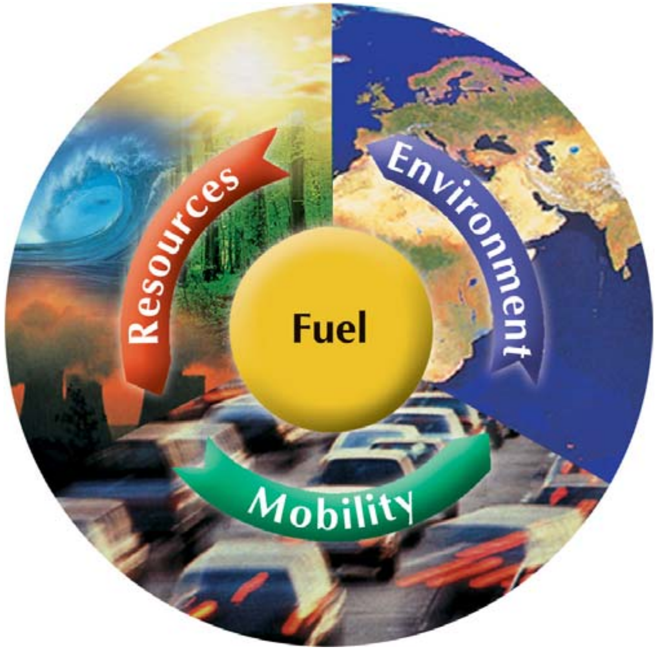

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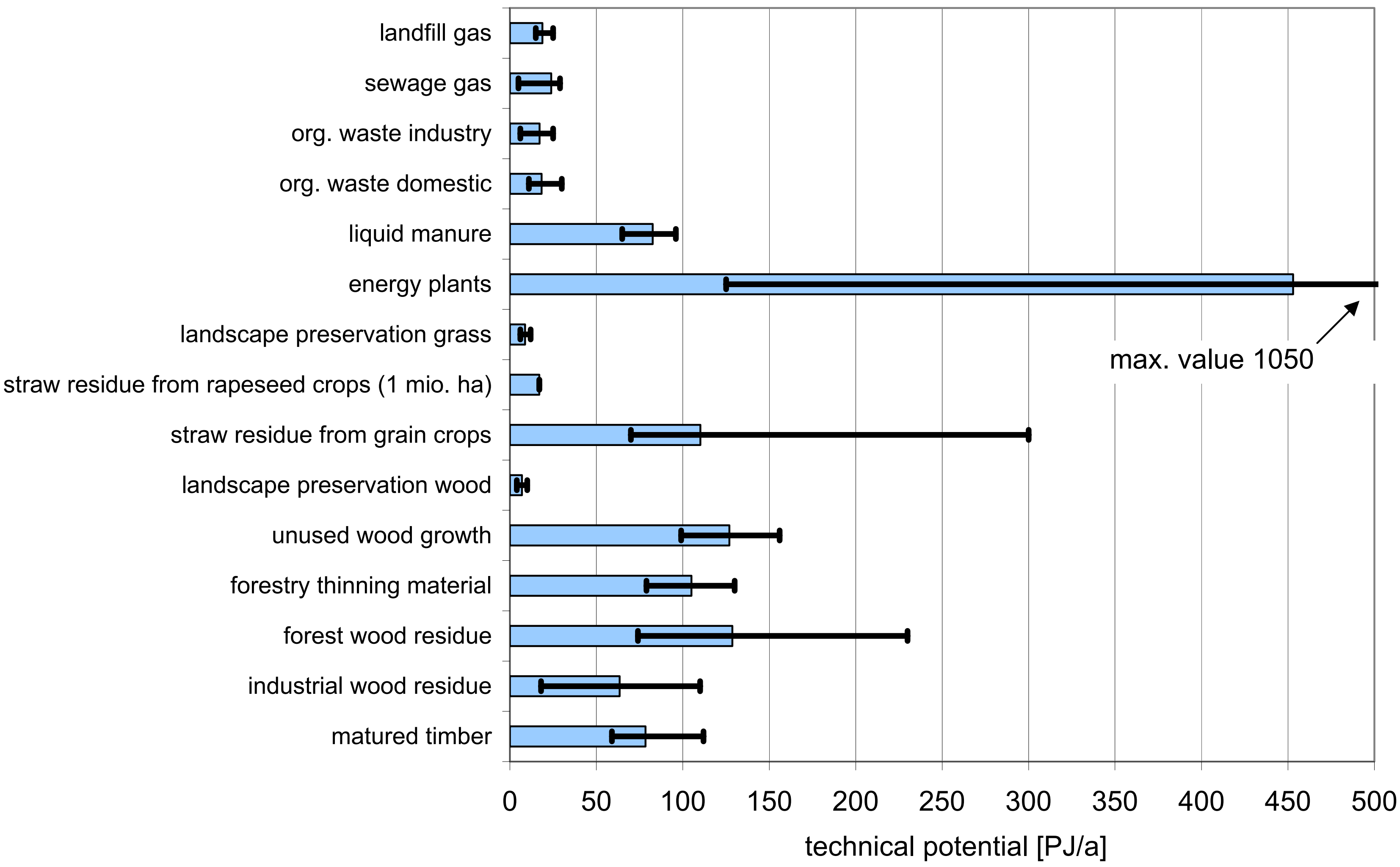
Biomass Potential in Germany

(Technical Biomass Potential for Energetic Use: ca. 1.260 PJ/a)



Biomass Potential in Germany

Technical Biomass Potential for Energetic Use:

→ **1 260 PJ/a**

Assumption: 2 Mio. Hectare for Energy Crops
(11.5 Mio. Hectare Arable Farm Land)

Corresponds to:

8.7 % of the Primary Energy Consumption

(14 438 PJ/a in 2004)

25 % of the Transport Fuel Consumption

(2 513 PJ/a in 2003;

calculated with an energetic

Conversion Factor Biomass-to-Fuel of 0.5)

ReFuels 4 FCs

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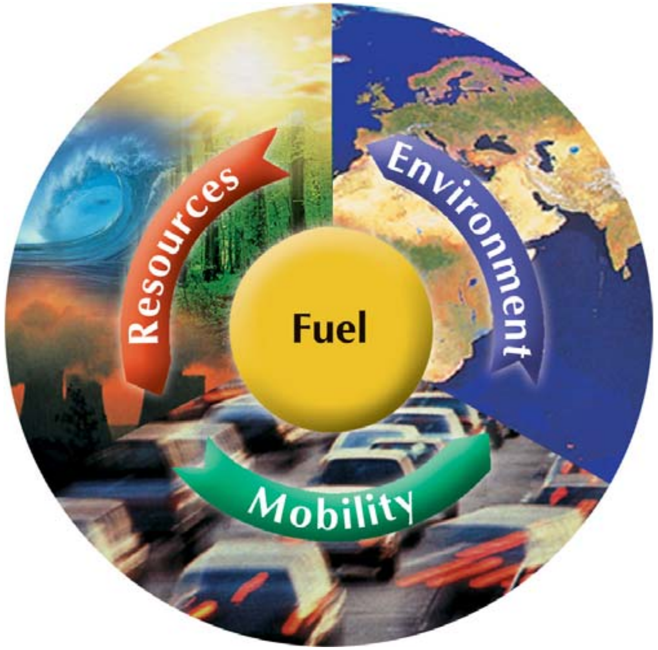

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Questions to be Addressed

What are the best Fuels for Stationary Applications ?

What are the best Fuels for the Transportation Sector ?

What are the best Fuels for Fuel Cells ?

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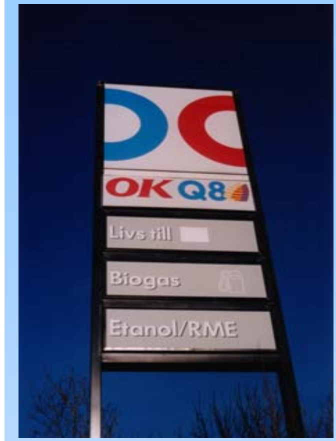
Promising Renewable Fuels for Stationary and Automotive Applications

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

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Promising Renewable Fuels for Stationary and Automotive Applications

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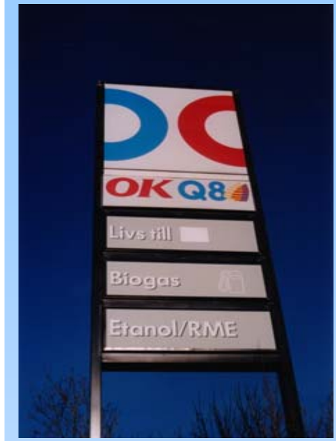

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- H_2 in NG (Natural Gas)
- SNG in NG

Red: Market Penetration Today

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Promising Renewable Fuels for Stationary and Automotive Applications

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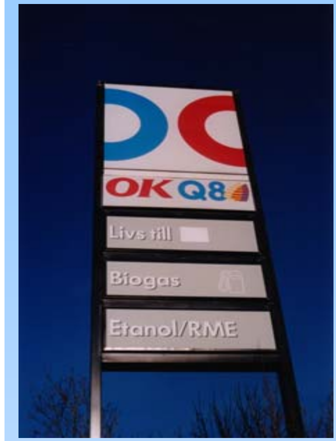

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- MeOH in Diesel
- EtOH in Diesel
- FT-HC in Diesel
- H_2 in NG (Natural Gas)
- SNG in NG

Red: Usability for Fuel Cells

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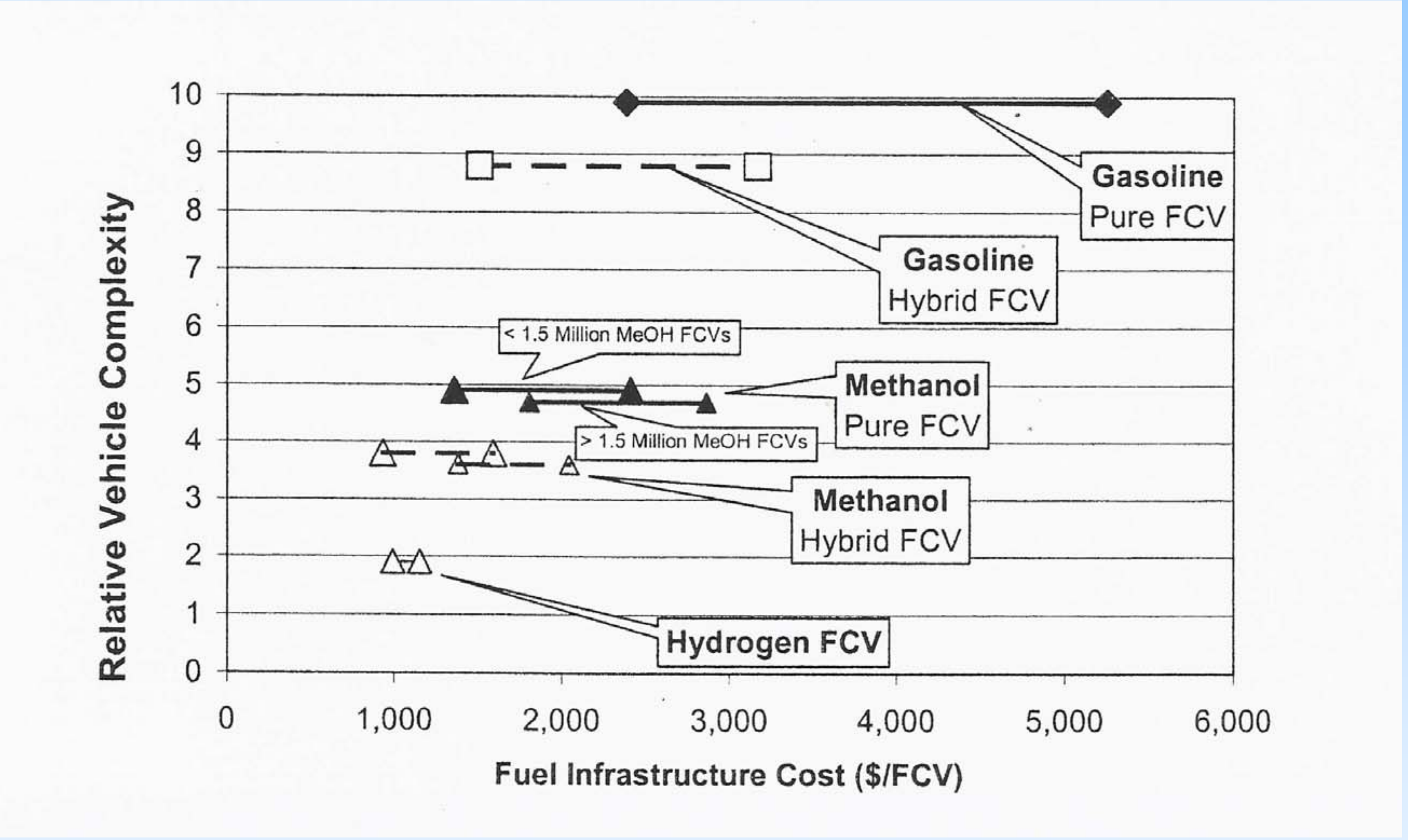
Vehicle Complexity vs. Fuel Infrastructure Costs per Vehicle



FCV: Fuel Cell Vehicle

Source: C.E. Thomas et al., IJHE 25, 551 (2000)

ReFuels 4 FCs

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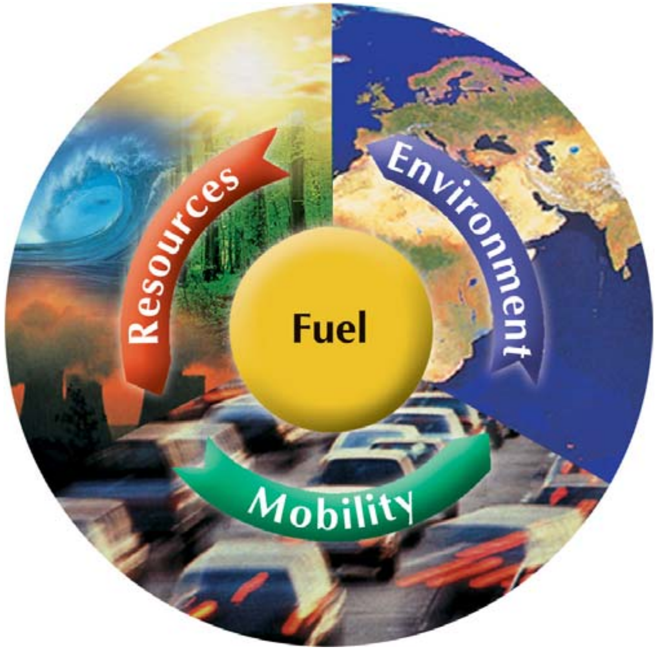

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"bw-cell":

Technology Development for Decentral CHP Generation in Baden-Württemberg

- Highly Efficient PEM-based Combined Heat and Power (CHP) Supply Systems

- Development of a 4 kW_e Prototype PEM Fuel Cell System for Home Energy Supply from Natural Gas

The “bw-cell” - ZSW Competence

- Concept Design / Process Simulation
- Manufacturing of Components
  - Fuel Cell Stack / Fuel Cell Subsystem
  - Gas Cleaning (Desulphurisation)
  - Gas Fine Cleaning (Selective Methanation)
  - DC/AC Inverter
  - Water Management
- System Integration
  - Process Control
  - Selection / Integration of Peripheral Components
  - Integration of FLOX®-Reformer

Fundamentals: Steam Reforming of NG

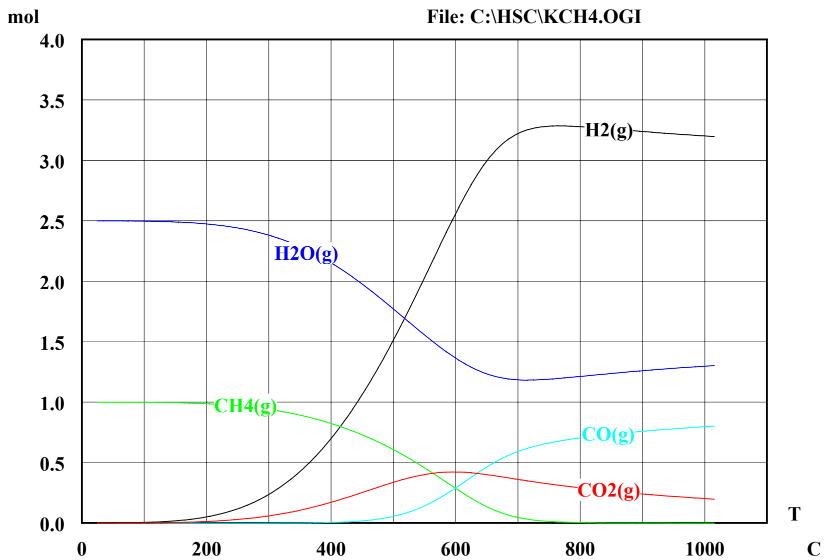
Reforming: $CH_4 + H_2O(g) \rightarrow 3\,H_2 + CO$ (ΔH_{298K} = 206 kJ/mol)

CO-Shift: $CO + H_2O(g) \rightarrow H_2 + CO_2$ (ΔH_{298K} = -41 kJ/mol)

Reaction Conditions: 700 - 900°C, 1 bar (Ni or Pt - Catalyst)

Equilibrium (1bar, s/c = 2.5)

Methane



Steam/Carbon - Ratio

$$\frac{s}{c} = \frac{\dot{n}_{H_2O}}{\dot{n}_{CH_4}}$$

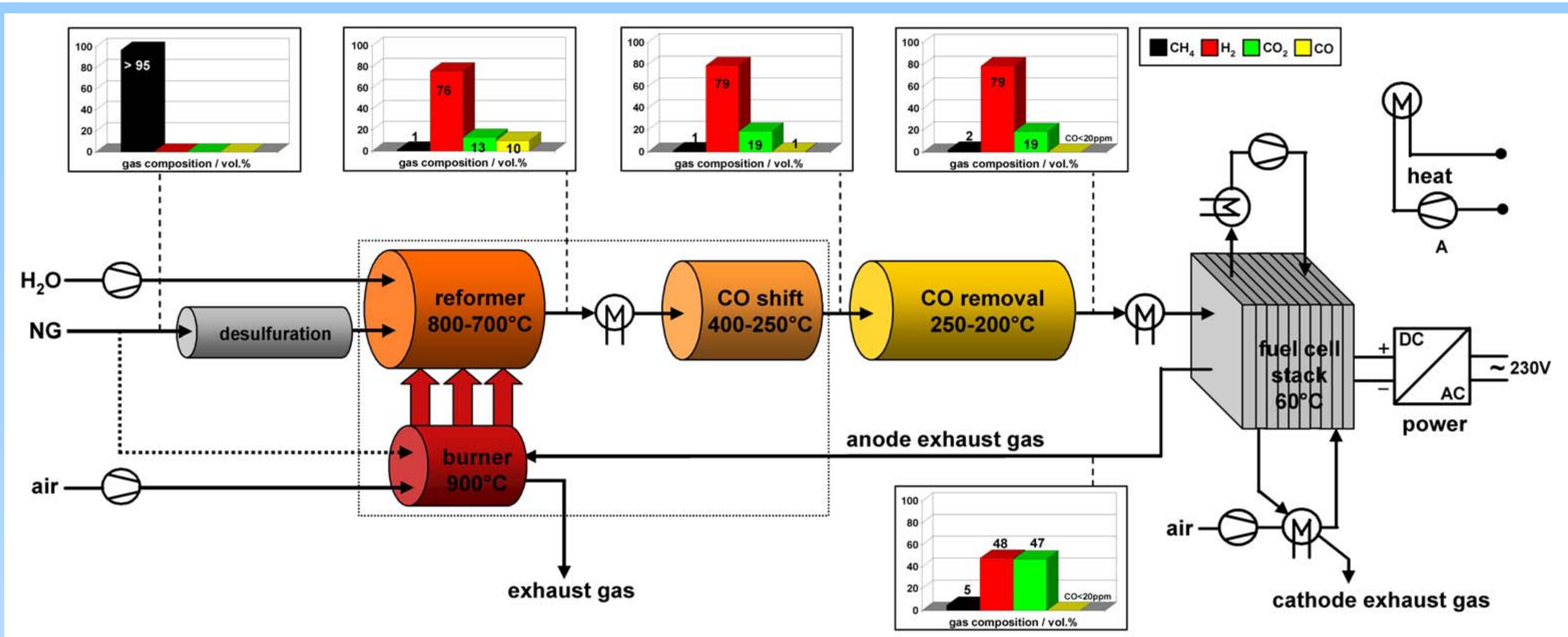
Space-Time-Velocity (SV)

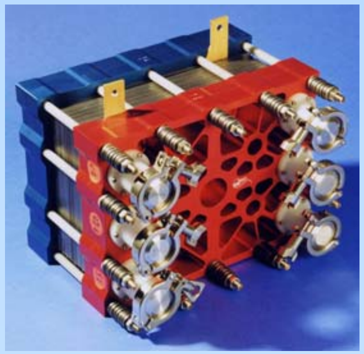
$$SV = \frac{\dot{V}_{Edukt,norm}}{V_{Kat}} = \frac{\dot{V}_{Feed} + \dot{V}_{H_2O}}{V_{Kat}}$$

Stoichiometry Factor

$$S = \frac{y_{H_2} - y_{CO_2}}{y_{CO} + y_{CO_2}}$$

The “bw-cell” - System Assembly





The “bw-cell”

Prototype 1 (2004):
200 x 70 x 150 cm³ / 0.5 m^3/kW_e

Prototype 2 (2005):
75 x 75 x 180 cm³ / < 0.25 m^3/kW_e

PEM Fuel Cell System "bw-cell": Technical Specifications (I)

„bw-cell" system (2nd generation)

feed	natural gas
electrical output	4,5 kW gross
	3,6 kW net *)
el. efficiency	> 30 %
dimensions	70*70*180 cm (< 0.25 m^3/kW_e)
weight	≈ 200 kg
emissions	NO_x, CO, C_xH_y incl. CH_4 < 10 vppm
start-up time	< 20 min. (from stand-by)
load changes	< 10 min. (50-100 %)

*) incl. peripheral and inverter losses related to the lower heating value (LHV) of natural gas

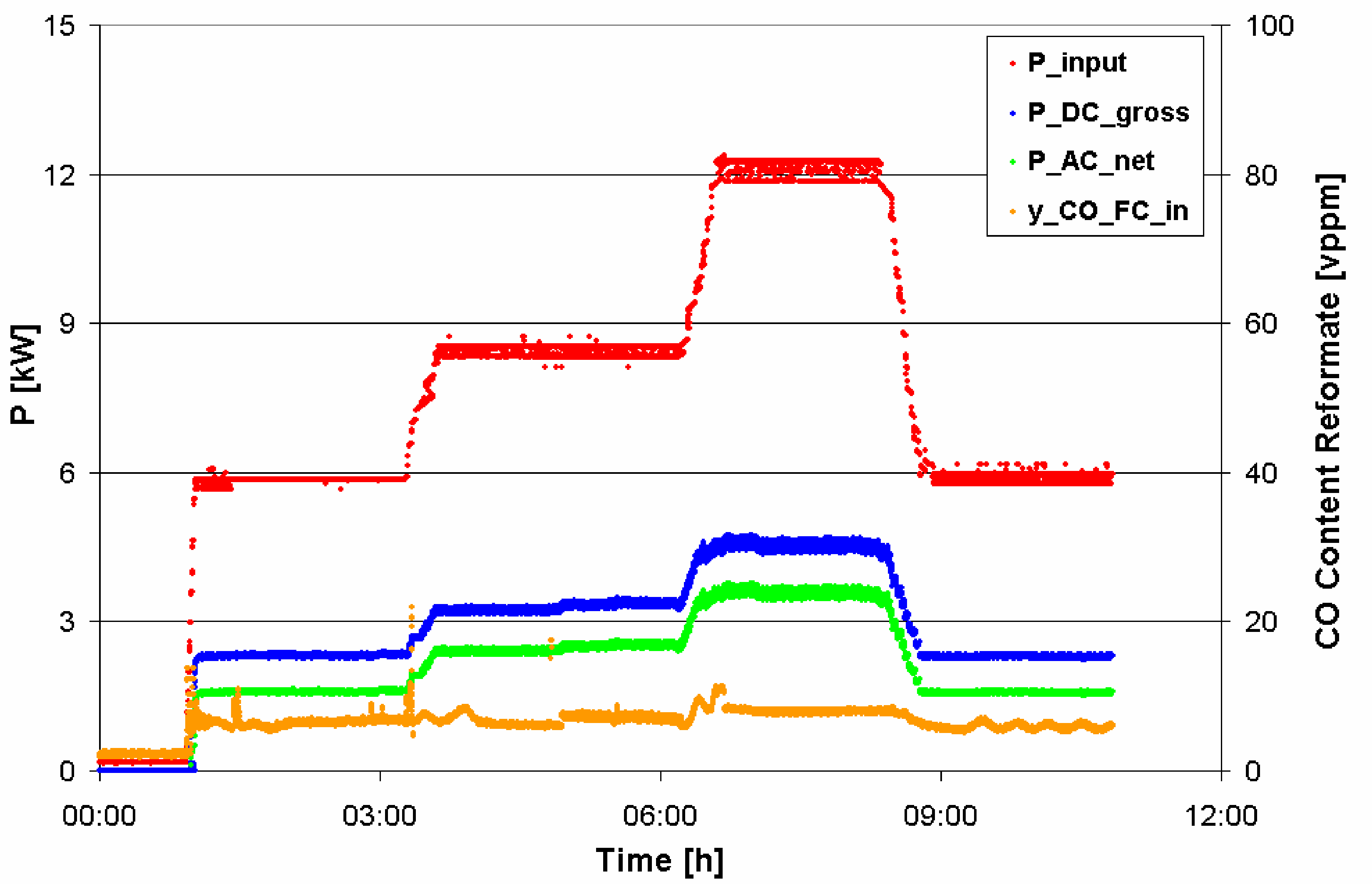
PEM Fuel Cell System “bw-cell”: Technical Specifications (II)

reformate gas generation system	
reformer	steam reformer with integrated
	CO shift (CO_{out} < 0.6 Vol.%)
	η_{ref} > 78 %
reformate	H_2 > 78 Vol.% (CH_4 < 1 Vol.%)
	reformate pressure > 300 mbar
CO removal	selective methanation
	(CO_{out} < 20 ppm)
fuel cell system	
DC power	4,5 kW
	> 700 mV @200 mA/cm²
	50 cells, 560 cm² active area
stack temperature	65 °C
H_2 conversion	> 75 %
pressure drop	anode < 20 mbar
	cathode < 20 mbar

PEM Fuel Cell System “bw-cell”: Further Special Features

- No Additional Burner Required
- Standby Ability
- High Reformate Pressure (up to 300 mbar) without Auxiliary Gas Compressor
- Low Pressure Drop in the ZSW Fuel Cell Stack (< 20 mbar)
- Fixed Bed Reactors (Use of Commercial Catalysts)
- Adaptability to Non-pipeline/Renewable Fuels like LPG, Ethanol, SNG etc.

The “bw-cell“
NG Input / Electric Output / CO Concentration



ReFuels 4 FCs

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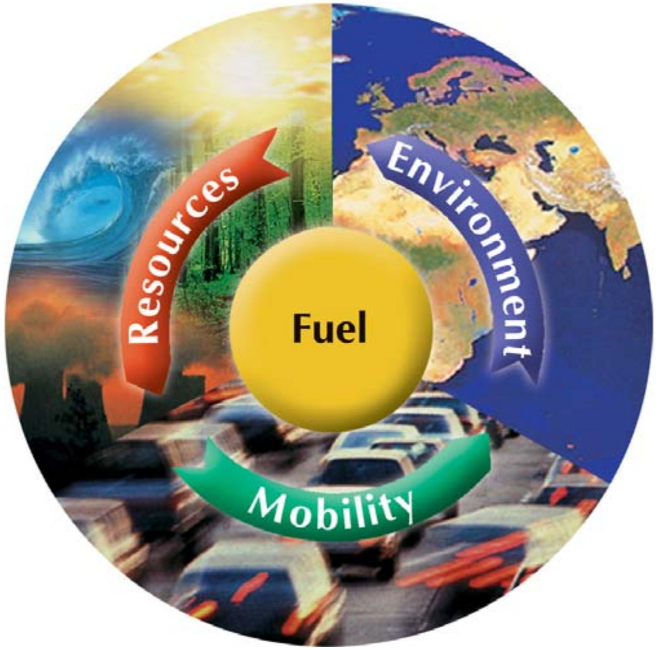

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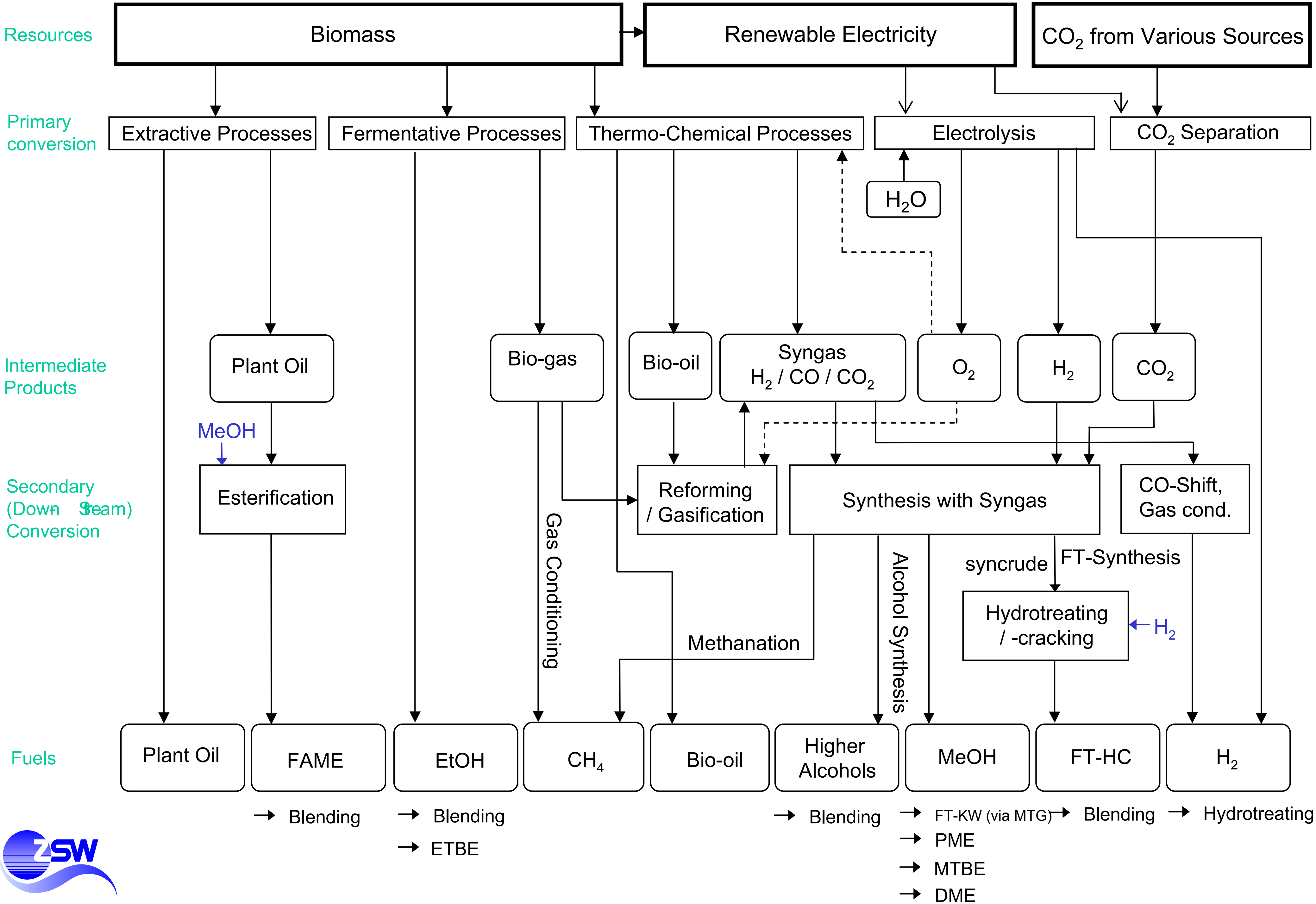
Generation Paths of Renewable Fuels



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SynFuels: Fuel Production from SynGas

Hydrogen

$CH_xO_y + (1 - y)\ H_2O \rightarrow CO + (0.5\,x + 1 - y)\ H_2$

$CO + H_2O\ (g) \rightarrow H_2 + CO_2$

Methanol

$CO + 2\ H_2 \rightarrow CH_3OH$

$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$

DME

$2\ CO + 4\ H_2 \rightarrow CH_3OCH_3 + H_2O$

$3\ CO + 3\ H_2 \rightarrow CH_3OCH_3 + CO_2$

Methane

$CO + 3\ H_2 \rightarrow CH_4 + H_2O$

$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$

Gasoline / Diesel

$CO + H_2 \rightarrow -CH_2- + H_2O$

$CO_2 + 2\ H_2 \rightarrow -CH_2- + 2\ H_2O$

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Methanol Properties (I)

- Liquid at ambient temperature (easy handling)
- High energy density (ca. 50 % of gasoline)
- Completely miscible with water
- Biodegradable
- More corrosive than gasoline (pipelines, tanks, seals)
- No lubricating effects e.g. in fuel pumps
- Adapted vehicles have been built (M100, M85)
  M100: pure MeOH;
  M85: 85 Vol.% MeOH in Gasoline

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Methanol Properties (II)

- Today MeOH is used in the fuel market for MTBE production from iso-butene, $(CH_3)_2C=CH_2$. Methyl tertiary butyl ether, $(CH_3)_3COCH_3$, is an octane booster to improve knock resistance of gasoline.
- Further utilisation “intermediate energy carrier” for the production of: FAME (fatty acid methyl ester), DME (dimethyl ether), Gasoline (MTG, methanol-to-gasoline)
- MeOH can easily be converted to H_2 at low temperatures (250 – 300°C) for fuel cell applications.

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Dimethyl Ether (DME) Properties

- Most simple ether (H_3C-O-CH_3)
- No C-C bonds (nearly particulate free exhaust gas emissions with internal combustion diesel engine)
- High Cetane number (55 – 60)
- Non-toxic (used as propellant in aerosol cans)
- Boiling Point -24.9 °C; liquid in pressure tanks (5 bar; to avoid evaporation at elevated T: ca. 30 bar)
  → Storage comparable to LPG

- Problem: Parking in Garages
  (density higher than air - same as LPG)

- Density of liquid: 0.67 kg/l

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Substitute Natural Gas (SNG) Properties

- Main component: CH_4
- SNG production from Renewable Energy
  - Fermentative route via bio-gas
    - CH_4 (and CO_2) are natural decomposition products of biomass
  - Synthetic route via syngas
  - via hydro-gasification with H_2 as gasification agent
- NG is an easy back-up system for SNG

- Gaseous, boiling point: - 162 °C (CH_4)
- Non-toxic
- Lighter than air (safety aspects)
- Energy density ca. 3.3 times higher than H_2
- Existing grid for natural gas
  - ca. 600 filling stations (Germany), ca. 450 (Italy), ca. 1250 (Europe) for compressed natural gas (CNG)

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Bio-Gas from Anaerobic Digester Plants

Bio-Gas: CH_4/CO_2

Commercially Available (decentral) Technology

Bio-Gas Digester Size:
100 – 1000 Nm^3

Feed/Year:
1000 – 10000 t/a

Source: ISET, Krautkremer

Conversion of Digestive Biomass to SNG

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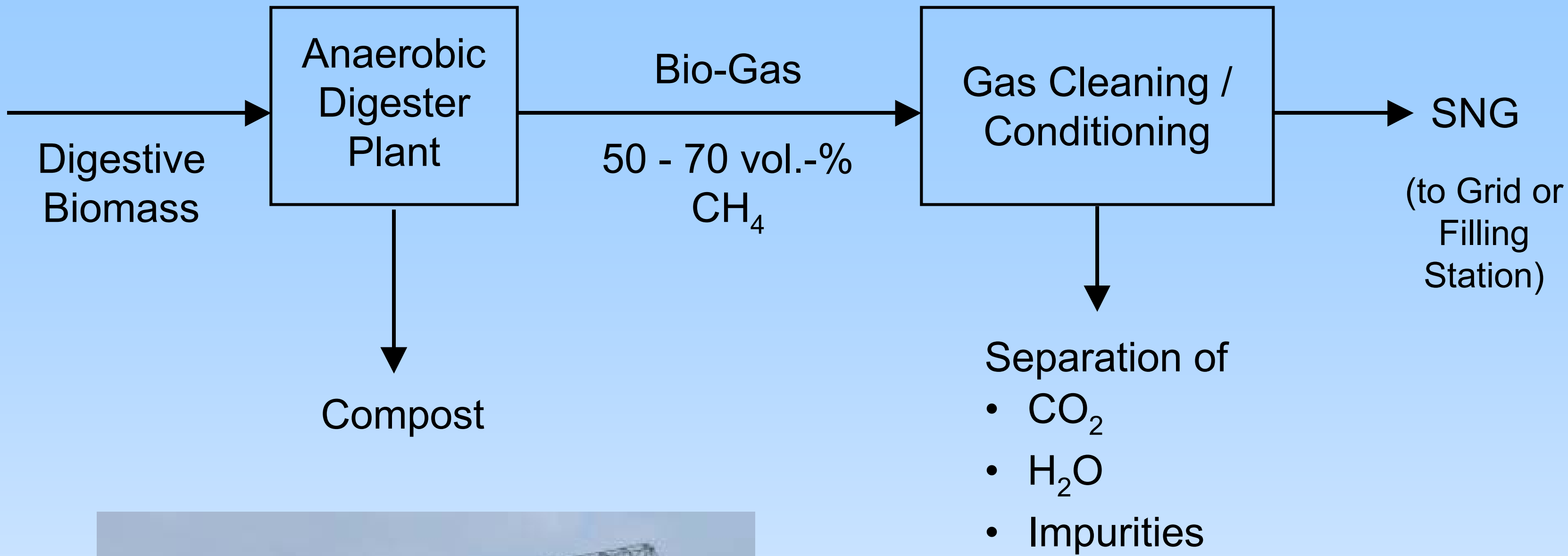

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AER-Process:

Thermochemical Biomass Conversion to Hydrogen

- Absorption Enhanced Reforming
- Gasification of Biomass to a Product Gas with a Hydrogen Content > 70 Vol.%

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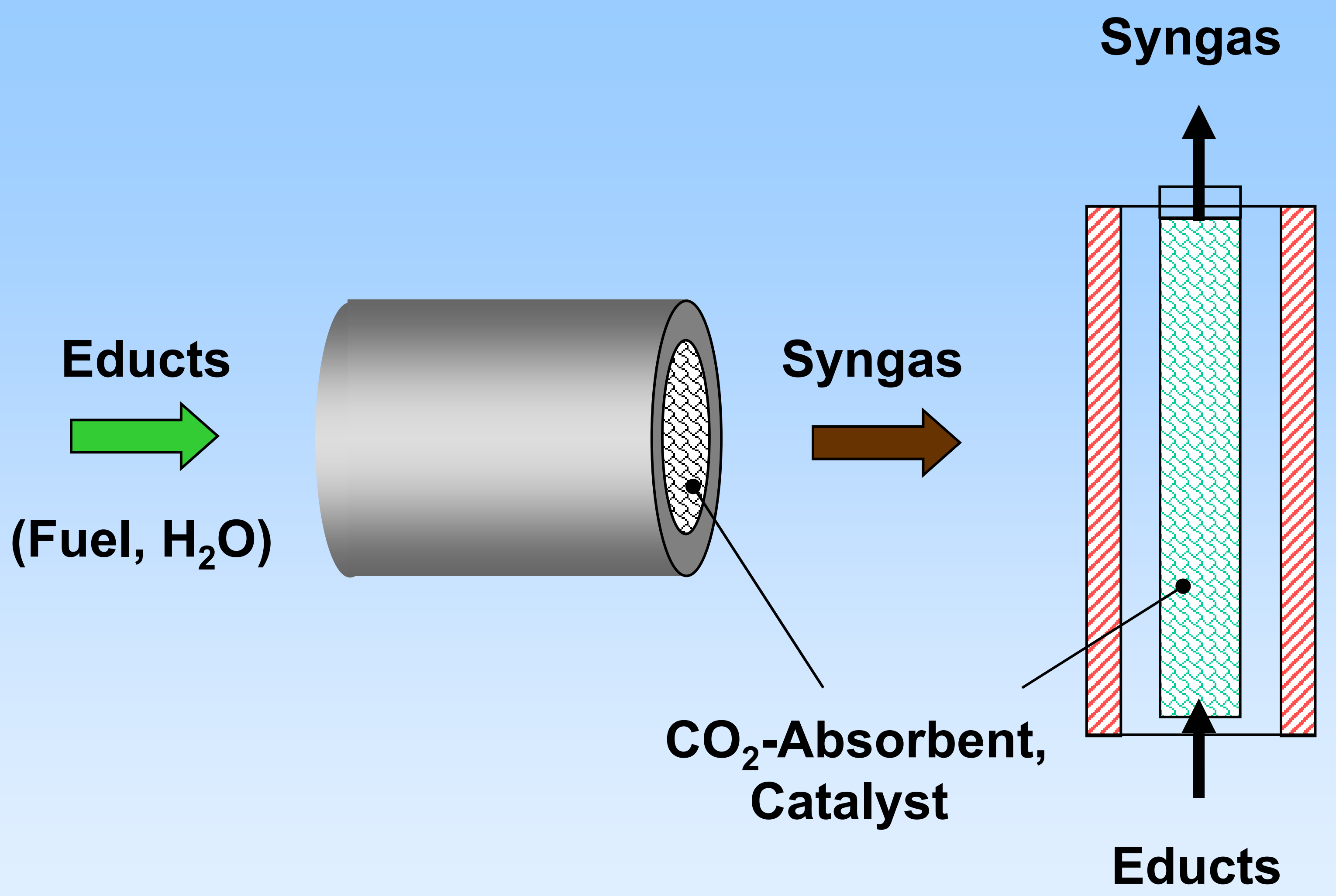
Thermochemical Fuel Conversion to Hydrogen: AER-Process in a Fixed Bed Reactor



- Goal: High H_2 Content in Syngas

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AER - Reactions (Absorption Enhanced Reforming)

Steam Reforming / Gasification of Biomass

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

CO Shift Reaction

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

Combined with a HT-CO_2-Absorption

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

Overall (600 - 700 °C, 1 bar)

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

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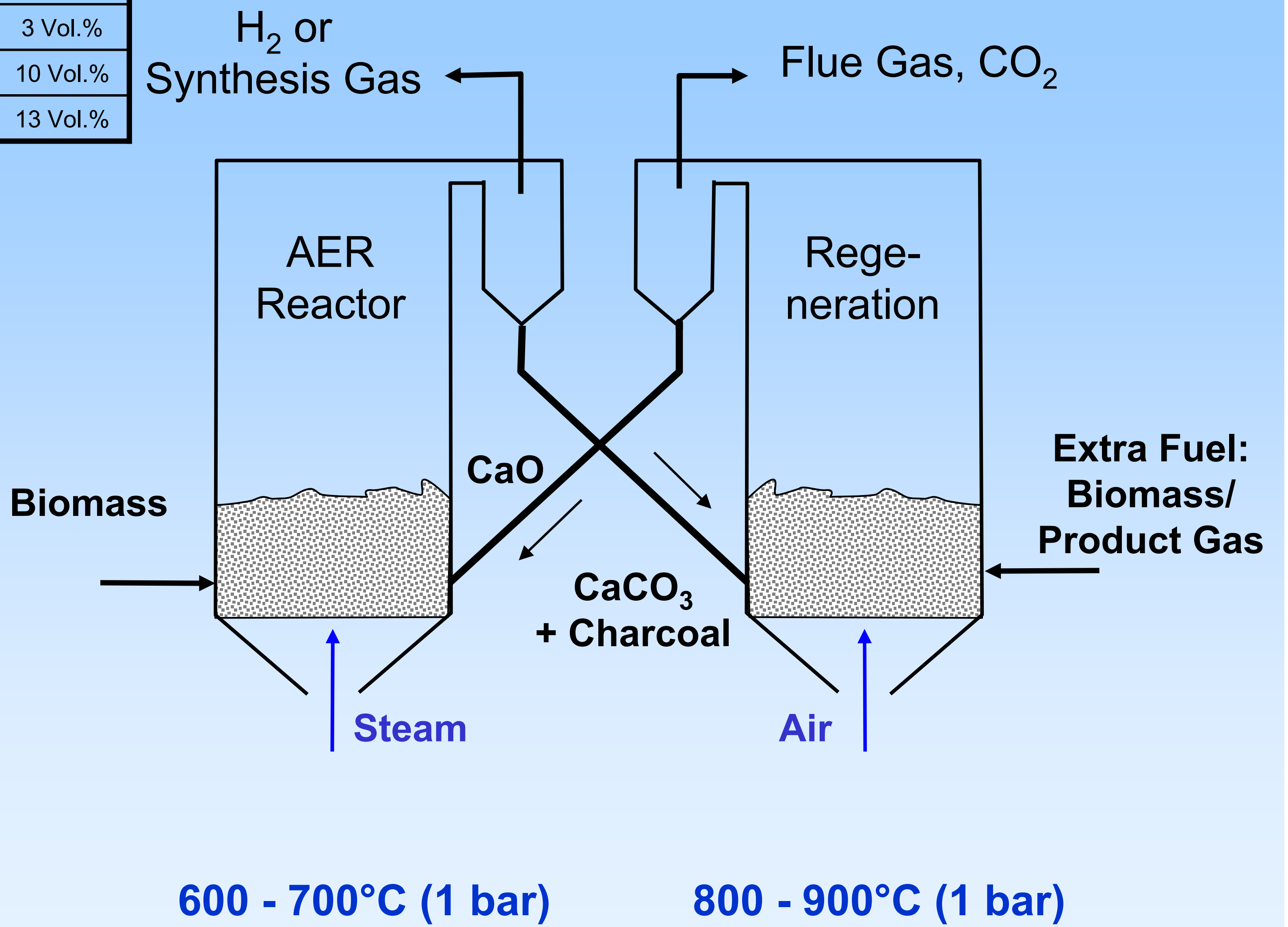
Biomass Gasification: AER Combined Fluidized Bed Process

H_2	68 Vol.%
CO	3 Vol.%
CO_2	10 Vol.%
CH_4	13 Vol.%



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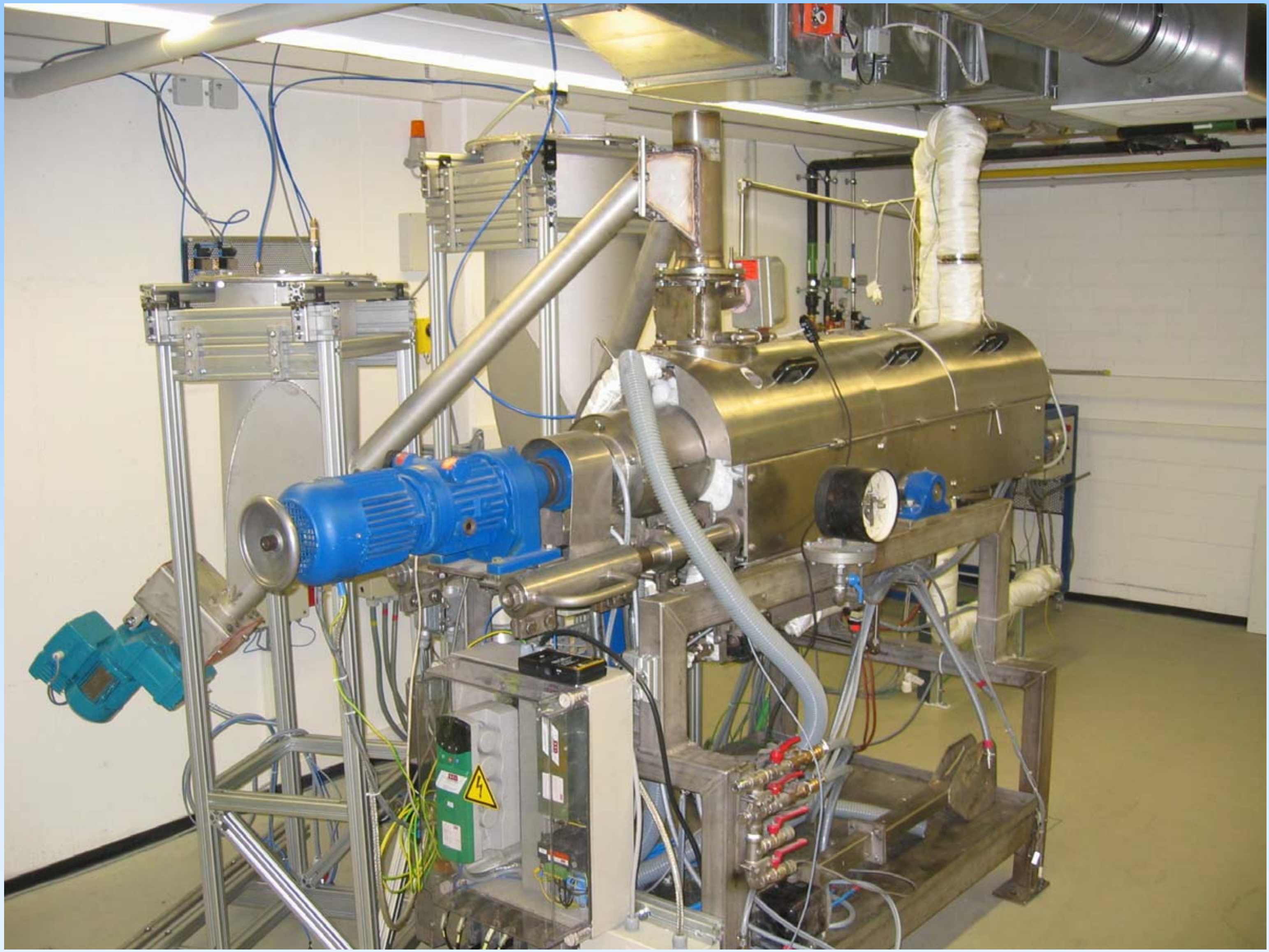
AER

Moving Bed Reactor: Pyrolysis Plant (AER Gasification of Wood Pellets)



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Fluisised Bed Reactor for CO_2-Absorption / -Desorption Experiments

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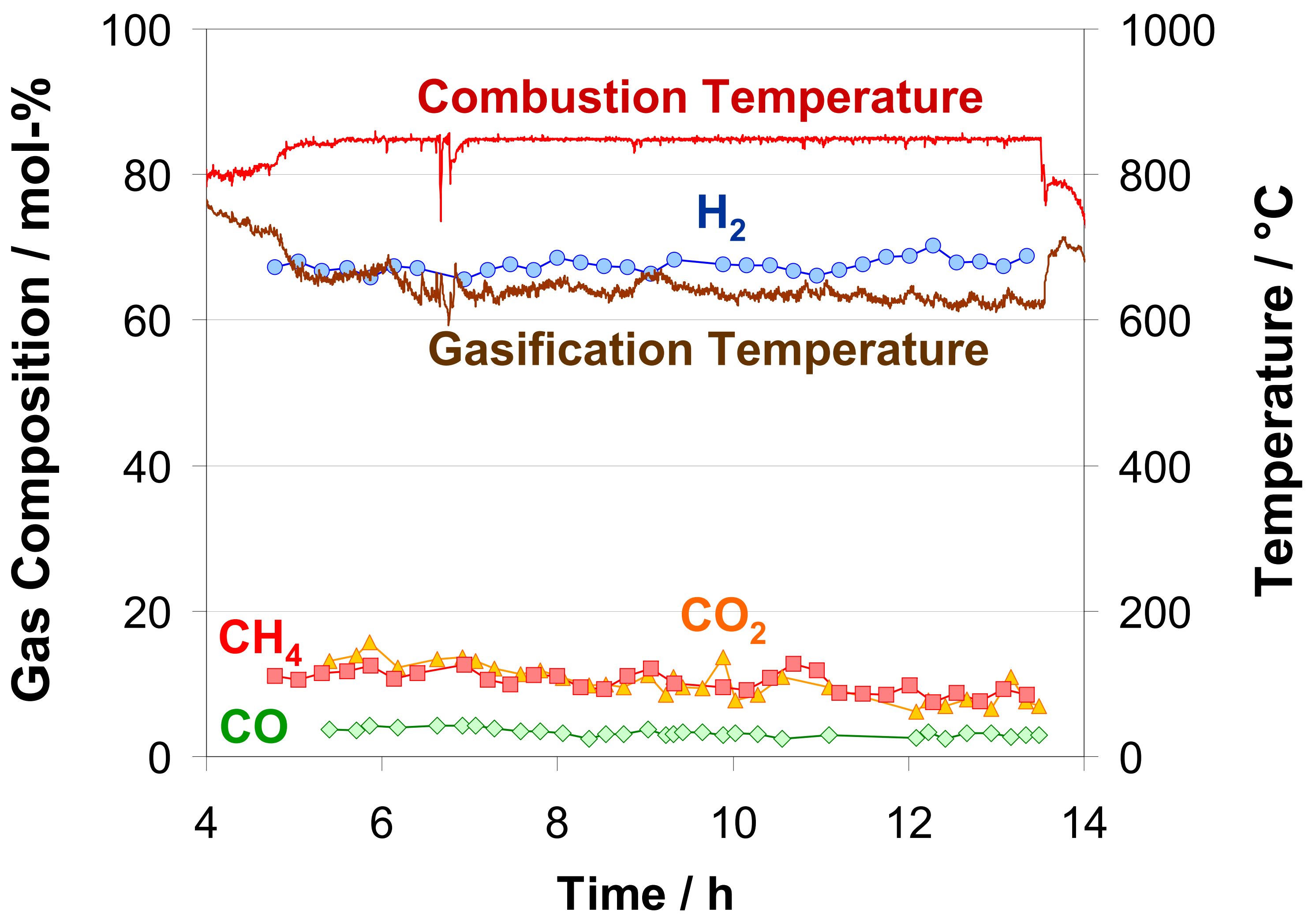
Results AER-GAS I: FB Product Gas Composition and Temperature versus Time

AER-Wood-Gasification; Bed-Material: Absorber & Ni-Olivine, FICFB - Gasifier: 100 kW_{th}



Source: Vienna Technical University

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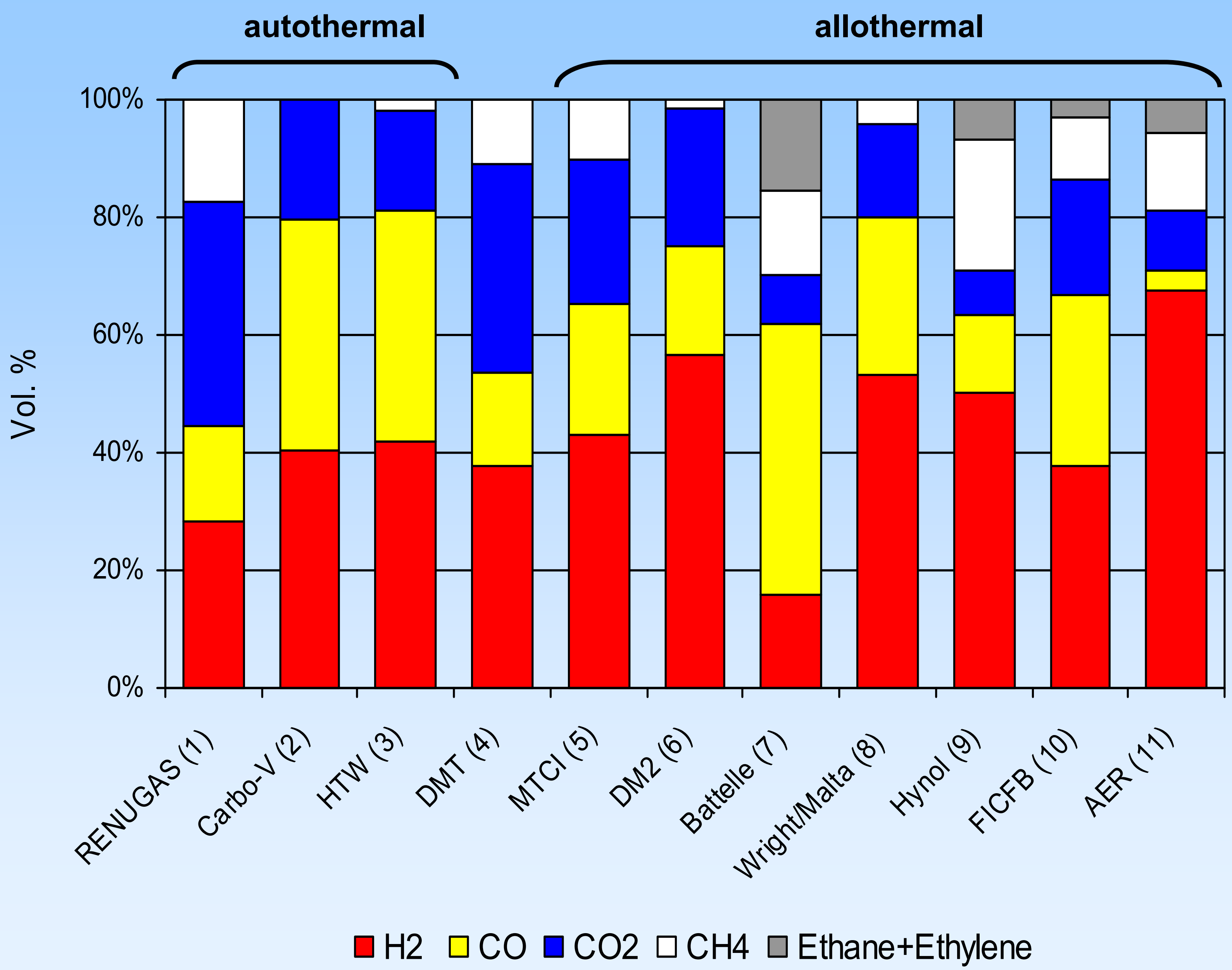
Results AER-GAS I: Highest H_2 Content in Producer Gas of Biomass Gasifiers



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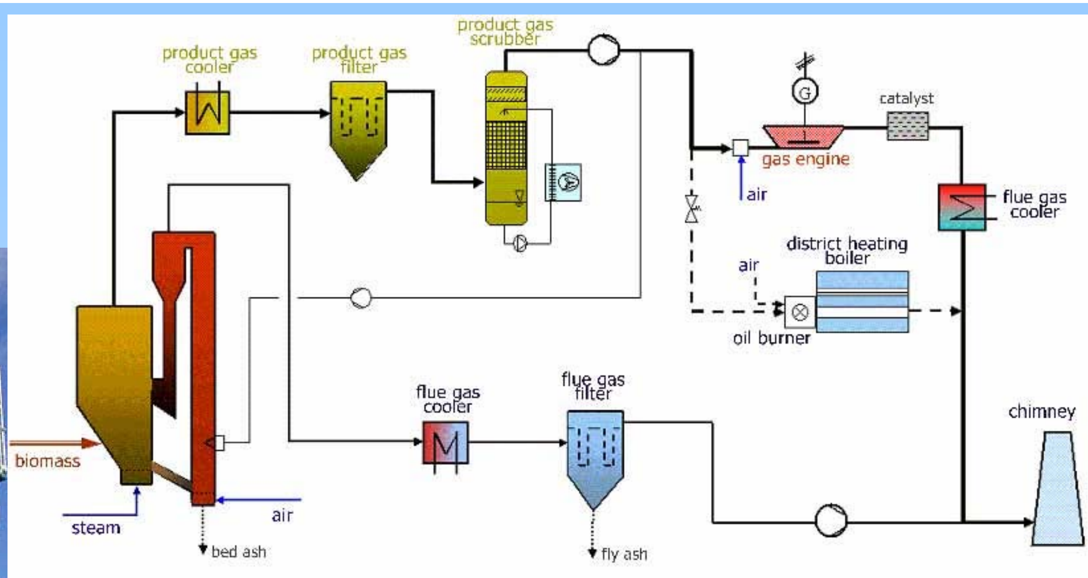
AER-GAS II: Test of AER-Process in Biomass 8 MW_{th} Power Plant Güssing / Austria



8 MW_{th} - 2 MW_e

Source: EEE

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AER-Gas II Consortium

ZSW	Sorbent Investigation (TGA), Tar Removal
ICE-HT	Sorbent Investigation and Improvement
IFE	Sorbent Investigation and Improvement
UOC	Catalytic Bed Materials Investigation
PAUL SCHERRER I PSI	Catalyst Investigation, *in situ* Tar Measurement
IVD	Fluidised Bed AER Reaction, Tar Mechanisms
Institute of Chemical Engineering	Fluidised Bed AER Reaction with Internal Regeneration
BKG	Test Campaign Power Plant Guessing
GE Jenbacher	Gas Engine for AER Product Gas

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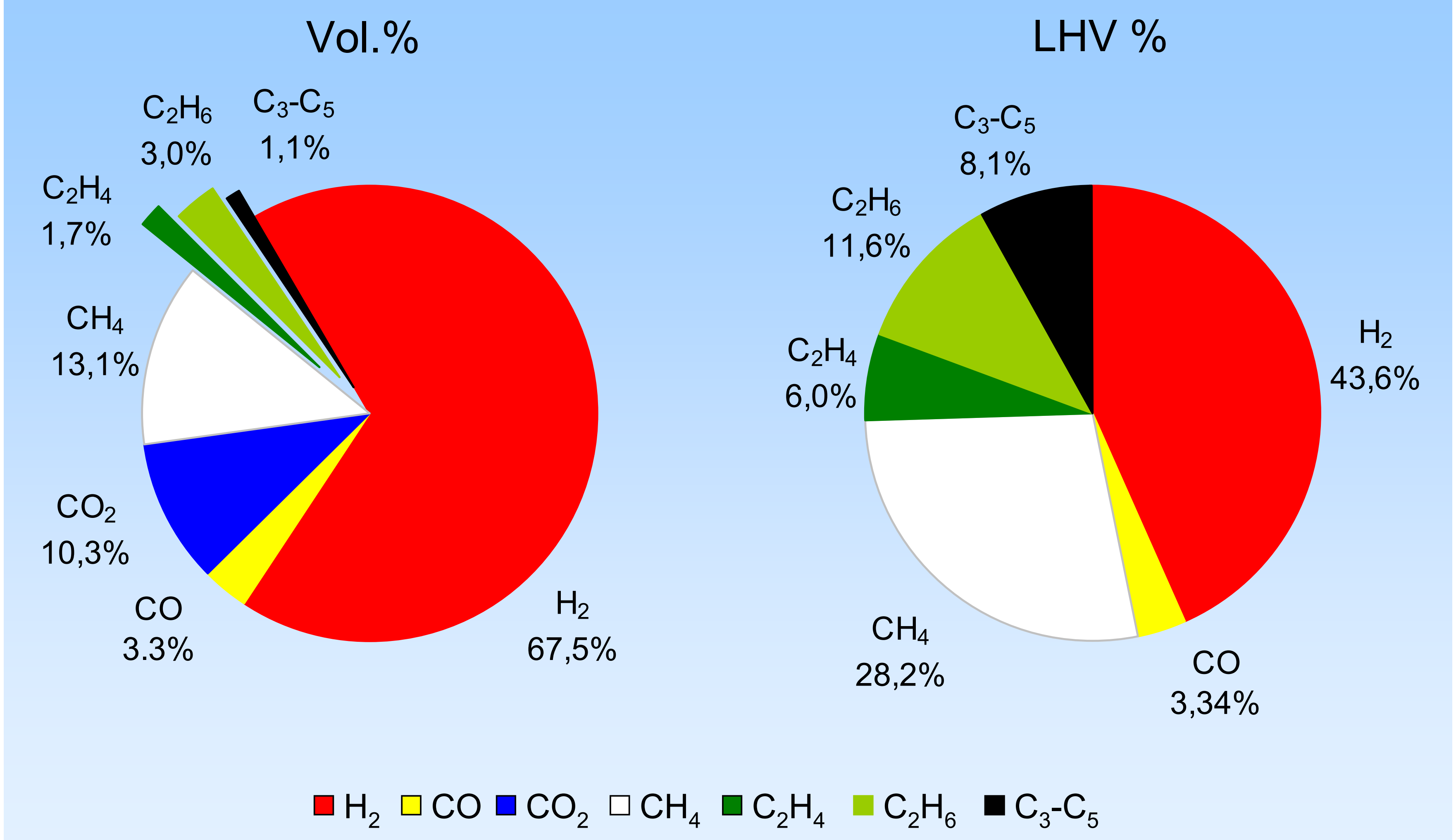
Product Gas from AER Biomass Gasification



SNG from AER-Gasifier

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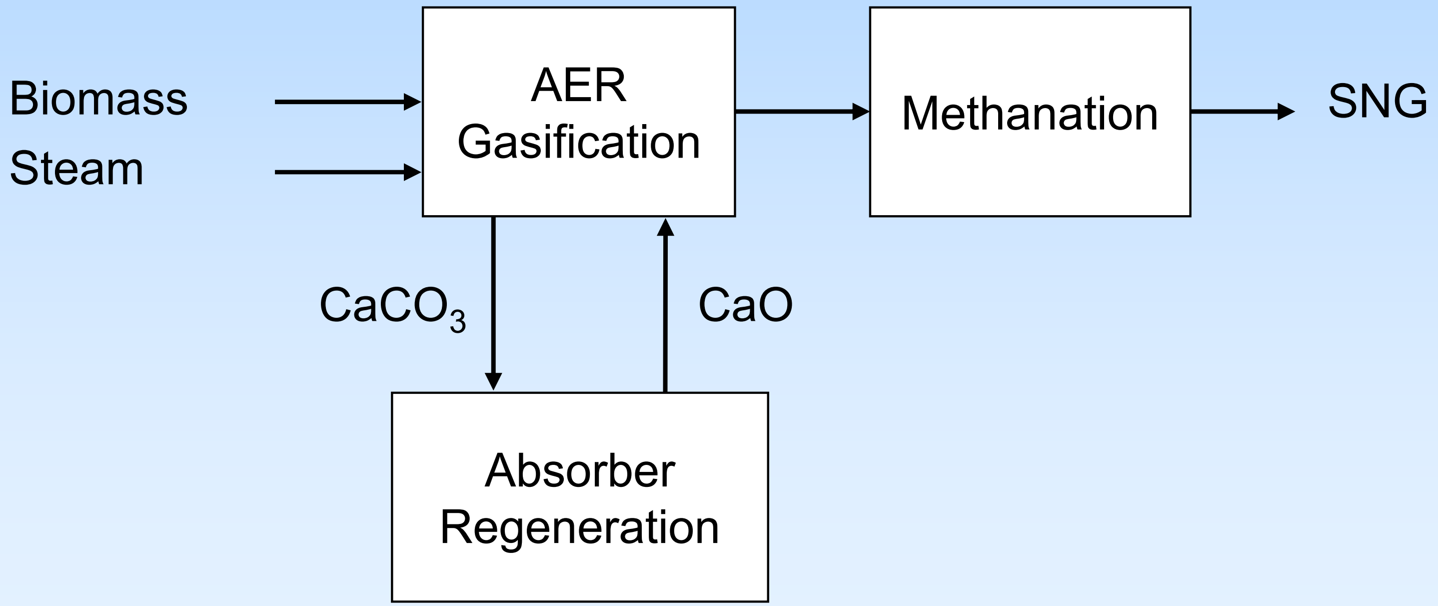
- High Quality SNG from Adjusted Bio-Syngas in 1 Process Step
- Energy Efficient Process
  - Low Gasification Temperature → High C_1-C_3 Content
  - Only a Part of the Bio-Syngas is Methanised (50 % of LHV)



AER: Absorption Enhanced Reforming

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AER

Methanation of CO_x in Bio-Syngas

$CO + 3\ H_2 \rightarrow CH_4 + H_2O$

$\Delta H_{298K} = -\ 206.158\ kJ/mol_{CH4}$

$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$

$\Delta H_{298K} = -\ 165.475\ kJ/mol_{CH4}$

$2\ CO + 2\ H_2 \rightarrow CH_4 + CO_2$

$\Delta H_{298K} = -\ 246.841\ kJ/mol_{CH4}$

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AER

Goal of the AER Biomass Gasification Process

- **Innovative Process with**
  - **70 Vol.-% H_2** in Raw Gas
  - **> 15 Vol.-% CH_4** (+ C_nH_m) in Raw Gas
  - **Low Tar Content in Raw Gas** < 500 mg/m_{NTP}^3
  - Utilisation of **Low Rank Biomass** (e.g. Straw)
- **Poly-Generation from Biomass**
  - **Electricity** *(Gas Engine; Future Option: MCFC)*
  - **District Heat**
  - **Fuel** *(Future Option: H_2, SNG, Syngas)*

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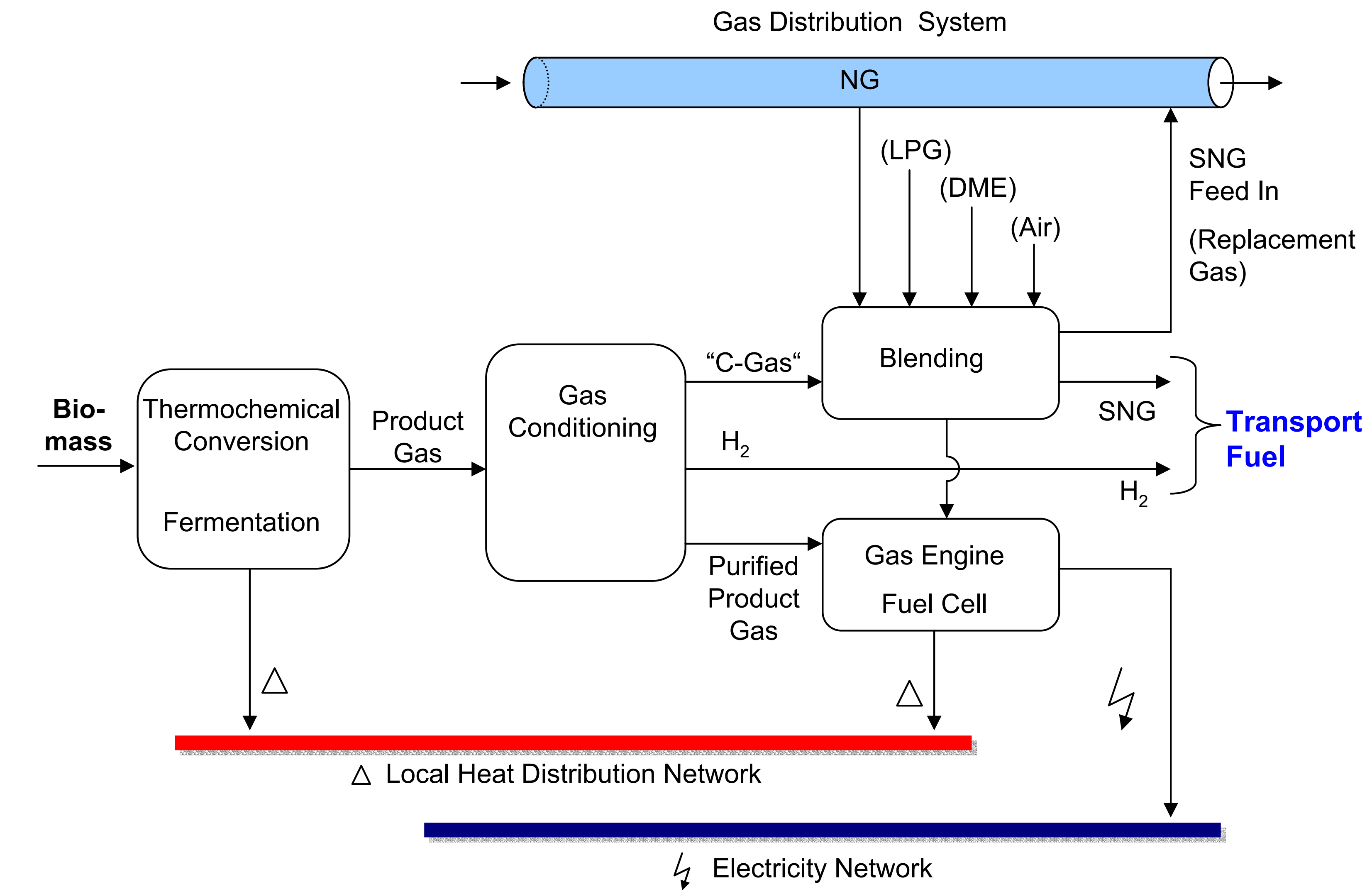
Poly-Generation Concept: Electricity, Heat and Transport Fuel from Biomass



ReFuels 4 FCs

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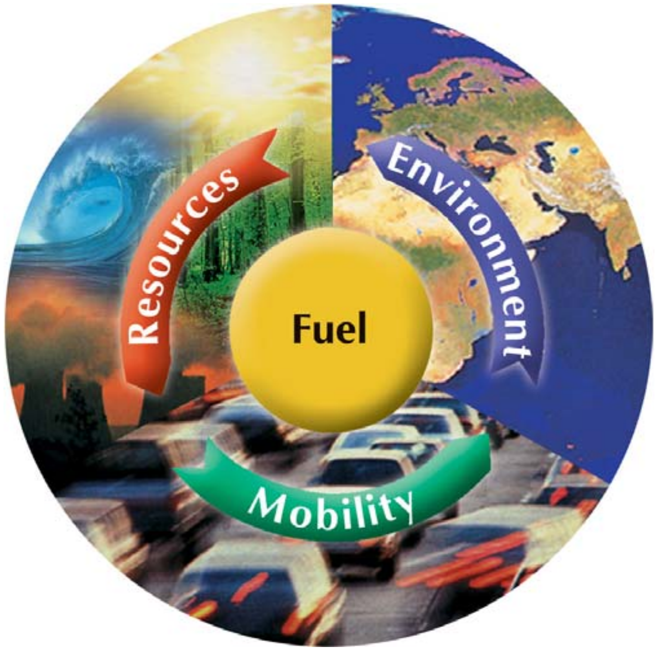

Contents:

Motivation
Biomass Resources for ReFuels
Promising ReFuels
Utilisation of (Re)Fuels in FCs (“bw-cell”)
ReFuel Production
Outlook

Centre for Solar Energy and Hydrogen Research
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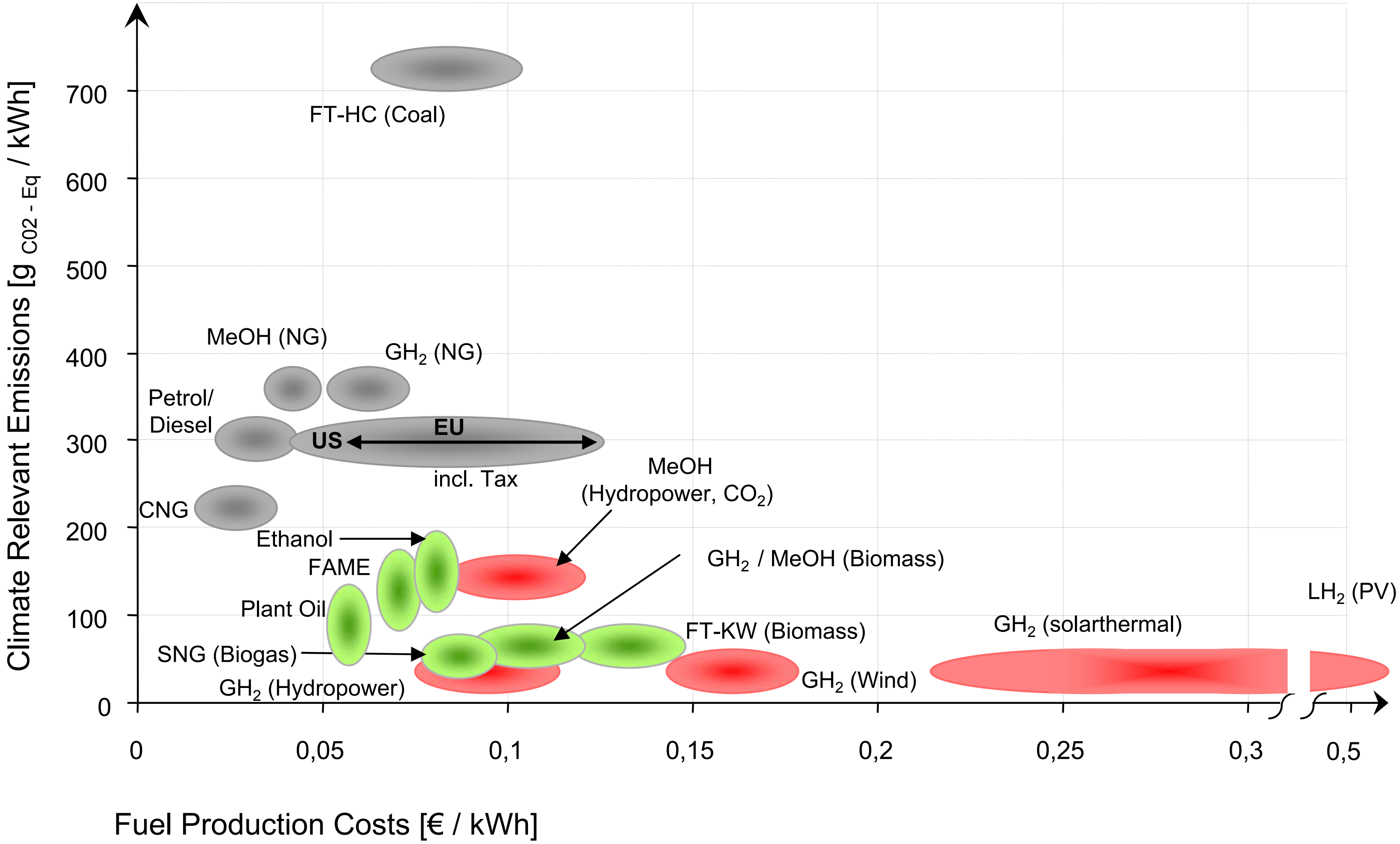
Climate Relevant Emissions and Costs



What are the best ReFuels 4 FCs ?

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- Road Transport

  ⇒ Hydrogen

- Gas Grid-Bounded Stationary Fuel Cells

  ⇒ SNG

- Non Gas Grid-Bounded Stationary Fuel Cells

  ⇒ MeOH, DME, EtOH ????

- "4C"-Market

  ⇒ Hydrogen, Methanol

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Open Questions

- What is the Optimum Plant Size for ReFuel Production (Centralized or Decentralized) ?

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Proceedings of ReFuelNet-Conference

Order:

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An Interesting Discussion !

Thanks for Your Kind Attention.