Großtechnische Produktion von Wasserstoff: Stand der Technik und neue Entwicklungen

Materials Valley Workshop

Hanau, 12. Mai 2011

Agenda

- Air Liquide S.A.
  - Lurgi GmbH
    - Air Liquide Forschung- und Entwicklung GmbH
- Wasserstofferzeugungsverfahren
- Steam Reforming
- Alternativen

World leader in gases for industry, health and the environment

- **Total revenue 2010 :** €13,5 billion
  - **80% outside of France**
  - **More than 20% in Americas**
- **Over 1 million customers in** 80 countries
- 43,600 employees
- **Highly international management**
- **42% of Air Liquide's revenue comes from gas applications which preserve life and the environment**
- **Over 60% of Air Liquide's R&D budget devoted to developing technologies designed to preserve the environment and life**

Energy

Environment

Health

High-Tech

Developing economies

Air Liquide's Research & Development

- Proactive and credible – Driver for innovation
- Global – 3 continents (centers, satellites, pilot plants)
- Network – 8 main R&D centers (France, Germany, USA, Japan)
- Commitment – annual innovation budget of 218 Mi€
- 2 500 inventions protected by 8 400 patents

International network of R&D centres

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DRTC *(USA)*

CRCD *(France)*

CTAS *(France)*

FRTC *(Germany)*

Gellep *(Germany)*
Satellite – R&D Teams in AL facility

ALL *(Japan)*

ITRI *(Taiwan)*
Satellite –R&D Teams at our customers' facilities

Houston *(USA)*
Satellite –R&D team in AL IM

Group R&D centres

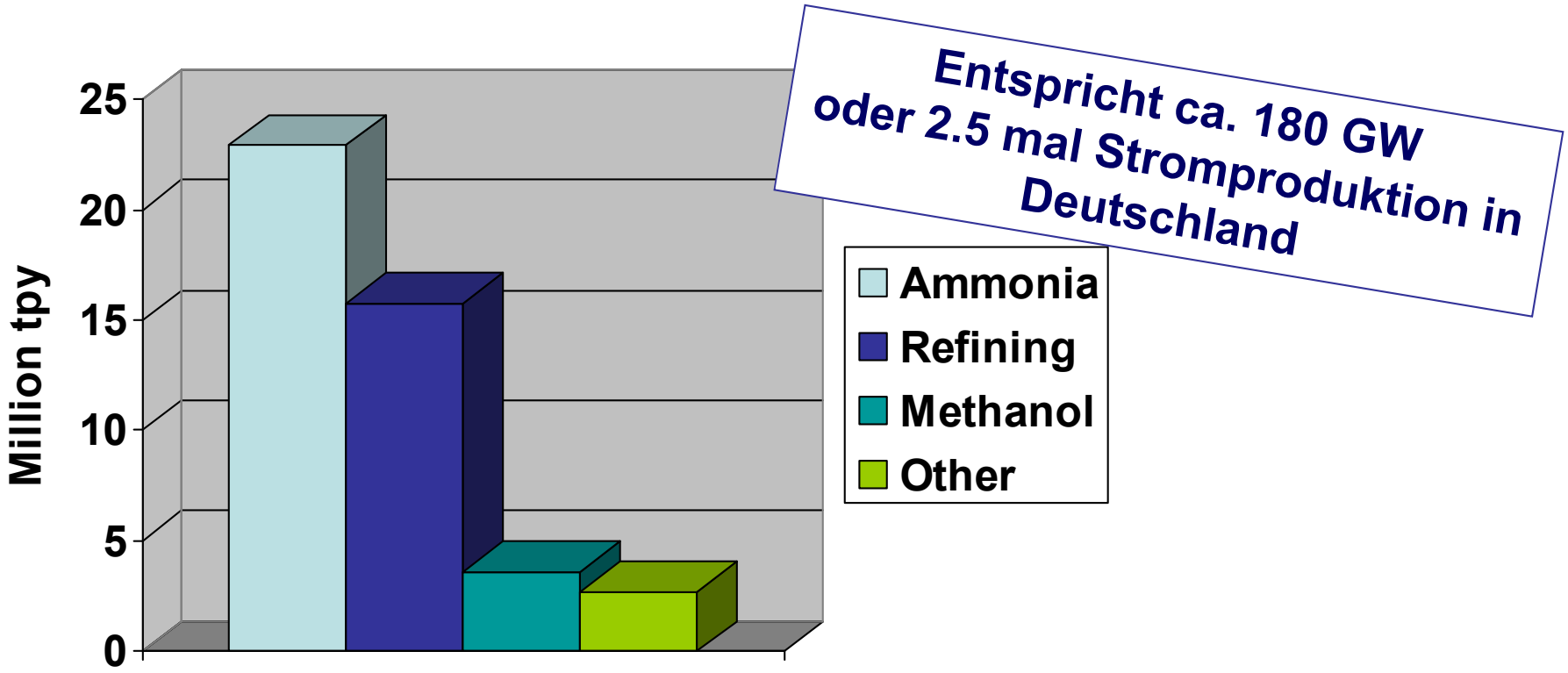
SEPPIC

Laboratoires ANIOS

S&M Schülke & Mayr

Lurgi

Wasserstoffverbrauch nach Segment



Quellen für Wasserstoff

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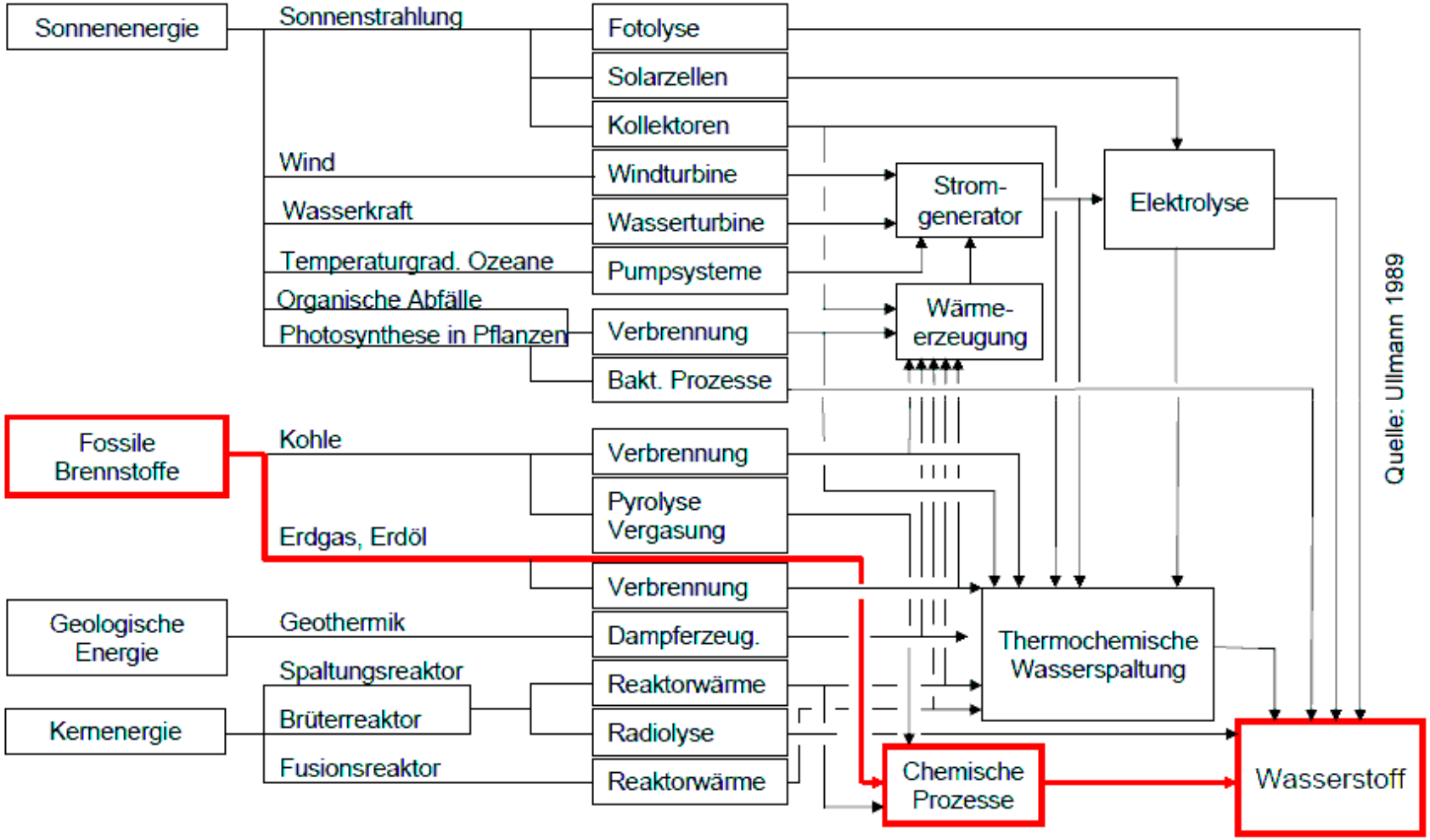
Primärenergiequellen, Rohstoffe u. Produktionsverfahren: Fossiler Hauptproduktionsweg

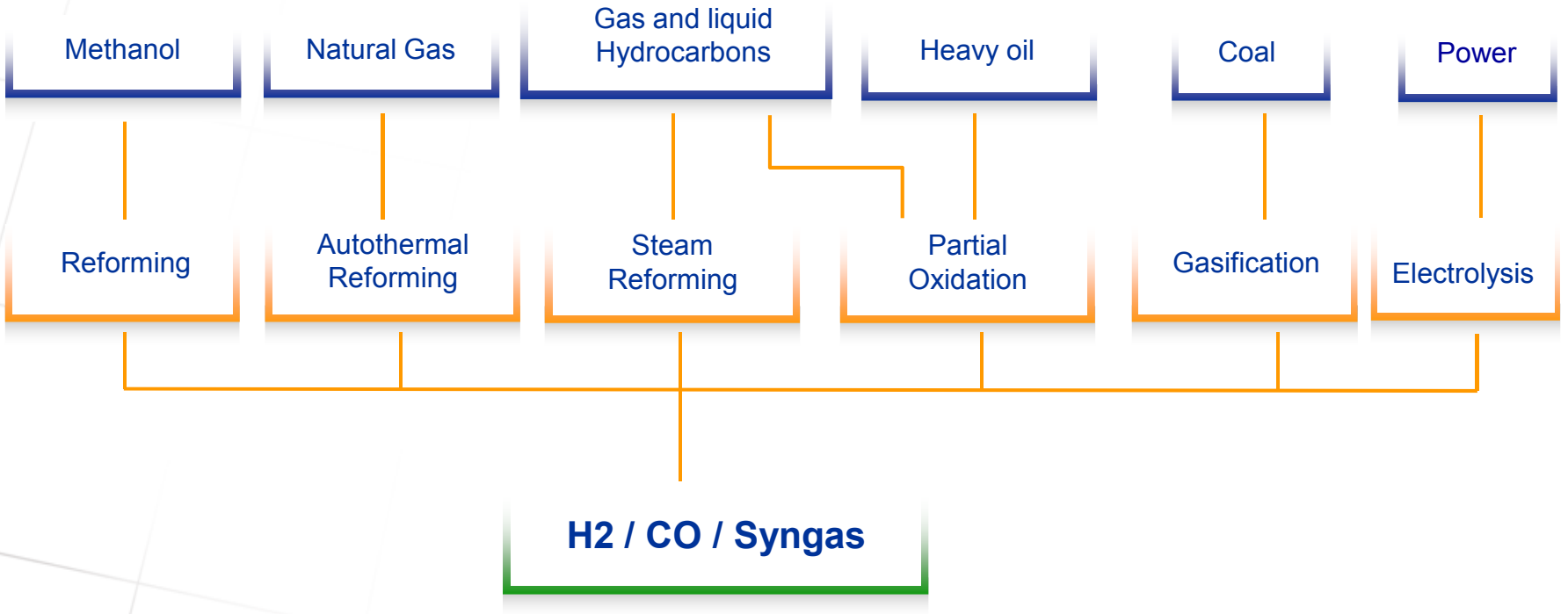


TUHH
Technische Universität Hamburg-Harburg
Dr.-Ing. Bernhard Neumann

Wasserstofftechnologie
Herstellung von Wasserstoff aus Kohlenwasserstoffen

Abb. 3

Ways to Hydrogen



Kommerzielle Wasserstofferzeugungstechnologien

- Steam Reforming
- Autothermal Reforming
- Combined Reforming
- Partial Oxidation / Multi Purpose Gasification
- Kohlevergasung
- Electrolyse
- Methanol-Reforming

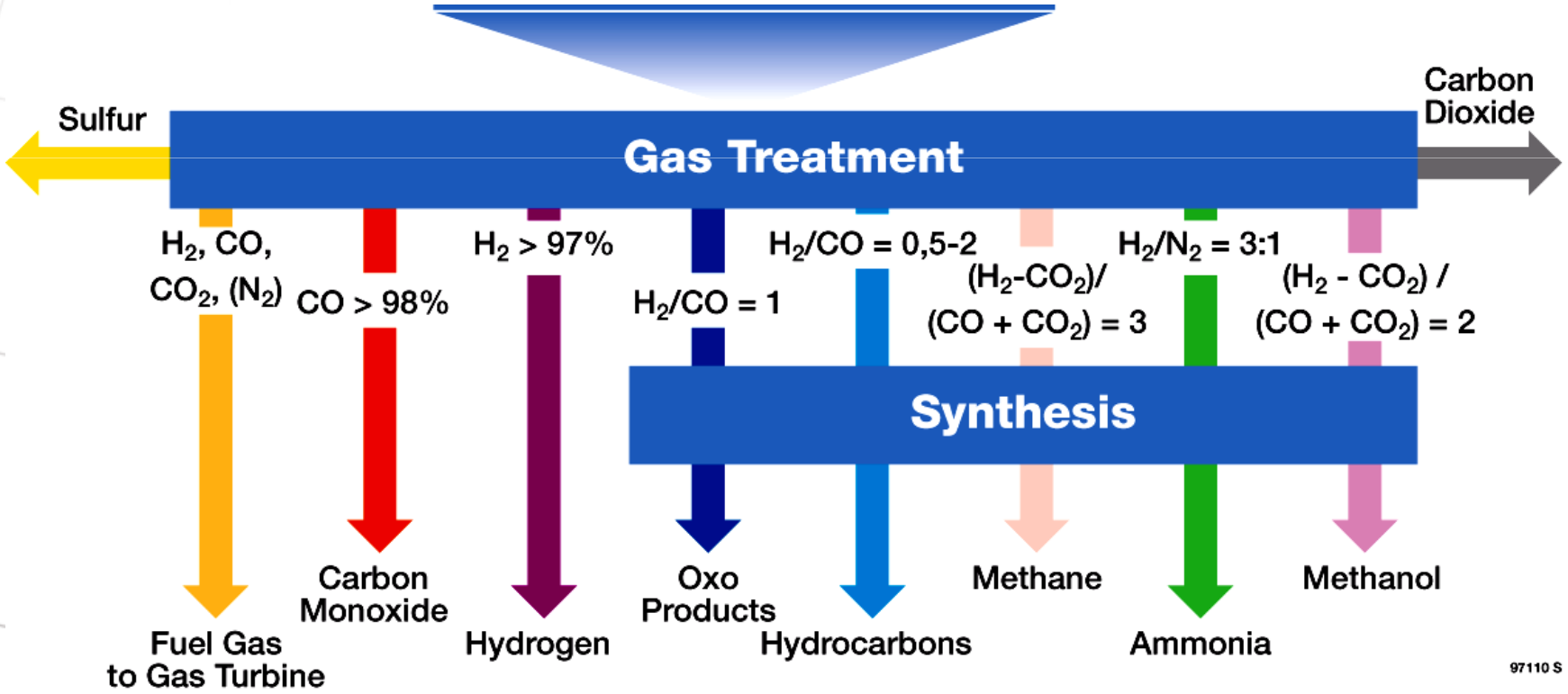
HyCO Projects – Process Feedstock

- **Steam Reforming / Autothermal Reforming**
  - Natural gas
  - LPG
  - Naphtha
  - Refinery off-gas
- **Partial Oxidation / Multi Purpose Gasification**
  - Natural gas
  - Residues
- **Gasification**
  - Coal
  - Biomass

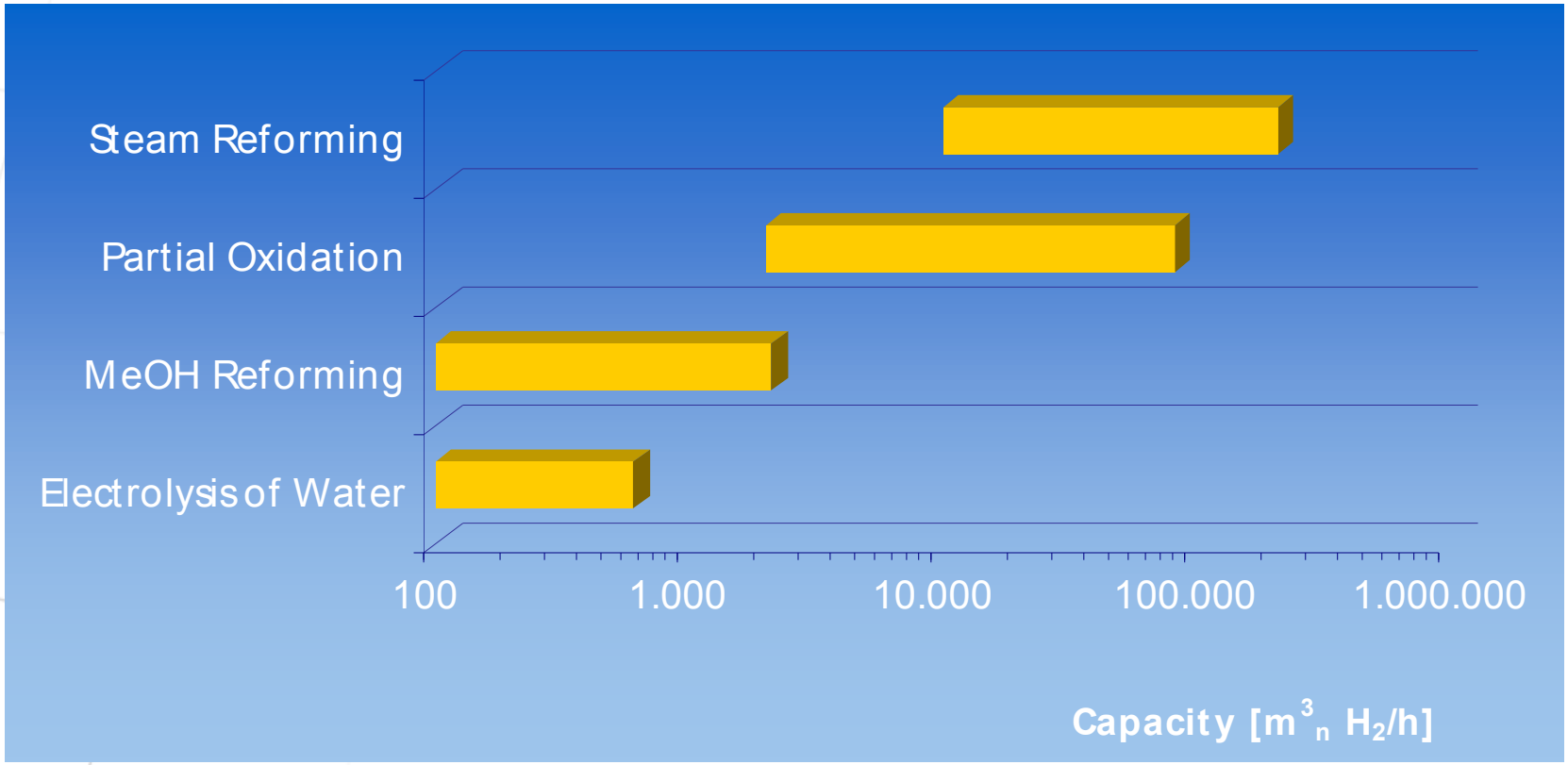
Downstream Products

The selection of the SG production technology depends mainly on:

- **Feedstock and oxygen availability and prices**
- **Plant size**
- **Downstream applications**



Typical Single-train Capacities



Syngas Generation Concepts

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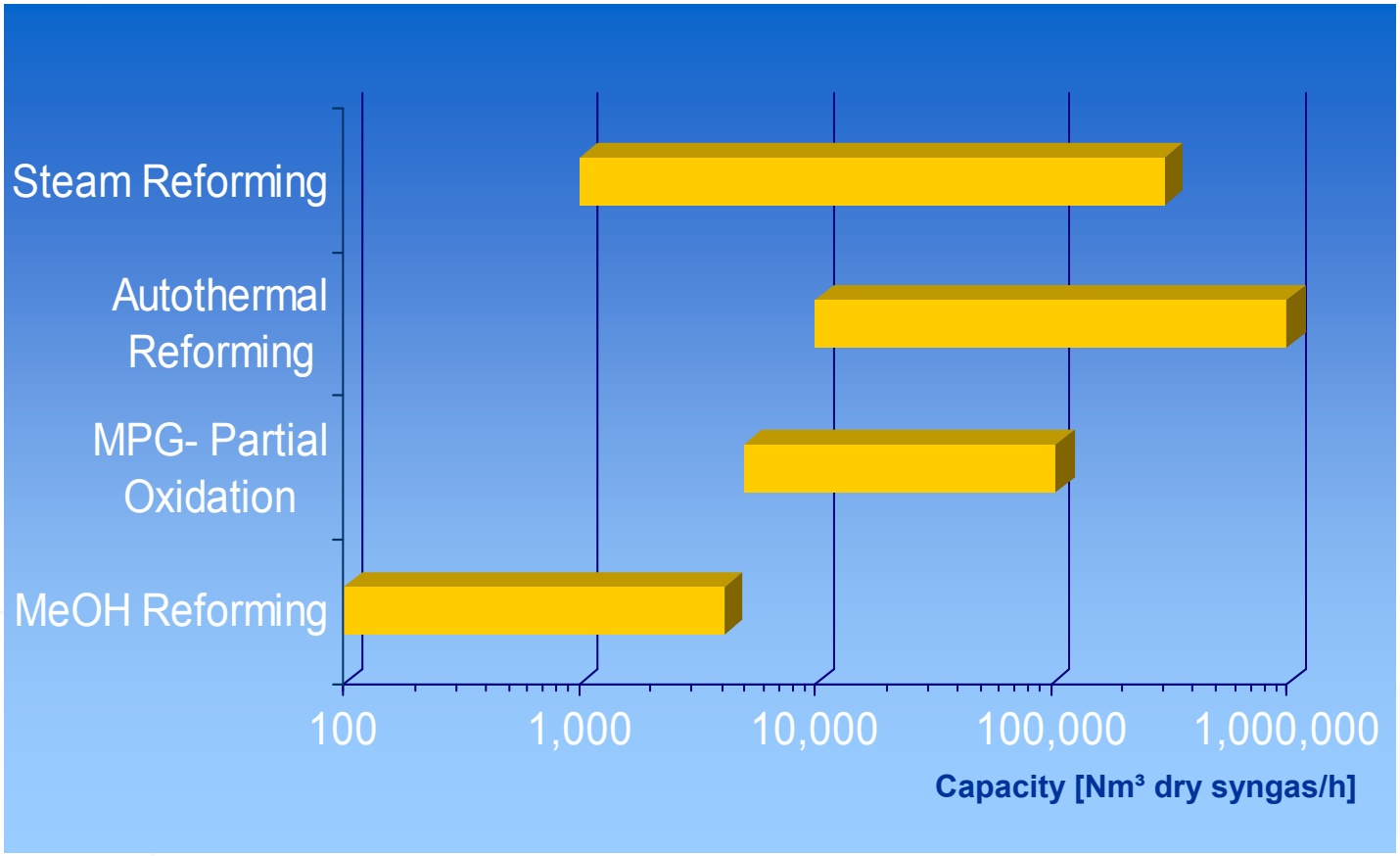
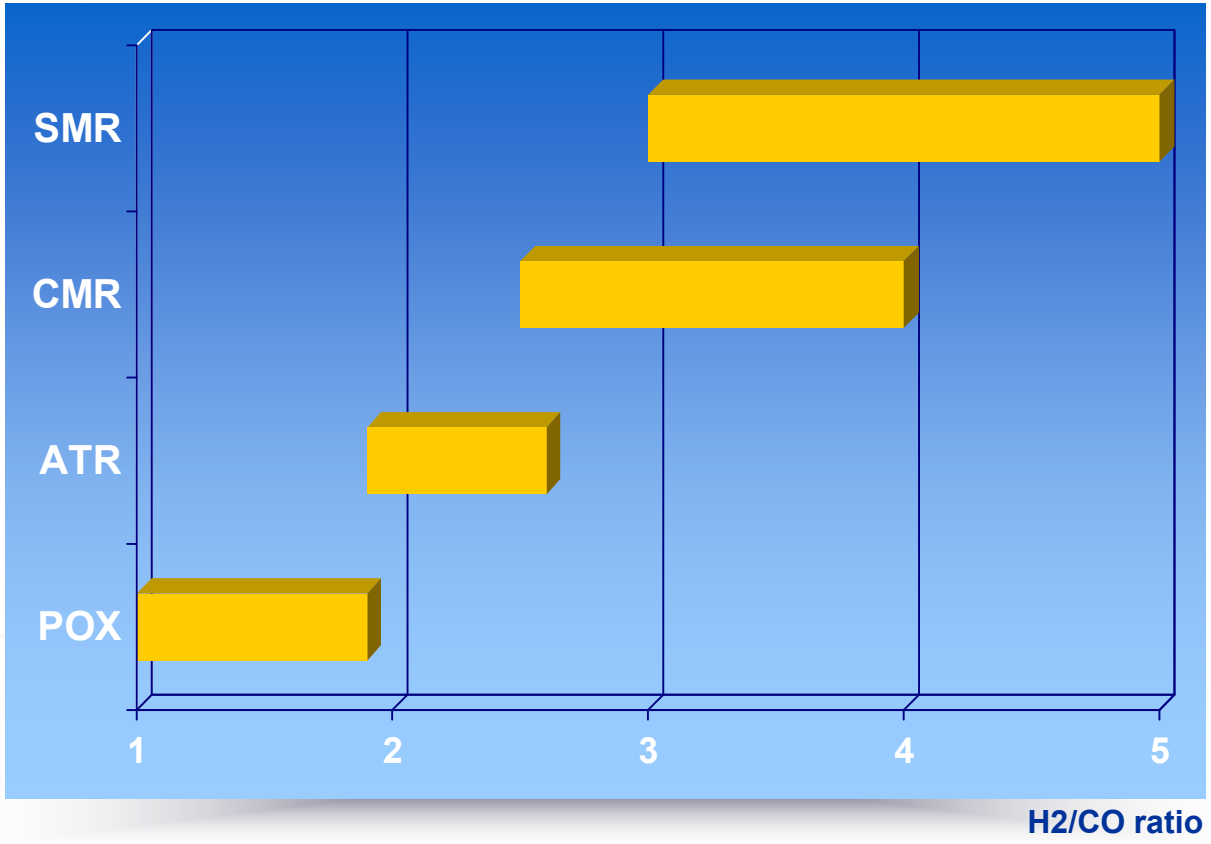
- **Typical single train capacities**



Syngas Generation Concepts

- **Achievable H_2/CO ratios for syngas generation**

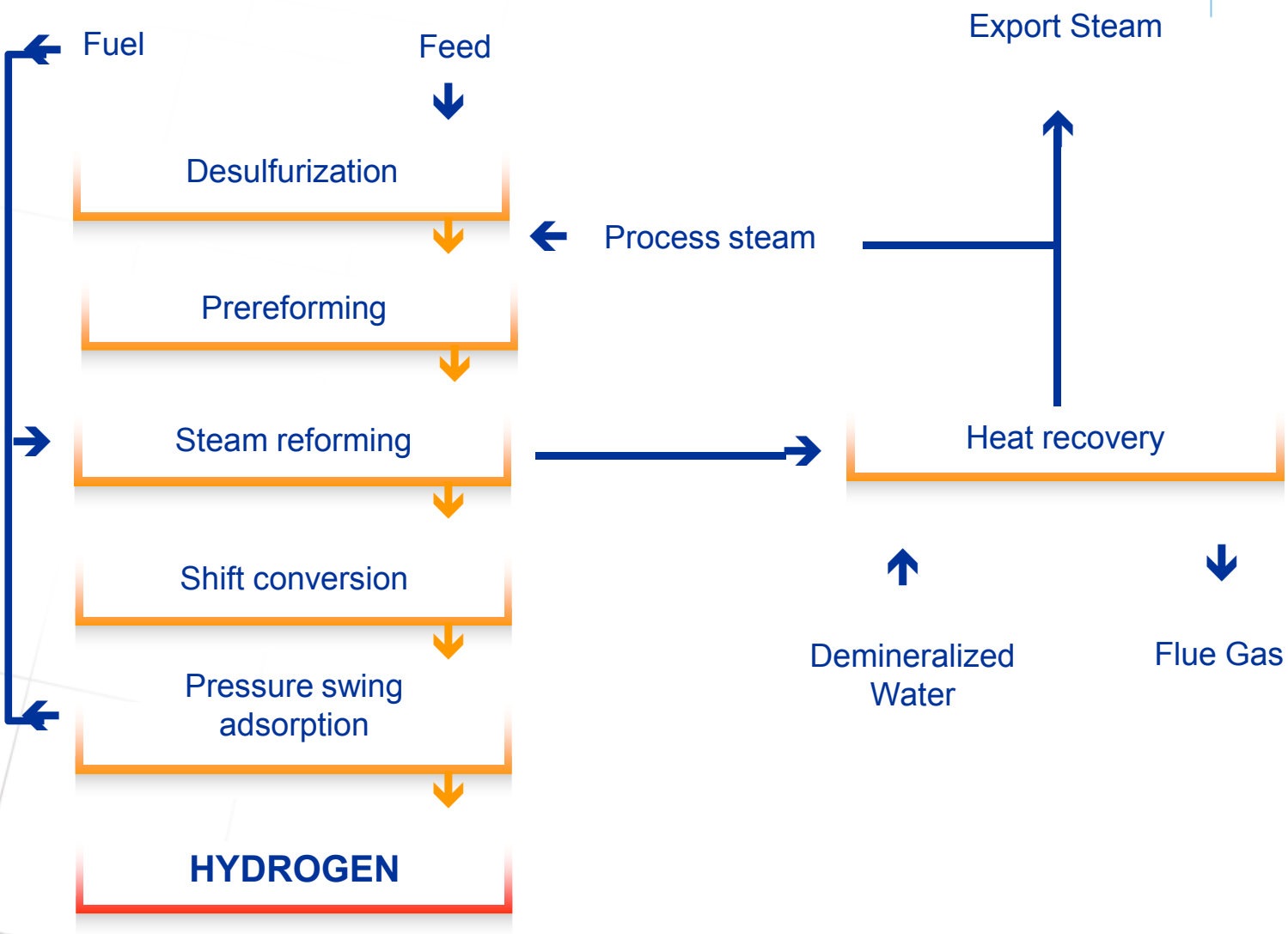


Feed Natural Gas

CMR= Combined Methane Reforming

Steam Reforming / SMR / Dampfreformierung

Steam Reforming



Desulfurization of Feedstock

$$S + H_2 \leftrightarrow H_2S$$

$$R-CH=CH-R' \leftrightarrow R-CH_2-CH_2-R'$$

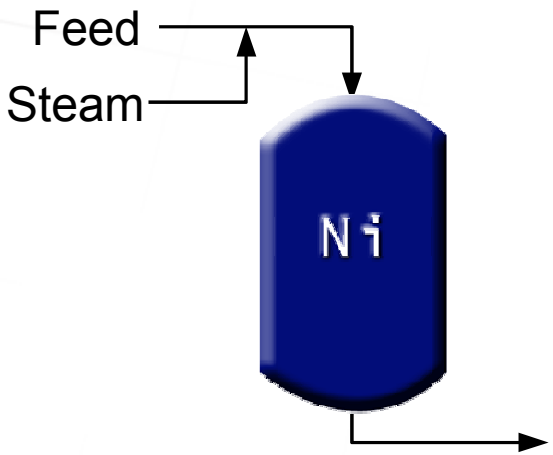
$$H_2S + ZnO \leftrightarrow H_2O + ZnS$$

H_2-content in feed: 2-5 vol.% → CoMo → ZnO → ZnO → **S-content at outlet: < 0.2 ppm**

Temperature: 350 - 400°C / 660 - 750°F

ΔT per % Olefins: 10°C / 18°F

Prereforming



$$C_nH_m + nH_2O \leftrightarrow nCO_2 + (n + m/2)H_2$$

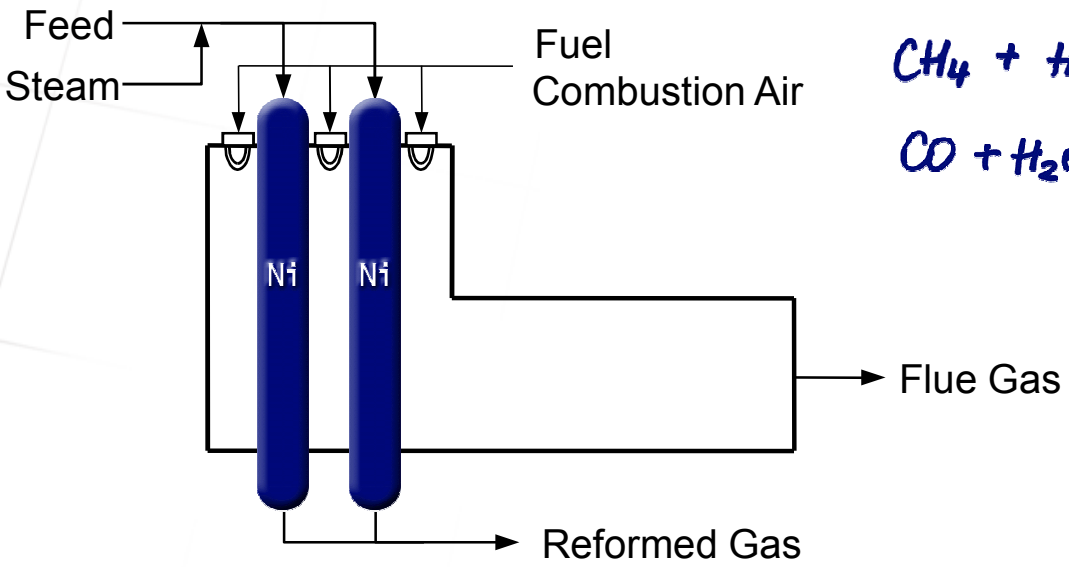
$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \text{ - HEAT}$$

$$CO + H^5O \leftrightarrow CO^5 + H^5$$

Temperature: **390 - 500°C**
735 - 930°F

H_2O/C: **1.1 - 2.0**

Steam Reforming



$$C_mH_m + mH_2O \leftrightarrow mCO_2 + (m + m/2)H_2$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 - HEAT$$

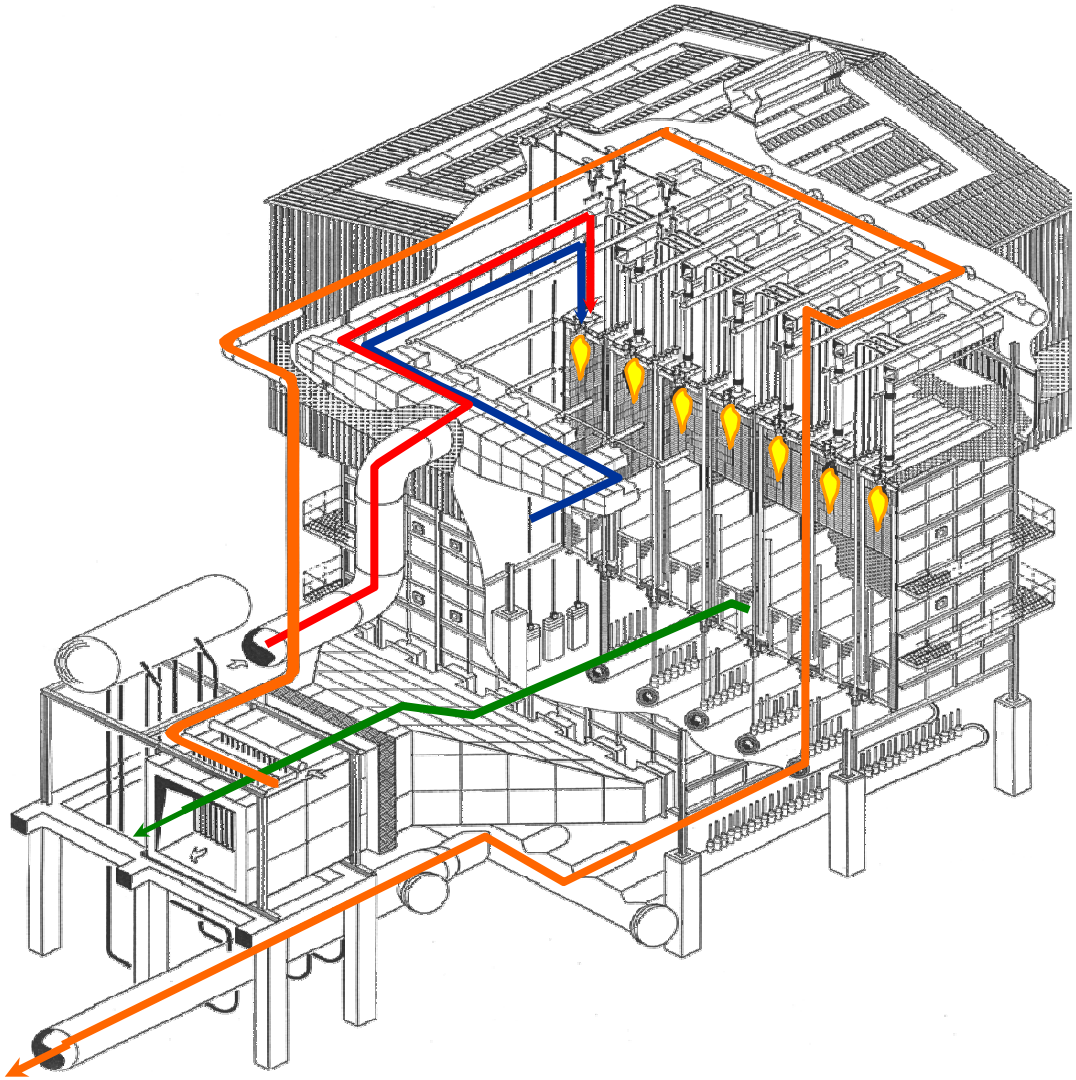
$$CO + H_2O \leftrightarrow CO_2 + H_2$$

Temperature: **700 - 950°C**
1290 - 1740°F

H_2O/C: **2.5 - 3.2**

Lurgi Steam Reformer®

- Process Gas
- Combustion Air
- Fuel Gas
- Flue Gas



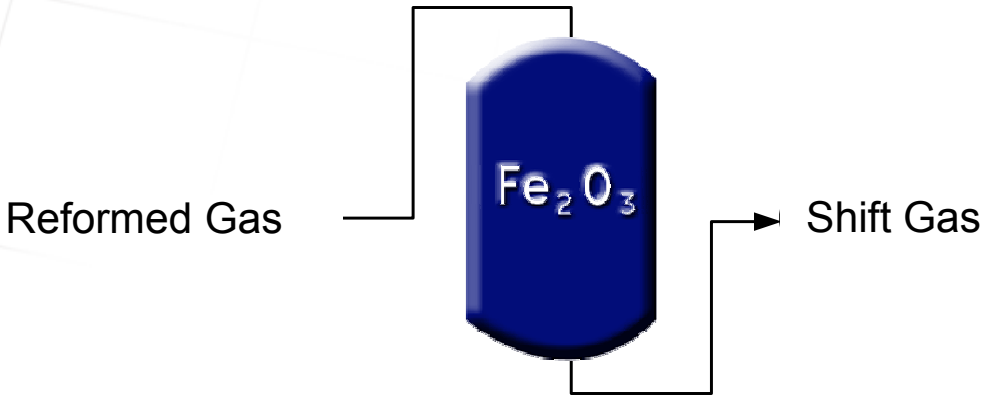
Lurgi Reformers

General Arrangement 1

Lurgi Steam Reformer ®

Reformerofen im Aufbau

CO-Shift



$$CO + H_2O \leftrightarrow CO_2 + H_2 + HEAT$$

Temperature: **320 - 400°C**
610 - 750°F

Temperature rise: **40 - 80°C**
72 - 144°F

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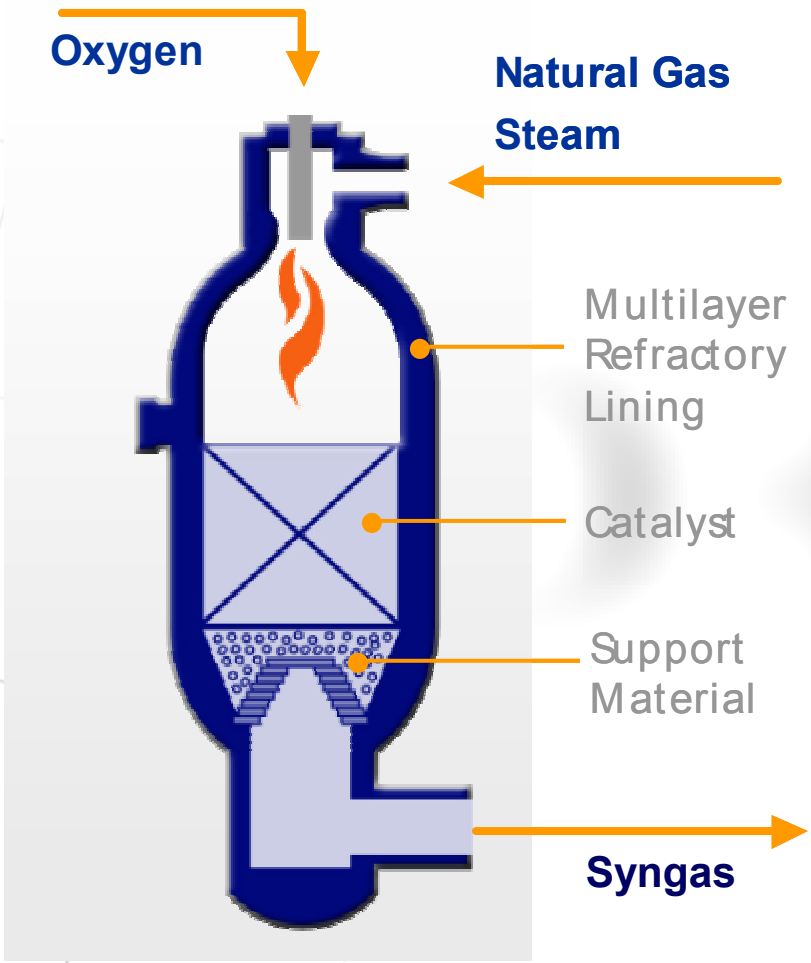
Sauerstoff basierte Verfahren

Autothermreforming (ATR)

Partielle Oxidation (Pox)

Technology – Autothermal Reforming



Combustion

$$CH_4 + 3/2\,O_2 \rightarrow CO + 2H_2O + HEAT$$

Catalytic reactions

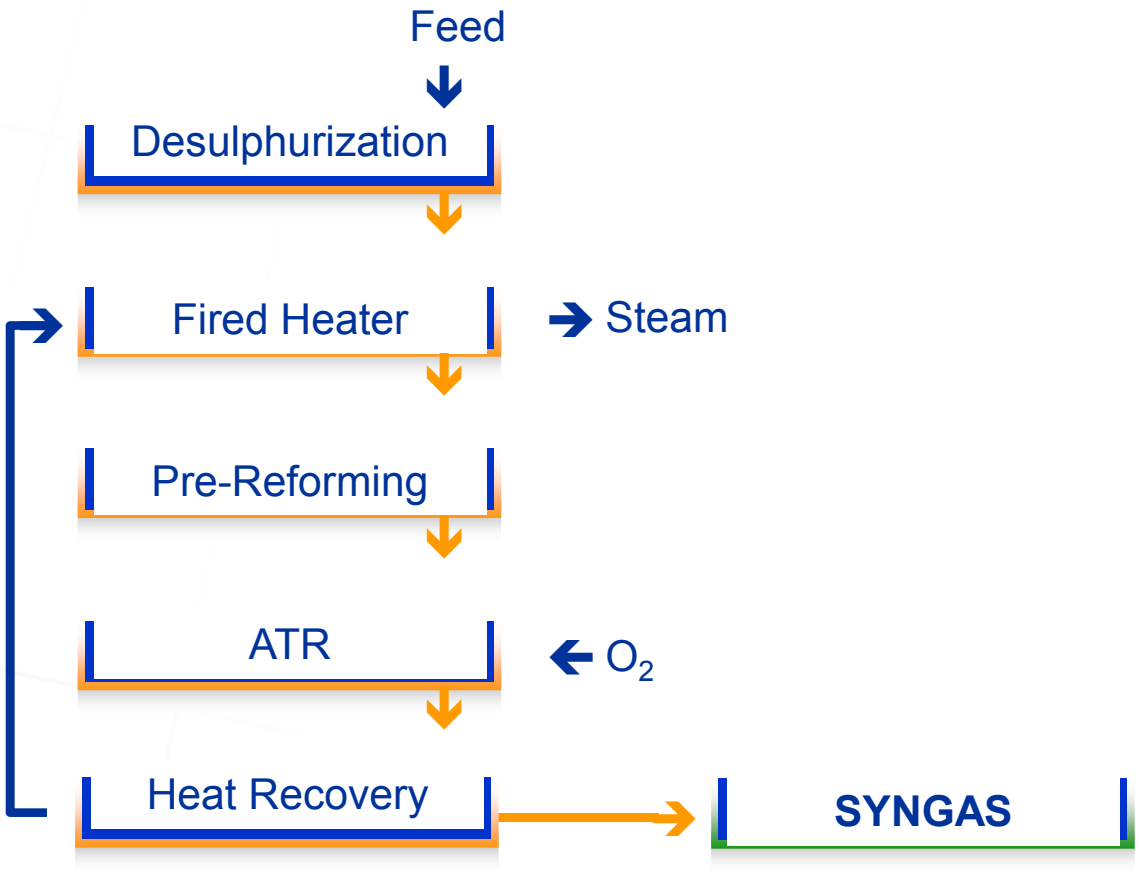
$$CH_4 + H_2O \longleftrightarrow CO + 3H_2 - HEAT$$

$$CO + H_2O \longleftrightarrow CO_2 + H_2 + HEAT$$

Temperature: **950–1050 °C**
1740 –1920 °F

Pressure: **30–40 bar**
435–580 psi

Autothermal Reforming



Vergleich ATR - SMR

Combined Reforming

Kaltim Methanol

2,000 mtpd

Start-Up 1998

Syngas Generation Concepts

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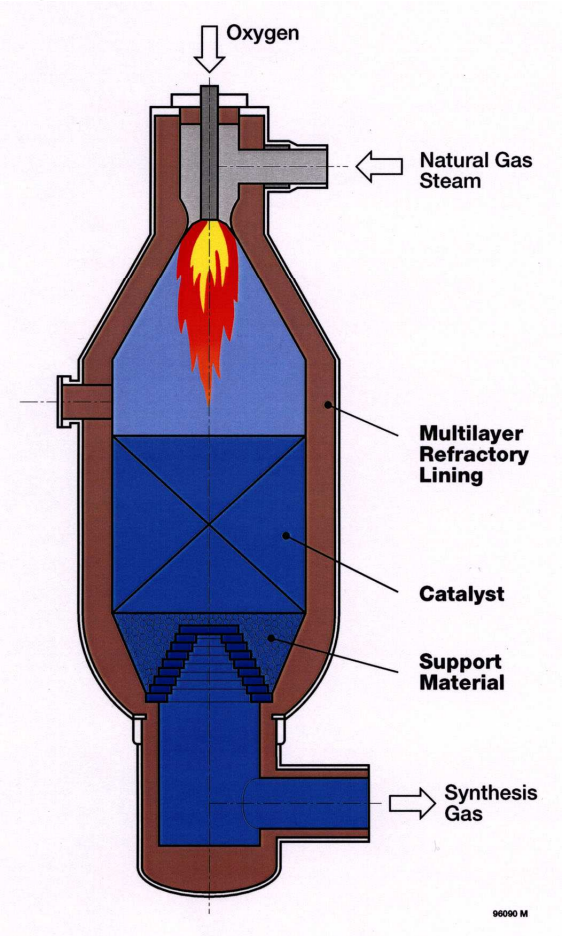
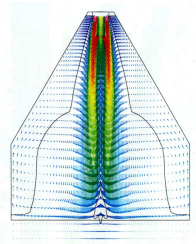
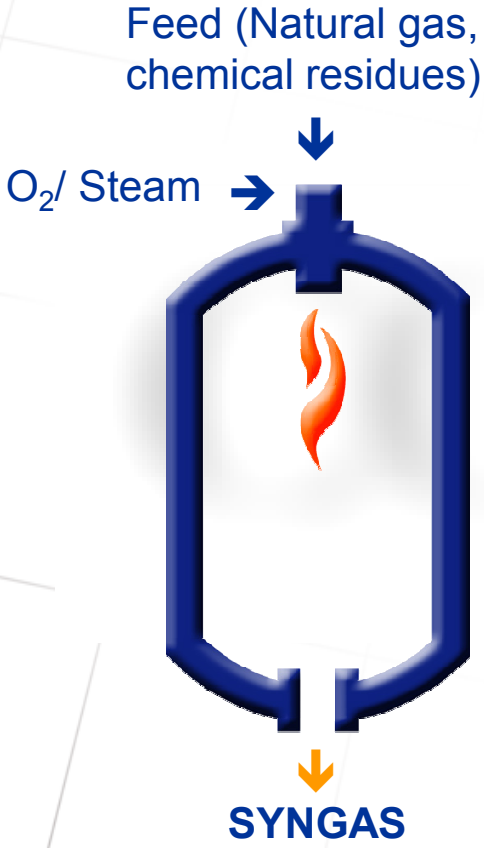
Autothermal Reforming





Multi Purpose Gasification MPG®



Partial oxidation

$$C_m H_m + m/2\ O_2 \rightarrow m\ CO_2 + m/2\ H_2 + HEAT$$

Steam reactions

$$C_m H_m + m\ H_2O \longleftrightarrow m\ CO + (m + m/2)\ H_2 - HEAT$$

$$CO + H_2O \longleftrightarrow CO_2 + H_2 + HEAT$$

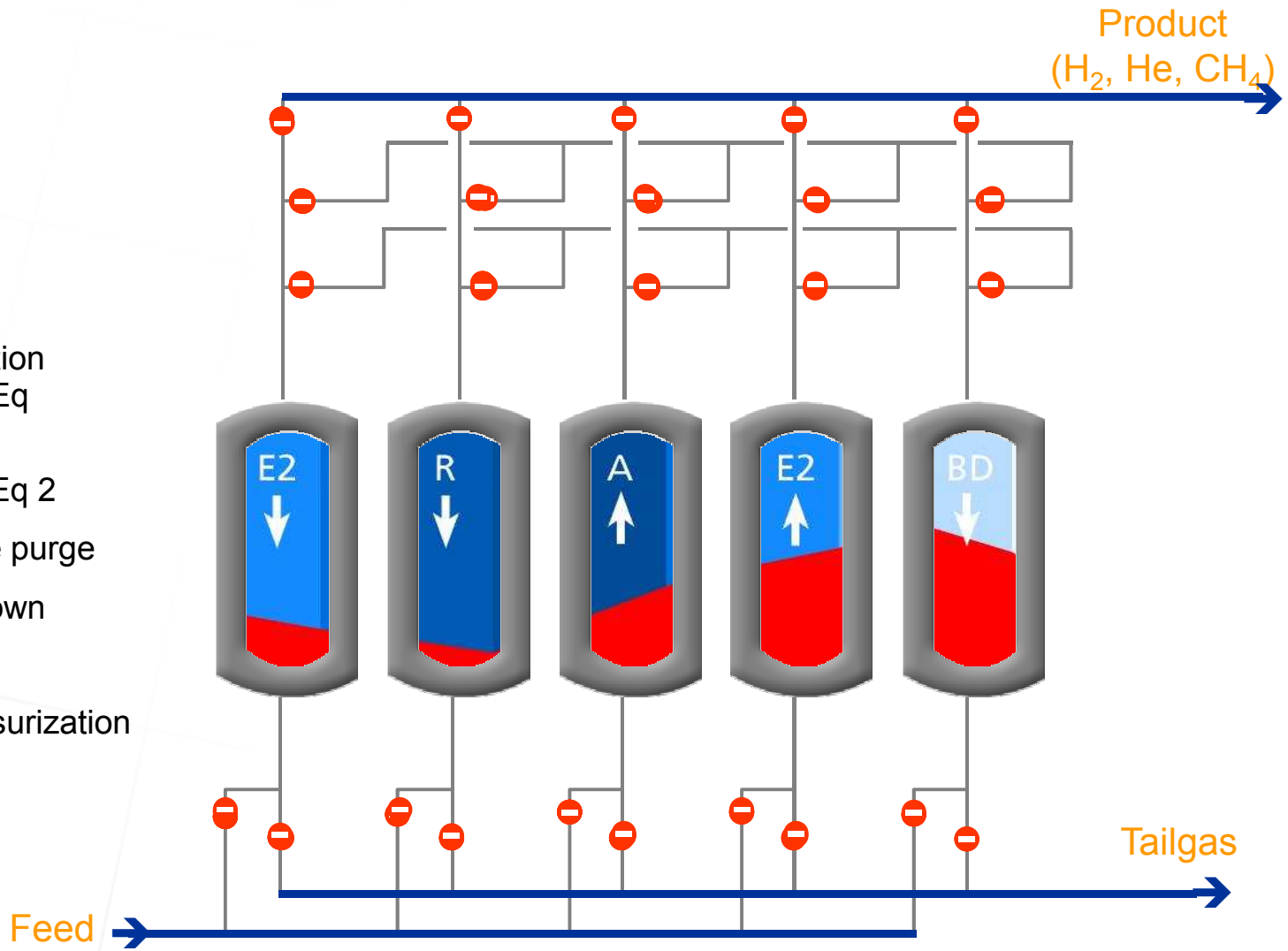
Temperature: **1200–1450 °C**
2190–2640 °F

Pressure: **30–70 bar**
435–1015 psi

Multi Purpose Gasification MPG®

Hydrogen Purification by PSA

A	Adsorption
E1	Press. Eq 1
E2	Press. Eq 2
PP	Provide purge
BD	Blow down
P	Purge
R	Repressurization



Hydrogen Product Specification

- **Hydrogen purity:**
  - Up to 99.9999 mol.% H_2
  - Influence on H_2-recovery of the PSA Unit
- **Specification for maximum hydrogen purity:**

Hydrogen purity	mol -%	> 99.9999
Water	ppm vol.	< 1
CH_4	ppm vol.	< 1
$CO + CO_2$	ppm vol.	< 1
N_2	ppm vol.	< 1

Reduktion der CO_2 Emissionen

Lurgi SMR – CO_2 Emissions

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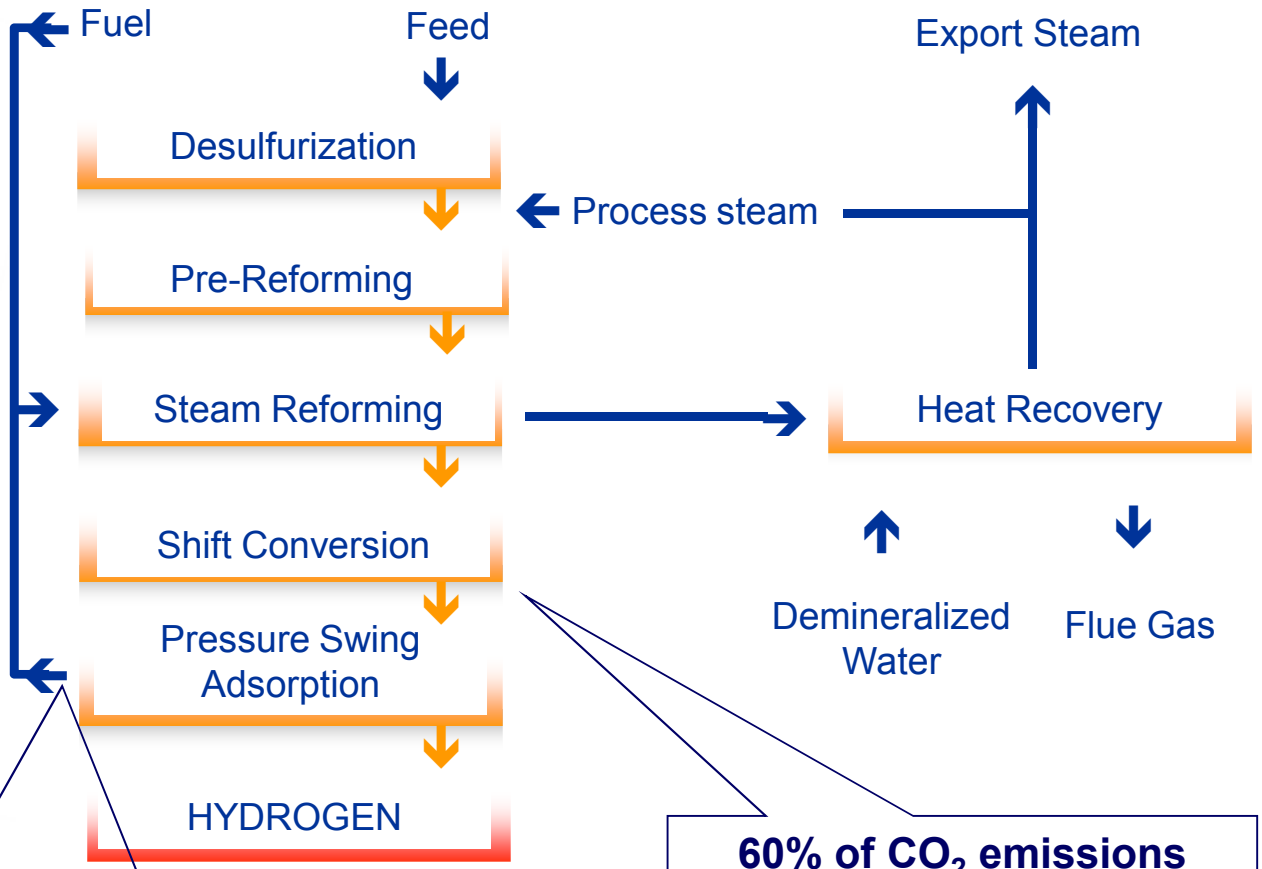
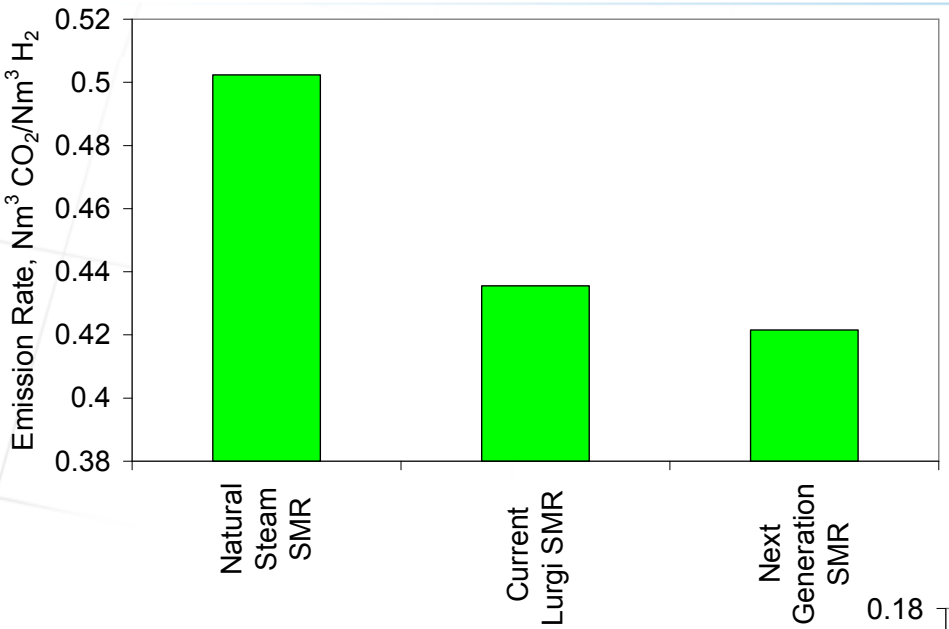
15% of CO_2 emissions come from burning natural gas fuel



25% of CO_2 emissions come from burning PSA tail gas (CO, CH_4) – Reformer and Shift Converter Temp. Can be optimized to Reduce

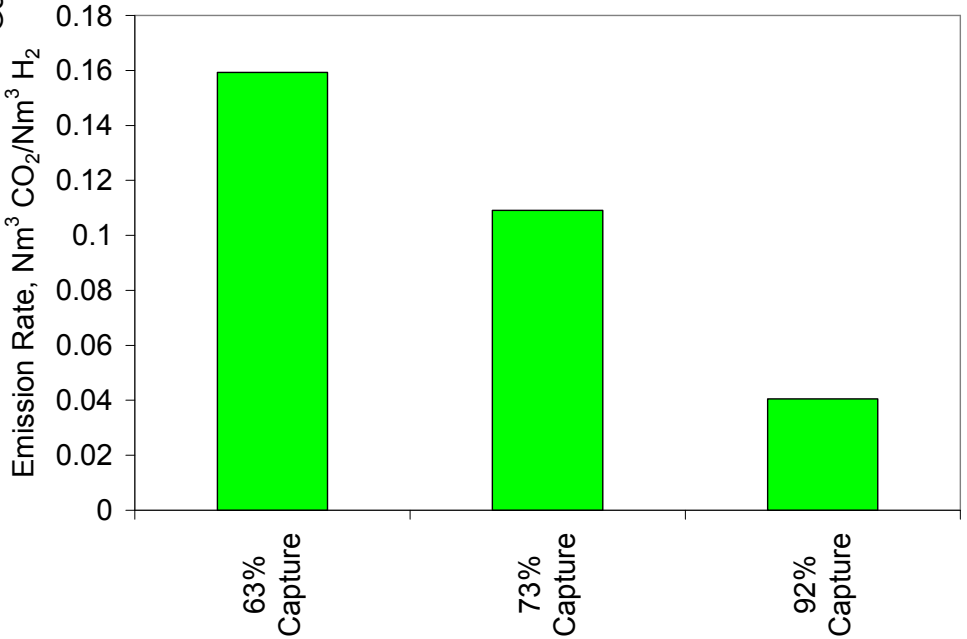
60% of CO_2 emissions come from SMR and Shift reactions producing CO_2 as byproduct

Next Generation SMR



Reduced Emissions prior to CO_2 Capture

High CO_2 Capture Rates



Reducing Cost of CO_2 Capture/Compression/Drying

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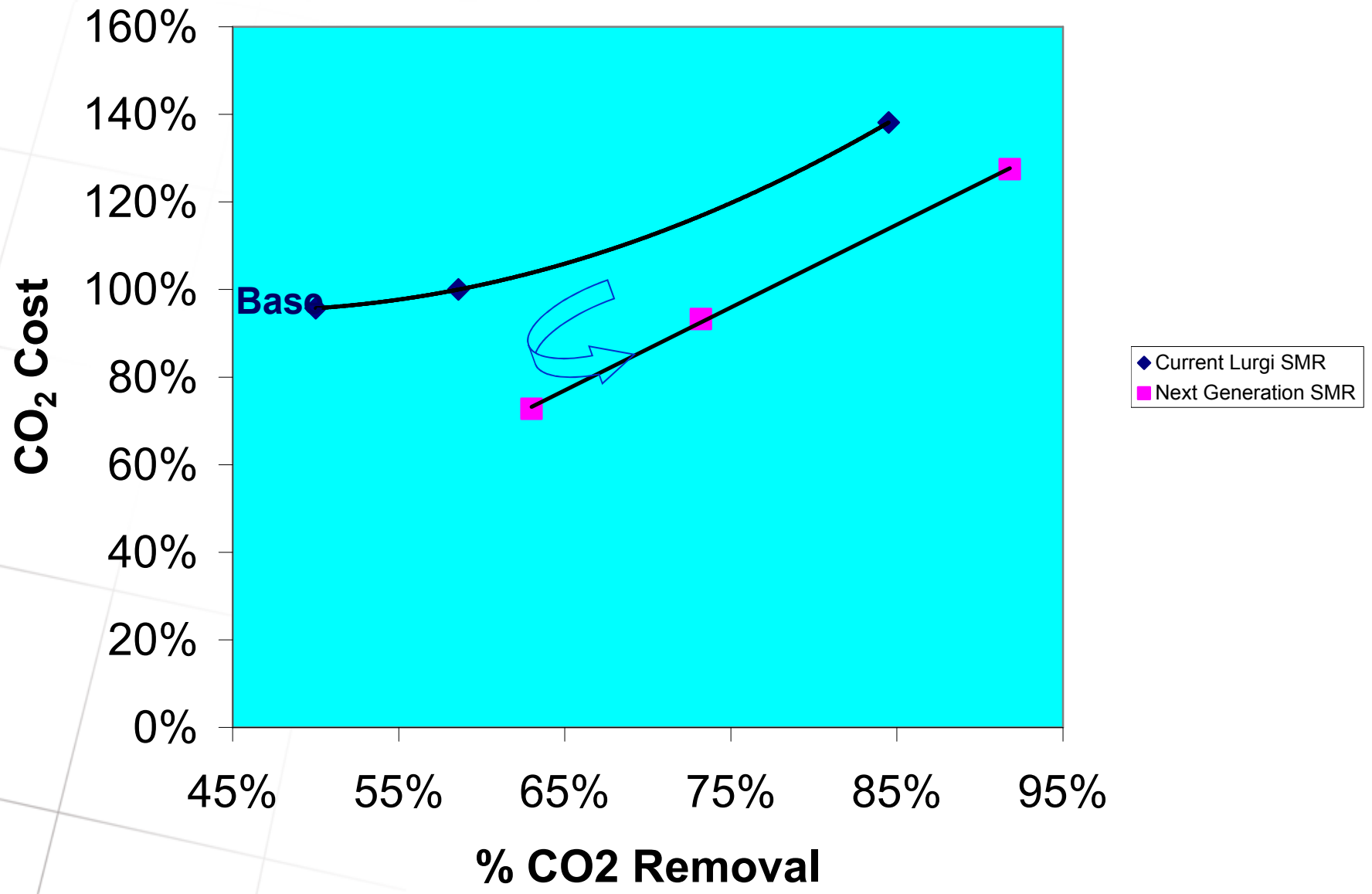

Nutzung von Biomasse

Biomass to Fuels: Bioliq Concept KIT, Karlsruhe

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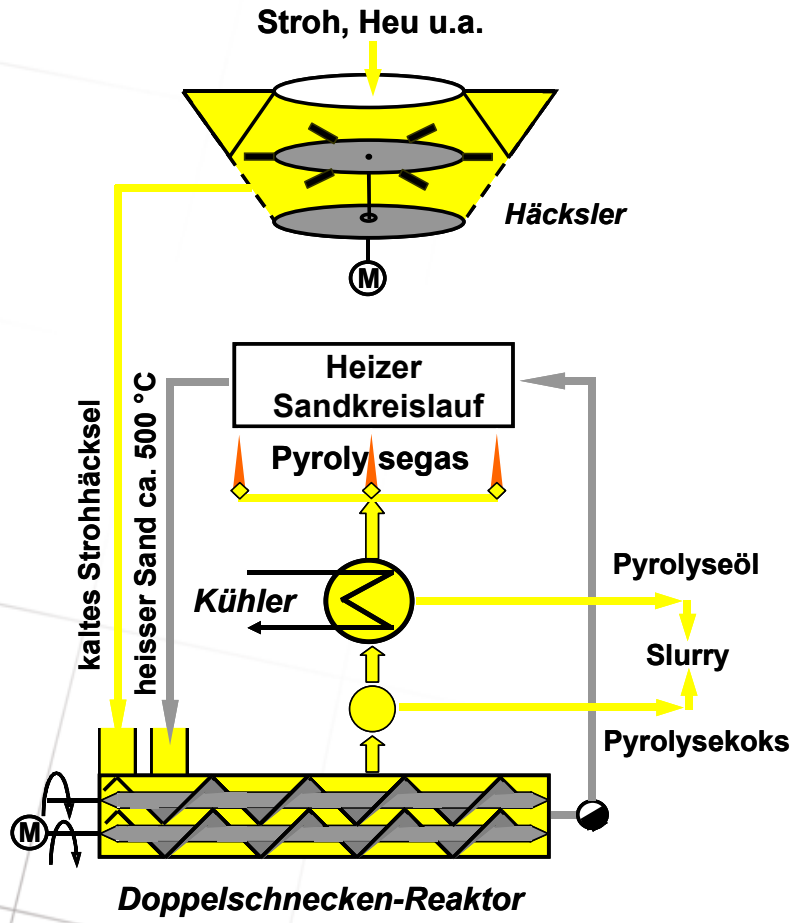
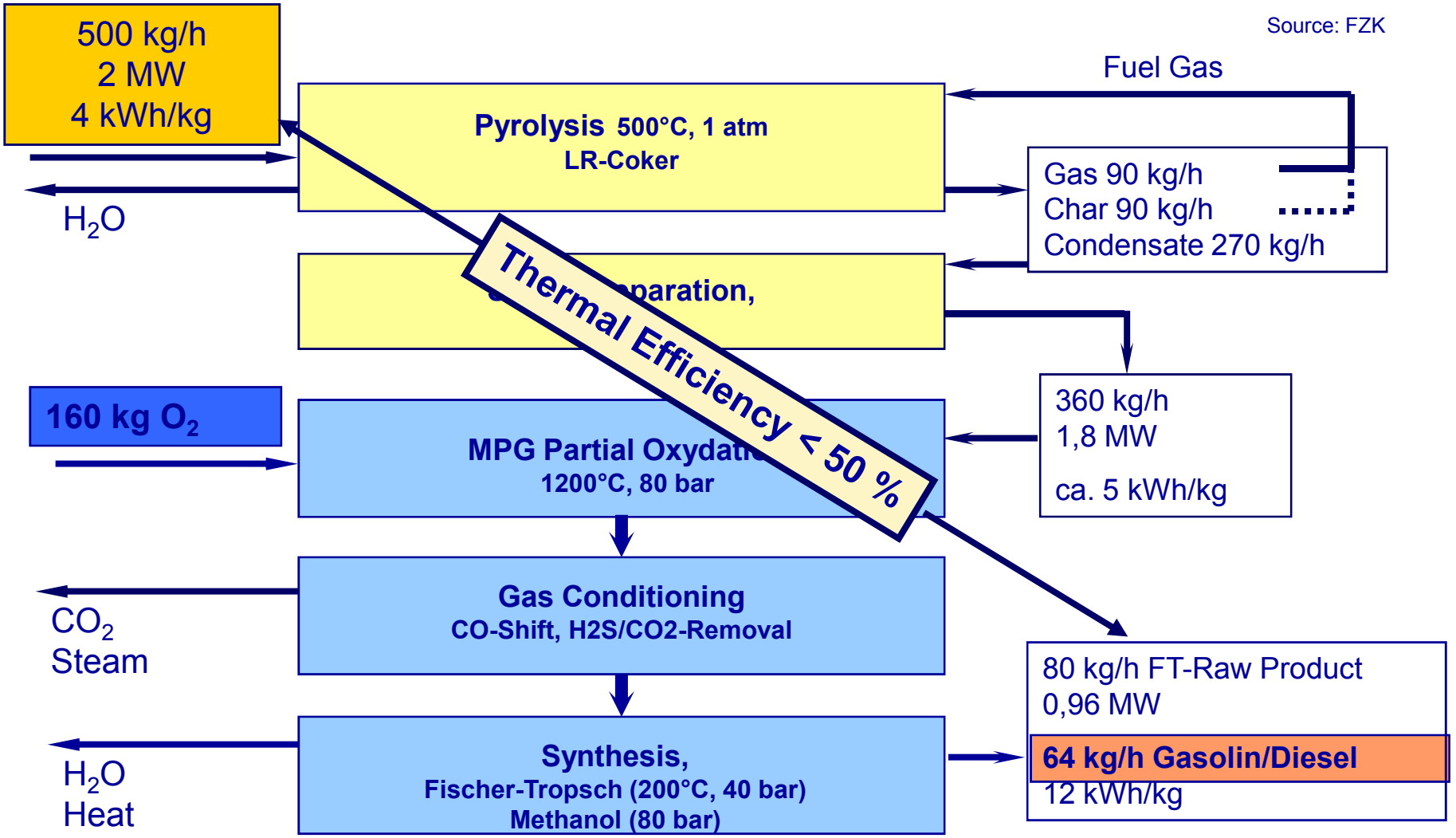
Bioliq1 : Pyrolyse von Biomasse mit LR-Coker (Lurgi-Ruhrgas Coker)

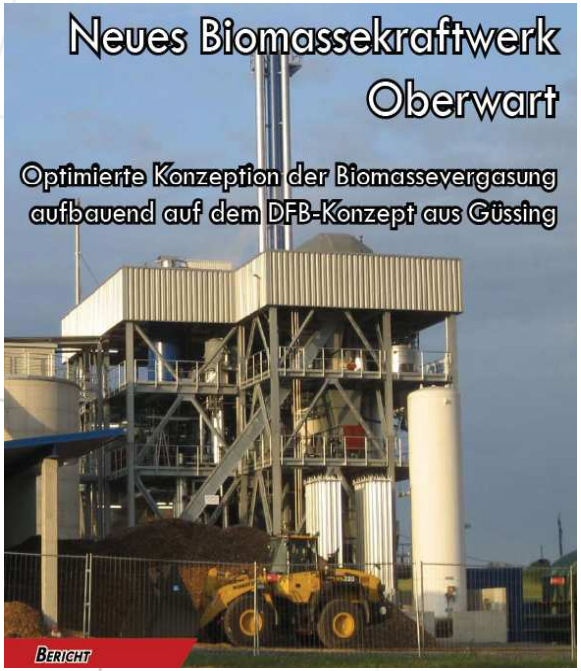


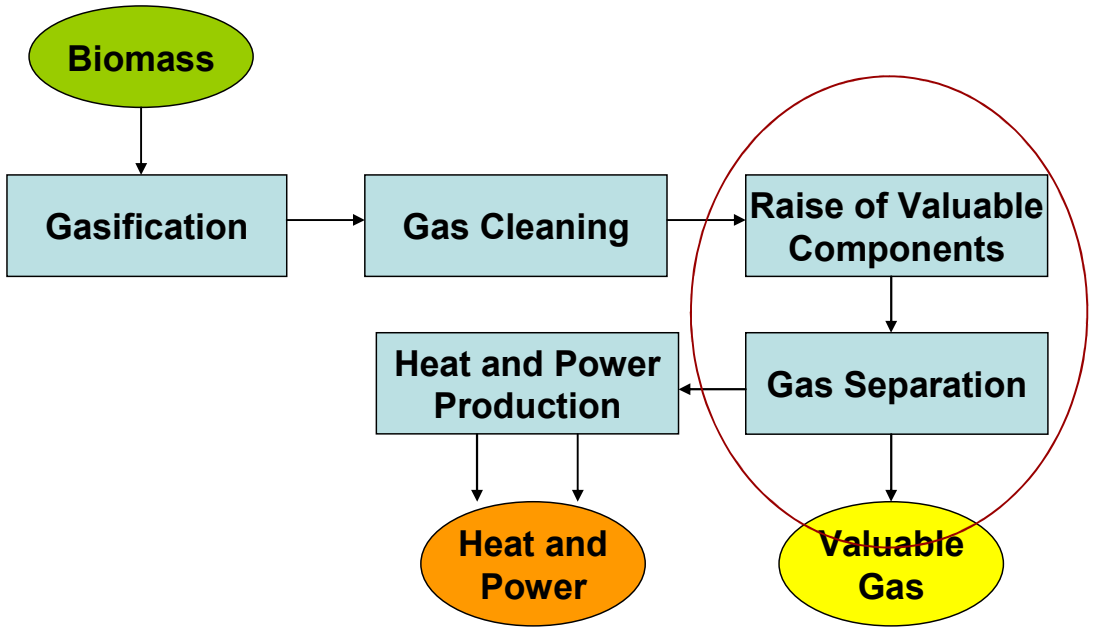
Biomass to Fuels: Bioliq Concept KIT, Karlsruhe



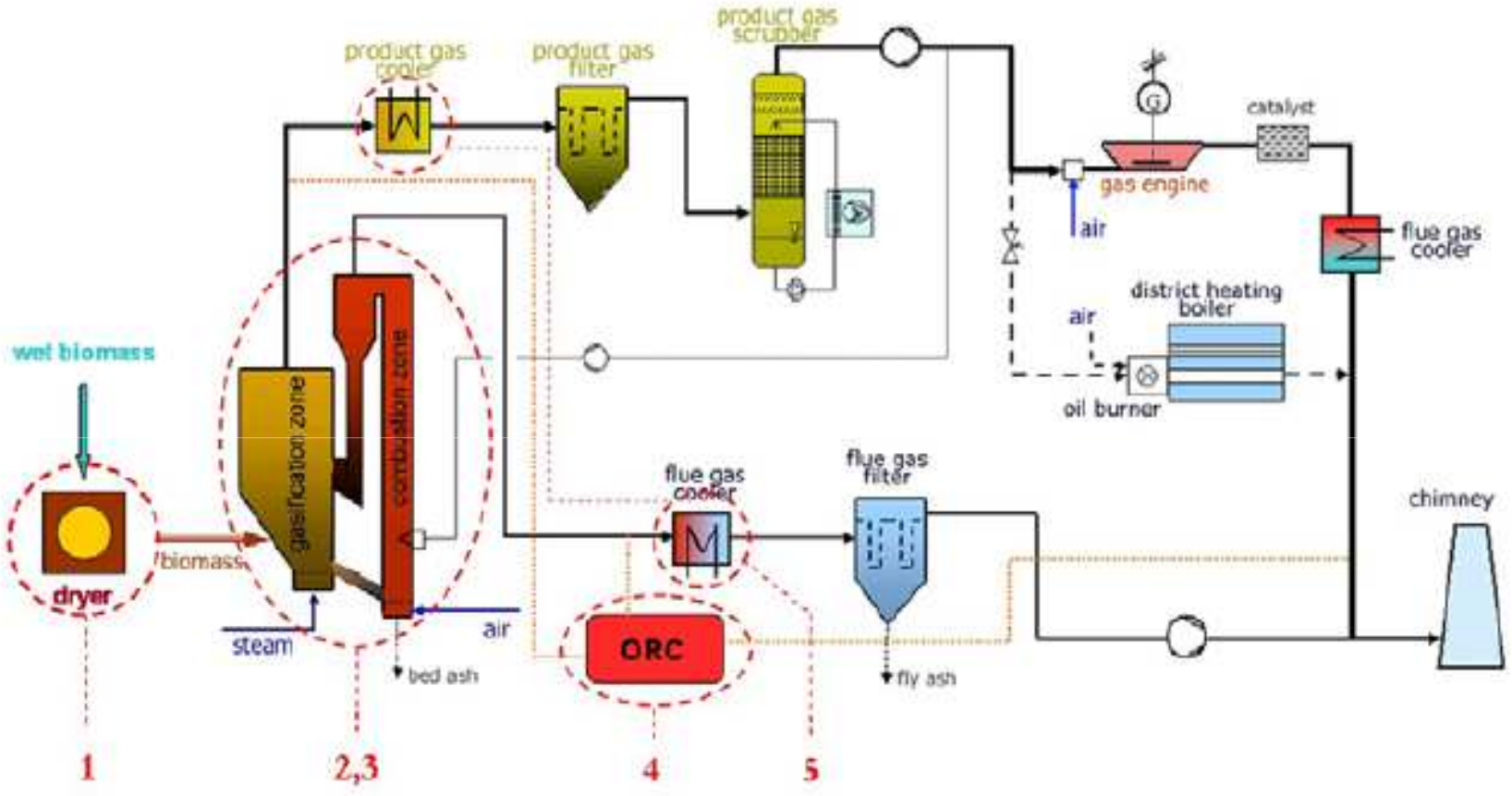
Increase Value of Gas from Biomass Gasification

- chemical conversion of individual constituents
  - increase of CH4 content by sulphur resistant methanation (SNG)
  - increase of H2 content by sorbent enhanced reforming and CO shift





Oberwart Block Flow Diagram



Vielen Dank für die Aufmerksamkeit
Kommentare ?