Pre-combustion – the method
Pre-combustion - principle

- Split the $C_xH_y$-molecules into $H_2$ and $CO_2$
- Transfer heating value from $C_xH_y$ to $H_2$
- Separate $CO_2$ from $H_2$

Pre-combustion - steps

1. Natural gas
   - Hydrogenator
   - Desulfurizer
   - Pre-reformer
   - Reformer
   - Syngas cooling
   - Water-gas shift
   - $CO_2$ removal
   - $H_2$-rich gas

2. Coal
   - Grinding & slurrying
   - Gasifier
   - Syngas cooling
   - Particle removal
   - Sour water-gas shift
   - $H_2S/CO_2$ removal
   - $H_2$-rich gas
   - Claus process
   - $S$
Pre-combustion – pre-reforming

\[ C_mH_n + H_2O \rightarrow CH_4 + CO_2 / CO \]

- It allows reducing the steam-to-carbon ratio in the main reformer and may contribute to less energy use in the main reformer.
- Pre-reformer can act as a “sulfur guard” by removing all sulfur to protect the main reformer catalyst and so increase its lifetime. The pre-reformer catalyst is Nickel based on either a magnesium oxide or magnesium alumina, of which the latter at low temperatures favours the chemisorption of sulfur.
- Increased fuel feed flexibility, as the pre-reformer smoothes out variations in the feed composition.

Pre-combustion – Reforming - 1

- Reaction with steam - **steam reforming** – heat is supplied from outside the reformer.
- Reaction with oxygen - **partial oxidation** – heat is generated within the reformer:
  - Partial oxidation with no catalyst - POX
  - Autothermal reforming (ATR) – combination of POX and SR
  - Catalytic Partial Oxidation (CPO)
Pre-combustion – Reforming - 2

Steam reforming (SR)

Pre-combustion – Reforming - 3

Auto-thermal reforming (ATR)

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Pre-combustion – Reforming - 4

\[ CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad \Delta H = 205.9 \text{ [kJ/mol]} \]
\[ CO + H_2O \rightleftharpoons H_2 + CO_2 \quad \Delta H = 41.2 \text{ [kJ/mol]} \]
\[ CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \quad \Delta H = -247 \text{ [kJ/mol]} \]
\[ CH_4 + \frac{1}{2}O_2 \rightleftharpoons CO + 2H_2 \quad \Delta H = -35.9 \text{ [kJ/mol]} \]
\[ (CH_4 + \frac{3}{2}O_2 \rightleftharpoons CO + 2H_2O) \quad \Delta H = -519.6 \text{ [kJ/mol]} \]

**Formation of coke**

\[ CH_4 \rightleftharpoons C + 2H_2 \quad \Delta H = 74.6 \text{ [kJ/mol]} \]
\[ 2CO \rightleftharpoons C + CO_2 \quad \Delta H = -172.5 \text{ [kJ/mol]} \]

Steam-to-carbon ratio (based on moles) or S/C-ratio. Typical values in the range 1.3-3.0.

Natural gas steam reforming = decomposition of methane by steam, to produce *synthesis gas* (CO+H₂)

\[ CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad (\Delta H_{298} = 206 \text{ kJ mol}^{-1}) \]
\[ CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (\Delta H_{298} = -41 \text{ kJ mol}^{-1}) \]
Natural gas auto-thermal reforming

\[
\begin{align*}
CH_4 + \frac{1}{2}O_2 &\rightleftharpoons CO + 2H_2 & (\Delta H_{298} = -36 \text{ kJ mol}^{-1}) \\
CH_4 + H_2O &\rightleftharpoons CO + 3H_2 & (\Delta H_{298} = 206 \text{ kJ mol}^{-1}) \\
CO + H_2O &\rightleftharpoons CO_2 + H_2 & (\Delta H_{298} = -41 \text{ kJ mol}^{-1})
\end{align*}
\]

Feed gas is prereformed and desulphurised. The gas is fed into an auto-termal reformer reactor at a typical pressure of 30-40 bar and temperature of 900-1000 ºC to produce syngas (H_2, CO, H_2O, CO_2, CH_4).

Pre-combustion – Reforming - 5

Steam reforming of methane for different steam-to-carbon ratios and pressures.
Oxygen-blown partial oxidation of methane for different steam-to-carbon ratios and pressures.

Pre-combustion – Reforming - 7

Achievable H₂/CO ratios of reforming technologies. The values within an interval depend mainly on steam-to-carbon ratio and reforming temperature.
**Pre-combustion – Gasification - 1**

Involving carbon

\[
\begin{align*}
C + 2H_2 & \rightleftharpoons CH_4 & \Delta H = -74.6 \text{ [kJ/mol]} \\
C + CO_2 & \rightleftharpoons 2CO & \Delta H = 172.5 \text{ [kJ/mol]} \\
C + H_2O_{(g)} & \rightleftharpoons CO + H_2 & \Delta H = 131.3 \text{ [kJ/mol]} \\
C + \frac{1}{2}O_2 & \rightleftharpoons CO & \Delta H = -110.5 \text{ [kJ/mol]}
\end{align*}
\]

Involving oxygen

\[
\begin{align*}
CO + \frac{1}{2}O_2 & \rightleftharpoons CO_2 & \Delta H = -283.0 \text{ [kJ/mol]} \\
H_2 + \frac{1}{2}O_2 & \rightleftharpoons H_2O_{(g)} & \Delta H = 241.8 \text{ [kJ/mol]}
\end{align*}
\]

Steam-to-carbon ratio (based on moles) or S/C-ratio. Typical values in the range 1.3-3.0.

---

**Pre-combustion – Gasification - 2**

Carbon conversion = 1 - \( \frac{\text{Unconverted solid C}}{\text{Carbon in coal feed}} \)

Cold gas efficiency = \( \frac{\text{Chemical energy in syngas}}{\text{Chemical energy in coal}} \)
### Pre-combustion – Gasification - 3

#### Flow Regime

<table>
<thead>
<tr>
<th>Flow Regime</th>
<th>Moving/Fixed Bed</th>
<th>Fluidized Bed</th>
<th>Entrained Flow</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Combustion analogy</strong></td>
<td>grate fired combustors</td>
<td>fluidized bed combustors</td>
<td>pulverized coal combustors</td>
</tr>
<tr>
<td><strong>Fuel Types</strong></td>
<td>solids only</td>
<td>solids only</td>
<td>solids or liquids</td>
</tr>
<tr>
<td><strong>Fuel Size</strong></td>
<td>5 - 50 mm</td>
<td>0.5 - 10 mm</td>
<td>&lt; 500 μm</td>
</tr>
<tr>
<td><strong>Residence time</strong></td>
<td>15 - 30 minutes</td>
<td>5 - 50 seconds</td>
<td>1 - 10 seconds</td>
</tr>
<tr>
<td><strong>Oxidant</strong></td>
<td>air- or oxygen-blown</td>
<td>air- or oxygen-blown</td>
<td>almost always oxygen-blown</td>
</tr>
<tr>
<td><strong>Gas Outlet Temperature</strong></td>
<td>400 - 600 °C</td>
<td>700 – 1000 °C</td>
<td>900 – 1600 °C</td>
</tr>
<tr>
<td><strong>Pressure</strong></td>
<td>10-35 bar</td>
<td>10-25 bar</td>
<td>25-80 bar</td>
</tr>
<tr>
<td><strong>Ash Handling</strong></td>
<td>slagging and non-slagging</td>
<td>non-slagging</td>
<td>always slagging</td>
</tr>
<tr>
<td><strong>Acceptability of fines</strong></td>
<td>Limited</td>
<td>Good</td>
<td>Unlimited</td>
</tr>
<tr>
<td><strong>Commercial Examples</strong></td>
<td>Sasol-Lurgi dry-ash, BGL (slagging)</td>
<td>HTW, KRW</td>
<td>GE, Shell, ConocoPhillips E-Gas, Siemens</td>
</tr>
</tbody>
</table>

#### Comments

- Moving beds are mechanically stirred, fixed beds are not. Gas and solid flows are always countercurrent in moving bed gasifiers.
- Bed temperature below ash fusion point to prevent agglomeration. Preferred for high-ash feedstocks and waste fuels. Low carbon conversion. Some methane and tars in syngas.
- Not preferred for high-ash fuels due to energy penalty of ash-melting. Unsuitable for fuels that are hard to atomize or pulverize. Pure syngas, high carbon conversion.

---

#### Pre-combustion – Gasification - 4

- Coal Flow Direction: Moving/fixed Bed
- Gas Flow Direction: Entrained Flow

- Moving beds are mechanically stirred, fixed beds are not. Gas and solid flows are always countercurrent in moving bed gasifiers.
- Bed temperature below ash fusion point to prevent agglomeration. Preferred for high-ash feedstocks and waste fuels. Low carbon conversion. Some methane and tars in syngas.
- Not preferred for high-ash fuels due to energy penalty of ash-melting. Unsuitable for fuels that are hard to atomize or pulverize. Pure syngas, high carbon conversion.
Pre-combustion – Gasification - 5

Siemens SFG gasifier

Pre-combustion – Gasification - 6

BGL gasifier
Pre-combustion – Syngas cooling

- Radiant syngas cooling
- Water quench
- Gas recycle quench
- Chemical quench
Pre-combustion – WGS -1

Water-gas shift:
Fixed-bed reactor with catalyst, 185-500 °C

\[ CO + H_2O \leftrightarrow H_2 + CO_2 \quad \Delta H = 41.2 \text{ [kJ/mol]} \]

Pre-combustion – WGS -2

WGS catalysts are

High-temperature shift catalyst
Active component: Fe\(_3\)O\(_4\) with Cr\(_2\)O\(_3\) as stabiliser
Operating conditions: 350-500 °C
Sulfur content in feed gas < 100 ppmv

Low-temperature shift catalysts
Active component: Cu supported by ZnO and Al\(_2\)O\(_3\)
Operating conditions: 185-275 °C
Sulfur content in feed gas < 0.1 ppmv

Sour shift catalysts
Active component: Sulfided Co and Mo (CoMoS)
Operating conditions: 250-500 °C
Sulfur content in feed gas > 300 ppmv
Pre-combustion – CO₂ capture

**Pressure** ≈ 20-70 bar
CO₂ partial pressure 3.5-27 bar

**CO₂ separation** from syngas:
Selexol, Rectisol, Purisol, (MDEA) are most commonly used
Pre-combustion – CO$_2$ capture

Selexol

---

Pre-combustion –

Level 1: Fuel
- Natural gas
- Coal

Level 2: Reforming/Gasification
- Steam reforming (SR)
- Auto-thermal reforming (ATR)
- Partial oxidation (POX)
- Oxygen-blown Internal O$_2$ prod.
- Oxygen-blown External O$_2$ prod.
- Air-blown

Level 3: Reformer heat supply method
- NG-fired
- H$_2$-fired
- Exhaust + H$_2$-fired
- Air-blown
- Oxygen-blown
- Oxygen-blown
- Oxygen-blown

H$_2$-separation
- H$_2$-membrane reforming reactor
- H$_2$-membrane Water/Gas shift
- H$_2$-membrane Low-temp
- H$_2$-membrane High-temp

CO$_2$-separation
- CO$_2$-membrane Reformer
- CO$_2$-membrane Water/Gas shift
- CO$_2$-Low-temp
- Gas diffusion membrane
- Amine absorption
- PSA
- Physical absorbents
Pre-combustion – IGCC without CO₂ capture

Coal feed → Gasifier → Quench/heat recovery → Particulate removal → Sulfur removal → H₂S → Quench water → Recovered heat

Air Separation Unit → N₂ → Compressed air → GT → ST → Generator

Raw syngas → Hydrogen-rich gas → Quench/heat recovery

N₂ → Air

Air → HRSG → GT → ST → Generator

Recovered heat

H₂S

CO₂ storage

NTNU Innovation and Creativity
Hydrogen Combustion in Gas Turbines

- Existing fuel distribution system and fuel nozzles not dimensioned for a fuel with a low volumetric heating value – high velocities, high pressure drop, choking of the fuel flow
  - Hydrogen-rich fuels require a significant design modification of fuel injection systems
- High formation of NO\(_X\) because of very high flame temperatures locally in the flame
- Location of the flame inside the combustor and an increase in the H\(_2\)O concentration on the product side may cause a too high heat flux on combustor walls or on fuel nozzles

Consequences – Dilution of H\(_2\) (N\(_2\), H\(_2\)O)

- Maximum temperature at exhaust or power turbine inlet
- Maximum torque or power output to load
- Mechanically limited compressor discharge pressure
- Mechanically limited compressor discharge temperature
- Mechanical overspeeding of a free compressor on a multi-shaft machine
- Aerodynamically limited maximum compressor discharge pressure, leading to surge
- Aerodynamic overspeeding of a free compressor on a two-shaft machine, leading to choke
Consequences – Dilution of $H_2 (N_2, H_2O)$

Lines of constant efficiency

Reduced flow rate $\frac{m\sqrt{T}}{p}$

$\frac{m\sqrt{T}}{p} \frac{R}{\sqrt{k}}$

Wobbe index

\[
Wobbe \ index = \frac{LHV}{\sqrt{\frac{\rho_{gas}}{\rho_{air}}}} = \frac{LHV}{\sqrt{\frac{MW_{gas} T_{air}}{MW_{air} T_{gas}}}}
\]

- The Wobbe index is used to compare the combustion energy output of different composition fuel gases in a burner
- Main indicator of the interchangeability of various fuels
- If two fuels have similar Wobbe index then it is likely that a given burner can change between the two fuels and operate in a similar manner
- Wobbe index does not relate flame temperature, heat transfer coefficients or temperature gradients
H₂-rich fuel in GT: NOₓ, Wobbe-index

Wobbe index for mixtures of hydrogen with methane (CH₄), nitrogen (N₂), steam (H₂O), carbon monoxide (CO) and CO₂. The temperatures of the air and fuel are both set to 15 °C for the calculation of the Wobbe index.

NOₓ formation in GT combustion

Relation between NOₓ emission and stoichiometric flame temperature, progressively reduced by steam dilution, for gas turbine diffusive combustion at 12–16 bar with different fuels. Nitrogen is the balance gas for 56% and 95% hydrogen.
Lesson:

With a Target Steam/Fuel Ratio of 0.13 a NOx level of 10 ppm. can be achieved without special measures.

Hydrogen Combustion in Gas Turbines
From Norm Schilling, GE

<table>
<thead>
<tr>
<th>Customer/Site</th>
<th>Model</th>
<th>No.</th>
<th>Gas</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antwerp</td>
<td>MS6000B</td>
<td>1</td>
<td>RFG</td>
<td>78% H2</td>
</tr>
<tr>
<td>Puerto Llano</td>
<td>MS6000B</td>
<td>2</td>
<td>RFG</td>
<td>Up to 50% H2</td>
</tr>
<tr>
<td>La Coruna</td>
<td>MS6000B</td>
<td>1</td>
<td>RFG</td>
<td>Up to 52% H2</td>
</tr>
<tr>
<td>Rotterdam</td>
<td>MS6000B</td>
<td>1</td>
<td>RFG</td>
<td>59% H2</td>
</tr>
<tr>
<td>AGIP/Milazzo</td>
<td>MS5001P</td>
<td>1</td>
<td>RFG</td>
<td>30% to 50% H2</td>
</tr>
<tr>
<td>Cochin Refineries</td>
<td>MS5001P</td>
<td>1</td>
<td>RFG</td>
<td>50% H2</td>
</tr>
<tr>
<td>Mobil/Paulsboro</td>
<td>MS5001P</td>
<td>2</td>
<td>RFG</td>
<td>20% to 60% H2</td>
</tr>
<tr>
<td>Uhde NUP</td>
<td>MS3002J</td>
<td>1</td>
<td>TG</td>
<td>~60% H2</td>
</tr>
<tr>
<td>Donges</td>
<td>GE10</td>
<td>1</td>
<td>RFG</td>
<td>76% H2</td>
</tr>
<tr>
<td>Zarqa Refinery</td>
<td>PGT10</td>
<td>1</td>
<td>RFG</td>
<td>82% H2</td>
</tr>
<tr>
<td>Exxon/Mobil Singapore</td>
<td>MS6001FA</td>
<td>2</td>
<td>IGCC</td>
<td>44.5% H2</td>
</tr>
<tr>
<td>Georgia Gulf</td>
<td>MS7001EA</td>
<td>3</td>
<td>Blend Methane+50% H2</td>
<td></td>
</tr>
<tr>
<td>SUV Vresova</td>
<td>MS9001E</td>
<td>2</td>
<td>IGCC</td>
<td>46.8% H2</td>
</tr>
<tr>
<td>BASF/Geismar</td>
<td>MS6001B</td>
<td>1</td>
<td>PG</td>
<td>Up to 80% H2</td>
</tr>
<tr>
<td>Koch Refinery</td>
<td>MS6001B</td>
<td>1</td>
<td>RFG</td>
<td>12% to 50% H2</td>
</tr>
<tr>
<td>Daeson Korea</td>
<td>MS6001B</td>
<td>1</td>
<td>PG</td>
<td>up to 95% H2</td>
</tr>
<tr>
<td>Shell Int'l</td>
<td>MS5001P</td>
<td>1</td>
<td>RFG</td>
<td>60% H2, propane</td>
</tr>
<tr>
<td>Reutgerswerke</td>
<td>MS3002J</td>
<td>1</td>
<td>PG</td>
<td>60% H2</td>
</tr>
<tr>
<td>Tenerife</td>
<td>MS6001B</td>
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<td>RFG</td>
<td>~70% H2</td>
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<tr>
<td>Cartagena</td>
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<td>1</td>
<td>RFG</td>
<td>66% H2</td>
</tr>
<tr>
<td>San Roque</td>
<td>MS6000B</td>
<td>2</td>
<td>RFG</td>
<td>70% H2</td>
</tr>
</tbody>
</table>

IGCC=Syngas; RFG=Refinery Gas; PG=Process Gas; TG=Tail Gas
Pre-combustion – Natural gas

- Reformer
- WGS
- CO₂ capture (amine, Selexol)
- PSA
- CO₂ capture
- High-purity H₂ for other purposes such as fuel cells
- Hydrogen-rich fuel to power plant
- Natural gas
- Steam
- Reforming
- WGS
- CO₂ capture

Pre-combustion – Gas Turbine Combined Cycle with Auto-Thermal Reforming

- Reformer
- ATR
- HTS
- LTS
- CO₂ capture
- Reforming/Shift
- Gas turbine
- Steam cycle
- HRSG
- Steam generation
- ST
- MIX
- Natural gas
- Exhaust
- Carbon capture
- Combined Cycle
- Pre-combustion
- Preheating
- Air/Exhaust
- Steam/Water
- Natural gas
- Syngas
- H₂-rich fuel
- T = Turbine, COMP = Compressor
- SF = Supplementary firing, HRSG = Heat recovery steam generator
- PRE = Pre-reformer, ATR = Auto-thermal reformer, H₂ - High temperature shift reactor, WR = Water removal, ABS = CO₂ absorber, FC = Fuel compressor
Pre-combustion – sorption-enhanced WGS

Integration of water gas-shift and CO₂ capture processes. By removing continuously CO₂ or hydrogen from the reactor, the equilibrium is shifted to the product side. The CO₂ or hydrogen is separated using a membrane integrated with the catalyst in the reactor.
Pre-combustion – sorption-enhanced reforming

Integration of the reforming/gasification, water gas-shift and CO₂ capture processes. By removing continuously CO₂ or hydrogen from the reactor, the equilibrium is shifted to the product side. The hydrogen (or CO₂) may be separated using a membrane. Heat may be transferred to the reactor or heat may be generated in the reactor by supplying oxygen to it.