Overview and Basics of Different Thermochemical Processes for Syngas Production

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Outline

• What is syngas?
• Importance of syngas production
• Options for syngas production
• Steam Methane Reforming
• Dry reforming
• Partial Oxidation
• Autothermal Reforming
• Gasification
• Pyrolysis
• Summary
What is syngas?

- Synthesis gas or syngas consist primarily of CO and H₂, although CO₂ and some unconverted hydrocarbons may be present in the gas mixture.
- The ratio of hydrogen to carbon monoxide varies according to the type of feed, method of production, and the end of the gas.
Importance of syngas production

- Syngas is a key intermediate in the chemical industry.

*2011

140 million tonnes per year

*2013

50 million tonnes per year

65 million tonnes per year
Importance of syngas production

- Requirements of the syngas composition vary with the subsequent synthesis.

<table>
<thead>
<tr>
<th>Process</th>
<th>Optimum Composition</th>
<th>Co-reactants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>$H_2/N_2 = 3$</td>
<td>-</td>
</tr>
<tr>
<td>Methanol</td>
<td>$(H_2-CO_2)/(CO+CO_2) = 2$</td>
<td>-</td>
</tr>
<tr>
<td>Fischer-Tropsch (high T)</td>
<td>$(H_2-CO_2)/(CO+CO_2) = 2$</td>
<td>-</td>
</tr>
<tr>
<td>Fischer-Tropsch (low T)</td>
<td>$H_2/CO \approx 2$</td>
<td>-</td>
</tr>
<tr>
<td>Synthetic Natural Gas</td>
<td>$(H_2-CO_2)/(CO+CO_2) = 3$</td>
<td>-</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>CO</td>
<td>Methanol</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>$O_2$</td>
<td>Methanol</td>
</tr>
<tr>
<td>Ethanol</td>
<td>$H_2/CO \approx 2$</td>
<td>Methanol</td>
</tr>
<tr>
<td>Higher alcohols</td>
<td>$H_2/CO \approx 1$</td>
<td>Olefins</td>
</tr>
<tr>
<td>Industrial Hydrogen</td>
<td>99.99% $H_2$</td>
<td>-</td>
</tr>
<tr>
<td>Hydrogen for Fuel Cells</td>
<td>&lt; 50 ppm CO</td>
<td>-</td>
</tr>
</tbody>
</table>
Importance of syngas production

• There is a growing worldwide demand for H₂ in refineries because of the need to process heavier and dirtier feedstock.
• Syngas is playing an increasing role in energy conversion.
• Syngas and H₂ production technologies can utilize energy more efficiently, supply ultraclean fuels, eliminate pollutant emissions at end-use systems, and cut emissions of GHG.
  o More efficient electrical power generation: IGCC and syngas-based fuel cells.
  o Ultraclean transport fuels such as liquid hydrocarbon fuels, methanol, dimethyl ether, and ethanol for transportation vehicles.
Options for syngas production

- Syngas can be produced from almost any carbon source (hydrocarbon feedstock), including natural gas, naphtha, residual oil, petroleum coke, coal, and biomass.
Options for Syngas Production from Gaseous and Liquid Hydrocarbons
Steamb Reforming

Steam Reforming of Natural Gas

- The lowest cost route for syngas production is based on the steam reforming of natural gas
- Steam methane reforming (SMR) is the reaction of methane with steam over a metal catalyst:
  - Supported Ni catalyst
  - Temperature range of 700 – 800 °C
  - Pressure range of 30 – 50 atm
  - High steam to carbon ratio between 2 - 6

\[ \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow 3\text{H}_2 + \text{CO} \quad \Delta H_{298} = +206 \text{ kJ mol}^{-1} \]
Steam Reforming
Steam Reforming of Natural Gas

- SMR process involves contributions from several different catalyzed reactions, e.g. Water-gas shift (WGS), Reverse water-gas shift (RWGS), Boudouard reaction and Methane decomposition reactions

\[
\begin{align*}
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad \Delta H_{298} = -41 \text{ kJ mol}^{-1} \\
\text{CO}_2 + \text{C} & \rightleftharpoons 2\text{CO} \quad \Delta H_{298} = +172 \text{ kJ mol}^{-1} \\
\text{CH}_4 & \rightarrow \text{C} + 2\text{H}_2 \quad \Delta H_{298} = +75 \text{ kJ mol}^{-1} \\
\text{CH}_4 + 2\text{H}_2\text{O} & \rightleftharpoons \text{CO} + 4\text{H}_2 \quad \Delta H_{298} = +165 \text{ kJ mol}^{-1} \\
\text{CH}_4 + \text{CO}_2 & \rightleftharpoons 2\text{CO} + 2\text{H}_2 \quad \Delta H_{298} = +247 \text{ kJ mol}^{-1} \\
\text{C} + \text{H}_2\text{O} & \rightarrow \text{CO} + \text{H}_2 \quad \Delta H_{298} = +131 \text{ kJ mol}^{-1} \\
\text{CO} + \frac{1}{2} \text{O}_2 & \rightarrow \text{CO}_2 \quad \Delta H_{298} = -283 \text{ kJ mol}^{-1}
\end{align*}
\]
Steam Reforming of Natural Gas

- SMR can be divided into four steps:
  - Feed pretreatment – Desulfurization
  - Reforming
  - H\textsubscript{2}/CO ratio adjustment - Water gas shift conversion
  - Downstream processing, e.g. hydrogen purification
Steam Reforming
Steam Reforming of Natural Gas

Desulfurization:
- Hydrogenator - Sulphur-containing to H₂S
- Zinc oxide bed - H₂S scrubbing

HTS conversion - Fe₂O₃/Cr₂O₃/MgO, ≈ 350 °C
LTS conversion – CuO/ZnO/Al₂O₃, ≈ 250 °C

Pressure swing adsorption (PSA) for the purification of H₂
CO₂ scrubbing

Steam Reforming
Steam Reforming of Other Hydrocarbons

- Reforming of other gaseous hydrocarbons (ethane, propane, and n-butane) have been explored for the production of $H_2$ for fuel cells.
- Endothermicity increases with increasing carbon number of the hydrocarbon.

$$\text{C}_2\text{H}_6 + 2\text{H}_2\text{O} \leftrightarrow 5\text{H}_2 + 2\text{CO} \quad \Delta H_{298} = +374 \text{ kJ mol}^{-1}$$

$$\text{C}_3\text{H}_8 + 3\text{H}_2\text{O} \leftrightarrow 7\text{H}_2 + 3\text{CO} \quad \Delta H_{298} = +498 \text{ kJ mol}^{-1}$$

$$\text{n-C}_4\text{H}_{10} + 4\text{H}_2\text{O} \leftrightarrow 9\text{H}_2 + 4\text{CO} \quad \Delta H_{298} = +651 \text{ kJ mol}^{-1}$$
Steam Reforming
Steam Reforming of Other Hydrocarbons

- Higher hydrocarbons such as naphtha are the preferred feedstock for the reforming process when natural gas is not available or surplus of various hydrocarbon streams is available.

\[ C_nH_m + nH_2O \leftrightarrow ((m+2n)/2)H_2 + nCO \quad \Delta H_{298} > 0 \]

- Steam reforming of alcohols, methanol and ethanol, for fuel cell applications.

\[ CH_3OH + H_2O \leftrightarrow 3H_2 + CO_2 \quad \Delta H_{298} = + 49 \text{ kJ mol}^{-1} \]
Steam Reforming
Steam Reforming of Biogas

- **Biogas** is a renewable source similar to natural gas. It is commercially produced in large quantities in anaerobic digesters and landfill gas recovery facilities.
- Biogas can be an alternative raw material to conventional steam reforming technology.

Steam Reforming

Steam Reforming of Biogas

- The enrichment and enhanced potential of use can only be achieved after removing the CO₂ and contaminants (moisture, H₂S…).
- The upgrading step results in high capital and operational costs and lowers the efficiency of the process.
Steam Reforming
Alternative Processes

- High energy requirements and CO$_2$ emissions.
- High S/C ratio to avoid catalyst deactivation.
- Need for CO shift in order to adjust the H$_2$/CO ratio.

**Alternative processes ...**

**Dry reforming**
- ✓ Environmental benefits
- ✓ Adequate H$_2$/CO ratio for synthesis of oxygenated derivatives
- ✗ Catalyst deactivation by carbon deposits

**Partial Oxidation**
- ✓ Adequate H$_2$/CO ratio for methanol synthesis and Fisher-Tropsch reaction
- ✓ Exothermic reactions
- ✗ Lower energy efficiency and selectivity

**Autothermal Reforming**
- ✓ Thermally neutral system
- ✓ Adequate H$_2$/CO ratio for oxygenated derivatives and Fisher-Tropsch reaction
- ✗ Excessive control system
Dry Reforming

\[ \text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{H}_2 + 2\text{CO} \quad \Delta H_{298} = + 247 \text{ kJ mol}^{-1} \]

- Dry reforming offers environmental benefits as it turns two GHG into valuable feedstock.
  - CO\(_2\) emissions for SMR = 0.35 - 0.42 m\(^3\) of CO\(_2\)/m\(^3\) of H\(_2\) produced vs. CO\(_2\) emissions for DR as low as 0.20 m\(^3\) of CO\(_2\)/m\(^3\) of H\(_2\)
- DR is the most effective process wherever CO\(_2\)-rich methane stream is available, carbon dioxide is a byproduct ready for utilization and/or in areas where water is restricted:
  - Natural gas that contains large amounts of CO\(_2\)
  - In power plants which emit a large amount of CO\(_2\) at relatively high temperature, in petrochemical industries, in the metallurgical industry (coke oven gases)
  - Valorisation of landfill gas and biogas
This novel process combines the catalytic and dielectric properties of carbon materials with microwave heating.

Under MW heating the mechanism for DR reaction is believed to be a combination of the catalytic methane decomposition reaction and the CO$_2$ gasification reaction. In situ regeneration of active centres.

Cheap carbon-based materials present good catalytic activity towards DR under microwave heating, whereas low conversions of CH$_4$ and CO$_2$ are achieved using the same catalysts under conventional heating.
Dry Reforming
Microwave-assisted dry reforming over carbon-based catalysts

Activated Carbon
700 °C
CH₄/CO₂ = 2:3
VHSV = 0.4 L/g h

AC + Ni/Al₂O₃
800 °C
CH₄/CO₂ = 1:1
VHSV = 3.0 L/g h

Partial Oxidation

- The partial oxidation of methane is a catalytic process in which methane reacts with oxygen in the presence of a catalyst.
- Syngas production is maximized at ≈ 1100 °C and atmospheric pressure, yielding near complete methane conversion and minimizing CO$_2$ production.
- POX of methane is an exothermic process and it requires a smaller amount of thermal energy. But it is considered an expensive process because a flow of pure O$_2$ is needed.
- The two reactants can cause an explosion if the reaction is not appropriately controlled.

$$\text{CH}_4 + \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \quad \Delta H_{298} = -36 \text{ kJ mol}^{-1}$$
Autothermal Reforming

- Autothermal reforming is the reaction of natural gas or liquid hydrocarbons with steam and oxygen.
- ATR is a combination of SR and POX. It is designed to save energy, because the thermal energy required for SR is generated in the POX.
- The oxidant can be air, enriched air, or oxygen, depending on the demands of the downstream purification processes. ATR reformer operates in the range of 900–1150 °C and 1-80 bar.

\[
\text{CH}_4 + \frac{1}{2}\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \frac{5}{2}\text{H}_2 + \text{CO}
\]
POX and ATR
Commercial status

- ATR and POX are being developed mostly for fuel processors of gasoline, diesel, and jet fuel, and for natural gas fueled fuel cell (PEMFC) cogeneration systems.

Johnson Matthey – Hot Spot ATR

Tokyo Gas Company – D-CPOx
Options for Syngas Production from Solid Hydrocarbons
Gasification

- Gasification is a process which occurs when a solid carbonaceous material reacts with an oxidizer (excluding oxygen) to produce a gaseous fuel-rich product.
- Gasification is the basis for using solid fuels such as coal, petcoke, heavy oils and biomass for the production of syngas.
- The different characteristics of the feedstocks determine the technology being optimum for the gasification to syngas.
Gasification

Gasification
Producer Gas

- **Producer gas** is the term used when syngas is obtained specifically from gasification.
- The producer gas is mainly composed of $\text{H}_2$, CO, CO$_2$, CH$_4$ and H$_2$O.
- The main contaminants are tars, dust, alkali metals and traces of ammonia (NH$_3$), hydrogen sulphide (H$_2$S) and hydrochloric acid (HCl).
Gasification

- Gasification reactions are endothermic. Gasification processes can be designed so to balance the exothermic and endothermic reactions.

**Gasification:**

\[
\begin{align*}
C + CO_2 & \leftrightarrow 2CO \\
C + H_2O & \rightarrow CO + H_2 \\
C + 2H_2O & \rightarrow CO_2 + H_2 \\
C + O_2 & \rightarrow CO_2 \\
\end{align*}
\]

\[\Delta H_{298} = + 172 \text{ kJ mol}^{-1}\]

\[\Delta H_{298} = + 131 \text{ kJ mol}^{-1}\]

\[\Delta H_{298} = + 190 \text{ kJ mol}^{-1}\]

\[\Delta H_{298} = - 394 \text{ kJ mol}^{-1}\]

\[\Delta H_{298} = - 111 \text{ kJ mol}^{-1}\]

**Partial Oxidation:**

\[\text{C} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}\]

\[\Delta H_{298} = - 111 \text{ kJ mol}^{-1}\]

**Water gas shift:**

\[\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2\]

\[\Delta H_{298} = - 41 \text{ kJ mol}^{-1}\]

**Methanation:**

\[\text{C} + 2\text{H}_2 \leftrightarrow \text{CH}_4\]

\[\Delta H_{298} = - 75 \text{ kJ mol}^{-1}\]

\[2\text{CO} + 2\text{H}_2 \leftrightarrow \text{CH}_4 + \text{CO}_2\]

\[\Delta H_{298} = - 247 \text{ kJ mol}^{-1}\]

\[\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}\]

\[\Delta H_{298} = - 165 \text{ kJ mol}^{-1}\]

\[\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}\]

\[\Delta H_{298} = - 242 \text{ kJ mol}^{-1}\]

\[\text{S} + \text{H}_2 \rightarrow \text{H}_2\text{S}\]

\[\Delta H_{298} = - 20 \text{ kJ mol}^{-1}\]
Coal gasification is a mature technology and gasification reactors have been commercially available for decades. Gasification of coal has been practiced commercially for nearly 200 years and a renewed interest is recently evident with concern over dwindling reserves of oil and gas and the use of renewable energy.

Optimum operation for syngas from coal:
- Under pressure
- Low surplus of oxygen to minimise CO\(_2\) production
- At high temperature to ensure complete combustion of tar components
Gasification technologies are normally classified into three groups: (i) moving bed gasifiers; (ii) fluid bed gasifiers; and (iii) entrained flow gasifiers.
Coal gasification for liquid hydrocarbon production using Fischer-Tropsch technology is largely used in South Africa.
Gasification
Integrated Gasification Combined Cycle (IGCC) & Co-gasification

- The integrated gasification combined cycle (IGCC) produces a fuel gas which is cooled, cleaned and burned in a gas engine to produce electric power. Heat recovered from the hot exhaust of the gas engine produces steam that powers a steam turbine generator to produce additional electric power.
• Many of the techniques used for coal gasification have their analogues in biomass gasification. However, the differences both in the combustible material and in the associated mineral matter, call in many cases for different solutions in detail.

• Most of the gasification reactors dedicated for fossil fuels utilization are unsuitable for biomass processing because of its high content of alkali and alkali earth metals, and relatively high amount of tars released in the process.
Gasification

Biomass Gasification

- An extensive review of gasifier manufacturers in Europe, USA and Canada identified 50 manufacturers offering ‘commercial’ biomass gasification plants.
- Biomass gasification is in use in a number of pilot and demonstration plants but only in a few industrial large commercial scale and operational units.

Sources: Maniatis K. Progress in biomass gasification: an overview
Gasification
Biomass Gasification – Syngas Cleaning

- Producer gas cleaning is a fundamental step in integrated biomass gasification systems.
- The level of cleaning that is required may vary substantially depending on the end-use technology and/or emission standards.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC engine</td>
<td>Gas turbine</td>
</tr>
<tr>
<td>Particulate</td>
<td>&lt;50 mg m(^{-3})</td>
</tr>
<tr>
<td>(soot, dust, char, ash)</td>
<td>(PM10)</td>
</tr>
<tr>
<td>Tars (condensible)</td>
<td>&lt;100 mg m(^{-3})</td>
</tr>
<tr>
<td>Inhibitory compounds</td>
<td></td>
</tr>
<tr>
<td>(class 2-heter atoms, BTX)</td>
<td></td>
</tr>
<tr>
<td>Sulfur</td>
<td>&lt;20 µL L(^{-1})</td>
</tr>
<tr>
<td>(H(_2)S, COS)</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>&lt;50 µL L(^{-1})</td>
</tr>
<tr>
<td>(NH(_3), HCN)</td>
<td></td>
</tr>
<tr>
<td>Alkali</td>
<td>&lt;0.024 µL L(^{-1})</td>
</tr>
<tr>
<td>Halides (primarily HCl)</td>
<td>1 µL L(^{-1})</td>
</tr>
</tbody>
</table>

Note: All values are at STP unless explicitly stated otherwise.

\(^a\) n.d. = not detectable; tars described in further detail in Section 2.2.

Gasification
Biomass Gasification – Commercial Status

**Enerkem Alberta Biofuels**

- **Feedstock**
  Post-sorted municipal solid waste
- **Products**
  Biomethanol, bioethanol, chemicals and other materials
- **Expected capacity**
  38 million litres per year
Gasification
Biomass Gasification – Commercial Status

Babcock & Wilcox Volund, Plant Harbore, Denmark

- Gasifier primary fuel – woodchips
- Gasifier output – 4 MWth

Source: Babcock & Wilcox Volund Plan Fact Sheet. Biomass Gasification Plants – Woodchips gasification
Pyrolysis is a thermochemical decomposition of a solid fuel in the absence of oxidizing agents.

The syngas production from pyrolysis takes places through the gasification of bio-oil and char.

Biorefining is the sustainable processing of biomass into a spectrum of marketable products and energy.

Syngas production and purification technologies are in the centre of future high efficient and low emission technologies.
Biomass & Waste Conversion Technologies: syngas production and biotechnological application