1 Routes to Syngas

1.1 General trends

1.1.1 Towards focus and sustainability

Synthesis gas (syngas) is a mixture of hydrogen, carbon monoxide and carbon dioxide. It may also contain nitrogen as applied for the ammonia synthesis. Syngas is a key intermediate in the chemical industry. It is used in a number of highly selective syntheses of a wide range of chemicals and fuels, and as a source of pure hydrogen and carbon monoxide. Syngas is playing an increasing role in energy conversion [418].

Synthesis gas can be produced from almost any carbon source ranging from natural gas and oil products to coal and biomass by oxidation with steam and oxygen. Hence it represents a key for creating flexibility for the chemical industry and for the manufacture of synthetic fuels (synfuels).

Figure 1.1 Conversion via syngas.

The conversion via syngas results in products plus heat (Figure 1.1). In most plants, the heat is utilised for running the plant. As an alternative, the heat may be exported, but that is not always necessary.

The present use of syngas is primarily for the manufacture of ammonia (in 2006, 124 million tonnes per year) and of methanol (in 2005, 33 million tonnes per year), followed by the use of pure hydrogen for hydrotreating in refineries as shown in Table 1.1.

The main commodity products based on natural gas are shown in Table 1.1 [420]. It is evident that the chemical conversion of natural gas
(approximately $7 \times 10^9$ GJ/y) is marginal to the total natural gas production $(3.07 \times 10^{12}$ Nm$^3$/y [78] or $1.17 \times 10^{11}$ GJ/y assuming a lower heating value (LHV) equal to 38 MJ/Nm$^3$). Recent trends in the use of syngas are dominated by the conversion of inexpensive remote natural gas into liquid fuels (“gas to liquids” or “GTL”) and by a possible role in a future “hydrogen economy” mainly associated with the use of fuel cells. These trends imply, on the one hand, the scale-up to large-scale GTL plants (more than 500,000 Nm$^3$ syngas/h) and, on the other hand, the scale-down to small, compact syngas units for fuel cells ($5–100$ Nm$^3$ syngas or H$_2$/h). These forecasts create new challenges for the technology and for the catalysis.

Table 1.1 Main chemical products based on natural gas.

<table>
<thead>
<tr>
<th>Product</th>
<th>Yearly prod. (mil. t/y)</th>
<th>Energy consumpt. (GJ/t)</th>
<th>Thermal LHV (mol / methane LHV)</th>
<th>Efficiency (mol / product LHV)</th>
<th>CO$_2$ (t/t)</th>
<th>Main technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>124</td>
<td>29</td>
<td>65</td>
<td>89</td>
<td>16$^a$</td>
<td>Syngas/synthesis</td>
</tr>
<tr>
<td>Ethylene</td>
<td>75</td>
<td>15$^b$</td>
<td>62</td>
<td>93</td>
<td>0.65</td>
<td>Steam cracking C$_2$H$_6$</td>
</tr>
<tr>
<td>Propylene</td>
<td>53</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Steam cracking C$_2$H$_6$</td>
</tr>
<tr>
<td>Methanol</td>
<td>32</td>
<td>28</td>
<td>72</td>
<td>84</td>
<td>0.28</td>
<td>Syngas/synthesis</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>20</td>
<td>12.6</td>
<td>84$^c$</td>
<td>92</td>
<td>0.9</td>
<td>Steam reforming</td>
</tr>
<tr>
<td>Synfuels</td>
<td>18$^d$</td>
<td>67</td>
<td>60</td>
<td>78</td>
<td>1.18</td>
<td>Syngas/synthesis</td>
</tr>
</tbody>
</table>

a) incl. CO$_2$ converted into urea
b) data kindly provided by F. Dautzenberg, ABB Lummus, 2005
c) CH$_4$ used for reaction heat; no steam export
d) excl. 3 million tonnes per year under construction

The data in Table 1.1 show that the practical efficiencies for natural gas conversion into products are approximately 80% of the ideal values expressed as:

$$\eta_{ideal} = \frac{\text{LHV product/mol}}{\text{LHV methane/mol}}$$

(1.1)

For endothermic reactions (ethylene, hydrogen), the LHV of the fuel providing the reaction heat should be added to the nominator.

The world energy production is dominated by fossil fuels as the main energy source. It amounted to 88% in 2007 with oil responsible for 37%
The energy consumption is growing fast in Asia, and China has become the world’s second largest consumer of oil, after the USA. The proved reserves of oil are concentrated in the Middle East (61%) and those of natural gas are also in the Middle East (41%), followed by Russia (23%) [78]. Coal is more evenly distributed between the continents.

Apart from the large reserves (Middle East, Russia), natural gas is present as associated gas in oil fields. However, as many fields are far from the marketplace and often off-shore, the gas there is called remote gas or stranded gas [102]. Part of the associated gas is reinjected to enhance the oil recovery, but unfortunately still a significant fraction is flared for convenience. The flared gas amounts to close to 5% of the total natural gas production (corresponding to about 1% of total world CO₂ production from fossil fuels) [263] [420].

So far, the proven reserves for oil have followed the increase in production as expressed by the reserves/production ratio (R/P ratio) staying at about 40 for oil over the last 20 years; however, at a steadily increasing cost of exploration and production. A big fraction of the reserves is present as oil sand (tar sand) and other non-conventional sources under active development [78]. This means that at the present world production, the oil reserves known today will be used up within about 40 years. This figure should be considered with care. It does not include reserves still to be found and it does not include the changes in consumption (for instance the growth in Asia). Furthermore, the R/P ratio for oil varies from region to region, being above 80 in the Middle East and below 20 in North America.

The R/P ratio (2007) for natural gas is about 60 and 122 for coal [78]. The total R/P for fossil fuels (based on oil equivalent) is less than 100 years. These figures emphasise the need for flexibility in the energy network and the need for alternative fuels. Oil is the most versatile of the fossil fuels with high energy density and it is easily transported.

The power industry is very flexible to feedstocks and it is feasible to transport coal over long distances to big centralised power plants close to deep water harbours. Natural gas is transported to the marketplace in pipelines over still longer distances or as liquified natural gas (LNG).
The automotive sector represents a special challenge as the energy conversion is strongly decentralised. So far oil-derived products have been the solution, but in view of the limited reserves of oil, a number of alternative fuels are being considered, such as liquefied petroleum gas (LPG), natural gas, methanol, dimethylether (DME), ethanol, biodiesel, synfuels and hydrogen. Biofuels represent a “sustainable” response to liquid fuels. It may be based on ethanol and biodiesel derived from conventional agricultural products or from synfuels via gasification of biomass. The alternative fuels may be blended with conventional fuels or used directly in internal combustion engines (ICE) or fuel cells. In Western Europe alternative fuels may amount to 20% of energy sources by 2020.

Globalisation has caused companies to concentrate on core business and critical mass. It has resulted in a restructure of the chemical industry into two types of focused companies [190]: the molecule suppliers (commodities and fine chemicals) and the problem solvers (functional chemicals like additives and pharmaceuticals). Each type has its own characteristics as reflected by the role of the catalyst [418].

The most important parameter for large-volume chemicals is production costs (variable and fixed costs). The variable costs are related to the feed costs, the use of energy, process selectivity and environmental costs.

Four trends have characterised plants for commodity chemicals:

- Location of cheap raw materials;
- Economy of scale;
- More integrated plants; and
- CO₂ footprint (tonnes CO₂ per tonne product).

Plants are moved to locations where raw materials are cheap. As illustrated in Figure 1.2, the ammonia production is hardly feasible at natural gas prices typical for Europe and USA (3–4 USD/GJ with high seasonal variations) [420]. As a result, new plants for commodity chemicals are built at locations (Middle East, Trinidad, Nigeria, West Australia…) with low natural gas prices (0.5–1 USD/GJ). It means that
the use of natural gas as feedstock may not be feasible where there is a big market for natural gas as fuel.

![Graph showing ammonia production costs](image)

**Figure 1.2 Ammonia production costs [420]. Reproduced with the permission of Springer.**

Plants have become larger to take advantage of the economy of scale. The economy of scale can be expressed by:

$$\text{Cost}_1 = \text{Cost}_2 \left( \frac{\text{capacity}_1}{\text{capacity}_2} \right)^n$$

(1.2)

$n$ typically varies between 0.6–0.9.

The economy of scale means choice of different technologies as they may be characterised by different values of $n$.

Today, ammonia plants are built with capacities up to more than 3000 metric tons per day (MTPD) and methanol plants are being considered at capacities of 10000 MTPD. This corresponds to the size of synthetic fuel plants based on FT synthesis (35,000 bpd). At the same time, as plants become bigger, there is a trend to miniturise chemical process plants and take advantage of mass production, the economy of numbers competing with the economy of scale. This is one of the key issues in the “hydrogen economy” and the application of fuel cells. Micro-structured
process equipment components such as heat exchangers, and new reactor concepts are becoming available. Plants have also become more integrated to minimise energy consumption.

It can be shown that the plant costs for a variety of processes correlate with the energy transfer (heat transfer, compression) within the process scheme [289]. As an example, the energy consumption of ammonia production has decreased over the last 50 years from about 40 GJ/t to 29 GJ/t corresponding to a thermal efficiency (LHV) of 65% or 73% of the theoretical minimum [169] [420].

Commodity plants depend on steady improvement and sophistication of the technology. Even small improvements of the process scheme may show short payback times. On the other hand, the uncertainties associated with new technology may easily outbalance the economic advantage of a new process. Improvement of one process step might easily result in less favourable performance of another process step. The high degree of integration means that the weakest part of the chain may determine the performance of the entire plant. As an example, there is a need for more coke-resistant catalysts and often deactivation phenomena determine the process layout and the optimum process conditions to be applied [404]. It is evident that catalyst life, i.e. on-stream factor, is crucial for large-scale commodity plants in contrast to batch-wise manufacture of fine chemicals.

A few days’ production stop because of a catalyst failure may be crucial for the plant economy. It means that secondary phenomena such as catalyst deactivation are important issues. For large-scale operation, economic arguments will limit the minimum space time yield to approximately 0.1 tonne product/m³ at a typical catalyst life of 5 years [289]. This corresponds to a catalyst consumption of less than 0.2 kg cat/t product. For ammonia synthesis a typical figure is 0.03 kg cat/t NH₃.

These risks mean that it has become more expensive to develop new process technology. New technology must be demonstrated to a larger extent – not only the basic principles, but also the solutions to a series of secondary problems [400] [418].

Many well-established processes are approaching their theoretically achievable efficiency, selectivity, etc. (refer to Table 1.1), but new
challenges have been introduced by objectives for sustainable growth formulated by society. This has not only led to the introduction of new products, but also necessitated the development of new processes. Environmental challenges represent major room for breakthroughs in the catalytic process industry.

For any process scheme, it is essential at an early stage to establish the overall mass balance and to estimate the $\Delta \rho$ as simply being the difference between the price of products and the price of feedstocks [418]. Hence, there has been a trend to develop processes using cheaper raw materials. The gain in $\Delta \rho$ could, however, be lost by lower selectivity or higher investments. Selectivity is crucial to achieving a high $\Delta \rho$. Low selectivity and conversion per pass result in low concentrations in process streams and hence more expensive separation systems.

It may be argued that energy efficiency is of less importance when natural gas is cheap, but high energy efficiency means small feed pretreat units and reduced requirements for utilities and hence less investments.

Moreover, high efficiency means less CO$_2$ production. As illustrated in Figure 1.3, the $\Delta \rho$ calculation should consider also the energy

![Figure 1.3 Simplified mass balance.](http://www.worldscibooks.com/chemistry/p717.html)
consumption and the by-products which may easily have a negative value. This may be expressed by the so-called E-factor [458] expressing the amount of by-product produced per kg of product.

The emissions may have great negative value. This may be reflected by the costs of carbon capture and storage (CCS) (refer to Section 1.4.2). The CO₂ emission expressed as a C-factor [106] [420] (tonnes CO₂ per tonne product, refer to Table 1.1) may become an important process parameter in the future. CO₂ emissions are often directly related to the energy consumption of the process.

As an example, a reduction of the energy required to produce ammonia from natural gas of 1 GJ/t means a reduction of CO₂ emissions of around 8.5 million tonnes CO₂/y, worldwide [416]. In many ammonia plants about 80% of the CO₂ is reacted with ammonia to urea from which it is, of course, liberated to the atmosphere when the urea is used as fertiliser.

On the other hand, CO₂-consuming processes will hardly change the picture from non-carbon containing fuel [416].

As an example, consider the methanol synthesis:

\[
\text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}
\]  

(1.3)

Even if hydrogen was made available from non-carbon containing fuel, the present world production of methanol via this reaction would only amount to 40 million t CO₂/y. This corresponds to the CO₂ emission from a 4000 MW coal-based power plant and should be compared with the total CO₂ emissions of approximately 27.5 \(10^9\) t CO₂/y (7.5 \(10^9\) t carbon/y). It means that CO₂ as a reactant will have little impact on the CO₂ problem. Again, the products will eventually end as CO₂.

A similar argument is valid for CO₂ reforming of natural gas.

1.1.2 Direct or indirect conversion

An important challenge in “C₁ chemistry” is to circumvent the syngas step by a direct conversion of methane into useful products. Still, yields are far from being economical [238] [287] [307]. The methane molecule is very stable, with a C-H bond energy of 439 kJ/mol; hence methane is resistant to many reactants. Electrophillic attack requires superacidic
conditions, and radical abstraction of a hydrogen atom by a reactant $Q$ requires that the $Q$-$H$ bond exceeds 439 kJ/mol [130]:

$$\text{CH}_4 + Q^\cdot \leftrightarrow \text{CH}_3 + QH$$

(1.4)

This is feasible when $Q$ is an oxidising agent. However, the product often has much weaker C-H bonds than methane, which implies that it is difficult to eliminate further reactions leading to complete oxidation.

$$\text{CH}_4 \xrightarrow{\text{O}_2} \text{CH}_4\text{O} \xrightarrow{\text{O}_2} \text{CO}_2 + 2\text{H}_2\text{O}$$

(1.5)

The direct conversion of CH$_4$ into methanol may have a high selectivity, but at a low conversion per pass. For example, Zhang et al. [537] reported a selectivity of 60% at a conversion of 12–13%. This corresponds to a yield of about 7.5%. This low yield per pass results in a large recycle ratio and a difficult separation associated with a low partial pressure of the product. This is illustrated by simple calculations in Figure 1.4 [410].

Figure 1.4 Recycle ratio and conversion. A selectivity of 95% at a conversion per pass of 5% means a large recycle ratio of approximately 10, and hence a difficult separation due to low partial pressure of the product. Reproduced with the permission of Springer [410].
A simple kinetic analysis of consecutive first-order reactions [410] may illustrate the problem. The data in Figure 1.5 show that the higher the ratio $k_2/k_1$, the lower the yield of the intermediate B.

![Graph showing the relationship between $Y_{max}$ and $k_2/k_1$.](image)

Figure 1.5 Consecutive reactions. Reactivities and maximum yields. Reproduced with the permission of Springer [410].

The direct oxidation of methane to methanol or formaldehyde has been a “dream reaction” for a long time [537]. Attempts include gas-phase reaction, catalytic reactions, and use of other oxidants than air. Selectivities may be high, but at a lower conversion per pass resulting in yields being inferior for industrial use.

High selectivity and conversion may not be sufficient. A process using superacid activation (Catalytica) for converting CH$_4$ via methyl bisulphate into methanol has the potential of achieving a high selectivity of 95% at a conversion of 90% [345]. However, the process would require a large sulphuric acid plant (1 mol SO$_3$/mol methanol) and a unit for concentrating a large recycle of diluted acid [410].

Other attempts have aimed at creating a carbon-carbon bond from methane, although most natural gas sources contain a fraction of ethane and other lower alkanes.
Most work in direct conversion has focused on the oxidative conversion of methane into ethylene [196] [307]. It has proven to be more promising than high-temperature pyrolysis of methane into primarily acetylene. However, the process suffers from ethane being a significant part of the products (low ΔΔ) and that above 20% of the converted methane is oxidised to carbon oxides. Under industrial conditions C2 yields are less than 20% at a conversion of 24–35% per pass. As a result, the process scheme ends up being rather complex, meaning that the oxidative coupling is not economically feasible with the present low selectivities to C2 hydrocarbons. Although the reaction scheme is elegant, the principles behind Figure 1.4 may explain why yields in oxidated coupling have never passed an apparent ceiling [292].

Catalytic partial oxidation at high temperature and ultra-short residence time over noble metals gauze has shown formation of olefins and oxygenates [206]. The feasibility of this route is still to be analysed. The indirect route via methanol appears to be a more promising route for olefins (see Section 2.6).

Direct conversion of methane to higher hydrocarbons without the assistance of oxygen is not favoured by thermodynamics. This constraint can be circumvented in a two-step process via carbides, but so far yields have been insignificant [279].

Other studies have explored the direct conversion of methane into benzene [420]. Selectivities of 70% were obtained close to equilibrium conversion at 600°C (12%).

From a thermodynamic point of view [145] the manufacture of synthetic transportation fuels should aim at a minimum change of the hydrogen content of the feedstock to that of the product (typically around H/C=2). It means that, in principle, it is more efficient to convert natural gas to paraffinic diesel than to aromatic rich gasoline. For coal the indirect conversion via syngas appears less efficient than the direct hydrogenation routes. However, these theoretical considerations should be supplemented with an analysis of the process steps and selectivities involved [145].

The main advantage of the indirect routes via syngas is the very high carbon efficiency. As an example, a modern methanol synthesis loop based on natural gas may operate with more than 50% conversion per
pass having a selectivity of 99.9% and a carbon efficiency above 95% (refer to Section 2.6.2). The synthesis gas routes are highly efficient as illustrated in Table 1.1, but they are capital intensive because they involve exchange of energy in the reformers and heat recovery units, as illustrated in Figure 1.6 [413].

![Figure 1.6 Indirect conversion of natural gas (numbers indicate the relative investments) [413]. Reproduced with the permission of Elsevier.](image)

Syngas manufacture may be responsible for approximately 60% of the investments of large-scale gas conversion plants based on natural gas. Therefore, there is great interest in optimising process schemes based on steam reforming and autothermal reforming as well as in exploring new routes for the syngas manufacture.

1.2 Manufacture by steam reforming of hydrocarbons

1.2.1 Reactions and thermodynamics

Steam reforming is the reaction between steam and hydrocarbons into a mixture of hydrogen, carbon monoxide, carbon dioxide and unconverted
reactants. Steam may be replaced by carbon dioxide as reactant. The reforming reactions are accompanied by the water-gas-shift reaction.

The term “steam reforming” should not be confused with catalytic reforming used for the conversion of paraffinic hydrocarbons to high octane hydrocarbons such as iso-alkanes and aromatics. A better term may be “oxygenolysis” [381] [389] as the reaction involves the breakage of C-H and C-C bonds by means of oxygen containing species.

A complete steam reforming reaction scheme can thus be written as:

Table 1.2 Steam reforming reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction</th>
<th>$\Delta H_{\text{298}}^0$</th>
<th>kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2$</td>
<td>-206</td>
<td></td>
</tr>
<tr>
<td>R2</td>
<td>$\text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4\text{H}_2$</td>
<td>-165</td>
<td></td>
</tr>
<tr>
<td>R3</td>
<td>$\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2$</td>
<td>-247</td>
<td></td>
</tr>
<tr>
<td>R4</td>
<td>$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>R5</td>
<td>$\text{C}_n\text{H}_m + n\text{H}_2\text{O} \leftrightarrow n\text{CO} + (n + 0.5m)\text{H}_2$</td>
<td>$&lt;0$</td>
<td></td>
</tr>
</tbody>
</table>

Although all reactions may describe specific operating conditions, only two out of the first four reactions are independent from a thermodynamic point of view, since the other two can be established as linear combinations of the two selected ones. Catalytic studies indicate that it is steam reforming of methane to carbon monoxide and the water-gas-shift reactions that are the independent reactions in addition to the steam reforming of higher hydrocarbons as the last reaction. This set of reactions (R1, R4, and R5 in Table 1.2) will consequently be used in the following.

The term “steam reforming” is also used for the reaction between steam and alcohols (methanol and ethanol) as well as liquid-phase reactions with carbohydrates or biomass (see Section 1.4).
The last reaction R5 in Table 1.2 is the reverse Fischer–Tropsch synthesis, but the conversion of higher hydrocarbons can be considered irreversible at normal reforming temperatures. The higher hydrocarbons react on the metal surface to C1 components or stay as carbonaceous deposits. At temperatures above 600–650°C, the catalytic reactions may be accompanied by thermal cracking.

The symbol “$\leftrightarrow$” indicates that a reaction is reversible, i.e. at a given temperature the reaction will not have full conversion. Usually only the last reaction is considered irreversible, so parts of methane and steam will remain in the mixture at outlet conditions.

Preparation of heat and mass balances for synthesis gas processes thus requires methods to calculate mass and heat balances and chemical equilibrium.

For a reaction system like the one shown above in Table 1.2 it is convenient to define the thermodynamic reference state as the enthalpy and free energy of formations as an ideal gas at 25°C (298.15 K). This definition allows direct calculation of heat duty in the enthalpy calculation without having to distinguish between the parts for heating and reaction.

Different functions may be used to represent the ideal gas heat capacity or enthalpy as a function of temperature; values in Appendix 1 are based on a fourth-degree polynomial for the enthalpy of formation, where the zero-order coefficient has been adjusted to obtain the enthalpy of formation at 25°C.

\[
H_i = \sum_{k=1}^{5} E_{ik} \cdot T^{k-1}
\]  

(1.6)

Appendix 1 shows the coefficients in the enthalpy polynomials for a number of characteristic synthesis gas reaction key components and a table with actual values of the ideal enthalpies of formation as a function of temperature.

The preparation of mass balances requires calculation of chemical equilibrium by solution of the following Equation (1.7) for the coupled reactions between all components:

\[
K_{eq,j} = \prod_{i=1}^{n} a_i^{Y_{ij}}
\]  

(1.7)
where \( v_{ij} \) is the stoichiometric coefficient for component \( i \) in reaction \( j \).

The right-hand side includes the activity, which rigorously is defined as:

\[
a_i = \frac{f_i^\text{gas}}{f_i^\circ} = \frac{y_i \cdot \varphi_i \cdot P}{f_i^\circ}
\]  

in which \( f \) is the fugacity, \( f^\circ \) the reference fugacity and \( \varphi \) the fugacity coefficient, which describes the deviation from an ideal gas. Preparation of syngas is carried out at high temperature and a modest pressure so the assumption of an ideal gas is acceptable when the operation is not close to the dew point of the mixture. This implies that the fugacity coefficient \( \varphi \) usually is set to unity. The equilibrium constant, \( K_{eq} \), is a function of temperature only, so the conversion in the steam reforming of methane reaction is favoured by a low pressure.

As the reference state for all components in the reactions is defined as an ideal gas at 25°C (298.15K) and 1.01325 bar, the value that must be used for \( f^\circ \) is 1.01325 bar. If another unit of measurement for pressure is used, the reference pressure must be changed correspondingly so that the activity becomes independent of pressure. If a component is a solid, such as carbon in carbon formation, the activity, \( a_i \), is unity, since the reference state for the Gibbs free energy of carbon is also defined as the solid state.

The temperature equation for the equilibrium constant is derived from thermodynamics using the Gibbs energy of formation, \( G^\circ \), the enthalpy of formation \( H^\circ \), and the temperature dependence as derived from:

\[
RT \ln(K_{eq,j}) = -\Delta G_j^\circ
\]

\[
\frac{\ln(K_{eq,j})}{dT} = \frac{\Delta H_j^\circ}{RT^2}
\]

After insertion of Equation (1.6) the final equation for the equilibrium constant is:

\[
\ln(K_{eq,j}) = C_{1,j} \cdot \ln(T) + \frac{C_{2,j}}{T} + C_{3,j} \cdot T + C_{4,j} \cdot T^2 + C_{5,j} \cdot T^3 + C_{6,j} \cdot T^4
\]

The basic reaction properties for some key reactions are shown in Table 1.3.
Table 1.3 Basic reaction properties for steam reforming reactions. Formation data at 25ºC. Data from [137] [375].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH°</th>
<th>ΔG°</th>
<th>ΔS°</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ + H₂O ↔ CO + H₂O ↔ CH₄ + CO₂ ↔ C₂H₆ + 2H₂O ↔ CO + 3H₂</td>
<td>206.15</td>
<td>142.12</td>
<td>0.2148</td>
</tr>
<tr>
<td>CO₂ + H₂</td>
<td>-41.16</td>
<td>-28.52</td>
<td>-0.0424</td>
</tr>
<tr>
<td>2CO + 2H₂</td>
<td>247.31</td>
<td>170.64</td>
<td>0.2572</td>
</tr>
<tr>
<td>2CO + 5H₂</td>
<td>347.27</td>
<td>215.53</td>
<td>0.4419</td>
</tr>
</tbody>
</table>

The definition of the standard state as the ideal gas of formation at 25ºC (298.15K) and 1.01325 bar implies that the absolute values of entropy will not fulfil the third law. The heat of reaction is defined as the heat of formation, but with the opposite sign so it is written as -ΔH°₂⁹₈.

Tables with equilibrium constants at selected temperatures for the main synthesis gas reactions are shown in Appendix 2.

The reforming reaction involving two stable molecules as methane and water is strongly endothermic and it leads to formation of more molecules. This means that the affinity for the reaction (-ΔG°) is established by the entropy term. The basic thermodynamic reaction properties as a function of temperature are shown for the methane reforming reaction in Figure 1.7.

It is seen that reaction enthalpy and entropy are weak functions of temperature, but also that they are positive in the entire interval implying that other heat sources are necessary for conversion. The free energy decreases strongly with temperature due to the corresponding increase in
\[ \Delta S \] giving more favourably equilibrium. Hence, the steam reforming reaction is entropy-driven.

![Figure 1.7 Steam reforming. Thermodynamic functions.](image)

Conversion at equilibrium is calculated by solving the coupled set of equations for \( K_{eq} \) for the two independent reactions R1 and R4 in Table 1.2.

A simplified method to find the conversions in the two reactions is available as will be shown below, but a general method which can solve any chemical equilibrium problem is preferred. For this purpose two methods may be used. The first is minimisation of the Gibbs free energy [316], whereas the other one is the solution for conversions [468]. The first one may be attractive from a theoretical point of view and it is readily combined with phase equilibrium, but the last one is preferred in catalysis, since no combination of reactions may proceed in all cases. The set of equations in Table 1.2 may be solved using the Newton–Raphson method with the conversions as independent variables. Some of the components (higher hydrocarbons or oxygen) may almost disappear in the final mixture so it is necessary to handle elimination of reactions with almost complete conversion.
Methane conversions as a function of temperature in the combined methane reforming and shift reactions are shown in Figure 1.8. It is seen that conversion is strongly favoured by high temperature, low pressure, and high steam-to-carbon ratio.

Example 1.1
A simplified method [276] may be used to solve the chemical equilibrium for the reactions R1, R4 and R5 in Table 1.2 and find the conversions $\xi_1$ and $\xi_4$ in the reactions R1 and R4.

Initially all higher hydrocarbons are converted quantitatively to CO and H$_2$ using Equation R5, whereafter the mole amounts in the initial
mixture are converted according to the ordinary stoichiometric conversion equations below:

\[
\begin{array}{c|c|c}
\text{In} & \text{Out} & y \\
y^{0}_{\text{CH}_4} & y^{0}_{\text{CH}_4} - \xi_1 & y_{\text{CH}_4} = (y^{0}_{\text{CH}_4} - \xi_1)/(1 + 2 \xi_1) \\
y^{0}_{\text{H}_2\text{O}} & y^{0}_{\text{H}_2\text{O}} - \xi_1 - \xi_4 & y_{\text{H}_2\text{O}} = (y^{0}_{\text{H}_2\text{O}} - \xi_1 - \xi_4)/(1 + 2 \xi_1) \\
y^{0}_{\text{CO}} & y^{0}_{\text{CO}} + \xi_1 - \xi_4 & y_{\text{CO}} = (y^{0}_{\text{CO}} + \xi_1 - \xi_4)/(1 + 2 \xi_1) \\
y^{0}_{\text{CO}_2} & y^{0}_{\text{CO}_2} + \xi_4 & y_{\text{CO}_2} = (y^{0}_{\text{CO}_2} + \xi_4)/(1 + 2 \xi_1) \\
y^{0}_{\text{H}_2} & y^{0}_{\text{H}_2} + 3\xi_1 + \xi_4 & y_{\text{H}_2} = (y^{0}_{\text{H}_2} + 3\xi_1 + \xi_4)/(1 + 2 \xi_1)
\end{array}
\]

The bottom line is the total amount before and after conversion. The normalisation is in principle with respect to the total amount of preconversion of higher hydrocarbons; here it is simply assumed that the sum of the initial mole fractions is unity.

Assuming ideal gas the mole fractions can now be inserted in the two equations for $K_{\text{eq}}$:

\[
K_{\text{eq,ref}} = \frac{y^{3}_{\text{H}_2} \cdot y_{\text{CO}} \cdot P^2}{y_{\text{CH}_4} \cdot y_{\text{H}_2\text{O}}}
\]

\[
K_{\text{eq,shf}} = \frac{y^{2}_{\text{H}_2} \cdot y_{\text{CO}_2}}{y_{\text{CO}} \cdot y_{\text{H}_2\text{O}}}
\]

Considering the shift reaction alone results in a second-order equation in the conversion $\xi_{\text{shf}}$, and this equation can be solved analytically after reformulation of the equilibrium equation as:

\[
\begin{align*}
\{ K_{\text{eq,shf}} y_{\text{CO}} & y_{\text{H}_2\text{O}} - y^{0}_{\text{H}_2} y^{0}_{\text{CO}_2} \} \xi_{\text{shf}}^2 + K_{\text{eq,shf}} (y^{0}_{\text{CO}} + y^{0}_{\text{H}_2\text{O}}) + (y^{0}_{\text{H}_2} + y^{0}_{\text{CO}_2}) = 0 \\
\text{or} & \\
A \xi_{\text{shf}}^2 + B \xi_{\text{shf}} + C = 0
\end{align*}
\]

The roots are:

\[
\xi_{\text{shf}} = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A} = \frac{-B \pm D}{2A}
\]
Both roots are real, but only the smallest one is used, since the largest one (by experience) may give negative mole fractions. –B is always positive, so the solution is in principle only relevant for –D, but since B and D numerically may have the same size, it is appropriate to use the + sign for the other root and then calculate the final root by using the fact that the product of the two roots is C/A.

The conversion in the shift reaction alone is then:

$$\xi_4 = \frac{2C}{-B + D}$$

This implies that for any value of $\xi_1$ the conversion in the shift reaction can be found analytically. The reforming reaction with known $\xi_4$ is a fourth-order equation in $\xi_1$. It can be solved analytically, but it is more practical to implement a combined method to solve the two equations [276]. This method uses bisection for the determination of $\xi_1$ with insertion of the correct value of $\xi_4$ for each step by solution of the quadratic equation. The equations are highly non-linear, so it is necessary to know the conversion limits. The lower limit may be set to zero here. It need only be considered if the reverse reaction must be considered. The upper limit is the minimum concentration of either CH₄ or H₂O+CO₂.

The method is suitable for implementation in a spreadsheet and can be written as:

1. Calculate the equilibrium constants for the two reactions from the data in Appendix 2.
2. Specify the lower and upper boundaries as $\xi_{1,\text{min}}$ and $\xi_{1,\text{max}}$.
3. Guess a new value of $\xi_1$ as the average of the minimum and maximum values.
4. Calculate new initial mole fractions assuming the conversion $\xi_4$ in the shift reaction is 0.
5. Find the conversion in the shift reaction from the analytical solution.
6. Calculate new mole fractions using both conversions.
7. Calculate the reaction quotient for the steam reforming reaction by inserting the new calculated mole fractions in the equilibrium expression.
8. If the reaction quotient is larger than the equilibrium constant, the conversion is too large, since the reaction quotient increases...
with conversion. Set the upper conversion limit to the calculated value of $\xi_1$ and jump to step 3.

9. If the reaction quotient is smaller than the equilibrium constant, the conversion is too small. Set the lower conversion limit to the calculated value of $\xi_1$ and jump to step 3.

The iteration is slow but safe and continues until the desired accuracy has been reached.

The steam reforming reactions are fast reactions due to the high temperature and the presence of the catalyst implying that the actual conversion will be close to the equilibrium conversion.

Figure 1.9 shows the conversions in the methane steam reforming and shift reactions, if they are treated as independent reactions. The conversion in the endothermic steam reforming is increasing with temperature, whereas the opposite is the case for the shift reaction.

![Figure 1.9 Temperature, conversion and temperature approach to equilibrium for steam reforming and shift.](image)

Using actual conversions as a measure of reaction extent is not convenient, since they must be relative to equilibrium conversions. Instead the so-called “temperature approach” to equilibrium is used,
which is the horizontal distance between the actual outlet temperature and the corresponding equilibrium temperature. This is illustrated in Figure 1.9 by use of the adiabatic reaction paths. The temperature approach to equilibrium is portrayed by horizontal dotted lines.

It is seen that an appropriate definition of the temperature approach is:

\[ \Delta T_{\text{app,ref}} = T_{\text{exit}} - T_{\text{eq}} \]
\[ \Delta T_{\text{app,shf}} = T_{\text{eq}} - T_{\text{exit}} \]  

(1.11)

\( T_{\text{eq}} \) is the temperature on the equilibrium curve having the same conversion or the same reaction quotient as the actual outlet gas.

By this definition the temperature approach will always be positive provided the reaction path is below the equilibrium curves.

It is true that if two of the reactions in the reaction set R1 to R4 in Table 1.2 are at equilibrium, the other two will also be at equilibrium. If, however, one of the reactions has an approach larger than zero, the other reactions will have different approaches and some may even have negative approaches. This also signifies that conversion and temperature approach in fact only has a practical meaning for the limiting reaction.

Example 1.2
The equilibrium conversion in the steam reforming of methane to carbon monoxide and hydrogen is determined from the two equilibrium expressions shown in Example 1.1. In this second example a large hydrogen plant making 100,000 Nm\(^3\)/h of H\(_2\) is considered.

Although some hydrogen must be present in the feed to keep the catalysts reduced, the feed is assumed to be pure CH\(_4\) with an actual flow equal to 500 mol/s and a temperature of 500ºC. The condition out of the tubular reformer is 875ºC and 31 bar (absolute) and the dry gas composition (mole %) has been measured at the outlet as: H\(_2\) 70.36, CO 13.65, CO\(_2\) 7.35 and CH\(_4\) 8.64.

Assume that the shift reaction is in equilibrium in order to calculate the unknown amount of water and then calculate the temperature approach to the steam reforming of methane reaction.

The equilibrium constant for the shift reaction at 875ºC is found in Appendix 2 to be 0.82838. The equation for the shift reaction can be rearranged as a function of the dry mole fractions and the unknown water mole fraction as:

\[ \text{Example 1.2} \]

The equilibrium conversion in the steam reforming of methane to carbon monoxide and hydrogen is determined from the two equilibrium expressions shown in Example 1.1. In this second example a large hydrogen plant making 100,000 Nm\(^3\)/h of H\(_2\) is considered.

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The equilibrium constant for the shift reaction at 875ºC is found in Appendix 2 to be 0.82838. The equation for the shift reaction can be rearranged as a function of the dry mole fractions and the unknown water mole fraction as:
Routes to Syngas

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Insertion of the specified dry mole fractions and the equilibrium constant gives:

\[ y_{H_2O} = 31.38 \text{ mole}\% \]

The wet mole fractions are now calculated, and these and the pressure are then inserted into the steam reforming equilibrium reaction to calculate the reaction quotient. The result is:

\[ Q_{ref} = 544 \Rightarrow T_{eq,ref} = 850^\circ C \Rightarrow \Delta T_{ref} = 25^\circ C \]

In addition to the steam reforming reactions carbon may also be formed according to the reactions in Table 1.4.

Table 1.4 Carbon-forming reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction</th>
<th>(-\Delta H_{298}^0)</th>
<th>kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>R6</td>
<td>( CH_4 \leftrightarrow C + 2H_2 )</td>
<td>-75</td>
<td></td>
</tr>
<tr>
<td>R7</td>
<td>( 2CO \leftrightarrow C + CO_2 )</td>
<td>172</td>
<td></td>
</tr>
<tr>
<td>R8</td>
<td>( CO + H_2 \leftrightarrow C + H_2O )</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>R9</td>
<td>( C_nH_m \rightarrow nC + 0.5mH_2 )</td>
<td>&lt;0</td>
<td></td>
</tr>
</tbody>
</table>

Two forms of carbon may be found. The first is ordinary graphite, but carbon may also be found in a whisker structure on the catalyst, which has another free energy of formation as will be discussed in Chapter 5.

The reaction properties are seen in Table 1.5 below. A table with equilibrium constants is found in Appendix 2.
Table 1.5 Basic reaction properties for carbon-forming reactions.
Data from [137] [375] for carbon as graphite. Data from [425] for carbon as whisker (refer to Section 5.3.1).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH° (kJ/mol)</th>
<th>ΔG° (kJ/mol)</th>
<th>ΔS° (kJ/mol/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ ↔ C + 2H₂</td>
<td>74.85</td>
<td>50.79</td>
<td>0.0807</td>
</tr>
<tr>
<td>CH₄ ↔ C_whisker + 2H₂</td>
<td>89.62</td>
<td>58.19</td>
<td>0.1054</td>
</tr>
<tr>
<td>2CO ↔ C + CO₂</td>
<td>-172.46</td>
<td>-119.85</td>
<td>-0.1765</td>
</tr>
<tr>
<td>CO + H₂ ↔ C + H₂O</td>
<td>-131.30</td>
<td>-91.32</td>
<td>-0.1341</td>
</tr>
</tbody>
</table>

(See notes to Table 1.3)

1.2.2 Product gas composition

The methane steam reforming reaction R1 in Table 1.2 results in a H₂/CO ratio close to 3. Steam can be replaced by CO₂, resulting in a H₂/CO ratio close to 1. The addition of oxygen in ATR and POX gives a lower H₂/CO ratio.

The H₂/CO ratio can be varied over a wider range, as illustrated in Figure 1.10, as the reforming reactions are coupled to the shift reaction. In the manufacture of hydrogen, the reforming process is followed by water gas shift carried out in the presence of an iron and/or copper catalyst at low temperatures (210–330°C) to ensure complete conversion of carbon monoxide (refer to Section 1.5). The conversion of methane is restricted by the thermodynamics of the reforming reactions. The endothermic steam (and CO₂) reforming reactions must be carried out at high temperature and low pressure to achieve maximum conversion, as illustrated in Figure 1.8.
As an example, modern hydrogen plants are normally designed for low steam-to-carbon ratios (refer to Section 2.2), although high steam-to-carbon ratios (4–5 molecules of H₂O/C atom) would result in higher conversion of the hydrocarbons. However, a low steam-to-carbon ratio (typically 2.5 or less) reduces the mass flow through the plant, the steam production, and thus the equipment sizes. The lowest investment is therefore generally obtained for plants designed for low steam-to-carbon ratios.

In principle, a low steam-to-carbon ratio increases the amount of unconverted methane from the reformer (Figure 1.8), but this can be compensated for by increasing the reformer outlet temperature, typically to 920°C. In synthesis plants, the unconverted methane flows downstream with the synthesis gas. Unconverted methane thus implies a larger syngas unit and results in restrictions on recycle ratios in the synthesis because of accumulation of the inert methane in the synthesis gas, which reduces the partial pressures of the syngas components.
Stoichiometric reforming according to Equations R1 and R3 in Table 1.2 at $\text{H}_2\text{O}/\text{CH}_4$ or $\text{CO}_2/\text{CH}_4$ ratios of 1 is rarely feasible [399], because it would result in incomplete conversion at the pressures that are economical for industrial syngas plants (20–50 bar). This is also true for mixed $\text{CO}_2/\text{H}_2\text{O}$ reforming as illustrated in Figure 1.11 [415]. The low-pressure manufacture of reducing gas for direct ore reduction is one exception (refer to Section 2.4.3).

Other thermodynamic constraints are related to the risk of carbon formation when too little oxidant is present (refer to Chapter 5).
The requirements to the composition of the syngas vary with the synthesis in question, as shown in Table 1.6.

Table 1.6 Syngas composition for various processes [415].

<table>
<thead>
<tr>
<th>Process</th>
<th>Stoichiometric composition</th>
<th>Co-reactants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>$\frac{H_2}{N_2} = 3$</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>$\frac{H_2}{CO + CO_2} = 2$</td>
<td></td>
</tr>
<tr>
<td>DME from hydrocarbons</td>
<td>$\frac{H_2}{CO + CO_2} = 2$</td>
<td></td>
</tr>
<tr>
<td>DME from coal gas</td>
<td>$\frac{H_2}{CO} = 1$</td>
<td></td>
</tr>
<tr>
<td>High-temp. Fischer–Tropsch</td>
<td>$\frac{H_2}{CO + CO_2} = 2$</td>
<td></td>
</tr>
<tr>
<td>Low-temp. Fischer–Tropsch</td>
<td>$\frac{H_2}{CO} = 2$</td>
<td></td>
</tr>
<tr>
<td>SNG</td>
<td>$\frac{H_2}{CO + CO_2} = 3$</td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td>CO</td>
<td>Methanol</td>
</tr>
<tr>
<td>Higher alcohols</td>
<td>$\frac{H_2}{CO} = 1$</td>
<td>Olefins</td>
</tr>
<tr>
<td>Industrial hydrogen</td>
<td>99.99 H₂</td>
<td></td>
</tr>
<tr>
<td>Hydrogen for PEMFC</td>
<td>&lt;50 ppm CO</td>
<td></td>
</tr>
<tr>
<td>Reducing gas (iron ore)</td>
<td>$\frac{CO_2 + H_2O}{H_2 + CO + CO_2 + H_2O} \leq 0.05$</td>
<td></td>
</tr>
</tbody>
</table>
1.2.3 Thermodynamics of higher hydrocarbons

Higher hydrocarbons are steam reformed according to Reaction R5 in Table 1.2. In natural gas mixtures and light hydrocarbon mixtures the components are identified as such, but in heavier hydrocarbon feedstocks such as naphthas, kerosene and diesel, the chemical compounds and composition are usually unknown. Instead, such mixtures are characterised by the following measurements:

- A distillation curve with initial and final boiling point. It is converted to a true boiling-point (TBP) curve;
- Specific gravity;
- The carbon to hydrogen (C/H) weight ratio;
- PNA distribution: Paraffin (alkane), Naphthene (cycloalkane), and Aromatic;
- Lower heating value (LHV);
- Refractive index;
- Liquid viscosity.

Except for the LHV, no reaction properties are thus measured. Correlations are available to estimate reaction properties using conventional refinery pseudo-component characterisation methods, but it is advantageous to calculate a mixture of real chemical compounds, which represent the measurements, as well as possible to be able to calculate accurate mass and energy balances over the plant.

This is carried out selecting a number of components, whose type is chosen approximately proportional with the PNA distribution and the C/H ratio. The components are selected in such a way that their normal boiling points are distributed equally on the measured TBP curve. For each additional measurement an equation is set up using proper mixing rules and the total equation system is solved using appropriate uncertainty factors. After solution of the equations, the resulting composition of the mixture will give accurate mass and energy balances in the syngas process.
1.2.4 The tubular reformer

The negative heat of reaction of the reforming reaction and the high exit temperatures at typical process conditions mean that heat must be supplied to the process, typically in a fired reactor, the tubular reformer [389] as shown in Figure 1.12. The product gas will normally be close to the equilibrium of Reactions R1 and R4 in Table 1.2 with an “approach to equilibrium” of about 5–10°C and 0°C for the two reactions, respectively.

Figure 1.12 Photo of a tubular reformer.
To illustrate the strong endothermicity, adiabatic steam reforming of methane (carried out with $\text{H}_2\text{O}/\text{CH}_4=2.5$ at a pressure of 20 bar abs and a feed temperature of 500ºC) will result in a temperature drop of approximately 12ºC for each 1% of methane converted.

The overall heat requirement can be estimated from enthalpy tables (see Appendix 1) when the product gas composition is known from equilibrium calculations.

**Example 1.3**
The heat input for a tubular reformer in a hydrogen plant (100,000 Nm$^3$/h) should be estimated. The outlet equilibrium properties of the feed were calculated in Example 1.2, so this example is a continuation of this with the purpose of calculating the heat balance over the tubular reformer.

The total inlet and outlet atomic balances for C and O are set up. The C balance can be used to calculate the total outlet flow by use of the wet composition found in Example 1.2. Similarly, the O balance can be used to calculate the water inlet flow as follows:

\[
\begin{align*}
\text{C:} & \quad \text{CH}_4,_{\text{in}} = \text{CH}_4,_{\text{out}} + \text{CO},_{\text{out}} + \text{CO}_2,_{\text{out}} \\
\text{O:} & \quad \text{H}_2\text{O},_{\text{in}} = \text{CO},_{\text{out}} + 2\text{CO}_2,_{\text{out}} + \text{H}_2\text{O},_{\text{out}} \\
gives & \quad F_{\text{out}} = 2459 \text{ mol/s} \\
& \quad \text{H}_2\text{O},_{\text{in}} = 1250 \text{ mol/s} \\
& \quad \text{CH}_4,_{\text{out}} = 146 \text{ mol/s} \\
& \quad \text{H}_2,_{\text{out}} + \text{CO},_{\text{out}} = 1417 \text{ mol/s}
\end{align*}
\]

The steam-to-carbon ratio in the feed is thus: $\text{H}_2\text{O}/\text{CH}_4=2.5$ and the total conversion of $\text{CH}_4$ is 71%.

If all CO in the product can be converted to $\text{H}_2$ in the subsequent shift reaction system, the total amount of product is 114,338 Nm$^3$/h of which 100,000 Nm$^3$/h or 88% in this case is recovered as final product.

A total heat balance over the tubular reformer can now be established by using the calculated component flows and the corresponding enthalpies of formation of the feed components at 500ºC and the product components at 875ºC from Appendix 1 as:
### Routes to Syngas

If an average heat of reaction equal to 225 kJ/mol (valid at 700°C) is used, it is found that in this case 75% of the total heat added is used in the reaction and the rest is used for heating of feed and product. The split between the two parts changes, of course, with H₂O/CH₄ ratio and other operating conditions.

The catalyst is normally nickel on a stable support (refer to Chapter 4). The catalyst properties are dictated by the severe operating conditions, including temperatures of 450–950°C and steam partial pressures of up to 30 bar. The intrinsic activity of the catalyst depends on the nickel surface area.

The catalyst is placed in a number of high-alloy reforming tubes placed in a furnace as shown in Figure 1.13. Tubular reformers are designed with a variety of tube and burner arrangements (as shown in Section 3.2.2). Such reformers are built today for capacities up to more than 300,000 Nm³ of H₂ (or syngas) /h.

---

**Table 1.1**

<table>
<thead>
<tr>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet:</td>
</tr>
<tr>
<td>Outlet:</td>
</tr>
<tr>
<td>(Q_{\text{added}} = -198500 - (-306975) = 108475 \text{kJ/s} \equiv 108 \text{MW})</td>
</tr>
</tbody>
</table>

---

**Figure 1.13** Reformer furnace and waste heat section [425]. Reproduced with the permission of Wiley.
Heat transfer takes place primarily (>95%) by radiation from the furnace gas and in a sidewall-fired furnace also from the furnace walls. The remaining transfer is by convection.

About 50% of the fuel combustion heat is transferred through the tubes for the reforming reactions and for heating up the gas to the exit temperature. The remaining combustion heat is recovered in the waste heat section (Figure 1.13).

It is possible to increase the amount of heat transferred to the process gas in the reformer from about 50% to about 80% of the supplied heat when using a convective heat exchange reformer in which the flue gas as well as the hot product gas are cooled by heat exchange with the process gas flowing through the catalyst bed. This results in a more compact piece of equipment [171]. However, in all types of heat-exchange reformers, the heat exchange is by convection, and this generally leads to lower average heat fluxes to protect the construction materials than in reformers with radiant heat transfer. Therefore, in principle the fired tubular reformers may appear the most economic solution for large-scale operation, but the convective reformer may be applied in combination with the tubular reformer for more efficient heat recovery by “chemical recuperation” [426] [427]. This is further discussed in Section 2.2 and Chapter 3.

1.2.5 Carbon formation. Higher hydrocarbons

Steam reforming involves the risk of carbon formation (Table 1.4). The formation of carbon may lead to breakdown of the catalyst and the build-up of carbon deposits and disintegrated catalyst pellets may cause partial or total blockage of the reforming tubes resulting in development of hot spots or hot tubes [389]. The parameters determining the risk of carbon formation are discussed in Chapter 5.

Higher hydrocarbons show a higher tendency for carbon formation on nickel than does methane and, therefore, special catalysts either containing alkali or rare earths or based on an active magnesia support are required (refer to Section 5.3.2) [389] [425].

Naphtha can be processed directly in the tubular reformer, as practiced in many industrial units, but the control of the preheat
temperature and heat flux profile may be critical [384]. This is a severe constraint as the heat required in the tubular reformer and hence the reformer costs may be reduced by increasing preheat temperature. However, the preheater may then work as a “steam cracker” producing olefins from higher hydrocarbons in the feed [532] (refer to Section 4.3.3). The olefins easily form carbon in the reformer. Apart from the pressure, the conditions in the tubular steam reformer and in the preheater are not far from that of a steam cracker in an ethylene plant.

These constraints are removed when using an adiabatic prereformer [394] [415] as illustrated in Figure 1.14. The prereforming catalyst is typically a highly active nickel catalyst. This catalyst also works as an effective sulphur guard for the tubular reformer and downstream catalysts, by removing any traces of sulphur still left after the desulphurisation section.

With proper desulphurisation, it is possible to convert naphtha and heavy distillate feedstocks such as kerosene and diesel in a prereformer into syngas with no trace of higher hydrocarbons [389] [405].
All higher hydrocarbons are converted in the prereformer in the temperature range of 350–550°C, and the reforming and shift reactions are brought into equilibrium. After a prereformer, it is possible to preheat to temperatures around 650°C, thus reducing the size of the tubular reformer. A revamp of an ammonia plant [457] by installing a prereformer and larger preheater involved the increase in the reformer inlet temperature from 520°C to 650°C. This resulted in reduced fuel consumption.

With low catalyst activity, the thermal cracking route (pyrolysis) may also take over in the reformer tube [389]. This is the situation in case of severe sulphur poisoning or in attempts to use non-metal catalysts with low activity. The risk of carbon formation depends on the type of hydrocarbon with the contents of aromatics being critical. Ethylene formed by pyrolysis results in rapid carbon formation on nickel (refer to Section 5.2). Ethylene may also be formed by oxidative coupling if air or oxygen is added to the feed – or by dehydration of ethanol.

1.2.6 Non-tubular reforming

In a tubular reformer, the tube diameter is selected from the mechanical considerations leaving the space velocity (catalyst volume) as a dependent parameter. This so-called tubular constraint can be illustrated by the simple example:

Note
For given tube length, L, flow, F, and transferred heat (reformer duty), Q, the number of tubes, n, is determined by the tube diameter, d, the average heat flux, q_{av}, and the space velocity, SV (Nm³/h/m³ cat). For constant inlet and outlet conditions, this means:

\[ Q = n \pi d L q_{av} \]

\[ Q = F = SV \cdot n \frac{4}{3} d_{i}^{2} \cdot L \]

(1.12)

from which:

\[ q_{av} \approx SV \cdot d_{i} \]

The tubular constraint (the last equation) can be made less restrictive by convective heat exchange reformers. This may involve the use of
catalysed heat transfer surfaces [188] [397] [488] in the form of plate type reformers and multi-channel reformers. This is discussed further in Section 3.3.8.

Another approach is to decouple the heat transfer and the reaction. This includes reheat schemes [403] [455] [548] in which the process gas is heated in a heater followed by reforming reaction in an adiabatic reactor as illustrated in Figure 1.15. However, many steps are required to reheat the gas because of the strong endothermicity of the reaction.

![Figure 1.15 Reheat scheme for steam reforming [403]. Reproduced with the permission of Japan Petr. Inst.](image)

A variation of the reheat process scheme is the use of a circulating catalyst bed using one bed for reaction and the other for heating up the catalyst [549]. This is also applied in other fluidised petrochemical processes [439]. However, for steam reforming the recirculation rate would be very high. Moreover, catalyst dust in downstream heat exchangers would result in methane formation by the reverse reforming reaction (methanation). Other attempts have aimed at utilising the high heat transfer in fluidised beds and supplying the heat by an external heater [10]. Other suggestions [262] have dealt with supplying the heat by addition of a CO₂ acceptor (CaO, etc.) to the fluidised bed. The heat
from the formation of carbonate is almost sufficient for the reforming reaction [262].

An alternative to the reforming process may be the use of a cyclic process [438] as illustrated in Figure 1.16. Hydrogen is generated by reacting steam with a metal (Cu, Fe, etc.). The resulting metal oxide is reduced by reaction with methane-forming steam and CO₂ at a pressure well suited for sequestration. The scheme involves a number of constraints relating to heats of reaction. The addition of air is necessary to ensure that the overall reaction becomes thermoneutral.

\[
\text{CH}_4 + 1.32\text{H}_2\text{O} + 0.34\text{O}_2 = 3.32\text{H}_2 + \text{CO}_2 \quad \Delta H^{\circ}_{298} = 0 \quad (1.13)
\]

Figure 1.16 Cyclic process for CO₂-free hydrogen [414]. Reproduced with the permission of Balzer.

1.3 Other manufacture routes

1.3.1 Partial oxidation

An alternative approach to steam reforming is to add oxygen to the feed and hence gain the necessary heat by internal combustion. It means that the steam formed by the combustion is condensed in the process stream instead of leaving as water vapour in the flue gas from the fired reformer. Hence, the higher heating value of the fuel is recovered in the partial
oxidation schemes in contrast to the lower heating value in the steam reforming process.

Partial oxidation can be carried out in three different ways as illustrated in Figure 1.17:

- Non-catalytic partial oxidation (POX);
- Autothermal reforming (ATR);
- Catalytic partial oxidation (CPO).

The non-catalytic partial oxidation [486] (POX, Texaco, Shell) needs high temperature to ensure complete conversion of methane and to reduce soot formation. Some soot is normally formed and is removed in a separate soot scrubber system downstream of the partial oxidation reactor. The thermal processes typically result in a product gas with $\text{H}_2/\text{CO}=1.7-1.8$. Gasification of heavy oil fractions, petcoke, coal and biomass may play an increasing role as these fractions are becoming more available and natural gas (NG) less available.

The autothermal reforming (ATR) process is a hybrid of partial oxidation and steam reforming using a burner and a fixed catalyst bed for
equilibration of the gas. This allows a decrease in the maximum temperature and hence the oxygen consumption can be lowered. On the other hand, the high temperature in POX units may result in lower contents of methane and carbon dioxide in the product gas than in ATR.

Soot formation in ATR can be eliminated by addition of a certain amount of steam to the feedstock and by special burner design. Steam can hardly be added to the non-catalytic processes without the risk of increased soot formation because of the resulting lower temperature. This means less flexibility for the composition of the syngas from POX units.

In catalytic partial oxidation (CPO) the chemical conversions take place in a catalytic reactor without a burner. In all cases of partial oxidation, some or all of the reactions listed in Table 1.7 are involved. The partial oxidation reactions are accompanied by the steam reforming and shift reactions (Table 1.2). The oxidation reactions are irreversible under all conditions of practical interest.

Table 1.7 Reactions occurring in partial oxidation of methane.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(-\Delta H_{298}^o) kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>R10 (\text{CH}_4 + 0.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2)</td>
<td>36</td>
</tr>
<tr>
<td>R11 (\text{CH}_4 + \text{O}_2 \rightarrow \text{CO} + \text{H}_2\text{O} + \text{H}_2)</td>
<td>278</td>
</tr>
<tr>
<td>R12 (\text{CH}_4 + 1.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O})</td>
<td>519</td>
</tr>
<tr>
<td>R13 (\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O})</td>
<td>802</td>
</tr>
</tbody>
</table>

The overall reaction in a partial oxidation reactor is strongly exothermic and no heat must be supplied to the reactor. The partial oxidation reactions may be accompanied by cracking of the hydrocarbons or by oxidative dehydrogenation into non-saturated compounds including olefins, poly-aromatics and soot. The control of the heat balance and the formation of by-products are main considerations in the design of partial oxidation reactors.
Two-step reforming features are a combination of tubular reforming (primary reformer) and oxygen-fired secondary (autothermal) reforming. In this concept the tubular reformer is operating at less severe operation, i.e. lower outlet temperatures (refer to Section 2.6.2).

1.3.2 Autothermal reforming

The ATR technology was pioneered by SBA and BASF in the 1930s [413], by Topsoe and SBA in the 1950s [331], and later Topsoe alone [107] [111] developed the technology at first for ammonia plants and later for large-scale gas-to-liquid plants. Today, ATR is a cost-effective technology for the synthesis gas section for a variety of applications [187].

![Figure 1.18 ATR reactor.](image_url)
The ATR reactor consists of a burner, a combustion chamber, and a fixed catalyst bed placed in a compact refractory lined vessel [107] as illustrated in Figure 1.18. Irrespective of whether the burner is thermal or catalytic or whether a fixed or a fluidised catalyst bed is used, the product gas will be determined by the thermodynamic equilibrium at the exit temperature, which in turn is determined by the adiabatic heat balance.

The feedstocks are hydrocarbons, steam, and either oxygen or air (or a mixture thereof). Optionally, carbon dioxide may be added to the hydrocarbon stream (refer to Section 2.4.2). The mixture of hydrocarbon and steam is preheated and mixed with oxygen in the burner. An adiabatic prereformer may be advantageous to eliminate thermal cracking of higher hydrocarbons in the preheater.

A turbulent diffusion flame ensuring intensive mixing is essential to avoid soot formation. The burner is designed to avoid excessive metal temperatures in order to ensure long lifetime [109].

Typically, the molar ratio of oxygen (as O\textsubscript{2}) to carbon in the hydrocarbon feed stream is 0.5–0.6 with oxygen as the oxidant [111] and the temperature of the flame core may be higher than 2000\textdegree C. Hence, the design of the combustion zone is made to minimise transfer of heat from the flame to the burner [107].

Thermal combustion reactions are very fast. The sub-stoichiometric combustion of methane is a complex process with many radical reactions [466]. The reaction pattern depends on the residence time/temperature distribution. Hence, it is important to couple the kinetic models with CFD simulations by post processing [466] or by direct coupling in more advanced calculations.

The sub-stoichiometric combustion involves the risk of soot formation as a result of pyrolysis reactions with acetylene and polycyclic aromatic hydrocarbons as soot precursors [107] [465]. The soot formation will start below a certain steam-to-carbon ratio depending on pressure and other operating parameters [111]. However, the data in Table 1.8 shows results from a soot-free pilot test (100 Nm\textsuperscript{3} NG/h) at a low steam-to-carbon ratio of 0.21 [111].

The methane steam reforming and shift reactions (Reactions R1 and R4 in Table 1.2) also occur thermally in the combustion zone, but far
from equilibrium for the reforming reaction, whereas the shift reaction remains close to equilibrium.

Table 1.8 ATR pilot test at low H₂O/C. H₂O/C=0.21, O₂/C=0.59, P=24.5 bar, T<sub>exit</sub>=1057°C. Product gas analysis vol% [111].

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>56.8</td>
</tr>
<tr>
<td>N₂</td>
<td>0.2</td>
</tr>
<tr>
<td>CO</td>
<td>29.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.9</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.0</td>
</tr>
<tr>
<td>H₂O</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>100.0%</td>
</tr>
</tbody>
</table>

H₂/CO=1.96, selectivity to H₂+CO (dry gas): 95%.

Soot precursors and residual methane are converted by steam reforming and shift reactions in the catalyst bed. These reactions are in equilibrium in the gas leaving the catalyst bed and the ATR reactor. The catalyst size and shape is optimised to have sufficient activity and low pressure drop to achieve a compact reactor design. The catalyst must be able to withstand the high temperature without excessive sintering or weakening and it should not contain components volatile at the extreme conditions. A catalyst with nickel on magnesium alumina spinel has proven to fulfil these requirements [107] [111].

Specific studies [3] have been made on the use of ATR for synthesis gas production for very large methanol and FT plants, considering the limitation by other parts of the plant, e.g. boilers, compressors, air separation units, etc.

1.3.3 Catalytic partial oxidation

In catalytic partial oxidation (CPO), the reactants are premixed and the reactions proceed on the catalytic reactor without a burner, in contrast to ATR [184]. The principle of a fixed-bed catalytic partial oxidation (CPO) is illustrated in Figure 1.19.

CPO with no flame was practiced in the 1950s [355] at low pressure and later by Lurgi at pressure [231]. The reaction was started by an
ignition catalyst. The addition of oxygen to a fluidised bed steam reformer has been studied by a number of groups [53] [429] including pilot scale operation [180] and lately with hydrogen membranes [100] [341].

![Figure 1.19 Principle of catalytic partial oxidation (CPO).](image)

Extensive studies of CPO reactions were carried out by Lanny Schmidt et al. [229] [443] using a millisecond fixed-bed reactor. It was possible to produce syngas over a rhodium monolith at residence times of milliseconds [229]. Platinum was less active than rhodium. It was shown [242] that the reactions take place in an oxidation zone as combined surface/gas-phase reactions followed by a steam reforming zone with equilibration of the steam reforming and shift reactions. It was also possible to convert liquid hydrocarbons [164], ethanol [434] and biomass [444] in the millisecond reactor.

The fixed-bed CPO technology has been studied at pilot scale [41] and at pressure. When operating at 20 bar [2] [41] and O₂/NG=0.56, it was possible to achieve stable conversions close to thermodynamic equilibrium.
The direct CPO reaction R10 in Table 1.7 appears to be the ideal solution for methanol and Fischer–Tropsch syntheses, as it provides a H₂/CO molar ratio of 2 and has a low heat of reaction:

\[
\text{CH}_4 + 0.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \quad (1.14)
\]

It is often considered a “dream reaction” with H₂/CO ratios lower than two at low conversions, but industrial utilisation would imply expensive recycle of non-converted methane as also discussed for direct conversion of methane (refer to Section 1.1.2). Other studies which claim high yields at low temperatures may be misleading [105].

![Figure 1.20 CPO catalyst and operating conditions][1]

Figure 1.20 CPO catalyst and operating conditions [410]. In a flat bed reactor the catalyst temperature may easily be significantly higher than the gas temperature, whereas the catalyst and gas temperatures may follow each other in a reactor operating at high Reynold numbers. Reproduced with the permission of Springer.

**Note**

High yields of carbon monoxide and hydrogen were claimed in CPO studies at reactor temperatures as low as 300°C [105] with product gas compositions corresponding to equilibrium of the reforming reaction at 600–700°C. However, it could be estimated [153] [410] that the catalyst surface might have had an over-temperature of 300–400°C because of strong film diffusion due to low Reynolds number \(N_{Re}\). Therefore, the
product gas most likely reflects the gas equilibrium at the catalyst surface. At low \( N_{Re} \) in a flat reactor operating with low conversion, the catalyst temperature may easily be higher than the gas temperature and close to that resulting from the adiabatic temperature increase at full conversion as illustrated in Figure 1.20. In an integral reactor operating at high \( N_{Re} \), the temperatures of the gas and the catalyst will increase simultaneously through the bed.

Measurements of conversions at CPO conditions reported in the literature are seldom showing conversions relative to the equilibrium conversions. Yields are often expressed as selectivities to hydrogen and carbon monoxide although the product gas in most situations is close to equilibrium for the reforming and shift reactions. Therefore selectivity data should be supplemented by calculation of approach to equilibrium, \( \Delta T_{ref} \) (Equation 1.11). Reported selectivities may be misleading. Even sophisticated catalyst compositions lead to equilibrated product gas as illustrated in Example 1.4 below.

Example 1.4
As an example, one study [27] claimed high selectivity to CO+H\(_2\) using a sophisticated catalyst at 775ºC. Equilibrium calculations are carried out for a stoichiometric mixture of CH\(_4\) and O\(_2\) reacting at 775ºC and ambient pressure according to:

\[
\begin{align*}
\text{CH}_4 + 0.5\text{O}_2 & \leftrightarrow \text{CO} + 2\text{H}_2 \\
K_{eq,ox} &= \frac{P_{\text{H}_2}^2 \cdot P_{\text{CO}}}{P_{\text{O}_2}^{0.5} \cdot P_{\text{CH}_4}} = 2.7210^{11}
\end{align*}
\]

From an equilibrium point of view all oxygen is reacted, but due to the presence of a catalyst, equilibrium is also established in the steam reforming and shift reactions:

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \leftrightarrow \text{CO} + 3\text{H}_2 \\
K_{eq,ref} &= \frac{P_{\text{H}_2}^3 \cdot P_{\text{CO}}}{P_{\text{CH}_4} \cdot P_{\text{H}_2}\text{O}} = 96.06 \\
\text{CO} + \text{H}_2\text{O} & \leftrightarrow \text{CO}_2 + \text{H}_2 \\
K_{eq,shf} &= \frac{P_{\text{H}_2} \cdot P_{\text{CO}_2}}{P_{\text{CO}} \cdot P_{\text{H}_2}\text{O}} = 1.1603
\end{align*}
\]

Values of the equilibrium constants are calculated using the data given in Appendix 2. It is seen that full conversion can be assumed in the oxygen reaction, so after solving the two remaining equations for
the unknown conversions using the principle in Example 1.1, the following equilibrium composition is found: CH₄ 3.53, H₂ 62.08, H₂O 2.24, CO 30.87 and CO₂ 1.29. This corresponds to a total conversion of CH₄ equal to 90% and selectivities to CO and H₂ equal to:

\[
\begin{align*}
\text{CH}_4\text{CO} &= \frac{\text{CO}}{\text{CO} + \text{CO}_2} 
\times 100 = 96\% \\
\text{CH}_4\text{H}_2 &= \frac{\text{H}_2}{\text{H}_2 + \text{H}_2\text{O}} 
\times 100 = 97\%
\end{align*}
\]

This is in fine agreement with measurements such as those published in [27] for CPO over transition metal catalysts. It should be noted that adding an inert makes the equilibrium even more favourable due to the decrease in partial pressures.

As shown in Table 1.8, the ATR process at low steam carbon ratio is very close to fulfilling H₂/CO=2 at selectivities above 90% for CO→H₂.

Figure 1.21 The dark reactor shows a CPO pilot (210 Nm³/h CO+H₂ and 25 bar) in front of a tubular reformer of twice the capacity. The size of the CPO catalyst bed is indicated.

Therefore, the product gas from CPO at high conversions will be close to the thermodynamic equilibrium of the steam reforming and water-gas-shift reactions [242]. For adiabatic operation, the exit
temperature is determined from a heat balance based on inlet flows and temperatures assuming that all oxygen is consumed.

If so, the same exit temperature is required in ATR and CPO to achieve similar syngas compositions for given feedgas streams. As the CPO requires a lower preheat temperature (approximately 250°C) than ATR (approximately 650°C), it means that CPO inherently has a higher oxygen consumption per tonne of product than does ATR.

Hence, CPO appears less feasible for large-scale operation. However, the compactness of the CPO reactor as illustrated in Figure 1.21 makes it attractive for smaller decentralised units (hydrogen, fuel cells, see Section 2.3).

1.3.4 Air-blown technologies and membranes

The partial oxidation routes have the advantages of eliminating the expensive heat transfer surfaces of the steam reforming processes, but they suffer from the necessity of an expensive oxygen plant which with the present technology will be based on cryogenic separation of air (Air Products, Air Liquide, Linde) [25]. The air separation units can be built at capacities of approximately 3500 tonnes O₂/d and above, but the investment may amount to 40% of the syngas unit.

The costs of oxygen plants have created a potential for air-blown technologies. However, with few exceptions (secondary reforming for ammonia: refer to Section 2.5; CO₂-free hydrogen for power: refer to Section 2.2; and fuel cells: refer to Section 2.3), the amount of nitrogen in the syngas is prohibitive for recycle syntheses, because of a huge accumulation of nitrogen. The use of air instead of oxygen results in large gas volumes and consequently big feed/effluent heat exchangers and compressors [2] [172] [408]. This may not be feasible for large-scale plants provided that the big purge streams (with low heating value) cannot be used for export of energy as steam or electricity.

One attempt to solve these problems has been the development of syngas technology based on oxygen ion selective membranes [95]. The membrane materials are non-porous and are composed by mixed metal oxides (perovskite, etc.) that conduct oxygen ions and electrons through the oxygen-deficient lattice structure. At high temperature, 700–1100°C,
it is possible to achieve the required diffusivities [95] [99]. The challenge is the tightness of ceramic scale and metal/ceramic joints. The technology resembles that for solid oxide fuel cells (SOFC), however, without the transport of electrons involved. This means that the driving force depends on $\ln\left[\frac{p_{O_2,1}}{p_{O_2,2}}\right]$ in contrast to a gas diffusion driven membrane with the driving force proportional to $\sqrt{\frac{p_{O_2,1}}{p_{O_2,2}}}$.

With the high driving force across the membrane, there is no need for compression of air to the process pressure. However, as illustrated in Figure 1.22 there is still a need for a big feed/effluent heat exchanger in the “ceramic membrane reforming” scheme. One design (Air Products) is based on planar membranes with air and process gas flows in micro-channels [95] [317]. This ITM (Ion Transport Membrane) technology has been demonstrated at pilot scale (28 Nm$^3$ syngas/h) involving temperatures and pressures up to 900°C and 28 bar, respectively.

![Figure 1.22 Comparison of ceramic membrane reforming (CMR) and ATR [409]. Reproduced with the permission of ACS.](image)

Other studies [99] [341] apply ion-selective membranes in fluid bed reactor concepts. The ITM technology may have a higher potential for air separation [71] as an alternative to the cryogenic technology.

### 1.3.5 Choice of technology

The choice of technology is dictated by the need for high conversion, the requirements of the syngas composition, and by the scale of operation.
For methanol, tubular reforming would be cheapest at low capacities, whereas the autothermal reforming is favoured at large capacities. This is caused by the economy of scale being different for the tubular reformer and the oxygen plant as illustrated in Figure 1.23 [408].

For the intermediate range representing the capacity of world-scale methanol plants, a combination of tubular reforming and a secondary oxygen blown reformer is normally the optimum solution. In this concept, the tubular reformer is operating at less severe conditions, i.e. lower outlet temperature (see Section 2.6.2).

![Figure 1.23 Impact of economy of scale](Figure 1.23 Impact of economy of scale [408]. Reproduced with the permission of Elsevier.)

For very large scale, autothermal reforming and POX remain the preferred choice. ATR has lower oxygen consumption than POX. POX has slightly lower contents of methane and CO\(_2\) in the product gas. CPO has a higher oxygen consumption than ATR and it may be difficult to scale up the premixing of reactants. The oxygen membrane technology
still operates at the maximum temperature of 900ºC, which means higher content of non-converted methane.

For small-scale operation, convective reformers are preferred due to compactness. The same is true for CPO units, in particular when an air-blown process is acceptable or when oxygen is available. The oxygen membrane technology may have a potential in such situations.

### 1.4 Other feedstocks

#### 1.4.1 Alcohols, oxygenates

The thermodynamic constraints described for steam reforming disappear when methanol is used as feed [411]. The reaction takes place over a copper catalyst being active above 200ºC and at the same time, the catalyst is not active for the methanation reaction (reverse reforming reaction R1 in Table 1.2). This means that a methane-free gas can be produced at low temperatures and at high pressures and that full conversion to CO₂ (and CO) hydrogen is achieved as illustrated in Figure 1.24. The heat of reaction is less than for steam reforming of hydrocarbons (Table 1.9). In contrast, the use of nickel catalysts results in methane-rich gases [125] [151] [392] and an overall exothermic process.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta H_{298}^{\circ} \text{kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>R14</td>
<td>( \text{CH}_3\text{OH} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 3\text{H}_2 ) -50</td>
</tr>
<tr>
<td>R15</td>
<td>( \text{CH}_3\text{OH} \leftrightarrow \text{CO} + 2\text{H}_2 ) -91</td>
</tr>
<tr>
<td>R16</td>
<td>( \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \leftrightarrow 2\text{CO}_2 + 6\text{H}_2 ) -173</td>
</tr>
<tr>
<td>R17</td>
<td>( (\text{CH}_3)_2\text{O} + \text{H}_2\text{O} \leftrightarrow 2\text{CO} + 4\text{H}_2 ) -205</td>
</tr>
<tr>
<td>R4</td>
<td>( \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 ) 41</td>
</tr>
</tbody>
</table>
Methanol reforming (decomposition) over Cu/Zn/Al catalysts [83] [258] [343] is a well-established technology [61] [260], mainly used for small hydrogen plants (less than 1000 Nm³/h). Since the amount of heat required per mole of hydrogen is far less than for steam reforming of natural gas, the equipment becomes much cheaper than the tubular reformer. On the other hand, the heat of evaporation on a mass basis of methanol is about four times higher than that of naphtha.

A methanol reformer is typically a reactor heated by electricity or indirectly by circulating heating oil [61]. A more advanced and compact scheme [183] applies steam condensing on the outside of catalyst tubes.

![Figure 1.24](image.png)

Figure 1.24 Steam reforming of methanol. Equilibrium composition (P=5 bar, T=280°C) [411]. Reproduced with the permission of Royal Soc. Chem.

The optimum choice of operating conditions [63] is around a steam-to-methanol ratio of 1.5 and a temperature in the range 250 to 300°C. The pressure does not influence the reaction rate, but very high pressures limit the equilibrium conversion, which otherwise is above 99%.

Methanol may be a suitable alternative in areas with expensive hydrocarbons considering the simplicity of the methanol reforming unit
Methanol from biomass may represent a sustainable route to hydrogen [485] (see Section 2.2).

DME is easily converted over Cu/Zn/Al catalysts [32] [191] [483] with little change in the layout of the plant [63]. Without water addition, decomposition of DME over a Cu/Al/Zn catalyst results in a syngas with H$_2$/CO=2. This route has been applied for small-scale supply of syngas, eliminating storage of carbon monoxide. By using methyl formate as feed, a syngas with H$_2$/CO=1 is achievable.

The three different methods of methanol (and DME) conversion are compared in the example below:

Table 1.10 Methanol conversion. Typical conditions.

<table>
<thead>
<tr>
<th>Process</th>
<th>Cat.</th>
<th>H$_2$O/C</th>
<th>$T_{\text{exit}}$ (ºC)</th>
<th>$P_{\text{exit}}$ (bar)</th>
<th>% Conv.</th>
<th>Product gas (vol.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH Reforming</td>
<td>Ni</td>
<td>1.5</td>
<td>350</td>
<td>20</td>
<td>100.0</td>
<td>0.7    0.0 8.5 24.7 66.1</td>
</tr>
<tr>
<td>MeOH Cracking</td>
<td>Cu</td>
<td>0.</td>
<td>350</td>
<td>20</td>
<td>99.3</td>
<td>66.6   33.3 0. 0. 0.</td>
</tr>
<tr>
<td>MeOH Cracking</td>
<td>Cu</td>
<td>1.5</td>
<td>285</td>
<td>20</td>
<td>99.8</td>
<td>64.5   2.0 20.1 0. 13.4</td>
</tr>
<tr>
<td>DME Cracking</td>
<td>Cu</td>
<td>1.5</td>
<td>285</td>
<td>20</td>
<td>81.1</td>
<td>69.5   19.9 9.9 0. 0.7</td>
</tr>
</tbody>
</table>

The interest in fuel cells for automotive applications has resulted in a large number of investigations of reforming of methanol [286] [501] for on-board reforming or for distributed units for hydrogen production. Compact units have been studied [183] using micro-channel or plate reformers [94] [340] [442] or a combination with selective hydrogen membranes [26] [40].

As copper catalysts are sensitive to exposure to air during shutdown and start-up of on-board reformers, there has been an interest in palladium catalysts for the methanol reforming process [103].

Ethanol has attracted interest as a feedstock for syngas [419], thereby coupling biotechnology to classic catalysis [369]. However, steam reforming of ethanol is not as simple as the conversion of methanol, because ethanol is easily dehydrated to ethylene, being a coal precursor.
Moreover, Reaction R16 in Table 1.9 involves the breakage of a carbon-carbon bond. This means that copper catalysts are not suitable, as they are poor catalysts for hydrogenolysis [462]. On the other hand, Group VIII metals like nickel being active for hydrogenolysis are also active for carbon formation (refer to Chapter 5). Therefore, there are many attempts to identify catalyst with stable performance [220] [359] [530]. It appears that noble metal catalysts (Ru, Rh) [280] [298] [359], promoted Co catalysts [299] [302], or bi-metallic catalysts such as Ni,Cu [539] look promising. Autothermal reforming of ethanol and other alcohols is an option [138] [147] [441], as it is for methanol.

The increased production of biodiesel leaves glycerol as a by-product which has been considered as a source for hydrogen by reforming [9].

Dumesic et al. [128] [248] found that aqueous phase reforming (APR) is a promising route for converting oxygenated hydrocarbons such as simple alcohols, ethylene glycol, glycerol and carbohydrates (sorbital, glucose, etc.) into hydrogen and carbon dioxide.

\[
C_nH_{2n}O_n + nH_2O \leftrightarrow 2nH_2 + nCO_2
\]  

(1.15)

The reaction is carried out at temperatures in the range 150–265°C over a platinum catalyst or bi-metallic catalysts [248] [249] (Pt, Ni Pt,Co) including a non-noble metal catalyst, Ni,Sn [247] [456]. Although there is high thermodynamic potential at the reaction conditions for the formation of methane and other hydrocarbons, the experimental data show reasonable selectivities for hydrogen. The addition of Sn to Ni almost eliminated the formation of methane [456].

Although carbohydrates (C\textsubscript{n}H\textsubscript{2n}O\textsubscript{n}) contain a lot of hydrogen, this is bound to oxygen, meaning that the “effective” hydrogen-to-carbon ratio is zero:

\[
C_nH_{2n}O_n \rightarrow nC + nH_2O
\]  

(1.16)

This is illustrated in Table 1.11, comparing with other molecules.

The liquid phase reforming by Dumesic et al. solves the problem by extracting oxygen as carbon dioxide, but then making hydrogen (Equation 1.15).
### 1.4.2 Coal, gasification

Coal conversion was considered in the 1970s as a reaction to the oil crisis. The target was the manufacture of substitute natural gas (SNG) via coal gasification and methanation (refer to Section 2.6.6). SNG was never introduced at large scale before oil prices decreased. The conversion of coal to liquid fuels was not feasible except under special circumstances (South Africa) because of the high investments in coal gasification. Coal gasification was also applied in combined cycle power plants (IGCC) in which the “syngas” was burned in a gas turbine followed by a steam turbine.

With the increasing use of coal, in particular in China [78], coal gasification has come into focus again [268]. Clean coal conversion is an issue in the US with its large coal reserves – however with an increasing demand on CO₂ capture and storage (CCS). Similar plans are considered in a number of countries. Gasification technologies have the advantage that CO₂ will be available at much higher pressures than envisaged by normal combustion. Gasification is the basis for using coal, petcoke, oil sand (tar sand) and biomass for the production of syngas. These fuels differ in properties and composition. Coals are normally classified in

---

Table 1.11 Gross formula from the very low H/C ratios is obtained.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Molecule – H₂O</th>
<th>H/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane, CH₄</td>
<td>CH₄</td>
<td>4</td>
</tr>
<tr>
<td>Heptane, C₇H₁₆</td>
<td>C₇H₁₆</td>
<td>2.3</td>
</tr>
<tr>
<td>Ethylene, C₂H₄</td>
<td>C₂H₄</td>
<td>2.0</td>
</tr>
<tr>
<td>Acetylene, C₂H₂</td>
<td>C₂H₂</td>
<td>1.0</td>
</tr>
<tr>
<td>Methanol, CH₂O</td>
<td>CH₂</td>
<td>2.0</td>
</tr>
<tr>
<td>DME/C₄H₄O</td>
<td>C₄H₄</td>
<td>2.0</td>
</tr>
<tr>
<td>Ethylglycol C₇H₆O₂</td>
<td>C₇H₂</td>
<td>1.0</td>
</tr>
<tr>
<td>Glycerol, C₃H₈O₃</td>
<td>C₃H₂</td>
<td>0.7</td>
</tr>
<tr>
<td>Glycose, C₆H₁₁O₅</td>
<td>C₆H₁₀</td>
<td>0.3</td>
</tr>
<tr>
<td>C₅H₁₀O₆</td>
<td>C</td>
<td>0</td>
</tr>
</tbody>
</table>
four groups, characterised by their content of fixed carbon and related heating value as listed in Table 1.12 [230].

The volatile matter increases from less than 8% in anthracite to more than 27 wt% in lignite. In addition, the content of water may vary from less than 5 wt% in anthracite to about 60% in German brown coal. Nitrogen (0.5–2%) will be converted into ammonia. The sulphur content may typically vary from 0.5–5 wt%. Sulphur will be converted to COS and H₂S. Sulphur will poison downstream synthesis catalysts and must be removed. Chlorine is normally below 1 wt%. Chlorine may cause corrosion problems in downstream equipment. Chlorine will react with ammonia from the nitrogen and deposition of ammonia chloride may foul waste heat boilers and limit their operating temperature [230].

<table>
<thead>
<tr>
<th>Classification</th>
<th>Fixed carbon⁵ (wt%)</th>
<th>Heating value⁶ (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracite</td>
<td>&gt;92</td>
<td>36-37</td>
</tr>
<tr>
<td>Bituminous carbon</td>
<td>78-92</td>
<td>32-36</td>
</tr>
<tr>
<td>Subbituminous carbon</td>
<td>73-78</td>
<td>28-32</td>
</tr>
<tr>
<td>Lignite (brown coal)</td>
<td>65-73</td>
<td>26-38</td>
</tr>
</tbody>
</table>

The ash may contain a number of components which are volatile at high temperatures such as As, Hg. The ash content may typically be around 10% in anthracite coal, but up to 40% in some coals considered for gasification [230]. The properties of the ash (melting point, etc.) are important parameters.

The C/H ratio in coal varies around 14 wt/wt in lignite to 25 wt/wt in anthracite as shown in Table 1.13.

Coke made from coal consists mainly of fixed carbon plus the ash. It is of high value for use in blast furnaces because of its strength.

Petroleum coke, pet coke and liquid refinery resid feedstocks are used for gasification. Pet coke is made from heavy residues in refineries by the coking process (delayed coking). Resids and pet coke are characterised by a low C/H ratio of 7–10 wt/wt and high content of sulphur 1–7 wt%.
These feedstocks typically contain vanadium (300–3500 mg/kg) which is volatile as V₂O₅ and nickel.

Table 1.13 H/C ratios of various fuels.

<table>
<thead>
<tr>
<th></th>
<th>C/H (wt/wt)</th>
<th>H/C (atom/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Naphtha C₇H₁₆</td>
<td>5.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Biomass</td>
<td>Approximately 9</td>
<td>1.3</td>
</tr>
<tr>
<td>Resid/asphalt</td>
<td>7–10</td>
<td>1.7–1.2</td>
</tr>
<tr>
<td>Lignite</td>
<td>14–17</td>
<td>0.9–0.7</td>
</tr>
<tr>
<td>Bitum. coal</td>
<td>14–19</td>
<td>0.9–0.10</td>
</tr>
<tr>
<td>Antracite</td>
<td>25</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Orimulsion is another liquid fuel being an emulsion of water and bitumen from the Orinoco fields in Venezuela. Like resids, it contains sulphur, vanadium and nickel. Oil sand resids are heavy hydrocarbons recovered from deposits in sandstone, for instance in Alberta, Canada.

The different characteristics of these feedstocks determine the technology being optimum for the gasification to syngas. The feed is characterised by the atomic amounts of C, H, O, N, S and halogens, X. Oxygen will usually be in deficit so it must be added to the gasifier.

The main gasification reactions are shown in Table 1.14.

Table 1.14 Gasification of carbon. Main gasification reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction</th>
<th>$-\Delta H_{298}^\circ$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R18</td>
<td>C + 0.5O₂ → CO</td>
<td>111</td>
</tr>
<tr>
<td>R19</td>
<td>C + O₂ → CO₂</td>
<td>394</td>
</tr>
<tr>
<td>R20</td>
<td>C + H₂O → CO + H₂</td>
<td>-131</td>
</tr>
<tr>
<td>R21</td>
<td>C + CO₂ → 2CO</td>
<td>-172</td>
</tr>
<tr>
<td>R22</td>
<td>C + 2H₂ → CH₄</td>
<td>75</td>
</tr>
<tr>
<td>R23</td>
<td>H₂ + 0.5O₂ → H₂O</td>
<td>242</td>
</tr>
<tr>
<td>R24</td>
<td>S + H₂ → H₂S</td>
<td>20</td>
</tr>
</tbody>
</table>
It is seen that combustion to CO produces 28% of the lower heating value of carbon. The remaining heating of the reactor can be used to drive the endothermic water gas reaction C [230]. In addition to these full conversion reactions the following six side reactions in Table 1.15 can also take place:

Table 1.15 Gasification of carbon. Equilibrium side reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction</th>
<th>$\Delta H^o_{298}$</th>
<th>kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>$\ce{CH_4 + H_2O &lt;-&gt; CO + 3H_2}$</td>
<td>-206</td>
<td></td>
</tr>
<tr>
<td>R4</td>
<td>$\ce{CO + H_2O &lt;-&gt; CO_2 + H_2}$</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>R25</td>
<td>$\ce{N_2 + 3H_2 &lt;-&gt; 2NH_3}$</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>R26</td>
<td>$\ce{N_2 + 2CH_4 &lt;-&gt; 2HCN + 3H_2}$</td>
<td>-285</td>
<td></td>
</tr>
<tr>
<td>R27</td>
<td>$\ce{CO + H_2O &lt;-&gt; HCOOH}$</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>R28</td>
<td>$\ce{H_2S + CO_2 &lt;-&gt; COS + H_2O}$</td>
<td>-29</td>
<td></td>
</tr>
</tbody>
</table>

The conversions in these reactions depend on the actual design of the coal gasifier. They are usually specified using experimentally determined temperature approaches to equilibrium.

The $\ce{H_2}/\ce{CO}$ ratio in the syngas relates to the $\ce{H}/\ce{C}$ ratio in the feed [230] (see Table 1.13) and to the addition of steam.

However, a simple adiabatic heat balance should be corrected for heat capacity of ash and at high temperature also heat of melting, heat losses, etc.

The optimum operation for syngas is: 1) under pressure to minimise compression of the larger syngas volume to the synthesis pressure; 2) at a low surplus of oxygen to minimise $\ce{CO_2}$ production and to reduce oxygen costs; and 3) at high temperature to ensure complete combustion of tar components to minimise the formation of methane.

The conditions for maximising $\ce{CO+H_2}$ production are illustrated in Figure 1.25.
These ideal conditions should be balanced by the constraints given by solving a number of secondary problems caused by the ash and other impurities as well as low temperature.

The gasification technologies are normally classified into 3 groups: moving bed gasifiers; fluid bed gasifiers; and entrained flow gasifiers. The main characteristics are summarised in Table 1.16. Typical raw gas compositions are shown in Table 1.17.

![Gasification of carbon yields of CO+H₂](image)

Figure 1.25 Gasification of carbon yields of CO+H₂. Discrete value of T. CO + H₂ refer to the left y-axis and H₂O to the right y-axis.

In the moving bed gasifier [230], the coal is added in the top via a hopper. It has a large consumption of oxygen and steam. The coal moves downwards by gravity in counter-current with the gas stream. This results in high efficiency and low oxygen consumption, but the low gas exit temperature means high methane (9–12 vol% dry gas) and tar in the product gas. Methane is a disadvantage for most syntheses, but an advantage for substitute natural gas. Tar results in difficulties in gas cleaning and recovery of water from the process condensate.
Table 1.16 Coal gasifiers. Main characteristics.

<table>
<thead>
<tr>
<th>Gasifier Type</th>
<th>Ash</th>
<th>$T_{\text{exit}}$ (°C)</th>
<th>$P$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moving bed:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lurgi–Sasol</td>
<td>Dry</td>
<td>650</td>
<td>25–30</td>
</tr>
<tr>
<td>BGL</td>
<td>Slagging</td>
<td>&gt;650</td>
<td></td>
</tr>
<tr>
<td>Fluid bed:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HT Winkler</td>
<td>Dry</td>
<td>900–1050</td>
<td>10</td>
</tr>
<tr>
<td>Entrained flow:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GE (Texaco)</td>
<td>Slagging</td>
<td>1250–1600°C</td>
<td>20–80</td>
</tr>
<tr>
<td>Shell</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prenflo</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E Gas (Dow)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Siemens (GSP)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The dry-ash gasifier is the preferred choice if the coal has a high ash content, provided the coal lumps have sufficient strength for the moving bed operation. If not, the fluidised bed technology may be preferred. The Winkler process, which is very flexible to coal quality, was used for the German lignite (Rheinbraun). It has been demonstrated for 10 bar. The entrained flow gasifiers operate with grained coal and oxygen in concurrent flows. The gasification takes place at high temperature and short residence time. This requires more oxygen but results in high feedstock flexibility and a tar-free product gas with high yields of CO+$\text{H}_2$. Furthermore, pressures up to 80 bar can be applied. Hence, entrained flow gasifiers are typically preferred for manufacture of syngas.

Table 1.17 Coal gasification. Typical composition of raw gas (vol%). Coal – Illinois No. 6 [461].

<table>
<thead>
<tr>
<th></th>
<th>Lurgi Dry ash</th>
<th>BGL</th>
<th>GE (Texaco)</th>
<th>Shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2$</td>
<td>16.1</td>
<td>26.4</td>
<td>29.8</td>
<td>30.0</td>
</tr>
<tr>
<td>$\text{CO}$</td>
<td>5.8</td>
<td>46.0</td>
<td>41.0</td>
<td>60.3</td>
</tr>
<tr>
<td>$\text{CH}_4$</td>
<td>3.6</td>
<td>4.2</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>11.8</td>
<td>2.9</td>
<td>10.2</td>
<td>1.6</td>
</tr>
<tr>
<td>$\text{H}_2\text{S}$</td>
<td>0.5</td>
<td>0.6</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>COS</td>
<td>-</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>$\text{N}_2$</td>
<td>0.1</td>
<td>3.8</td>
<td>0.7</td>
<td>0.1</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>61.8</td>
<td>16.3</td>
<td>17.1</td>
<td>3.6</td>
</tr>
<tr>
<td>$\text{NH}_3$</td>
<td>0.3</td>
<td>0.3</td>
<td>0.2</td>
<td>2.0</td>
</tr>
<tr>
<td>HCN</td>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
</tr>
</tbody>
</table>
The various gasifiers differ in method of feeding and in waste heat recovery [230]. The GE (Texaco) gasifier feeds coal in a waste slurry (paste) which means that oxygen is used for evaporation of water. However, the slurry feed system allows a much higher pressure (up to 70–80 bar) than possible for gasifiers with dry feeding systems.

The cooling of the exit gas takes place in a simple water quench. The Shell and Prenflo gasifiers are a result of a joint optimisation of the Koppers Totzek atmospheric gasifier. They apply dry feeding of coal and heat recovery in a downstream boiler. This is in principle more efficient, but the boiler is expensive and subject to fouling. The Prenflo gasifier is now marketed with the option of having a water quench and GE is studying systems for dry feeding. In this way, the gasification technologies are approaching each other.

The GE (Texaco) and the Shell gasifiers have been used for decades for gasification of natural gas and liquid hydrocarbons (heavy oil, resid).

The E-gasifier [230] applies a coal slurry feed as the GE gasifier, but with a two-stage feeding where the second stage has a function as “chemical quench”. The tar in the product gas is recycled to the first combustion stage. The Siemens gasifier [230] is a further development of the Schwarze Pumpe gasifier (GSP). It operates in process steps close to an optimum by using dry feeding and a two-step heat recovery using a boiler followed by a quench, thus avoiding the low-temperature problems of a boiler. There is still room for improving the gasification technology.

![Figure 1.26 Coal conversion. Principal flow sheet.](image-url)
impurities and units for removal of CO₂ and recovery of sulphur. As a rule of thumb, the investments for a coal-based synthesis plant is around three times higher than those for a natural gas-based plant. This does not include the costs of CO₂ sequestration.

Carbon capture and storage (CCS) may well dictate the acceptance of coal conversion in the future [30]. Capture of CO₂ by absorption using the wet scrubbing processes is well-known technology in the process industry (refer to Section 1.5.3). CO₂ is already stored when used for re-injection in oil fields for enhanced oil recovery. In nature, CO₂ has been stored in geological cavities for millions of years with no sign of leakages and there appears to be plenty of capacity for geological sequestration. However, the experience is limited and there are a number of concerns in relation to leakages, chemical reactions, pollution of ground water, etc. There is a need for more research and demonstration projects to create a solid basis for public acceptance. The CO₂ capture is the most expensive part of CCS [315]. The costs of the absorption process is almost proportional to the partial pressure of CO₂. For power plants, three options for CO₂ capture are considered: post combustion (flue gas); pre-combustion (as in IGCC power plant); and oxy-fuel (using oxygen for combustion).

Post-combustion capture of CO₂ in the flue gas is expensive and reduces the efficiency of a power plant, whereas gasification under pressure yields a higher CO₂ partial pressure with lower cost of loss in efficiency. Oxy-fuel is an attempt to increase the partial pressure of CO₂ (and to eliminate NOₓ formation). A gasification-based syngas plant resembles an IGCC plant. The captured CO₂ must be compressed before sequestration, at best to a super-critical liquid (critical pressure of CO₂, 73.8 bar), which means a reduction of the volume to 0.3%. This requires a significant amount of energy.

Example 1.5
A 4000 MW coal-based power plant has an efficiency equal to 40% based on the LHV of the fuel. The coal can be assumed to be pure C and it has an LHV equal to 27 MJ/kg.

The total amount of feed is:
This is also the total emission of CO₂ in the flue gas from the plant. (P_{CO₂}=0.2 \text{ bar}).

If this amount is to be compressed for CCS, a simplified expression for the minimum work is (see Section 2.1.3):

\[ W_{\text{compression}} \approx C_{\text{feed}}RT \ln \left( \frac{73.8}{0.2} \right) = 30.9 \cdot 8.3144 \cdot 298.15 \cdot 5.91 = 452 \text{ MW} \]

In a gasification plant the CO₂ is available at 1 bar after the CO₂ wash. This means a reduction in compression energy to 329 MW or 0.24 GJ/tonne CO₂ based on the amount of C in the feed.

The example illustrates that CCS means that the efficiency of an IGCC power plant will decrease from 43% to 35% [418]. The capture costs are already a part of syngas-based plants, but the energy for CO₂ compression is similar to that of IGCC plants.

1.4.3 Biomass

Sequestration of CO₂ should not be an issue of gasification of biomass to syngas. Biomass covers a wide field of materials ranging from vegetable biomass such as wood, straw, grain, black liquor from the paper industry, animal biomass and various waste. Gasification of biomass may be an alternative to biochemical routes [419]. However, there are still problems to be solved.

Biomass differs from coal and heavy refinery products [230]. It has a smaller heating value (10–20 MJ/kg), low sulphur and, in particular straw has a high content of chlorides. The ash will typically have a low melting point and be aggressive. The fixed carbon is below 15%. It means that it is difficult to achieve high temperatures in gasification without using excess oxygen in the air stream. The relatively low temperatures (8–900°C) means that the product gas will have a high content of tar components which may be difficult to remove. At present, a number of gasifiers are under development. It appears that fluid bed gasifiers [127] [230] are being preferred (Carbona, Foster Wheeler, Güssing).
Biomass can be co-gasified in entrained coal gasifiers, provided there are no milling (grinding) problems.

A special entrained flow gasifier was developed by Chemrec for gasification of black liquor from the paper industry. If successful, there is a huge potential for this niche market [478].

Biomass has another disadvantage as feedstock which is related to its very low energy density (approximately 3.7 GJ/m$^3$), which is almost ten times lower than that of oil. It means that there are severe logistics problems. Except for grain, it is not economic to transport biomass over long distances. This may be solved by using a two-step procedure [225] with a decentralised flash pyrolysis [133] to a bio-oil which can be gasified in gasifiers similar to those used for heavy refinery products [230]. It was also shown that bio-oil and solid biomass could be gasified in the millisecond CPO unit [435]. Another catalytic route being explored is gasification (steam reforming) of biomass to hydrogen and carbon dioxide in super critical water (T>374°C, P>221 bar) [445]. Potassium carbonate improves the rate [76]. Other attempts have used nickel catalysts [132].

1.5 Gas treatment

1.5.1 Purification

Most of the catalysts for syngas manufacture and downstream syntheses are sensitive to poisoning – in particular sulphur. Therefore, there is a need to purify the feedstock for the reforming processes and to purify the raw gas from gasification of heavy feedstocks which cannot be purified before gasification. Modern process plants take full advantage of high catalyst activity by operating at more severe and economic conditions. This has sharpened the requirements to purification. Characteristic reactions are seen in Table 1.18.
Table 1.18 Reactions for gas purification.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction</th>
<th>$\Delta H^\circ_{298}$</th>
<th>kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>R29</td>
<td>$H_2S + Cu \leftrightarrow Cu - S + H_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R30</td>
<td>$H_2S + ZnO \leftrightarrow ZnS + H_2O$</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>R31</td>
<td>$SO_2 + 3H_2 \leftrightarrow H_2S + 2H_2O$</td>
<td>207</td>
<td></td>
</tr>
<tr>
<td>R32</td>
<td>$COS + H_2O \leftrightarrow H_2S + CO_2$</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>R33</td>
<td>$RSH + H_2 \leftrightarrow RH + H_2S$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R34</td>
<td>$HCN + H_2O \leftrightarrow NH_3 + CO$</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

Sulphur in natural gas is present mainly as hydrogen sulphide, lower mercaptanes and thioethers. Hydrogen sulphide is easily absorbed on zinc oxide (Table 1.18). The uptake takes place in three zones as illustrated in Figure 1.27 [391]. A layer of complete conversion – with solid state diffusion as rate-determining step – to bulk zinc sulphide is followed by a front for bulk saturation with gas diffusion in the pore system as rate-determining step and a chemisorption front adsorbing the traces of sulphur passing through the absorption fronts.

Figure 1.27 Sulphur profile in a zinc-oxide bed.
It means that the H$_2$S/H$_2$O ratio of the gas leaving the reactor is determined by the chemisorption equilibrium and not the bulk phase equilibrium.

Commercial zinc-oxide absorbents are a compromise of saturation level (kg S/m$^3$ bed), porosity (high diffusivity), and high chemisorption capacity (purity, surface area). In practice, this means that sulphur is removed to the ppb range provided the gas is dry. The ZnO reactor typically operates at 350–400°C, but is effective also at low temperature, although with longer absorption front and lower saturation value.

Although lower mercaptanes are partly withheld by zinc oxide, a hyrodesulphurisation step is normally installed prior to the zinc-oxide vessel. The hydrogenation catalyst is a Co(Ni)Mo/Al$_2$O$_3$ catalyst operating at 350–400°C and it converts organic sulphur into hydrogen sulphide (Table 1.18). The HDS step needs a (recycle) stream of hydrogen for the reaction. Without hydrogen present, thioethers and thiophenes will pass unconverted through the reactor. The hydrogen-to-feed ratio varies with the feedstock in question. A recycle hydrogen stream may often contain CO$_2$, which may result in H$_2$O by reverse shift over the HDS catalyst. This may have an impact on the equilibrium over the zinc oxide (Table 1.18). Carbon oxides may also cause a lower activity of the HDS catalyst.

A zinc-oxide mass containing copper may take care of traces of sulphur passing through the zinc oxide by establishing the chemisorption equilibrium over copper, which is independent of the presence of water (Table 1.18). The prereformer catalyst establishes the H$_2$S/Ni chemisorption equilibrium at a much lower value than H$_2$S/Cu (refer to Section 5.4). However, it is expensive to use the prereformer catalyst as a desulphurisation mass.

In this way, it is possible to desulphurise a range of hydrocarbon feedstocks from natural gas to heavy naphtha to a level of less than 10 ppb.

In the 1960s, the analytical limit for sulphur was 0.2 ppm [126] [391] and this stayed in process design manuals of several contractors for years. Surface science and better analytical methods have demonstrated that real limits are in the low ppb range (refer to Section 5.4).
Chlorine, which will be present as HCl or organic chlorine compounds, is a poison, in particular for copper catalysts [391] and it may cause stress corrosion in the equipment. Chlorine can be removed by promoted alumina. Chlorine may be present in certain refinery off-gases and in landfill gas. Chlorine may also originate from failure in the water purification system. If so, it will pass the guard bed and should be captured by a guard in the low-temperature shift reactor (see Section 1.5.2).

Ammonia is not a poison for metal catalysts (Ni, Cu, Fe), but it may deactivate acidic zeolite catalysts and HDS catalyst. It can be removed over a low-temperature bed with zeolite.

The raw dust-free syngas from purification of coal and heavy hydrocarbons contains sulphur as COS and H₂S (Table 1.18) according to the equilibrium (see Appendix 2). COS can be removed by a promoted zinc oxide [246].

1.5.2 Water gas shift

The water-gas-shift (WGS) reaction R4 in Table 1.2 is used to adjust the H₂/CO ratio of the syngas (refer to Figure 1.10). For ammonia and hydrogen plants, as much CO as possible should be converted into H₂. This involves the WGS reaction. The reaction is exothermic, meaning that low temperatures are required for high conversion. The WGS accompanies the steam reforming and the partial oxidation reactions, and the equilibrium is established at the high exit temperatures, but the WGS processes operate at lower temperatures. Many materials are active for WGS [214] (even rusty surfaces in sample lines may be active and cause misleading analyses).

Depending on the operating conditions, three different types of WGS processes are applied [232] [303] [391]. High-temperature shift (300–500°C) over a robust catalyst is used for primary conversion. Medium temperature shift (200–330°C) is used for special purposes. Low-temperature shift (185–250°C) is used to achieve maximum conversion. Sour gas shift (350°C) is used to operate under high sulphur conditions and low H₂/CO (raw coal gas, etc).
The high-temperature shift process is typically carried out in adiabatic reactors at an inlet temperature above 300°C and with a temperature increase up to 500°C. The catalyst is a robust Fe-Cu-Cr catalyst [68]. Chromium, which prevents sintering, is present as an iron chromium internal spinel [175] [361]. The activity is improved by promotion with a low percent copper, which will be present as small metallic crystallites on the iron chromium spinel [232] [266]. This will also inhibit the formation of hydrocarbons at low H₂/CO ratios [96]. It was shown [235] [391] that the activity for this reaction could be related to the phase transition into iron-carbide, which is a Fischer–Tropsch catalyst:

\[
5\text{Fe}_3\text{O}_4 + 32\text{CO} \leftrightarrow 3\text{Fe}_5\text{C}_2 + 26\text{CO}_2
\] (1.17)

The transformation point can be determined by means of the “principle of equilibrated gas” [235] (refer to Section 5.2.3).

The catalyst is robust towards sulphur [67] [68]. However, this can hardly be utilised as the product gas leaving the steam reformer is practically sulphur-free and because the raw syngas from a coal gasifier will have the potential for carbide formation due to the low H₂/CO ratio (see below).

Low-Temperature Shift (LTS) catalysts are copper-based catalysts which operate at temperatures as low as 185–225°C [232] [303] [391]. They may in principle operate at even lower temperatures, but limited by the dew point of the process gas. The commercial catalysts are typically based on Cu/ZnO/Al₂O₃. The active phase is copper in close connection with zinc oxide. Although the activity relates to the copper surface area, the role of the zinc oxide is still being discussed [216] [232], as is the reaction mechanism [207] [337].

Another approach is the use of a Cu/ZnO/Cr₂O₃ catalyst [232] [69] [329].

The LTS catalyst resembles the methanol synthesis catalyst and promotion is required to eliminate the by-product formation of methanol [97]. The activation of copper catalysts is strongly exothermic and should be carried out with care. The phase transitions during activation have been followed through in situ measurements using EXAFS and XRD [124].
Sulphur is a poison for copper catalysts, but due to the presence of zinc oxide, the catalyst has a high sulphur capacity.

The LTS catalysts lose activity during operation due to sintering. After a large decrease, the activity levels off as shown in Figure 1.28. The sintering is accelerated by chlorine apparently promoting transport of copper while migrating through the catalyst bed [391].

The performance of the LTS catalyst can be analysed by a model including the absorption and chemisorption parts for the uptake of sulphur and chlorine as well as the progression of sintering as illustrated in Figure 1.28.

It may be advantageous to carry out the WGS reaction on the raw syngas from gasification of coal and heavy hydrocarbons by a so-called sour shift catalyst. This allows removal of CO₂ and H₂S in the same wash system (see Section 1.5.3). It requires a catalyst that is sulphur-tolerant and capable of working at low H₂O/C ratios. The conventional iron-based HTS catalyst can operate in the presence of sulphur, but it requires addition of significant amounts of steam to eliminate the problem of the carbide formation reaction. This problem is solved by using a molybdenum sulphide-based catalyst [168] [232]. The catalyst is promoted and is based on alumina support. It requires the presence of
sulphur to maintain the sulphide phase \[245\]. It can operate in the temperature range 200–500°C with low steam/dry gas ratios.

The recent interest in compact fuel cell units for automotive applications has led to development of WGS catalysts based on noble metals \[134\] \[277\], which in contrast to the iron- and copper-based catalysts can withstand exposure to air during start-up and shutdown.

### 1.5.3 Acid gas removal

In many syngas plants, it is necessary to adjust the syngas composition by removal of carbon dioxide. In gasification-based plants, there is also a need to remove hydrogen sulphide. In large plants, this is done by absorption processes in which the gas is contacted with a solvent in a packed absorption tower. There are in principle two types of processes based on physical and chemical absorption, respectively. Main commercial processes are listed in Table 1.19 \[281\] \[284\]. The physical absorption processes (Recticol, Selexol) are driven by ordinary gas solubility. The solvent circulation rate, (size of tower, heat exchange) depends on the total quantity of gas and hence they are best suited for syngases with high contents of CO\(_2\) and H\(_2\)S. In contrast the design of the chemical absorption processes (MEA, Benfield) is related to the concentration of CO\(_2\) (and H\(_2\)S) and they are the preferred choice for gases with low partial pressures. The chemical processes require energy to release CO\(_2\). This is normally done by heating. The selection of process depends on parameters such as selectivity (co-absorption of useful gas components), required purity, etc.

<table>
<thead>
<tr>
<th>Solvent</th>
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<tbody>
<tr>
<td>Chemical</td>
</tr>
<tr>
<td>MEA</td>
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<td>DEA</td>
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<td>Benfield</td>
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<td>Physical</td>
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<tr>
<td>Rectisol</td>
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<td>Selexol</td>
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Table 1.19 Absorption processes for acid gas removal.
The physical wash processes can be designed so that \( \text{H}_2\text{S} \) and \( \text{CO}_2 \) are absorbed separately, meaning that both gases can be recovered at high concentration. The \( \text{CO}_2 \) stream may be compressed for CCS (refer to Section 1.4.2). The \( \text{H}_2\text{S} \) stream is converted either into elementary sulphur by the Claus process or into concentrated sulphuric acid by the WSA process [291].