

9 Fuel Processing

Hydrogen—the most abundant element on Earth—is on its way to becoming the world’s fuel of choice. An extremely clean and efficient fuel, hydrogen is utilized much more than most people realize. Industrial production of hydrogen is an annual US\$ 100 billion-plus business, and growing rapidly every year, especially in developing countries. Hydrogen plays an integral part in countless products, each used throughout our daily lives. Perhaps, more importantly, hydrogen is the fuel of choice for fuel cells. These advanced power systems have provided internal power for manned spacecraft, and now offer nearly unlimited potential for distributed energy systems and emission-free automobiles and buses. Cost of fuel cells, production of fuel cell materials and a ready supply of fuel hydrogen have been major stumbling blocks to realizing this potential. However, industry leaders have invested many millions of dollars in fuel cell related research programmes, in an effort to enable this technology to reach the consumer in the near term. To employ hydrogen as a fuel, it must be broken out of its parent hydrocarbon molecule and delivered to the user, whether it be as simple as methane (CH_4) or more complicated like diesel (approximately $\text{C}_{12}\text{H}_{24}$). This is a process, which has been inconvenient and expensive. However, there have now been several breakthroughs in this technology around the globe.

Most fuel cells involve electrochemical oxidation of hydrogen on the anode.¹ There are only a few examples of direct conversion of other fuels on the anode.^{2,3} In high temperature fuel cells, it is possible to convert the fuel to hydrogen inside the cell utilizing the heat from the electrochemical reaction,¹ but otherwise it is necessary to convert the primary fuel outside the stack into a hydrogen-rich gas which is fed to the anode. The primary fuel may be hydrocarbons, ranging from natural gas to kerosene or coal gas. Secondary fuels such as methanol may also be used in special applications, example, for automotive purposes. The coupling of fuel processing with the fuel cell operation is essential to achieve high plant efficiency.¹

The ideal electrical efficiency, η_{ideal} , of a fuel cell is defined by (9.1) assuming that all reactants and products are in their standard state:

$$\eta_{\text{ideal}} = \Delta G^\circ / \Delta H^\circ \quad (9.1)$$

where, ΔG° and ΔH° refer to the net fuel cell reaction.

Figure 9.1 shows η_{ideal} vs temperature for various fuels converted electrochemically in the cell. For methane, η_{ideal} is close to 100% and independent of temperature (reflecting that the entropy of the combustion reaction is almost zero). For methanol, (with $\Delta S^\circ > 0$), η_{ideal} is above 1 and increases with temperature. However, the advantage of using methanol is partly lost because methanol is manufactured from natural gas with an efficiency of about 65% lower heating value (LHV). Similarly, η_{ideal} for hydrogen fuel is less than 100% and decreases strongly with temperature ($\Delta S^\circ < 0$). If a fuel was able to operate at efficiencies close to an ideal efficiency

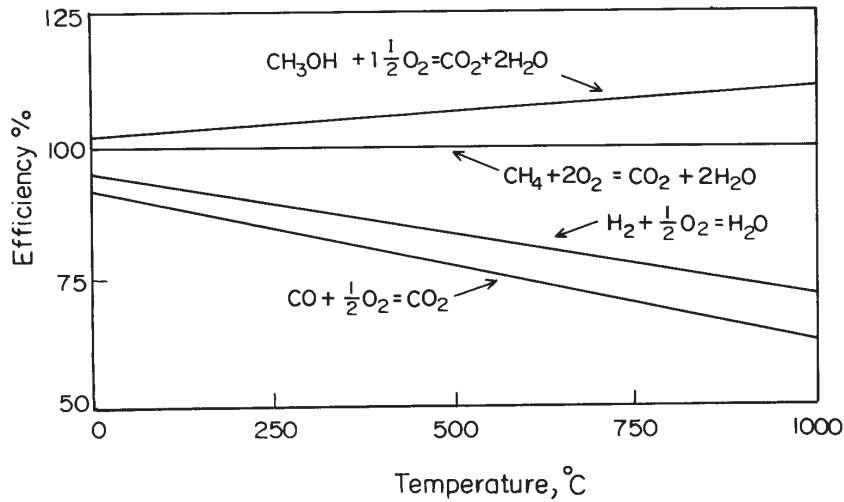


Figure 9.1 Ideal electric efficiencies for various fuels¹

above 100%, it would mean that the temperature would decrease. This could be compensated for by the supply of heat at the operating temperature of the fuel cell. For low temperature fuel cells, it would imply that low quality steam could be converted into electricity.

These ideal efficiencies show the upper limits of the practical efficiencies. The reversible voltage is reduced due to the actual activities of the reactants and products in the cell, as expressed by the Nernst equation and by the polarization on the cathode and anode, and the internal resistance of the electrolyte when current is drawn from the cell. The fuel cell does not utilize all the fuel since this would give a very low voltage at the outlet due to the reduction in the Nernst potential. The fuel utilization ranges from 60% to 80% and it is the main task of the fuel processing system (FSP) to utilize the unconverted fuel most efficiently. If it is just burned, the unconverted fuel can be utilized in a boiler, however, linked to a 'Carnot cycle' with much lower efficiency. A more efficient way is to recycle the unconverted fuel to the cell, thus obtaining a higher overall conversion.

Catalysis is likely to become a key element in the conversion of liquid or gaseous fuels into hydrogen for fuel cells. This conversion, commonly referred to as fuel processing, most often involves either *hydrocarbons*, like methane, propane/LPG and higher liquid hydrocarbons, or *alcohols*, like, methanol and ethanol, although in principle, any hydrogen-containing compound may be applied, such as even dimethyl ether and ammonia. It is even possible to convert other fuels—directly or indirectly—into fuel cells.^{4,5} Known examples comprise methanol, methane and carbon monoxide. However, most fuel cells are based on the electrochemical oxidation of hydrogen, although higher electrical efficiencies may be achieved when applying other fuels, for instance, methane in the solid oxide fuel cell where indeed, in some cases, ideal electrical efficiencies in excess of 100% may, in principle, be obtained.⁶

The chemical process and petrochemical industries use hydrogen in many different processes and have manufactured hydrogen for decades. The various pathways of hydrogen production

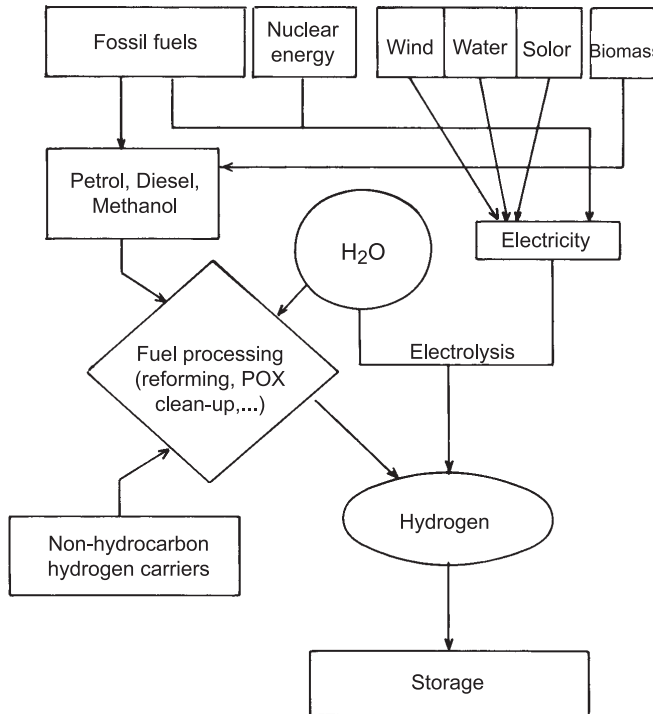


Figure 9.2 Different pathways of hydrogen production

are given in Fig. 9.2. The automotive fuel processor is distinct from the larger industrial-scale, stationary hydrogen generators in several respects, which include the following requirements:

- Hydrogen production levels with the automotive fuel processor are several orders of magnitude smaller than those in chemical plants;
- Having severe constraints on size and weight, the automotive fuel processor should be compact and lightweight;
- The automotive fuel processor should have the ability to cycle through frequent start-up and shut-down (one or more per day);
- The automotive fuel processor's hydrogen production rate should be responsive to changes in demand, which can vary from 5% to 100% of the rated processing rate;
- The automotive fuel processor has to meet very strict cost targets;
- The automotive fuel processor should be reliable in its performance, although its total lifetime is shorter by an order of magnitude (compared to stationary systems).

The conversion of fuels to hydrogen is carried out by one of three major techniques: steam reforming (SR), partial oxidation (PO) reforming, and auto thermal reforming (ATR). Apart from these techniques, some of the hydrogen storage forms will also be discussed.

When hydrogen for use in fuel cells is typically generated in a fuel processor from available fuels ($C_nH_mO_p$) by means of the reforming reaction (through the reforming process, the three principal pathways, namely, steam reforming, partial oxidation and autothermal reforming), it demonstrates that the process is most efficient when conducted under conditions of thermoneutrality ($\Delta H_r = 0$). The reforming efficiency is correlated with the fuel properties to show that it depends on the values of n and m , and on the heat of formation of the fuel.⁷ Steam reforming is known to produce high concentrations of hydrogen in the product. The partial oxidation and autothermal reforming processes are more attractive for practical applications; contrary to belief, they are also capable of higher reforming efficiencies than are steam reformers.

The theoretical maximum for fuel processing efficiencies of different types of fuels (alkanes, olefins, naphthenes, aromatics, olefins and oxygenates) with varying chain lengths was examined. The average values of n , m and p were calculated via component analysis and the heat of formation was estimated by Ahmed and Krumpelt.⁷ Figure 9.3 is a plot of the efficiencies as a function of the hydrogen-to-carbon (H/C) atomic ratio in the fuel. The efficiency increases with the H/C ratio.

The generation of hydrogen, or hydrogen-rich product streams, by reforming of hydrocarbons or alcohols, may from a thermodynamic point of view, be categorized in two basically different types of processes. One is endothermic—steam reforming (SR) in which the hydrocarbon or alcohol feed is reacted with steam. The heat required for the reaction is supplied from external sources, either by combustion of part of the feed, or by burning off combustible gases or by a combination of both. The other is exothermic, partial oxidation (POX), where the feed reacts directly with air, enriched air or (in large plants) pure oxygen at a carefully balanced oxygen-to-fuel ratio. In this case, the overall process becomes net heat producing. In either of the processes, heat management and, as part thereof, thermal integration of the fuel processor and the fuel cell, becomes key to achieve high overall plant efficiencies.

Steam reforming (SR) is probably the most common method for producing hydrogen in the chemical process industry.

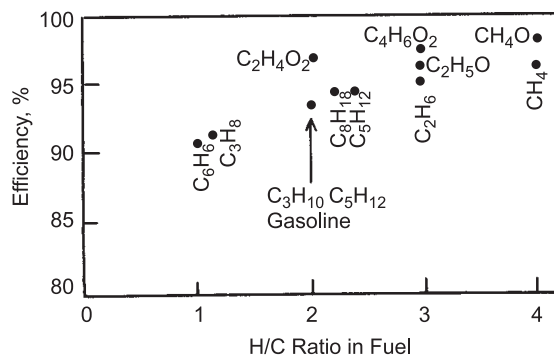
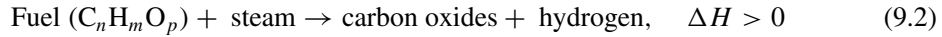
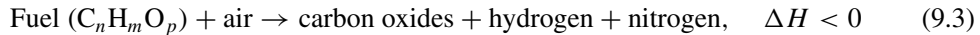


Figure 9.3 The effect of hydrogen-to-carbon ratio in the fuel on the theoretical (maximum) fuel processing efficiency⁷



In this process, steam reacts with the fuel (example, natural gas) in the presence of a catalyst to produce hydrogen, carbon monoxide and carbon dioxide. These reformers are well suited for long periods of steady-state operation and can deliver relatively high concentrations of hydrogen (>70% on a dry basis). The carbon monoxide and carbon dioxide are removed from the reformate gas stream by a variety of reactions and scrubbing techniques, such as the water gas shift reaction, methanation, CO₂ absorption in amine solutions, and pressure swing adsorption. The primary SR reaction is strongly endothermic, and reactor designs are typically limited by heat transfer, rather than by reaction kinetics. Consequently, the reactors are designed to promote heat exchange and tend to be large and heavy. Indirect heat transfer (across a wall) makes conventional steam reformers less attractive for the rapid start and dynamic response needed in automotive applications.

Partial oxidation (POX) reformers react the fuel with a substoichiometric amount of oxygen. The initial oxidation reaction results in heat generation and high temperatures.



The heat generated from the oxidation reaction raises the gas temperature to over 1,000 °C, whereby it is relatively easy to steam-reform the remaining (usually methane and other pyrolysis products) or added hydrocarbons or oxygenates, by injecting an appropriate amount of steam into this gas mixture. The oxidation step may be conducted with or without a catalyst.

Autothermal reformers (ATR) combine the heat effects of the POX and SR reactions by feeding the fuel, water and air together into the reactor:



This process is carried out in the presence of a catalyst, which controls the reaction pathways and thereby determines the relative extents of the oxidation and SR reactions. The SR reaction absorbs part of the heat generated by the oxidation reaction, limiting the maximum temperature in the reactor. The net result is a slightly exothermic process. But in order to achieve the desired conversion and product selectivity, an appropriate catalyst is essential. The lower-temperature process provides many benefits for automotive applications, including the following:

- Lower temperatures favour the water gas shift reaction, which results in a higher selectivity for carbon dioxide and hydrogen,



- High-temperature processes require more thermal integration (that is, heat exchange between the cooler, incoming reactants, and the hot effluent).
- For a given mass, the energy required to heat the reformer to its operating temperature is directly proportional to its operating temperature. Thus, lower temperatures will mean less fuel consumed during start-up.

- The lower-temperature reactor hardware can be built from a wider choice of materials, which can lower manufacturing costs.
- Higher-temperature processes, in order to reduce heat loss, need more insulation, which adds to the size and cost.

The processing of hydrocarbon and oxygenated fuels always require due consideration to the possibility of coke formation. Thermodynamic equilibrium calculations are useful for obtaining guidelines on the conditions that favour coking. Liebhafsky and Cairns⁸ calculated the carbon deposition boundaries for a C–H–O system with temperature. These diagrams may be used to estimate coke-free operating zones. Faster computers and available software have also made it easy to calculate for specific feed and reaction combinations. Some of the results are shown in Fig. 9.4. The figure shows the minimum temperatures required to prevent carbon formation during reforming of isooctane (2,2,4-trimethylpentane), for five feed stoichiometries. For partial oxidation at an oxygen-to-carbon (O/C) atomic ratio of 1, carbon is formed upto 1,180 °C. If the O/C ratio is maintained at 1, while the source of oxygen is changed by the addition of water, carbon formation can be avoided at 1,030 °C under auto thermal conditions. If all the oxygen comes from water (steam reforming), as depicted by the third column, carbon is avoided at temperatures above 950 °C. If the O/C ratio is increased to 2, the temperature required to avoid carbon is further reduced. Thus, the O/C ratio has a very strong bearing on carbon formation. The distribution of the source of oxygen also plays an important role, as shown in the figure—using water as the source of oxygen lowers the temperature needed to avoid coke formation.

Figure 9.4 shows that the SR reaction is less likely to form carbon than is the auto thermal reaction. For kinetic considerations, practical reformers usually operate at temperatures above 600 °C. Since carbon formation is not predicted at 600 °C and O/C = 2, the ATR reaction is more attractive⁹ wherever size and weight constraints are acute (as in automobiles).

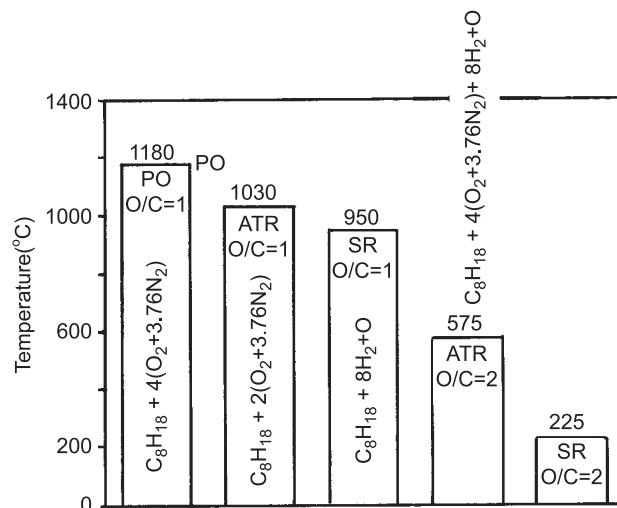


Figure 9.4 Reactor temperature required to prevent the formation of carbon during reforming 2,2,4-trimethylpentane, assuming thermodynamic equilibrium

Catalytic steam reforming (CSR) is usually performed to obtain hydrogen from light hydrocarbons or alcohols. As it is an endothermic process, energy must be supplied to the system. Steam reforming is the most common reforming process because it yields the highest amount of hydrogen. In contrast, partial oxidation is an exothermic process that can be initiated by a simple combustion process. The POX of heavier hydrocarbons is carried out where natural gas is not readily available or where an abundance of oil is predominant. Coal gasification is a similar process, which can also deliver hydrogen, although this reaction is again endothermic. Reviews of on-board hydrogen generation have been published.^{10,11}

Ideally, after reformations, only H_2 and CO_2 should be present but, because of the water gas shift reaction, CO is also present, which poisons the catalysts in most fuel cells that operate below 250 °C. A gas clean up is therefore necessary. After the reformer, a high and low temperature reactor shifts the reaction equilibrium towards H_2 formation. A preferential oxidation (PROX) reactor can then be used, which selectively oxidizes CO to CO_2 , to reduce the CO content in the fuel stream to as low as 5 ppm, dependent on the number of PROX reactors. A membrane can also be used which selectively blocks the permeation of CO (usually a Pd/Ag membrane). The CO can then be burnt to CO_2 and removed from the system. Methanation is another form of gas clean up.

The electrolysis of water is one of the few processes which does not rely on fossil fuels to produce hydrogen. It is also one of the cleanest methods, where pure hydrogen (and oxygen) is obtained. Hydrogen may be generated from other carriers, such as ammonia (NH_3), hydrazine (N_2H_4), carbon fibers and metal hydrides.

Hydrogen is inherently present in fossil fuels, in water, and in secondary sources like biogas and waste materials. It is also a main product or a by-product in many chemical reactions. It is, however, important to be able to produce hydrogen as economically as possible in fuel cell applications.

9.1 Processing Hydrogen from Alcohols

9.1.1 General

Alcohols, and more specifically, methanol, are convenient storage systems for hydrogen. These liquids can easily be transported through the existing infrastructure and have fewer constraints concerning safety than, for instance, gaseous hydrogen storage. The technical synthesis of methanol is based on natural gas feedstock, which is easily and readily available. A direct conversion of methanol in fuel cells is attractive, due to the simplicity of the system without the need for a reformer, and can be achieved in MCFCs and SOFCs or DMFCs.

However, a research effort is in progress, which, if successful, will diminish considerably the capital costs of small reforming reactors.

Methanol SR can be considered to consist of either the decomposition of methanol followed by the water gas shift reaction, or as the reaction of methanol with steam to form CO_2 , which can be followed by a reverse shift reaction: both mechanisms are explained in subsequent sections. Partial oxidation of methanol is usually not preferred, as steam reforming is more effective for hydrogen production.

9.1.2 Partial oxidation (POX)

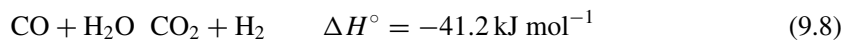
POX of methanol (9.6), is exothermic and occurs over ZnO-supported Pd catalysts with a very high selectivity towards hydrogen.



It was found, though, that at higher temperatures, the selectivity for H₂ improved but the overall catalytic activity decreased. Methanol reforming over Pd/ZnO catalysts also seems to agree with a POX scheme followed by an SR step, which improves the selectivity. Methanol decomposition may also play a role in the methanol reforming reaction over this type of catalyst.

9.1.3 Steam reforming (SR)

As mentioned before, the SR^{12,13,14} of methanol can follow two different pathways. The first involves the decomposition of methanol into CO and hydrogen, (9.7) followed by a water gas shift reaction (9.8).



The second mechanism consists of the reaction of water and methanol to CO₂ and hydrogen, (9.9) which can be followed by a reverse shift reaction, (9.10)



Methanol SR (Fig. 9.5)¹⁵ occurs when methanol and water are mixed and then vapourized and heated to about 300 °C. The vapour mixture is passed over a catalyst, where the reaction occurs. At 300 °C, the decomposition of methanol readily occurs, as well as the two steam reforming reaction pathways described above, to convert methanol into hydrogen.

SR of methanol is usually catalyzed by Cu/ZnO type catalysts and can be performed in fixed-bed reactors. The catalytic burner provides the heat for the reaction. The basic burner structure is a ceramic hollow cylinder to which fuel gas mixed with air is supplied. Pure methanol from the tank is used for the start-up operation, but during continuous operation, the methanol feed can be diluted with retaliate from the anode off-gas (when connected to a fuel system). The products can be separated, as necessary.

SR of methanol is much less endothermic ($\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2$, $-\Delta H_{298}^\circ = -49 \text{ kJ mol}^{-1}$) than that of hydrocarbons. Thus, more than 99% conversion is readily achieved at low temperatures, 200–300 °C, using copper-based catalysts. No methanation occurs and conversion and product distribution is not very pressure sensitive. Although highly active Pd catalysts have been reported,¹⁶ those based on copper are preferred for economical reasons.

As a result of the relatively low temperatures the equilibrated product gas is rich in hydrogen and, consequently, low in CO even at moderate steam to methanol ratios (Fig. 9.6). The optimum

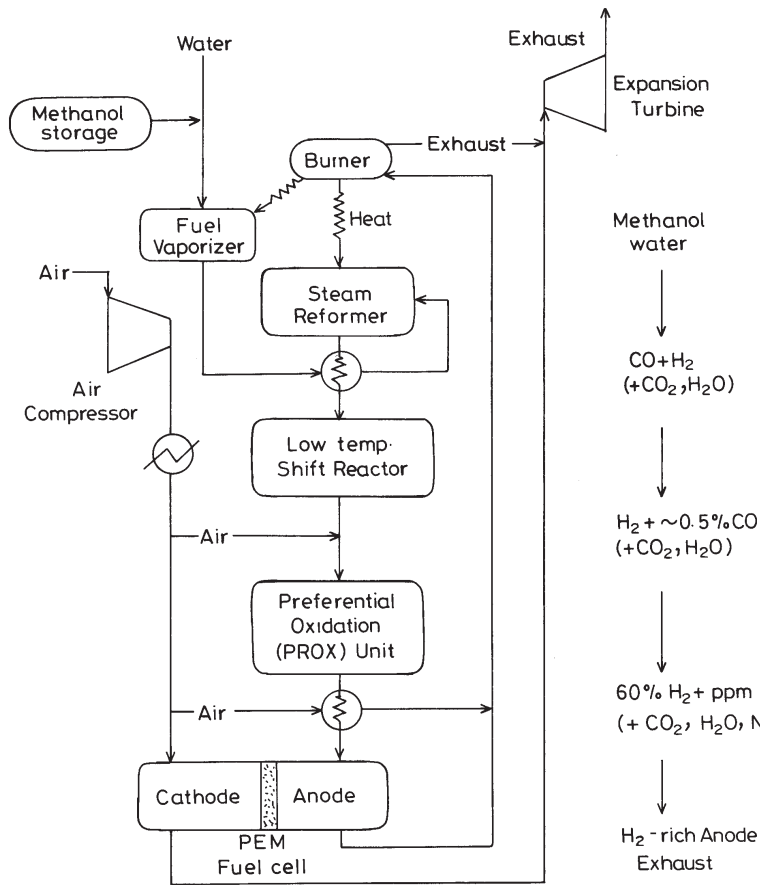


Figure 9.5 The methanol steam reforming reaction

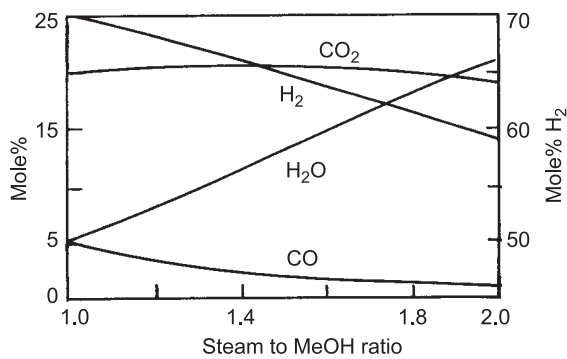


Figure 9.6 Steam reforming of methanol. Variation in equilibrium composition with steam to methanol ratio (280 °C, 5 bar)

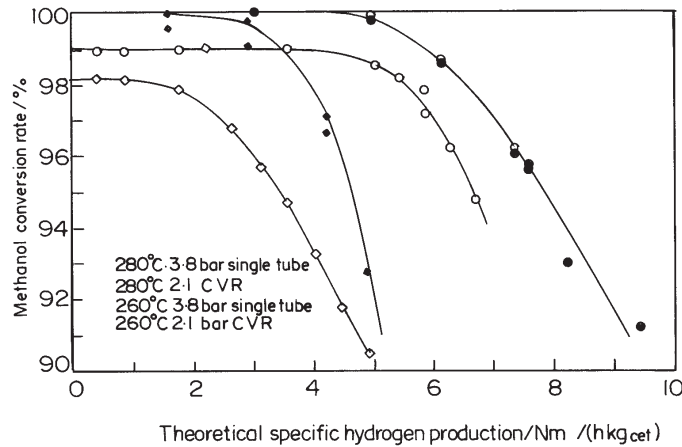


Figure 9.7 Methanol reforming (steam: methanol molar ratio = 1.5): conversion against specific hydrogen production at different temperatures and pressures²¹

steam to carbon ratio is typically between 1.2 and 1.5. The methanol SR process is relatively well understood.^{17–20} The main application is in small hydrogen plants, that is, less than about $1,000 \text{ Nm}^3 \text{ h}^{-1}$. The technology is also considered by several groups to be an attractive solution for on-board hydrogen generation for automotive purposes, because the methanol fuel processor is considerably simpler than its hydrocarbon-based counterpart.

Emonts et al.²¹ evaluated the performance of a 50 kW (LHV hydrogen) methanol reformer and, with a stationary performance test showed a specific hydrogen production of $6.7 \text{ Nm}^3 / (\text{kg}_{\text{cat}} \text{ h})$ at a methanol conversion of 95%. This study correlates methanol conversion with specific hydrogen productivity in terms of $\text{Nm}^3 / (\text{kg}_{\text{cat}} \text{ h})$ at two different pressures and temperatures, 3.8/21 bar and 260/280 °C, respectively, and a molar steam to methanol ratio of 1.5 (Fig. 9.7).

As can be seen, the higher pressures lead to a modest decrease in equilibrium conversion; this decrease becomes more pronounced at lower temperatures. The endothermicity of the SR reaction is reflected by the large increase in productivity upon a mere 20 °C increase in operating temperature. This effect of temperature emphasizes the desirability of developing more temperature tolerant copper-based reforming catalysts.

Ethanol and higher alcohols may also be converted. However, as this involves breaking of one or more C–C bonds, the process is far from being as facile as it is for methanol, and higher temperatures are generally required. Ethanol easily becomes dehydrated, forming ethylene, which leads to carbon formation. At modest temperatures, below approximately 450 °C, efficient bond cleavage is obtained over an $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst to yield a mixture of essentially methane and carbon dioxide.²² However, nickel is an effective catalyst for carbon formation from ethylene, if formed (Fig. 9.8). Cu/Ni-based catalysts that are active below 300 °C have been reported.²³ Other catalyst systems studied include Co, Cu/Zn, Cu/Zn/Cr and noble metals supported on different carriers.^{24–26} These studies indicate that SR of ethanol proceeds via an acetaldehyde intermediate.^{25–28} Acetic acid is also commonly observed and a reaction mechanism involving two parallel pathways from a common intermediate, acetaldehyde, has been proposed:²⁷ one

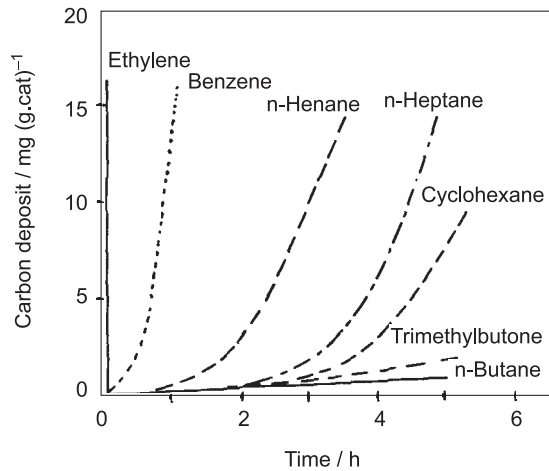


Figure 9.8 Rate of carbon formation for selected hydrocarbons [40]

involving the direct decarbonylation of acetaldehyde, forming CO and CH₄; the other going from acetaldehyde via acetic acid to CO, CO₂ and H₂.

9.1.4 Autothermal reforming

This type of methanol reforming combines the endothermic SR reaction with the POX of methanol in an adiabatic system (9.5–9.9). A spherical reactor system was calculated to be the most attractive configuration for an autothermal process. In this configuration, an inner oxidation catalyst bed is combined with an outer sphere for SR to promote internal heat exchange and maximize the product selectivity.²⁸

Autothermal systems can be very productive, fast starting and compact. A single compact catalyst bed, which converts methanol, water and air into a reformat composed mostly of CO₂ and H₂, has been built. Also, methanol can be converted as proposed by the so-called HotSpot^(TM) fuel processor concept.^{29–31} The first step in this process is believed to be total oxidation of part of the methanol, supplying the heat for subsequent SR. Thus, in the current terminology, we are dealing with *flameless autothermal reforming* (ATR) rather than methanol-based CPO fuel processing. The catalyst is a combined noble metal/base metal catalyst with the noble metal acting as a process initiator by catalyzing the total oxidation reaction. The fuel processor features a modular design to enable different maximum power output at similar response times. Ethanol has also been proposed as a feed for partial oxidation.³²

9.1.5 Membrane reactors

This type of reforming unit combines the process of steam reforming (or cracking, dependent on the conditions) with a semi-permeable membrane, which extracts the product, reducing its

concentration, and thereby, the reaction yields are higher. For the methanol reforming reaction, the hydrogen partial pressure in the product depends less on the reaction and more on the back-pressure across the membrane. With a membrane reactor, pure hydrogen was obtained³³ with a total efficiency of 80%. With better membranes and catalysts, the loss of hydrogen could be kept to 5%.

9.2 Producing Hydrogen from Hydrocarbons

Natural gas is abundant in most places over the world as a fossil fuel. Other natural resources, such as oil, coal and coal gas, can also be found in most regions. As was the case for methanol, hydrogen has to be liberated from the hydrocarbons by one of the mentioned processes: CSR, POX, or ATR. Natural gas can be used directly without external reforming in the high temperature fuel cells.

9.2.1 Catalytic steam reforming

Catalytic steam reforming (CSR)³⁴ (Fig. 9.9)³⁵ was recognized as a process in the early 19th century and has been developed since. A series of patents were filed in the 1920s when researchers in USA were interested in broadening the possible uses of CSR into different fields. Europe and Japan quickly followed and new routes for the CSR of different hydrocarbons were found. Now a days, CSR is one of the principal processes for the production of H₂ and syngas (synthetic gas; a mixture of H₂ and CO). Although partial oxidation and coal gasification also play a vital role in hydrogen production, CSR is cheaper and more energy efficient than the former two methods.³⁶

The most important route to hydrogen is SR of either natural gas (9.11) or liquid hydrocarbons as exemplified in (9.12) for pure component *n*-heptane. For small-scale hydrogen plants and for automotive applications, SR of methanol (9.13) may be an attractive alternative.

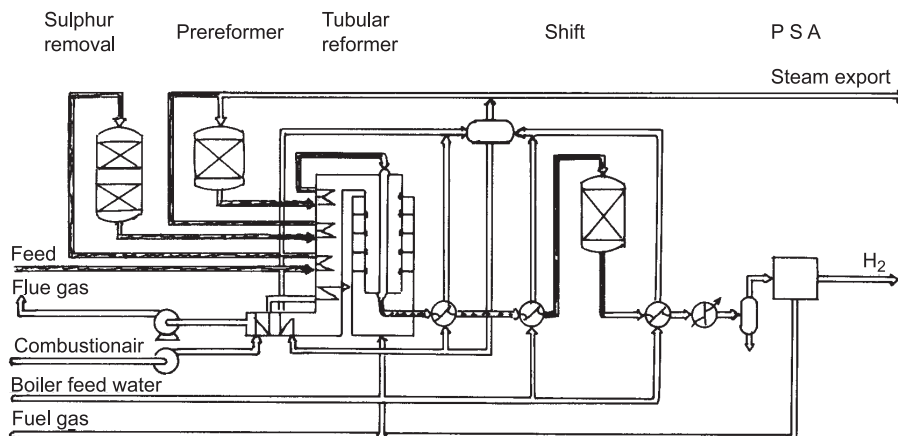
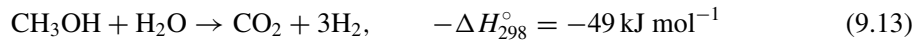
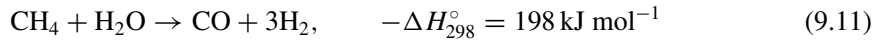
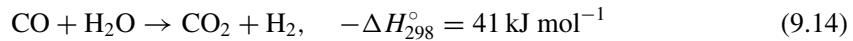


Figure 9.9 The hydrocarbon steam reforming reaction



In the reactions (9.11–9.13), the water gas shift (WGS) reaction participates independently:



All reactions are reversible. Under the preferred reforming conditions, however, the position of the thermodynamic equilibrium makes reactions (9.12) and (9.13) essentially irreversible, but due to the WGS reaction, the equilibrated product inevitably contains steam and carbon oxides along with the desired hydrogen product. Group VIII metals catalyze SR of hydrocarbons, with Ni being the most cost-effective.

SR of methane is strongly endothermic—more so per carbon atom than any of the higher hydrocarbon homologues. Methane SR is, also in practice, a reversible reaction. In order to ensure a high methane conversion, therefore, it is necessary to operate at high temperature, low pressure and relatively high steam-to-carbon ratios (Fig. 9.10).

In conventional tubular SR, the heat is transferred to the process by placing the reformer tubes in a fired furnace. One constraint imposed by this layout is that only about 50% of the furnace heat is transferred to the reforming process. The remainder is recovered in a waste heat section typically serving to produce steam and to preheat feed streams. This figure may, however, be significantly increased when applying heat exchange reforming in which both the flue gas and the high temperature product gas is cooled by heat exchange with the process gas within the reformer itself.^{37–39}

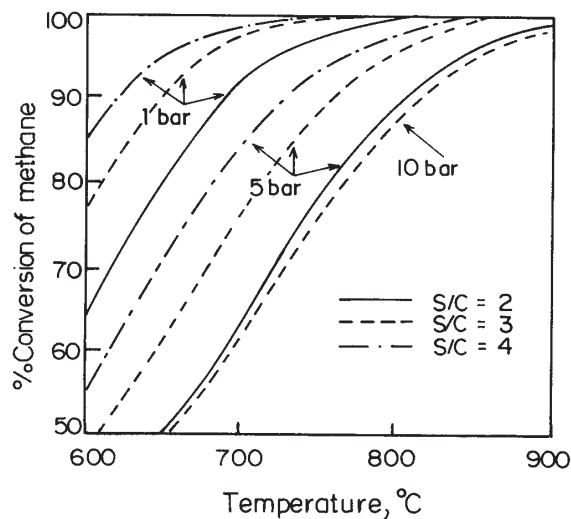


Figure 9.10 Steam reforming of methane: equilibrium conversion against temperature, pressure and steam/carbon ratio

Light distillate naphtha is an attractive feedstock in areas where natural gas is not readily available. The conversion of higher hydrocarbons takes place by irreversible adsorption to the nickel surface, and subsequent breakage of terminal C–C bonds one by one until, eventually, the hydrocarbon is converted into C₁ components. However, reaction rates of individual hydrocarbons over a given catalyst are often quite different from one particular component to the other. And, even though most of the higher hydrocarbons react faster than methane, they are at the same time also susceptible to non-catalytic thermal cracking.⁴⁰ At temperatures above 600–650 °C, that is, at the temperatures characteristic to SR, the thermal reactions begin to compete with the catalytic processes, and this increases as the catalyst activity decreases, example, due to sulphur poisoning. The thermal cracking—or pyrolysis—of the higher hydrocarbons produces olefins, which are precursors for coke formation. In particular, ethylene leads to rapid carbon formation.

In general, the heavier the hydrocarbon feedstock, the slower the reaction rate⁴¹ and the higher the risk of pyrolysis. This problem of carbon formation may be solved effectively by the insertion of a low temperature, fixed bed adiabatic *pre-reformer*⁴⁰ prior to the primary steam reformer. In the adiabatic pre-reformer, the higher hydrocarbons are completely converted into C₁ fragments (CH₄, CO and CO₂). This is quite similar to the process taking place in conventional reforming, but the relatively low temperatures (350–550 °C) in the pre-reformer eliminate the potential for carbon formation. Moreover, the pre-reformer allows for higher inlet temperatures in the primary reformer, thereby reducing its size.

Catalysts

SR of most hydrocarbons occurs only over appropriate catalysts (therefore, CSR), apart from at very high temperatures, whereas in some cases, SR can occur without a catalyst (methanol decomposition can be carried out above a certain temperature without catalyst). Catalysts for SR are usually group VIII metals, in which Ni appears to be the most active. The addition of ceramic oxide stabilizers (α – Al₂O₃ and other oxides) can improve the catalytic activity and can prevent coke formation. Catalysts appear in their oxide form and can be activated by some reducing agents like H₂ and NH₃. Reduction of the metal oxide results in free metal particles, which can take part in the reaction to produce more free metal sites and so on.

Coke formation

Depending on the catalytic selectivity and on the saturation (carbon to hydrogen ratio) of the hydrocarbons, the decomposition of the hydrocarbon may be favoured over the reaction with steam. This process, called coke formation, can deactivate the catalyst in different ways. The carbon so formed can diffuse through the metal crystal and disrupt the catalyst structure but the catalyst surface properties remain unchanged. Metal crystallites (< 2nm) or promotion of the catalysts with alkaline material also reduces coke formation.

9.2.2 Partial oxidation

Methane and other hydrocarbons can be converted to hydrogen by partial oxidation. Partial oxidation,^{42–44} may be catalyzed or uncatalyzed. Partial oxidation (Fig. 9.11)¹⁵ is a reforming

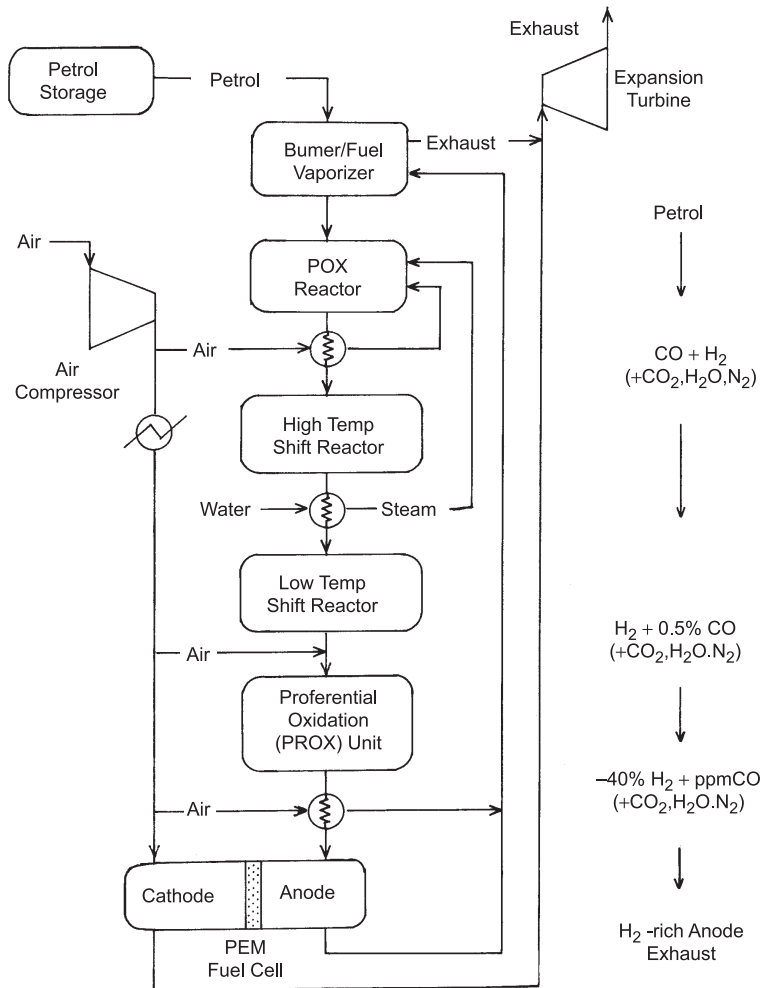


Figure 9.11 The partial oxidation of hydrocarbons to hydrogen

process in which the fuel is partially combusted; it is exothermic and provides heat for other reactions in the reforming system (usually in combination with SR). The oxygen fed into the system is substoichiometric, so that both, CO and CO₂ are formed. A gas shift reaction can transform the CO from the first reaction further into CO₂. The principle reactions are given in (9.15) and (9.16).



By proper adjustment of oxygen-to-carbon and steam-to-carbon ratios, the partial combustion in the thermal zone ($\text{CH}_4 + 3/2\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O}$, $-\Delta H_{298}^\circ = 519 \text{ kJ mol}^{-1}$) supplies the heat

for the subsequent endothermic steam reforming (9.11) and shift (9.15) reactions taking place in the catalytic zone in which soot precursors are effectively broken down. Thus, the product gas composition is fixed thermodynamically through the pressure, exit temperature, steam to carbon and oxygen to carbon ratios.⁴⁵

The *non-catalytic partial oxidation*⁴⁶ 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 scrubber system at the downstream of the POX reactor. The thermal processes typically result in a product gas with $H_2 : CO = 1.7-1.8$.

Catalytic partial oxidation has been the subject of intensified research efforts in recent years. In CPO, the reaction is initiated catalytically (flameless) as opposed to ATR and POX. It has been shown⁴⁷⁻⁵¹ that under extremely short residence times, in the order of milliseconds, methane may be partially oxidized, forming H_2 and CO as the main products.

For natural gas conversion, the preferred catalysts are based on Ni and, in particular, Rh^{49,52,53} and selectivities higher than 90% may be achieved at conversions beyond 90%. The main side reactions are further oxidation of the hydrogen/carbon monoxide product. Most studies have been made near atmospheric pressure. Experiments carried out at elevated pressures^{54,55} do not indicate dramatic changes in product distribution.

Among the virtues of CPO is that the reaction, according to (9.15), is nearly thermo neutral and has a low net energy demand. However, these advantages may easily be offset by the competing total oxidation reactions, which significantly enhance process exothermicity. Another characteristic is that, ideally, the reaction is kinetically controlled. This is due to the short contact times and to the oxidation reactions being faster than the equilibrating steam reforming and shift reactions. Thus, by selecting a proper interval in the region of milli-second residence times,⁵⁶ it is possible to avoid the slower SR reactions interfering to any significant extent. However, despite the high selectivities to carbon monoxide and hydrogen, the competing total oxidation reactions remain a major problem and, in practice, gas compositions are close to equilibrium with respect to reactions (9.11) and (9.14). Today, similar product selectivities as for CPO may be obtained by ATR.^{45,57,58} Many studies fail to report data on the approach to equilibrium. Often, this renders the discussion on selectivities confusing.

The CPO reaction is complicated and a comprehensive understanding is presently lacking. The complexity of the technology is compounded by the fact that, although the process is essentially adiabatic, it is characterized by high catalyst surface temperatures^{50,56} which leads to thermal non-equilibrium between the solid and the gaseous phases. Given the process being conducted at high temperatures and extremely short contact times, that is, within the domain of kinetic control, it is evident that heat and mass transfer play a decisive role in determining process characteristics, temperature and concentration profiles,^{56,59} which eventually may change the entire product spectrum. As addressed in several papers^{51,56,60} careful examination of factors such as gas mixing and flow patterns, radiation, reactor and catalyst geometry, are of utmost importance to further uncover the fundamentals of CPO.

For petrol fuel processing for automotive applications, small air blown reformers are the preferred choice and CPO reformer prototypes have been developed.

When using air as oxidant, NO_x components can be formed at high temperatures ($> 1,400^\circ C$). Methane POX occurs over heterogeneous selective catalysts, whereby Ni/Al_2O_3 has a high

selectivity for CO_2/H_2 at reforming temperatures of 850°C . $\text{Ni/La/Al}_2\text{O}_3$ was found to have lower activity and selectivity. At lower temperatures, different catalysts were tested and it was shown that $\text{Co/La/Al}_2\text{O}_3$ is active at 750°C but not at lower temperatures; whilst an $\text{Fe/La/Al}_2\text{O}_3$ catalyst could be used at 600°C but it provided a low conversion and low selectivity.⁶¹

9.2.3 Autothermal reforming

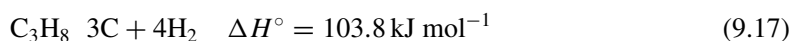
Autothermic conversion of methane to hydrogen occurs readily at 850°C , where a POX process is combined with a CSR. An improved performance was found for single-bed configurations, as opposed to two-bed systems, due to the better heat exchange possibilities in a single bed reactor. A 60%–65% methane conversion could be attained with a selectivity of 80% towards hydrogen production. Systems employing the autothermic conversion of hydrocarbons are being used internally for MCFCs and SOFCs and can be used externally for other fuel cell systems.

9.2.4 Membrane reactors

It is also possible for the reforming of hydrocarbons to be combined directly, as described for methanol reforming, using a membrane in order to selectively shift the reforming reactions towards formation of the product. Membrane reactors³⁵ are more economic at lower temperatures but they need a minimum temperature of around 650°C , otherwise their fuel consumption and feed supply pressure is too high. A very selective membrane is needed to perform the separation of the substances.

9.2.5 Propane cracking

The decomposition of hydrocarbons (propane, methane, and so forth) is endothermic but provides some advantages to the reactor design. A simple design can be chosen, as no shift converter or steam generator is necessary. The reaction for propane cracking⁶² is given by [9.18].



This reaction occurs at above 800°C , so a heat source (such as a propane burner) is needed. The carbon by-product accumulates on the surface of the catalysts, thus eventually blocking the whole surface area. The catalyst can be regenerated, however, by passing air over the surface to burn off the carbon. Some small amounts of CO and CO_2 are produced during the cracking process, which can be removed by methanation, selective oxidation or catalytic burning.

9.2.6 Coal gasification

Coal gasification is endothermic and a high temperature is needed for the reaction to proceed. Solid coal is treated with oxygen and steam to produce a syngas mixture according to equation 9.18. The

reaction process can be very complex, however, as coal comes in many forms and compositions. The process, therefore, has to be adjusted for each type of coal mined. This type of hydrogen production is mainly used in large power plants (> 20 MW).



9.3 Hydrogen from Other Sources

Ammonia (NH_3) is an easily liquefied gas produced by the reaction of methane with steam and air. It is easy to find transport facilities and is widely used in many applications (fertilizers, for instance). Decomposition of NH_3 occurs to produce hydrogen by cracking at high temperatures.



An ammonia fuel cell power plant was developed by the Analytical Power Corporation (Boston, MA, USA) using an ammonia cracker to power the fuel cells. The biggest advantage of ammonia over hydrocarbons is the lack of carbonaceous species, which can decompose alkaline fuel cells or poison the other low temperature fuel cells.⁶³

Electrolysis of water is a major issue in hydrogen production: Hydrogen produced by water electrolysis is pure and, most of all, the process can be completely emission free if the electricity used to electrolyze the water is from a renewable source, such as hydropower or wind energy. Hydro-electric power plants could enhance the energy storage by using the electricity to produce hydrogen. Solar energy is also a clean method for water electrolysis.

Another renewable method to produce hydrogen comes in a rather unlikely form. It was recently reported that some type of algae can be tricked into producing hydrogen instead of their normal photosynthesis processes that lead to oxygen. The plants utilize stored carbohydrates and other biochemical materials to generate hydrogen using just sunlight and water. It should, therefore, be possible to extract hydrogen from these algae by growing them in a closed system and venting off the produced hydrogen.⁶⁴

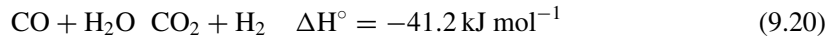
9.4 Gas Clean-up

Reforming hydrocarbons into hydrogen always produces small amounts of CO in the gas stream. This contaminant must be taken out of the fuel stream before being fed into low temperature fuel cells. The gas clean-up can be done in several ways. The first step is a water gas shift conversion of some of the CO into CO_2 , thereby producing more hydrogen, which is the reason why this is called the shift reaction. The next step, to reduce the CO level, can be carried out by different techniques. The three most common ones are selective oxidation, methanation, and the use of a selective membrane.

9.4.1 The shift reaction

The shift reaction involves the conversion of CO into CO_2 using steam as an oxidant (14). This hydrogen forming reaction is exothermic and is usually carried out over a catalyst. The reformat

clean-up includes both, a high and a low temperature shift step. The high temperature shift reactor uses Fe_3O_4 catalysts and temperatures above 350°C to produce CO_2 and H_2 from CO and steam. The low temperature reactors operate at around 200°C and employ CuO/ZnO catalysts.



For SOFCs and MCFCs, a separate shift reactor is not necessary, as CO can be used in the cell by direct oxidation, or an internal shift reaction can occur in this system. When using an internal reforming system, the H_2 produced by the reforming step is directly used at the anode, thereby shifting the reforming step oxidized or shifted with steam to hydrogen and CO_2 .

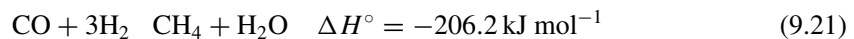
After the low temperature shift reaction, the fuel stream still contains CO (0.5%–1%), still too high for low temperature fuel cells. Therefore, a further clean up has to be carried out.

9.4.2 Selective oxidation

Selective removal of CO occurs over some catalysts, which only oxidize CO and not hydrogen. The fuel stream is fed in a bed over these catalysts and oxygen is introduced. Catalysts used for this purpose are usually alumina-supported structures: ruthenium and rhodium supported on alumina are amongst the most active catalysts. Near to complete CO conversion can be achieved at temperatures as low as 100°C . Copper particles dispersed on alumina are cheaper, are easier to make, and, combined with ZnO , they also have a high catalytic activity for CO oxidation. The activity depends on the Cu particle size, with smaller particles being more active. Selective oxidation prevents the loss of hydrogen as opposed to the methanation process.^{65,66}

9.4.3 Methanation

A different approach to CO removal is taken by the methanation process. In this process, CO is treated with hydrogen to form methane and water. The amount of hydrogen needed to carry out this reaction is, however, three times the amount of CO removed, (9.21).



CO_2 present in the gas stream can, however, react with the hydrogen produced in a reverse shift reaction; the CO produced thereby would defeat the purpose of the whole process. Methanation can remove CO but severe restrictions are necessary to make this process viable in a gas clean-up system.

9.4.4 Membranes

Palladium alloy membranes can be effective in the removal of CO from the fuel stream. The gas is fed through the membrane, but only the hydrogen can permeate. They require rather large pressure differences and a relatively high temperature, which could make them less efficient, depending

Table 9.1 Characteristics of fuel cells

Fuel Cell Type	Cell Temperature (°C)	Maximum CO content (ppm)	Primary fuel
PEMFC	70–80	50	H ₂ , MeOH
PAFC	200	500	H ₂
MCFC	600–650	No limit	H ₂ , CH ₄ , CO, MeOH
SOFC	700–1,000	No limit	H ₂ , CH ₄ , CO, MeOH

on whether the heat can be provided by the fuel cell systems or not. The use of membranes was already mentioned, whereby the methanol steam reforming and the reforming of hydrocarbons can be directly combined with a membrane to produce clean hydrogen.^{28,35,67}

A combined system with different catalytic stages can prove to be the best answer to the problem of gas clean-up. The second cleaning step should take the CO level down to around 10–100 ppm, which can then be fed through the fuel cell with minimal losses.

Whereas high temperature fuel cells (MCFC and SOFC) are capable of converting methane, CO and alcohols, and others in the anode chamber by internal reforming, the PAFC and the PEM cells do not tolerate excessive amounts of CO, as indicated in Table 9.1

For the PAFC, it is possible to reach a level of < 500 ppm (0.05 vol.%) CO by means of high and low temperature WGS reactors as shown in Fig. 9.12. The fuel processor system consists of a hydrodesulphurisation unit, a heat exchange reformer (to minimize waste heat production) and two WGS reactors, bringing the CO content down to < 0.05%. The anode off-gas is used as fuel for the reformer and the flue gas is used to preheat the feed and the cathode air.

The PEMFC does not tolerate more than in the order of 50 ppm CO; the lower the CO concentration, the higher the efficiency of the cell. Therefore, further purification is required, which makes hydrocarbon powered fuel processors for PEMFCs very complicated relative to the

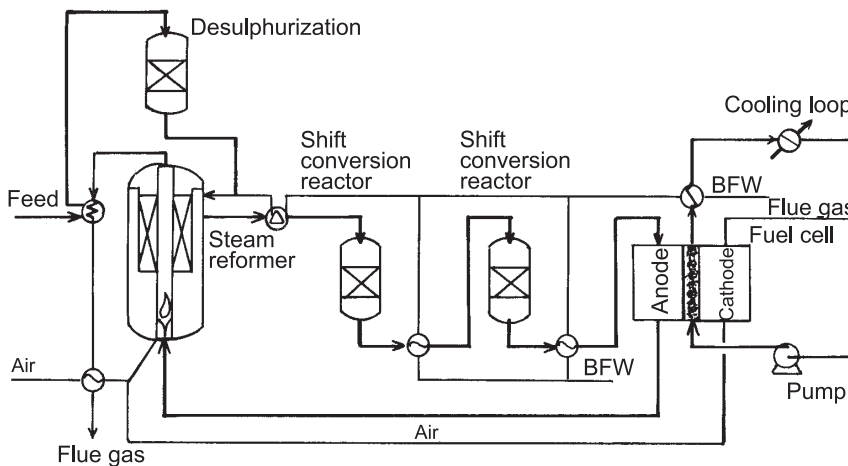


Figure 9.12 Schematic diagram of FPS for phosphoric acid fuel cell

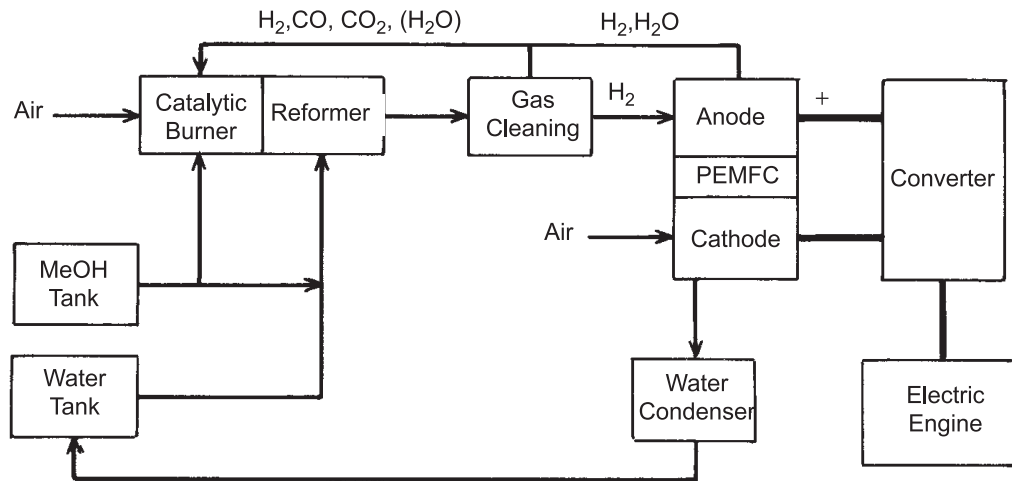


Figure 9.13 Principal flow diagram of methanol powered FPS for automotive application

methanol-based ones which do not require shift of the reformat gas prior to the final CO clean-up. Currently, among the processes for CO removal, selective oxidation appears to be the preferred solution.^{68–71} Alternatives include CO-selective methanation^{29,72} or the use of hydrogen-selective palladium alloy membranes.^{73–75} Figure 9.13 shows a principal flow diagram of a fuel processing system for automotive use based on methanol steam reforming.

One inherent problem of the PEMFCs is that they require low operating temperatures in order to avoid deterioration of the Nafion[®] type polymer membranes. Enabling a higher working temperature of the fuel cell would alleviate the constraints with respect to CO content and might even completely eliminate the need for the final purification step. This would lead to great simplifications in the design and operation of the fuel processor. Another aspect relating to the polymer membrane is the potential of applying the PEMFC as a direct methanol fuel cell. However, current polymers are permeable to methanol. Higher resistance towards methanol crossover might pave the way for direct methanol fuel cells. Therefore, very interesting perspectives arise if alternative ion conducting polymers could be developed, capable of operating at higher temperatures and providing an effective methanol barrier, or capable of doing any one of them. Acid-doped polybenzimidazole membranes appear to possess the potential of accomplishing either or both of these objectives.^{76,77} Another option might involve the use of dimethyl ether instead of methanol.

9.4.5 Fuel cell type determines extent of fuel processing required

The type of fuel cell to be used and the type of application determine the nature and extent of fuel processing required. At least six different types of fuel cells have been demonstrated for electric power generation. Except for the direct methanol fuel cell, all fuel cell types require some degree of fuel processing. The extent of fuel processing required—the allowable levels of carbon monoxide

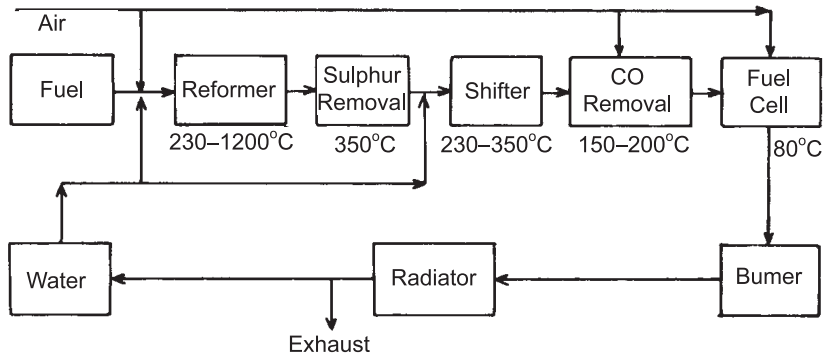


Figure 9.14 Schematic diagram of polymer electrolyte fuel cell system incorporating fuel processor

and other trace species (such as ammonia, hydrogen sulfide) in the reformat—is determined primarily by the operating temperature of the fuel cell. In general, the higher-temperature fuel cells have greater tolerance to non-hydrogen species in the fuel gas. For example, the solid oxide fuel cell (SOFC) being developed for operation above 773 K can readily oxidize carbon monoxide electrochemically. At the end of the fuel cell temperature spectrum, the 353 K polymer electrolyte fuel cell needs a fuel gas with a low (< 50 ppm) content of carbon monoxide and an even lower (< 0.1 ppm) concentration of hydrogen sulfide.

Figure 9.14 is a schematic diagram of a fuel cell power system, which highlights the different fuel processor components that are needed for the low temperature polymer electrolyte fuel cell system. The CO clean-up devices, and perhaps the sulphur removal unit, downstream of the reformer will not be needed for the SOFC stack.

9.5 Hydrogen Storage

Hydrogen can be stored either as a pure compound in gaseous or liquid form or as hydrogen bound in metals and chemicals. Hydrogen storage in hydrocarbons and other energy carriers such as ammonia and hydrazine was discussed earlier. Other, mostly physical forms of hydrogen storage will be discussed here.

9.5.1 Pure hydrogen

It is well known that hydrogen/air mixtures are explosive and most people still have the images of the Hindenburg or the Challenger disaster imprinted in their minds. Most other gases, however, are far more explosive than hydrogen and, in case of a leak, hydrogen disperses so quickly that it is very difficult to ignite. Safety measures are one of the major implications when it comes to commercialization of hydrogen fuel cells, although necessary safety measures can easily be taken and implemented in all applications.

For simplicity, it would be best to store hydrogen directly on board the vehicle or next to the stationary application. In this way, problems with reformed hydrogen, which contains contaminants that can degrade the fuel cell performance, are avoided. Unfortunately, the storage of gaseous hydrogen is not an easy task. Compressing hydrogen into a tank can be achieved, but a restricting factor, especially for transportation applications, is the size and mass of these tanks. With tanks of acceptable size and mass, the driving range of vehicles is restricted and much lower compared to the prevailing systems. Gaseous hydrogen is used, however, to fuel buses and on-site cars, as long ranges are not required and small tanks can be used.

Liquid has the highest energy density of any form of hydrogen storage. Liquid hydrogen tanks should be extremely well insulated (boiling point - 253 °C) and even then a loss of around 1%–2% per day of the stored hydrogen by evaporation occurs. Another problem with liquid hydrogen storage is the amount of energy necessary to convert the hydrogen into a liquid.

Although existing refuelling stations could be employed for refilling hydrogen tanks in both liquid and gaseous forms, it is still necessary to completely reorganize these stations, which could be rather expensive and time consuming. Localized refilling stations can be employed, especially for fleet refill purposes. A project running at the Munich airport (Germany) uses cars running on hydrogen for special transports from the terminal to the plane. The filling station is one of Europe's first and it also provides hydrogen for a fleet of buses running at the same airport. The NECAR4 prototype hydrogen car from Daimler-Chrysler was also a guest at the hydrogen refuelling station.

9.5.2 Hydrogen in other structures

The storage of hydrogen in metals or other structures is sometimes incorrectly called solid hydrogen. In principle, the hydrogen is stored as atomic hydrogen or as a gas absorbed into the structure. Metal hydrides are commonly used for hydrogen storage: a metal alloy exposed to hydrogen can form a metal hydride. The condition under which a metal alloy forms a metal hydride depends on the type of alloy. The release of hydrogen usually involves the heating of the metal hydride. Metal hydrides are common and can be used for different applications: hydrogen storage is only one of them. A database with properties, processing details, and applications of metal hydrides can be found on the internet.⁷⁸

A special case of metal hydride storage is found in the so-called power balls. These power balls store sodium hydride very effectively: they are produced by coating sodium hydride pellets in a waterproof skin and the balls are then stored in water. To release the fuel, mechanical breakage of the skin of individual balls releases fuel as necessary. The reaction for the stored NaH with water produces hydrogen and sodium hydroxide. The released hydrogen bubbles to the top of the containing vessel and can be used for fuel cells.⁷⁹

Another hot topic in hydrogen storage is the use of graphite nanostructures, which store hydrogen in gaseous form within their crystal structure. These graphite structures can be obtained in tubular form (nanotubes) or as fibers. Both forms are highly conductive, flexible and mechanically stable. The storage of hydrogen is achieved by absorption of the hydrogen gas in the crystal structure under elevated pressures and temperatures. The absorbed hydrogen is claimed to be more densely packed in the material than is possible by compressing hydrogen gas.⁸⁰

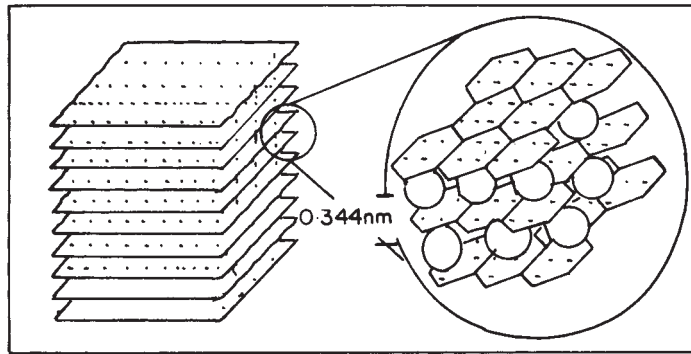


Figure 9.15 Hydrogen adsorption (grey dots) in graphite (plate like) nanofiber multilayers

Nanotubes can be considered elongated fullerenes with open ends, in which all carbon atoms are arranged in a sheet of hexagons. This sheet of hexagons can be either rolled along its main axis to form an electrically conducting tube or made perpendicular to this axis to form an insulator. Controversial reports state that single walled nanotubes have a hydrogen storage capacity of 4.2 wt% (a H:C atomic ratio of 0.52). Most of the absorbed hydrogen is claimed to be released at ambient pressure and temperature, whilst the residual hydrogen could be obtained by slightly heating the samples.^{81,82} Multiple walled nanotubes are reported to be even more promising.

Other, also controversial, studies report graphite nanofibers are even better than nanotubes.⁸³ They have been reported to store about 20–30 liters of hydrogen per gram of material, which is about ten times as much compared to metal hydrides. Carbon nanofibers are predicted to store up to three times their own mass in hydrogen under pressure at room temperature. This would be far more than any natural hydrogen storage in hydrocarbons (the highest storage, methane, is 25 wt%). The key to this enormous storage capacity is believed to be the regular, close-packed structure of the nanofibers. The fibers pack into dense, layered plates with gaps in between. Multiple layers of hydrogen could fit into the spaces⁸⁴ if the interaction with the carbon molecules is strong enough (Fig. 9.15). However, several groups could not confirm the spectacular claims and therefore caution is advised with respect to these storage materials.⁸⁵

Carbon nanomaterials could be cost-effective as long as an efficient production method can be found. Scaling up the production process is necessary to attain economical feasibility. Charging the materials with hydrogen still takes quite a long time and the pressures employed to pack the hydrogen in the crystal structure can be rather high. Reproducibility is also a factor, which needs to be approached for commercializing this technique; thus far, many results have been published and, while some are very promising, many of them have proved to be irreproducible. Nevertheless, nanostructured carbon materials could prove to play an important role in hydrogen storage systems.

Glass micro spheres⁸⁰ have been used for the purpose of hydrogen storage as well. At high temperatures, hydrogen gas can permeate through glass. At lower temperatures, the gas is locked in the trapped form. The storage capacity of these structures is smaller than that of the carbon nanofibers but they could compete as a more reliable method.

Zeolites can store hydrogen in a similar manner. The gas can be forced into the pores of molecular sieves under elevated temperatures and pressures. Cooling the matrix again traps the hydrogen, which can be released by heating. The amount of hydrogen, which can be stored, depends on the cation of the zeolite. Potassium zeolites have been found to store more hydrogen than rubidium and still more than sodium zeolites.^{86,87}

The entire scope, from fuel to fuel cell system to vehicle to infrastructure, has to be taken into account when comparing different storage forms and fuel processing techniques for fuel cells. A combination of existing technologies should be feasible to design a system, which is compatible with every one of the fuel cell applications. With modern and future technologies, it should be possible to find enough options for hydrogen production and storage; so, the problem of hydrogen storage should not hinder the commercialization of fuel cells.

9.6 Challenges and Opportunities for Fuel Processing Research

The concepts and steps of fuel processing are illustrated in Fig. 9.16.⁸⁸ There are challenges and opportunities for research and development on fuel processing for fuel cells. Based on the studies reported in literature, some key issues can be summarized, as shown in Fig. 9.17, for fuel processing for fuel cells. From a preliminary analysis of current situations, it appears necessary for further research to develop (1) effective ways for ultra-deep removal of sulphur from hydrocarbon fuels before reforming; (2) more energy-efficient and compact processors for on-site or on-board fuel reforming; (3) more effective removal of inorganic sulphur (H_2S) after fuel reforming; (4) non-pyrophoric, and more active catalysts for water gas shift reactions at medium and low temperatures; (5) highly selective and active catalysts for preferential oxidation of CO to enable maximum

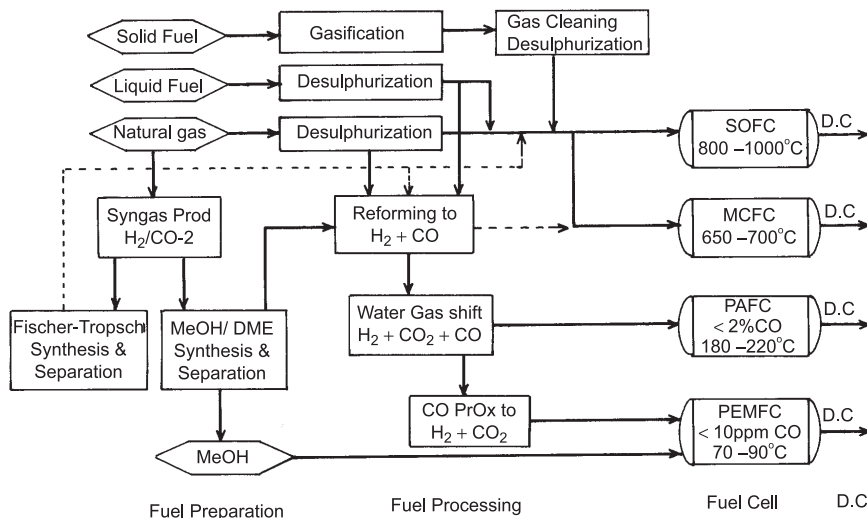


Figure 9.16 The concepts and steps for fuel processing of gaseous, liquid and solid fuels for high temperature and low temperature applications⁸⁸

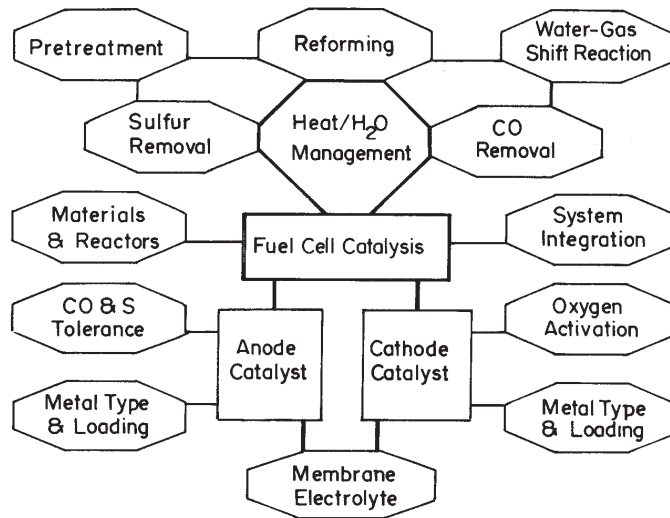


Figure 9.17 Some key issues for research and development on fuel processor for fuel cells

production of H₂; (6) high-performance electrode catalysts such as CO-tolerant electrodes with lower costs or lower loading of precious metals, and suitable proton-exchange membranes at higher (than current) temperatures for PEMFC.

It should be noted that by using fuel processing for hydrogen production in multiple steps, the net efficiency of the fuel cell system is reduced, and its efficiency advantage is consequently reduced, although such an indirect fuel cell system would still display a significant efficiency advantage. In this context, it is important to develop highly efficient and compact fuel processors for fuel cell applications.

9.7 Conclusion

The call for clean energy is the main driver in the development of fuel processing for both, stationary and mobile applications. Fuel processing technology for the generation of hydrogen is receiving a fresh look because of new applications in fuel cell power generation. The fuel processor system design can vary significantly, depending on the type of fuel cell, the specific application and the type of fuel. Several fuel processor designs are likely to emerge, for different applications and fuel cell types and for different fuels. The technology is available, but further progress in catalyst and development of components, system design and integration, cost reduction and not the least, successful field test programmes are required for fuel processors to eventually gain general consumer acceptance.

Of the three reforming pathways, the steam reforming process yields the highest hydrogen concentration in the product. However, for practical applications, the partial oxidation and autothermal reforming processes are attractive because they can be made more energy efficient and hardware can be smaller and lighter.

The need for smaller, lighter and more responsive fuel processors producing a high-purity, hydrogen-rich gas has created opportunities for alternative technologies in reforming, scrubbing and separation processes.

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