

Hydrogen generation from natural gas for the fuel cell systems of tomorrow

Andrew L. Dicks

British Gas plc., Gas Research Centre, Ashby Road, Loughborough, Leic. LE11 3QU, UK

Abstract

In most cases hydrogen is the preferred fuel for use in the present generation of fuel cells being developed for commercial applications. Of all the potential sources of hydrogen, natural gas offers many advantages. It is widely available, clean, and can be converted to hydrogen relatively easily. When catalytic steam reforming is used to generate hydrogen from natural gas, it is essential that sulfur compounds in the natural gas are removed upstream of the reformer and various types of desulfurisation processes are available. In addition, the quality of fuel required for each type of fuel cell varies according to the anode material used, and the cell temperature. Low temperature cells will not tolerate high concentrations of carbon monoxide, whereas the molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC) anodes contain nickel on which it is possible to electrochemically oxidise carbon monoxide directly. The ability to internally reform fuel gas is a feature of the MCFC and SOFC. Internal reforming can give benefits in terms of increased electrical efficiency owing to the reduction in the required cell cooling and therefore parasitic system losses. Direct electrocatalysis of hydrocarbon oxidation has been the elusive goal of fuel cell developers over many years and recent laboratory results are encouraging. This paper reviews the principal methods of converting natural gas into hydrogen, namely catalytic steam reforming, autothermic reforming, pyrolysis and partial oxidation; it reviews currently available purification techniques and discusses some recent advances in internal reforming and the direct use of natural gas in fuel cells.

Keywords: Hydrogen generation; Natural gas; Fuel cells; Development

1. Introduction

Fuel cells offer a means of converting the chemical energy of a fuel directly into electricity in one step and therefore differ fundamentally from most conventional methods of power generation. However, this only holds if the cells can be run directly on the primary fuel. Of all of the fuels that have been tested in fuel cells, hydrogen has the highest reactivity. At temperatures below 300 °C most hydrocarbons and alcohols, e.g. methanol, have very low catalytic reaction rates and often unwanted, and poisoning side-products are formed. At high temperatures direct electrochemical oxidation may be feasible and this is discussed later, but for most practical fuel cell systems currently under development, it is necessary first to produce hydrogen from an available primary fuel source. This must be done as efficiently as possible.

Fig. 1 shows the most obvious pathways for the production of hydrogen from different primary energy sources. The links between the energy resources and hydrogen have led to hydrogen being viewed as an intermediate energy vector having many potential end uses from substituting various fuel

and electric duties to use as a raw material in chemicals manufacture. Fuel cells provide the most efficient means of converting the chemical energy in the hydrogen molecule into electricity.

In the long term, as fossil fuel prices rise due to depletion of reserves and as global warming worsens, hydrogen may become more attractive as an energy vector and fuel. In the hydrogen economy, renewable energy sources may be used to generate hydrogen, e.g. by water electrolysis. In the short- and medium-term however, fossil fuels can be used to produce hydrogen for fuel cell plant and so provide a basis on which they can enter the commercial world.

This paper discusses the availability and properties of natural gas that make it the primary fuel of choice for fuel cells. It reviews the currently available purification techniques and describes the principal methods of converting natural gas into hydrogen, namely catalytic steam reforming, autothermic reforming, pyrolysis and partial oxidation. Some recent advances in internal reforming (reforming within the fuel cell itself) and the direct use of natural gas in fuel cells (without reforming) are also presented.

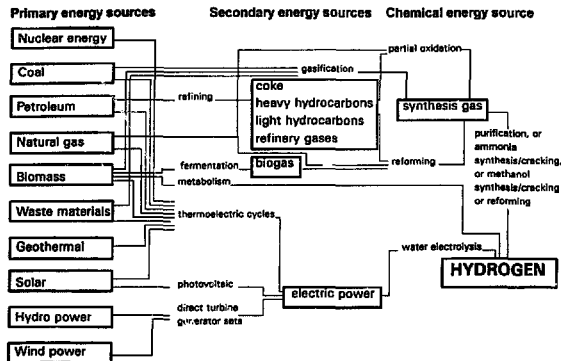


Fig. 1. Sources and production of hydrogen.

2. Availability of natural gas

Of all the potential sources of hydrogen for fuel cells, natural gas offers many advantages. Firstly it is relatively abundant around the world. In 1992 the annual world commercial production of natural gas was $2106 \times 10^9 \text{ m}^3$. Natural gas is transmitted via large pipeline systems in many of the developed countries: in the USA, Europe particularly in the UK, The Netherlands and Germany, and in Japan. There is also a significant transfer of natural gas by pipeline between countries. It is notable that in 1992, $58.3 \times 10^9 \text{ m}^3$, representing 3% of all gas produced was shipped from Canada to the USA, while $25 \times 10^9 \text{ m}^3$ was piped from the North Sea and $60.7 \times 10^9 \text{ m}^3$ were piped from the former Soviet Union to Germany through Poland, with a further $38.4 \times 10^9 \text{ m}^3$ to Eastern European countries [1].

In addition to piped natural gas there is a large international trade in liquefied natural gas (LNG). The largest amount shipped by tanker is into Japan. In 1992 this amounted to $25 \times 10^9 \text{ m}^3$ from Indonesia alone with additional supplies from Brunei and the Middle East. Smaller amounts are currently shipped from Algeria to the east coast of the USA and to Europe.

The proven reserves of natural gas together with an established infrastructure and trade in LNG clearly indicate that natural gas is the most available primary fuel. Natural gas also has a high energy content and, whether at high pressure in suitably designed vessels or cryogenically in the form of LNG, it provides an excellent means of energy storage.

Currently, steam reforming of natural gas provides the cheapest source of industrial hydrogen. Although the cost of hydrogen is related to both the fuel price and the processing costs (and therefore the scale of the operation), it is estimated that steam reforming will continue to provide the cheapest source of hydrogen over the next 15 to 20 years. This is illustrated in Fig. 2 which shows recent estimates of the costs of producing hydrogen by electrolysis, by biomass gasifica-

tion and by steam methane reforming (SMR). For comparison the present costs of industrial methanol and ethanol are also shown since these are often cited as possible fuels for mobile applications.

3. Properties of natural gas

Although the chemical composition of natural gas varies according to the source, the principal component is methane — the remainder being small amounts of low molecular weight hydrocarbons and often nitrogen and CO_2 . Many natural gases contain a small amount of sulfur, which is usually present as simple compounds such as hydrogen sulfide, carbonyl sulfide or mercaptans. Natural gas is the cleanest of all primary fossil fuels and is the most environmentally acceptable in terms of its products of combustion. When considering converting natural gas into hydrogen this property is also important, to minimise side products and keep environmental emissions to a minimum.

Table 1 shows typical compositions of a range of natural gases. It should be noted that in many countries compounds containing sulfur are added to the gas before distribution, to act as an odorant to help in the detection of leaks. For example, in the UK a cocktail of mercaptans and diethyl sulfide are added as the gas is processed onshore, whereas in The Netherlands tetrahydrothiophene is added.

Many utilities enrich their natural gas with other compounds to raise the heating value and flame speed to meet a required specification or to compensate for seasonal variations in composition. Occasionally, mixtures of butane-air or propane-air are also added to boost supplies during periods of high demand. So, although methane is the principal constituent of natural gas, significant quantities of other compounds will be present which can affect the performance of the fuel cell and which may pose particular processing difficulties.

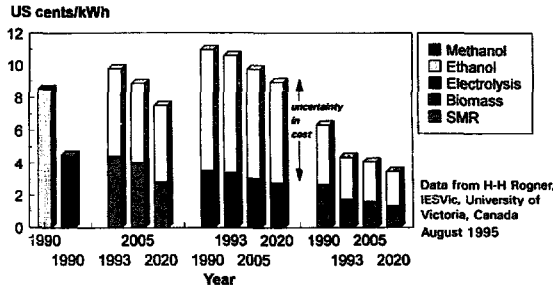


Fig. 2. Costs of hydrogen production, SMR: steam/methane reforming.

Table 1
Typical analyses of natural gases from different sources

Component	North Sea	Qatar	Netherlands	Pakistan	Ekofisk
CH ₄ (%)	94.86	76.6	81.4	93.48	85.5
C ₂ H ₆ (%)	3.90	12.59	2.9	0.24	8.36
C ₃ H ₈ (%)		2.38	0.4	0.24	2.85
i-C ₄ H ₁₀ (%)	0.15	0.11		0.04	0.86
n-C ₄ H ₁₀ (%)		0.21	0.1	0.06	
C ₅ ⁺ (%)		0.02		0.41	0.22
N ₂ (%)	0.79	0.24	14.2	4.02	0.43
S (ppm)	4	1.02	1	N/A	30

4. Purification of natural gas

Certain constraints are imposed on the fuel for each type of fuel cell. Platinum anode catalysts are poisoned by sulfur and CO which means that high fuel purity is required for the solid polymer fuel cell (SPFC) and to a lesser extent the phosphoric acid fuel cell (PAFC). On the other hand, the high temperature SOFC and MCFC are able to oxidise CO directly on the anode so these cells place less of a constraint on the fuel quality.

The most serious contaminant in natural gas is sulfur, present as H₂S, COS or other organic sulfur compounds. The concentration of these compounds in UK natural gas is typically:

Hydrogen sulphide (H ₂ S)	0–0.5 ppm (v/v)
Diethyl sulphide ((C ₂ H ₅) ₂ S)	3.0 ppm (v/v)
Tertiary butyl mercaptan ((CH ₃) ₃ CHS)	0.9 ppm (v/v)
Ethyl mercaptan ((C ₂ H ₅)HS)	0.4 ppm (v/v)

There is a statutory maximum level of 3.3 ppm of H₂S allowed in the British Gas transmission system (British Gas Act, 1986).

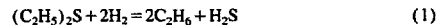
Sulfur is a poison for nickel steam reforming catalysts and for many anode catalysts including platinum. The adsorption of sulfur on nickel is reversible at low concentrations; adsorbed sulfur may be removed by switching to a sulfur-free feed or by steaming the catalyst for a few hours. If the

surface concentration of sulfur is allowed to increase, bulk sulfidation occurs causing permanent poisoning of the catalyst. The sensitivity of nickel to sulfur poisoning decreases as the temperature is raised and there is evidence that the SOFC is able to tolerate higher concentrations of sulfur in the feed than the MCFC [2,3]. Time is also an important factor in sulfur poisoning. In a packed bed steam reforming reactor, sulfur is first adsorbed on a narrow band of catalyst at the top of the bed. As time progresses sulfur moves through the catalyst bed and can eventually migrate with the process gases out of the reactor and poison shift catalyst or the anode surface in the fuel cell.

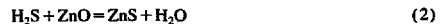
Sulfur removal is therefore essential if any hydrocarbon fuel is going to be steam-reformed. Typically, the levels need to be reduced to 0.2 ppm (v/v) or lower.

4.1. High temperature desulfurisation

For large scale hydrogen production, hydrodesulfurisation (HDS) is invariably the preferred method of sulfur removal. In this process the natural gas is mixed with a small quantity of hydrogen and passed over a hot bed of catalyst (usually cobalt and molybdenum oxides supported on alumina). Any organic sulfur is reduced to H₂S and hydrocarbon by reactions of the following kind:



The H₂S produced can then be removed by adsorption on a bed of ZnO catalyst:



Undesirable hydrocracking reactions can occur over HDS catalysts if they become reduced to the metals by a hydrogen-rich feed gas, and the sulfur concentrations are very low. Alkene hydrogenation can also cause problems if these are present in significant quantities. Fortunately, such problems are unlikely with most natural gases.

The optimum temperature for most HDS catalysis is between 350 and 400 °C, and the catalyst and zinc oxide adsorbent can be placed in the same vessel since ZnO can

remove H₂S to below 0.5 ppm at these temperatures. The reformer for HDS can be obtained by recycling some of the reformer product and such schemes have been reported by Ohnishi (Osaka Gas) [4] and Ikeda (UTC) [5].

The ICI PURASPEC process is another high temperature desulfurisation method that is similar to HDS in that two catalyst beds are employed, operating at 350 °C. In the first bed, organic sulfur compounds are thermally cracked to H₂S which is then absorbed on the second bed containing ZnO. The process, which has been demonstrated as suitable for desulfurising natural gas at elevated pressures by British Gas, does not require hydrogen.

4.2. Low temperature desulfurisation

The Osaka Gas mixed metal and metal oxide catalyst [6] provides a low temperature method of desulfurisation. The catalyst is claimed to remove organic sulfur and H₂S at room temperature, reducing start-up time for a fuel cell-based power generator. Tests combining the Osaka Gas high performance desulfurisation with conventional HDS claim to have resulted in a fuel gas for a 50 kW PAFC pilot plant containing less than 0.1 ppb.

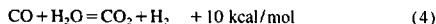
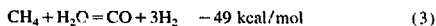
Low temperature adsorption processes are available that do not need hydrogen; the two most widely used are activated carbon and molecular sieves. Activated carbon can be chemically impregnated to enhance the adsorption of H₂S, and it is acceptable for use in small-scale systems for relatively short time periods. In both cases the adsorbents can be reactivated by raising the bed temperatures. For larger systems, these methods are impracticable because of the large quantities of adsorbent required and problems associated with its reactivation and disposal of the desorbed sulfur.

Finally, the Sulfatrac process has been developed in the USA from the well-known iron oxide adsorption process [7]. The adsorbent uses proprietary iron compounds on an inert substrate. It operates at low temperatures (down to 4 °C), and is able to remove H₂S and mercaptans in a single vessel.

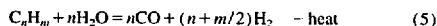
5. Chemistry of methane conversion

5.1. Steam reforming

Steam reforming is a mature technology, practised industrially on a large scale for hydrogen production. The reforming reaction (3) and water-gas shift reaction (4) are carried out over a supported nickel catalyst at elevated temperatures, typically above 500 °C.



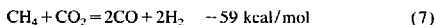
The higher hydrocarbons in natural gas also react with steam in a similar fashion:



Reactions (3) and (4) are reversible and are normally at equilibrium as the reaction rates are very fast. The product gas from a conventional reformer reactor is therefore governed by thermodynamics. Steam is normally added well in excess of the stoichiometric requirement of reaction (3) so that the equilibrium of reaction (4) moves towards more CO₂ rather than CO. This is to avoid carbon deposition through the Boudouard reaction (6) which is also catalysed by nickel:



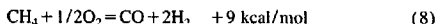
Steam may be replaced completely (or in part) by CO₂ which gives a more favourable H₂/CO ratio for some applications:



The equilibrium constants for all of these reactions are well known and it is possible to predict the outlet composition of a reformer knowing the atomic ratios of H/C and O/C present, and the pressure and temperature. Usually the predicted equilibrium outlet composition is close to the measured values, and small differences are expressed as an 'approach to equilibrium temperature'.

5.2. Partial oxidation

Methane and other hydrocarbons may be converted to hydrogen via partial oxidation which may be catalysed or non-catalysed:

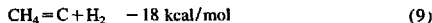


It should be noted that less hydrogen is produced per mole of methane by reaction (8) than reaction (3). Fuel cell systems employing partial oxidation therefore generally have lower electrical generation efficiencies than those employing steam reforming where unused heat from the fuel cell may be used for supplying the endothermic reforming reaction (3). However, for certain applications the lower efficiency may be offset by advantages such as compactness, rapid start-up, responsiveness to load change, and overall cost.

Several metals have been found to catalyse reactions (3)–(8), but nickel is generally preferred on cost grounds. In commercial steam reforming catalysts, the nickel is supported on a refractory oxide such as alumina, magnesia or mixed ceramics which are able to tolerate high temperatures. The physical form has evolved over many years to maximise the activity and rate of heat transfer within the reformer reactor. The catalyst pellet size is a compromise between ensuring good packing, mechanical stability and low pressure drop. The pressure drop is in turn governed by the vessel size and mass velocity for which the reactor is designed.

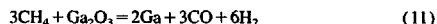
5.3. Thermal cracking and chemical reduction of metal oxides

If methane or other hydrocarbons are heated in the absence of air, they will decompose to produce hydrogen and carbon thus:



In principle these reactions can produce very pure hydrogen since no carbon oxides are formed. However such an advantage is outweighed by the problems of disposing of the solid carbon by-product. Thermal cracking is therefore normally viewed as a reaction to avoid except in some specialised applications.

Another alternative chemical route to hydrogen is through the reduction of certain metal oxides at high temperatures. Thus, at temperatures in the 900–1100 °C range, gallium oxide can be reduced to the metal using methane:



The gallium can then be oxidised using air or an oxygen-rich gas back to the oxide. Tungsten has also been investigated for such a process. The main problem with such methods is that the activity of the metal decreases over repeated oxidation and reduction cycles.

6. Carbon deposition

For a given steam–methane ratio it is possible to predict the thermodynamic likelihood of carbon deposition via the Boudouard reaction (6) from a gas mixture containing carbon oxides, hydrogen, steam and methane. However, it has been well established that the thermodynamic minimum steam–methane ratio for carbon deposition over nickel catalysts is lower than the thermodynamic data for graphite formation would predict. The reason is that the form of carbon deposited on nickel has a lower free energy of formation than graphite. On nickel it has been fairly well established that the key reactions occur over a surface layer of carbon atoms. If these are allowed to build up, e.g. because of low steam partial pressure, a filament or whisker of carbon can start to grow attached to a nickel crystallite. Such carbon filaments can generate massive forces within catalyst pellets and once started can lead to rapid catalyst breakdown, and the blocking of reactor tubes. Fig. 3 shows carbon filaments formed on a catalyst used for internal reforming in an MCFC.

Carbon may also be formed by thermal cracking of hydrocarbons. Reactions (9) and (10) tend to lead to a surface, pyrolytic carbon which in a catalyst can encapsulate the nickel particles, again causing deactivation. Reactions (9) and (10) have the greatest risk of occurring at the inlet to a reformer where there is almost no hydrogen present. At this point the likelihood of carbon deposition occurring is governed not so much by equilibrium considerations as by the relative kinetics of the carbon-forming reactions and the carbon-removal (gasification) reactions.

Higher hydrocarbons have a greater propensity for carbon deposition than methane. Thermal or steam cracking of hydrocarbons can occur above 600–650 °C even in the absence of nickel catalysts. The cracking leads to olefins and

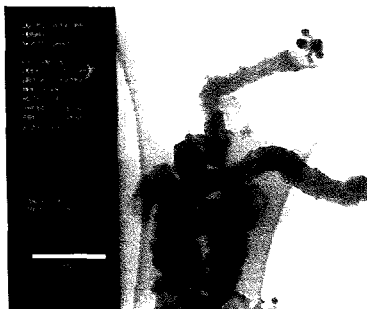


Fig. 3. Micrograph showing carbon filaments on a supported nickel catalyst used in a DIR-MCFC with low steam–carbon ration in the fuel gas.

then to a carbonaceous polymer which can dehydrogenate to produce coke. For this reason, it is common to carry out some pre-reforming of natural gas to remove the C_2 + hydrocarbons before the gas is fed to the main reformer. Pre-reforming can be carried out adiabatically at relatively low temperatures where the carbon deposition reactions do not occur. Typically pre-reforming is done in the 250–500 °C range [8].

Much work has been done to reduce the propensity for carbon deposition on nickel catalysts. This can be done for example by the addition of potassium. It has also been found that controlled passivation of catalyst with sulfur can reduce carbon formation [9]. Fortunately carbon filaments do not appear to form on precious metals such as ruthenium or rhodium which are also active for steam reforming, so if cost is not an issue, the use of precious metal catalysts can significantly reduce the risk of carbon deposition.

7. Steam reforming process technology

Many reviews have been given concerning conventional catalytic steam reforming process technology [9–11]. Most large scale steam reforming is carried out for ammonia production and externally heated metallic reformer tubes, packed with catalyst pellets, are used. Reformer plants vary in size, typically the smallest being about 100 Nm^3/h capacity and the largest currently in existence has a maximum hydrogen production rate of 140 000 Nm^3/h . Large plants invariably have two stages of reforming. The primary (externally heated) reformer tubes operate between an inlet of about 500 °C and an outlet of 750 °C. The gas from these tubes passes through secondary adiabatic (unheated) reactors in which air is added. Historically the air addition is required to produce a product containing H_2 and N_2 in the right proportions for ammonia synthesis. However, dividing the reaction between two catalysts also reduces the duty on each and commercial catalysts have lifetimes in excess of ten years.

Improvements in large scale hydrogen production are made in small evolutionary steps. The more recent developments have been the ICI Leading Concept Ammonia (LCA) process [10] and the Topsoe SPARG process [12]. Another widely adopted improvement is the use of gas turbines to provide combustion air for the primary reformer burners.

Large scale reformers could be feasibly used for supplying hydrogen to fuel cell plant applications at the 100 MW scale. For integration with fuel cell plant, however, smaller reformers are generally required. Several other characteristics are also desirable: high reformer efficiency (improved heat and mass transfer), good load changing capability, and low cost through use of cheaper materials and production methods. Several novel reformer technologies have been identified which address these requirements. These are described in the following sections.

7.1. Compact regenerative reformers

This type of reformer allows the feed, product, combusted and the partially reformed gases to exchange heat by directing them through flow pathways within the reformer. They have been designed especially for fuel cell systems and they offer high thermal efficiency, compactness and an ability to withstand thermal cycling. These reformers can be divided into two types:

1. Reformers with multi-tube assembly extending into the burner cavity, e.g. UTC multi-tube cylindrical reformer [13,14] (Fig. 4), and
2. Reformers with a central burner, e.g. Haldor Topsoe Heat Exchange Reformer [15], KTI compact reformer [16], and Osaka Gas compact reformer [4].

Fig. 5 shows the Topsoe compact reformer which is probably the best known of the central burner type. The burner is located at the bottom of a pressure vessel and pressurised

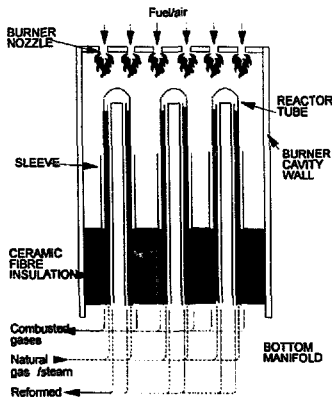


Fig. 4. UTC multi-tube cylindrical reformer.

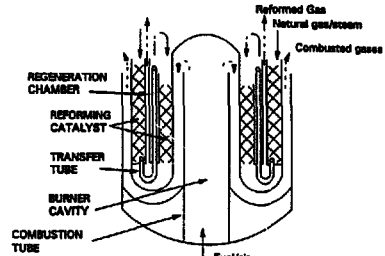


Fig. 5. Haldor-Topsoe heat exchange reformer.

combustion, typically at 4.5 bar is used. Feed gas is passed downwards through the first catalyst bed where it is heated to around 675 °C by convection from both the combustion products and the reformed product gas both flowing counter-current to the feed. On leaving the first bed of catalyst, the partially reformed gas is transferred through a set of tubes to the top of the second reforming section. The gas flows down through the catalyst, being heated to typically 830 °C by convection from the co-currently flowing combustion products and also by radiation from the combustion tube. The combination of co-current and counter-current heat transfer minimises metal temperatures.

The advantages of such a reformer are small size and suitability at a small scale; pressurised combustion giving good heat utilisation; improved start-up and load following, and low cost.

But it still has difficulties; there are mass transfer limitations from the gas phase to the catalyst pellets, and there are the heat transfer limitations of the tubes. Heat recovery is constrained by the design, i.e. the heat recovery system is integral to the reactor. High temperature materials are still needed and the size, cost and performance do not meet the target needs for many fuel cell systems.

7.2. Plate reformers

In the plate reformer concept, see Fig. 6, a stack of alternate combustion and reforming chambers are separated by plates. The chambers are filled with suitable catalysts. Alternatively either side of each plate can be coated with combustion catalyst and reforming catalyst. The heat from the combustion reaction is used to drive the endothermic reforming reactions. Plate reformers have the advantage that they are very compact and that they offer a means of reducing heat transfer resistances to a minimum. The use of a combustion catalyst means that low heating value gases can be burnt, such as fuel cell exhaust gases, without the need for a supplementary burner fuel. Catalyst coating requires a method of adhering the catalyst to a plate so that the catalyst is capable of operating for long periods at high temperatures without deactivation or surface cracking. Plate reformers are being developed by IHI [17], British Gas [18] and others.

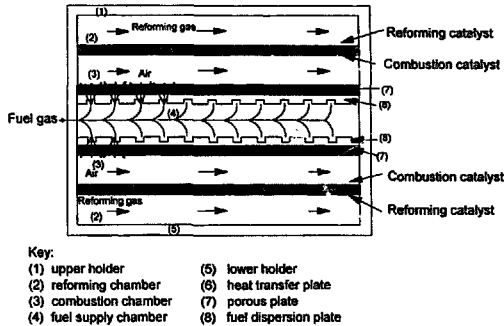


Fig. 6. Plate reformer concept.

7.3. Spiral steam reformer

In the spiral geometry reformer proposed by Astanovsky [19], shown in Fig. 7, feed gas enters an internal heat exchanger where it is heated to 810 °C by the reformed gas. The reforming section of the reactor is an annular space in the upper section. Catalyst is arranged in spiral shaped passageways formed by hollow walls. The heated gas enters the

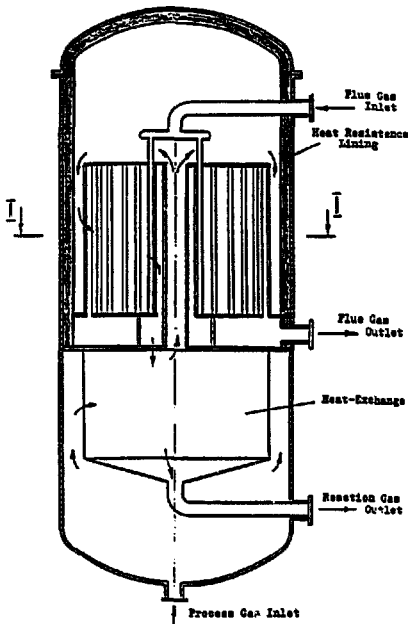


Fig. 7. Spiral steam reformer.

catalyst bed from its outer section and is directed horizontally inwards as the reforming reaction occurs. Heat for the reforming reaction is provided by the combusted gases which are flowing in the hollow wall. The reformed gases leave the catalyst at 860 °C and pass to the heat exchanger where they are cooled to about 310 °C. The advantages of this design are the high heat transfer area and high catalyst effectiveness brought about by the use of fine catalyst particles (1–4 mm).

7.4. TECT reformer

Tokyo Gas Research Institute have been conducting small scale trials (10 kW) on a radiating solid type reformer [20]. The Thermal Energy Conversion and Transfer Technology (TECT) reformer employs a porous solid medium which radiates heat to the reforming gas. The design has not yet been able to demonstrate an increase in thermal efficiency or reduction in size compared with a conventional reformer.

7.5. Membrane reformers

Hydrogen is able to selectively permeate through palladium or palladium alloy membranes. This has led to the consideration of steam reformers. Reactors have now been demonstrated in the laboratory where hydrogen, produced by steam reforming, is selectively removed from the reactor using a palladium membrane [21]. The removal of hydrogen increases the methane conversion level and the hydrogen produced is very pure. Such a reformer could therefore be ideally suited for the SPFC, since additional reactors to perform the shift reaction and carbon monoxide removal would not be required. The membrane thickness of a developed reactor is likely to be in the 0.01–0.1 mm range.

Hydrogen is also able to semi-selectively permeate through certain ceramic membranes. Although the permeate will contain quantities of impurities such as CO₂, CO, H₂O and CH₄, ceramic membranes are cheaper than palladium membranes

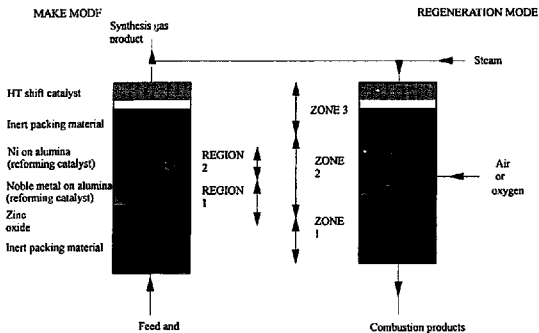


Fig. 8. Intensified combined reactor (IFC).

and are more robust. The use of such membranes is being studied by British Gas and others [22].

7.6. Intensified combined reactor

International Fuel Cells have a patent [23] for hydrogen production where the desulfurisation, steam reforming and the high temperature shift reactions are carried out in a single vessel. The vessel design is simple in comparison with the regenerative steam reformers such as the Haldor Topsoe Heat Exchange Reformer. IFC claims that high thermal efficiencies can be achieved without the use of passageways to exchange heat between the combustor gases and the reformer gases. Instead, heat to the endothermic steam reforming reactions is provided by the packing and catalytic material in the vessel. The packing material is heated in a cyclic operation firstly by steam and alternatively by combusting gases within the vessel. This is illustrated in Fig. 8 where two identical reactors are used. At any given time one vessel is producing hydrogen, i.e. in the make mode, whilst the other vessel is being heated, i.e. in the regeneration mode.

7.7. Non-catalytic partial oxidation reformers

If the temperature of reaction is high enough it is possible to carry out steam reforming without a catalyst and several technologies have been proposed to do this. Calcott and Deague [24] have described a reactor for producing CO and H₂-rich gas with little or no CO₂ and steam. A fuel (called the primary fuel) mixed with air or oxygen is introduced to the cylindrical reactor through nozzles. The arrangement of nozzles causes the mixture to swirl and form a compact, self contained and thoroughly mixed combustion zone. The primary fuel is completely combusted to CO₂ and H₂O which then react with a secondary fuel downstream of the combustion zone to form a synthesis gas mixture (see Fig. 9). The actual reactor consists only of a refractory-lined tube. The high intensity combustion zone causes fast combustion reactions, resulting in a compact reactor with temperatures of around 1200 °C. Texaco and Shell have proprietary processes that also require very high temperatures (about 1400 °C), and Topsoe have also developed a non-catalytic process [25].

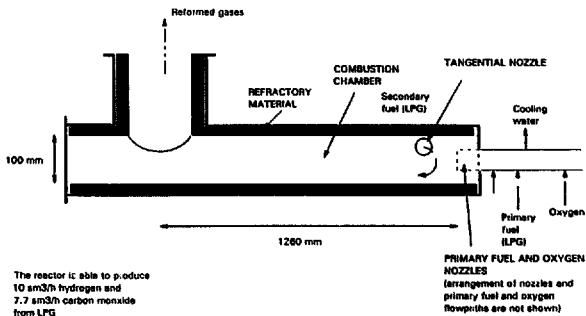


Fig. 9. Non-catalytic partial oxidation reformer (Calcott).

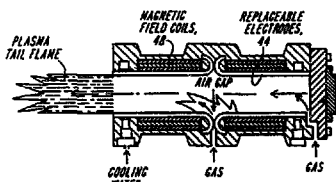


Fig. 10. Plasmatron reformer.

Recently the concept of carrying out steam reforming in an electric plasma has been proposed [26]. This type of reactor (Fig. 10) potentially has the advantage of being compact, operating at a moderate temperature with a fast start-up capability and good response to changes in load.

7.8. Catalytic partial oxidation reactors

Catalytic partial oxidation reactors can operate at lower temperatures than non-catalytic reactors and they require less pre-heating. Two categories of partial oxidation reactor can be identified, depending on whether or not steam is added with the fuel and oxidant.

In the absence of added steam, a number of substances can catalyse the partial oxidation of methane. Ashcroft [27] showed that lanthanide ruthenium oxide catalysts ($\text{Ln}_2\text{Ru}_2\text{O}_7$, where Ln is a lanthanide) are able to partially oxidise mixtures of CH_4 , O_2 and N_2 at atmospheric pressure and about 775 °C. Methane conversion was found to be 97%, and the product was a mixture of CO and H_2 containing little CO_2 or H_2O . Further work by Green et al. [28] showed that at similar temperatures and space velocities methane can be partially oxidised using the British Gas CRGF Ni– Al_2O_3 catalyst as well as supported metal catalysts such as 1% Ru, 1% Rh and 1% Pd on Al_2O_3 .

The Hot Spot reactor developed by Johnson–Matthey [29] utilises a partial oxidation catalyst (platinum and chromium oxide on a refractory support). The novel feature of this reactor is the hot spot created in the catalyst bed caused by point injection of the air–hydrocarbon mixture (Fig. 11). This arrangement eliminates the need for pre-heating the fuel and air during operation although for start-up on natural gas, the fuel should be pre-heated to around 500 °C. Alternatively, the reactor may be started from ambient temperature by introducing an initiating fuel such as methanol or a hydrogen rich gas. These compounds are oxidised by air at ambient temperature over the catalyst which serves to raise the catalyst bed temperature.

If steam is added as well as air and fuel to a partial oxidation reactor, it is possible to balance the heat generated by the exothermic partial oxidation reaction and the endothermic steam reforming reaction. The reactor is then said to be autothermal. For fuel cell applications (especially for low temperature cells) autothermal reactors have the advantage over steam reformers that they do not require an external heat

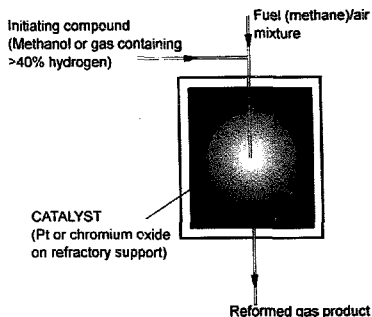


Fig. 11. Johnson Matthey 'Hot-Spot' reactor.

source. They have a faster start-up time than steam reformers and the reactors can be started without steam addition. This latter feature means that fuel can be supplied to the fuel cell before steam is raised, which is particularly attractive when the fuel cell system employs anode recycle.

Several types of autothermal reformer are available industrially, and others are under development. The ICI LCA process splits the reactions between two vessels. In the first, natural gas and steam are partially reformed over a nickel catalyst. The products pass to a second vessel where air is added and an exothermic reaction takes place over a monolithic catalyst. Heat from the second reactor is recycled to the first.

In the Combined Autothermal Reformer (CAR) from UHDE [30] the partial oxidation and reforming reactions take place in the same vessel. Natural gas is split into two streams. The first stream is mixed with steam and enters the top of the reactor. The gas passes downwards through vertical tubes containing reforming catalyst. The reformed gases then enter a partial oxidation chamber where the remainder of the natural gas and air–oxygen are injected. Partial oxidation takes place without catalyst and the products are fed upwards to transfer heat to the reformer tubes. The CAR was developed for large scale hydrogen, methanol and ammonia production, and may not be directly applicable to fuel cell systems.

The Davy McKee Company has a patent [31] for an autothermal reforming reactor in which the novel feature is the mixing of fuel, steam and oxidant streams prior to entering the catalyst bed. The mixing is carried out in a number of long tubes whose diameter is designed to ensure turbulent flow. The mixed gas stream can then be passed over the catalyst at high space velocities. One advantage of this design is that relatively inexpensive materials may be considered for catalysts, however the high throughputs may make the system unattractive for moderate fuel cell power plants.

Haldor Topsoe have developed an autothermal reformer using a proprietary burner and fixed catalyst bed. With this design the outlet temperature can be reduced to 900–1100 °C

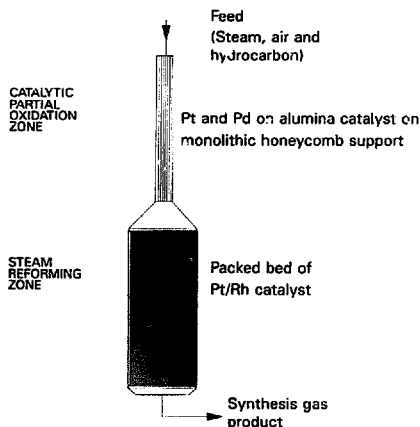


Fig. 12. Engelhard autothermal reformer.

with very low steam–methane ratios, whilst avoiding carbon deposition [32].

Engelhard (cited in Ref. [33]) have developed an autothermal reactor specifically for fuel cells (Fig. 12). This has been demonstrated to produce a hydrogen-rich fuel from diesel oil. The reactor achieves high conversion of the heavy hydrocarbons with low air addition rates and without carbon deposition owing to the use of platinum group metals in the reforming catalyst. The reformer comprises two sections, a catalytic partial oxidation zone followed by a steam reforming zone. The partial oxidation is carried out over Pd–Pt–Al₂O₃ on a honeycomb monolithic catalyst; a packed bed of supported Pt–Rh catalyst is used for the steam reforming.

7.9. Methane decomposition

Universal Oil Products have developed the HYPRO process [34] for the thermal cracking of methane or natural gas. A fluidised bed reactor is used in which methane is decomposed at about 850 °C and carbon is deposited onto a Ni–Al₂O₃ catalyst. The catalyst is continuously removed and fed to a regenerator where the carbon is burnt off by injecting air and supplemental natural gas. In contrast to the HYPRO process, the process described by UTC [35] utilises an expendable nickel catalyst or metal–glass fibre material on which to collect the product carbon. If catalytic glass fibre is used, it is claimed that the temperature of operation can be as low as 750 °C.

8. Internal reforming

The MCFC and the SOFC both operate at high enough temperatures to allow natural gas to be reformed within the

fuel cell stack. Internal reforming lowers the requirement for cell cooling and, by eliminating the external reformer, capital costs are also reduced.

There are two basic internal reforming concepts, and these are usually referred to as direct (DIR) and indirect (IIR) internal reforming. With DIR, reforming takes place either directly on the anode or within the fuel channel of the cell. Heat and steam are supplied directly from the electrochemical reaction. The electrochemical reaction also helps to drive the reforming reaction to completion by removing the hydrogen as it is formed. DIR results in high conversion and high cell efficiencies, even at the relatively low temperature of the MCFC. With IIR, the reforming reaction takes place in a compartment which is in close thermal contact with the cell. This gives the advantage of good heat transfer from the cell but without the hydrogen and steam synergy between the anode electrochemical reaction and the reforming reaction.

8.1. Internal reforming in the MCFC

Energy Research Corporation (ERC) in the USA, and several Japanese developers have built IIR-MCFC stacks. However, DIR provides the biggest challenge to MCFC developers. There are two main reasons. Firstly, a catalyst has to be found that is able to operate for extended periods in the presence of a corrosive alkali environment. Secondly, the catalyst needs to provide sufficient activity so that the rate of the reforming reaction is matched to the rate of the electrochemical reaction. This is to ensure that temperature variations across the cell are kept to a minimum, to reduce thermal stress, and thereby help ensure long stack life. Recycle of anode gas, cathode gas, or both may also be used to even out the temperature distribution across the stack.

The major developers of direct internal reforming are Mitsubishi Electric Co. (MELCO) and ECN, in collaboration with British Gas. MELCO have demonstrated DIR in stacks of 10 kW to 50 kW [36]. ECN have demonstrated a 1 kW stack, and plan to demonstrate DIR at the 10 kW scale shortly. For the ECN work, British Gas has been supplying catalyst, which unlike conventional steam reforming catalysts are able to operate in an MCFC environment for several thousand hours without significant deactivation [37].

8.2. Internal reforming in the SOFC

In the SOFC, the reforming of natural gas can be catalysed by the nickel cermet anode material at 1000 °C. Over nickel cermet the kinetics of methane reforming have been fairly well established, at least at high temperatures [38–40]. Recent work at British Gas [41] has demonstrated that over Ni–ceria anodes the rate of steam reforming is given by:

$$\text{rate} = kP_{\text{CH}_4},$$

$$\text{when } 1.6 \text{ kPa} < P_{\text{CH}_4} < 18 \text{ kPa}$$

$$\text{and } 5.4 \text{ kPa} < P_{\text{H}_2\text{O}} < 39 \text{ kPa}.$$

In cells running at low current densities (below 100 mA/cm²) the reforming reaction is not affected by the cell operation and the measured cell voltage–current curve running on methane–steam is close to the theoretical curve. We have also found little evidence for significant mass transfer influences on the reforming kinetics although Rechenauer and Achenbach [40] have suggested that previously reported dependencies of reaction rate on the steam–methane ratio may be due to mass transfer effects. Tests have, however, showed that there are significant differences in reforming activity on the anodes of cells of different compositions and from different sources.

Operation of the anode in a 98% H₂–2% steam environment resulted in very little change in the microstructure of the anode over a period of 50 h. Increasing the steam partial pressure, however, results in some sintering of nickel in the anode.

Westinghouse [42,43] have demonstrated that sulfur poisons the anode, but that degradation can recover when sulfur in the feed is removed. High steam concentrations are known to degrade anodes and recent work by British Gas has shown that operation of a cell on steam–methane, rather than hydrogen, results in an increase in sintering of the nickel in the anode.

With internal reforming systems it is possible to provide steam for the reaction by recirculating anode exhaust gas. This was first demonstrated by Westinghouse [43] several years ago. If natural gas is used as fuel directly on the anode of an SOFC, it has been demonstrated that there is a greater propensity for carbon deposition than when methane is used as fuel. It is widely assumed, therefore, that some pre-reforming of natural gas will be required for SOFC operation, and current designs have pre-reformers located close to the stack.

9. Direct use of natural gas in fuel cells

The complete oxidation of methane to CO₂ and H₂O is a highly exothermic reaction ($\Delta H^0 = 46 \text{ kJ mol}^{-1}$) and the entropy change on combustion is very small. Thus, if it were possible to combust methane directly in a fuel cell (without any intermediate reactions) the thermodynamic efficiency would be close to 100%. One problem, however, is that in a cell employing an oxide-conducting electrolyte, water is produced on the anode and, therefore, the cell may become effectively internal reforming.

Attempts to run fuel cells directly on methane were attempted in the 1960s with mixed success. Brummer [44] tested several anode materials in the PAFC but the SOFC appeared to be the most favoured type of cell for direct oxidation. This was first investigated by General Electric who devised an SOFC in which methane decomposed to produce carbon which acted as the anode. This did not prove to be feasible however and the earliest significant results were obtained in 1971 by Sandler [45]. He oxidised a methane–oxygen mixture over platinum and silver anodes in an SOFC

using calcium-stabilized zirconia electrolyte. Mason [46] in 1980 tested both silver and gold anodes but concluded that the electrolyte (in this case scandia-stabilised zirconia) rather than the electrode, dominates the electrooxidation of methane. A few years later, Otsuka et al. [47] tested several anode materials in a 'steam reforming' SOFC in which methane was fed to the anode and oxygen was provided at the cathode by decomposition of steam.

Mori [48] recently has tested platinum anodes in cells utilising BaCeO₃ electrolytes. Methane conversion exceeded 30% and current densities up to 600 mA/cm² were obtained at 1000 °C. An iron anode with a YSZ electrolyte also converted methane to CO and H₂ with high selectivity. Steele et al. [49] have investigated several materials and found that those with a perovskite structure (LaMnO₃) proved to be effective for direct oxidation of methane to CO₂ and water with a conversion of 35%. Titanium oxides have also been examined by several groups but the best performance so far seems to be that of Mogensen et al. [50]. They have operated the YSZ cell at 800–1000 °C using mixed ion-conducting oxides of ceria–gadolinia. They claim to have measured rates of methane oxidation nearly large enough to make their fuel cell a competitive power generator. Unfortunately none of these materials have emerged from the laboratory into a practical working fuel cell design. This is clearly an area of study where an incorporation of reactor design, heterogeneous catalysis and materials science could make such fuel cells viable power generators for the future.

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