

Conversion of hydrocarbons and alcohols for fuel cells

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Abstract

The growing demand for clean and efficient energy systems is the driving force in the development of fuel processing technology for providing hydrogen or hydrogen-containing gaseous fuels for power generation in fuel cells. Successful development of low cost, efficient fuel processing systems will be critical to the commercialisation of this technology. This article reviews various reforming technologies available for the generation of such fuels from hydrocarbons and alcohols. It also briefly addresses the issue of carbon monoxide clean-up and the question of selecting the appropriate fuel(s) for small/medium scale fuel processors for stationary and automotive applications. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Fuel processor; Steam reforming; Partial oxidation; Fuel cell; Hydrocarbon; Alcohol

1. Introduction

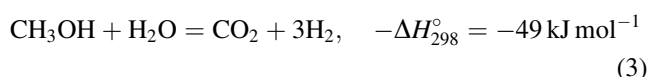
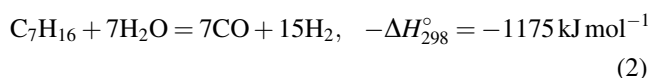
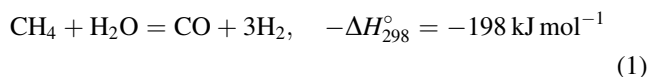
Catalysis is likely to become a key element in the conversion of liquid or gaseous fuels into hydrogen for fuel cells. This conversion, commonly referred to as fuel processing, most often involves either *hydrocarbons*, like methane, propane/LPG, and higher, liquid hydrocarbons or *alcohols*, e.g. methanol and ethanol, although, in principle, any hydrogen-containing compound may be applied, such as dimethyl ether and ammonia. It is even possible to convert other fuels than hydrogen—directly or indirectly—in the fuel cell [1,2]. 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 and indeed, in some cases, ideal electrical efficiencies in excess of 100% may, in principle, be obtained [3].

The generation of hydrogen, or hydrogen-rich product streams, by reforming of hydrocarbons or alcohols, may from a thermodynamic point of view, be categorised in two basically different types of processes. One is—endothermic—steam reforming 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, by burning combustible off gases or by a combination of both. The other is—exothermic—partial oxidation, where the feed reacts directly with air, enriched air or (in large plants) pure oxygen at a carefully balanced

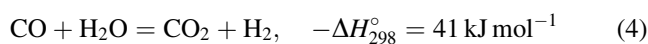
oxygen to fuel ratio. In this case, the overall process becomes net heat producing. In either of the processes heat management and, as part thereof, thermal integration of the fuel processor and the fuel cell becomes key to achieve high overall plant efficiencies.

2. Steam reforming

The most important route to hydrogen is steam reforming of either natural gas (Eq. (1)) or liquid hydrocarbons as exemplified in (2) by pure component *n*-heptane. For small scale hydrogen plants and for automotive applications, steam reforming of methanol (3) may be an attractive alternative.



In all of the reactions (1)–(3), 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 (2) and (3) essentially

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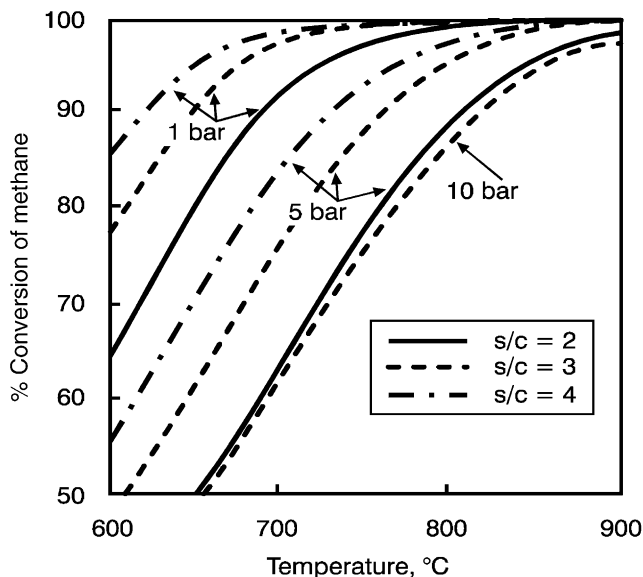


Fig. 1. Steam reforming of methane. Equilibrium conversion against temperature, pressure and steam/carbon ratio.

irreversible, but due to the WGS reaction, the equilibrated product inevitably contains steam and carbon oxides along with the desired hydrogen product. Steam reforming of hydrocarbons is catalysed by group VIII metals, with Ni being the most cost-effective.

Steam reforming of *methane* is strongly endothermic—more so per carbon atom than any of the higher hydrocarbon homologues. Methane steam reforming 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. 1).

In conventional tubular steam reforming, 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 [4–6].

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, subsequent breakage of terminal C–C bonds one by one until, eventually, the hydrocarbon is converted into C_1 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 higher hydrocarbons react faster than methane, they are at the same time also susceptible to non-catalytic thermal cracking [7]. At temperatures above

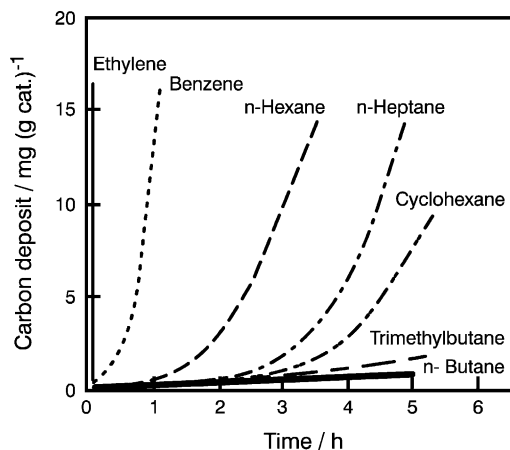


Fig. 2. Rate of carbon formation for selected different hydrocarbons [7].

600–650 °C, i.e. at the temperatures characteristic to steam reforming, the thermal reactions begin to compete with the catalytic processes and increasingly so as the catalyst activity decreases, e.g. 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 (Fig. 2).

In general, the heavier the hydrocarbon feedstock, the slower the reaction rate [8] 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 *prereformer* [7] prior to the primary steam reformer. In the adiabatic prereformer, the higher hydrocarbons are completely converted into C_1 fragments (CH_4 , CO and CO_2). This is quite similar to the process taking place in conventional reforming, but the relatively low temperatures (350–550 °C) in the prereformer eliminate the potential for carbon formation. Moreover, the prereformer allows for higher inlet temperatures in the primary reformer, thereby reducing its size.

The *steam reforming of methanol* is much less endothermic (Eq. (3)) 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 [9], 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. 3). The optimum steam to carbon ratio is typically between 1.2 and 1.5. The methanol steam reforming process is relatively well-understood [10–13]. The main application is in small hydrogen plants, i.e. less than about $1000 \text{ N m}^3 \text{ h}^{-1}$. 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.

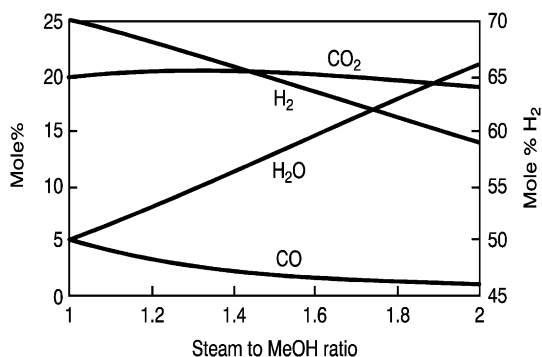


Fig. 3. Steam reforming of methanol. Variation in equilibrium composition with steam to methanol ratio (280 °C, 5 bar).

As part of a recent study [14], the performance of a 50 kW (LHV H₂) methanol reformer was evaluated. Stationary performance tests showed a specific hydrogen production of 6.7 N m³/(kg_{cat} h) at a methanol conversion of 95%. Fig. 4 correlates methanol conversion with specific hydrogen productivity in terms of N m³/(kg_{cat} 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.

As can be seen, the higher pressure leads to a modest decrease in equilibrium conversion, this decrease becoming more pronounced the lower the temperature. The endothermicity of the steam reforming reaction is reflected by the large increase in productivity upon a mere 20 °C increase in operating temperature. This effect of temperature emphasises 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 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 a Ni/Al₂O₃ catalyst to yield a mixture of essentially methane and carbon dioxide [15]. However, nickel is a very effective catalyst for carbon formation from ethylene, if formed (cf. Fig. 2). Cu/Ni-based catalysts active below 300 °C have been reported [16]. Other catalyst systems studied include those based on Co, Cu/Zn, Cu/Zn/Cr and noble metals supported on different carriers [17–19]. These studies indicate that steam reforming of ethanol proceeds via an acetaldehyde intermediate [18–21]. Acetic acid is also commonly observed and a reaction mechanism involving two parallel pathways from common intermediate acetaldehyde has been proposed [20]: one involves the direct decarbonylation of acetaldehyde forming CO and CH₄; the other goes from acetaldehyde via acetic acid to CO, CO₂ and H₂.

3. Partial oxidation

Partial oxidation reactions may be carried out either by catalytic partial oxidation (CPO), by non-catalytic partial oxidation or by autothermal reforming (ATR), the latter being a combination of non-catalytic oxidation and steam reforming.

The *autothermal reformer* [22] consists of a thermal and a catalytic zone. The feed is introduced to a burner and mixed intensively with steam and a substoichiometric amount of oxygen or air. In the combustion (thermal) zone, part of the feed reacts essentially according to

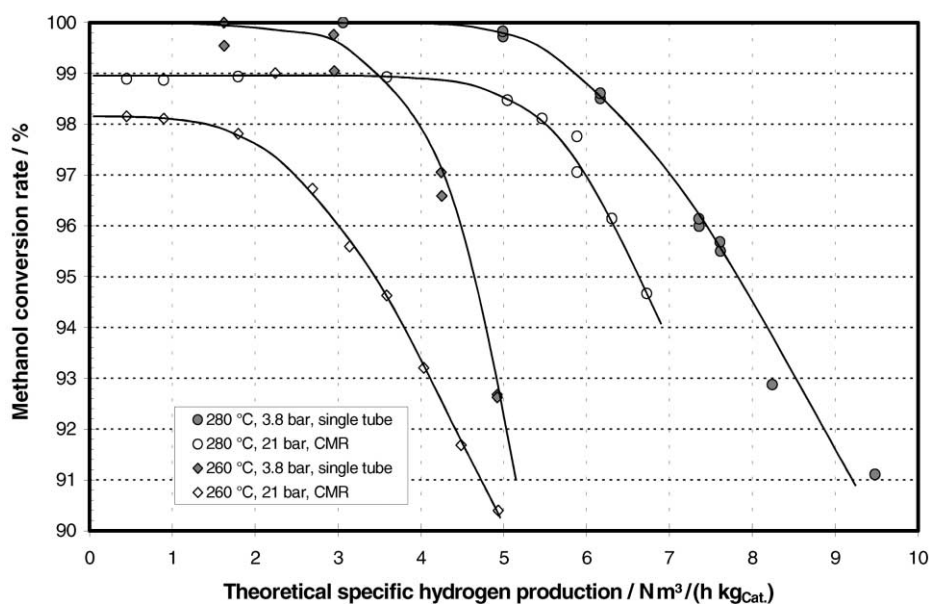
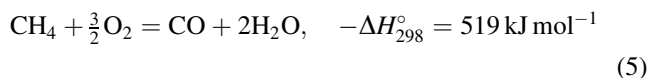
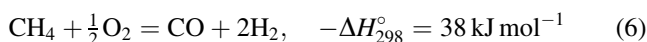


Fig. 4. Methanol reforming (steam:methanol molar ratio = 1.5): conversion against specific hydrogen production at different pressures and temperatures [14].

By proper adjustment of oxygen to carbon and steam to carbon ratios, the partial combustion in the thermal zone (Eq. (5)) supplies the heat for the subsequent endothermic steam reforming (Eq. (1)) and shift (Eq. (4)) 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 [23].

The *non-catalytic partial oxidation* [24] 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 downstream of the partial oxidation reactor. The thermal processes typically result in a product gas with $H_2:CO = 1.7\text{--}1.8$.

Catalytic partial oxidation has been subject to intensified research efforts in recent years. In CPO, the reaction is initiated catalytically (flameless) as opposed to ATR and POX. It has been shown [25–29] that under extremely short residence times, in the order of milliseconds, methane may be partially oxidised forming H_2 and CO as the main products:



For natural gas conversion preferred catalysts are based on Ni and, in particular, Rh [27,30,31] and selectivities higher than 90% may be achieved at conversions beyond 90%. The main side reactions are competitive, further oxidation of the hydrogen/carbon monoxide product. Most studies have been made near atmospheric pressure. Experiments carried out at elevated pressure [32,33] do not indicate dramatic changes in product distribution.

Among the virtues of catalytic partial oxidation is that the reaction, according to Eq. (6), is virtually thermoneutral 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 much faster than the equilibrating steam reforming and shift reactions. Thus, by selecting a proper interval in the region of millisecond residence times [34], it is possible to avoid the slower steam reforming 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 Eqs. (1) and (4). Today, similar product selectivities as for CPO may be obtained by ATR [23,35,36]. Many papers 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 characterised by high catalyst surface temperatures [28,34] which leads to thermal

non-equilibrium between the solid and gaseous phases. Given the process being conducted at high temperatures and extremely short contact times, i.e. 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 [34,37], which eventually may change the entire product spectrum. As addressed in several papers [29,34,38] careful examination of factors such as gas mixing and flow patterns, radiation, reactor and catalyst geometry, etc. are of utmost importance to further uncover the fundamentals of catalytic partial oxidation.

For gasoline fuel processing for automotive applications, small air blown reformers are the preferred choice and CPO reformer prototypes have been developed [39].

Also, *methanol* can be converted as proposed by the so-called HotSpotTM fuel processor concept [40–42]. The first step in this process is believed to be total oxidation of part of the methanol, supplying the heat for subsequent steam reforming. Thus, in the current terminology, we are dealing here with *flameless* 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 catalysing 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 [43].

4. Carbon monoxide clean-up

Whereas high temperature fuel cells (MCFC and SOFC) are capable of converting methane, CO and alcohols, etc. in the anode chamber by internal reforming, the PAFC and the PEM cells do not tolerate excessive amounts of CO as indicated in Table 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. 5. The fuel processor system consists of a hydrodesulphurisation unit, a heat exchange reformer (to minimise 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

Table 1
Fuel cell characteristics

	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	700–1000	No limit	H ₂ , CH ₄ , CO, MeOH

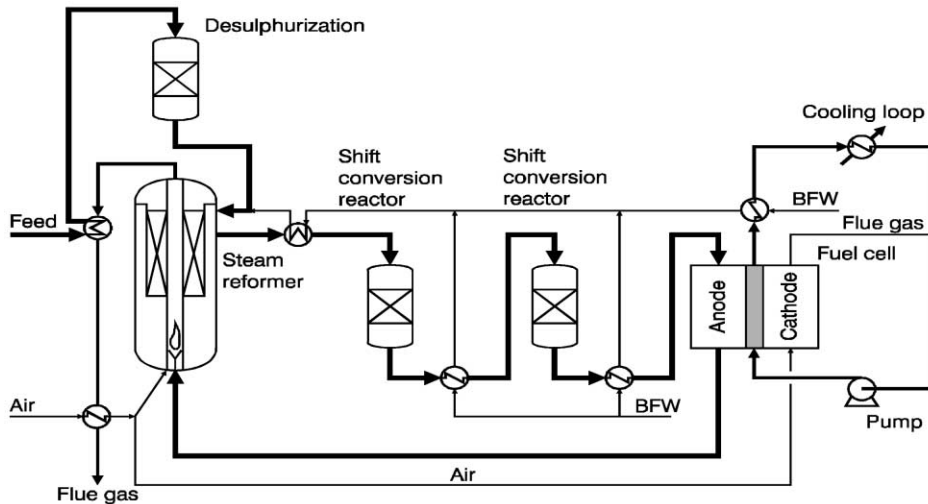


Fig. 5. Schematic diagram of FPS for phosphoric acid fuel cell.

required, which makes hydrocarbon powered fuel processors for PEMFC's so complicated relative to the 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 [44–47]. Alternatives include CO-selective methanation [40,48] or the use of hydrogen-selective Pd-alloy membranes [49–51]. Fig. 6 shows a principal flow diagram of fuel processing system for automotive use based on methanol steam reforming.

One inherent problem to the PEMFC's 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 [2]. 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/or providing an effective methanol barrier. Acid-doped poly-benzimidazole membranes appear to possess the potential of accomplishing either or both of these objectives [53,54]. Another option might involve the use of dimethyl ether instead of methanol.

5. The fuel choice

The PEMFC is the preferred solution for automotive application. However, while there is little doubt about hydrocarbons—natural gas, LPG or liquids—being the preferred fuels for *stationary* plants, there is considerable more ambiguity as to what is currently being the fuel of choice for *automotive* on-board hydrogen manufacture. The conversion of methanol is less complex than gasoline reforming and, moreover, more efficient on-board the vehicle.

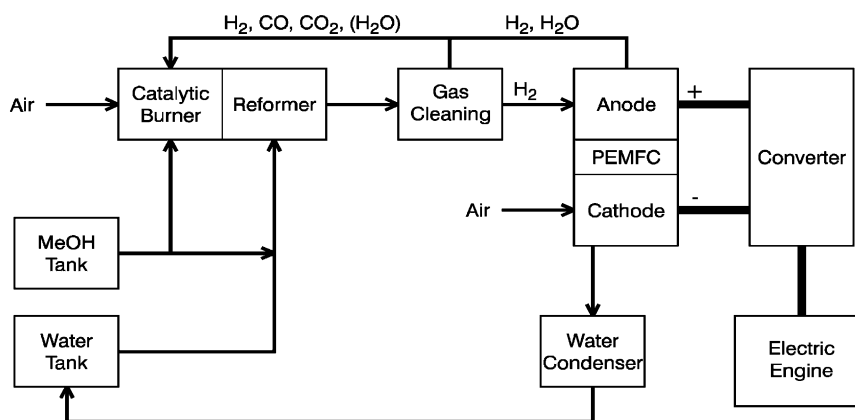


Fig. 6. Principal flow diagram of methanol-powered FPS for automotive application [52].

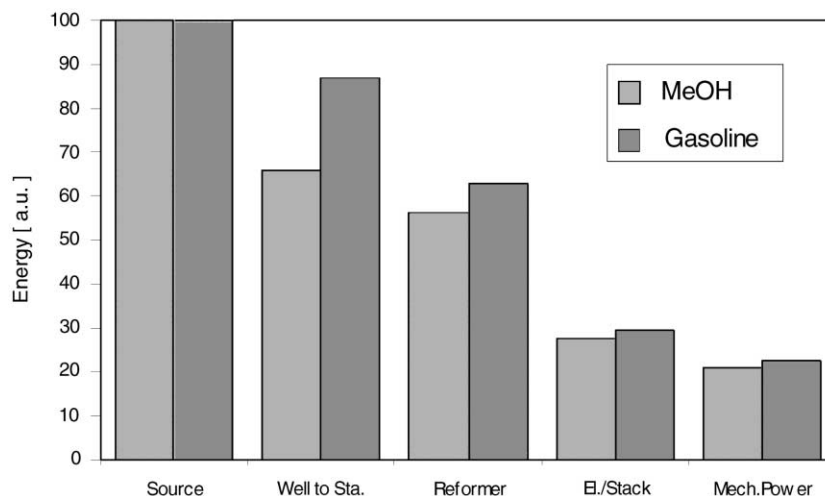


Fig. 7. Well-to-wheel efficiencies for methanol (manufactured from natural gas) and “gasoline” (no penalty applied for polishing “gasoline” to fuel processing grade) [55].

Table 2
Comparison of specific passenger car emissions (mg/km)

	CO	NO _x	Organic gases
Euro 2005 (gasoline)	1000	80	100
Euro 2005 (diesel)	500	250	50
Calif. ULEV	1312	43	34
Calif. SULEV	625	12	6
PEMFC (MeOH)	0.3	<0.01	0.9

However, as methanol manufacture, e.g. from natural gas is more energy consuming the two technologies come out fairly equal [55] when looked at on a well-to-wheel basis (Fig. 7).

With respect to carbon dioxide emissions, the situation is, by nature, very similar. The primary advantages of vehicles based on PEMFCs, whether being powered by methanol or gasoline, consist in the extremely low local NO_x, CO, organics and particulate emissions. Table 2 compares data obtained in a study [14] of a compact methanol reformer with future emission standards. Even when emissions associated with the well-to-station step are included, these are still below SULEV standards.

Obviously, such “near-zero” local emissions will become “true-zero” if direct hydrogen vehicles become available on a commercial scale. On-board storage of hydrogen would make drive trains far less complicated. However, direct hydrogen is not viable at present. Apart from special applications, it will require a breakthrough in materials development [56] as well as establishment of a hydrogen infrastructure.

6. Conclusions

Catalysis offers a variety of options for the conversion of hydrocarbons and alcohols into hydrogen for fuel cells.

Natural gas, whenever available, is the obvious choice for large scale hydrogen manufacture. This will also be true for smaller scale stationary units, e.g. for future on-site hydrogen manufacture at gas stations and for an emerging market for decentralised combined heat and power generation in residential areas, companies and institutions. In remote areas or in other locations where a natural gas infrastructure is not established, alternative fuels such as propane/LPG and higher, liquid hydrocarbons represent competitive alternatives, thus emphasising the aspect of fuel flexibility.

For automotive purposes, pure hydrogen is the preferred fuel due to simplicity in design, low cost and high efficiency. However, on a medium term time horizon, it is difficult to envisage hydrogen penetrating the market beyond centrally fuelled fleets. In the meantime, fuel processor development, integration with the fuel cell stack and auxiliaries remains a difficult technical challenge. Furthermore, as to fuel choice and specifications, there still appears to be a profound lack of consensus among world class organisations for what may be a transitional solution bridging the gap to direct hydrogen. This is as other, in defining the basis for a rational fuel and system selection. These uncertainties must be resolved in order for fuel cell power trains to constitute a serious alternative to conventional—and currently improving—engine technology.

The call for clean energy is the main driver in the development of fuel processing technology for both stationary and mobile applications. 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 component development, system design and integration, cost reduction and not least successful field test programmes is required for fuel processors to eventually gain general customer acceptance.

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