

ADVANCES IN HYDROCARBON TECHNOLOGIES

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ABSTRACT

This paper provides an overview about today's and future trends in using hydrocarbon technologies and related hydrogen technologies. The content of this presentation is devoted to hydrogen/bio-hydrogen production – with focus on-board fuel reforming and vehicular hydrogen storage. Hydrogen storage is widely recognized as a major technological barrier to the successful implementation of fuel cells for transportation and portable applications. The paper shows that GTL technology is undergoing a renewal of its innovative process. For more detailed information the interested reader is invited to consult the dedicated papers cited throughout the overview.

Key words: Hydrogen, on board fuel reforming, fuel cells, GTL, hydrogen storage

1. INTRODUCTION

The hydrogen and catalysts became one of the most powerful tools in the natural gas and petroleum sectors in the last century. Catalysis with focus on hydrocarbon conversion and formation – covers nowadays a broad range of process related to the upgrading of crude oil and natural gas. Although it is often mentioned that field of GTL-technologies (F-T synthesis) is mature and there is not much compasses for researcher, the increasing demand of natural gas has become gas conversion technologies a challenging task for refiners as well as for researchers. There, the importance of the catalysts and hydrogen is not only focused on its development but also tremendous work has to be done for catalysts formulation and hydrogen production and storage. The intention of this contribution is to review the basic aspects dealing with actual and future trends towards hydrocarbon technologies for:

- hydrogen / biohydrogen production,
- on-board fuel reforming,
- hydrogen storage,
- fuel cells,
- natural gas conversion/ gas conversion (GTL).

Thus, specific processes or a sequence of them can be selected or approved. The major objective is to cover the following elements of enormous interest in today's hydrocarbon technologies:

1. to stress the recent advances in hydrogen technologies and GTL technologies based on the literature;
2. address the limitation when using hydrogen technologies.

By hydrogen production I mean extracting and isolating hydrogen in the form of independent molecules, at the level of purity required for a given application. The processes naturally depend on the starting point, and the currently dominant scheme of production from methane only makes sense if the energy is initially contained in methane or can easily be transformed to methane. Thus in the case of fossil fuels, the transformation of natural gas into hydrogen is relatively easy and that of oils a little bit more elaborate, while transformation of coal requires an initial step of high-temperature gasification.

To reduce dependence on imported oil, a number of strategies are under consideration including the increased use of gasoline hybrid vehicles in the near term. For the long term, however, petroleum substitution is required and that necessitates the development of alternative energy carriers. Hydrogen has the potential to be an attractive alternative energy carrier, particularly for the transportation sector [1-10]. It can be clean, efficient and derived from diverse domestic resources, such as renewables (biomass, hydro, wind, solar geothermal) as well as fossil fuels and nuclear energy. In the case of fossil fuels, natural gas is likely to be used for the distributed production of hydrogen in the near term, before the infrastructure required for centralized hydrogen production and hydrogen delivery is developed. In the long term, centralized production, using coal with carbon sequestration or nuclear energy (thought high temperature water splitting or thermochemical cycles), could be employed to produce hydrogen using a number of delivery options. Hydrogen can then be employed in high-efficiency power generation systems, including internal combustion engines or fuel cells for both vehicular transportation and distributed electricity generation.

There are three primary barriers that must be overcome to enable industry commercialization of hydrogen fuel cell vehicles: (1) on-board hydrogen storage systems are needed that allow a vehicle driving range of greater than 500 km while meeting vehicle packaging, cost and performance requirements; (2) fuel cell system cost must be lowered to \$30 per kilowatt by 2015 while meeting performance and durability requirements; (3) the cost of safe and efficient hydrogen production and delivery must be lowered to be competitive with gasoline (a target of \$2.00 to \$3.00 per gallon gasoline equivalent, delivered, untaxed, by 2015) independent of production pathway and without adverse environmental impact.

2. HYDROGEN TECHNOLOGIES

The pollution from motor cars is, particularly in city areas, becoming increasingly unacceptable to people living in, visiting or working in the cities of the world. Demands for zero-emission have been voiced, and the automobile industry is facing louder and louder criticism for not addressing the problem. The simplest solution to reducing emissions is about 36% implying a fuel-to-wheel efficiency to make the vehicle more efficient. For fuel cell cars, the hydrogen fuel-to-wheel efficiency is about 36 %, implying a fuel-to-wheel efficiency of around 25 % for the chain starting from hydrogen production from natural gas, over proton exchange membrane (PEM) fuel cells and electric motors to wheels, all for a standard mixed driving cycle.

On a weight basis, hydrogen has nearly three times the energy content of gasoline (120 MJ/kg for hydrogen versus 44 MJ/kg for gasoline). However, on a volume basis the situation is reversed and hydrogen has only about a quarter of the energy content of gasoline (8 MJ/l for liquid hydrogen versus 32 MJ/l for gasoline). On-board storage in the range of 5-13 kg [1 kg hydrogen = gallon of gasoline energy equivalent, or gge] of hydrogen is required to encompass the full platform of light-duty automotive fuel cell vehicles. Engine power plants with efficiencies less than PEM fuel cells would require a larger payload of hydrogen to achieve a comparable driving range.

The Freedom CAR partnership was expanded in 2003 to include major energy companies (BP America, Chevron Corporation, ConocoPhillips, Exxon Mobil Corporation and Shell Hydrogen (U.S)) and is now known as the FreedomCAR and Fuel Partnership [12]. The performance targets developed are system and application driven, based on achieving similar performance and cost levels as current gasoline fuel storage systems for light-duty vehicles. The storage system includes the tank, valves, regulators, piping, mounting brackets, insulation, added cooling capacity, thermal management and any other balance-of-plant components in addition to the first charge of hydrogen and any storage media such as solid adsorbent or liquid used to store the hydrogen.

Currently, research priorities are on achieving the volumetric and gravimetric capacity targets in Table 1, while also paying attention to energy and temperature requirements for hydrogen release as well as kinetics of hydrogen charging and discharging. It is important to note that to achieve system-level of 2 kWh/kg (6 wt. % hydrogen) and 1,5 kWh/l (0,045 kg hydrogen/l) in 2010, the gravimetric and volumetric capacities of the material/media alone must clearly be higher than the system-level targets. To restate, development of a hydrogen storage material/media (e.g. metal hydride, carbon nanostructured material) that meets 6 wt. % or 45 g/l is not sufficient to meet the system targets. Depending on the material and on the system design, material capacities may need to be a factor of 1.2-2 times higher than capacity targets. Given the wide number of options for specific materials and system designs, only system level targets are specified.

Table 1 U.S. DOE hydrogen storage system performance targets [13, 14]

Storage parameter	Units	2007	2010	2015
U.S. DOE technical targets for on-board hydrogen storage systems				
System gravimetric capacity: usable, specific-energy from H ₂ (net useful energy/max system mass)	kWh/kg (kg H ₂ /kg system)	1.5 (0.045)	2 (0.06)	2 (0.06)
System volumetric capacity: usable energy density from H ₂ (net useful energy /max system volume)	kWh/l (kg H ₂ /l system)	1.2. (0.036)	1.5 (0.045)	2.7. (0.081)
Storage system cost (and fuel cost)	\$/ kWh net (\$/kg H ₂)	6 (200)	4 (133)	2 (67)
	\$/ gge at pump	-	2-3	2-3

2.1. Production of hydrogen

Hydrogen is the most abundant element in the universe. Hydrogen is produced on a large scale mainly by steam reforming, partial oxidation, coal gasification and electrolysis. Its current worldwide production is around 5×10^{11} N m³ per year [15]. It is primarily used as feedstock in the chemical industry, for instance, in the manufacture of ammonia and methanol, and in refinery reprocessing and conversion processes. However, with the environmental regulations becoming more stringent, there is now growing interest in the use of hydrogen as an alternative fuel. Its combustion does not result in any emission other than water vapor (although under certain air hydrogen ratios, NO_x can also be produced) and hence it is the least polluting fuel that could be used in an internal combustion engine. It can also be used in a fuel cell for the production of electricity for stationary application and mobile electric vehicle operations.

Different technologies are suited for application a scale determined both by the type of application and by the characteristic of the technology itself. If the cost of given technology exhibits an economy of scale, it is preferred to use that technology in a centralised fashion. If the technology is cheapest in smaller units (for fixed overall production), the situation is of course opposite, but this is rare, and a more common situation is that the cost is insensitive to scale of production. This allows the kind of applications aimed for to determine the scale employed. However, there may also be specific scale requirements set by the type of usage. For example, technology for passenger cars must have a size and weight suitable for typical motor vehicles. Here one finds little flexibility, due to existing infrastructure such as roads, size of garages and parking spaces, etc. Generally, if a new technology requires changes in infrastructure, both the cost and the inconvenience associated with changing to it must be taken into consideration.

The identification of hydrogen production by reverse operation of low temperature fuel cells as a technology not suffering by small scale of operation explains the interest in developing this technology for dispersed (decentralised) employment.

2.1.1. Dry reforming

As an alternative to conventional steam reforming, methane could be reformed in steam of carbon dioxide rather than steam of water,



Advantages of this reaction could be the disposal of CO₂ and the possibility of operating at fairly low temperatures, for example in combination with conventional steam reforming [16,17].

Syn-gas production technology plays a central role in petrochemistry. Methane reforming reaction with carbon dioxide (dry reforming) was first studied by Fischer and Tropsch (1928) over a number of base metal catalysts. Calculations indicate that the reaction is thermodynamically favored above 913 K. It is more endothermic than steam reforming. Carbon deposition is predicted, and carbon formation over metal catalysts during the carbon dioxide reforming reaction has been observed. An industrial process, the CALCOR PROCESS, has been developed, which uses methane and a large excess of CO₂ to make CO rich synthesis, a nickel based catalyst is indicated. The SPARG process is essentially the same a conventional steam methane reformer for the addition of sulfur to the catalyst [16].

Recently renewed attention in both academic and industrial research has been focused on the CO₂ – reforming reaction. The main problem of the CO₂ – reforming reaction is that CO₂ is at the

bottom of a potential energy well and its use in the dry reforming reaction requires a very large energy input. Two themes in particular are under investigation:

- (i) the development of new catalysts that are inactive towards the carbon formation reactions; In the works [35-37] employed the La_2NiO_4 – zeolite coupled membrane catalyst to combat the problem of catalyst deactivation due to coking in the CO_2 reforming of methane over nickel catalysts;
- (ii) the possibility of producing syn – gas with CO_2 reforming reactions performed in rapidly separating of the products CO and H_2 conditions from the reactants.

In recent years, the CH_4/CO_2 reforming reaction leading to the formation of syngas with low H_2/CO ratios has received renewed attention in the context of natural gas upgrading. Although noble metals have been found to be active and selective catalysts, their high costs limit their application. Other metals, such as cobalt and nickel, have been reported to be the alternatives [18] but they are easily deactivated due to metal volatilization and carbon deposition. The use of alkaline earth compounds, such as calcium and magnesium oxides, to modify nickel has been found to be satisfactory [19]. A series of complex oxide catalysts, such as LaNiO_3 , $\text{La}_{0.8}\text{Ca}(\text{or Sr})_{0.2}\text{NiO}_3$, $\text{LaNi}_{1-x}\text{CO}_x\text{O}_3$ (where $x = 0.2 - 1$) [20] with perovskite structure have been found to be resistant to coking. Bolt et al. [21] have reported that the catalyst with discontinuous interfacial NiAl_2O_4 layer showed less sintering of nickel. Recently, Gao et al. have reported that the La_2NiO_4 mixed oxide catalyst was more stable than LaNiO_3 at high temperatures ($500\text{--}850^\circ\text{C}$) and exhibited better activity in methane dissociation reaction [22]. Due to the interaction between the rare-earth and nickel entities, both nickel stability and catalyst life time are improved by the addition of rare earth to the nickel catalyst [23].

The coupling of catalysis with separation through membranes is becoming feasible for practical application. The technology is rather new and novel. According to Le Chatelier-Braun's law, if an external force leads to the separation of a specified component from a system at equilibrium, the system adjusts so as to minimize the effect of the applied force and thereby produces more of the removed component. Hence by combining reaction and membrane separation in a membrane reactor, one can possibly enhance product selectivity and achieve higher conversion at lower temperatures. There are other advantages in the employment of membrane separation in a reactor, such as simplified downstream separation and recovery savings on energy consumption, and life-prolonging of reactor materials and catalysts.

It has been pointed out that the steam reforming of methane, up to 100% conversion can be accomplished in palladium-membrane reactors at temperatures as low as 500°C , while carbon deposition can be avoided entirely [24]. We have not come across any application of membrane reactors in the CO_2 reforming of methane in the literature. To separate molecules other than H_2 , palladium and its alloys are not suitable. Currently, composite membranes, consisting of thin layers of zeolite film on a porous supporting structure, are under development to cater for such need. Molecules are separated on the basis of molecular size through these porous membranes. Both permselectivity and mechanical durability are essential factors and the development of the sol-gel procedures for the deposition of thin microporous ($< 2\text{ nm}$) and mesoporous ($2\text{ to }50\text{ nm}$) layers on macroporous ($> 50\text{ nm}$) supports has enabled the engineering of porous membranes suitable for industrial applications [25]. Thin microporous layers have been obtained by depositing polymeric silica sols on- γ -alumina supports [26]. Yan et al. [27] have prepared ZSM-5 membranes on porous alumina with good permselectivities (permeability at 185°C : 10.1 , 5.9 , and $0.19 \times 10^{-8}\text{ mol m}^{-2}\text{ s}^{-1}\text{ Pa}^{-1}$ for hydrogen, n-butane and isobutane, respectively) by in situ hydrothermal synthesis. Similarly, a continuous silicalite-1 membrane has been prepared on the inner wall of a porous alumina tube by Noble and Falconer [28]. It goes without saying that a continuous zeolite layer without pinholes or cracks is crucial for reaching high permselectivities. Matsukata et al. [29] have prepared a crackless zeolite layer on porous alumina. The thickness of the zeolite layers in membranes thus prepared is in the range of $40\text{--}500\text{ }\mu\text{m}$. Further study of the mechanism of thin layer formation is likely to lead to thinner and better permeable membranes.

The use of membranes as intrinsically active catalysts, or a catalyst support by depositing a catalytically active component on it has not been very successful in a reactor due to low catalyst loading per unit volume of reactor. Recently, collaboration has been established between Gao and Au in the application of the membrane techniques in the reforming of methane by CO_2 . Work has been done to adopt the La_2NiO_4 – Zeolite coupled membrane (thickness $\sim 0.1\text{ }\mu\text{m}$) being developed by Gao and coworkers [30] in a microreactor for the reforming reaction. The relative permeance of the membrane is $\text{CH}_4 : \text{CO}_2 : \text{CO} : \text{H}_2 = 1 : 6 : 30 : 70$. The novel part of their approach is to combine catalysis with membrane separation: both La_2NiO_4 and zeolite membranes are deposited on the inner and outer walls a porous alumina tube and catalytic reaction and product separation occur simultaneously in the reactor.

As far as the mechanism of the CH₄/CO₂ reforming reaction is concerned, there are quite a number of proposed schemes: Solomosi scheme [31], Rostrub-Nielsen scheme [32], Goula scheme [33] and Brandford scheme [34]. According to the proposed schemes, the dissociative adsorption of CH₄ is considered to be the initial and rate determining step and CO₂ activation can be promoted by CH_x and H species on the surface. However, the CH₄/CO₂ results of Au et al. over Ni/SiO₂ [35] and Rh/SiO₂ [36,37] catalysts indicate that the reaction pathways for the formation of CO in the CO₂ reforming of methane can be represented as two different pathways for the formation of CO, i., e., the oxidation of CH_x species and the dissociation of CO₂; and the latter takes place prior to the former in the process of carbon dioxide reforming of methane over the SiO₂-supported nickel and rhodium catalysts. Similar conclusions have been drawn in the studies of CH₄/CO₂ reforming over Ni/SiO₂ by Kroll et al. [38].

Lee et al. [39] have studied of tri-reforming of methane to synthesize syngas with desirable H₂/CO ratios by simultaneous oxy-CO₂-steam reforming of methane. Results of tri-reforming of CH₄ by three catalysts (Ni/Ce – ZrO₂, Ni/ZrO₂ and Haldor Topsoe R-67-7H) are showed that the coke on the reactor wall and the surface of catalyst were reduced dramatically. It was found that the weak acidic sites, basic site and redox ability of Ce-ZrO₂ play an important role in tri-reforming of methane conversion.

The mechanism and the rate-determining steps of CO₂ reforming of methane were investigated over the typical Ni/α-Al₂O₃ catalyst in a wide temperature range of 550-750°C using steady-state and transient kinetic methods [40]. The methane dissociation reached equilibrium with Ni-H species above 650°C. The surface oxygen species originating from CO₂ became removable and reacted with CH_x species above 575°C. The reaction of CH_x with CO₂ was slower than that of CH₄ dissociation above 650°C, leading to the durative carbon deposition on the catalyst. The formation of hydrogen is a rapid or equilibrium step in the reforming reaction.

3. VEHICLE ON-BOARD FUEL REFORMING

The question of suitability for decentralised hydrogen production becomes more critical in the case of vehicle-integrated production systems, which must be economic at small scale.

The basis for on-board production of hydrogen in principle could be fuels such as fossil fuels or biofuels, notably gasoline, as well as methanol, ethanol and similar intermediate stages between fuels produced from natural organic or from more artificial industrial primary materials. Of these, only methanol can be obtained by a reforming process similar to that of natural gas, at moderate temperatures of 200-300°C. Reforming of other hydrocarbons usually requires temperatures above 800°C. Methanol is also interesting because of its similarity to gasoline in terms of fuelling infrastructure. The methanol energy content of 21 MJ kg⁻¹ or 17 GJ m⁻³ is lower than that of gasoline, but because fuel cell cars are more efficient than gasoline cars, the fuel tank size will be similar.

Fuel cells (FCs) are electrochemical devices that convert the chemical energy of a fuel and an oxidant directly into electricity and heat on a continuous basis. A fuel cell consists of an electrolyte and two electrodes. A fuel such as hydrogen is continuously oxidized at the negative anode while an oxidant such as oxygen is continuously reduced at the positive cathode. The electrochemical reactions take place at the electrodes to produce a direct electric current. FCs use hydrogen as a fuel which results in the formation of water vapor only and thus they provide clean energy. FCs offer high conversion efficiency and hence are promising. The current status of fuel technology for mobile and stationary application has recently been discussed [41].

Among the various types of fuel cells, the proton exchange membrane fuel cells (PEMFCs), the solid oxide fuel cells (SOFCs) and the molten carbonate fuel cells (MCFCs) have attracted considerable interest. SOFCs and MCFCs operate at high temperatures (around 973 K) and are used for stationary power generation. PEMFCs are primarily used for automotive applications. PEMFCs can be characterized into two categories: reformed and direct systems. Reformed systems required the use of an external reformer to reform fuel (methane, methanol, ethanol, gasoline, etc.) into hydrogen for use in the fuel cell. In direct systems the fuel is oxidized at the surface of the electrode without treatment. They have a low operating temperature (353 K), high current density and low CO tolerance (10 ppm). They use hydrogen as the fuel and this can be supplied as pure hydrogen. Thus, fuel cell vehicles can be equipped with pressurized hydrogen tanks, thereby ensuring a continuous supply of fuel. Alternately, hydrogen can be stored as a liquid in cryogenic tanks at 20 K. These ways of storing hydrogen are however inconvenient. Moreover, the use of compressed hydrogen involves safety aspects. Also, there is no proper infrastructure for hydrogen transport and distribution. Therefore, in practice, other hydrogen containing fuels are used.

A number of hydrogen generation routes have been explored [42]. Methanol, ethanol, ammonia, naphtha, diesel fuel and natural gas are some possible sources of hydrogen for fuel cells. In addition,

petroleum distillates, LPG, oil, gasified coal and even gas from landfills and wastewater treatment plants can also be processed to supply hydrogen^[43]. For stationary applications, natural gas is the fuel of choice due to its availability and ease in distribution. For automotive application naphtha and diesel fuel are the most convenient fuels since they can be easily transported. However, PEMFCs are very sensitive to impurities in fuel and have a sulphur specification less than 1 ppm^[44]. Gasoline has a 30 ppm sulphur standard in USA while hydrogen from coal gasification may contain 100-200 ppm sulphur. Catalytic cracking of ammonia generates a CO₂-free mixture containing 75% hydrogen. However, ammonia is toxic and poses a problem of generating nitrogen oxides during catalytic combustion of the cell effluent^[45]. Methanol, which is mainly prepared by syn-gas conversion, has a favorable H:C ratio of 4, is largely distributed and is available in abundance. Moreover, it can be transported and reformed more easily than natural gas. However, its main drawback is its high toxicity. Ethanol is more promising since is less toxic. It can also be more easily stored and safely handled. Most importantly, it can be produced in large amounts from biomass such as agricultural wastes and forestry residues and hence is a renewable resource, as against methanol and gasoline. This could prove advantageous in tropical countries with a warm climate where there are large plantations of corn and sugarcane. The bio-ethanol thus produced is free from sulphur, which otherwise may poison the fuel cell catalyst^[46]. The use of biomass as a new feedstock for hydrogen production or energy source has attracted considerable attention in recent years, because it is an environmentally friendly and renewable rich source (the worldwide amount of biomass in 2006: 1.5×10^{11} tones). The most promising option to generate hydrogen from bio-oil is a via steam reforming followed by a water gas shift reaction^[125].

3.1. Steam reforming of naphtha (gasoline)

Generating hydrogen by the steam reforming of hydrocarbons is a well-known technology. Tailoring the process for fuel-cell powered vehicles, however, introduces additional constraints. Here, the purity of hydrogen becomes essential to avoid poisoning the electrodes of the fuel-cell system. This could necessitate a selective membrane separation technology. This can be accomplished using palladium-silver membrane, which can be integrated directly to the reaction system (membrane reactor) or separately employed in later stages. The first choice (membrane reactor), however, offers attractive features regarding energy density of the whole system, which is an important criterion to judge the performance of fuel-cell-powered-vehicles. Compactness is also enhanced because conversion levels in such membrane reactors are increased. A significant amount of research work on membrane reactors is underway^[47,48] and there are also signs of successful technological developments^[49].

The flowsheet for the direct generation of hydrogen using steam reforming of naphtha on-board vehicle, which is suggested here, is shown in Fig. 1. The process can be described as follows: naphtha feedstock is vaporized and passed through a bed of zinc oxide to remove sulfur contamination, which is a potential poison for reforming catalyst and fuel-cell electrodes. Naphtha is then passed through the reformer, where it is catalytically reacted with steam to produce a mixture of steam, H₂, CO, CO₂, and CH₄. Heat is supplied to the reformer by the combustion of either a portion of the incoming naphtha or a portion of the generated hydrogen. The gas mixture is then cooled down by the incoming process water and directed to the low temperature (LT) shift reactor, where CO is converted catalytically to CO₂. The remaining traces of CO are further converted to CH₄ in the methanator and the gas mixture at this point contains about 53% H₂, 17% CO₂, 28% H₂O, and some traces of CH₄. Both the shift and methanation reactions are exothermic. Before directing the product gas mixture to the selective membrane, it is compressed to 0.3 MPa. The pure hydrogen stream is then sent to the anode of fuel cell and the unused H₂ from the fuel cell is combusted to provide the required heat in the reformer. This unconverted H₂ is assumed to be 30% of the amount entering the fuel cell (corresponding to 70% conversion in the fuel cell). The other stream leaving the membrane separator, which has less H₂, undergoes a process to recover water. This water will be combined with the water recovered from the fuel cell and circulated back to the reformer after being vaporized by the reformer products and then heated to the reformer temperature^[50].

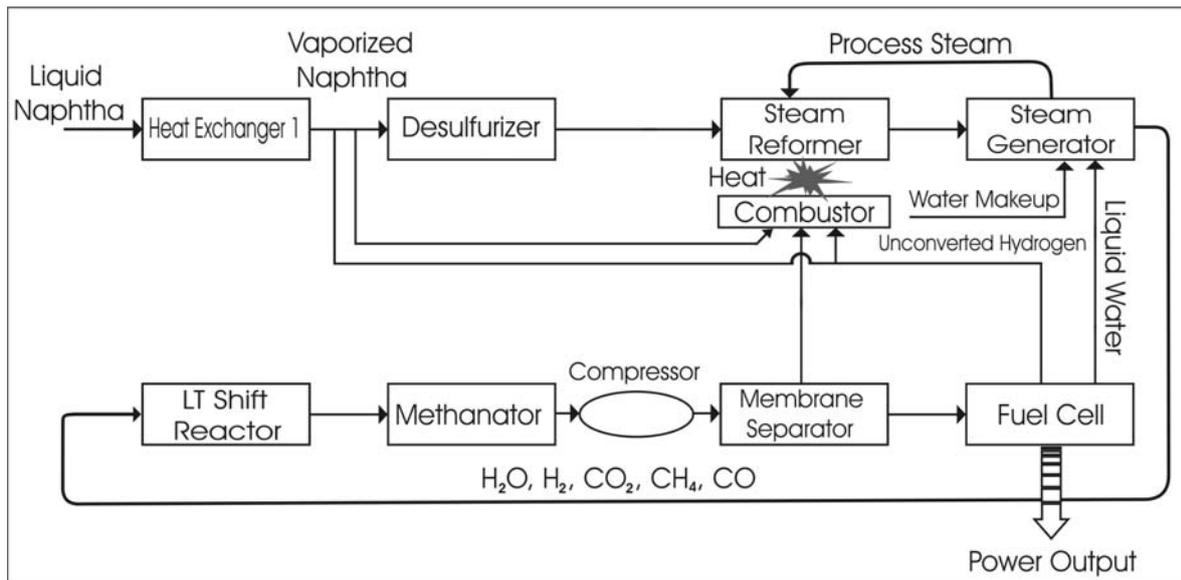


Fig.1. Schematic diagram of the flowsheet for the production of hydrogen by steam reforming of naphtha.^[50]

For the peak load of 50 kW, it is found that 14 l/h naphtha is needed, which means that a 70 l fuel tank in the vehicle is sufficient for 5 h drive. The amount of water needed is not critical factor, since it is generated in the fuel cell and quantities of watermakeup can be kept at the minimum level. In the desulfurization step, it is found that about 1.6 l of a bed of ZnO is capable of handling a stream of naphtha with 1500 ppm of sulfur for 45 h of continuous operation before regeneration or replacement based on operation at 1 MPa. Operation at lower pressure level will increase the desulfurization catalyst requirements, maybe to a prohibitive level. Over the reformer LHSV range of 1–4 h⁻¹, the amount of the supported nickel catalyst varies from 14 to 4 l, respectively. For the LT shift reactor the amount of catalyst required ranges from 4 to 60 l on going from 300 to 4000 h⁻¹ typical GHSV. The catalyst here is CuO-ZnO supported on Al₂O₃. The last methanation step to remove traces of poisonous CO requires about 3.5 l nickel supported by various oxide. The selective separate hydrogen, it is suggested to use a palladium–silver membrane, which is reported to give ultra–pure hydrogen^[50].

3.2. On – board diesel fuel processing

The fuel gas for the SOFC stack is generated by catalytic partial oxidation of diesel fuel, using a reformer without additional water supply. A time near market entry is desired to use synergetic effects in fuel cell improvement and system integration as well, and commercialization of fuel cells is expected to proceed first through SOFC systems for stationary and auxiliary power units (APU) application, initially using conventional fuels^[51].

Webasto's APU consists of three major sub-units^[52]. First, the fuel processing unit has to generate a homogeneous fuel/air mixture for the reforming catalyst. Then, this catalyst converts the diesel fuel with oxygen into a hydrogen and carbon monoxide rich fuel gas which is fed to the SOFC stack. The reformer as well as the subsequent SOFC operate at the same temperature level of approximately 800°C. Due to the high temperature level of the fuel cell stack, the carbon monoxide containing gas can be fed directly to the SOFC without any shifting devices between the reformer and the fuel cell. Downstream of the SOFC, the unconverted part of the fuel gas leaving the anode compartment is combusted in an afterburner with an intergrated heat exchanger to use the thermal energy for the pre-heating of the cathode air. Auxiliary components like diesel pumps and air blowers complete the set-up to a stand-alone system. All core components are located in one thermally insulated hotbox and operate near ambient pressure. By this, conventional blowers and pumps can be used, so no expensive mass flow controllers or air-compressors are necessary for operation. Fig. 2 shows a block diagram of the system set-up.

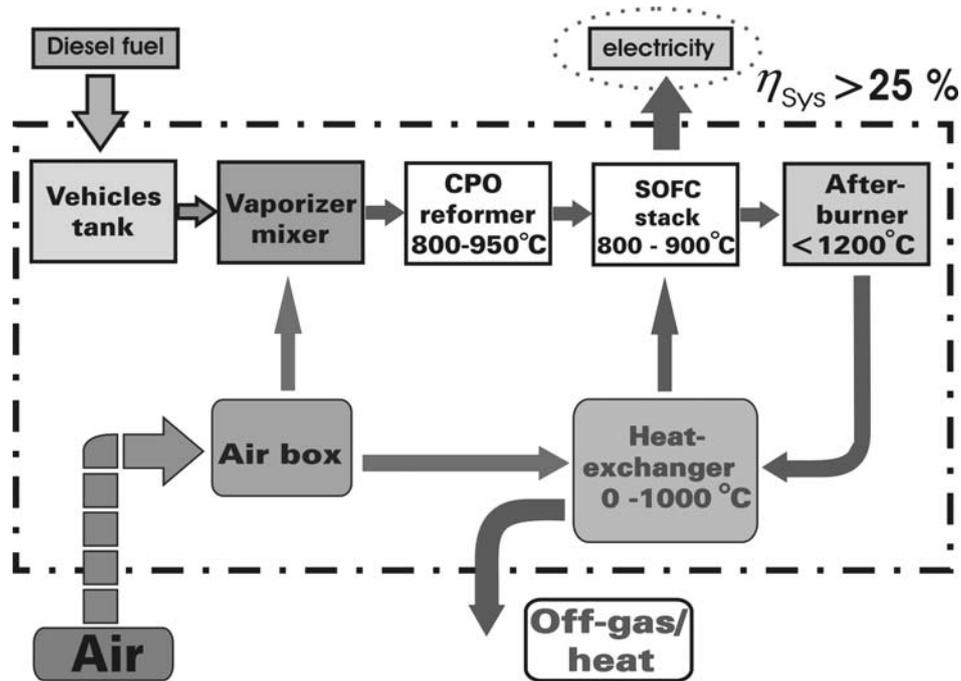
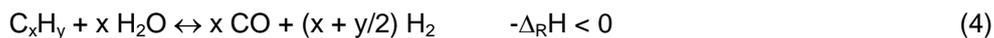


Fig.2 Set-up of Webasto's SOFC-APU system. [52]

In general, different technologies can be used for the generation of a fuel gas for an SOFC from liquid fuels. The pyrolysis of hydrocarbons (Eq.(2)) occurs at high temperatures, and besides hydrogen, solid carbon is formed, that accumulates in the reactor. The catalytic partial oxidation (CPO) with a sub-stoichiometric ratio of oxygen to hydrocarbons is weakly exothermic, and H_2 and CO are the major products (Eq. (3)). For the endothermal steam reforming (SR), water is used for the conversion of the hydrocarbons (Eq. (4)). The autothermal reforming (ATR) combines the CPO and the SR in a way, that a thermoneutral process results [1,2].



The CPO of hydrocarbons is chosen as reformer technology. Though the addition of water has a beneficial influence on the hydrogen content and decreases the catalyst temperatures due to the endothermal steam reforming reactions, the higher system complexity and the need of an additional reactant stream for SR and ATR is counterproductive.

The measurements at different air-numbers λ and molar system steam to carbon ratios S/C were made, to detect the most suitable ones for the CPO of diesel fuel. For this purpose, a reference fuel ($C_{13} - C_{15}$ alkane blend, sulphur content < 1 ppm per weight) was used with a boiling range between 235 and 265°C. Experiments were carried out in a laboratory scale reactor, using a heating coil for water vaporization and a diesel fuel pre-heater. The fuel was heated up to approximately 220°C and mixed with the air/steam flow, having a temperature higher than 350°C. Thus, the fuel is completely vaporized and fed to the catalyst sample [52].

The fuel processor units consist mainly of a metal-felt vaporizer with a ceramic glow plug, radial distributed air inlet holes and downstream located pre-catalyst, made from a catalytic monolith (Cordierit). For the system start, the reformer is operated in burner mode at an air-number λ of approximately 1.3. After the temperature of the stack reaches 500°C, the air-number λ is reduced to values between 0.6 and 0.8 to prevent oxidation of the SOFC anode. The system is heated up further until the desired operation temperature of approximately 850°C is reached. At this time, a stack power of 340 W_e can be delivered at a stack voltage of 22 VDC.

At present, a third generation of a stand-alone APU system is under test and the first results are very promising. At the same time, a further improved system is under construction with an aspired net

power of 1 kW_e and start times less than 1 h. System overall efficiency is expected to be more than 20 %.

3.3. Direct and gradual internal reforming of methane.

SOFCs are promising candidates for generating power while preserving the environment. Nowadays most SOFC developers use fuel containing a significant proportion of hydrogen. From this point of view, the most interesting fuel for SOFC systems remains methane (natural gas, biogas). Nevertheless, nowadays natural gas is directly available whereas hydrogen must be produced and thus direct internal reforming (DIR) is a very hopeful method. Indeed, gradual internal reforming (GIR)^[53] or DIR within SOFC anode^[54] allow the conversion of methane into hydrogen without using a separate reformer. Such a concept is convenient for high-temperature fuel cells in which the steam reforming reaction can be sustained with catalysts. The reforming reaction at the anode and the water gas shift reaction are carried out over a supported catalyst such as nickel. These reactions provide the system with the dihydrogen required by electrochemical reaction. SOFC internal reforming is thus designed by closely coupling the catalytic reforming reaction and the electrochemical oxidation reaction within the anode of the cell.

The anode material is a nickel and yttrium stabilized zirconia cermet (Ni - YSZ). DIR and also GIR involves adding the reforming function to the SOFC anode (Fig. 3)^[53,56] a direct production of hydrogen from methane being possible due to high temperature in the fuel cell.

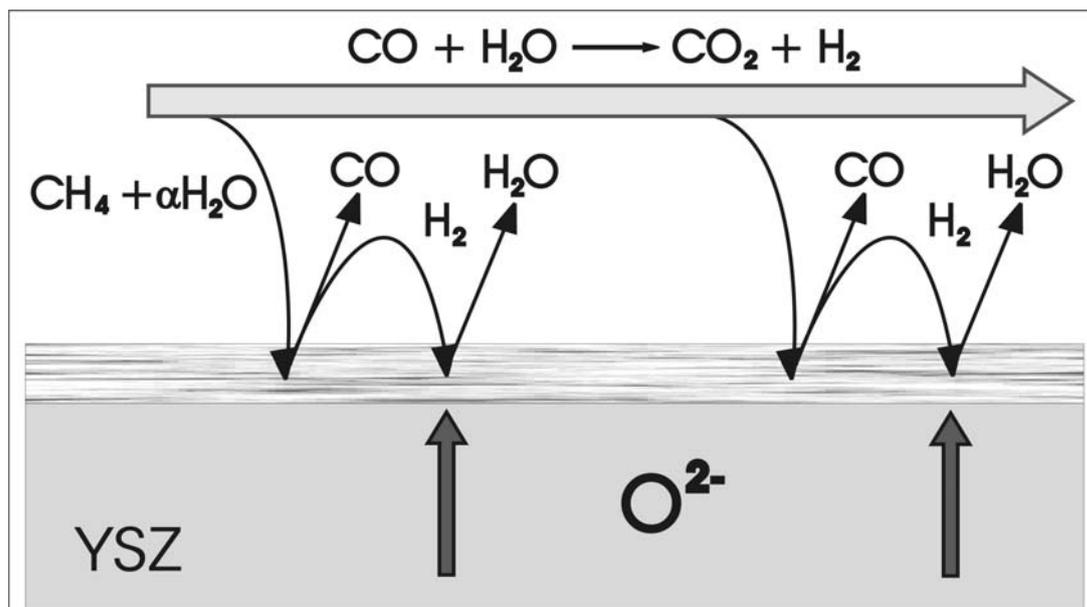
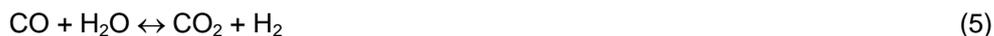


Fig.3 DIR or GIR of methane by steam.

[54]

Methane can thus be converted into H₂ and CO through the steam reforming reaction (Eq. 4) and the water gas shift (Eq. 5) while hydrogen is electrochemically oxidized within the anode.



However, unlike DIR, where the steam is fed in large amounts, the GIR process requires a very small quantity of steam since it uses the steam generated by the electrochemical reaction in the steam reforming reaction. Moreover, in DIR, because of the great difference between the reaction rates of the endothermic methane reforming reaction and the exothermic electrochemical hydrogen oxidation, cooling effects arise resulting in a temperature drop at the cell inlet^[57]. With operation in GIR, a delocalization of the steam reforming reaction along the cell may occur and, consequently, it would imply homogenization of the temperature gradient. However, at these working temperatures, Boudouard and cracking reaction can also be favored. Carbon formation is consequently possible, with the risk of carbon deposits polluting the anode. A carbon deposit on the anode surface can

obviously block the fuel supply and the transfer of the oxide ions, leading to a decrease in the power efficiency of the cell [56].

3.4. Methanol-to-hydrogen production.

Compressed and liquefied hydrogen are limited for use in automobiles by low energy density and safety precautions for containers and by the requirement of creating a new infrastructure for fuelling, so there is a strong interest in converting conventional fuels to hydrogen on-board. It is primarily to avoid having to make large changes to the current gasoline and diesel fuel filling stations that schemes based on methanol as the fuel distributed to the vehicle fuel tank have been explored. The energy density of methanol given above corresponds to $4.4 \text{ kWh litre}^{-1}$, which is roughly half that of gasoline. Hydrogen is then formed on-board by a methanol reformer before being fed to the fuel cell to produce the electric power for an electric motor. The set-up is illustrated in Fig. 4. Prototype vehicles with this set-up have been tested in recent years [58-60].

Methanol, CH_3OH , may eventually be used directly in a fuel cell without the extra step of reforming to H_2 . Such fuel cells are similar to proton exchange membrane and are called direct methanol fuel cells (DMFCs). Over the last 40 years, there has been extensive research on DMFCs and direct ethanol fuel cells (DEFCs). A theoretical investigation into the comparison of direct methanol and direct ethanol fuel cells shows that DEFCs have higher theoretical energy densities compared to DMFCs. The energy density of DEFCs is 8.01 kW/kg , compared to 6.09 kW/kg for a DMFCs. The major problem associated with using ethanol as a fuel is the low reaction kinetics of ethanol oxidation versus methanol oxidation [126].

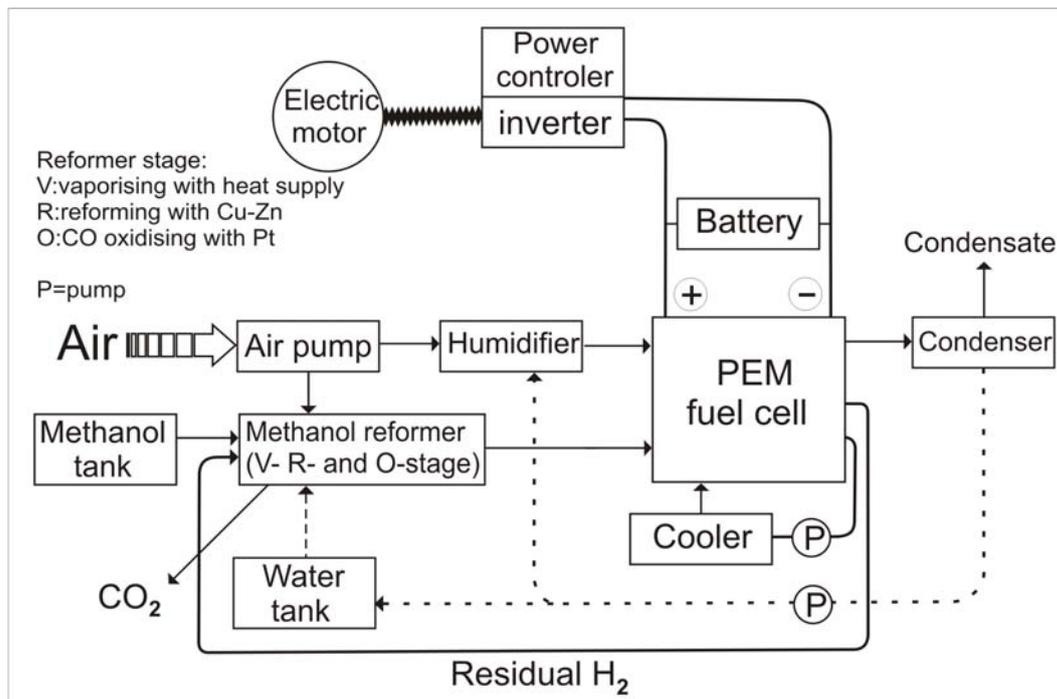
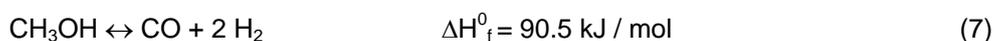
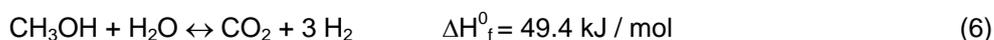


Fig.4 Layout of methanol-to-hydrogen vehicle power system with fuel cell and electric motor. [58]

As methanol may serve as a substitute for hydrogen in fuel cells and an intermediate fuel that can be used to produce hydrogen, its own production is of relevance and will be discussed in brief. Methanol may be produced from fossil sources such as natural gas or from biological material. Conventional steam reforming of natural gas may produce methanol.

Methanol steam reforming refers to the chemical reaction between methanol and water vapor for the production of hydrogen gas. This process is typically carried out in the presence of metal oxide catalysts at temperature ranging from 200 to 300°C . The chemical reactions taking place during the reforming process are outlined as follows:



Reaction (6) is the main reforming reaction which gives the stoichiometric conversion of methanol to hydrogen. It can be regarded as the overall effect of methanol decomposition reaction to CO and H₂O and the water-gas shift reaction. The amount of carbon monoxide (CO) as intermediate product formed in the process is determined from the relative kinetics of these two reactions. Appropriate feed ratio of methanol to water, proper control of temperature and pressure in the reformer are required to minimize the amount of CO formed in the process. Steam reforming of methanol is an endothermic reaction. Therefore the temperature is difficult to control inside the reactor which affects the performance.

The water-gas shift reaction or its reverse may be operating as well, (7).



with $\Delta H^0 = -41 \text{ kJ mol}^{-1}$. This could lead to CO contamination of the hydrogen stream, which is unacceptable for fuel cell types such as the proton exchange membrane or alkaline fuel cells (above ppm level) and only little acceptable (up to 2%) for phosphorous acid fuel cells. Fortunately, the CO production is low at the modest temperatures needed for steam reforming, and adjusting the amount or surplus steam (H₂O) may be to force the reaction (8) to go towards the left at the rate achieving the desired reduction of CO [61]. At the high end of the temperature regime, this control of CO becomes more difficult. However, use of suitable membrane reactors with separate catalysts for steam reforming and water-gas shift allows this problem to be overcome [62-64]. A typical thermal efficiency of hydrogen formation by this method is 74 %, with near 100 % conversion of the methanol feed.

It is possible to make the process autothermal, i.e. to avoid having to heat the reactants, by adding the possibility of the exothermic partial oxidation process.



Here $\Delta H^0 = -155 \text{ kJ mol}^{-1}$. By suitable combination of (6) and (9) the overall enthalpy difference may become approximately zero. There are still problems in controlling the temperature across the reactor, because the oxidation reaction (9) is considerably faster than the steam reforming (6). Proposed solutions include the use of a catalyst filament wire design leading to near-laminar flow through the reactor [61].

Catalysts traditionally used for the steam reforming process include a Cu-Zn catalyst containing mole fractions of 0.38 CuO, 0.41 ZnO and 0.21 Al₂O₃ [63, 65] and a metallic Cu-Zn catalyst in case of the wire concept [61].

Micro-channel reactor with catalyst coating in steam reforming of methanol is a promising candidate for portable electronics in order to get the compactness in the structure of fuel processor, the advantages with respect to transient behavior, hydrodynamics and heat and mass transfer characteristics. The main feature of micro-structured reactors is the high surface-area-to-volume ratio in comparison to conventional chemical reactors. Heat-transfer coefficient in this micro-channel reactor is also significantly higher than that for traditional heat exchangers. The high heat-exchanging efficiency allows to carry out reactions under isothermal conditions. In addition to heat transport, mass transport is also improved considerably in micro-structured reactors. He flows in the micro-channels are mostly laminar, directed, and highly symmetric. Process parameters such as pressure, temperature, residence time, and flow rate are more easily controlled in this reactor. Micro-structured reactors also give opportunities for new production concepts. Depending on demand, more micro-structured reactors or such subunits could be connected in parallel so that the required intermediate products and end-products can be produced [72].

The first use of wall-coated reactor for steam reforming of methanol was reported by de Wild and Verhaak [73]. They used the washcoated plate-fin type heat exchanger for the reaction. The washcoated heat exchanger showed better performance as compared to packed beds. The problem in micro-channel reactors lies on low durability of the catalyst. There is limited literature concerning the durability of the catalyst where catalyst deactivation at faster rate has been reported [73,74]. More catalyst loading and increase in porosity inside the coating are required in order to increase the durability of the catalyst. There are four types of catalyst for steam reforming of methanol in the literature under this category of the reactor: CuO/ZnO/Al₂O₃, CuO/Cr₂O₃/Al₂O₃, CuO/CeO₂/Al₂O₃ and Pd/ZnO. In the micro-channel reactor, CuO/ZnO/Al₂O₃ catalyst coating was used by [75-77] and [78]. Another [79-83] studied CuO/Cr₂O₃/Al₂O₃, CuO/CeO₂/Al₂O₃ and Pd/ZnO catalyst respectively. For CuO/ZnO/Al₂O₃ catalyst, all the groups except [78] utilized commercial catalyst and the coating was made with the slurry of catalyst powder and alumina/zirconia sol. Before coating of the catalyst, the micro-channel sheets was undercoated with the alumina/zirconia sol in order to enhance the adhesion

between catalyst powders and the substrate structure. For CuO/Cr₂O₃/Al₂O₃ and CuO/CeO₂/Al₂O₃ catalyst, [79-81] used the alumina binder prepared by mixing of γ -alumina powder, water, PVA (binder) and acetic acid.

A novel catalyst fabricated from Al-Cu-Fe quasicrystal can be used for steam reforming of methanol [71]. A dense Pd/Ag membrane reactor was developed for methanol steam reforming [83]. Hydrogen production from methanol by oxidative steam reforming was carried out in a membrane reactor [84].

For higher hydrocarbons, such as gasoline steam reforming has to be performed at high temperature. Using conventional Ni catalysts, the temperature must exceed 900°C, but addition of Co, Mo and Re or use of zeolites allows a reduction of the temperature by some 10 % [66,67].

Small-scale applications of fuel cells, aimed at increasing operation time before recharge over that of current battery technology, have simulated the development of miniature reformers for both methanol and other hydrocarbons [68,70]. Although the thermal efficiency of these devices aiming at use in conjunction with fuel cells rated in the range of 10 mW to 100 W is lower than for larger units, system efficiencies compare favourably with those of existing devices in the same power range.

3.5. Steam reforming of ethanol.

Ethanol is more promising because is less toxic than methanol. It can also be more easily stored and safety handled. Most importantly, it can be produced in large amounts from biomass such as agricultural wastes and forestry residues and hence is a renewable resource, as against methanol and gasoline. This could prove advantageous in tropical countries with a warm climate where there are large plantations of corn and sugarcane. The bio-ethanol thus produced is free from sulphur, which otherwise may poison the fuel cell catalyst. Similar, it is free from metals as well. Bio-ethanol, which is a dilute aqueous solution containing around 12 wt. % ethanol, could be directly subjected to steam reforming thereby eliminating one unit operation of distillation required to produce pure ethanol. The entire process could therefore be economically attractive. Above all, ethanol is CO₂ neutral since the CO₂ that is produced in this process is consumed by biomass growth and a closed carbon cycle is operated while the use of methanol and gasoline adds to CO₂ emissions. Thus, the use of ethanol will not contribute to global warming.

The first step in the conversion of ethanol to hydrogen is reforming. This reaction is carried out in the range of temperatures 673-1273 K. Reforming can be either by steam (steam reforming), or by humidified air (partial oxidation reforming), or by a mixture of air and steam (auto-thermal reforming). Here, attention is focussed on the steam reforming reaction. This yields a H₂-rich gas containing CO, which is a poison for PEMFCs. Except for use in high temperature cells, the CO concentration must be reduced to a very low level (around 10 ppm). A water gas shift reactor is therefore used to reduce the CO content of this gas stream. After high temperature and low temperature water gas shift (HTS and LTS), the residual CO is then reduced further to ppm level in a CO preferential oxidation (PROX) reactor [85]. This product gas is then suitable for feeding PEMFCs.

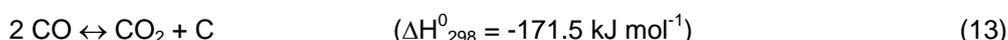
Thermodynamics aspects of ethanol steam reforming have received a fair amount of attention in the published literature. The reaction is strongly endothermic and produces only H₂ and CO₂ if ethanol reacts in the most desirable way. The basic reaction scheme is as follows:



However, other undesirable products such as CO and CH₄ are also usually formed during reaction. Aupretre et al. [122] have discussed the main reactions in ethanol steam reforming that account for the formation of these by-products:



Other reactions that can also occur are: ethanol dehydrogenation to acetaldehyde, ethanol dehydration to ethylene, ethanol decomposition to CO₂ and CH₄ or CO, CH₄ and H₂. Coke formation may occur as per the following Boudouard reaction:



Another possible route for the formation of carbon is through ethylene:



From the thermodynamic standpoint, since reaction (10) is endothermic and results in increase in number of moles, increasing the temperature and lowering the pressure is in favor of ethanol reforming. At 500 K, steam reforming of ethanol does not occur ($\Delta G > 0$). However, ethanol decomposition can easily occur at this temperature since the value of ΔG is sufficiently negative [86].

Vasudeva et al. [87] found that H_2 yields as high as 5.5 mol/mol of ethanol in the feed can be obtained at equilibrium at temperatures around 773-873 K with water-to-ethanol molar ratios of above 20. They suggested that carbon formation occurs only at low water-to-ethanol ratios (<2) and low temperatures (883 K).

The steam reforming of ethanol over Ni, Co, Ni/Cu and noble metals (Pd, Pt, Rh) has been extensively studied. The greatest concern lies in developing an active catalyst that inhibits coke formation and CO production [87].

In the presented review [87], catalytic steam reforming of ethanol for H_2 production is discussed in-depth. The effects of process variables such as temperature, pressure and the water-to-ethanol molar ratio in the feed on the H_2 yield at equilibrium are discussed. An overview of previous studies using Ni, Co, Ni/Cu and noble metals (Pd, Pt, Rh) is given. The catalyst performance characteristics suggest strong metal-support interaction. The reaction pathway is complex and a number of undesirable side reactions occur thereby affecting the selectivity to H_2 . Catalyst coking is mainly due to the formation of ethylene by ethanol dehydration. The use of a two-layer fixed bed reactor is therefore promising: at low temperatures, ethanol should first be converted by dehydrogenation over Cu into acetaldehyde which has a lower coking activity. The resulting mixture can then be passed at low temperatures around 723 K over a bed containing a mixture of Ni catalyst and a chemisorbent. While Ni will be active in steam reforming of acetaldehyde thus formed, the selective removal of CO_2 from the product mixture by chemisorption will enable production of H_2 -rich streams can be fed to a PEMFC.

Recently, Haryanto et al. [123] have reviewed steam reforming of ethanol, examined the various catalysts reported till date and presented a comparative analysis. They concluded that the ethanol conversion and H_2 production varies greatly with the reaction conditions, the type of catalyst and the method of catalyst preparation. The importance of process engineering related aspects is evident and these need to be discussed at length. This article is aimed at fulfilling this need. It reviews the available literature on catalytic steam reforming of ethanol. All published information on this topic is analyzed and presented in a coherent manner. The role of the catalyst composition and the process conditions in determining product distribution is elucidated. The possible reaction pathways and the kinetic and thermodynamic considerations have also been discussed. The coupling of ethanol steam reforming with selective removal of CO_2 by chemisorption to produce high-purity H_2 at low temperatures has been discussed. It is expected that this will provide an insight into steam reforming of ethanol.

Haga et al. [88] and Sahoo et al. [89] studied the catalytic properties of Co among other metals and found that selectivity to H_2 was in the order $\text{Co} > \text{Ni} > \text{Rh} > \text{Pt}, \text{Ru}, \text{Cu}$. Metals alone may not assist hydrogen production significantly. So performance of metal catalysts could be improved using supports. The nature of the support also plays a key role in determining the selectivity to H_2 . Choice of the support is hence crucial.

Al_2O_3 is commonly used as a support in the steam reforming reaction. However, it is acidic and promotes dehydration of ethanol to ethylene, which in turn polymerizes to form coke on the catalyst surface (Eq. 14). In contrast, MgO is basic. ZnO also has basic characteristics. CeO_2 is also basic and has redox properties [90-92].

4. VEHICULAR HYDROGEN STORAGE APPROACHES.

Current on-board hydrogen storage approaches include compressed hydrogen gas, cryogenic and liquid hydrogen, metal hydrides, high surface area sorbents (such as carbonbased nanostructured materials), and chemical hydrogen storage [13,14]. Compressed and cryogenic hydrogen, metal hydrides, high surface area sorbents, and carbon/based materials are categorized as "reversible" on/board, because these approaches may be recharged with hydrogen on-board the vehicle, similar to refueling with gasoline today. Systems that bind hydrogen with low binding energy (less than 20 - 25 kJ/mol H_2) can undergo relatively easy charging and discharging of hydrogen under conditions that may be applicable at refueling stations. For chemical hydrogen storage approaches as well as selected metal hydrides, the hydrogen is incorporated in much stronger bonds (e.g. with bond energies typically in excess of 60 - 100 kJ/mol H_2). Once the hydrogen is released, for use during vehicle operation, recharging with hydrogen under operating conditions convenient at a refueling

station is problematic. Such systems are referred to as “regenerable off-board”, which requires the spent media to be recovered from the vehicle and then regenerated with hydrogen either at the fueling station or at a centralized processing facility. Materials with binding energies between 25 and 60 kJ/mol H₂ may require substantial thermal management during recharging on-board the vehicle.

Both reversible on-board storage and regenerable off-board storage approaches have advantages and disadvantages. DOE is currently supporting research in both areas with a schedule for down-select decisions planned as materials are designed, developed and tested. Referring to Fig. 5 again, the current status of vehicular hydrogen storage systems is shown in comparison to DOE 2010 and 2015 performance targets. These values are system estimates provided by developers and the R&D community, and are updated by DOE as progress is reported. One can see that none of the current systems meet the combined gravimetric, volumetric, and cost targets for either 2010 or 2015.

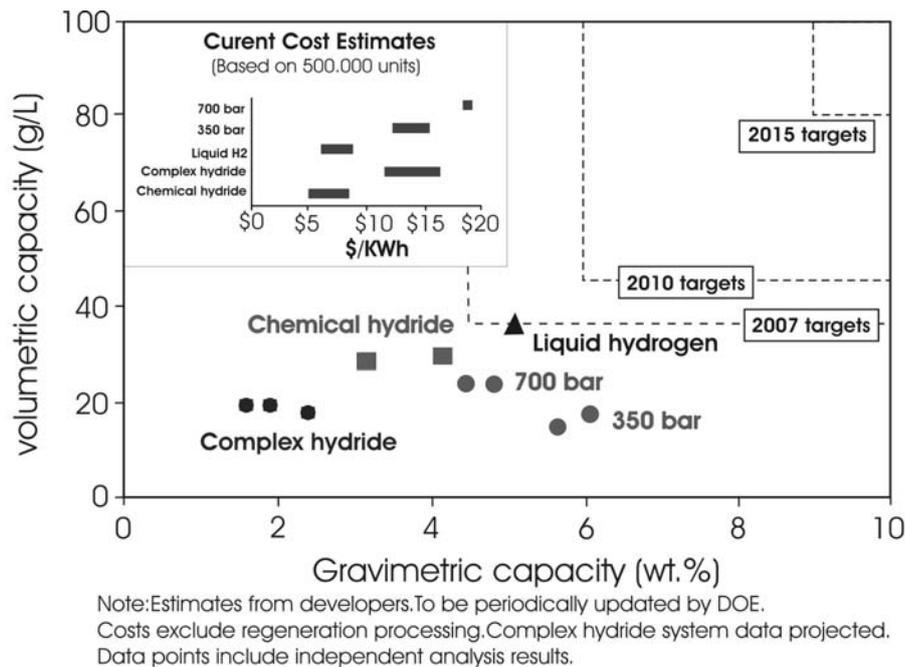


Fig.5 Current status of hydrogen storage system capacity and cost^[14]

4.1 Reversible on-board approaches

4.1.1 Compressed hydrogen gas

Carbon fiber-reinforced composite tanks for 35 MPa and 70 MPa compressed hydrogen are under development and are already in use in prototype hydrogen-powered vehicles ^[95]. The driving range of fuel cell vehicles with compressed hydrogen tanks depends on the vehicle type, design and the amount of stored hydrogen. For example, the General Motors HydroGen3 fuel cell vehicle (Opel Zafira minivan with a target curb weight of 1590 kg) is specified for a 270 km driving range with 3.1 kg of hydrogen at 70 MPa ^[96]. By increasing the amount of compressed hydrogen gas beyond 3 kg, a longer driving range can be achieved, but at more cost, weight and reduced passenger and cargo space on the vehicle. Volumetric capacity, limits of high pressure and cost are thus key challenges for compressed hydrogen tanks. Refueling or filling time, compression energy penalty (e.g. 15-20 % of the lower heating value of hydrogen) and heat management requirements during refilling also need to be considered ^[94].

4.1.2. Liquid hydrogen tanks.

Liquid hydrogen (LH₂) tanks can, in principle, store more hydrogen in a given volume than compressed gas tanks, since the volumetric capacity of liquid hydrogen is 0.070 kg/l (compared to 0.039 kg/l at 70 MPa) ^[97]. Key issues with LH₂ tanks are hydrogen boil-off, the energy required for hydrogen liquefaction, as well as tank cost. However, the driving range for vehicles using liquid hydrogen, excluding the effects of boil-off, can be longer than that for compressed hydrogen. For example, the General Motors HydroGen3 Opel Zafira minivan is specified with a driving range of 400 km with 4.6 kg liquid hydrogen, versus 270 km described above for the 70 MPa tank ^[96].

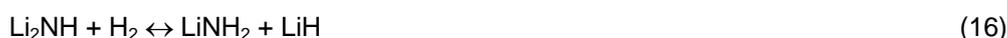
4.1.3. Metal hydrides.

Some metal hydrides have the potential for reversible on-board hydrogen storage and release the relatively low temperatures and pressures required for fuel cell vehicles [98].

Complex metal hydrides such as alanates have the potential for higher gravimetric hydrogen capacities in the operational window than conventional metal hydrides such as LaNi_5H_6 . Sodium alanate can store and release hydrogen reversibly through chemical reactions conducted at modest temperature and pressure when catalyzed with titanium dopants, as discovered by Bogdanovic and co-workers, according to the following reactions [99,100].



In practise, material (not system) gravimetric capacities are currently only 3 – 4 % [101]. In metal hydride systems based on lithium amide, the following reversible reaction takes place at 325 °C and 0.1 MPa [102]:



In this reaction, 6.5 wt. % hydrogen can be reversibly stored. However, the temperature is outside of the vehicular operating window using the waste heat of a PEM fuel cell.

Another example of a system that received significant attention since the recent work Vajo et al. is “destabilized” lithium borohydride (LiBH_4) with over 9 wt. % material capacity demonstrated [103, 104]. Further improvements will be pursued by nanoengineering and catalyst development.

4.1.4. High surface area sorbents and carbon-based materials.

While metals hydrides offer high volumetric capacities through dissociative absorption of hydrogen, high surface area sorbents offer the advantages of fast hydrogen kinetics and low hydrogen binding energies and, hence, potentially fewer thermal management issues during hydrogen charging and discharging. Single-walled carbon nanotubes (SWNTs), among several other high surface area sorbents (e.g. carbon nanofibres, graphite materials, metal-organic frameworks, aerogels, etc.) are being studied for hydrogen storage within the DOE program and by others. Transition metal atoms bound to fullerenes have recently been proposed as potential adsorbents for the high density, room temperature and ambient pressure storage of hydrogen based on theoretical studies [105,106]. It is indicated that stable scandium-based organometallic buckyball fullerenes might adsorb and desorb as many as 11 hydrogen atoms per scandium atom, leading to a theoretical maximum reversible hydrogen storage density of close to 9 wt. %. These materials have yet to be synthesized to confirm theoretical predictions. At a pressure of 2.5 GPa, the mole ratio between the stored hydrogen atoms a C atoms on the (20,0) nanotube (nanocontainer) is an impressive 1:1, corresponding to a weight ratio of 7.7 % [124].

4.2. Chemical hydrogen storage: regenerable off-board.

Chemical hydrogen storage may offer options with high energy densities and potential ease of use, particularly if systems involve liquids that may be easily dispensed using infrastructure similar to today’s gasoline refueling stations. Most of these reactions are irreversible, so the spent storage material would have to be regenerated off-board the vehicle because they cannot be reconstituted simply by applying an overpressure of hydrogen gas at modest temperature and pressure.

4.2.1. Hydrolysis reactions.

Hydrolysis reactions involve the reaction of chemical hydrides with water to produce hydrogen. The reaction of sodium borohydride solutions has been the most studied to date [106]. This reaction is:



Another hydrolysis reaction that is presently being investigated is the reaction of MgH_2 with water, to form $\text{Mg}(\text{OH})_2$ and H_2 [107]. In this case, particles of MgH_2 are contained in a non-aqueous slurry to inhibit premature water reaction when hydrogen generation is not required. Material-based capacities

for the MgH_2 slurry reaction with water can be as high as 11 wt. %. However, water must also be carried on-board the vehicle in addition to the slurry and the Mg(OH)_2 must be regenerated off-board.

4.2.2. Hydrogenation/dehydrogenation reactions.

The hydrogenation and dehydrogenation of organic liquids offer a potential advantage by not requiring water on-board as a co-reactant. For simple organic compounds, dehydrogenation is endothermic, so external heat must be applied. One early example is the decalin-to-naphthalene reaction, which can release 7.3 wt. % hydrogen at 21 °C via the reaction ^[109]:



Recently, new organic liquid hydrogen storage media have been developed by Air Products ^[110] that demonstrate the beneficial effect of heteroatom substitution on the thermodynamics of dehydrogenation. These liquids, including an example of N-ethyl carbazole, have shown 5-7 wt. % gravimetric hydrogen storage capacity and greater than 0.050 kg/l hydrogen volumetric capacity (material capacities only). Because this hydrogen release reaction is endothermic, it can use waste heat from the fuel cell (or internal combustion engine) and on-board heat rejection may not be an issue. Furthermore, the spent fuel regeneration (hydrogenation) reaction is endothermic, so it may be possible to couple the reaction efficiently at the regeneration plant to optimize energy recovery and to reduce cost.

4.2.3. Ammonia borane and other boron hydrides.

There are a number of boron hydride materials that have a high hydrogen content. Ammonia borane (AB, NH_3BH_3), is isoelectronic with ethane and has a high hydrogen storage capacity (up to 19.6 wt. % for release of three hydrogen molecules). Unlike ethane, hydrogen release from AB is exothermic. Products of dehydrogenation can include compounds such as cyclotriborazane (one hydrogen molecule released), borazine (two hydrogen molecules released), and polymeric analogues. The thermodynamics of these pathways is being determined both theoretically ^[112] and experimentally.

Autrey and co-workers ^[111] have shown that incorporating solid ammonia-borane into a mesoporous silica scaffold enhances hydrogen release through the formation of $(\text{NH}_2\text{BH}_2)_n$ and $(\text{NHBH})_n$ compounds at relatively low temperature (even at 80°C, with a 6 wt. % material capacity, including the scaffold).

4.2.4. Ammonia.

Ammonia, NH_3 , which has a boiling point of -33.5°C , has a high capacity for hydrogen storage, 17.6 wt. %. However, in order to release hydrogen from ammonia (an endothermic reaction), high fuel processing temperatures, and therefore large reactor mass and volume would be required. Other considerations include safety and toxicity issues, both actual and perceived, as well as the incompatibility of PEM fuel cells in the presence of trace levels of ammonia (> 0.1 ppm).

4.2.5. Alane.

Alane, AlH_3 , is another metal hydride being investigated as a material for hydrogen storage. The chemical formula of alane contains a theoretical 10 wt. % of H_2 , and a theoretical density of hydrogen in the compound (148 g H_2/l) that is more than double the density of liquid H_2 . In a collaborative effort at Brookhaven National Laboratory ^[113], it was found that the addition of LiH reduces the desorption temperature. The onset of hydrogen desorption of alane has been lowered to below 125°C, with hydrogen yields of 7-8 wt. % (based on material only) below 175°C. However, in order to utilize AlH_3 as an on-board storage technology, significant issues need to be resolved. First of all, the desorption should be lowered further to make the release of H_2 compatible with the waste heat generated by PEM fuel cell system ($\sim 80^\circ\text{C}$). Secondly, there is no practical, low-cost method to regenerate the spent Al powder back into AlH_3 . Finally, the infrastructure implications of a solid-state hydride storage option that is not rechargeable on-board the vehicle have yet to be fully explored.

5. GAS CONVERSION TECHNOLOGIES/NATURAL GAS UPGRADING.

The evolution of the known crude oil and natural gas reserves world-wide indicates a dramatic increase in the latter compared to a leveling off concerning the crude oil. This trend is expected to continue, which will in addition to the price development with respect to the crude oil based upgrading – most likely generate a gradual shift towards the application of natural gas as a feedstock for the production of fuels and petrochemicals ^[114,115]. This situation has forced an enhanced global interest in processes, which can convert natural gas into liquids and higher added value products – without going via methanol as intermediate. This route is known as the “gas to liquids (GTL)” – technology, based on the Fischer-Tropsch route. The interest to manufacture fuels and petrochemicals from natural gas is driven by desire to apply this technology directly, for example at remote natural gas field sites, in order to minimize transportation costs and gas burning at the recovery sites ^[116].

The following sub-chapters will deal with “GTL” – technology, based on the Fischer-Tropsch route as well as the methanol to hydrocarbon conversions, where zeolites and related microporous materials have been demonstrated to be superior catalysts ^[121].

5.1. “Gas to Liquids (GTL)”/conversion of synthesis gas to fuel.

Fuels production directly from syngas (in former times obtained from coal) has been reported by Fischer and Tropsch in 1923 for the first time ^[117], using an alkali-promoted iron catalyst. Fuels manufactured via the Fischer-Tropsch route reveal an excellent quality since they consist mainly for linear paraffins and α -olefins and do not contain sulfur and aromatics. A Co-containing catalyst is applied for the production of heavy paraffins via Fischer-Tropsch route starting with natural gas, a technology developed by Shell and named the “Shell Middle Distillate Synthesis (SMDS)” route ^[118, 119]. In addition, diesel fuel (or gasoline) is produced by hydrocracking of the more or less sulfur and nitrogen-free wax obtained through the SMDS process using noble metal containing zeolites. The more restricted fuel specifications currently introduced in order to reduce the environmental impact of hazardous emissions represent a driving force with respect to an increased use of fuels prepared via the Fischer-Tropsch route as a blending component of the gasoline and diesel pools in the future.

Besides the SMDS technology an alternative has been presented by SASOL/Chevron termed as the “Slurry-Phase-Distillate” process, again based on the Fischer-Tropsch route producing wax (using a Co-containing catalyst) followed by a hydrocracking step in order to get diesel or gasoline ^[120].

The methanol or gasoline (MTG) plant in New Zealand has been combined with a methane steam reforming unit for production of synthesis gas and a methanol plant to produce gasoline from natural gas. The process economics can be improved considerably by a clever combination and close integration of the different steps. In the TIGAS process developed by Haldor Topsoe AS for the manufacture of gasoline in a pilot plant scale, the methanol synthesis and the MTG reactions are integrated –without the separation of methanol as an intermediate product. A multi-functional catalyst has been developed, however, these process technologies do not usually apply catalysts based on zeolites or related microporous materials ^[116]. Finally, ExxonMobil has introduced the so-called “Advanced Gas Conversion for the 21st Century” (AGC-21) technology, again based on the Fischer-Tropsch route ^[120].

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