

15. Hydrogen

15.1 Introduction

Cars, trucks and buses can burn pure hydrogen in an internal combustion engine, or use it in a fuel cell to drive an electric motor. The fuel cell option is generally considered preferable for the long term, because although it requires more changes to existing vehicle design, it allows for higher efficiency and hence a longer range on the same amount of fuel. This section will thus consider the upstream emissions associated with producing hydrogen of the purity required for fuel cells.

Hydrogen is the chemical element with the smallest molecular mass. Hydrogen is not found as a free element on earth. Because of its high reactivity, it is always bonded to other molecules. As a result hydrogen for automotive use has to be man made.

The hydrogen energy content per unit mass is high. Compared to petrol for example, it is three times as high. On a volume basis, the energy content of hydrogen is relatively small. Both properties can be found in Table 15.1

Table 15.1
Physical properties of hydrogen

	Lower calorific value Mass basis (MJ/kg)	Lower calorific value Volume basis (MJ/L)
Hydrogen	119.9	8.9*
Petrol	41.2	31.0
Diesel oil	42.9	36.1

* Liquid hydrogen at -253°C

Gaseous hydrogen is very light (90 grams per cubic metre [g/Nm^3]) at ambient conditions and rises in air. Burning hydrogen rises in air as well. This is in contrast to burning petrol, for example, which stays at ground level.

All mixtures of hydrogen and air with a volumetric hydrogen content between 4% and 75% are inflammable. Compared to mixtures of petrol and air, this is a wide range. Hydrogen can burn in mixtures with air from very lean (excessive air) to rich (excessive fuel). The ignition energy is very low, so the combustion process can be initiated easily. The flame propagation speed of burning hydrogen is high. In an experimental spark ignited engine with direct gaseous hydrogen injection, flame speeds up to 40 m/s have been measured, at various engine speeds. The flame speeds obtained with internal mixture formation were significantly higher than those with external mixture formation (Meier et al., 1994). These high flame speeds necessitate engine adaptation.

The important safety aspects for handling hydrogen are discussed in the next section.

15.2 Full Fuel-Cycle Analysis

15.2.1 Tailpipe

We consider only fuel-cell powered vehicles. Such hydrogen vehicles have virtually no emissions, even of NO_x, because fuel cells operate at temperatures that are so much lower than internal combustion engines that NO_x is not formed from the nitrogen and oxygen in the air. Theoretically, a hydrogen-fuelled fuel cell vehicle emits only water vapour.

DaimlerChrysler in Europe established a subsidiary, EvoBus GmbH to fit a limited number of vehicles with the latest generation of fuel cells and use them in buses being used for public transport.

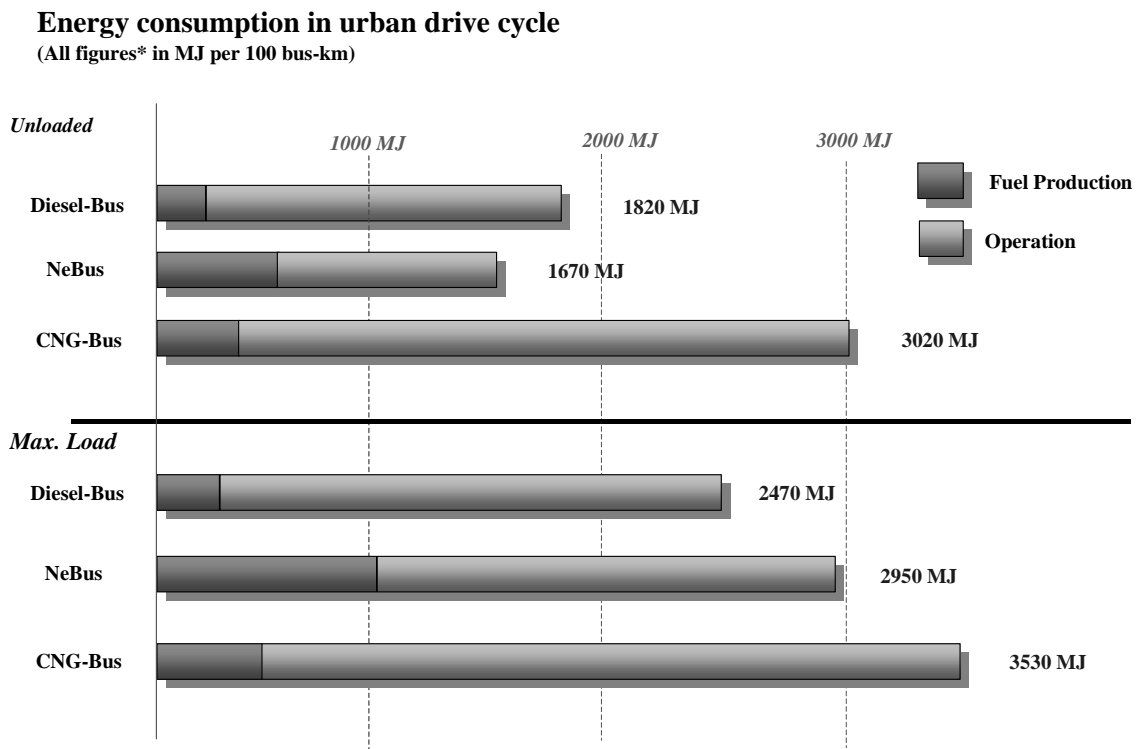


Figure 15.1
Energy consumption in urban drive cycle for buses (Graham, 2000)

During March 2000, a hydrogen fuel cell bus (NeBus) was exhibited in Perth and Melbourne. Figure 15.1 reproduces the energy consumption for the NeBus along with some comparative energy consumption (Graham, 2000). During operation, though energy is being used, this study will assume that the tailpipe emissions are purely water vapour.

Following on from these demonstrations, Perth will operate three fuel cell buses by late 2002. BP will invest more than \$1 million in Western Australia to establish a hydrogen manufacture and supply chain. A small purification unit at the BP Kwinana refinery will produce the requisite high quality hydrogen for the buses.

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15.2.2 Upstream

Production of Hydrogen

Hydrogen can be produced through steam reforming of natural gas, cleanup of industrial by-product gases, or electrolysis of water. This section will consider only steam reforming of natural gas.

The main commercial processes specific for the manufacture of hydrogen are steam reforming of natural gas or other hydrocarbons, coal gasification, and water electrolysis. Relatively small quantities of hydrogen are produced by steam reforming of naphtha and partial oxidation of natural gas. Oil refineries also recover hydrogen from some of their process units, most commonly from reformers.

Overall, the main chemical reactions used in these processes are as follows :



Worldwide, hydrogen as a raw material for the chemical industry is produced predominantly from natural gas (about 70%), with other petroleum feedstocks, coal, and water electrolysis accounting for the remainder. Process steps involved in natural gas reforming are illustrated in Figure 15.2.

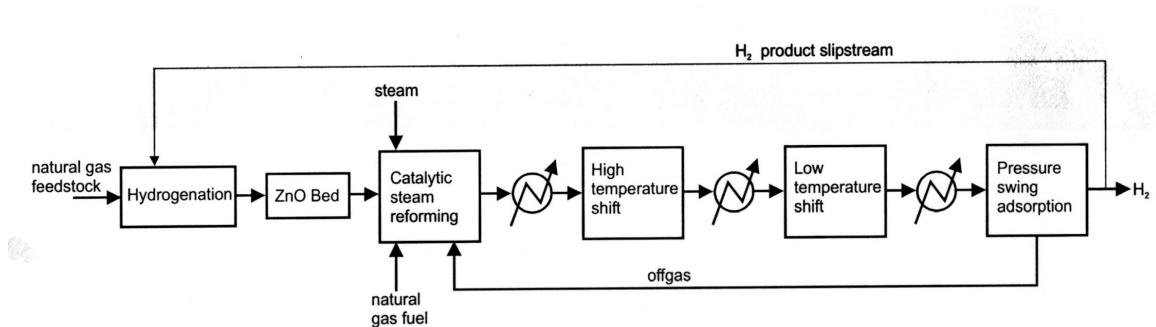


Figure 15.2
Diagram of the process for hydrogen production from natural gas incorporating PSA purification (from Spath and Mann, 2001).

In steam reforming, hydrocarbons contained in natural gas (mostly methane) are converted to synthesis gas (mixture of H₂, CO, CO₂) by reaction with steam over a catalyst in a primary reformer furnace. This process is usually operated at 800–870°C and 2.2–2.9 MPa, using a Ni-based catalyst.

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Because hydrocarbon feeds for steam reforming should be free of sulfur, feed desulfurisation is required ahead of the steam reformer. The desulfurisation step usually consists of passing the sulfur-containing natural gas feed at about 300–400°C over a CoMo catalyst in the presence of 2–5% H₂ to convert organic sulfur compounds to H₂S.

This is then followed by adsorption of H₂S over a ZnO guard bed to reduce the sulfur level to less than 0.1 ppmwt which is the level that the reforming catalyst can tolerate.

The gas and process steam mixture is then introduced into the primary reformer. This reformer is a direct natural gas fired chamber containing rows of nickel-alloy tubes filled with the catalyst pellets. The gas leaving the primary reformer is about 76.7% H₂, 12% CO, 10% CO₂, and 1.3% CH₄. Up to 95% conversion of CH₄ can be achieved in the primary reformer.

In the next step, the CO is converted to CO₂ and hydrogen by the water gas shift (WGS) reaction step:



The combination of this reaction with those occurring in the reformer gives the overall reaction stoichiometry presented earlier.

This reaction is first conducted on a chromium-promoted iron oxide catalyst in the high temperature shift (HTS) reactor at about 370°C at the inlet. Converted gases are cooled outside of the HTS and are sent to the low temperature shift (LTS) converter at about 200–215°C to complete the water gas shift reaction. The LTS catalyst is a copper–zinc oxide catalyst supported on alumina. The product gas after WGS contains about 77% H₂, 18% CO₂, 0.30% CO, and 4.7% CH₄.

The gas is then cooled and CO₂ scrubbed out by hot potassium carbonate or other processes such as MEA, methyldiethanolamine (MDEA) or other similar technology. The scrubbed gas contains about 98.2% H₂, 0.3% CO, 0.01% CO₂, and 1.5% CH₄.

Remaining carbon oxides are converted to methane by passing the gases reheated to about 315°C over a methanation catalyst, usually containing about 35% Ni supported on refractory material. Over this catalyst, CO and CO₂ are hydrogenated to CH₄. A typical hydrogen product is 98% H₂ and 2% CH₄.

As an alternative to scrubbing out the CO₂ followed by methanation, the shifted gas can be purified by pressure-swing adsorption (PSA) when high purity hydrogen is desirable. PSA is used in nearly all cases where high purity (>99%) hydrogen is needed. Pressure-swing adsorption utilizes the fact that larger molecules such as CO, CO₂ and CH₄ can be separated from the smaller hydrogen gas molecule by selective adsorption on high surface area materials such as molecular sieves. Hydrogen has a very weak affinity for adsorption. The process of pressure-swing adsorption is capable of producing very pure (>99.9%) hydrogen at recoveries of 70–90%, depending on the number of adsorption stages.

In applications where an ultra-pure hydrogen is required, for example in proton exchange membrane (PEM) fuel cells used in vehicles, final purification may be achieved by using palladium membranes. This process utilises the fact that hydrogen diffuses through palladium metal at high temperatures (about 600°C).

Upstream emissions in hydrogen production arise from natural gas recovery and purification, heat requirements of the steam reformer and energy demand of all process units. Further emissions arise from the chemistry of the process as illustrated by chemical equations. In a

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sense, hydrogen production can be seen as “decarbonisation” of natural gas, with all carbon converted into carbon dioxide.

Spath and Mann (2001) recently revised their earlier calculations in relation to the life cycle assessment of hydrogen production from natural gas steam reforming. Their updated estimates have been used in the quantitative parts of the life-cycle calculations.

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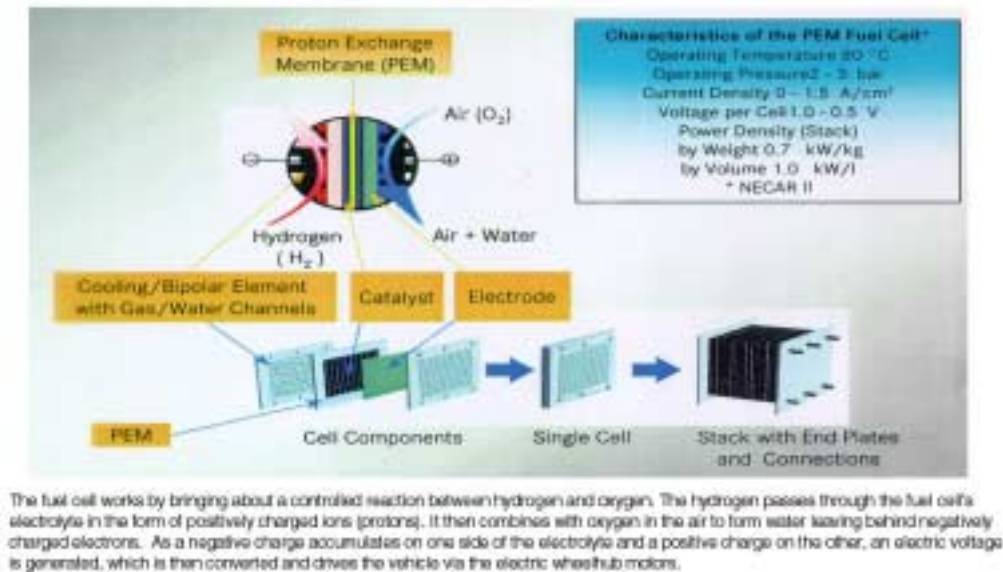


Figure 15.3
Proton exchange membrane fuel cell (source: DaimlerChrysler)

Figure 15.3 depicts the details of a PEM fuel cell. Because fuel cell vehicles are in a very early state of development, it is difficult to predict what the energy consumption of this type of vehicles will be in a mature situation. However, some indications can be given. From previous research it was found that the energy efficiency of a fuel cell vehicle without regenerative braking is 42 - 48%, from vehicle tank to wheels. For fuel cell vehicles with regenerative braking, this figure is 46-55% (van Walwijk et al., 1996). These figures are supported by a recent publication of Mercedes Benz. For a concept fuel cell van (rolling laboratory type), a part load efficiency of 40% is reported (van Walwijk et al., 1996).

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15.3 Results

15.3.1 Emissions per unit energy

Table 15.2
Embodied emissions (per MJ) for hydrogen (from natural gas)

Full Lifecycle	Units	LS diesel	Hydrogen (from natural gas)
Greenhouse	kg CO ₂	0.0834	0.0832
HC total	g HC	0.138	0.033
HC urban	g HC	0.110	0.001
NOx total	g NOx	1.016	0.053
NOx urban	g NOx	0.986	0.035
CO total	g CO	0.249	0.012
CO urban	g CO	0.240	0.005
PM10 total	mg PM10	39.7	0.7
PM10 urban	mg PM10	39.3	0.4
Energy embodied	MJ LHV	1.16	1.41

Table15.3
Precombustion emissions (per MJ) for hydrogen (from natural gas)

Precombustion	Units	LS diesel	Hydrogen (from natural gas)
Greenhouse	kg CO ₂	0.0167	0.0832
HC total	g HC	0.0548	0.0332
HC urban	g HC	0.126	0.001
NOx total	g NOx	0.073	0.053
NOx urban	g NOx	0.043	0.035
CO total	g CO	0.019	0.012
CO urban	g CO	0.010	0.005
PM10 total	mg PM10	4.4	0.676
PM10 urban	mg PM10	4	0.435
Energy embodied	MJ LHV	1.16	1.41

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Table 15.4
Summary of embodied emissions from hydrogen

		LS diesel	Hydrogen (from natural gas)
Greenhouse kg	Precombustion	0.0167	0.0832
Greenhouse kg	Combustion	0.0667	0.0000
HC total g	Precombustion	0.0548	0.0332
HC total g	Combustion	0.0835	0.0000
HC urban g	Precombustion	0.1262	0.0011
HC urban g	Combustion	0.0835	0.0000
NOx total g	Precombustion	0.0726	0.0527
NOx total g	Combustion	0.944	0.000
NOx urban g	Precombustion	0.043	0.035
NOx urban g	Combustion	0.944	0.000
CO total g	Precombustion	0.0191	0.0121
CO total g	Combustion	0.2301	0.0000
CO urban g	Precombustion	0.0096	0.0046
CO urban g	Combustion	0.2301	0.0000
PM10 total mg	Precombustion	4.40	0.68
PM10 total mg	Combustion	35.26	0.00
PM10 urban mg	Precombustion	4.00	0.44
PM10 urban mg	Combustion	35.26	0.00
Energy embodied MJ	Precombustion	1.16	1.41
Energy embodied MJ	Combustion	0	0

15.3.2 Emissions per unit distance

Table 15.5
Embodied emissions (per km) for hydrogen (from natural gas)

Full Lifecycle	Units	LS diesel	Hydrogen (from natural gas)
Greenhouse	kg CO ₂	0.9250	0.8970
HC total	g HC	1.509	0.358
HC urban	g HC	1.192	0.012
NOx total	g NOx	11.250	0.568
NOx urban	g NOx	10.638	0.372
CO total	g CO	2.723	0.131
CO urban	g CO	2.612	0.049
PM10 total	mg PM10	438.4	7.3
PM10 urban	mg PM10	423.1	4.7
Energy embodied	MJ LHV	12.7	15.2

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Table 15.6
Precombustion emissions (per km) for hydrogen (from natural gas)

Precombustion	Units	LS diesel	Hydrogen (from natural gas)
Greenhouse	kg CO ₂	0.2060	0.8970
HC total	g HC	0.609	0.358
HC urban	g HC	0.292	0.012
NOx total	g NOx	1.080	0.568
NOx urban	g NOx	0.468	0.372
CO total	g CO	0.243	0.131
CO urban	g CO	0.132	0.049
PM10 total	mg PM10	58.4	7.28
PM10 urban	mg PM10	43.1	4.68
Energy embodied	MJ LHV	12.7	15.2

Table 15.7
Embodied emissions summary (per km) for hydrogen (from natural gas)

		LS diesel	Hydrogen (from natural gas)
Greenhouse kg	Precombustion	0.2060	0.8970
Greenhouse kg	Combustion	0.7190	0.0000
HC total g	Precombustion	0.6090	0.3580
HC total g	Combustion	0.9000	0.0000
HC urban g	Precombustion	0.2920	0.0120
HC urban g	Combustion	0.9000	0.0000
NOx total g	Precombustion	1.0800	0.5680
NOx total g	Combustion	10.170	0.000
NOx urban g	Precombustion	0.468	0.372
NOx urban g	Combustion	10.170	0.000
CO total g	Precombustion	0.2430	0.1310
CO total g	Combustion	2.4800	0.0000
CO urban g	Precombustion	0.1320	0.0492
CO urban g	Combustion	2.4800	0.0000
PM10 total mg	Precombustion	58.40	7.28
PM10 total mg	Combustion	380.00	0.00
PM10 urban mg	Precombustion	43.10	4.68
PM10 urban mg	Combustion	380.00	0.00
Energy embodied MJ	Precombustion	12.70	15.20
Energy embodied MJ	Combustion	0	0

There is insufficient information with which to estimate quantitatively the uncertainties associated with the use of hydrogen as a fuel.

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15.4 Viability and Functionality

Important advantages of fuel cells are: high energy efficiency, because the efficiency is not limited to the maximum efficiency of thermal energy processes; low emissions during operation, though manufacturing of fuel cells may cause emissions; and low noise production.

However, fuel cells have some disadvantages as well. Compared to internal combustion engines, the disadvantages are: fuel cells are very expensive; and fuel cells are large and heavy per kW output. Most research concentrates on reducing these disadvantages.

Three different methods for on-board hydrogen storage have been considered (van Walwijk et al., 1996):

- high pressure hydrogen gas
- hydride, where hydrogen is chemically bound to a metallic material
- cryogenic storage of liquid hydrogen, at low temperature.

The storage method used for the NeBus is shown in Figure 15.4.

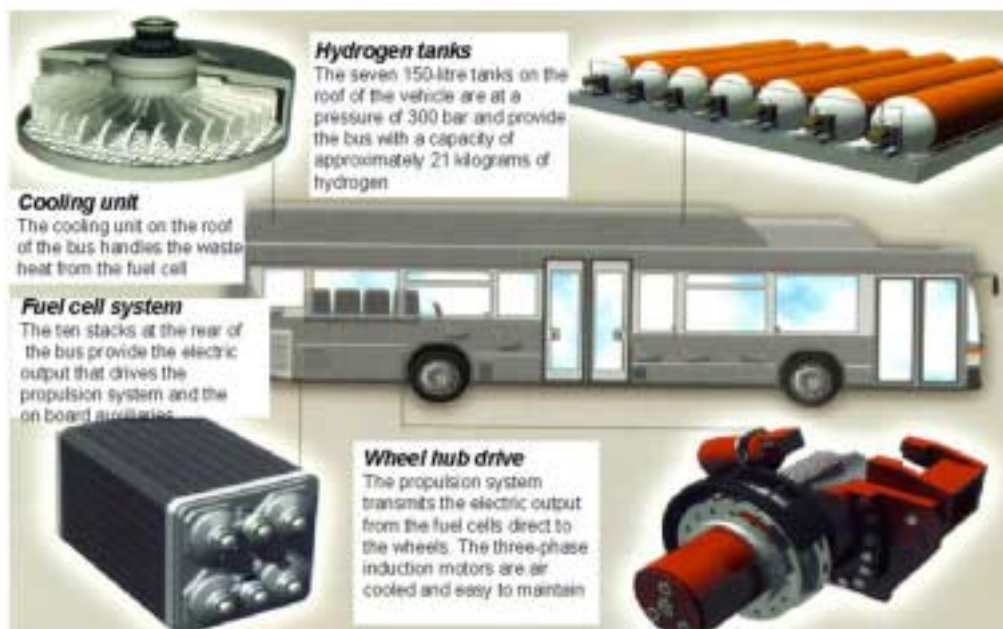


Figure 15.4
Storage method for the NeBus hydrogen bus

15.4.1 Safety

Safety is an important issue regarding hydrogen production, transport and use in a vehicle (refuelling, on-board storage and in case of collisions). In this section, safety aspects of hydrogen when used as fuel for road vehicles are discussed. First, the circumstances in which hydrogen can be dangerous and the reasons for this, are discussed.

Hydrogen rises when it is released into the open air. Its safety is then similar to that of conventional fuels. However, in closed rooms, hydrogen is more dangerous than conventional fuels. Hydrogen can burn in mixtures with air from very lean - with excess air - to very rich .

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The flame propagation speed is very high, which gives the combustion an explosive character. A spark from a light switch can start the combustion process for example. A (local) pressure peak can also ignite hydrogen-air mixtures. These pressure peaks are not found in the open air but may occur in closed rooms at locations where different pressure waves interfere.

Two notorious accidents contributed to the general concern regarding the safety of hydrogen. In 1937, the 'Hindenburg' airship burnt down in a few seconds, and in 1990 a Space Shuttle exploded just after take-off. Both had hydrogen on-board. At the accident with the 'Hindenburg' relatively few spectators were hurt because the burning hydrogen rose in the air. Because of the high flame propagation speed, an accidental hydrogen fire never lasts long.

Refuelling of hydrogen vehicles is discussed later. To avoid explosions, evaporating hydrogen is extracted during the refuelling process. For example, BMW has developed a fully automatic refuelling system which may be safely used by anyone. For on-board storage of hydrogen, some hydrogen has to be vented when a hydrogen vehicle is not used over a longer period of time, because the fuel tank cannot be 100% isolated. A safety valve in the vehicle tank prevents excessive tank pressures. Sensors inside the vehicle can detect hydrogen and the vehicle windows can be opened automatically if so required. Evaporative hydrogen losses will also occur when the vehicle is parked in a garage. To avoid ignitable mixtures of hydrogen in air, four different measures can be taken:

- Hydrogen can be exhausted by a spark free venting system
- A small fuel cell can be mounted in the vehicle. Evaporating hydrogen can then be used in this fuel cell to generate electricity, which can be stored in the vehicle batteries to be used later. This type of fuel cell has not been developed yet.
- Evaporated hydrogen can be stored in a metallic hydride, in which it is chemically bound to a metallic material. More information on hydride storage can be found in section 12.5. It has to be kept in mind that heat is generated when hydrogen is being stored in a metallic hydride.
- When the hydrogen vehicle is equipped with a fuel cell instead of a combustion engine, the fuel cell can be used to convert the evaporated hydrogen automatically into electrical energy which may be stored in the batteries.

The safety of hydrogen fuel systems is important during vehicle collisions. There is substantial testing designed to ensure leakproof hydride tanks, and to place the vehicle tank inside the safety cage of vehicles so as to reduce the risk of damage to the tank during a collision.

Van Walwijk et al. (1996) report that accidents with hydrogen vehicles are no worse than those with LPG or natural gas. However, they also point out that no results from collision tests with hydrogen vehicles could be found in the literature.

15.4.2 Warranty

Hydrogen powered vehicles are supplied by the engine manufacturer.

15.4.3 Functionality of the fuel under the full range of Australian conditions

There is no reason to expect any lack of functionality of hydrogen under Australian conditions.

15.4.4 Fuel energy density and vehicle operational range

The driving ranges of comparable diesel and hydrogen vehicles are different, when the mass of fuel tank and fuel are the same. It is smaller for hydrogen vehicles. The diesel vehicle can

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drive twice the distance. The specifications for the DaimlerChrysler NeBus specify 7 roof-mounted pressure resistant cylinders (weighing 1,900 kg) to give a range of 250 km, with a passenger capacity of 34 seated and 24 standing (58 passengers). These figures are similar in range to earlier generation CNG buses and compare to a typical range of 400 km for an equivalent diesel bus (Cannon and Sun, 2000).

BMW has been working on liquid storage systems. Mass and storage volume are acceptable. A disadvantage is the storage temperature of -253°C for liquid hydrogen, which requires an insulated vehicle tank. In a vehicle, the storage tank is not refrigerated. This results in evaporative losses when the engine is not running. Due to the unavoidable leaking of heat to the storage tank, some hydrogen will evaporate. This gas must be able to escape (or must be used) to avoid excessive pressures and to maintain a low temperature in the vehicle tank. The fact that the energy of the heat is used as evaporation energy helps to maintain a low temperature in the vehicle as well. With appropriate insulation and a tank pressure of 5 bar, it is possible to avoid venting for three or four days. After that period, the evaporative losses continue.

15.4.5 Refuelling requirements

To refill a hydrogen vehicle, an onward (for liquid hydrogen) and a return (for gaseous hydrogen from the vehicle tank) hose are connected to avoid losses of hydrogen during refuelling. BMW has developed a refuelling system in which, after connecting the hoses to the vehicle, the complete system - including the vehicle part - is flushed with helium before the refuelling commences. This is to avoid ignitable mixtures of hydrogen and air. After the system has been flushed, the refuelling of the vehicle may commence.

Most hydrogen vehicles are being refuelled with liquid hydrogen. When refuelling a cold hydrogen tank with liquid hydrogen, approximately 10% of the hydrogen will become gaseous upon entering the tank. For warm vehicles, the percentage can increase up to 25%. These evaporative losses are being exhausted back to the storage tank of the refuelling station. In this way losses of hydrogen can be avoided, including the loss of energy, which is directly related to a loss of hydrogen.

Refuelling time of vehicles with a tank for liquid hydrogen at (-253°C) is between three and ten minutes, when the vehicle tank is cold. However, an empty vehicle tank will slowly warm up to ambient temperature. Refuelling of a tank that is at ambient temperature has to be done relatively slowly. The refuelling time of a hydrogen vehicle can thus rise to ten times the refuelling time of a petrol vehicle.

Refuelling time of hydrogen vehicles with metallic hydride storage tanks is lengthy compared to conventionally fuelled vehicles. Heat is generated when the hydrogen is bound to the metallic hydride. This heat has to be removed during the refuelling process.

15.5 Health Issues

There are no air pollutant or greenhouse gas emissions during operation. The only emissions that may be of concern arise during precombustion.

15.5.1 Production and transport

Upstream emissions in hydrogen production arise from natural gas recovery and purification, heat requirements of the steam reformer and energy demand of all process units. Further emissions arise from the chemistry of the process.

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Particulate matter

The LCA estimate for hydrogen urban precombustion (truck) PM10 emissions of 5 mg/km is substantially less than the LSD estimate of 43 mg/km.

Air toxics

The LCA estimate for hydrogen urban precombustion (truck) HC emissions of 0.012 g/km is substantially less than the LSD estimate of 0.292 g/km.

The public health effects of air toxics will be mainly associated with combustion emissions in large urban centres. An accompanying disk to this report provides details of air toxic emissions from upstream activities.

15.5.2 Use

We consider only fuel-cell powered vehicles. Such hydrogen vehicles have virtually no emissions, even of NO_x, because fuel cells operate at temperatures that are so much lower than internal combustion engines that NO_x is not formed from the nitrogen and oxygen in the air. Theoretically, a hydrogen fuelled fuel cell vehicle emits only water vapour.

Particulate matter

The LCA estimate for hydrogen combustion (truck) PM10 emissions of 0 mg/km is substantially less than the LSD estimate of 380 mg/km.

Air toxics

The LCA estimate for hydrogen combustion (truck) HC emissions of 0 g/km is substantially less than the LSD estimate of 0.900 g/km.

15.5.3 Summary

Hydrogen upstream emissions of both particles and HC are substantially less than LSD. Hydrogen has no tailpipe emissions of particles or air toxics.

15.6 OHS Issues

There are a range of OHS issues that must be considered when handling hydrogen.

Safety is an important issue regarding hydrogen production, transport and use in a vehicle (refuelling, on-board storage and in case of collisions). Hydrogen rises when it is released into the open air. Its safety is then similar to that of conventional fuels. However, in closed rooms, hydrogen is more dangerous than conventional fuels. Hydrogen can burn in mixtures with air from very lean - with excess air - to very rich. The flame propagation speed is very high, which gives the combustion an explosive character. A spark from a light switch can start the combustion process for example. A (local) pressure peak can also ignite hydrogen-air mixtures. These pressure peaks are not found in the open air but may occur in closed rooms at locations where different pressure waves interfere.

Safety is also an important issue for on-board storage of hydrogen. It has already been discussed in the section on viability and functionality.

15.7 Vapour Pressure Issues

Most hydrogen vehicles are being refuelled with liquid hydrogen. Evaporative losses during refuelling can be exhausted back to the storage tank of the refuelling station. In this way losses of hydrogen can be avoided, including the loss of energy, which is directly related to a loss of hydrogen.

15.8 Environmental Impact and Benefits

Hydrogen is a gaseous fuel with no air pollutant or greenhouse gas emissions. It thus cannot contaminate soil or water. Provided that an environmentally sustainable system can be produced then the use of hydrogen would be highly beneficial. Manins (1992) proposed an innovative scheme based on using tidal power to dissociate hydrogen and thus run a hydrogen economy. The theoretical potential is great for environmental benefits provided the technology can be implemented.

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