MODULE 2:

Hydrogen Use

College of the Desert

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The Fuel Cell Engine Company

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MODULE 2: HYDROGEN USE

CONTENTS

OBJECTIVES

At the completion of this module, the technician will understand:

- the processes by which hydrogen is extracted from other substances
- how hydrogen is stored, and the inherent advantages and disadvantages of each method
- how hydrogen is transported, and the inherent advantages and disadvantages of each method

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Key Points & Notes

2.1 Hydrogen Manufacture

The fundamental question underlying the use of hydrogen as a fuel is, Where do we get it from? Despite its abundance in the universe, hydrogen does not occur freely on earth, as it reacts very readily with other elements. For this reason, the vast majority of hydrogen is bound into molecular compounds.

To obtain hydrogen means to remove it from these other molecules. With respect to the energy required, it is easy to remove hydrogen from compounds that are at a higher energy state, such as fossil fuels. This process releases energy, reducing the amount of process energy required. It takes more energy to extract hydrogen from compounds that are at a lower energy state, such as water, as energy has to be added to the process.

The process of extracting hydrogen from fossil fuels is called reforming. Today, this is the principal and least expensive method of producing hydrogen. Unfortunately, reforming emits pollutants and consumes non-renewable fuels.

The process of extracting hydrogen from water is called electrolysis. In principal, electrolysis can be entirely non-polluting and renewable, but it requires the input of large amounts of electrical energy. Consequently, the total environmental impact of acquiring hydrogen through electrolysis is largely dependent on the impacts of the source power.

One way to assess the comparative environmental impact of electrolysis and the reforming of various fuels is by comparing the total amount of carbon dioxide emitted. A recent study used a Mercedes-Benz A-Class car as the basis for comparison, and calculated the total carbon dioxide emissions per 1000 km of travel. The total carbon dioxide emissions include those from the car’s tailpipe, the fuel processor, and the powerplant that supplied the energy to the fuel processor.

The results of the study, shown in Figure 2-1, clearly indicate that environmental cleanliness of hydrogen is directly linked to its mode of manufacture. Although not included in the study, hydrogen derived from renewable, non-fossil energy sources would likely have no carbon dioxide emissions.

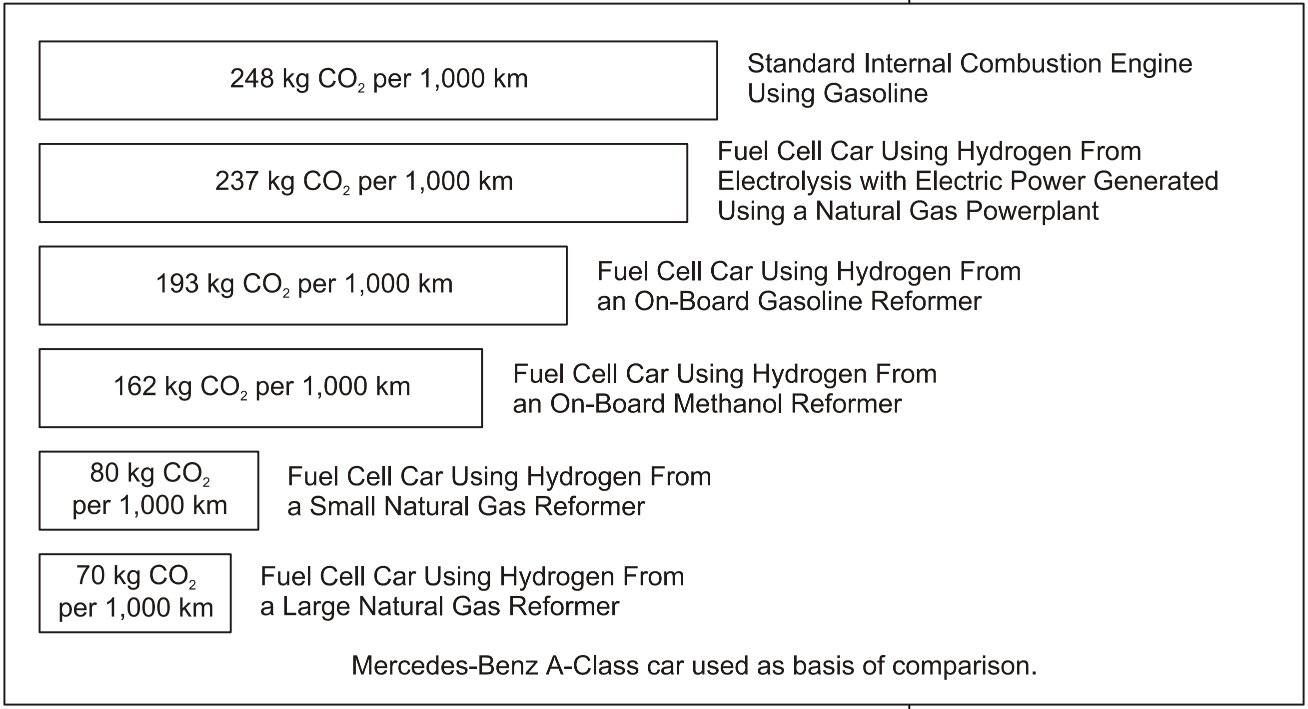


Figure 2-1 Total Carbon Dioxide Emissions for Comparative Hydrogen Production Methods

Alternative methods of hydrogen production include thermochemical water decomposition, photoconversions, photobiological processes, production from biomass, and industrial processes. Although some of these methods show promise for the future, they are still largely experimental and capable of supplying only small amounts of hydrogen.

Hydrogen can be produced on a large scale at dedicated hydrogen production plants, or on a small scale at local production facilities. Large-scale production benefits from economies of scale and plants can be located near power and water, but suffers from the difficulties of hydrogen transportation. Some methods of hydrogen production, such as from coal or biomass, can only be undertaken on a large scale.

Small scale production can reduce the problems of hydrogen transportation by using energy that is easily brought to the facility, such as electricity, natural gas or solar. On the downside, the amount of equipment required for the amount of hydrogen produced is significantly higher than for large-scale facilities, due to the economy of scale.

At the extreme small scale, fossil fuels could be reformed to hydrogen on board a fuel cell vehicle, but the systems are complex and costly.

Key Points & Notes

Currently, the vast majority of all hydrogen manufactured worldwide originates from fossil fuels, as a byproduct in chemical industries, or crude oil refining processes. Hydrogen production from renewable energy is not yet feasible on a large scale.

Production of hydrogen currently costs from 3 to 15 times more than natural gas, and from 1.5 to 9 times more than gasoline, depending on the method used. When extracted from fossil fuels, the initial production and refining of the fuel further increases the total cost.

2.1.1 Electrolysis

In electrolysis, electricity is used to decompose water into its elemental components: hydrogen and oxygen. Electrolysis is often touted as the preferred method of hydrogen production as it is the only process that need not rely on fossil fuels. It also has high product purity, and is feasible on small and large scales. Electrolysis can operate over a wide range of electrical energy capacities, for example, taking advantages of more abundant electricity at night.

At the heart of electrolysis is an electrolyzer. An electrolyzer is a series of cells each with a positive and negative electrode. The electrodes are immersed in water that has been made electrically conductive, achieved by adding hydrogen or hydroxyl ions, usually in the form of alkaline potassium hydroxide (KOH).

The anode (positive electrode) is typically made of nickel and copper and is coated with oxides of metals such as manganese, tungsten and ruthenium. The anode metals allow quick pairing of atomic oxygen into oxygen pairs at the electrode surface.

The cathode (negative electrode) is typically made of nickel, coated with small quantities of platinum as a catalyst. The catalyst allows quick pairing of atomic hydrogen into pairs at the electrode surface and thereby increases the rate of hydrogen production. Without the catalyst, atomic hydrogen would build up on the electrode and block current flow.

A gas separator, or diaphragm, is used to prevent intermixing of the hydrogen and oxygen although it allows free passage of ions. It is usually made of an asbestos-based material, and tends to break apart above 176 °F (80 °C).

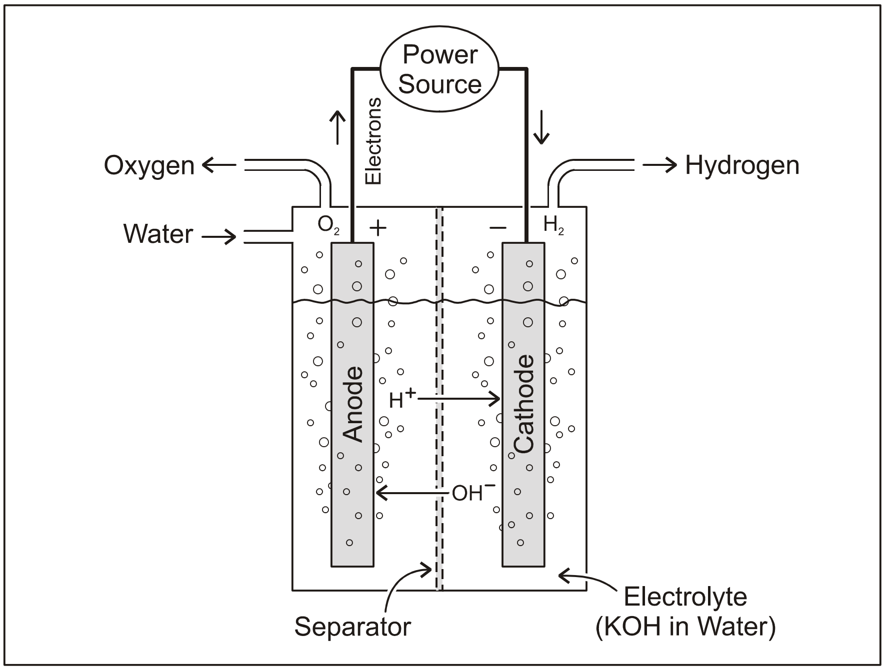


Figure 2-2 Typical Electrolysis Cell

The reactions at the cathode are:

(1) $K^+ + e^- \Rightarrow K$	a positively charged potassium ion is reduced
(2) $K + H_2O \Rightarrow K^+ + H + OH^-$	the ion reacts with water to form a hydrogen atom and a hydroxyl ion
(3) $H + H \Rightarrow H_2$	the highly reactive hydrogen atom then bonds to the metal of the cathode and combines with another bound hydrogen atom to form a hydrogen molecule that leaves the cathode as a gas

The reactions at the anode are:

(1) $OH^- \Rightarrow OH + e^-$	a negatively charged hydroxyl ion is oxidized
(2) $OH \Rightarrow \frac{1}{2}H_2O + \frac{1}{2}O$	the ion reacts to form water and an oxygen atom

(3) $O + O \Rightarrow O_2$ — the highly reactive oxygen atom then bonds to the metal of the anode and combines with another bound oxygen atom to form an oxygen molecule that leaves the anode as a gas

The rate of hydrogen generation is related to the current density (the amount of current divided by the electrode area measured in amps per area). In general, the higher the current density, the higher the source voltage required, and the higher the power cost per unit of hydrogen. However, higher voltages decrease the overall size of the electrolyzer and therefore result in a lower capital cost. State-of-the-art electrolyzers are reliable, have energy efficiencies of 65 to 80% and operate at current densities of about 186 A/ft^2 (2000 A/m^2).

This large electrolyzer consumes a maximum of 240 HP (180 kW) of electrical power while generating 1,400 sft^3/hr (660 slpm) of hydrogen. The hydrogen is delivered at up to 5,000 psig (345 barg) using an integral compressor.

This small electrolyzer consumes 10 HP (7.5 kW) of electrical power while generating a maximum of 42 sft^3/hr (20 slpm) of hydrogen. The hydrogen is delivered at 30 to 100 psig (1 to 6.9 barg) at 99.7% purity.

Figure 2-3 Electrolyzers

A fuel cell reverses the process of electrolysis. Electrolysis adds electrical energy to low-energy water to release two high-energy gases. A fuel cell allows the gases to react and combine to form water, releasing electrical power. Both processes release heat, which represents an energy loss.

For electrolysis, the amount of electrical energy required can be somewhat offset by adding heat energy to the reaction. The minimum amount of voltage required to decompose water is 1.23 V at 77 °F (25 °C). At this voltage, the reaction requires heat energy from the outside to proceed. At 1.47 V (and same temperature) no input heat is required. At greater voltages (and same temperature) heat is released into the surroundings during water decomposition.

Operating the electrolyzer at lower voltages with added heat is advantageous, as heat energy is usually cheaper than electricity, and can be recirculated within the process. Furthermore, the efficiency of the electrolysis increases with increased operating temperature.

When viewed together with fuel cells, hydrogen produced through electrolysis can be seen as a way of storing electrical energy as a gas until it is needed. Hydrogen produced by electrolysis is therefore the energy carrier, not the energy source. The energy source derives from an external power generating plant. In this sense, the process of electrolysis is not very different from charging a battery, which also stores electrical energy. Viewed as an electricity storage medium, hydrogen is competitive with batteries in terms of weight and cost.

To be truly clean, the electrical power stored during electrolysis must derive from non-polluting, renewable sources. If the power is derived from natural gas or coal, the pollution has not been eliminated, only pushed upstream. In addition, every energy transformation has an associate energy loss. Consequently, fossil fuels may be used with greater efficiency by means other than by driving the electrolysis of hydrogen. Furthermore, the cost of burning fossil fuels to generate electricity for electrolysis is three to five times that of reforming the hydrogen directly from the fossil fuel.

Key Points & Notes

The approximate efficiencies of modern thermal power stations are:

Nuclear: 30–33%
Natural gas: 30–40%
Coal: 33–38%
Oil: 34–40%

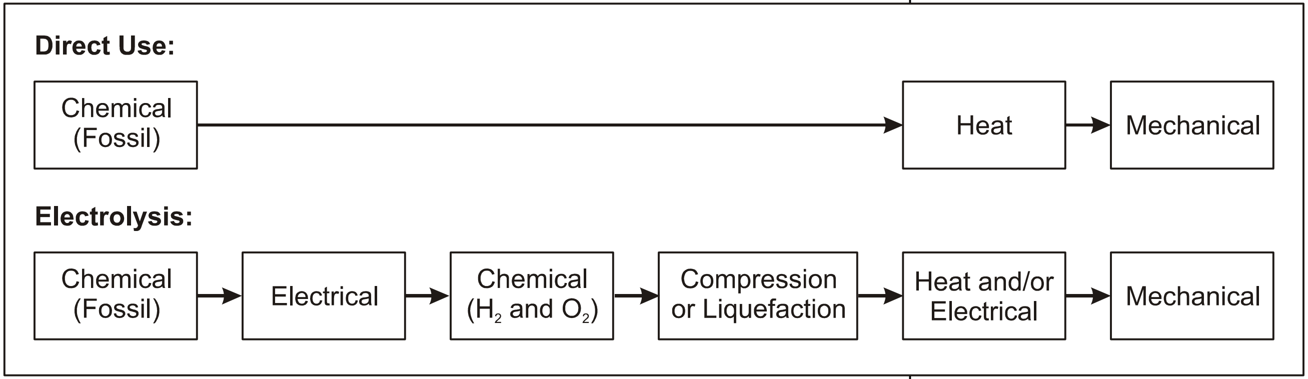


Figure 2-4 Energy Transformation Processes Based on Fossil Fuels

Non-polluting renewable energy sources include hydroelectric, solar photovoltaic, solar thermal and wind. These methods of power generation are applicable only in specific geographic or climatic conditions. Furthermore, with the exception of hydroelectric, each of these power sources is intermittent. Despite growth in the use of these energy sources, they currently provide a very small amount of the power consumed today.

Hydroelectric power generation uses the energy of moving water to turn turbines that in turn rotate generators. Hydroelectric power is only feasible in areas with major rivers that undergo significant changes in height. Most suitable locations worldwide have already been developed. Hydroelectric power is a cheap source of clean power especially when utilizing excess, off-peak power. The efficiency of hydroelectric power generation can top 80%. This is probably the optimum form of renewable energy although the environmental and ecological cost of dams is high.

Solar electric power generation uses banks of solar cells to convert the energy of the sun directly into electrical power. Solar power is only feasible in areas with significant amounts of intense sunlight and requires large tracts of land to generate sufficient levels of power. The efficiency of solar cells currently ranges from 3 to 17%.

Key Points & Notes

This solar cell array contains tracking and flat cells which can generate a combined rated total of 50 HP (37 kW) in bright sunlight. The power is supplied at 360 VDC with a maximum current of 103 A.

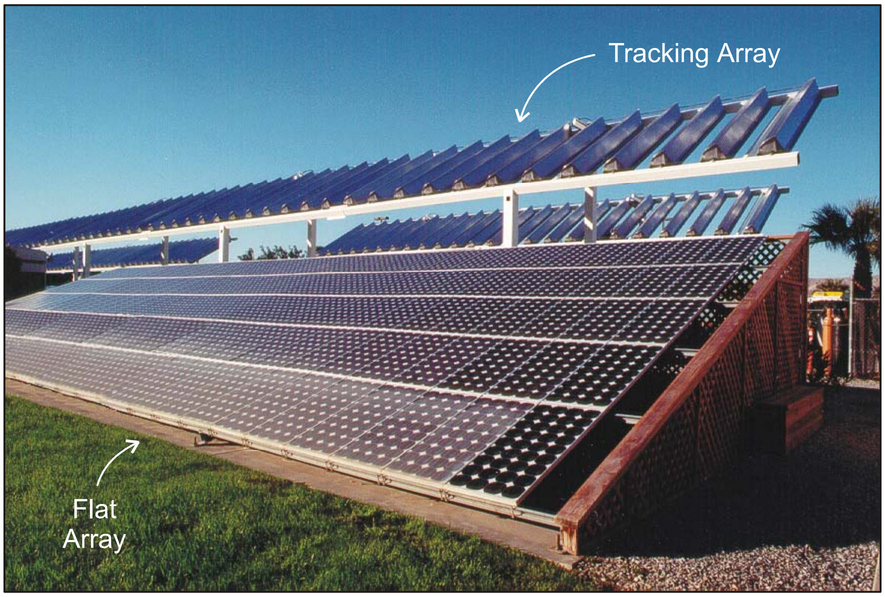


Figure 2-5 Solar Cell Array

Solar thermal power generation starts by concentrating the sun's heat into a fluid that has a high heat-carrying capacity, such as oil. The oil's heat is transferred through heat exchangers to water, generating steam for a steam turbine generator. Like solar electric power generation, solar thermal power generation is only feasible in areas with significant amounts of intense sunlight and requires large tracts of land in order to generate sufficient levels of power. The overall efficiency of converting sunlight to electricity for these systems is about 8 to 24% depending on the type of technology used.

Wind power generation uses the energy of moving air to turn turbines that in turn rotate generators. Wind power is only feasible in areas with favorable wind conditions and requires large tracts of land in order to generate sufficient levels of power. Wind has low energy density and wind turbines operating at optimum conditions (design speed) may obtain 30% efficiency at best. Real-world operating conditions may reduce this efficiency considerably.

Wind Turbines

Although a renewable energy source in conjunction with electrolysis would eliminate the dependence on fossil fuels, it does not reduce the number of energy transformations required to produce mechanical work using hydrogen. If clean, renewable power were available, it could also be used in other ways that require fewer energy transformations, such as direct storage in batteries or to compress air for propulsion.

Another consideration associated with electrolysis is the source of water. Water is already a precious commodity, and would be consumed in vast quantities in order to support a large hydrogen economy. The water would also have to be purified prior to use, increasing its cost.

2.1.2 Reforming

Reforming is a chemical process that reacts hydrogen-containing fuels in the presence of steam, oxygen, or both into a hydrogen-rich gas stream. When applied to solid fuels the reforming process is called gasification. The resulting hydrogen-rich gas mixture is called reformate. The equipment used to produce reformate is known as a reformer or fuel processor.

The specific composition of the reformate depends on the source fuel and the process used, but it always contains other compounds such as nitrogen, carbon dioxide, carbon monoxide and some of the unreacted source fuel. When hydrogen is removed from the reformate, the remaining gas mixture is called raffinate.

In essence, reforming a fossil fuel consists of the following steps:

1. Feedstock purification (including sulfur removal).
2. Steam reforming or oxidation of feedstock to form hydrogen and carbon oxides.
3. Primary purification—conversion of carbon monoxide to carbon dioxide.
4. Secondary purification—further reduction of carbon monoxide.

The reforming reactions require the input of water and heat. Overall reformer thermal efficiency is calculated as the LHV of the product hydrogen divided by the LHV of the total input fuel. This thermal efficiency depends on the efficiencies of the individual processes, the effectiveness to which heat can be transferred from one process to another, and the amount of energy that can be recovered through means such as turbochargers. In the end, high temperature reformer efficiencies are approximately 65% and low temperature methanol reformers can achieve 70 to 75%.

The advantages of reforming fossil fuels are that they:

- uses existing fuel infrastructures
- reduces the need to transport and store hydrogen

- does not need the input of large amounts of energy as in electrolysis
- is less expensive than other hydrogen production methods

The disadvantages of reformers are that they:

- can have relatively long warm-up times
- are difficult to apply to vehicle engines because of irregular demands for power (transient response)
- are complex, large and expensive
- introduce additional losses into the energy conversion process, especially those that have small thermal mass
- use non-renewable fossil fuels
- generate pollution

The pollution generated by reformers take three forms:

- carbon dioxide emissions
- incomplete reactions, leaving carbon monoxide and some of the source fuel in the reformate
- production of pollutants through combustion, such as nitrous oxides

Reforming fossil fuels only makes sense if the hydrogen is needed directly, as in a fuel cell engine. For internal combustion engines, it is always more efficient to use the fossil fuel directly without passing it through a reformer first.

Medium- or large-size reformers can be installed at fuel cell vehicle fueling stations. At these scales, the equipment complexity, warmup time and transient response are not issues, pollutants can be controlled more effectively, and existing power infrastructures can be used. The facility must store only small amounts of hydrogen, and hydrogen transportation is avoided.

Small-size reformers can be installed in fuel cell vehicles to entirely eliminate the problems associated with fueling, storing and handling hydrogen directly. In fact, many fuel cell experts think that the true challenge in fuel cell engine design now lies in the development of an efficient, compact, reliable and highly integrated fuel processor. Other experts think that the use of on-board reformers will never pose a realistic solution due to their size, complexity and cost.

Figure 2-6 Medium-Scale Natural Gas Reformer

2.1.2.1 Potential Reforming Fuels

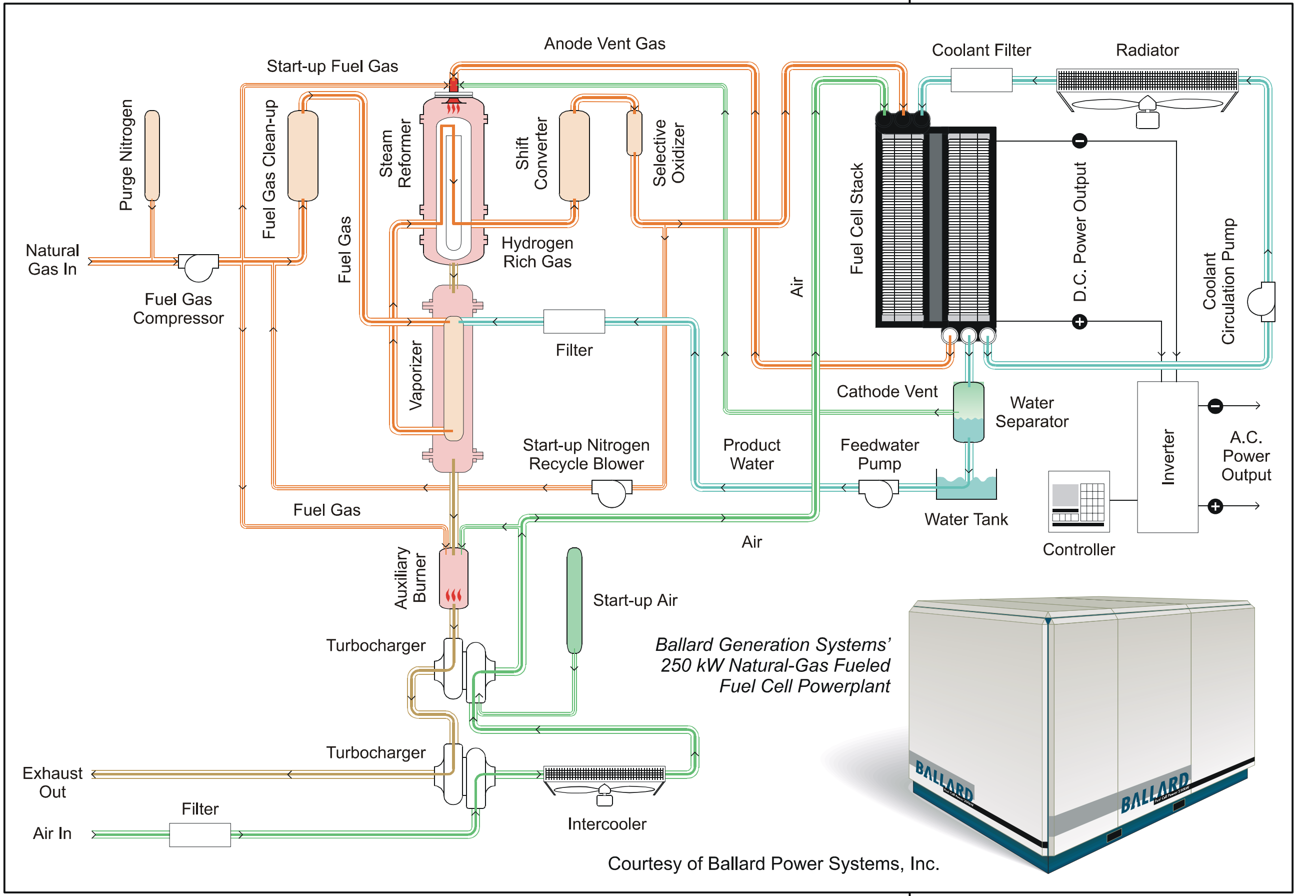
In theory, any hydrocarbon or alcohol fuel can serve as a feedstock to the reforming process. Naturally, fuels with existing distribution infrastructures are the most commonly used.

Methane (Natural Gas)

Natural gas has a well-established infrastructure and is the most economical of all reforming feedstocks. Natural gas contains low levels of sulfur compounds (primarily mercaptans) that must be removed, as they would block active catalyst sites in the reformer and fuel cells. These sulfur compounds requires fuel purification (hydro-desulfurization) prior to reforming.

Key Points & Notes

This natural gas reformer uses a partial oxidation reation, a water/gas shift reaction, and pressure swing adsorption techniques to generate up to 4,200 sft^3/hr (1,980 slpm) of hydrogen. The hydrogen purity is 99.999%. Maximum water consumption is 4,000 gal/day (15,100 L/day).



Courtesy of Ballard Power Systems, Inc.

Figure 2-7 Typical Fuel Cell Process Schematic with Integral Natural Gas Stationary Reformer

Since methane is a gas at atmospheric conditions, it cannot be used to advantage on an on-board vehicular fuel processor, although it is an excellent source for stationary fuel reformers. Propane has similar reforming characteristics to natural gas.

Methanol

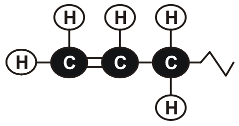
Methanol is readily available and is a favorite for on-board vehicular fuel processors as it can be reformed at relatively low temperatures of 390 to 570 °F (200 to 300 °C). However, methanol has lower energy content and energy density than liquid hydrocarbon fuels.

Gasoline and Diesel

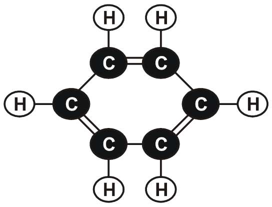
Gasoline and diesel have very well established infrastructures but have a lower hydrogen-to-carbon ratio than other feedstocks. This results in a lower hydrogen yield relative to the amount of waste gas. In general, heavier hydrocarbons also contain sulfur trapped in long chains and cyclic compounds that typically require higher processing pressures of 90 to 650 psig (6 to 45 barg) to remove.

In addition, petroleum products include compounds called olefins and aromatics that result from the refining process. Olefins are highly reactive and tend to form polymer gums or carbon. Aromatics are very stable and difficult to reform and may form carbon. Both gum and carbon formation block active catalyst sites and their formation are highly dependent on processing temperature. The presence of sulfur, olefin and aromatic compounds requires fuel purification and pre-reforming processes prior to reforming.

Key Points & Notes



Olefin



Aromatic

Coal

Coal has enormous supply potential but suffers from high impurity levels, low hydrogen yield, and is difficult to handle. Coal could only be reformed at large dedicated facilities and therefore faces the problems associated with transporting and storing hydrogen. Currently, coal reforming is the most expensive of all reforming methods.

Reformate Composition Comparison

Typical reformate compositions are indicated in Table 2-1. For each source fuel, the yield is calculated based on both steam reforming and partial oxidation (POX) reforming techniques. In both cases, the resulting carbon monoxide is then converted to carbon dioxide using a water/gas shift reaction followed by a selective oxidation reaction. (These techniques are described in the sections that follow.)

	Methane		Methanol		Gasoline/Diesel		Coal	
	Steam	POX	Steam	POX	Steam	POX	Steam	POX
Hydrogen	75.7%	47.3%	71.1%	37.8%	71.1%	37.8%	63.1%	23.6%
Nitrogen	1.9%	33.5%	1.9%	39.8%	1.9%	39.8%	1.9%	49.2%
Carbon Dioxide	19.9%	16.7%	24.5%	19.9%	24.5%	19.9%	32.5%	24.7%
Source Fuel/Other	2.5%	2.5%	2.5%	2.5%	2.5%	2.5%	2.5%	2.5%

Table 2-1 Typical Reformate Compositions

All oxygen is added in the form of air. Any excess water used in the reforming or purification reactions may contribute to the humidification of the gas mixture, but is not indicated as a portion of the overall mixture.

Reformate can be used directly in (PEM) fuel cells instead of pure hydrogen although this has five important implications:

- Firstly, the carbon monoxide and source fuel impurities must be reduced to acceptable levels, as they are fuel cell poisons.
- Secondly, any unreacted *liquid* source fuel that passes into the fuel cells obstructs the power generation reaction.
- Thirdly, although nitrogen, carbon dioxide and gaseous source fuels pass through the fuel cells without detrimental effect, they dilute the amount of hydrogen present so that the fuel cell stacks and affiliated system equipment must be larger than if running on pure hydrogen.
- Fourthly, the presence of gases other than hydrogen precludes the use of the fuel in a "dead-ended" manner: pure hydrogen can be recirculated through a fuel cell until entirely consumed, whereas reformate must pass through and be vented to prevent the steady accumulation of non-reactive gases. Since fuel cells must operate with more fuel than is stoichiometrically required, this results in direct hydrogen wastage with an associated overall loss in efficiency.
- Fifthly, use of reformate usually eliminates the need for a fuel humidifier since the reforming process leaves the gas saturated with water.

2.1.2.2 Types of Reformers

Reformers are of three basic types: steam reformers, partial oxidation reactors and thermal decomposition reactors. A fourth type results from the combination of partial oxidation and steam reforming in a single reactor, called an autothermal reformer.

Steam Reformers

Steam reformers are currently the most efficient, economical and widely used technique of hydrogen production. Steam reforming is based on the principal that hydrogen-containing fuels decompose in the presence of steam over nickel-based catalysts to produce a mixture of hydrogen and carbon monoxide. The steam reforming process is illustrated schematically in Figure 2-8. The overall reaction for generic hydrocarbons is:

$$C_nH_m + n\ H_2O + heat \Rightarrow n\ CO + (n + m/2)\ H_2$$

Key Points & Notes

When applied to methane, the overall reaction reduces to:

$CH_4 + H_2O + heat \Rightarrow CO_2 + 2\ H_2$

For methanol:

$CH_3OH + H_2O + heat \Rightarrow CO_2 + 3\ H_2$

Key Points & Notes

The output products also contain some unreacted source fuel and water. In addition, only light hydrocarbons can be completely vaporized without leaving a carbon residue. The carbon monoxide must be converted to carbon dioxide using supplementary processes (Section 2.1.2.3).

A great benefit of steam reforming is that the hydrogen present in the water is released during the reaction and contributes to the overall hydrogen yield.

The steam reforming process typically requires temperatures of 840 to 1700 °F (450 °C to 925 °C) and pressures of approximately 290 to 500 psig (20 to 35 barg). These temperatures are achieved through combustion of a portion of the reformate. These flame temperatures are too low to form nitrous oxides, which begin forming at temperatures above 2700 °F (1480 °C).

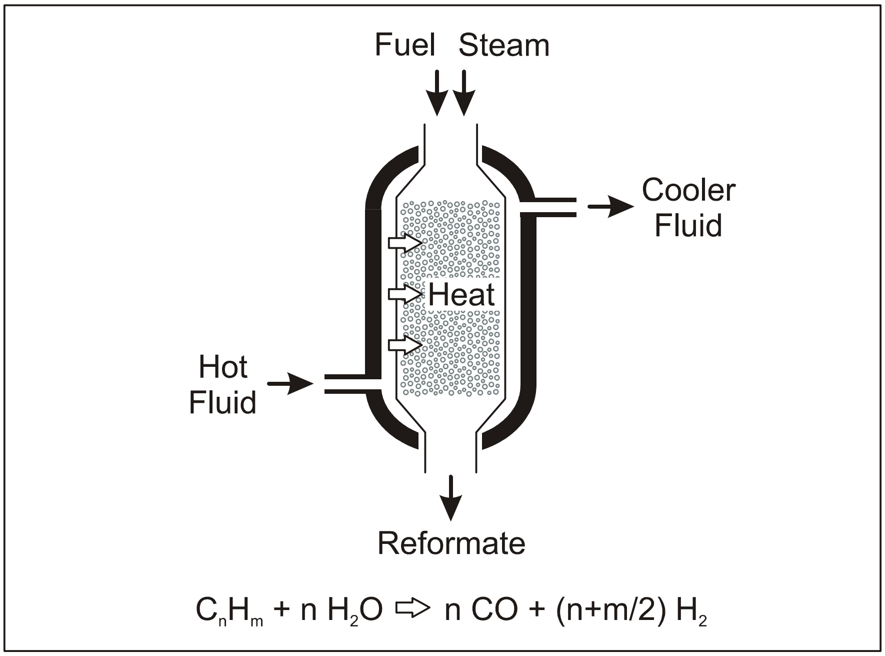
Since the overall steam reforming reaction is endothermic (uses heat), the bulk of the heat energy can be recovered by feeding it back into the process. The extent to which the heat energy is recovered determines the thermal efficiency of the reformer, and can be as high as 85%. This high thermal efficiency is the primary feature of steam reformers.

Thermal efficiencies can reach 90% when steam reforming methanol. This is because the decomposition reaction occurs at the much lower temperatures of 390 to 570 °F (200 to 300 °C), decreasing thermal losses accordingly.

In addition to temperature and pressure, the fuel-to-water ratio plays a significant role in promoting the formation of hydrogen while suppressing undesired reactions. This water must either be drawn from an external source, or, if used in conjunction with a fuel cell, drawn from the fuel cell product water stream.

The complex interactions between the fuel-to-water ratio, available heat, thermal mass and hydrogen demand result in relatively slow startup characteristics and poor response to transient demands for steam reformers. As a result, steam reformers for automotive applications require complex control systems and creative engineering practices. Designs must be optimized to provide high surface area for heat transfer, high thermal inertia during transients and compact reactor dimensions.

Key Points & Notes



$$C_nH_m + n\,H_2O \Rightarrow n\,CO + (n+m/2)\,H_2$$

Figure 2-8 Steam Reforming Process

Steam reformers are not inherently compact. For a typical car, a methanol steam reformer would need a catalyst volume of 1.3 to 1.8 gallons (5 to 7 L) and a tank volume for the methanol/water mixture about three times the size of a comparable gasoline or diesel tank.

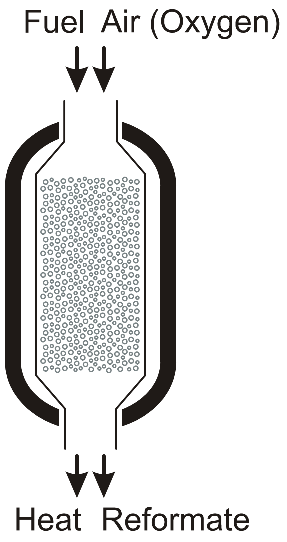
Partial Oxidation Reformers

Partial oxidation reformers (or “POX” reformers) react a lean mixture of oxygen (air) with fuel to produce a mixture of hydrogen and carbon monoxide. The partial oxidation process is illustrated schematically in Figure 2-9. The overall reaction for generic hydrocarbons is:

$$C_nH_m + n/2\,O_2 \Rightarrow n\,CO + m/2\,H_2 + \text{heat}$$

Since partial oxidation reformers use oxygen from air, nitrogen passes through the reactor along with the reaction products, thereby diluting the fuel stream. The output products also contain some unreacted source fuel. The carbon monoxide must be converted to carbon dioxide using supplementary processes (Section 2.1.2.3).

Unlike stream reformers, partial oxidation reformers are typically used to reform heavier hydrocarbons such as gasoline, diesel and heavy oil. A form of partial oxidation is used to gasify coal although the presence of sulfur and large amounts of ash, both of which must be removed, further complicates this process. These processes do not use catalysts and occur at 2100 to 2400 °F (1150 to 1315 °C) and on the order of 880 psig (60 barg). Lighter hydrocarbons, such as methane, can be partially oxidized using catalysts at 1090 °F (590 °C).



$$C_nH_m + (n/2)\ O_2 \Rightarrow n\ CO + (m/2)\ H_2$$

Figure 2-9 Partial Oxidation Process

Partial oxidation reformers offer both disadvantages and advantages compared to stream reformers. The key disadvantages of partial oxidation reformers are higher operating temperatures and pressures, lower thermal efficiency and lower hydrogen yield. The lower thermal efficiency stems primarily from the fact that the oxidation process in exothermic (releases heat). This means that a significant portion of the inlet fuel energy ends up as heat, which cannot be utilized by the reactor itself, nor by the fuel cell. The lower yield results from the fact that additional hydrogen is not added to the reaction in the form of water. The hydrogen yield is also diluted by large amounts of nitrogen when the oxygen is added in the form of air.

Larger heat rejection requirements also result in higher parasitic cooling losses. In a pressurized partial oxidation reactor, some of the waste energy can be recovered using a burner/turboexpander combination to help pressurize the fuel cell process air. Nonetheless, exothermic partial oxidation reformers always face an overall efficiency handicap of 5 to 10% compared to endothermic steam reformers.

The effect of increased hydrogen dilution (due to the presence of nitrogen) increases the size of supplemental reformate purification equipment, and requires a larger fuel cell stack for a given power output.

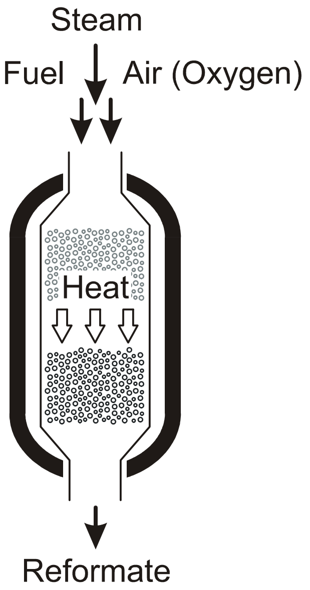
The key advantages of partial oxidation reformers are their relative compactness, and potentially good startup and load-following characteristics. The improvement in these areas is related to the exothermic nature of the oxidation reaction — there is no time lag for heat transfer from external sources. Furthermore, partial oxidation processes offer the potential to use readily available gasoline and diesel supplies.

Autothermal Reformers

Autothermal reformers attempt to combine the compactness and load following capabilities of partial oxidation reactors with the efficiency of steam reformers by combining the two reactors in one unit. The autothermal process is illustrated schematically in Figure 2-10. The overall reactions for generic hydrocarbons are:

$$C_nH_m + n/2\ O_2 \Rightarrow n\ CO + m/2\ H_2 + \text{heat}$$

$$C_nH_m + n\ H_2O + \text{heat} \Rightarrow n\ CO + (n + m/2)\ H_2$$



$$C_nH_m + (n/2)\ O_2 \Rightarrow n\ CO + (m/2)\ H_2$$

$$C_nH_m + n\ H_2O \Rightarrow n\ CO + (n+m/2)\ H_2$$

Figure 2-10 Autothermal Process

In an autothermal reformer, fuel, steam and oxygen (or air) are fed over a mixed catalyst bed that supports both partial oxidation and steam reforming reactions. The heat generated

Key Points & Notes

by the partial oxidation reaction provides the heat required for the steam reforming reaction, and removes the need for an external burner or heat source. This process requires careful thermal integration and tight controls to ensure heat balance and temperature matching between the two reactions.

While autothermal reformers overcome some of the efficiency limitations of partial oxidation reformers, they still operate at efficiencies below those of steam reformers and result in a dilute hydrogen stream. Furthermore, autothermal reformers are the least developed of all reformer systems and still require significant engineering effort before they become practical.

Thermal Decomposition Reformers

Thermal decomposition reformers (or "catalytic crackers") use heat to break down source fuels yielding high purity hydrogen (>95%) and solid carbon. The thermal decomposition process is illustrated schematically in Figure 2-11. The overall reaction for generic hydrocarbons is:

$$C_nH_m + \text{heat} \Rightarrow n\,C + m/2\,H_2$$

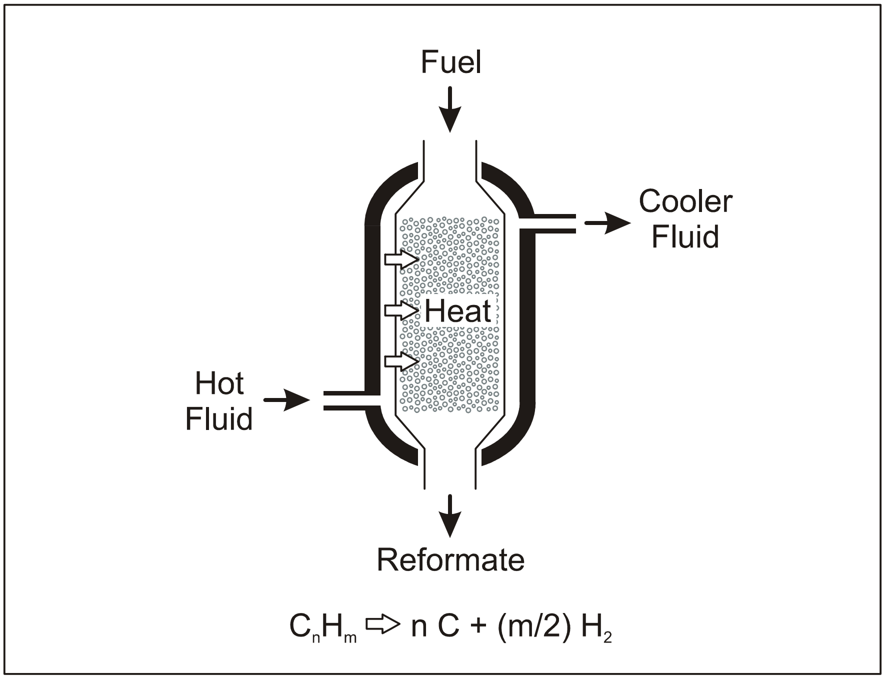


Figure 2-11 Thermal Decomposition Process

Thermal decomposition reformers are very compact with quick startup and load-following characteristics but have the lowest thermal efficiency of any of the reforming systems (55–65%). The thermal efficiency is so low partly because a great deal of the source fuel's energy remains trapped in the product carbon (rather than in the lower energy forms of carbon monoxide or carbon dioxide). Efficiencies would improve significantly if the product carbon could be burned for heat generation, but this would lead to undesirable emission levels of nitrous oxides and would substantially increase system complexity.

2.1.2.3 Reformate Purification

Steam, partial oxidation and autothermal reformers all convert the carbon contained in the source fuel into carbon monoxide. Depending on the feedstock, the reformate stream can also include sulfur compounds, liquid methanol other contaminants. All of these compounds poison or degrade fuel cell performance and must be removed to very low levels. For example, alkaline fuel cells can tolerate no more than 3% (by volume) carbon monoxide, and PEM fuel cells can tolerate no more than 50 ppm carbon monoxide. Other reformate gases, such as nitrogen and carbon dioxide, dilute fuel cell performance but do not damage the cells.

Reformate purification is a two-stage process. In the first stage, the bulk of the carbon monoxide is transformed into carbon dioxide using a water/gas shift reaction. In the second stage, the amount of carbon monoxide is further reduced using selective oxidation or methanation reactions, and/or the hydrogen is extracted from the reformate stream using a pressure swing adsorption process or by means of metal separation membranes.

The amount of reformate purification chosen is a trade-off between fuel cell longevity and performance, and overall system complexity, size and cost.

Water/Gas Shift Reaction

The water/gas shift reaction reacts carbon monoxide with steam over a catalyst to produce a mixture of hydrogen and carbon dioxide. The shift reaction process is illustrated schematically in Figure 2-12. The overall reaction is:

$$CO + H_2O \Leftrightarrow CO_2 + H_2 + \text{heat}$$

The water/gas shift reaction can be performed using high-temperature catalysts that support the reaction in excess of 570 °F (300 °C), or using low-temperature catalysts that support the reaction to about 285 °F (150 °C).

The water/gas shift reaction is an exothermic process; this heat can be recovered and used in other parts of the reforming process to improve the overall thermal efficiency. Some shift reaction catalysts also oxidize exothermically when exposed to air. This can result in high temperatures that can pose a fire hazard and/or damage the catalyst.

Key Points & Notes

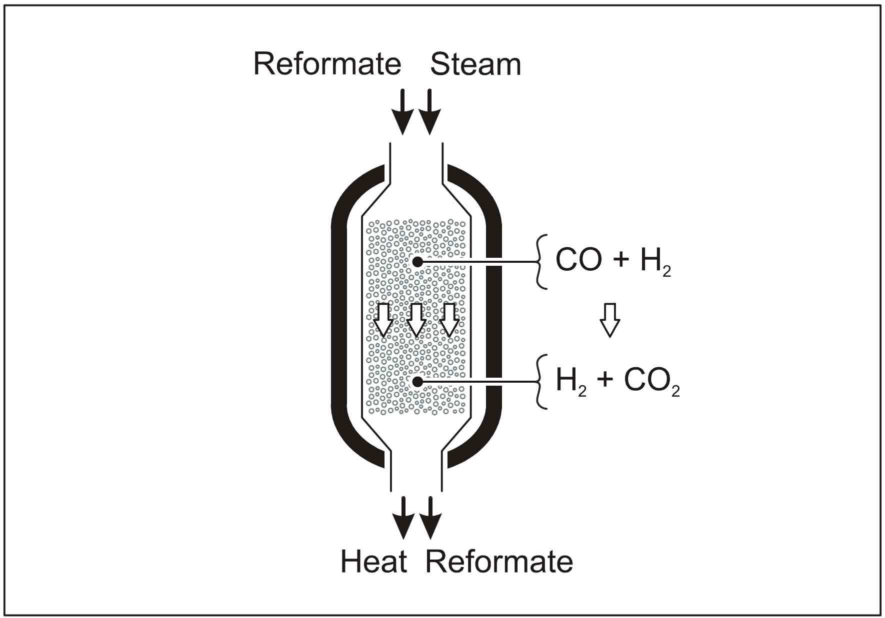


Figure 2-12 Water/Gas Shift Reaction Process

Like in a steam reformer, the water for the shift reaction must either be drawn from an external source, or if used in conjunction with a fuel cell, drawn from the fuel cell product water stream.

The water/gas shift reaction is an efficient method of eliminating the bulk of carbon monoxide in a reformate stream. Carbon monoxide typically comprises between 15 and 60% of the reformate stream, depending on the feedstock used. The water/gas shift reaction can reduce this to levels less than 1%, and even as low as 0.2%.

Selective Oxidation

Selective oxidation (or “selox”) is a chemical process that reacts carbon monoxide with oxygen (air) over a catalyst to produce carbon dioxide. The selective oxidation process is illustrated schematically in Figure 2-13. The catalyst bed facilitates both of the following competing reactions:

$$CO + \tfrac{1}{2}O_2 \Rightarrow CO_2 + \text{heat}$$

$$H_2 + \tfrac{1}{2}O_2 \Rightarrow H_2O + \text{heat}$$

The former reaction is preferred and is selected by controlling the temperature profile within the selective oxidizer. Temperatures that are too high favor the water-producing

Key Points & Notes

reaction whereas temperatures that are too low result in condensation. The selective oxidation reaction is an exothermic process; this heat can be recovered and used in other parts of the reforming process to improve the overall thermal efficiency.

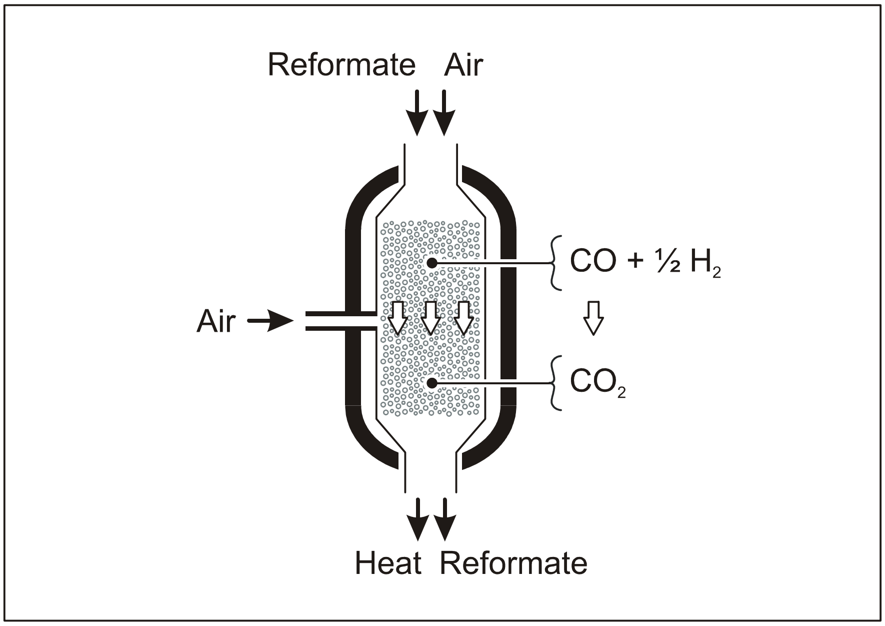


Figure 2-13 Selective Oxidation Process

Selective oxidation is the most compact of all purification methods and is capable of reducing carbon monoxide content to very low levels, such as 5 to 10 ppm. The main drawback of selective oxidizers is that they require complex control systems, especially to maintain low carbon monoxide levels during load transients.

Methanation

Methanation is a chemical process that reacts carbon monoxide and carbon dioxide with hydrogen to produce methane and water. The methanation process is illustrated schematically in Figure 2-14. The overall reactions are:

$$CO + 3\ H_2 \Rightarrow CH_4 + H_2O + \text{heat}$$

$$CO_2 + 4\ H_2 \Rightarrow CH_4 + 2\ H_2O + \text{heat}$$

These reactions are the opposite of those that occur during steam reforming of methane and are therefore reversing the hydrogen production initially accomplished. If this process were performed on the reformate stream directly, virtually all of the product hydrogen would be consumed with no net yield. However, if the carbon dioxide is removed prior to methanation using some other means (such as pressure swing adsorption), the remaining carbon monoxide can be successfully reduced to very low levels with little loss in overall hydrogen yield.

When reforming methanol, the methanation process has the side benefit of simultaneously converting previously unreacted methanol into carbon dioxide, hydrogen or methane. This not only increases the hydrogen yield, but also reduces the chance of liquid methanol entering the fuel cells where it can obstruct the power generation reaction.

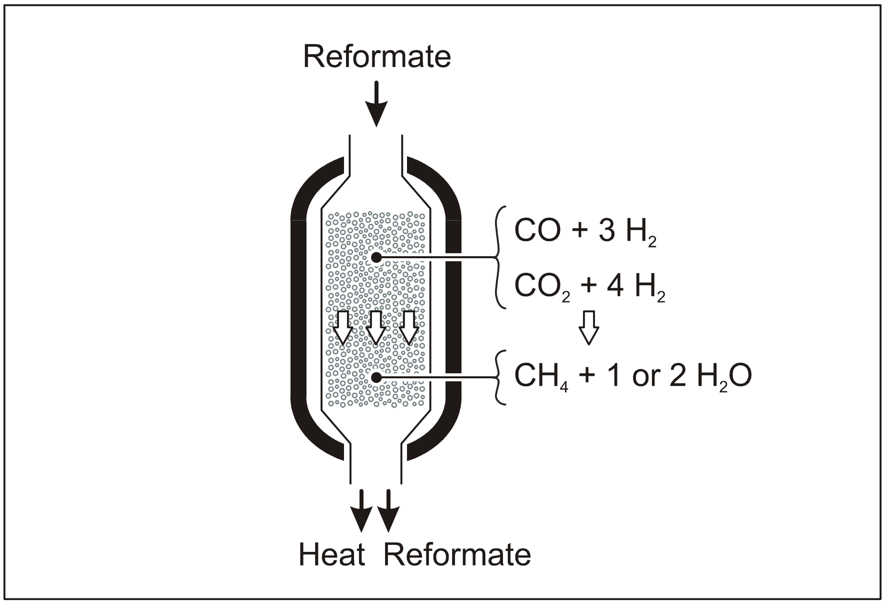


Figure 2-14 Methanation Process

Pressure Swing Adsorption (PSA)

Pressure swing adsorption (or “PSA”) is a common industrial method of separating a gas mixture into its various components. This technology has been used extensively in combination with steam reformers to extract hydrogen on an industrial scale. Very high purity is attainable (99.99%) while recovering up to 85% of the available hydrogen.

At the heart of the pressure swing adsorption process are materials called zeolites. A zeolite is a mineral with a highly structured crystalline surface that attracts gas molecules to its surface and holds them there through physical adsorption (*adsorb* means “to stick to the surface of”. This is different from *absorb* that means “to penetrate into the surface of”). Many different types of zeolites are manufactured commercially, each capable of selectively adsorbing specific gases or groups of gases. Combinations of zeolites can therefore be tailored to form “molecular sieves” capable of trapping unwanted gases while allowing desired gases to pass

Key Points & Notes

unaffected. Pressure swing adsorption devices are routinely built to separate oxygen from air in the same manner that hydrogen is separated from fuel.

Physical adsorption involves relatively weak “van der Waals” and electrostatic forces. These bonds are easily broken when subjected to pressure and flow variations. This principle is used to flush the trapped unwanted gases out of the zeolites after the purified product has been removed. The pressure difference between the initial gas mixture and the exhaust stream drives the process; hence the term pressure swing adsorption. Repeated cycles result in a continuous flow of purified product.

Specifically, the pressure swing adsorption process involves four primary phases that together make up a complete cycle. During the first, or “feed pressurization” phase, reformate gas is introduced to the zeolite bed at high pressure. During the second, or “production” phase, the unwanted gases are adsorbed by the zeolites while purified hydrogen concentrates at the top of the bed and is drawn off. During the third, or “depressurization” phase, the pressure is reduced and some of the unwanted gases are expelled. During the fourth, or “low pressure purge” phase, some of the pure hydrogen gas is back-flushed through the bed at low pressure in order to desorb and purge out the remaining unwanted gases. The pressure swing adsorption process is illustrated schematically in Figure 2-15.

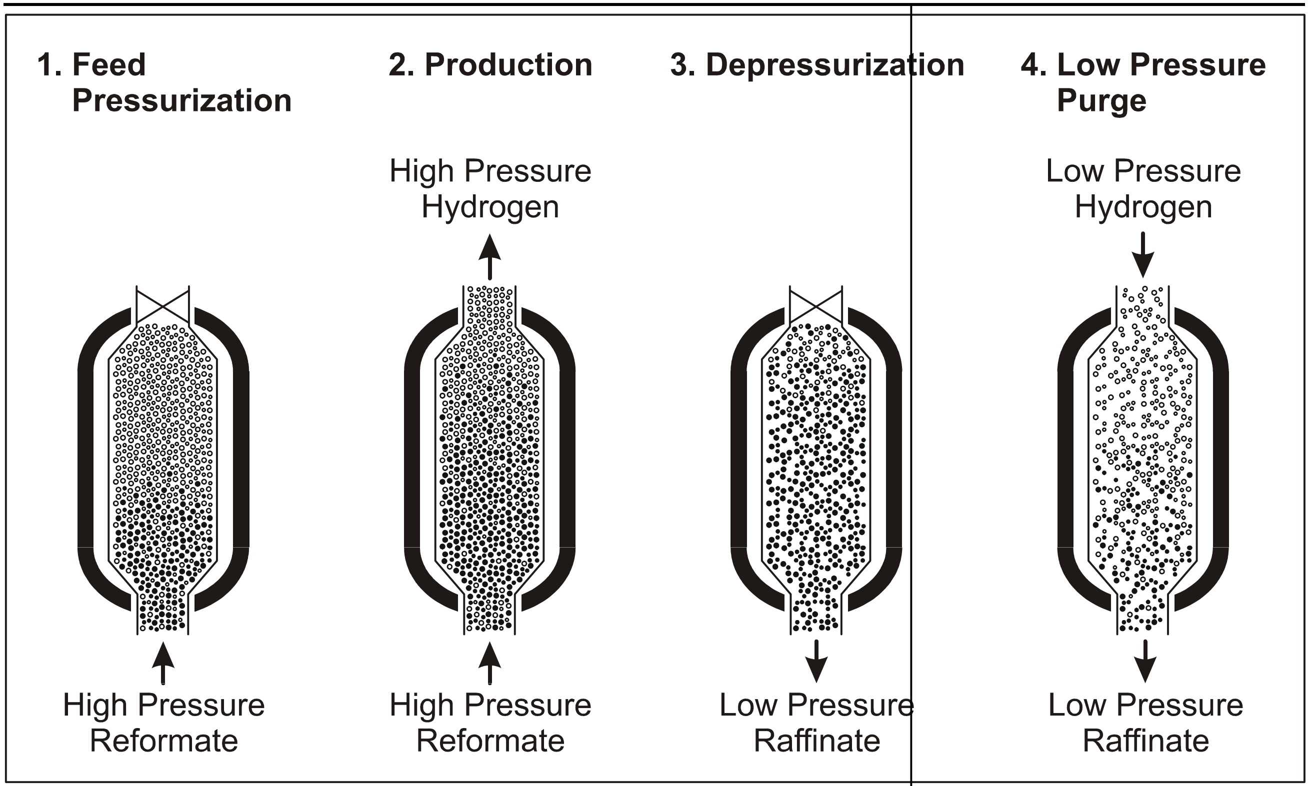


Figure 2-15 Pressure Swing Adsorption Process

Conventional pressure swing adsorption machines use stationary beds filled with small porous pellets formed of zeolite crystals mixed with a clay binder. These pellets can be as small as 0.5 mm in diameter but are more typically 2 or 3 mm in diameter. This configuration results in a very high surface area and therefore large adsorption capacity, but the size and arrangement of the pellets inhibits rapid gas transfer in and out of the pellets.

When operated quickly, the pellet arrangement results in a high pressure drop, fluidization (the pellets lift with the gas and act like a fluid), and attrition (the pellets rub together, break apart, and disappear). To compensate, conventional machines must operate at very low speed (typically at 0.5 cycles/min) and tend to be large. However, new developments in pressure swing adsorption technology use a proprietary adsorbent structure and novel rotary valve technology that allow two orders of magnitude increase in the gas separation cycle speed without fluidization or attrition. This allows the construction of devices that are a fraction of the size of conventional units with the potential for use on-board vehicles.

Courtesy of QuestAir Technologies Inc.

Figure 2-16 QuestAir Technologies' State-of-the-Art Compact Pressure Swing Adsorption Device

The greatest problem associated with using pressure swing adsorption in conjunction with fuel cells is the fact that the gases that come into contact with the zeolites must be completely dry. This is because water adsorbs onto the surface of the zeolites and forms strong bonds that involve electron transfer and other strong forces. This is known as *chemical* adsorption, and is different from the *physical* adsorption that occurs with the waste gases.

Chemical adsorption bonds are too strong to be broken using pressure and flow fluctuations. As a result, these bonds displace potential physical adsorption bonds and render the zeolite bed less effective, ultimately disrupting the pressure swing adsorption process. Once formed, chemical adsorption bonds require heat to be broken. To prevent these bonds from forming, a desiccant must be used to adsorb water from the incoming wet gas stream before it comes into contact with the zeolites. This can be done concurrent with, and within the same machine as, the gas separation process so that there are two pressure swing adsorption cycles operating — one for water separation and the other for hydrogen.

Metal Separation Membranes

Metal separation membranes present an impermeable physical barrier to all gases except hydrogen.

Key Points & Notes

To function, the reformate must be delivered to the membrane across a pressure gradient. Up to 85% of the hydrogen then diffuses from the high pressure (300 psig; 20 barg) reformate stream to form a low-pressure (30 psig; 2 barg) stream of very high purity (>99.999%). The remaining high-pressure raffinate can be combusted to provide heat for the reforming process. The metal separation membrane process is illustrated schematically in Figure 2-17.

The advantages of metal separation membranes are that they provide high purity, undiluted hydrogen in a compact, simple and reliable manner. Metal separation membranes are also well suited to thermal integration with steam reformers and respond well to thermal transients.

The primary disadvantage of metal separation membranes is their very high material and construction costs. Traditionally, metal separation membranes are the most costly of all purification techniques, owing to their use of silver palladium or other alloys and the need to eliminate all pinholes and sealing leaks. However, new developments using thin film membranes promise to lower the materials cost to practical levels.

Other drawbacks to metal separation membranes include the need to re-humidify the hydrogen prior to use by fuel cells, and the need for a pressurized reformer. The use of a pressurized reformer results in increased reformer weight and size, although this is offset somewhat by the elimination of other purification equipment.

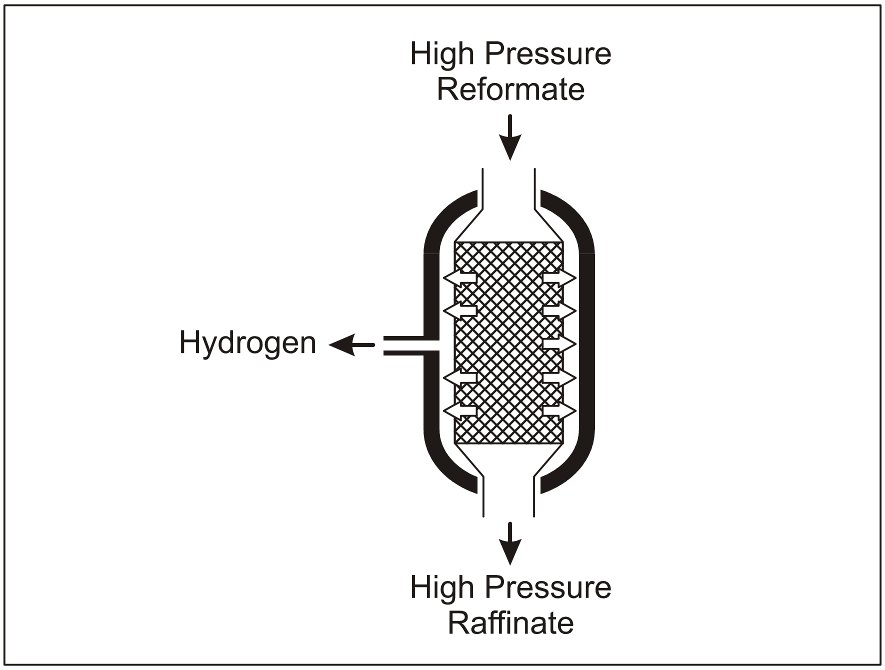


Figure 2-17 Metal Separation Membrane Process

2.1.2.4 Heat Generation

Heat is an essential part of any reforming process. For endothermic reactions, such as steam reforming and thermal decomposition, heat must be supplied from an external source. For exothermic reactions, such as partial oxidation and autothermal reactions, heat is generated internally by the reaction itself.

The water/gas shift, selective oxidation, and methanation reformate purification reactions are also exothermic. Central to the thermal efficiency of a reformer is the thermal integration of both the reforming and purification stages. Through careful engineering design, heat can be moved from one part of the process to another, reducing the amount of net heat that must be added or removed.

Exothermic reactions have better startup and transient response than endothermic reactions as the heat of reaction is immediately available without the time lag associated with adding heat. Despite this advantage, exothermic processes can require complex control strategies in order to control temperatures and avoid overheating catalysts and materials over the entire operating range. Excess heat from exothermic reactions must be dissipated through a cooling system.

Endothermic reactions require the addition of heat in concert with the instantaneous load demand. To some extent, this problem can be lessened by designing reformers with high thermal inertia that tend to smooth out the differences between transient peaks and valleys. Nevertheless, heat must be added using burners and complicated control systems that attempt to provide the required heat on demand.

Key Points & Notes

Typical burner designs use flames or catalytic combustors, with or without a thermal buffer. Burners are usually fueled using the hydrogen-depleted raffinate, the fuel cell anode exhaust stream, a portion of the reformate, or some of the source fuel. Combustion can lead to NOx emissions if the burner temperature exceeds 2700 °F (1480 °C).

Flame Burners

Flame burners generate heat through the direct combustion of the fuel with air.

Flame burners can supply the radiant heat of combustion directly to a metal reactor wall. This is a very common approach for high temperature steam reformers, and can also be applied in low temperature reforming systems.

Flame burning has the advantage of mechanical simplicity, although hot spots can easily occur where the flame contacts the reactor. This can lead to localized overheating and catalyst degradation, especially when used in a low temperature application. To overcome this, a thermal buffer can be used as an intermediate heat transfer medium, smoothening out the temperature profile.

Thermal buffers usually take the form of flue gases or thermal fluids, such as heating oils. Oils are applicable only to low-temperature reformer designs. Oils are particularly advantageous since they have high heat capacity, which allows heat to be stored in a small amount of fluid at temperatures significantly lower than that of the flame. This high heat capacity also allows the reformer to operate at a nearly constant temperature for optimum efficiency. Heat from an oil buffer can be transferred to the reformer and to the vaporizer beds through a coiled tube embedded in the vessel walls. Overheating remains a concern, though, as thermal oils begin to degrade above 645 °F (340 °C).

Catalytic Combustors

Catalytic combustors generate heat through the combustion of fuel with air over a catalyst such as platinum. This process allows for complete combustion without flames at lower temperatures than would be required without the catalyst. Combustion temperatures can be maintained at temperatures of 1290 °F (700 °C) or less using very lean air/fuel mixtures.

Key Points & Notes

Like flame burners, catalytic combustors can supply the heat of combustion directly to a metal reactor wall or by way of a thermal buffer. In either case, the lower combustion temperature decreases the chance of overheating, either in the reactor or in the thermal oil.

Catalytic combustors also offer the advantages of very complete fuel combustion, low emissions (less than 5 ppm CO and no NOx), and very effective and responsive temperature control. Response to load changes is very fast, which is excellent where rapid startup and good transient response are required.

The disadvantages of catalytic combustors are the increased capital cost associated with the catalyst, and the potential for catalyst poisoning in the event of fuel impurities.

2.1.3 Thermochemical Water Decomposition

In thermochemical water decomposition, heat alone is used to decompose water. This process is similar to electrolysis, with the difference that all the energy is added as heat and none as electricity. The maximum theoretical efficiency for this process is about 50%.

Water decomposes directly at very high temperatures (>4500 °F; 2500 °C) which is too high to be practical. Instead, chemical reagents are used to decompose water in multi-step chemical reactions in the following sequence:

1. Oxygen production
2. Hydrogen production
3. Materials regeneration

These reactions take the generic form of:

$$AB + H_2O + \text{heat} \Rightarrow A\,H_2 + B\,O$$

$$A\,H_2 + \text{heat} \Rightarrow A + H_2$$

$$2\,BO + \text{heat} \Rightarrow 2B + O_2$$

$$A + B + \text{heat} \Rightarrow AB$$

This is essentially an oxidation-reduction reaction where A and B are chemical compounds that commonly include iron, oxygen or chlorine. This process can take place at about 1290 °F (700 °C).

Selection of the specific chemical compounds for the reaction series depends on such factors as the:

- amount of energy needed for each step
- stability of the reactants for each step
- ability for the products of one step to be easily reacted in the next
- reaction time
- reaction yield
- individual reaction temperature
- pressure and flow requirements
- number of steps
- amount of cleanup required
- composition of waste products

In addition, as with any other chemical process, heat recovery, mass transfer and materials issues affect the overall system design.

Thermochemical water decomposition, like electrolysis, is only as renewable and environmentally clean as its energy source. If waste heat is used from other processes, the resulting hydrogen increases the overall efficiency of the heat-generating parent process. If heat is obtained by burning fossil fuels, the resulting hydrogen will likely have generated more pollution than would have been by using the source fuel directly.

2.1.4 Photo Conversion

Photo conversion is an electrolysis process by which the electricity needed to decompose water into hydrogen and oxygen is generated directly using solar energy.

Water cannot absorb solar energy directly since it is transparent to the required wavelengths. The most common process uses a series of cells, each with a pair of semi-conductor photoelectrodes immersed in a watery electrolyte and separated by a membrane that allows ion transfer but prevents gas mixing. The cathode, is made of a “p-type” semiconductor material (that has an excess of positive “holes”). The anode, is made of a “n-type” semiconductor material (that has an excess of electrons). This is similar to a solar cell.

When the anode is illuminated by sunlight, electrons absorb the light energy and pass through an external circuit to the cathode. This creates an "electron-hole" pair. The positive hole subsequently reacts with the water to create positive hydrogen ions and gaseous oxygen. The hydrogen ions pass through the membrane to recombine with the electrons at the cathode, resulting in hydrogen gas. Thus, the overall process results in photoelectrolysis of the water.

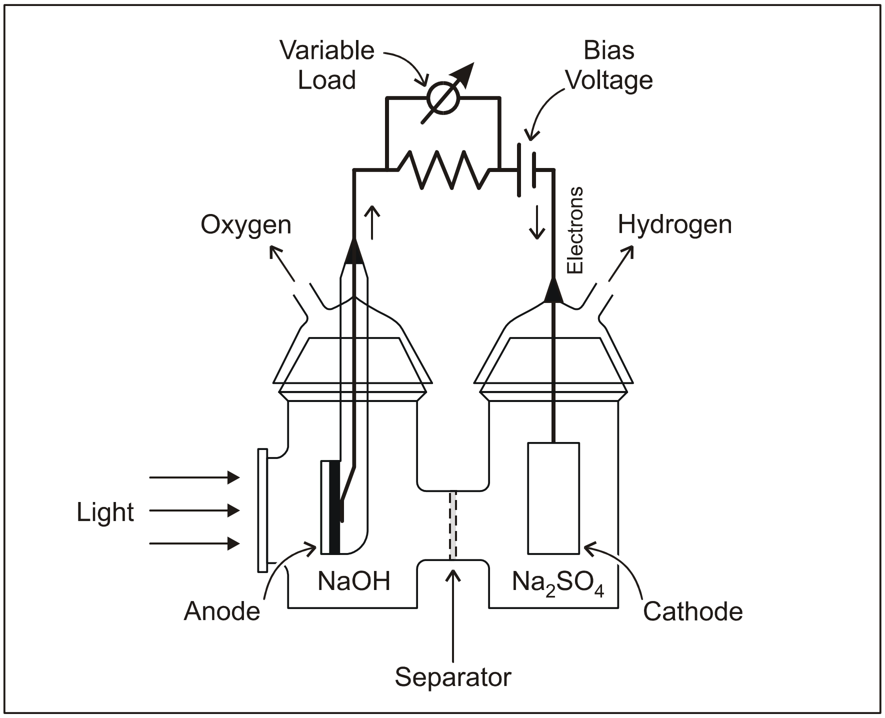


Figure 2-18 Semiconductor Photo Conversion Cell

A related method uses photochemical catalysts, suspended in alkaline or acidic solutions, as opposed to semiconductors. These catalysts absorb photon energy upon illumination, which creates an electric charge that drives a water-splitting reaction.

Like any solar energy power generation process, photo conversion can only work in areas of prolonged, concentrated sunlight. Furthermore, this type of system has maximum efficiencies of between 8 and 12%.

Photobiological Processes

Light energy can also produce hydrogen through photobiological processes, using biological systems such as cyanobacteria (blue-green) algae, photosynthetic algae or eukaryotic (green) algae. In principle, these algae contain hydrogen-metabolizing enzymes that feed off base compounds in an anaerobic environment and release hydrogen gas in the process. These algae use compounds such as water, whey, starches, sugar refinery waste, and distillery waste as electron donors. Unfortunately, the efficiency of these processes is very low; typically less than 1%.

2.1.5 Production from Biomass

Hydrogen can be produced from the decomposition of biomass. Biomass comprises all manner of plant and animal material that can be converted into energy. Biomass is organic in nature and can be derived from a variety of sources including residues, wastes and crops. Residues include the materials left over after the harvest of crops or trees. Wastes include those from food processing plants, sewage and municipal solid waste. Crops include those that can be grown specifically for their energy content, such as soybeans, trees and woody plants, among many others.

Key Points & Notes

Potential U.S. biomass supplies for energy purposes have been estimated to be the energy equivalent of 7 million barrels of oil per day: 40% from biomass waste resources and 60% from biomass energy crops grown on 80 million acres of excess agricultural lands.

The appeal of hydrogen production from biomass is the obvious abundance of waste materials and its subsequent potential to supply large amounts of hydrogen. The primary problems are that the process is land and water intensive, and is hampered by the difficulties associated with handling solids. Furthermore, the associated technology is not well developed with the result that it is currently the most expensive means of obtaining hydrogen.

Hydrogen production from biomass takes two primary forms; thermochemical conversion and anaerobic digestion.

Thermochemical Conversion

Thermochemical conversion is a multistage process that includes feedstock pre-processing, gasification, gas cleanup, steam reforming, shift reaction and hydrogen separation (or alternatively, methanol synthesis and purification).

Gasification is at the heart of the thermochemical conversion process. Gasification occurs through the thermal decomposition (or “pyrolysis”) of organic matter with the help of an auxiliary gas such as air, oxygen, or hydrogen to yield primarily gaseous products.

Typically, the feedstock reacts with steam and air (oxygen), at a temperature dictated by the feedstock characteristics, to rapidly yield a mixture of hydrogen, carbon monoxide, carbon dioxide, water and methane along with hydrogen sulfide and other trace impurities.

Hydrogen content is determined by the process temperatures and pressures and can constitute about 20% of the gas mixture. A major disadvantage of direct biomass gasification is the co-production of tars, phenolics and acids. Effective separation and purification of the decomposition products and efficient gas cleanup for the removal of tars and oils remain as technical challenges.

Catalysts can be used to increase production efficiencies, reduce tar formation and eliminate the need for oxygen. The process can become even more profitable if undertaken under pressure, as the equipment needed becomes smaller and less expensive.

Anaerobic Digestion

Anaerobic digestion (or "methane fermentation") is a multi-stage process in which the waste from one set of organisms is the food for another set. This process takes place in an anaerobic environment, usually in a digester, in the presence of a population of anaerobic bacteria.

Anaerobic digestion consists of three basic processes. First, cellulose and hemicellulose are broken down by enzymes to form soluble organic compounds. Then the soluble organic materials are converted to hydrogen, carbon dioxide, formate and acetate by acid-producing bacteria. Finally, methane is produced from those substances by methane-producing bacteria.

The resulting methane gas production is very slow at ambient temperatures, and the digester temperature must be increased to the order of 100 °F (37 °C). The resultant gas has medium fuel value, and the concentration of methane is only slightly higher than its carbon dioxide content. As a result of these two factors, anaerobic digestion processes use almost as much energy as they produce, or even more, depending on the design of the digester and the operating conditions. Although hydrogen can be obtained from methane through steam reforming, this additional step requires too much energy to be cost effective.

2.1.6 Industrial Processes

Hydrogen is produced as a byproduct of some conventional industrial processes. Hydrogen is:

- a byproduct of chlorine and polyvinylchloride production
- a by-product of the sodium hydroxide industry
- produced among other light gases in crude oil refineries
- produced from coal in coke oven gases
- emitted in chemical dehydrogenation processes

Key Points & Notes

Industrial Plant

Generally these by-product sources have insufficient capacity and are too costly to supply large quantities of hydrogen.

Key Points & Notes

2.2 Hydrogen Storage

Key Points & Notes

If the greatest challenge in hydrogen use is to extract it, the second greatest challenge is how to store it. As seen in Section 1, hydrogen has the lowest gas density and the second-lowest boiling point of all known substances, making it a challenge to store as either a gas or a liquid. As a gas, it requires very large storage volumes and pressures. As a liquid, it requires a cryogenic storage system.

Hydrogen’s low density, both as a gas and a liquid, also results in very low energy density. Stated otherwise, a given volume of hydrogen contains less energy than the same volume of other fuels. This also increases the relative storage tank size, as more hydrogen is required to meet a given vehicle’s range requirements. The amount of hydrogen needed for fuel cells is offset somewhat by the fact that it is used more efficiently than when burned in an internal combustion engine, so less fuel is required to achieve the same result.

Despite its low volumetric energy density, hydrogen has the highest energy-to-weight ratio of any fuel. Unfortunately, this weight advantage is usually overshadowed by the high weight of the hydrogen storage tanks and associated equipment. Thus, most hydrogen storage systems are considerably bulkier and/or heavier than those used for gasoline or diesel fuels.

For all practical purposes, hydrogen can be stored as either a high-pressure gas, a liquid in cryogenic containers, or a gas chemically bound to certain metals (hydrides). The volume and weight of each of these systems is compared to gasoline, methanol and battery storage systems (each containing 990,000 Btu (1,044,500 kJ) of stored energy; equivalent to 8.4 gallons of gasoline) in Figure 2-19. Ironically, the best way to store hydrogen is in the form of hydrocarbon fuels although it requires additional systems to extract it.

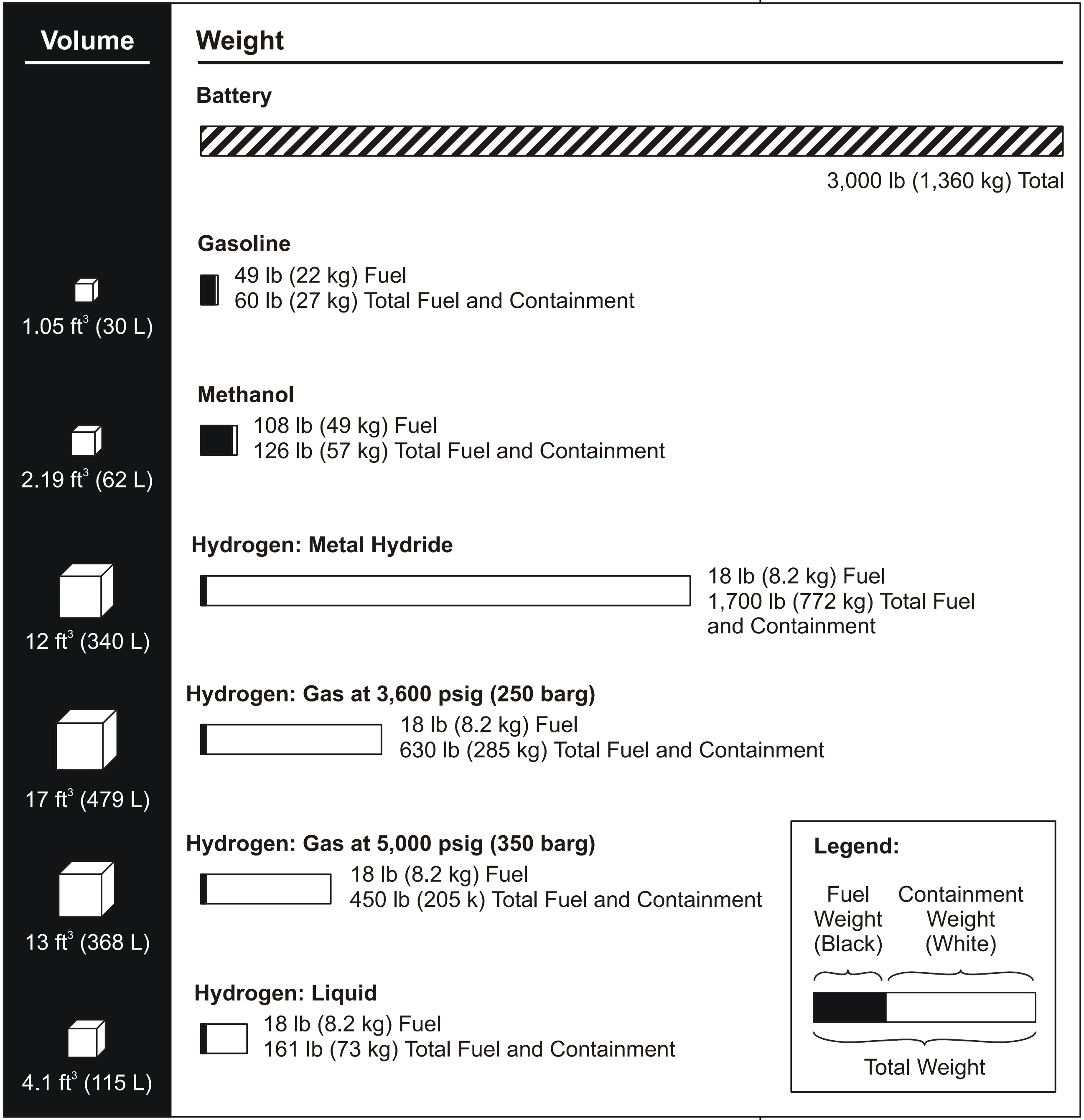


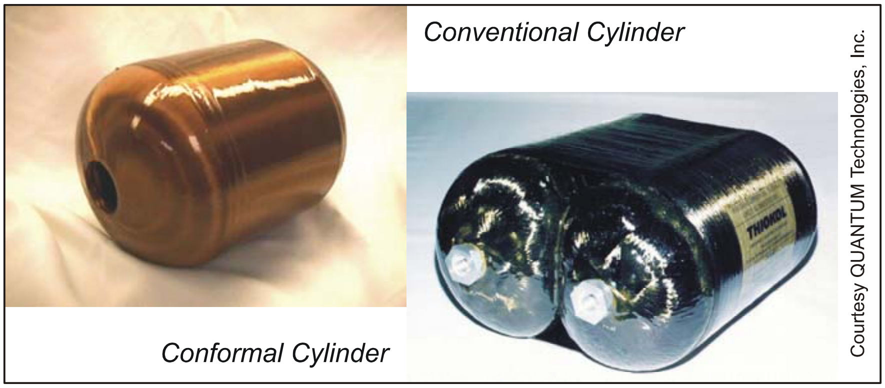
Figure 2-19 Storage Volume and Weight of Comparative Fuels Each With 990,000 Btu (1,044,500 kJ) of Stored Energy

2.2.1 High Pressure Gas

High-pressure gas storage systems are the most common and most highly developed methods of storing hydrogen. Most existing fuel cell vehicles use this form of hydrogen storage.

High-pressure hydrogen is stored in cylinders, similar to those used for compressed natural gas. Most cylinders have a cylindrically shaped sidewall section with hemispherical end domes, although new conformal designs use multiple cylinders in tandem and distort the cylindrical shape in order to increase the usable volume.

Ports in the middle of each end dome allow the gas to flow into and out of the cylinder, with end bosses that control the gas flow. One end boss acts primarily as a plug, although it includes a pressure relief device vent port and may contain pressure and temperature transducers to measure gas conditions within the cylinder. The other end boss is a sophisticated portal device that includes a solenoid valve, an excess flow valve, a manual isolation valve, a check valve and a pressure relief device vent port.



Courtesy QUANTUM Technologies, Inc.

Figure 2-20 High Pressure Hydrogen Cylinder Designs

The solenoid valve is normally closed and isolates the cylinder whenever the vehicle is shut down. The excess flow valve closes whenever the gas flow leaving the cylinder is too great (such as if a pipe bursts). The manual isolation valve allows the cylinder contents to be either isolated or vented manually in the event of solenoid valve failure. The check valve allows fueling while the solenoid valve is closed. The pressure relief devices (at either end of the cylinder) release the cylinder contents when exposed to fire.

High-pressure gas cylinders must be made of thick-walled, high strength materials and must be very durable. Cylinders are classified into four types according to their materials of construction.

Key Points & Notes

The terminology "high pressure gas" usually denotes pressures above 3000 psig (207 barg) when used in relation to gas storage systems. However, any gas pressure above 30 psig (2 barg) has the potential to cause serious human injury and should be considered "high" in human terms.

Key Points & Notes

Desig-nation	Description	% Load Taken by Metal vs. Composite
Type 1	A cylinder made wholly of steel or aluminum	100 / 0
Type 2	A cylinder with a metal line of steel or aluminum and a hoop-wrapped (circumferential) composite overwrap	55 / 45
Type 3	A cylinder with a thin metal liner of steel or aluminum and a fully wound composite overwrap	20 / 80
Type 4	A cylinder with a plastic liner and a fully wound composite overwrap	0 / 100

Table 2-2 High Pressure Gas Cylinder Classifications

In general, the less metal used, the lower the weight. For this reason, Type 3 cylinders are usually used in hydrogen applications, and Type 4 cylinders will likely gain prominence in the future. Specific weights depend on individual manufacturers, but as a point of reference, a 3.5 ft^3 (100 L) Type 1 (steel) cylinder weighs about 220 lb (100 kg) a Type 3 (aluminum/composite) cylinder weighs about 143 lb (65 kg), and a Type 4 cylinder weighs about 66 lb (30 kg).

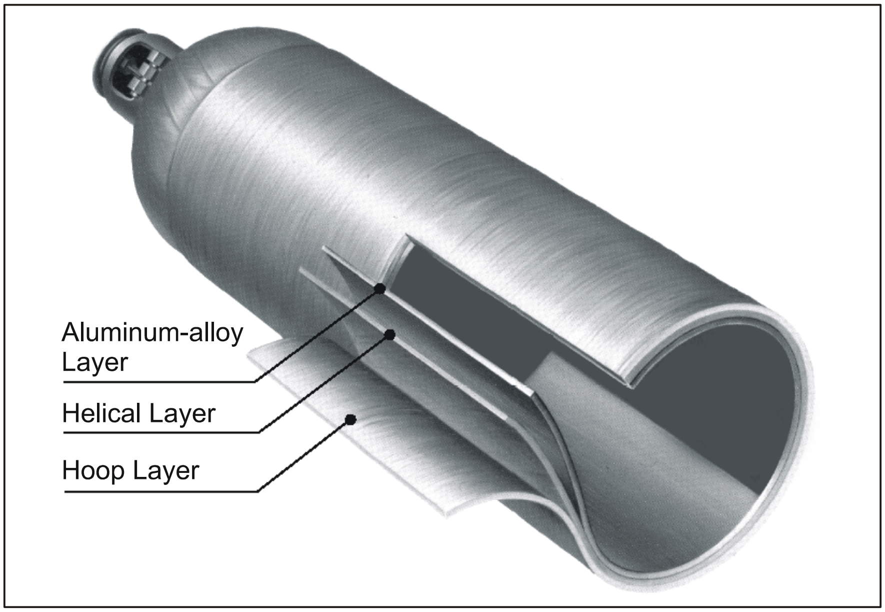
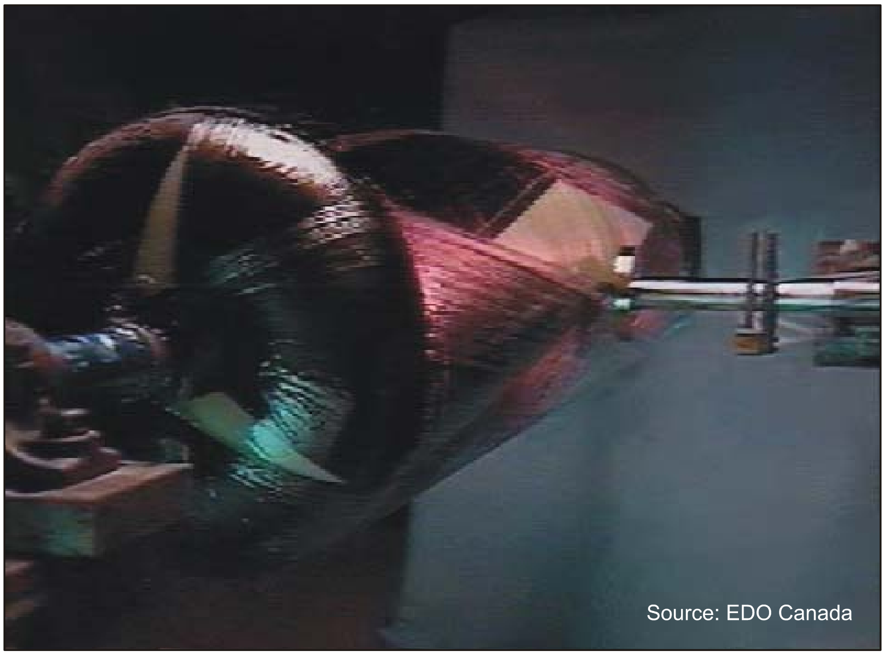


Figure 2-21: Type 3 Cylinder Construction

Type 3 cylinders derive most of their strength from the composite overwrap that is wound around the inner liner. This composite consists of high-strength fibers (usually carbon) that are wrapped around the cylinder in many layers and glued together by a resin such as epoxy.

Key Points & Notes



Source: EDO Canada

Figure 2-22: Composite Cylinder During Manufacturing

The combination of fibers and resin used in a composite cylinder is extremely strong provided that the fibers and resin remain undamaged. Composite surfaces are less tough than metal surfaces and are more susceptible to physical damage (cuts, abrasion, impacts, etc.) and chemical damage (ammonia, acids, etc.), although they are less susceptible to corrosion.

Cylinder manufacturers strive to attain the highest storage pressures possible in order to reduce the required storage volume. High-pressure cylinders typically store hydrogen at up to 3600 psig (250 barg) although new designs have been certified for 5000 psig (350 barg) operation. State-of-the-art technology currently under development has exceeded the accepted burst test standard of 23,500 psig (1620 barg) using a 10,000 psig (700 barg) Type 4 cylinder.

High temperatures from hot ambient conditions, or as a result of compression during fueling, may increase storage pressures by 10% or more. Any gas stored at these high pressures is extremely dangerous and is capable of releasing a gas stream with explosive force or propelling small projectiles like a bullet. An unrestrained cylinder could turn into a rocket if the gas were suddenly released through a small opening.

Despite the potential danger, high-pressure cylinders have an excellent safety record. Cylinder designs must conform to

Cylinders are certified for a specific gas and must survive rigorous tests before being put into service.

rigorous standards and survive certification tests that demonstrate:

- no failures during 13,000 pressure cycles to 100% service pressure plus 5000 cycles to 125% service pressure. Some standards also demand 30 cycles to 166% service pressure.
- no failures (after pre-conditioning) during 5000 pressure cycles to 100% service pressure at 140 °F (60 °C) followed by 5000 cycles at –40 °F (–40 °C).
- burst pressure of 2.25 to 3.0 times the service pressure, depending on the standard.
- impact resistance to flaws, drops and pendulum impact.
- safe venting of contents when exposed to a bonfire.
- no fragmentation when exposed to gunfire.

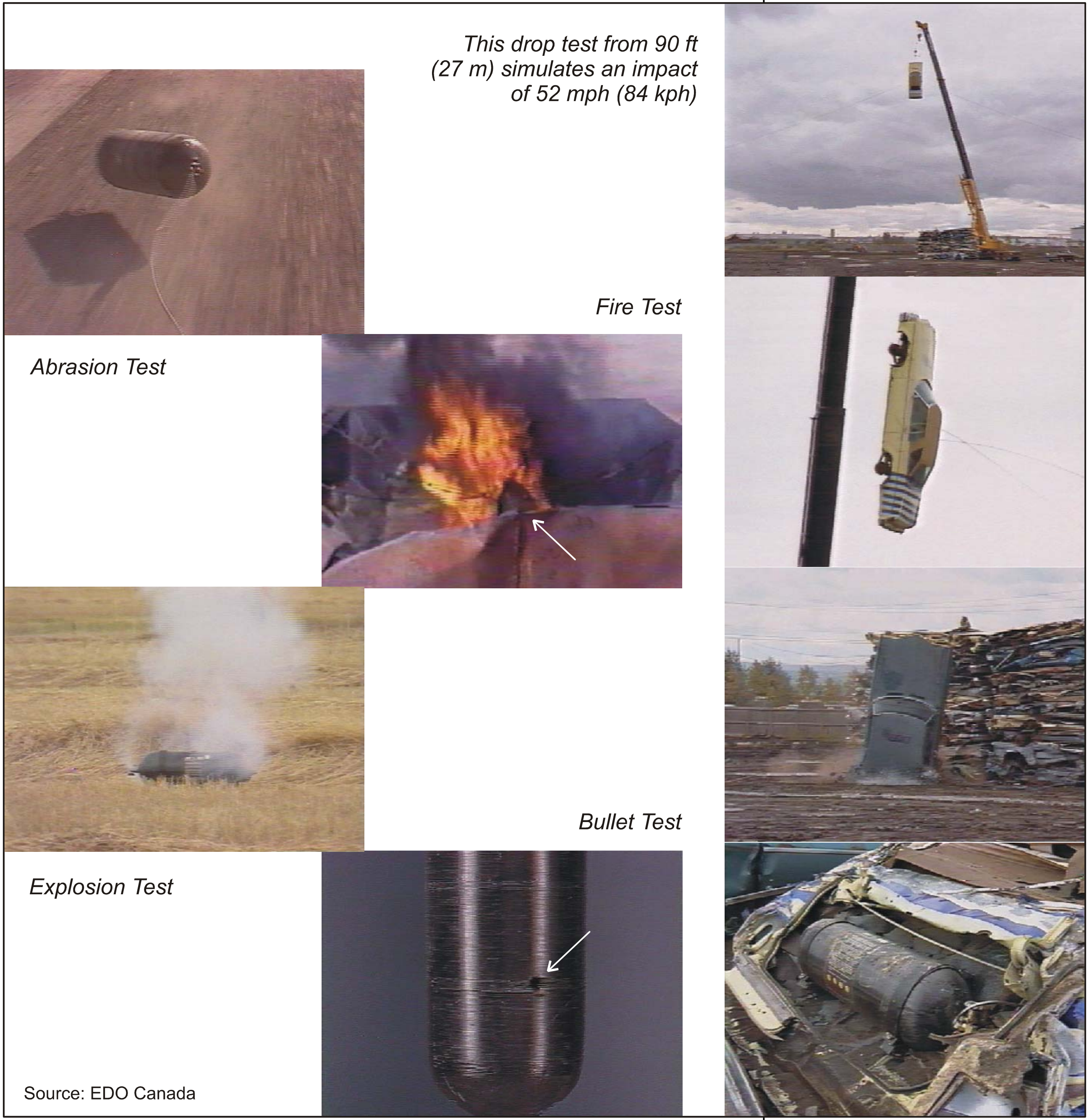
Some cylinder tests performed on a Type 4 cylinder are illustrated Figure 2-23.

During manufacture, each cylinder is subjected to hydrostatic and leak tests, and selected cylinders from each lot are subjected to cyclic and burst tests. Cylinders are labeled by the manufacturer as to the construction standard, serial number, service pressure, maximum fill pressure, and end-of-service date. Cylinders that are not subjected to severe external abuse or gas pressures above normal service levels can expect a service life of 15 years or 11,250 fills. Inspections and leak tests are a routine part of cylinder maintenance.

A typical vehicle application uses a series of cylinders mounted on a common manifold. At a service pressure of 3600 psig (250 barg), the fuel storage system weighs nearly four times that of a comparable liquid hydrogen storage system and occupies more than four times the space. When compared to gasoline, the gaseous hydrogen storage system is 15 times greater by volume and 23 times by weight. To put this into perspective, approximately 50% of a transit bus roof must be covered with hydrogen cylinders in order to replace its standard diesel tank.

Despite this volume, the entire weight of hydrogen fuel is only 90 to 110 lb (40 to 50 kg), which is negligible compared to the weight of the cylinders and associated equipment. Storing gas at an even higher pressure results in a smaller storage volume, but the overall storage weight to hydrogen volume does not change much as the cylinders must be more robust. The current record for the highest hydrogen storage by weight ever recorded at 11.3% as achieved using a 5,000 psig (350 barg) Type 4 cylinder.

Key Points & Notes



This drop test from 90 ft (27 m) simulates an impact of 52 mph (84 kph)

Abrasion Test

Fire Test

Explosion Test

Bullet Test

Source: EDO Canada

Figure 2-23: Cylinder Qualification Tests

Gas compression is an energy intensive process. The higher the end pressure, the greater the amount of energy required. However, the *incremental* energy required to achieve higher and higher pressures decreases so that the initial compression is the most energy intensive part of the process.

The energy economy of higher compression levels is counterbalanced by an incremental decrease in gas density at higher pressures, so that further compression packs less hydrogen mass into the cylinders (even if suitable cylinders were to exist). A useful way of understanding the energy cost of compression is as a percentage of the total energy content (LHV) of the hydrogen being stored. In these terms, approximately 5% of the LHV is required to compress the gas to 5000 psig (350 barg). Exact energy usage depends on the flow capacity and efficiency of the compressors used.

2.2.2 Liquid

Liquid hydrogen storage systems overcome many of the weight and size problems associated with high-pressure gas storage systems, albeit at cryogenic temperatures.

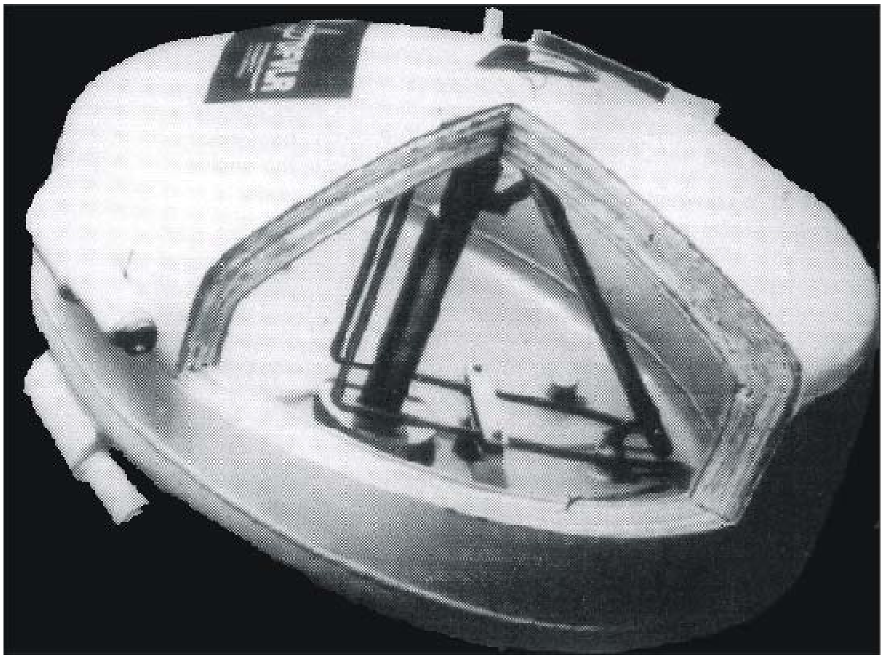


Figure 2-24: Automotive Liquid Hydrogen Tank, Sectioned

Liquid hydrogen can be stored just below its normal boiling point of –424 °F (–253 °C; 20 K) at or close to ambient pressure in a double-walled, super-insulating tank (or "dewar"). This insulation takes the form of a vacuum jacket, much like in a Thermos bottle. Liquid hydrogen tanks do not need to be as strong as high-pressure gas cylinders although they do need to be adequately robust for automotive use.

Hydrogen cannot be stored in liquid form indefinitely. All tanks, no matter how good the insulation, allow some heat to transfer from the ambient surroundings. The heat leakage rate depends on the design and size of tank — in this case,

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bigger is better. This heat causes some of the hydrogen to vaporize and the tank pressure to increase. Stationary liquid hydrogen storage tanks are often spherical since this shape offers the smallest surface area for a given volume, and therefore presents the smallest heat transfer area.

Tanks have a maximum overpressure capacity of about 72 psi (5 bar); if the hydrogen is not consumed as quickly as it vaporizes, the pressure builds to a point where it vents through a pressure relief valve. This vented hydrogen is not only a direct loss of usable fuel, but it also poses a flammability hazard if the vehicle is parked indoors. Provision must be made to vent the hydrogen safely without the potential for accumulation. Current automotive hydrogen tank technology provides a venting (or "boil-off") rate of about 1 to 2% per day.

Liquid Hydrogen Filling Tank

Hydrogen can be drawn from the tank either as a liquid or as gas. When used in an internal combustion engine, liquid hydrogen can be injected directly into the cylinders in order to increase the amount of fuel combusted in each power stroke. When used in a fuel cell engine, gaseous hydrogen can be drawn off at sufficient pressure to feed the power generating reaction.

Although liquid hydrogen storage systems eliminate the danger associated with high pressures, they introduce dangers associated with low temperatures. A severe frostbite hazard exists in association with the liquid hydrogen, its vapors and contact surfaces. Carbon steel exposed to temperatures below –22 °F (–30 °C), either directly or indirectly, becomes brittle and is susceptible to fracture. Air may liquefy on the outside of exposed liquid hydrogen lines or under insulation resulting in an oxygen concentration that poses a fire or explosion hazard if it drips onto combustible materials.

Liquid hydrogen is considerably more dense than gaseous hydrogen but is still much more bulky than gasoline on an equivalent energy basis. Liquid hydrogen storage systems can be four to ten times larger and heavier than an equivalent gasoline tank.

Hydrogen liquefaction is a very energy intensive process due to the extremely low temperatures involved. Liquefaction involves several steps, including:

1. Compression of hydrogen gas using reciprocating compressors; pre-cooling of the compressed gas to liquid nitrogen temperatures –319 °F (–195 °C; 78 K)

2. Expansion through turbines
3. Catalytic conversion to its stable "parahydrogen" form (Section 1.1)

In total, the energy required for the liquefaction process is the equivalent of up to 40% of the LHV of hydrogen. Once in liquid form, hydrogen is relatively efficient to transport and easy to use. Clearly, to maximize the energy investment paid during liquefaction, it is prudent to store and use the hydrogen directly as a liquid whenever possible.

The worst scenario in terms of energy investment is to liquefy the hydrogen, transport it in liquid form, re-convert it to a gas, and store in on-board a vehicle as a high pressure gas. This erodes the net available energy twice, once during liquefaction and again during compression, while still being left with the disadvantages of a bulky and heavy on-board gaseous fuel storage system.

2.2.3 Metal Hydrides

Rare Earth Hydrides

Metal hydride storage systems are based on the principle that some metals readily absorb gaseous hydrogen under conditions of high pressure and moderate temperature to form metal hydrides. These metal hydrides release the hydrogen gas when heated at low pressure and relatively high temperature. In essence, the metals soak up and release hydrogen like a sponge.

The advantages of metal hydride storage systems revolve around the fact that the hydrogen becomes part of the chemical structure of the metal itself and therefore does not require high pressures or cryogenic temperatures for operation. Since hydrogen is released from the hydride for use at low pressure (and must be released before it can burn rapidly), hydrides are the most intrinsically safe of all methods of storing hydrogen.

There are many types of specific metal hydrides, but they are primarily based on metal alloys of magnesium, nickel, iron and titanium. In general, metal hydrides can be divided into those with a low or high hydrogen desorption (release) temperature.

The high temperature hydrides may be less expensive and hold more hydrogen than the low temperature hydrides, but require significant amounts of heat in order to release the hydrogen. Low temperature hydrides can get sufficient heat from an engine, but high temperature hydrides require an external source of heat.

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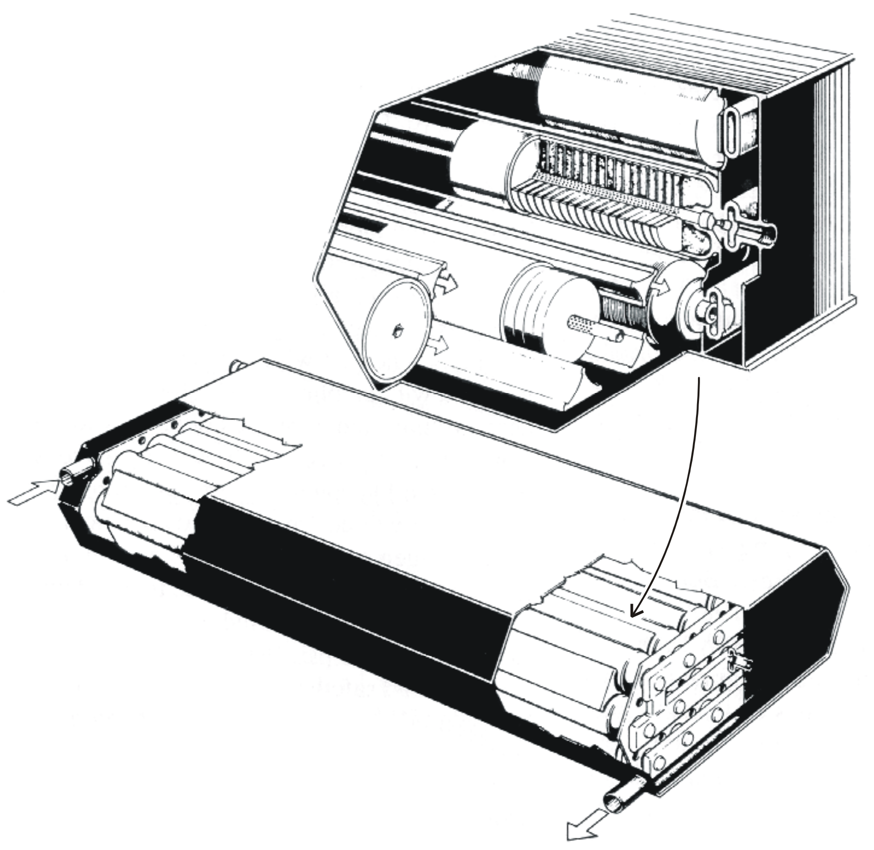

Figure 2-25: Metal Hydride Vehicle Storage Tank, Sectioned

The low desorption temperatures associated with some hydrides can be a problem since the gas releases too readily at ambient conditions. To overcome this, low temperature hydrides need to be pressurized, increasing the complexity of the process. The characteristics of typical metal hydrides are summarized in Table 2-3.

The main disadvantage of metal hydride storage systems is not so much the temperatures and pressures needed to release the hydrogen, but rather their low mass energy density. Even the best metal hydrides contain only 8% hydrogen by weight and therefore tend to be very heavy and expensive. Metal hydride storage systems can be up to 30 times heavier and ten times larger than a gasoline tank with the same energy content.

Another disadvantage of metal hydride storage systems is that they must be charged with only very pure hydrogen or they become contaminated with a corresponding loss of capacity. Oxygen and water are prime culprits as they chemically adsorb onto the metal surface displacing potential hydrogen bonds. The storage capacity lost through contamination can to some extent be reactivated with heat.

Characteristic	Low Temperature				High Temperature		
	$Ti_2Ni\text{-}H_{2,5}$	$FeTi\text{-}H_2$	$VH\text{-}VH_2$	$LaNi_5\text{-}H_{6,7}$	$Mg_2Cu\text{-}H_3$	$Mg_2Ni\text{-}H_4$	Mg-H
Alloy mass that can absorb hydrogen	1.61%	1.87%	1.92%	1.55%	2.67%	3.71%	8.25%
Hydride mass equivalent to the energy in 0.264 gal (1 L) of gasoline	342 lb 155 kg	295 lb 134 kg	286 lb 130 kg	355 lb 161 kg	No Data	149 lb 67.5 kg	79 lb 35 kg
Alloy mass necessary to accumulate 5.5 lb (2.5 kg) of hydrogen	478 lb 217 kg	414 lb 188 kg	401 lb 182 kg	496 lb 225 kg	No Data	209 lb 95 kg	110 lb 50 kg
Desorption temperature at 145 psig (10 barg)	93 ºF 34 ºC 307 K	125 ºF 52 ºC 325 K	127 ºF 53 ºC 326 K	163 ºF 73 ºC 346 K	604 ºF 318 ºC 591 K	662 ºF 350 ºC 623 K	683 ºF 362 ºC 635 K
Desorption temperature at 22 psig (1.5 barg)	26 ºF –3 ºC 270 K	44 ºF 7 ºC 280 K	59 ºF 15 ºC 288 K	70 ºF 21 ºC 294 K	480 ºF 245 ºC 522 K	512 ºF 267 ºC 540 K	565 ºF 296 ºC 569 K
Charging	Easy	No Data	No Data	Very Difficult	No Data	Difficult	Very Difficult
Safety	Safe	No Data	No Data	No Data	Highly Flammable	Safe	Highly Flammable

Table 2-3 Metal Hydride Characteristics

A further problem associated with metal hydrides relates to their structure. Metal hydrides are typically produced in a granular or powder form so that they have a large surface for gas storage. These particles are susceptible to attrition, which both reduces their effectiveness and may plug relief systems or other piping.

No specific metal hydride has outstanding performance on all accounts (high absorption capacity, high density, low heat requirement and low cost). In some cases, a mixture of low and high temperature hydrides can be used to maintain some of the advantages inherent to each while at the same time introducing some of disadvantages of each.

Alkaline Earth Hydrides

A recent hydride variation that offers some advantages over previous methods involves the use of pelletized sodium, potassium or lithium compounds. These hydride compounds react with water to release hydrogen without the addition of heat.

The most commercially developed process involves the use of sodium hydroxide (NaOH), which is abundantly available as a waste material from paper, paint, textiles, plastic, petroleum and other industries. Sodium hydroxide is converted to sodium hydride (NaH) by driving off the oxygen through the addition of heat as follows:

$$2\ NaOH + heat \Rightarrow 2\ NaH + O_2$$

The sodium hydride can then be pelletized, using a process similar to that used to pelletize charcoal briquettes, and coated with a waterproof plastic coating or skin. In this form, the sodium is non-volatile and can be transported easily. To release the hydrogen, the pellets are cut as needed while immersed in water to react as follows:

$$NaH\ (solid) + H_2O\ (liquid) \Rightarrow NaOH\ (liquid) + H_2\ (gas)$$

This reaction is fast, and results in a hydrogen pressure of 125 to 150 psig (8.6 to 10.3 barg). The resulting sodium hydroxide can be retrieved and returned to the original process for reuse.

This process shares the advantages with other hydrides of not requiring high pressures or cryogenic temperatures for operation. It has the added advantages of not requiring heat to release the hydrogen, overcomes contamination and structural problems, and can be handled with relative ease.

Like other hydride systems, sodium hydrides are heavy and have a mass energy density that is comparable with high temperature hydride systems as indicated in Table 2-4. Disadvantages of the sodium hydride process include the mechanical complications related to cutting the pellets in a controlled fashion, and the materials reclamation issues that surround the waste sodium hydroxide and used plastic coatings.

Characteristic	NaH
Alloy mass that can absorb hydrogen	4.4%
Hydride mass equivalent to the energy in 0.264 gal (1 L) of gasoline	90 lb 41 kg
Alloy mass necessary to accumulate 5.5 lb (2.5 kg) hydrogen	130 lb 59 kg

Table 2-4 Sodium Hydride Characteristics

This sodium hydride process is interesting as a combination of hydrogen generation and storage in one step. Like electrolysis, the hydrogen in sodium hydride is an energy carrier, not an energy source, since the source sodium hydroxide is at a low energy state and must be “charged” through the addition of heat energy. As before, this process

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is only as renewable and environmentally friendly as the source energy. Also like electrolysis, water is consumed during hydrogen release.

2.2.4 Other Storage Methods

A variety of other hydrogen storage methods are currently being researched, and are not currently commercially viable. Among these are carbon adsorption, glass microsphere and iron oxidation techniques.

Carbon Adsorption

Carbon adsorption is a technique similar to that employed with metal hydrides wherein hydrogen is bound chemically onto the surface of highly porous carbon granules. The carbon is adsorbed at –300 to –120 °F (–185 to –85 °C) and 300 to 700 psi (21 to 48 barg). The amount of carbon adsorption increases at lower temperatures. Heat in excess of 300 °F (150 °C) releases the hydrogen.

Glass Microsphere

Glass microsphere storage systems use tiny, hollow glass balls into which hydrogen is forced under very high pressure. Once stored, the balls can be stored at ambient conditions without hydrogen loss. Moderate heat releases the hydrogen again. Experiments are being done to increase the hydrogen release rate by crushing the spheres.

Iron Oxidation

Iron oxidation is a process by which hydrogen is formed when sponge iron (the raw ingredient for steel-making furnaces) is reacted with steam as follows:

$$Fe + H_2O \Leftrightarrow FeO + H_2$$

$$3\ FeO + H_2O \Leftrightarrow Fe_3O_4 + H_2$$

The byproduct of this process is rust. Once the iron is fully rusted, it must be exchanged for a new tank and then be converted back to sponge iron using industrial methods. The steam and heat needed for the on-board reaction could potentially be provided by the exhaust of an internal combustion engine or the coolant stream of a fuel cell engine.

Although iron is cheap, it is heavy, so the process is only 4.5% effective by weight. Furthermore, a catalyst (which is expensive) is required to maintain the reaction at practical temperatures of 175 to 390 °F (80 to 200 °C).

2.3 Hydrogen Transportation

Key Points & Notes

Hydrogen transportation issues are directly related to hydrogen storage issues. In general, compact forms of hydrogen storage are more economical to transport and diffuse forms are more costly.

2.3.1 Pipelines

Pipelines can carry hydrogen as gas or as a liquid.

Gas Pipelines

Gaseous hydrogen can be transported by pipeline in a similar fashion as natural gas.

Hydrogen, being less dense than natural gas, results in less mass transport for a given pipeline size and operating pressure. In addition, the energy density of hydrogen is only one-third that of natural gas on a volumetric basis; hence, three times the amount of hydrogen gas must be pumped through a pipeline to transmit an equivalent amount of energy.

There are 285,000 miles of natural gas pipelines throughout the continental US with a daily movement of over 50 billion standard cubic feet (sft^3) and a capacity of approximately 90 billion sft^3/day.

To compensate for both of these properties, hydrogen pipelines need to be designed to operate at higher pressure in order to be practical. All pumps and other equipment must be hydrogen compatible. Furthermore, hydrogen pipelines must be resistant to hydrogen embrittlement in order to prevent cracking.

Existing hydrogen gas pipelines operate in some parts of the world. In the US there are 450 miles (725 km) of pipelines, including those in Texas, Indiana, New Jersey and Louisiana. Several hydrogen pipelines exist in Canada. In Europe, pipelines operate within Germany (210 km) and between Belgium and France (400 km), among several others. Compared to pipelines of others gases, these lengths are very short, however, they indicate that the high cost of transporting hydrogen by gas pipeline is already worth it in some areas.

Hydrogen Pipeline

Liquid Hydrogen Pipelines

Hydrogen can be transported in a pipeline as a liquid, but liquid hydrogen pipelines have been accomplished over very short distances only. These pipelines require thorough insulation in order to maintain cryogenic temperatures and prevent the formation of a two-phase (liquid/gas) flow. If exposed to air, the low pipeline temperature would cause air to liquefy and oxygen to concentrate on the surface of the pipe, increasing the fire hazard.

2.3.2 Mobile Transport

Key Points & Notes

Mobile transport includes transport by truck, rail or barge. The hydrogen is stored in tanks appropriate to hydrogen storage method and transport medium.

Gas Transport

Hydrogen as a high-pressure gas can be transported in cylinders at pressures ranging from 2200 to 5800 psig (150 to 400 barg).

For trucks, specially designed tube trailers carry a number of large, high-strength steel tubes linked together through a common manifold. This design works well in providing small quantities of hydrogen, but is very inefficient in terms of transport energy. The weight of cylinders required is such that the gas is only 2 to 4% of the cargo weight.

Figure 2-26: Tube Trailer

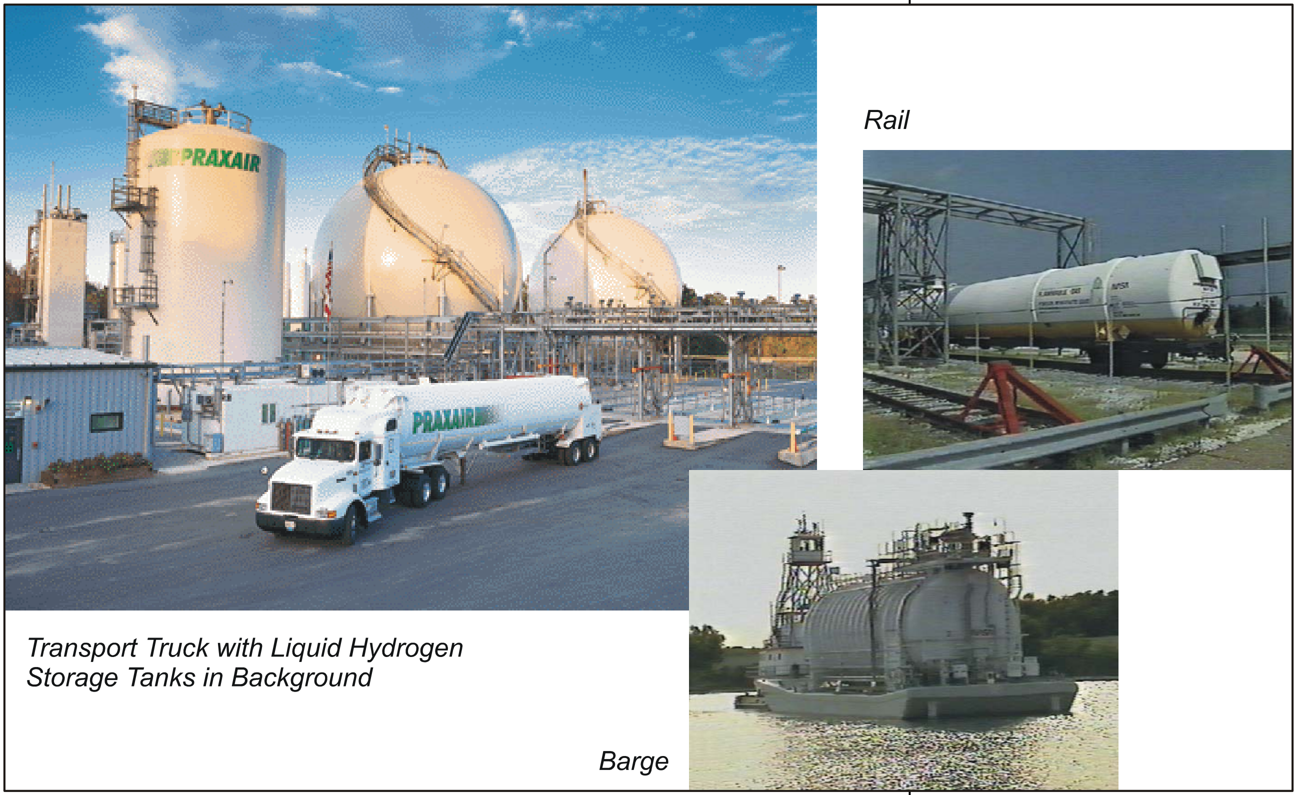
This tube trailer holds 104,000 sft^3 (2,945 sm^3) of hydrogen at 3,160 psig (218 barg). The two additional tubes on the ground next to the tube trailer hold an additional 12,500 sft^3 (354 sm^3) of hydrogen at 4,000 psig (275 barg).

Liquid Transport

Hydrogen can be transported by truck, rail or barge as a cryogenic liquid in double-walled, super-insulated vacuum-lined tanks. Transporting liquid hydrogen is far more efficient than as a high-pressure gas, particularly where larger quantities are needed. On the downside, maintenance costs are much higher for liquid transportation.

As a point of reference, 150 lb (70 kg) of liquid hydrogen occupies a volume of 35.3 ft^3 (1000 L) and requires a transport container weighing between 440 and 660 lb (200 to 300 kg). The same weight of hydrogen, transported as a gas or hydride would require between two and five tons of containers. The liquid option is obviously much more efficient.

Liquid hydrogen transport trailers include standard 40-foot and 80-foot truck trailers. The largest containers used in transport reach 7,000,000 ft^3 (200,000 m^3).



Rail

Transport Truck with Liquid Hydrogen Storage Tanks in Background

Barge

Figure 2-27: Liquid Hydrogen Transport

2.3.3 Site Manufacture

Site manufacture of hydrogen sidesteps the issue of transporting it. The energy for the manufacture of hydrogen is moved to the site, rather than the hydrogen itself. The energy might be in the form of electrical power to an electrolysis system, or a fossil fuel piped or trucked to a reformer.

By manufacturing hydrogen at or near the location where it is required, the high cost and energy inefficiency of transport is avoided, and advantage is taken of the high transport efficiency of other forms of energy.