HYDROGEN

1. Introduction

Hydrogen, the lightest element, has three isotopes: hydrogen [12385-13-6], H, at wt 1.0078; deuterium [16873-17-9], D, at wt 2.0141; and tritium [15086-10-9], T, at wt 3.0161 (1). Hydrogen is very abundant, being one of the atoms composing water; deuterium and tritium occur naturally on Earth, but at very low levels. Tritium, a radioactive low energy beta-emitter with a half-life of 12.26 yr (2), is useful as a tracer in hydrogen reactions (see DEUTERIUM AND TRITIUM; RADIOACTIVE TRACERS).

Whereas hydrogen atoms exist under certain conditions, the normal state of pure hydrogen is the hydrogen molecule [1333-74-0], H_2, which is the lightest of all gases. Molecular hydrogen is a product of many reactions, but is present at only low levels (0.1 ppm) in the Earth's atmosphere. The hydrogen molecule exists in two forms, designated *ortho*-hydrogen and *para*-hydrogen, depending on the nuclear spins of the atoms. Many physical and thermodynamic properties of H_2 depend on the nuclear spin orientation, but the chemical properties of the two forms are the same.

Hydrogen is a very stable molecule having a bond strength of 436 kJ/mol (104 kcal/mol), and is not particularly reactive under normal conditions. However, at elevated temperatures and with the aid of catalysts, H_2 undergoes many reactions. Hydrogen forms compounds with almost every other element, often by direct reaction of the elements. The explanation for its ability to form compounds with such chemically dissimilar elements as alkali metals, halogens, transition metals, and carbon lies in the intermediate electronegativity of the hydrogen atom.

Hydrogen can be liquefied and stored as a cryogenic liquid (LHy). LHy first found in important use as rocket fuel for the U.S. space program and was subsequently introduced to the industrial market. Hydrogen is viewed as an important player in the future energy equation for ultraclean transportation fuels (see HYDROGEN ENERGY). Fuel cells are receiving significant R&D funding by the world's automobile manufacturers and some of the major oil companies in large consortiums. Upon combustion, hydrogen returns to water, accompanied by virtually no pollution and no greenhouse gas production, in contrast to hydrocarbon-based fuels (see AIR POLLUTION; ATMOSPHERIC MODELING).

2. Physical and Thermodynamic Properties

The spins of the atomic nuclei in a hydrogen molecule can be coupled in two distinct ways: with nuclear spins parallel (*ortho*-hydrogen) or nuclear spins antiparallel (*para*-hydrogen). Because molecular spins are quantized, *ortho*- and *para*-hydrogen exist in different quantum states. As a result, there are differences in many properties of the two forms of hydrogen. In particular, those properties that involve heat, such as enthalpy, entropy, and thermal conductivity, can show definite differences for *ortho*-vs *para*-hydrogen. Other thermodynamic properties show little difference.

The equilibrium between *ortho*- and *para*-hydrogen is a function of temperature. Equilibrium compositions for various temperatures ranging from absolute zero to 500 K are shown in Table 1. For any given hydrogen sample, equilibrium conditions of *ortho*- and *para*-hydrogen are often not realized, however, because the uncatalyzed interconversion of the two forms is relatively slow at low temperatures. At high temperatures, where molecular dissociation occurs, self-conversion rates are more rapid. Hence, when hydrogen is prepared, the equilibrium ortho–para ratio characteristic of the temperature of preparation can persist for relatively long periods of time at other temperatures.

Table 1. **Temperature Dependence of the Equilibrium *Ortho*-, *Para*-Hydrogen Composition**[a,b]

Temperature, K	*para*-Hydrogen at equilibrium, %	H^c, kJ/mol[d]
0	100.0	
10	100.0	−1.0627
20	99.82	
25	99.01	
30	97.02	
35	93.45	
40	88.73	
50	77.05	−1.062
75	51.86	
100	38.62	−0.9710
150	28.60	
200	25.97	−0.3302
300	25.07	−0.0556
500 and higher	25.00	

[a] Refs. 3–5.
[b] Normal hydrogen contains ca 3 : 1 ratio of *ortho*- to *para*-hydrogen. See text.
[c] Heat of reaction of the conversion of normal to *para*-hydrogen.
[d] To convert kJ to kcal, divide by 4.184.

The equilibrium 3:1 ratio of *ortho*-to *para*-hydrogen that occurs at about room temperature is called normal hydrogen. Physical properties are typically given for normal hydrogen and for *para*-hydrogen (20.4 K equilibrium hydrogen). *para*-Hydrogen is the lower energy form of hydrogen. The equilibrium mixture at very low temperatures is almost pure *para*-hydrogen, and the conversion of *ortho*-hydrogen to *para*-hydrogen is an exothermic process. The energy released on conversion of normal hydrogen to *para*-hydrogen is given in Table 1 for several temperatures; additional data are also available (5). The energy released on converting liquid normal hydrogen to 90% *para*-hydrogen is sufficient to vaporize 64% of the original liquid (6). For this reason, catalysts have been developed that rapidly convert normal to *para*-hydrogen, greatly facilitating the storage of liquid hydrogen. Many materials have been found to catalyze this conversion, including hydrous iron(III) oxide, rare earths, uranium compounds, and carbon (7–11). Strong magnetic fields also enhance the ortho–para conversion rate.

For the deuterium molecule [7782-39-0], D_2, the ortho–para relationship is the opposite of that in H_2, ie, the ortho form is the more prevalent one at low temperatures. For instance, at 20 K, the equilibrium concentration of D_2 is 97.97% ortho, and at 220 K it is 66.66% *ortho*-deuterium (12).

Tables 2,3, and 4 outline many of the physical and thermodynamic properties of *para*- and normal hydrogen in the solid, liquid, and gaseous states, respectively. Extensive tabulations of all the thermodynamic and transport properties listed in these tables from the triple point to 3000 K and at 0.01–100 MPa (1–14,500 psi) are available (5,39). Additional properties, including accommodation coefficients, thermal diffusivity, virial coefficients, index of refraction, Joule-Thomson coefficients, Prandtl numbers, vapor pressures, infrared absorption, and heat transfer and thermal transpiration parameters are also available (5,40). Thermodynamic properties for hydrogen at 300–20,000 K and 10 Pa to 10.4 MPa (10^{-4} – 103 atm) (41) and transport properties at 1,000–30,000 K

Table 2. **Physical and Thermodynamic Properties of Solid Hydrogen**

	Hydrogen		
Property	*para-*	Normal	Refs.
mp, K (triple point)	13.803	13.947	13–15
vapor pressure at mp, kPa[a]	7.04	7.20	15,16
vapor pressure at 10 K, kPa[a]	0.257	0.231	16
density at mp, $(\text{mol/cm}^3) \times 10^3$	42.91	43.01	17,18
heat of fusion at mp, J/mol[b]	117.5	117.1	15
heat of sublimation at mp, J/mol[b]	1023.0	1028.4	19,20
C_p at 10 K, J/(mol · K)[b]	20.79	20.79	21
enthalpy at mp, J/mol[b,c]	−740.2	321.6	14,15,18,19
internal energy at mp, J/mol[b,c]	−740.4	317.9	15,22
entropy at mp, J/(mol · K)[b,c]	1.49	20.3	14,15,18,19
thermal conductivity at mp, mW/(cm· K)	9.0	9.0	23
dielectric constant at mp	1.286	1.287	24
heat of dissociation at 0 K, kJ/mol[b]	431.952	430.889	16

[a] To convert kPa to mm Hg, multiply by 7.5.

[b] To convert J to cal, divide by 4.184.

[c] Base point (zero values) for enthalpy, internal energy, and entropy are 0 K for the ideal gas at 101.3 kPa (1 atm) pressure.

Table 3. **Physical and Thermodynamic Properties of Liquid Hydrogen**

Property	Hydrogen		Refs.
	para-	Normal	
mp, K (triple point)	13.803	13.947	13–15
normal bp, K	20.268	20.380	13–15
critical temperature, K	32.976	33.18	13–15
critical pressure, kPa^{a}	1292.8	1315	13–15
critical volume, cm^{3}/mol	64.144	66.934	13–15, 17, 18
density at bp, mol/cm^{3}	0.03511	0.03520	13–15, 17, 18
density at mp, mol/cm^{3}	0.038207	0.03830	13–15, 17, 18
compressibility factor, $Z = PV/RT$			
at mp	0.001606	0.001621	15, 22
bp	0.01712	0.01698	15, 22
critical point	0.3025	0.3191	15, 22
adiabatic compressibility, $(-\partial V/V\partial P)_s$, MPa^{-1b}			
at triple point	0.00813	0.00813	25
bp	0.0119	0.0119	25
coefficient of volume expansion, $(-\partial V/V\partial T)_p$, K^{-1}			
at triple point	0.0102	0.0102	26
bp	0.0164	0.0164	26
heat of vaporization, J/mol^{c}			
at triple point	905.5	911.3	15, 22
bp	898.3	899.1	15, 22
C_p, J/(mol · K)^{c}			
at triple point	13.13	13.23	13–15, 17, 18
bp	19.53	19.70	13–15, 17, 18
C_v, J/(mol · K)^{c}			
at triple point	9.50	9.53	13–15, 17, 18
bp	11.57	11.60	13–15, 17, 18
enthalpy, J/mol			
at triple point	−622.7	438.7	13–15, 17, 18
bp	−516.6	548.3	13–15, 17, 18
internal energy, J/mol^{c,d}			
at triple point	−622.9	435.0	13–15, 17, 18
bp	−519.5	545.7	13–15, 17, 18
entropy, J/(mol · K)^{c,d}			
at triple point	10.00	28.7	13–15, 17, 18
bp	16.08	34.92	13–15, 17, 18
velocity of sound, m/s			
at triple point	1273	1282	13, 15, 27–29
bp	1093	1101	13, 15, 27–29
viscosity, mPa · s(= cp)			
at triple point	0.026	0.0256	15, 29–32
bp	0.0133	0.0133	15, 29–32
thermal conductivity, mW/(cm · K)			
at triple point	0.73	0.73	15, 28, 30, 31, 33
bp	0.99	0.99	15, 28, 30, 31, 33
dielectric constant			
at triple point	1.252	1.253	15, 24
bp	1.230	1.231	15, 24
surface tension, mN/m (= dyn/cm)			
at triple point	2.99	3.00	15, 34
bp	1.93	1.94	15, 34

Table 3 (*Continued*)

Property	Hydrogen *para-*	Hydrogen Normal	Refs.
isothermal compressibility, $1/V(\partial V/V\partial P)_T$, MPa^{-1b}			
at triple point	−0.0110	−0.0110	35
bp	−0.0199	−0.0199	35

[a] To convert kPa to mm Hg, multiply by 7.5

[b] To convert MPa to atm, divide by 0.101.

[c] To convert J to cal, divide by 4.184.

[d] Base point (zero values) for enthalpy, internal energy, and entropy are 0 K for the ideal gas at 101.3 kPa (1 atm) pressure.

and 0.1–3.0 MPa (1–30 atm) (42) have been compiled. Enthalpy–entropy tabulations for hydrogen over the range 3–100,000 K and 0.001–101.3 MPa (0.01–1000 atm) have been made (43). Many physical properties for the other isotopes of hydrogen (deuterium and tritium) have also been compiled (44).

As can be seen from Tables 2,3,4, many of the corresponding physical properties of normal and *para*-hydrogen are significantly different from each other.

Table 4. **Physical and Thermodynamic Properties of Gaseous Hydrogen**[a]

Property	Hydrogen *para-*	Hydrogen Normal	Refs.
density at 0°C, (mol/cm^3) × 10^3	0.05459	0.04460	13,14,17,18
compressibility factor, $Z = PV/RT$, at 0°C	1.0005	1.00042	15,22
adiabatic compressibility, $(-\partial V/V\partial P)_s$, at 300 K, MPa^{-1b}	7.12	7.03	25
coefficient of volume expansion, $(\partial V/V\partial P)_p$, at 300 K, K^{-1}	0.00333	0.00333	26
C_p at 0°C, J/(mol · K)^c	30.35	28.59	13–15,17,18
C_v at 0°C, J/(mol · K)^c	21.87	20.30	13–15,17,18
enthalpy at 0°C, J/mol^{c,d}	7656.6	7749.2	13–15,17,18
internal energy at 0°C, J/mol^{c,d}	5384.5	5477.1	13–15,17,18
entropy at 0°C, J/(mol · K)^{c,d}	127.77	139.59	13–15,17,18
velocity of sound at 0°C, m/s	1246	1246	13,15,27–29
viscosity at 0°C, mPa · s(= cP)	0.00839	0.00839	15,29–32
thermal conductivity at 0°C, mW/(cm · K)	1.841	1.740	15,28,30,31,33
dielectric constant at 0°C	1.00027	1.000271	15,24
isothermal compressibility $1/V(\partial V/\partial P)_T$, at 300 K, MPa^{-1b}	−9.86	−9.86	35
self-diffusion coefficient at 0°C, cm^2/s		1.285	36
gas diffusivity in water at 25°C, cm^2/s		4.8×10^{-5}	37
Lennard-Jones parameters			
collision diameter, σ, m × 10^{10}		2.928	38
interaction parameter, ϵ/k, K		37.00	38
heat of dissociation at 298.16 K, kJ/mol^c	435.935	435.881	16

[a] All values at 101.3 kPa (1 atm).

[b] To convert MPa to atm, divide by 0.101.

[c] To convert J to cal, divide by 4.184.

[d] Base point (zero values) for enthalpy, internal energy, and entropy are 0 K for the ideal gas at 101.3 kPa (1 atm) pressure.

These differences have often been used to advantage in analysis. For instance, at 120–190 K the thermal conductivity for *para*-hydrogen is more than 50% greater than that of *ortho*-hydrogen. Hence, thermal conductivity offers a means of determining the ortho–para ratio of a given hydrogen sample. The thermal conductivity of hydrogen gas is the highest of all common gases, about seven times that of air. Thus thermal conductivity is also used to detect hydrogen in the presence of other gases. Second and third viral coefficients for *para*- hydrogen have been tabulated from 14 to 500 K (45,46). Equations are given for calculating the virial coefficients over this temperature range. These values of the virial coefficients for *para*-hydrogen agree with values for normal hydrogen at 100 K (47).

Expansion from high to low pressures at room temperature cools most gases. Hydrogen is an exception in that it heats upon expansion at room temperature. Only below the inversion temperature, which is a function of pressure, does hydrogen cool upon expansion. Values of the Joule-Thomson expansion coefficients for hydrogen have been tabulated up to 253 MPa (36,700 psi) (48), and the Joule-Thomson inversion curve for *para*-hydrogen has been determined (49,50).

The vapor pressure of liquid *para*-hydrogen as a function of temperature can be calculated from the following equation (51):

$$\ln(P/P_t) = ax + bx^2 + cx^3 + d(1-x)^e$$

where $a = 3.05300134164$; $b = 2.80810925813$; $c = -0.655461216567$; $d = 1.59514439374$; $e = 1.5814454428$; $x = (1 - T_t / T)/(1 - T_t / T_c)$; $T_t = 13.8$ K; $T_c = 32.938$ K; $P_t = 0.007042$ MPa; T, the temperature, is in K; and P, the vapor pressure, is in MPa. The vapor pressure of liquid normal hydrogen as a function of temperature can be calculated from the following equation (16):

$$\log_{10} P = -A/T + B + CT$$

where $A = 44.9569$; $B = 6.79177$; $C = 0.020537$; T is temperature in K; and P is vapor pressure in Pa. Tables of vapor pressure for liquid and solid normal hydrogen (52), sublimation pressures of *para*-hydrogen from 1 K to the triple point (53), and equations for estimating sublimation pressures of normal and *para*-hydrogen (16) are all available in the literature.

Hydrogen gas diffuses rapidly through many materials, including metals. This property is used in separating hydrogen from other gases and in purifying hydrogen on an industrial scale. Hydrogen diffusion through metals is also used as an analytical technique for hydrogen determination in gas chromatography (54). Hydrogen is only slightly soluble in water but is somewhat more soluble in organic compounds. For instance, at 0°C and 0.1 MPa (1 atm) pressure, the solubility of H_2 in water (STP) is $0.0214\ \text{cm}^3/\text{g}$; in benzene the solubility is $0.0585\ \text{cm}^3/\text{g}$ (55). A method has been outlined for estimating the solubility of hydrogen gas in various solvents as a function of temperature and pressure (56). The solubility of hydrogen in water as a function of temperature and pressure in the range 0–100°C and 0.1–10 MPa (1–100 atm) is available (55), as is the solubility of hydrogen in a number of other aqueous solutions as well as organic solvents (55).

Table 5. **Vapor Pressures of Hydrogen Isotopes, Normal Species**[a,b]

Parameter	Temperature, K	Vapor pressure, kPa[c]		
		H_2	D_2	T_2
bp of T_2	25.04	323.0	147.9	101.3
bp of D_2	23.67	237.6	101.3	66.72
triple point of T_2	20.62	108.0	37.24	21.60
bp of H_2	20.38	101.3	34.01	19.24[d]
triple point of D_2	18.73	59.63	17.13	8.012[d]
triple point of H_2	13.95	7.199	0.674[d]	0.197[d]

[a] Refs. 16 and 60.

[b] Liquid unless at triple point or otherwise indicated.

[c] To convert kPa to mm Hg, multiple by 7.5.

[d] Solid.

Solid hydrogen usually exists in the hexagonal close-packed form. The unit cell dimensions are $a_0 = 378$ pm and $c_0 = 616$ pm. Solid deuterium also exists in the hexagonal close-packed configuration, and $a_0 = 354$ pm, $c_0 = 591$ pm (57–59).

In addition to H_2, D_2, and molecular tritium [100028-17-8], T_2, the following isotopic mixtures exist: HD [13983-20-5], HT [14885-60-0], and DT [14885-61-1]. Table 5 lists the vapor pressures of normal H_2, D_2, and T_2 at the respective boiling points and triple points. As the molecular weight of the isotope increases, the triple point and boiling point temperatures also increase. Other physical constants also differ for the heavy isotopes. A 98% *ortho*–2% *para*-deuterium mixture (the low temperature form) has the following critical properties: $P_c = 1.650$ MPa(16.28 atm), $T_c = 38.26$ K, $V_c = 60.3$ cm/mol3 (61). The thermal conductivity of gas-phase deuterium is about 0.73 times that of gas-phase hydrogen. This thermal conductivity difference offers a convenient method for analysis of H_2–D_2 mixtures. Other physical properties of D_2, T_2, HD, DT, and HT are listed in the literature (60).

A mixture of solid and liquid *para*-hydrogen, termed slush hydrogen, is thought to be better for fuel purposes than liquid normal hydrogen because of the greater density and higher heat capacity of the solid–liquid mixture. Some thermodynamic properties of slush hydrogen and oxygen are given in the literature (62). As of this writing the National Aeronautics and Space Administration (NASA) is researching the possibility of using slush hydrogen as a fuel for the space shuttle and for hypersonic planes. Slush hydrogen is a highly energetic hydrogen slurry that takes up 15% less volume than conventional liquid hydrogen. Use of slush hydrogen could cut a plane's gross lift-off weight by as much as 30% (63). The slush is made by passing liquid hydrogen through a vessel cooled by helium and collecting solid hydrogen that forms on the vessel walls.

Solid hydrogen is known to undergo phase transitions as the pressure is increased. One phase of solid hydrogen that is postulated to exist under conditions of extreme pressure is metallic hydrogen (64–66). Metallization of hydrogen at extremely high pressures was first predicted from theory in 1935. Metallic hydrogen, predicted to have unusual properties, including very high temperature superconductivity, could store 100 times more energy compared with the same mass of liquid hydrogen.

Hydrogen gas chemisorbs on the surface of many metals in an important step for many catalytic reactions. A method for estimating the heat of hydrogen chemisorption on transition metals has been developed (67). These values and metal–hydrogen bond energies for 21 transition metals are available (67).

3. Chemical Properties

3.1. Hydrogen-Producing Reactions. *Industrial.* The main means of producing hydrogen industrially are steam reforming of hydrocarbons

$$CH_4 + H_2O \longrightarrow CO + 3\,H_2$$

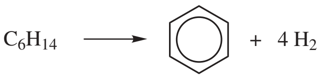
partial oxidation of hydrocarbons

$$C_nH_{2n} + \frac{n}{2}\,O_2 \longrightarrow n\,CO + n\,H_2$$

and water electrolysis

$$2\,H_2O \longrightarrow 2\,H_2 + O_2$$

Mixtures of $CO{-}H_2$ produced from hydrocarbons, as shown in the first two of these reactions, are called synthesis gas. Synthesis gas is a commercial intermediate from which a wide variety of chemicals are produced. A principal, and frequently the only source of hydrogen used in refineries is a by-product of the catalytic reforming process for making octane-contributing components for gasoline (see Gasoline and other motor fuels), eg,



Hydrogen is also a significant by-product of other industrial processes, such as steam pyrolysis (68) of hydrocarbons to produce ethylene (qv), eg,

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

This by-product hydrogen can be used as fuel or purified and used in other chemical or refinery operations.

Laboratory. Hydrogen is produced on a laboratory scale from the action of an aqueous acid on a metal or from the reaction of an alkali metal in water:

$$Zn + 2HCl \longrightarrow H_2 + ZnCl_2$$
$$2\,Na + 2\,H_2O \longrightarrow H_2 + 2\,NaOH$$

These reactions can be carried out at room temperature. Hydrogen gas can also be produced on a laboratory scale by the electrolysis of an aqueous solution.

Production of hydrogen through electrolysis is also used industrially. This involves the following reaction at the cathode of the electrochemical cell:

$$H^+ \text{ (aq)} + e^- \longrightarrow 1/2\ H_2$$

Hydrogen atoms can be produced in significant quantities in the gas phase by the action of radiation on or by extreme heating of H_2 (3000 K). Although hydrogen atoms are very reactive, these atoms can persist in the pure state for significant periods of time because of the inability to recombine without a third body to absorb the energy of bond formation.

3.2. Bonding of Hydrogen to Other Atoms. The hydrogen atom can either lose the 1*s* valence electron when bonding to other atoms, to form the H^+ ion, or conversely, it can gain an electron in the valence shell to form the hydride ion, H^- (see HYDRIDES). The formation of the H^+ ion is a very endothermic process:

$$1/2\ H_2 \text{ (g)} \longrightarrow H^+ \text{ (g)} + e^- \qquad \Delta H = 1310 \text{ kJ/mol (313.1 kcal/mol)}$$

Hence, H^+ exists only when hydrogen is bonded to the most electronegative atoms. In aqueous solutions, H^+ hydrates to form H_3O^+ ion.

The formation of the hydride ion is also endothermic:

$$1/2\ H_2 \text{ (g)} + e^- \longrightarrow H^- \text{ (g)} \qquad \Delta H = 151 \text{ kJ/mol (36.1 kcal/mol)}$$

Hydride ions only form when hydrogen reacts with very electropositive materials.

Most hydrogen compounds are formed through covalent bonding of hydrogen to the other atoms. Hydrogen can bond with itself to form the hydrogen molecule. Because the hydrogen molecule has a high bond strength (436 kJ/mol or 104 kcal/mol), it is not particularly reactive under normal conditions. For this reason, high temperatures and catalysts are often used in reactions involving hydrogen.

3.3. Reactions of Synthesis Gas. The main hydrogen manufacturing processes produce synthesis gas, a mixture of H_2 and CO. Synthesis gas can have a variety of H_2-to-CO ratios, and the water gas shift reaction is used to reduce the CO level and produce additional hydrogen, or to adjust the H_2-to-CO ratio to one more beneficial to subsequent processing (69):

$$CO + H_2O \longrightarrow CO_2 + H_2$$

Synthesis gas is used mainly to produce ammonia (qv) and methanol (qv) (70).

$$CO + 2\ H_2 \longrightarrow CH_3OH$$
$$3\ H_2 + N_2 \longrightarrow 2\ NH_3$$

In methanol production, zinc copper–chromium catalysts are used with reaction conditions of 200–400°C and pressures ≥10 MPa (100 atm) (71,72). Methanol is an industrial solvent and chemical intermediate from which formaldehyde (qv), acetic acid, methyl chloride, and methylamines are made (70). The gasoline additive methyl *tert*-butyl ether (MTBE), used for octane boosting, is produced from methanol and isobutene. Methanol production has received increased attention owing to the possibility of methanol-based fuels (see ALCOHOL FUELS). Ammonia production is an exothermic reaction thermodynamically favored by low temperatures, but high temperatures are needed to get reasonable rates of reaction. The approximate equilibrium constant K_p for the equation as written at 1 MPa (10 atm) is 7.08×10^{-4} at 350°C and 1.45×10^{-5} at 500°C (73). Industrially, the reaction is catalyzed with promoted iron oxides (74). Other materials such as ruthenium also catalyze this reaction (75). Operating conditions in an industrial plant cover a wide range of pressures [14–101 MPa (140–1000 atm)] and temperatures (ca 400–520°C). Ammonia is used to produce a wide variety of other chemicals, including nitrogen-based fertilizers (qv).

Synthesis gas is used in the production of substitute natural gas (SNG), ie, methane, and higher hydrocarbons,

$$\mathrm{CO} + 3\,\mathrm{H_2} \longrightarrow \mathrm{CH_4} + \mathrm{H_2O}$$

$$m\,\mathrm{CO} + (2m+1)\,\mathrm{H_2} \longrightarrow \mathrm{C}_m\mathrm{H}_{2m+2} + m\,\mathrm{H_2O}$$

as well as in the production of olefins (qv), glycols (qv), and higher alcohols (see ALCOHOLS, HIGHER ALIPHATIC). Several reviews are available summarizing these reactions (76,77). The first reaction, called methanation, is used not only to produce methane (SNG) but also to remove small quantities of carbon monoxide from a gas stream (78) (see FUELS, SYNTHETIC–GASEOUS FUELS). Nickel catalysts are used with temperatures of about 315°C. Other catalysts have also been used for methanation (79–82).

The second reaction is called the Fischer-Tropsch synthesis of hydrocarbons. Depending on the conditions and catalysts, a wide range of hydrocarbons from very light materials up to heavy waxes can be produced. Catalysts for the Fischer-Tropsch reaction include iron, cobalt, nickel, and ruthenium. Reaction temperatures range from about 150 to 350°C; reaction pressures range from 0.1 to tens of MPa (1 to several hundred atm) (77). The Fischer-Tropsch process was developed industrially under the designation of the Synthol process by the M. W. Kellogg Co. from 1940 to 1960 (83).

Ethylene glycol, propylene glycol, and glycerol (qv) as well as higher alcohols can be prepared from synthesis gas. A series of patents describes this reaction, catalyzed by a rhodium homogeneous catalyst (84–86). Hydroformulation, also called the oxo process (qv), is a well-established industrial reaction involving synthesis gas. An aldehyde such as *n*-butyraldehyde, an important chemical intermediate (87), is produced from an olefin using homogeneous catalysis:

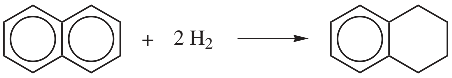
$$\mathrm{CH_3CH{=}CH_2} + \mathrm{CO} + \mathrm{H_2} \longrightarrow \mathrm{CH_3CH_2CH_2CHO}$$

A second principal application for this reaction is the production of higher alcohols from the aldehydes made from the olefins (88). These alcohols are used to manufacture detergents (see Detergency; Surfactants):

$$\mathrm{RCH_2CH_2CHO} + \mathrm{H_2} \longrightarrow \mathrm{R(CH_2)_3OH}$$

Other reactions that involve synthesis gas are various hydrogenation reactions, for example,

$$H_2 + CH_3C{\equiv}CH \longrightarrow CH_3CH{\equiv}CH_2$$

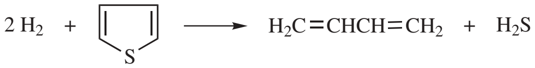


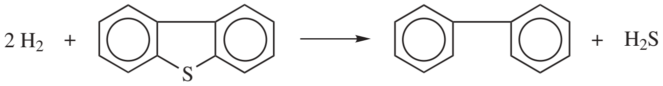
In hydrogenation, it is often desirable to hydrogenate selectively, leaving some unsaturated bonds intact. A review of hydrogenation reactions is available (89).

3.4. Other Reactions of Hydrogen.

Heteroatom Removal from Fuels. Sulfur, nitrogen, and oxygen are heteroatoms, which are abundant in many fuel sources such as petroleum (qv), coal (qv), and oil shale (qv). These elements are considered pollutants and detriments to the refining process. Hydrogen is used to reduce the levels of these contaminants. Coal contains both inorganic sulfur, ie, pyrite [1309-36-0], FeS_2, and organic sulfur, which undergo the following reactions when subjected to hydrogen at high temperatures (90–93):

$$FeS_2 + H_2 \longrightarrow FeS + H_2S$$
$$FeS + H_2 \longrightarrow Fe + H_2S$$

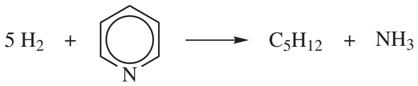


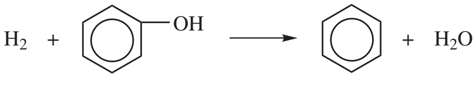


Thiophene[110-02-1], C_4H_4S, and dibenzothiophene [132-65-0], $C_{12}H_8S$, are models for the organic sulfur compounds found in coal, as well as in petroleum and oil shale. Cobalt–molybdenum and nickel–molybdenum catalysts are used to promote the removal of organic sulfur (see COAL CONVERSION PROCESSES, CLEANING AND DESULFURIZATION). Hydrogen also reacts with other sulfur compounds:

$$RSH + H_2 \longrightarrow RH + H_2S$$
$$COS + H_2 \longrightarrow H_2S + CO$$

Petroleum, particularly shale oil, also contains organic oxygen and nitrogen compounds. Model reactions for the removal of these materials with hydrogen include





As a Reducing Agent. Hydrogen reacts with a number of metal oxides at elevated temperatures to produce the metal and water. Examples of these reactions are

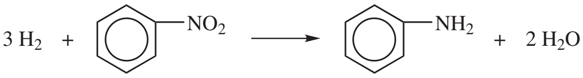
$$FeO + H_2 \longrightarrow Fe + H_2O$$
$$Cr_2O_3 + 3\,H_2 \longrightarrow 2\,Cr + 3\,H_2O$$
$$NiO + H_2 \longrightarrow Ni + H_2O$$
$$Bi_2O_3 + 3\,H_2 \longrightarrow 2\,Bi + 3\,H_2O$$

Reduction of metal oxides with hydrogen is of interest in the metals refining industry (94,95) (see METALLURGY). Hydrogen is also used to reduce sulfites to sulfides in one step in the removal of SO_2 pollutants (see AIR POLLUTION) (96). Hydrogen reacts directly with SO_2 under catalytic conditions to produce elemental sulfur and H_2S (97,98). Under certain conditions, hydrogen reacts with nitric oxide, an atmospheric pollutant and contributor to photochemical smog, to produce N_2:

$$2\,NO + 2\,H_2 \longrightarrow N_2 + 2\,H_2O$$

A ruthenium catalyst is particularly active for promoting this reaction.

Organic compounds can also be reduced with hydrogen:



$$2\,H_2 + RCOOH \longrightarrow RCH_2OH + H_2O$$
$$H_2 + RCHO \longrightarrow RCH_2OH$$

3.5. Reactions of Hydrogen and Other Elements. Hydrogen forms compounds with almost every other element. Direct reaction of the elements is possible in many cases. Hydrogen combines directly with the halogens, X_2, to form the corresponding hydrogen halide.

$$H_2 + X_2 \longrightarrow 2\,HX$$

The reaction with fluorine occurs spontaneously and explosively, even in the dark at low temperatures. This hydrogen–fluorine reaction is of interest in rocket propellant systems (99–102) (see EXPLOSIVES AND PROPELLANTS, PROPELLANTS). The reactions with chlorine and bromine are radical-chain reactions initiated by heat or radiation (103–105). The hydrogen–iodine reaction can be carried out thermally or catalytically (106).

Hydrogen combines directly with oxygen, either thermally or with the aid of a catalyst.

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

Many materials catalyze this reaction, among them metals and metal oxides such as Pt, Pd, NiO, and Co_3O_4 (107–109). One application for this reaction is in the removal of trace impurities of oxygen in a nitrogen stream using a palladium catalyst (110). Oxygen–hydrogen mixtures present a hazard because the mixture ignites explosively under certain conditions. Many studies have been made of the explosion and detonation limits of a hydrogen–oxygen system (111,112). Industrially one of the most important reactions of hydrogen is in the production of ammonia where synthesis gas is most often employed. Hydrogen reacts with graphite to form methane:

$$2\,H_2 + C_{(\text{graphite})} \longrightarrow CH_4$$

Thermodynamically, the formation of methane is favored at low temperatures. The equilibrium constant K_p is $10^{8.82}$ at 300 K and is $10^{-1.0}$ at 1000 K (113). High temperatures and catalysts are needed to achieve appreciable rates of carbon gasification, however. This reaction was studied in the range 820–1020 K, and it was found that nickel catalysts speed the reaction by three to four orders of magnitude (114). The literature for the carbon–hydrogen reaction has been surveyed (115).

Hydrogen reacts directly with a number of metallic elements to form hydrides (qv). The ionic or saline hydrides are formed from the reaction of hydrogen with the alkali metals and with some of the alkaline-earth metals. The saline hydrides are salt-like in character and contain the hydride, ie, H^-, ion. Saline hydrides form when pure metals and H_2 react at elevated temperatures (300–700°C). Examples of these reactions are

$$Li + 1/2\,H_2 \longrightarrow LiH$$
$$Ca + H_2 \longrightarrow CaH_2$$

The saline hydrides are very reactive and are strong reducing agents. All saline hydrides decompose in water, often violently, to form hydrogen:

$$NaH + H_2O \longrightarrow H_2 + NaOH$$

Catalysts can be beneficial in the preparation of some saline hydrides (116).

Other metals also form compounds with hydrogen, either through direct heating of the elements, or during electrolysis with the metal as an electrode. These metallic hydrogen compounds, also called hydrides, are in fact covalently bonded and do not contain H^-. Many metallic hydrides are nonstoichiometric in nature and appear to be metal alloys, having properties typical of metals, such as high electrical conductivity. Some compounds, such as MgH_2, are intermediate in properties between the saline hydrides and the metallic hydrides. A review of hydrides is available (117).

3.6. Reactions of Atomic Hydrogen.

Atomic hydrogen is a very strong reducing agent and a highly reactive radical that can be produced by various means. Subjecting H_2 at 0.1 MPa (1 atm) pressure to a temperature of 4000 K produces about 62% hydrogen atoms (118).

$$H_2 \longrightarrow 2\,H$$

Hydrogen atoms can also be formed on catalytic surfaces, during electrolysis and upon decomposition of hydrocarbon radicals.

$$CH_3CH_2 \longrightarrow CH_2{=\!=}CH_2 + H$$

Hydrogen atoms are thought to play a principal role in the mechanistic steps of many reactions, including hydrocarbon thermolysis (119). Some reactions of atomic hydrogen with olefins and paraffins are the following (120–122):

$$\begin{aligned} H + C_4H_8 &\longrightarrow CH_2 + C_3H_6 \\ H + C_3H_6 &\longrightarrow C_3H_7 \\ H + C_2H_6 &\longrightarrow H_2 + C_2H_5 \end{aligned}$$

Other reactions (118,123) of atomic hydrogen include

$$\begin{aligned} H + Cl_2 &\longrightarrow HCl + Cl \\ H + O_2 &\longrightarrow O + OH \\ H + O_3 &\longrightarrow HO + O_2 \\ H + NO_2 &\longrightarrow HO + NO \end{aligned}$$

Hydrogen atoms also react with a graphite surface at elevated temperatures to produce methane and acetylene (124,125).

3.7. Absorption of Hydrogen in Metals. Many metals and alloys absorb hydrogen in large amounts. A striking example is a palladium electrode which, during electrolysis, can absorb several hundred times its volume of hydrogen. The absorption is largely reversible for palladium and for some other metals and alloys. Many metals can store more hydrogen per unit volume than a liquid-hydrogen Dewar vessel (126). Thus the hydrogen is compressed in the metal to a density greater than in the liquid state. Some metal systems that have been studied are TiFe, $LaNi_5$, $SmCo_5$, Mg_2Ni, Mg_2Ca, YCo_5, and $ThCo_5$ (127–131). These systems are being developed for energy storage.

Hydrogen diffuses and absorbs in many metals, with detrimental effects. Hydrogen exposure, under certain conditions, can seriously weaken and embrittle steel (qv) and other metals. In one study, iron (qv) in a hydrogen atmosphere at high pressures and 400–450°C degenerated in all mechanical properties (139). It is thought that atomic hydrogen on the surface of the metal diffuses to voids in the metal, forming hydrogen gas at very great pressures. Eventually, the metal may yield to the high hydrogen pressures (133). The limits to the use of steel in hydrogen service and additives to improve resistance to hydrogen attack have been discussed (134,135).

Hydrogen at elevated temperatures can also attack the carbon in steel, forming methane bubbles that can link to form cracks. Alloying materials such as molybdenum and chromium combine with the carbon in steel to prevent decarburization by hydrogen (132).

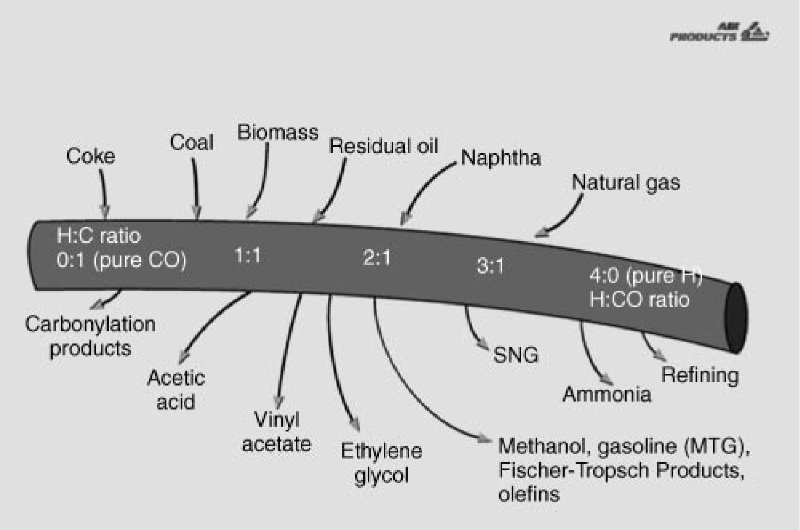


Fig. 1. Syngas feeds and products.

4. Sources and Supplies

Several new processes that are varying mixtures of synthesis gas are of interest for new routes to chemicals utilizing different feedstocks and hence different economics.

Figure 1 illustrates the broad range of hydrogen feedstock sources from light hydrocarbons to solids and end products, which use pure hydrogen through mixtures of HyCO syngas to pure carbon monoxide.

A principal source of hydrogen in refineries is the by-product production of hydrogen from catalytic reforming to produce high octane gasoline (Fig. 2). Typical volumes of hydrogen produced range from 600 scf/bbl (16.8 m^3/bbl) up to 1400 scf/bbl (39.2 m^3/bbl) depending on the type of catalytic reforming process employed. Industrial volumes range from the low end of 0.14×10^6 m^3/d (5×10^6) 5 million standard cubic feet (5×10^6 SCF) per day up to as high as 2.8×10^6 m^3/d (100×10^6 SCF/d) from a modern single catalystic reformer.

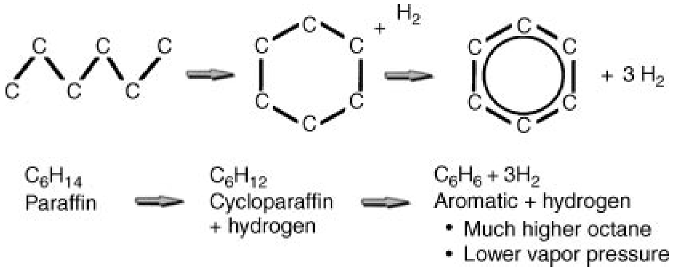


Fig. 2. Catalytic reforming.

In the 1990s, with the advent of U.S. Clean Air Act Amendments (CAAA) requiring reformulated gasoline (RFG) for approximately 25–30% of the U.S. and the subsequent California Air Resources Board (CARB) regulations in 1996, benzene in ghasoline has been restricted and catalytic reforming by-product hydrogen has become less of a source for refiners. Clearner fuel regulations are progressing around the world and are increasing the demand for hydrogen for refiners significantly.

Hydrogen is also a significant by-product of several chemical processes. A principal commercial source utilized extensively today is the steam cracking of ethane and heavier feedstocks (propane, butane, and naphtha).

Generally, the hydrogen by-product from an ethylene plant can be used directly by a refiner within their refinery hydrogen loop. However if the hydrogen is utilized in a chemical process as a feed source for an industrial gas pipeline system, such as the U.S. Gulf Coast, it is purified in a H_2-pressure swing adsorption (PSA) unit from a typical 85–95% H_2 off-gas need to factored into blending with other hydrogen streams within a refinery and can cause loss of the H_2 stream during excursions of high CO content, which acts as a poison to some refining catalysts. The hydrogen concentration and volume of the off-gas stream from ethylene crackers depends on the feedstocks and capacity of the crackers. Generally, the U.S. Gulf Coast plants have ethylene crackers using an ethane and propane (E/P) feed and yield on the order of magnitude of $1.12–1.4 \times 10^6$ m^3/d (40 to 50 $\times 10^6$ SCF) of hydrogen per 6.8×10^{10} kg/yr (1.5×10^9 lb/yr) facility. In Europe and in the Asia-Pacific region, the majority of ethylene crackers operate on naphtha feedstocks, which yields a pyrolysis gasoline product requiring hydrogenation to stabilize it prior to shipment or sale. As a result of the heavier feedstock, and the internal need for hydrogen, the net yield from this source is typically only $0.56–0.7 \times 10^6$ m^3/d (40 to 50 $\times 10^6$ SCF) of hydrogen per 6.8×10^{10} kg/yr (1.5×10^9 lb/yr) facility. In Europe and in the Asia-Pacific region, the majority of ethylene crackers operate on naphtha feedstocks, which yields a pyrolysis gasoline product requiring hydrogenation to stabilize it prior to shipment or sale. As a result of the heavier feedstock, and the internal need for hydrogen, the net yield from this source is typically only $0.56–0.7 \times 10^6$ m^3/d ($20–25 \times 10^6$ SCF) of hydrogen at a lower purity level. Figure 3 illustrates

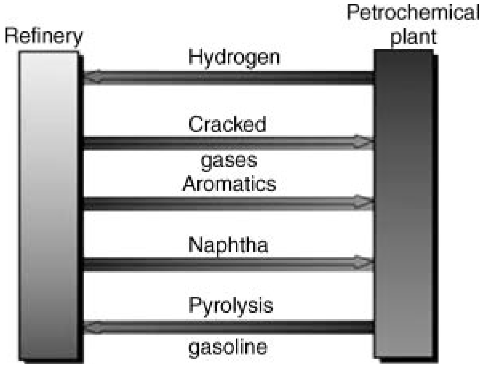


Fig. 3. Integrated refinery/petrochemical complex.

the flow of intermediate streams between refining and petrochemicals plants, including hydrogen.

4.1. Chlor-Alkali. Hydrogen is also a significant by-product of chlor-alkali processes, since chlorine manufacture is significant around the world. However, some of the facilities are not located in proximity to another refinery or chemical complex, so the hydrogen by-product is typically burned as a fuel. There are three types of chlor-alkali processes: (*1*) mercury cells; (*2*) diaphragm; and (*3*) the newer membrane cells. The hydrogen purity ranges from 95 to 98+%, with impurities of air, water, carbon oxides, methane and HCl. In addition the mercury cells contain amounts of mercury that must be removed prior to use. The hydrogen off-gas yield is approximately 0.028×10^6 m^3/d (1×10^6 SCE/d) per 100 t/d of chlorine production at a pressure of 103 kPa.

4.2. Other Chemical Processes. Several other chemical processes yield a by-product hydrogen stream, which is commercially recovered today. These include styrene manufacture from ethylbenzene and the gasoline additive methyl *tert*-butyl ether (MTBE), where the site includes the step of dehydrogenation of isobutane to isobutene and then reaction with methanol. Ammonia and methanol processes have purge gas streams which have volumes of hydrgoen at sufficient purity to justify recovery and purification of the hydrogen.

A relatively new manufacturing process to produce carbon black yields a hydrogen stream of approximately $0.14 \times 10^6 m^3$/d (5×10^6 SCF/d). The Kvaerner process involves the thermal reduction of hydrocarbons to carbon black and hydrogen and was commercialized in 1998.

5. Manufacture and Production

The main commercial processes for the on-purpose production of hydrogen are steam reforming, partial oxidation (coal, coke, resid), or electrolysis of water. Hydrogen is also commercially produced as a by-product of chemical processes (ethylene crackers, styrene, MTBE etc) or gasoline manufacturing (catalytic reforming).

These processes all produce hydrogen from hydrocarbons and water.

steam reforming	$CH_4 + 2\,H_2O \longrightarrow CO_2 + 4\,H_2$
naphtha reforming	$C_nH_{2n} + 2 + n\,H_2O \longrightarrow n\,CO + (2n + 1)\,H_2$
resid partial oxidation	$CH_{1.8} + 0.98\,H_2O + 0.51\,O_2 \longrightarrow CO_2 + 1.88\,H_2$
coal gasification	$CH_{0.8} + 0.6\,H_2O + 0.7\,O_2 \longrightarrow CO_2 + H_2$
water electrolysis	$2H_2O \longrightarrow 2\,H_2 + O_2$

Selection of the differing processes is dependent on a number of criteria: (*1*) the availability and relative cost of the different feedstocks; (*2*) capital costs; (*3*) operating costs; (*4*) environmental considerations, and (*5*) end use of the hydrogen or syngas. Generally, as the feedstocks go from natural gas to light hydrocarbons to heavy hydrocarbons and then to solid feedstocks, the processing difficulty and capital costs increase. Partial oxidation (POX) plants also

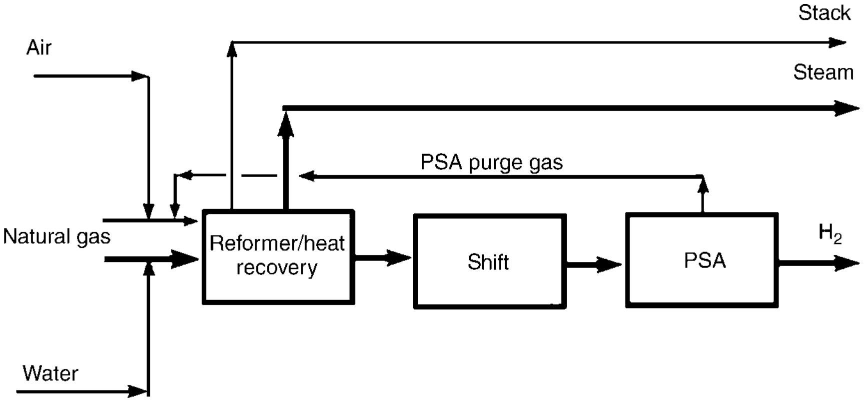


Fig. 4. Steam–methane reformer.

require an air separation plant to produce the oxygen, larger water gas shift and CO_2 removal facilities and gas cleanup systems due to impurities present in the solid feedstocks (such as sulfur).

Heavier fractions, such as vacuum residue, deasphalter bottoms, refinery sludges, and petroleum coke, can be processed into hydrogen using POX technology, however, the low hydrogen content of these feeds combined with a high capital and operating cost requires that they be available at very low or negative cost for a hydrogen only facility. The heavier feeds are more suited to syngas production or where the raw syngas is processed for hydrogen with a syngas by product.

5.1. Steam Methane Reforming (SMR).

In the U.S., over 95% of on-purpose hydrogen production is supplied by steam methane reforming of light hydrocarbons (Fig. 4). Many existing refinery and chemical hydrogen plants produce a medium-purity (95%–97%) hydrogen product by removing the carbon dioxide in an absorption system and methanating any remaining carbon oxides. Since the 1980s most SMRs use pressure swing adsorption (PSA) technology to recover and purify the hydrogen to purities above 99.9%. These PSA-based hydrogen plants have higher efficiencies than conventional low-purity plants because of additional export steam credits.

When natural gas is used as the feed to a steam reformer, the basic reactions are

Reforming

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad \text{Endothermic}$$

$$\Delta H^{+}25°C = 206 \text{ kJ/gmol } (49.3 \text{ kcal/gmol})$$

Shift

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \text{Exothermic}$$

$$\Delta H^{+}25°C = -41 \text{ kJ/g mol } (-9 \text{ H kcal/gmol})$$

Overall

$$CH_4 + 2\,H_2O \longrightarrow CO_2 + 4\,H_2$$

The reforming reaction is highly endothermic and accompanied by an increase in the total number of moles. Hence, it is favored by high temperature and low pressure. For light hydrocarbon feeds such as natural gas, a single nickel-based catalyst is employed. However, for heavier feeds such as naphtha, two catalysts are usually preferred. The reforming reaction is equilibrium-limited. It is favored by high temperature 788–880°C, low pressure (1.4–3.8 MPa), and a high steam-to-carbon ratio (2.5 to 4). These conditions minimize methane slip at the reformed outlet and yield an equilibrium mixture that is rich in hydrogen.

The shift reaction is exothermic and independent of pressure. It is also equilibrium limited and favored by low temperature (343–371°C) and high steam concentration. Normally, the shift catalyst is based on iron oxide.

It is clear that a steam reformer has the capability to also produce carbon dioxide (CO_2), carbon monoxide (CO) and synthesis gas ($CO + H_2$), which are valuable coproducts in some geographic areas. Also owing to the high temperatures, varying amounts of steam must be generated by heat recovery from the reformer furnace. This steam can be exported to the refinery or petrochemical facility for process needs and/or converted into electricity. By-products such as carbon dioxide, steam, and electricity have a large impact on plant design and economics. In addition, other utilities such as boiler feed water, cooling water, instrument air, and nitrogen are required to support operation of a hydrogen plant. Hence the needs can be combined with those of the host site to further reduce the total system supply costs.

Ammonia. Ammonia is the largest consumption process for hydrogen synthesis gas, with refining ranked second largest hydrogen market and methanol the third largest consumer of synthesis gas. The majority of the commercial ammonia processes utilize natural gas as the feedstock and are directly integrated with the synthesis loop to produce ammonia rather, than producing hydrogen as a product first. Therefore, they are generally regarded as consumers of natural gas (or heavier hydrocarbons) rather than hydrogen. The exception to this rule has been the recent emergence of several small ammonia plants based on off-gas hydrogen sourcing and pipeline nitrogen, for a direct conversion to ammonia process.

The majority of ammonia is produced by reforming natural gas into hydrogen in a primary steam reformer and then passing the resultant H_2, CO, CO_2, and residual CH_4 through a secondary reformer, where air is introduced to create the necessary 3:1 molar ratio of H_2 and N_2 mixture. The CO_2 is generally removed by an absorption process and then the CO is removed via methanation catalyst. There are small amounts of methane and argon in the mixture, which is necessary to purge from the ammonia synthesis loop.

The overall ammonia synthesis reactions is outlined below:

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

Methanol. Similar to the ammonia process, methanol is manufactured from a synthesis gas (hydrogen, carbon monoxide, carbon dioxide) rather than a separate hydrogen product. Similarly, natural gas or heavier hydrocarbons are the principal feedstock for commercial plants producing methanol. The recent trend has been for very large world scale methanol plants to be constructed in countries where there is an excess of natural gas reserves remote to major markets which is utilized at low feedstock pricing by the governments to attract capital to build the methanol plants and export the methanol to the end use markets to generate trade credits. This trend is expected to continue resulting in shutdown of older, smaller facilities in North America and Europe based on higher natural gas costs ($1.75–2.50/ $\times 10^6$ BTU's vs $0.25–0.50/ $\times$ 10^6. Approximately 40% of the U.S. methanol market demand is for use in MTBE production. At the time of this report, MTBE is the process of being banned in CARB gasoline by December 31, 2002, which is currently being studied by the EPA for the other 49 states (Blue Ribbon Committee, July 1999).

The majority of the world's methanol production is based upon natural gas reforming, with the balance based on heavier liquid hydrocarbons. The steam reforming reaction produces excess hydrogen (H_2) relative to carbon monoxide (CO) that is required to feed a methanol synthesis loop and generally, carbon dioxide (CO_2) from an external nearby source (ammonia plant) is added to the loop, or H_2 is purged from the methanol loop and burned as fule or sold as an off-gas hydrogen source.

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The overall methanol synthesis reaction is

$$\mathrm{CO + 2\,H_2 \rightleftharpoons CH_3OH}$$
$$\mathrm{CO_2 + 3\,H_2 \rightleftharpoons CH_3OH + H_2O}$$

Alternative Feedstocks. Refinery naphtha streams can also be used as feedstrock for steam reforming plants. Naphthas consists of a wide range of hydrocarbons with an initial boiling point of 44–56°C and a final boiling of 103–154°C. Naphtha is used in many steam reformers throughout the world. Naphthas are one of the primary feedstocks in the Asia-Pacific region where natural gas in not readily available. In the case where naphtha is used versus natural gas, the steam-to-carbon ratios must be elevated and special catalysts used to prevent cracking and carbon formation. With the higher steam-to-carbon ratios, the plants are generally less efficient.

Process and Plant Design. The main processing steps are feed compression and purification, steam reforming and shift conversion, pressure swing adsorption purification, product compression and steam generation. A detailed process flow diagram is shown in Figure 5.

Feed gas at elevated pressure has to be preheated, and desulfurized before it can be fed to the reformer furnace. When the feed contains olefins and/or organic sulfur, hydrogenation of the feed using a Co–Mo or Ni–Mo catalyst is necessary. Hydrogenation saturates the olefins to prevent cracking and carbon formation at the reformer inlet. Likewise, it is necessary to convert the organic sulfur (mercaptans, thiophenes, etc) to H_2S before desulfurization.

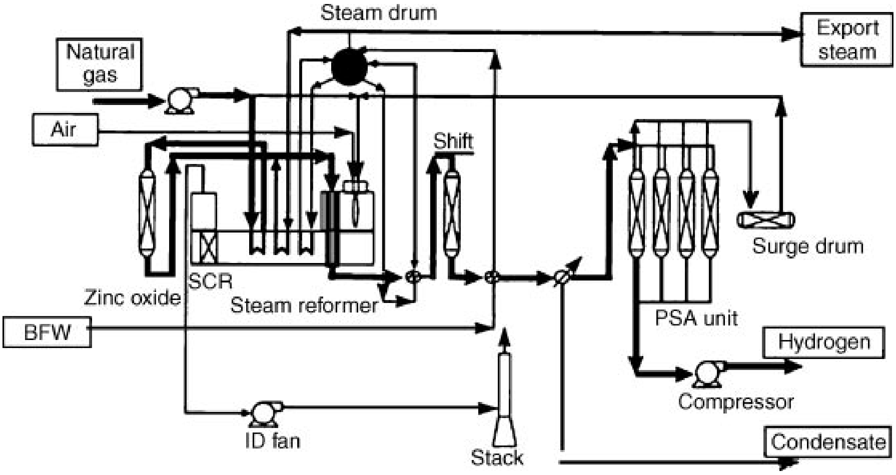

Fig. 5. Steam–methane reforming process flow diagram.

Desulfurization of the feed gas, which is usually carried out with a zinc oxide bed, is needed since sulfur can poison the reformer catalyst.

After purification, the feed gas is mixed with process steawem at an appropriate steam-to-carbon mole ratio. The catalyst converts the feed gas to an equilibrium mixture of hydrogen, methane, and carbon oxides. Most of the carbon monoxide in the reformer product is converted to carbon dioxide and additional hydrogen in the shift reactor.

After cooling, pure hydrogen is recovered from the shift product by a pressure swing adsorption (PSA) unit. Typically, a PSA produces hydrogen at 99.9%, although the hydrogen purity can be as high as 99.999% (136,137). The adsorbent, which is a mixture of activated carbon and zeolites, removes all of the contaminants from the hydrogen product in a single step. When CO_2 is desired as a coproduct, it can be recovered in one of two ways depending on the desired H_2 purity In modern plants, CO_2 is recovered from the process gases upstream of the PSA using a solvent system. In older hydrogen plants or when a lower purity (96 to 97%) hydrogen is acceptable, a solvent system and methanator purification system can be used instead of the PSA.

Process Economics. For small SMRs, the capital portion of the unit cost of hydrogen is significant and may be as high as 65%, with the balance being comprised of operating and energy costs (natural gas and power). As the size of the SMR increases, the capital contribution scales to a factor approximating 0.6. The economics of a large steam reformer are highly site specific. For a specific plant size and location, capital investment is a function of the feedstock and product purity and pressure, degree of utility integration, and reliability criteria. As an example the total capital cost of a "generic" 1.4 $m^3/d \times 10^6$ (50 SCF) steam reformer based on natural gas is $\$60 \times 10^6$, which includes $\$10 \times 10^6$ in plant offsites. The unit cost of hydrogen from a $1.4 \times 10^6 m^3/d$ (50×10^6 CFD) SMR plant (minimum steam case) is ~40% capital and operating costs and ~60% energy and utilities. It is important to recognize that the unit cost of hydrogen can be reduced by building a larger plant. The capital cost savings can thus be passed on to the customers in the form of lower hydrogen cost. Building a larger hydrogen plant many be justifiable in situations, where there are additional customers in the vicinity, who can be connected by pipeline such as those operated by industrial gas companies.

5.2. Partial Oxidation. Partial oxidation of hydrocarbons is a well practiced process, which has principally been licensed by Texaco and Shell around the world. The process is carried out by feeding preheated hydrocarbons, preheated oxygen and steam to a specially designed burner in an insulated reactor vessel designed for a specific residence time. The process is designed to achieve a partial oxidation of the hydrocarbons, using substoichiometric oxygen for complete combustion. The overall reaction is as follows:

$$C_nH_m + n/2\,O_2 \longrightarrow n\,CO + m/2\,H_2$$

Figure 6 illustrates a Texaco gasification process. There are three phases comprising the overall reaction including heating and cracking, reaction, and soaking.

In the heating cracking phase, preheated hydrocarbons leaving the atomizer are intimately contacted with the steam-preheated oxygen mixture. The atomized hydrocarbon is heated and vaporized by back radiation from the flame front and the reactor walls. Some cracking to carbon methane and hydrocarbon radicals occurs during this brief phase.

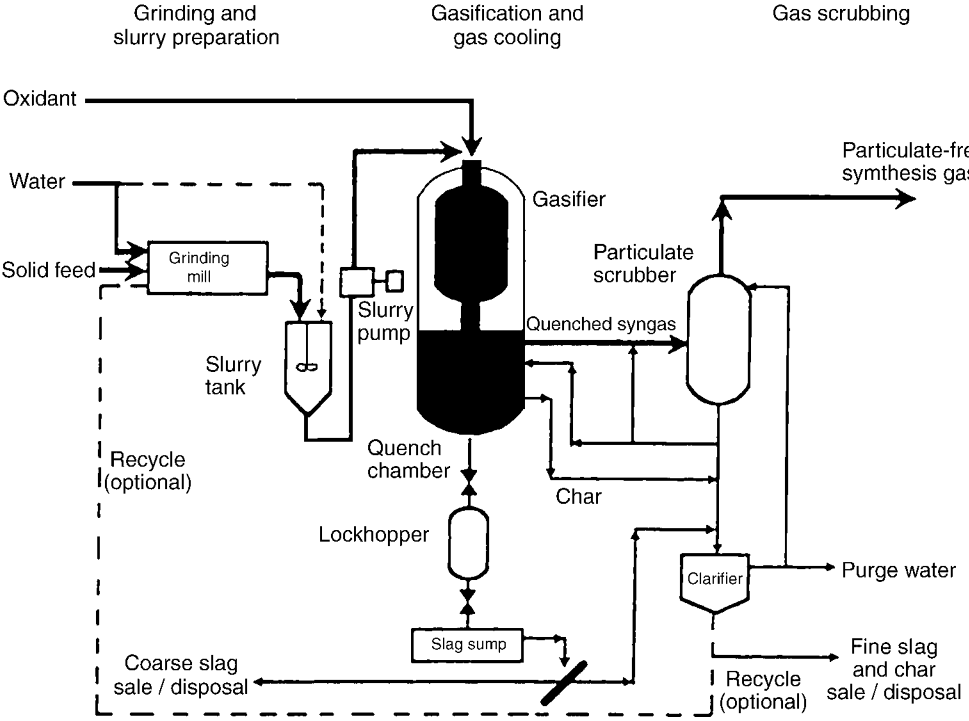

Fig. 6. Texaco gasification process.

In the reaction phase, hydrocarbons react with oxygen to the highly exothermic combustion reaction. Practically all of the oxygen is consumed in this phase.

$$C_nH_m + (n + m/4)\ O_2 \longrightarrow n\ CO_2 + m/2\ H_2O$$

The remaining unoxidized hydrocarbons react endothermically with steam and the combustion products from the primary reaction. The main endothermic reaction is the reforming of hydrocarbon by water vapor.

$$C_nH_m + n\ H_2O\ O_2 \rightleftarrows n\ CO + (n + m/2)\ H_2$$

Typical high-temprature, entrained flow gasifier operating conditions are: Temparature, 1270–1409°C; pressure, 2.7–8.2 MPa; and residence time, 2–5 s.

The basic gasification reactions are affected only slightly by pressure; consequently, gasification pressure generally is selected for best fit with downstream processing requirements. Refinery gasification projects often require air separation plants producing 1,000 tons/day of oxygen at delivary pressures ranging from 2.7 MPa to as high as 8.6 MPa.

In the final soaking phase, a portion of the carbon is consumed in reactions with CO_2 and steam. Some carbon, approximately 1–3 wt.% of the oil feed ends up in the product syngas and must be removed and recycled to the reactor. For natural gas fed gasifiers, the carbon content is much lower at about 0.2 w%.

The final composition of the gas is detemined by the degree of water gas shift equilibrium which occurs at the reactor outlet waste-heat exchanger or the quench section.

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

Sulfur in the feed is converted into H_2S with small amounts of COS, which needs to be removed via an amine scrubbing system.

Economic Process. It is critical in the evaluation of partial oxidation as an alternative hydrogen production technology to size the gasification facility to match the available markets for the ultimate and end products: steam, electricity, hydrogen, and/or syngas for chemicals. Most gasifiers, however, are of such a size, as dictated by feedstock availability, that product sales will be necessary beyond the host site to provide the econimics required for the capital investment in a POX unit.

An example of the relative size of a gasifier project is given below:

Gasification 1,000 ton of petroleum coke could produce 1,000 ton of ammonia.

Gasification of 1,000 b/d of heavy oil could produce about 32 MW of net electrical power.

Alternatively, carbon monoxide and hydrogen are basic chemical building blocks for production of many chemicals. If hydrogen is the desired primary end product, the carbon monoxide may be reacted almost entirely to produce hydrogen via steam shift.

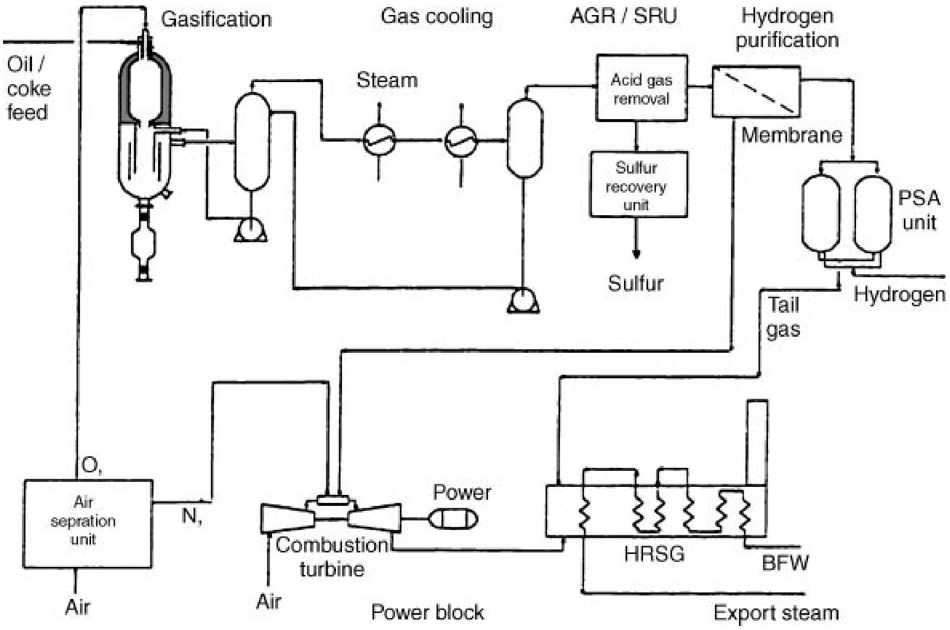

Fig. 7. Texaco gasification power system coproduction flow sheet.

The prediminant configuration for a refinery gasification unit utilizing coke or heavy resid involves the coproduction of hydrogen with power generation as shown in Figure 7.

Generally, the partial oxidation units in place in refineries shift all or a majority of the syngas to hydrogen for use internally fro their hydroprocessing units. Examples of refineries utilizing POX include: Star Enterprise/Convent, La; Equilon (JV of Shell and Texaco)/Wilmington, Calif; and Shell/Pernis, The Netherlands.

An example of the economics for a large POX unit are illustrated in Table 6 below. The capital cost of the Texaco facility including the air separation plant is approximately $\$275 \times 10^6$, excluding offsite utilities for the facility. The basis for the economics are 2,200 tld of coke feed, 140 MW Net Power Export (plus 140 MW internal consumption), Ca 40, 825 kg/h steam production and 0.7×10^6 m^3/d ($25 \times 10^6/d$) of hydrogen production.

Another interesting aspect of the POX of heavy fuels is the current deregulation of the power industry in the U.S. and the U.K. and potentially in Europe.

Table 6. **Economic Sensitivities For POX of Coke**

Variable	Base	Range	Return%
power internal, $/kwh	0.04	0.03–0.05	13–17
power export, $/kwh	0.025	0.02–0.04	14–18
hydrogen $/M m^3	0.028	0.017–0.056/Mm^3	14–17
steam, $/Mkg	1.15 Mkg	0.90–2.27/Mm^3	15–16
coke price, $/t	5	15 to ($ 5)	13–17

Large refiners are evaluating the economics of becoming net exporters of power, shutting down old boilers in light of the current declining price (late 1998) for coke. The recent financial crisis in the Asia-Pacific region has depressed demand for coke imports form the U.S., which combined with the fact that U.S. exports are close to 80% of the approximately 100,000 tld of coke production has led to negative price at the refinery gate. The key question is the long term pricing, which has fluctuated as a commodity over the past with market demand and supply.

5.3. New Production Methods. *Microhydrogen generators.* Recent advances in small-scale hydrogen production via steam methane reforming, partial oxidation, and autothermal reforming of hydrocarbons such as natural gas, propane, methanol etc, offer the promise of economic on-site hydrogen production at capacities below 0.028×10^6/d 1×10^6/d SCF pd. These units have been developed as low cost fuel processors to provide a hydrogen rich feed gas for fuel cells and are now being integrated with advanced small scale hydrogen purification units to enable the production of pure hydorgen. These reformers are designed to operate at lower pressures than the large central plants; are generally made from less exotic alloys; use compact convective heat transfer to reduce heat exchanger area needed; use standerdized designs; and will mass produced and hence will be cheaper than the large conventional reformers (138). These innovations combined with advances in small low cost hydrogen PSA systems offer the advantages of on-site production to small scale users(139).

Electrolysis. The electrolytic process uses electrical energy to split water into hydrogen and water. Electrolysis is a well proven process to convert water to hydrogen, and is used industrially on a limited scale. Electrolysis is a very clean, reliable process, and the hydrogen produced is very pure. The main drawback with the process is that the electricity used to drive the process is usually 3–5 times more expensive than the fossil-fuel energy used to generate it. However, electrolysis combined with electric energy produced from renewable sources such as solar photovoltaic cell, wind or hydroelectric power can become important in the future to produce hydrogen in a sustainable way (140). (See ELECTROCHEMICAL PROCESSING, INORGANIC).

When direct current is passed between two electrodes placed in water the following eletrode reactions occur:

$$\begin{array}{ll} \text{Cathode:} & 2\,H_2O + 2e^- \longrightarrow H_2 + 2\,OH^- \\ \text{Anode:} & 2\,OH^- \longrightarrow \frac{1}{2}\,O_2 + H_2O + 2e^- \end{array}$$

The reversible voltage, i.e., the theoretical minimum voltage needed to get the reaction to proceed at 25°C is 1.23V. In practice, however, a higher operating voltage is necessary to overcome internal cell resistances, due to irreversible processes at the electrodes. Typical cell voltages are about 1.85–2.05 V. The energy requirement is typically about 4–5 kWh/Nm^3, and the water consumption is about 1 1/Nm^3, of hydrogen produced.

Two types of electrolysis processes have been commercially developed: (1) an aqueous alkaline system; (2) and a solid polymer electrolyte (SPE) also known as proton exchange membrane (PEM). A third process, high temperature steam dlectrolysis (700–1000°C) is under development.

Aqueous Alkaline Electrolysis. Aqueous alkaline electrolysis traditionally employs potassium hydroxide (25–30%) added to the water to improve the electrical conductivity. A diaphragm is used to separate the cathode and anode and keep the product oxigen and hydrogen from mixing. The cells operate at 70–90°C.

Solid Polymer Electrolyte. The electrolyte is typically Nafion, an ion-exchange polymer membrane developed by Du Pont, which has sulfonic acid groups attached to the perfluoro polymer backbone. These units have relatively low internal resistance and can operate at higher temperatures than alkaline electrolysis units.

High-Temparature Steam Electolysis. The main advantage with this approach is that at higher temperatures, particularly above 700°C, there is a noticeable decrease in the decomposition cell voltage, e.g., at 1200 K, the theoretical decomposition voltage is 0.9 V. Thus at the high temperatures, less electrical energy, and more heat energy is required to produce hydrogen than at lower temperatures. Since heat energy is cheaper than electricity, the overall process will have a cost advantage. A ceramic such as yttria is used as the electrolyte, and O^{-2}ions are transported through the ceramic material. This technology is in the development stage.

Photolysis. Photolytic process are under development to enable the harnessing of sunlight to promote water splitting and provide and unlimited supply of hydrogen. Several approaches are being pursued. In photoelectrochemical (PEC) systems, inorganic materials are used for the directr conversion of solar energy into hydrogen semiconductor electrode. Hydrogen production efficiencies of 7–8% have been achieved thus far (141). In photobiological systems, photosynthetic algae and bacteria, absorb solar energy and use it for water splitting in the process of generating plant tissue. The hydrogen production seems to be a presursor step prior to fixiing the hydrogen with carbon from CO_2. The hydrogen yield is very low, about 1–2%. These processes are still in the early research stages (142).

Biomass Conversion. Various gasification processes are under development for the conversion of biomass, which includes materials such as agricultural crops and wastes, sewage sludge and municipal solid wastes, into synthesis gas, consisting of CO, H_2, CO_2, and some CH_4, followed by shift conversion and gas separation to produce hydrogen (143). This process is analogous to the process for making hydrogen from coal via gasification and the gasifier technologies themselves are adaptations of technologies originally developed for coal. Various biomass gasification technologies are under active commercial demonstration and were expected to be available in 2000. Since biomass is renewable material, the carbon dioxide released to the atmosphere in the biomass conversion process will be absorbed in creating new biomass and thus there is no net increase in atmospheric carbon dioxide (see FUELS FROM BIOMASS).

6. Shipment and Storage

6.1. Distribution Methods.

A full range of hydrogen supply options is generally available to industry in the U.S. and Europe and increasingly in

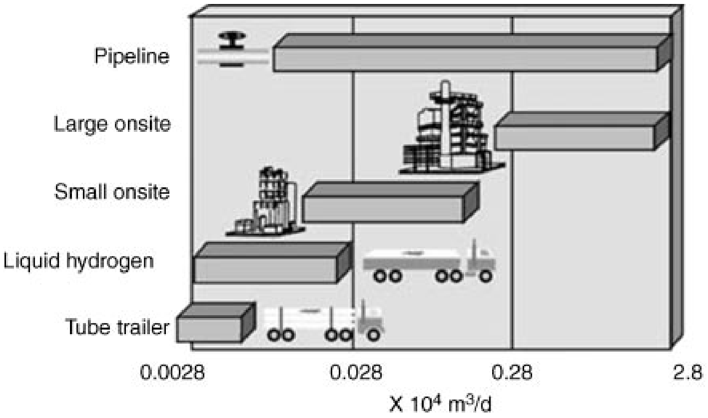

Fig. 8. Hydrogen supply selection chart to convert m^3/d to SCF/d, multiply by 35.71.

Latin America and Asia-Pacific region. Figure 8 illustrates the various distribution methods available, with a specific distribution method more economic in a given volume range. Pipelines are generally the low cost source of supply if available to the customer. If a new dedicated production (supply) of hydrogen is required, SMR or POX facility, then it will generally be located close to the use point (demand) or a point in the facility where utilities are available.

More specifically, industrial gas companies have expanded hydrogen, carbon monoxide and syngas pipelines extensively in the 1990s, growing with refiners and petrochemical companies needs at competetive pricing and increased reliability of supply due to multiple sources. Major pipeline systems are located in the Texs and Louisiana Gulf Cost and in Northern Europe (France, The Netherlands and Germany), which were established in the 1960s or early 1970s. Examples of where HyCO pipelines have expanded in the 1990s include Alberta, Canada; Camacari, Brazil; Southern California, U.S.; Mab Tha Phut, Thailand. The estimated total coverage of HyCO pipelines exceeds 1,000 miles (11609 km) on four continents.

6.2. Hydrogen Storage. The methods for storage of hydrogen include compressed gas or cryogenic liquid, adsorbed on solid materials such as carbon, and as chemically bound hydrogen in metal hydrides.

Hydrogen Gas. Hydrogen at ambient temperatures can be compressed in high pressure tanks which are easy to handle. Pressures range from below 1034 kpa to about 41.9 Mpa. The pressure vessels are periodically inspected and tested to ensure safety. Pressure vessels are typically made of low carbon steel, although special alloys and high strength nonmetallic composites are also availabel. High pressure tube storage is, however, confined to relatively small gas volumes because of the high capital cost of the storage and the gas compression costs.

Liquid Hydrogen. Hydrogen at 20 K and atmospheric pressure is stored in superinsulated tanks called “dewars”. Extremely low storage temperature always caused some heat leak into the container and cosequent “boil-off” loss of some hydrogen. Typically a cryogenic storage tank may lose about 1–2% per day of the contained hydrogen.

Metal Hydrides. Metal hydrides are intermetallic compounds that reversibly take up and release hydrogen (144). Each metal hydride is characterized by a unique equilibrium pressure–temperature curve called an isochore. At pressures above, and temparatures below the isochore, the metal hydride is formed. At pressures below, and temperatures above the isochore, the metal hydride decomposes to the metal hydride decomposes to the metal and hydrogen. High temperature hydrides such as MgH_2, $MgNiH_4$ have decomposition temperatures of 250–300°C at 101.3 kpa 1 atm, high hydrogen capacities of about 3.6–7.6 wt% (based on metal weight alone). Low temperature hydrides such as $FeTiH_x$, $LaNi_5H_6$, etc, that have decomposition temperatures below 50°C at 4.04 kpa have relatively low hydrogen capacities of about 1.4–1.8 wt%. The heat of formation needs to be removed as hydrogen is charged to these metals at ambient temperatures, and heating is required to subsequently release the hydrogen. The advantages of metal hydride storage include compactness, stability, and intrinsic safety of the system. Its theoretical volumetric hydrogen storage density is equal to or greater than liquid hydrogen. However, the volumetric storage densities of actual systems is somewhat lower taking into account the pressure vessel container, and by the need for internal heat transfer systems and perhaps thermal insulation. Drawbacks of metal hydrides include their high costs, their low gravimetric storage dinsity, typically between 1–5 wt%, and the fact that very pure hydrogen is required to form the metal hydride. The use of metal hydrides to store hydrogen is not yet of commercial importance. Current research activities are focused on increasing the gravimetic capacity, reactivity, and life of the alloys.

Glass Microspheres. A novel approach to hydrogen containment is the use of high strength glass microspheres with 25–500 μm in diameter and 1 μm wall thickness (145). The glass microshperes are permeable to hydrogen only at high temperatures (300–400°C) when hydrogen is charged at high pressure up to 250–600 atm. On cooling the hydrogen inside the microsperes is trapped at high pressure. The microspheres store about 10–15 wt% hydrogen (on glass weight alone). The microspheres can now be safely carried in nonpressurized containers. To release the hydrogen from the microspheres, they must be heated once again. These materials are in the early stages of laboratory development and offer the promise of very efficient storage and transport of hydrogen.

Carbon Storage. Activated carbon has a good capacity for the adsoption of hydrogen. This physisorption effect is most pronounced at cryogenic temperatures. Volumetric capacity of 50 g/L has been reported at 77 K and 354 kpa pressure (146). A recently discovered option for hydrogen storage is adsorption on carbon nanotubes. These tiny tubelike configurations of carbon have a very large surface area per unit weight. These tiny tubelike configurations of cabon have a very large surface area per unit weight. These materials have the potential to store large amounts of hydrogen. Reports by one group claims that 10 wt% hydrogen could be stored on these single-wall-nanotubes (147) at room temperature. As of this writing (1998) there is a great deal of research going into the use of carbon nanotubes and nanofibers to store hydrogen at ambient temperatures and pressures of about 10 MPa for vehical onboard hydrogen storage.

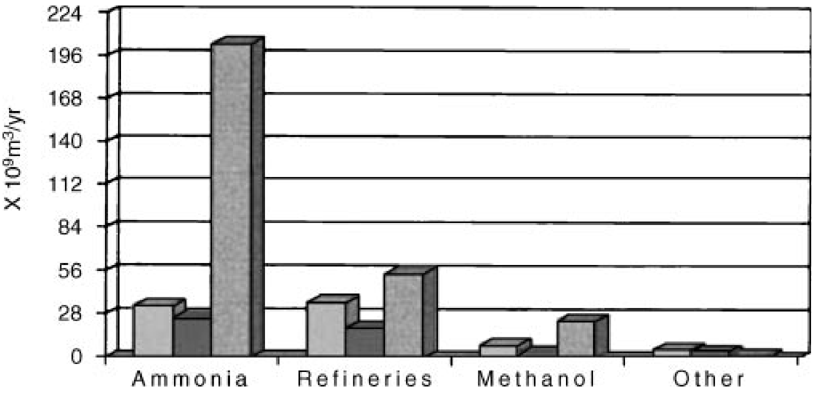

Fig. 9. Hydrogen use by end market. U. S.; Western Europe; other.

7. Economic Aspects

The estimated total world production/ consumption of on-purpose hydrogen and syngas is approximately 420×109 m^3/yr [15,000 billion standard cubic feet per year (BSCFY)]. Figure 9 illustrates the distribution of this capacity by major market and Figure 10 by geographic region.

Ammonia use is very large and estimated to grow by only 2–3 % per year, Hydrogen use for refining, methanol and other is expected to grow (3–40%) over the next ten years.

7.1. Hydrogen Producers.

Ammonia and methanol producers, petroleum refiners and third-party hydrogen suppliers are the largest producers of hydrogen on a world-wide scale. The information on some of the largest companies in each of these categories factors.

Ammonia. The manufacture of ammonia represents the largest use of hydrogen and accounts for over 60% of the worldwide consumption of on-purpose hydrogen. The hydrogen for this market is essentially always generated on-site

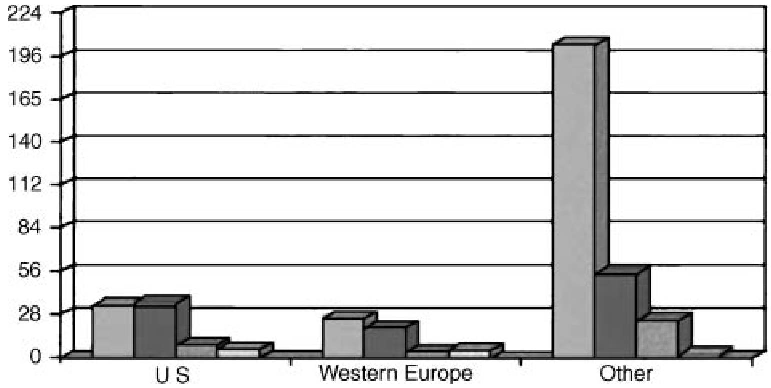

Fig. 10. Hydrogen use by geographic region. Ammonia; refineries; methanol; other.

by the ammonia manufacturer, as compared to say, petroleum refineries, where third party supply of hydrogen is becoming more prevalent. Global ammonia production in 1996, at around 103×10^6 metric tons, consumed an estimated 264×10^9 m^3 ($9{,}435 \times 109$ SCF) of hydrogen.

In the Americas, large producers of ammonia and consequently of hydrogen include Farmland Industries, PCS Nitrogen Fertilizer, Terra and CF Industries in the U.S: Agrium in Canada, Petroquimica in Mexico and PCS Nitrogen Trinidad in Trinidad and Tobago. Kemira, Hydro Agri, and Zaklady Azotowe are some of the major producers in Europe. Socialist Asia and the former USSR are the largest producers of ammonia in the world. Together, these two regions account for an estimated 38% of the world's ammonia production.

Ammonia consumption is expected to rise at an annual rate of about 2.5% over the next five years.

Methanol. The manufacture of methanol represents the third largest use of hydrogen, after ammonia manufacture and hydrogen consumption in petroleum refineries. Methanol manufacture accounts for about 9% of the worldwide consumption of on-purpose hydrogen. Similar to ammonia, the hydrogen for this market is typically generated on-site by the manufacturer and not purchased from a third party. The hydrogen is produced as part of a carbon monoxide, hydrogen mixture. Global methoanol production in 1996, at around 24×106 metic tons, consumed an estimated 36.9×10^9 m^3 ($1{,}319 \times 10^9$ SCF) of hydrogen.

Methanex and SABIC are the two largest methanol producers in the world accounting for over 20% and 5% of global production, respectively.

In the Americas, large producers of methanol include Celanese, Beaumont Methanol Limited Partnership, Borden Chemicals and Plastics and Lyondell Methanol Company in the U.S. and Methanex Corporation in Canada and Chile.

Methanor VoF in the Netherlands, Statoil in Norway and the Mitteldeutsche Erdoel refinery in Germany are some of the major methanol producers in Europe. Saudi Arabia, Indonesia and Malaysia are some of the countries in the rest of the world with significant methanol production.

Global methanol demand is expected to rise at 3–4% per year over the next five years.

Petroleum Refineries. Refiners two major sources of hydrogen are by-product hydrogen from catalytic reformers (which varies with the requirement to produce high octane gasoline) and on-purpose production from hydrocarbons (the majority is based on steam methane or naphtha reforming). The top six on-purpose hydrogen producers among the world's petroleum refiners include Shell, Exxon, Mobil, Chevron, Texaco and Indemitsu with a total hydrogen capacity ranging from $8.4–14 \times 10^6\,m^3/d$ ($300–500 \times 10^6$).

Third Party Hydrogen Supply. Major suppliers of third party hydrogen across the world included Air Products, Praxair, Air Liquide, Linde AG and BOC. Third party hydrogen supply accounts for about 10% of the non-ammonia–methanol hydrogen market.

Hydrogen Prices. The price of hydrogen on the merchant market is determinded in large measure by the mode of supply and proximity to the manufacturing location or supply infrastructure. Table 7 provides representative prices in the U.S. for the common modes of supply of significant quantities of merchant hydrogen.

Table 7. **Representative Prices for Common Modes of Supply of Hydrogen**

Supply mode	Typical volume × 10^6 (SCFD)	Typical price (\$/1000 SCF)
pipeline	2–50	1.25–2.25
large on-site plant	10–100	1.50–2.75
small on-site plant	0.5–10	3.00–6.00
delivered as liquid H_2 (Lhy)	0.01–1.0	6.00–18.00
delivered as gaseous H_2 (Bhy)	0.001–0.1	12.00–50.00

Suppliers of Hydrogen and Syngas Plants. There are numerous suppliers of on-purpose hydrogen and syngas plant equipment and technology to the ammonia, methanol and petroleum refining industries today. The major suppliers of steam reforming technology equipment include: Technip (formerly Kinetics Technology Inc.); Haldor Topsoe; Linde AG; Howe Baker; Foster Wheeler Corp.; Lurgi; MW Kellogg Corp.; and of partial oxidation technology: Texaco Development Corp. and Shell.

8. Specifications

Typical product specifications for liquid and gaseous hydrogen are grow on Table 8 and 9.

9. Analytical Methods

The determination of hydrogen content of an organic compound consists of complete combustion of a known quantity of the material to produce water and carbon dioxide, and determination of the amount of water. The amount of hydrogen present in the initial material is calculated from the amount of water produced. This technique can be performed on macro (0.1–0.2 g), micro (2–10 mg), or submicro (0.02–0.2 mg) scale. Micro determinations are the most common. There are many variations of the method of combustion and determination of water (148,149). The oldest and probably most reliable technique for water determination

Table 8. **Specification for Industrial Purity Hydrogen Supplied as a Cryogenic Liquid**[a]

Component	Maximum Acceptable Limit
oxygen	1.0 ppm v/v
nitrogen	5.0 ppm v/v
methane	4.0 ppm v/v
carbon dioxide	0.5 ppm v/v
carbon monoxide	0.5 ppm v/v
water	1.0 ppm v/v
water (dew point)	−105 F @ 101.3 kPa

Table 9. **Specification for Industrial Purity Hydrogen Supplied as a Gas in High Pressure Tube Trailers**[a]

Component	Maximum acceptable limit
oxygen	10.0 ppm v/v
nitrogen	400.0 ppm v/v
methane	10.0 ppm v/v
carbon monoxide	10.0 ppm v/v
water	7.8 ppm v/v
water (dew point)	−80 F at 101.3 kPa

[a] Total purity: 99.95 vol%.

is a gravimetric one where the water is absorbed onto a desiccant, such as magnesium perchlorate. In the macro technique, which is the most accurate, hydrogen content of a compound can be routinely determined to within ±0.02%. Instrumental methods, such as gas chromatography (qv) (150) and mass spectrometry (qv) (151), can also be used to determine water of combustion.

Methods are available for determining the hydrogen content of metals (152–158). A combustion technique, similar to that for hydrocarbons, has been used. The metal is placed in a strong oxidizing agent and ignited in oxygen. The amount of water resulting indicates the amount of hydrogen present in the metal. Other methods of analyzing for hydrogen in metals are vacuum fusion and hot extraction techniques in which the metal is heated in a vacuum and the hydrogen content of the metal is released as H_2 (152). Analysis for the hydrogen gas is most often by gas chromatography (154–157) or mass spectrometry (153).

To determine quantitatively the amount of hydrogen present in a gas mixture, gas chromatography using a thermal conductivity detector is often employed. This technique can determine hydrogen in the presence of oxygen and nitrogen (159), and in the very complex gas streams that might be found in a refinery environment (160–164) involving H_2, He, O_2, H_2S, N_2, CO, CO_2, and various hydrocarbons. In one technique, hydrogen's unique ability to diffuse through metals is used in a gas chromatography: hydrogen is separated from a gas stream by diffusion through a metal and is quantitatively determined (54). Gas chromatography has also been used to determine the amounts of trace impurities in hydrogen (165). The isotopes of hydrogen gas (H_2, HD, D_2) can be separated using gas chromatography (166).

Thermal conductivity is used as an analytical tool in the determination of hydrogen. Because the thermal conductivities of *ortho*- and *para*-hydrogen are different, thermal conductivity detectors are used to determine the ortho:para ratio of a hydrogen sample (167,168). In one method (169), an analyzer is described which splits a hydrogen sample of unknown ortho:para ratio into two separate streams, one of which is converted to normal hydrogen with a catalyst. The measured difference in thermal conductivity between the two streams is proportional to the ortho:para ratio of the sample.

Hydrogen has a very high thermal conductivity compared to that of most other gases. This difference is used to detect hydrogen in the presence of other gases. In one method (170), hydrogen is oxidized selectively over a catalyst in a gas mixture. The amount of hydrogen initially present is determined by the thermal conductivity of the gas mixture before and after the removal of hydrogen. The thermal conductivity difference between H_2 and D_2 has led to a method for determining the D_2 content of an H_2 sample (171–173). The deuterium content of water can be determined in a similar way after decomposing the water into hydrogen and oxygen.

Mass spectrometry has been used to determine the amount of H_2 in complex gas mixtures (174), including those resulting from hydrocarbon pyrolysis (68). Mass spectrometry can also be used to measure hydrogen as water from hydrocarbon combustion (151,175). Moreover, this technique is also excellent for determining the deuterium:hydrogen ratio in a sample (176,177).

Nuclear magnetic resonance (nmr) is a nondestructive means of measuring the amount of hydrogen in various materials; for example, nmr has been used to determine the hydrogen content of coals (178).

Several methods have been developed for detecting traces of hydrogen in the atmosphere (179–182). In one method (179), hydrogen in the atmosphere reacts with HgO to produce mercury vapor. The amount of Hg vapor produced, which is proportional to the amount of hydrogen present, is monitored by the Hg absorption of 253.7 nm light. This method is reported to detect H_2 at 0.5 ppm levels to within $\pm 3\%$; the limit of detection is 0.01 ppm H_2. Another technique for detecting small quantities of hydrogen in a gas uses sound velocity as a measure of the amount of hydrogen present (183). It is reported that very small quantities of hydrogen cause detectable increases in sound velocity.

The detection of trace impurities in hydrogen typically involves an enrichment process to concentrate the impurities. Large volumes of hydrogen are passed over an absorbent material such as SiO_2 at very low temperatures. The impurities in the hydrogen are concentrated on the SiO_2, then desorbed and analyzed with gas chromatography (165), by mass spectrometry (184,185) or by other means (186). It is claimed that traces of methane in H_2, He, and Ne in the ppb range can be detected using this method (165). Detection of carbon monoxide in hydrogen at 2 ppm levels is claimed (186). Determination of traces of impurities in hydrogen by other techniques is also possible (171,174,187,188). Although hydrogen gas is not directly detectable by infrared spectroscopy, other compounds present are often detectable. The determination of methane in H_2 at levels from 0.005% to 2% is reported using infrared spectroscopy (187).

10. Environmental Concerns

There are two environmental considerations associated with hydrogen: (*1*) nitrogen oxides (NO_x) formation when high hydrogen content gases are burned in a fuel system; and (*2*) emissions (NO_x and SO_x) associated with the production of hydrogen.

Nitric oxide (NO) comprises by far the greatest fraction of oxides of nitrogen (NO_x), which are formed as undesirable by-products of combustion. NO_x can generally by subdivided into two categories depending on its origin: thermal NO_x or fuel NO_x arises from the high temperature chain reaction of molecular nitrogen and oxygen in the combustion mixture of burners, such as arises owing to the burning of hydrogen off-gas streams in a furnace burner. Fuel NO_x arises form the oxidation of nitrogenous compounds chemically bound in liquid or solid fuels. Total NO_x emissions are the sum of the various components of NO_x formation. In combustion of gaseous fuels, where fuel-bound nitrogen is negligible, total NO_x is thermal NO_x, which is promarily NO (over 95%). After exiting the furnace stack, the NO slowly oxidizes to NO_2 in the atmosphere, which then reacts with sunlight to form ozone in the lower atmosphere and hence what is known as smog pollution in major cities.

The first concern can be mitigated by the recovery of hydrogen and reuse within therefining or chemical facility, thereby reducing the volume of hydrogen burned in the fuel system. Stricter environmental regulations are requiring facilities to use low NO_x burners in their furnaces or heaters. Increasingly, this environmental concern and the lower heating value of hydrogen relative to methane (natural gas) is entering the economic considerations of recovering the hydrogen in chemical plants and refineries. In one situation, the environmental and operating permits required a ethylene producer to find a continuous use (chemical or refining) for the by-product hydrogen from their new ethylene train.

The second concern can be addressed by using the latest environmental controls for NO_x control and sulfur removal in the design of a steam methane reforming (SMR) or partical oxidation facility. It should be recognized that environmental controls add significantly to the capital and operating costs of a hydrogen production facility.

The SMR process is the more environmentally acceptable of the two processes to produce hydrogen. In state-of-the-art SMR facilities, such as those required in California, NO_x is regulatic through a series of control features. Low NO_x burners utilize staged fuel combustion and flue gas recirculation to minimize NO_x production. Staged fuel combustion involves introducing the fuels at different locations to create two combustion zones. NO_x is reduced in the first zone because of low adiabatic flame temperatures resulting from the lean combustion conditions; NO_x is reduced in the second zone because of a quenching effect and lower flame temperature resulting from the inert combustion products.

Low NO_x burner technology is currently not able to meet the strict California regulations (BAAQMD) alone and therefore, new SMRs also require the addition of a selective catalytic reduction (SCR) unit to the stack. With a SCR unit, liquid ammonia is vaporized and injected into the flue gas, which passes over a honeycomb-shaped vanadium pentoxide catalyst–titanium dioxide catalyst. The ammonia reacts with NO_x in the presence of oxygen to form nitrogen and water vapor. By varying the ammonia injection rate, NO_x is controlled to the desired level. In California or other states, hydrogen plant flue gas stack require a Continuous Emissions Monitoring System (CEMS) to continuously monitor the stack emissions, which are electronically reported to the Air Quality Management Districts (AQMD). Sulfur removal (H_2S) from SMRs is generally accomplished through feed gas removal in a fixed bed adsorption system. Organic sulfur compounds in heavier hydrocarbon gaseous refinery offgases or naphtha feeds are generally removed in a cobalt–molybdenum catalyst system and stripped as hydrogen sulfide (H_2S).

Control of emissions from partical oxidation facilities adds more complexity and significant costs as the feedstocks progress from natural gas to heavy fuel oil to coal or coke. Coal or coke gasification facilities have issues associated with the solids handling aspects of storing and feeding them to the PO_x unit. In addition, the PO_x process creates ash and slag solids from the gasification step whose disposal is regulated under current environmental laws. Heavy feedstocks, such as coal, coke or heavy resids, also contain significant quantities of sulfur compounds, which create H_2S and carbonyl sulfides in the raw syngas these compounds must be separated and recovered in sulfur recovery unit (SRU) as elemental sulfur. Condensate streams from gasifiers also contain hydrogen cyanide, soluble metals and ammonia, which requires processing prior to disposal.

Partial oxidation of heavy liquid hydrocarbons requires similar treatment to solids gasification, however the amount of the pollutants is generally less. The soot generated in the gasifier is recycled back to the gasifier to minimize disposal costs.

11. Recycling and Disposal

Many purge, off-gas or by-product streams in refineries and related petrochemical and chemical operations contain hydrogen in significant volume and concentrations to warrant recovery and recycling of the hydrogen to other processes versus disposal as a fuel gas stream to recover the Btu value only. Table 10 illustrates various hydrogen off-gases and their compositions. Examples from refinery streams included a by-product of naphtha reforming (high octane gasoline), various hydrotreater and hydrocracker purges, by-product of ethylene manufacturing, methanol or ammonia purges and a by-product of chlor-alkali manufacture.

Some of these streams can be sent directly to other refining or chemical processing units so the hydrogen gas can be effectively managed within the overall facility to gain the maximum utilization of the hydrogen prior to its disposal as a fuel stream. A good example of hydrogen management within a refinery is the cascading of hydrogen purges from high severity, high pressure hydrocrackers or hydrorefining units to lower pressure, less severity hydrotreaters. However,

Table 10. **Typical Hydrogen Content of Various Off-gases and By-product Streams**

Off-gas source	Typical hydrogen concentration vol%
naphtha reformer	68–90
hydroprocessing	
high pressure	75–90
low Pressure	50–75
fluid catalytic cracking	10–20
toluene HDA	50–60
MTBE manufacture	85–90
styrene manufacture	80–85
ethylene manufacture	70–95
methanol manufacture	70–90
chlor-alkali manufacture	95–98

Table 11. **Hydrogen Recovery Technology Characteristics**[a]

Characteristic	Membrane	Adsorption	Cryogenics
hydrogen purity, %	<95	99.9+	95–99
hydrogen recovery,%	<90	75 to 90	90–98
hydrogen product pressure	feed pressure	feed pressure	variable
by products available	no	no	yes
feed pressure, upa	1,4–124	1.0–12.4	1.7–12.4

[a] To Convert MPa to Psi, multiply by 145.

a number of refining and chemical processes require high purity hydrogen and, therefore, these offgas streams must be purified prior to use. Hydrogen recovery technologies include membranes, adsorption systems and cryogenics. Each of technologies has its own unique capabilities and constraints (see Table 11).

11.1. Cryogenics. Cryogenic recovery and purification of hydrogen is a well established technology for the recovery and purification of hydrogen from refinery and petrochemical streams. It has the highest capital cost of the three main technology choices, but can provide multiple product recoveries, such as liquid hydrocarbons (propane, butane) in refineries or ethylene and propylene for petrochemical use. The process is particularly well-suited for feed gas streams containing 40–80 vol% hydrogen, which are available above 2.8 mpa. In most cases, all of the refrigeration requirements are provided by the expansion of the rejected hydrocarbons.

A typical cryogenic unit with natural gas liquids (NGL) recovery partially condenses the feed to produce a hydrocarbon liquid cut, a fuel stream and a hydrogen product. The hydrocarbon liquid cut is separated into a methane rich fuel stram and C3+ cut in a demethanizer column. A propane refrigeration system and feed gas expander are required to provide the necessary energy for separation.

11.2. Adsorption. Pressure swing adsorption (PSA) technology has been utillized in refineries and chemical plants since its introduction in the mid 1960s. Hydrogen (H_2) PSA technology has evolved from a 4-bed system initially to the more typical 8 to 12 bed systems ranging in product recovery from $0.028–3.36 \times 10^6 m^3/d$ ($1–120 \times 10^6$ SCF) hydrogen systems. The PSA system is a low capital option and consists of skidded components, carbon steel construction, switching valves, and various adsorbents. The H_2 PSA system removes multiple impurities in a multiple-bed system through a series of steps including adsorption, stepwise depressuring, purging, and stepwise repressuring. The use of multiple switching valves and microprocessors for control provide a continuous flow of hydrogen product. Unrecovered hydrogen and the impurities are produced at 34 Pa typically to maximize the hydrogen recovery and then compressed to be inserted into the fuel header system. H_2 PSA units provide hydrogen product at essentially the feed pressure and at high purity, with recoveries generally lower than alternative technologies. The ability to produce hydrogen at high purity provides a benefit to refiners by reducing inerts into the make-up hydrogen to a high pressure hydroprocessing unit such as a hydrocracker or FCC Gas Oil hydrotheater. In petrochemicals, cyclohexane manufacture is an example where higher purity is a benefit. Feed impurities are less of a problem compared

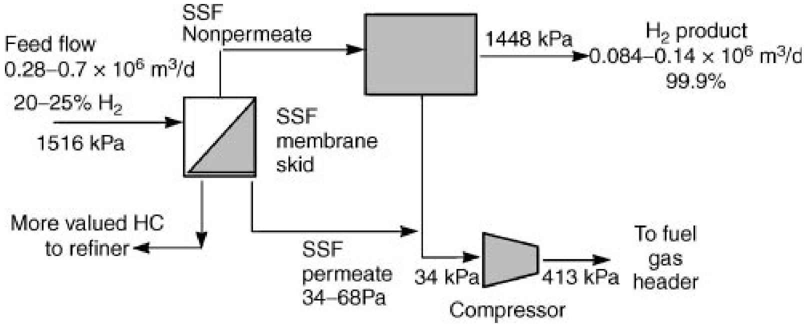

Fig. 11. H_2 Recovery from refinery off-gas. SSF membrane features: hydrocarbons permeate through membrane; H_2 remains at feed pressure; and hydrocarbons separation.

to membranes. Heavy hydrocarbons, however are a problem if they are irreversibly adsorbed, which may require the use of a temperature swing adsorption (TSA) guard bed.

Hydrogen recovered from gas feeds at lower pressures and lower hydrogen concentrations is generally uneconomical today.

A novel technology (Air Products) is under commercial development to address hydrogen recovery from these streams. Selective Surface Flow (SSF) membrane technology presents an opportunity to recover H_2 from previously untapped sources at an economic cost. Applying the ability of the SSF membrane to remove linear and branched C_2 through C_6 hydrocarbons from hydrogen containing streams while retaining the H_2 rich stream at near feed pressure, allows the novel membrane to be integrated with other long-proven process technologies. A simplified process flow diagram is shown in Figure 11.

11.3. Membranes.

Membranes have been used in refineries and petrochemical plants starting in the late 1970s. Membranes operate on the principle of selective gas permeation. Every gas entering the membrane separator has a characteristic permeation rate that is a function of its ability to dissolve in, diffuse through and dissolve out of the hollow fiber membrane. The permeation rate is the product of the solubility and diffusivity rates of the gas in the membrane. Membrane separators, use these relative permeation rates to selectively separate a “fast” gas such as hydrogen, from the slow gas components, such as methane, in a process gas stream.

The membrane separator consists of a compact bundle of hollow fibers which are sealed at one end and open at the other. The open ended fibers are held in a tube sheet. The bundle is contained within a coded pressure vessel. The pressurized feed gas enters at the side inlet of the membrane and flows up through the membrane into the inside of the hollow fibers (shell side). The fast gases selectively permeate through the membrane into the inside of the hollow fibers (tube side) which is at lower pressure. The permeate stream is collected in a manifold at the lower end of the membrane. The retentate gas exits through the upper end of the membrane at essentially the same pressure as the entering feed gas.

Shells are configured in series and/or parallel groups to achieve the performance required by the customer application. They have been used extensively to recover hydrogen from high pressure purge streams in ammonia or methanol plants or hydrocrackers in refineries. Hydrogen purity, although lower than with other technologies, is often quite adequate for a refiner's needs. A common disadvantage of membranes is that the hydrogen is produced at pressures much lower than the feed pressure and generally requires compression to utilize the hydrogen stream in a process. Feed impurities, such as H_2S or aromatics are a concern, since they may damage the membrane. Heavy hydrocarbons may liquefy and impair the membrane units performance. However, elevating the temperature of the stream to avoid the condensation of heavy hydrocarbons on the membrane fibers typically solves the problems.

11.4. Technology Selection. Customers, working with equipment suppliers of these separation technologies, must determine which off-gas streams can provide economical hydrogen for the end use. Many off-gas streams can be eliminated from consideration because the pressure or concentration of hydrogen is below an economic level of recovery relative to other sourcing options. Without liquids recovery to offset the higher capital costs, cryogenic separation is generally less competitive relative to other technologies.

If the amenable off gases provide sufficient volume of hydrogen to meet the new demands in the refinery or petrochemical plant, then hydrogen recovery will provide the solution alone. If the demand for hydrogen exceeds the recovered volume, then other options such as expanding an existing SMR at the site, constructing a new SMR, or connecting to a popeline source from a third party, such as an industrial gas supplier must be considered.

12. Health and Safety Factors

Hydrogen gas is not considered toxic but it can cause suffocation by the exclusion of air. The main hazard associated with the use of hydrogen lies in its extremely wide flammability limits in oxygen or air. Some of the properties of hydrogen Important in safety considerations are shown in Table 12.

Hydrogen is odorless and colorless and is, therefore, not easily detectable. Also hydrogen burns with a pale blue, nearly invisible flame. Hydrogen is easily ignited with low ignition energy, including static electricity. Hydrogen is the

Table 12. **Properties of Hydrogen Important in Safety Considerations**

Property	Value	Ref.
limits in air, vol%		
Flammability	4.0–75.0	189
Detonation	18.3–59.0	190
limits in oxygen, vol%		
flammability	4.5–94.0	191
detonation	15.0–90.0	
autoignition temperature, C	585	192
burning velocity in air, cm/s	265–325	192
detonation velocity in air, km/s	1.48–2.15	192

lightest gas known, and can accumulate in the top of enclosed spaces without proper ventilation. It may leak out of a pressurized gas system which is gas-tight to air or other gases. Hydrogen systems should be periodically checked for leaks with leak detection solutions, or hand-held flammable gas monitors. The detonation, and flammability limits for hydrogen-air mixtures are much wider than those of gasoline–air or methane–air mixtures (192)

Contact with liquid hydrogen can cause tissue freezing and severe cryogenic burns. When spilled, liquid hydrogen will vaporize rapidly forming a potentially explosive and oxygen vapor cloud. Visibility may be boscured in this vapor cloud.

Mandatory regulations governing the distribution of liquid or gaseous hydrogen are listed in the *Code of Federal Regulations* (193,194). The National Fire Protection Association has published specific requirements for liquid and gaseous hydrogen storage and delivery systems at consumer sites (195,196).

Hydrogen does not cases any adverse ecological effects.

13. Uses

The demand for and supply of hydrogen is currently concentrated in three main markets worldwide: refining, petrochemicals, and chemicals. Hydrogen is one of the most important industrial commodities used to desulfurize or hydrogenate various petroleum products derived from crude oil into transportation fuels; Nitrogen is used to produce ammonia and urea (fertilizers) and chemicals such as methanol, cyclohexane, oxoalcohols and polyurethane intermediates (TDI and MDI).

13.1. Refining. In the last decade, the worldwide refining industry has been impacted by several trends that have increased hydrogen demand significantly. First, in aggregate, crude oil has been getting heavier and more sour. This has led to highter hydrogen consumption in a refinery for upgrading the crude oil into light transportation fuels and removing the sulfur and nitrogen compounds. This long-term trend is expected to continue into the next century as more heavy crude oil production is sold into the marketplace through joint ventures of producing countries (PDVSA, PEMEX, Saudi Aramco) at specific facilities.

Petrochemicals and Chemicals. Some of the key or large uses of hydrogen in the petrochemical and chemical industries are outlined below.

Cyclohexane. Cyclohexane is most commonly produced by the hydrogenation of benzene. Cyclohexane is a raw material for the production of nylon fibers and resins. These two uses account for 90% of cyclohexane consumption. Most cyclohexane plants tend to be at or near refineries that process sweet crude or chlorine-caustic plants that have excess hydrogen.

Hexamethylene Diamine (HMDA). Hexamethylene diamine is produced by the hydrogenation of adiponitrile. Most HMDA is consumed in making nylon fibers and resins.

Toluene Diamine (TDA). Toluene diamine is produced by the catalytic hyrdrogenation of dinitrotoluene. TDA is then reacted with phosgene to produce toluene diisocyanate (TDI). TDI is used for flexible foam manufacture.

Aniline. The most common route for the production of aniline is by the hydrogenation of nitrobenzene. The largest use of aniline is in the production of MDI (rigid foam manufacture). MDI consumption is growing rapidly due to a strong construction market and several new applications.

1,4 Butanediol. One of the synthesis routes for 1,4 butanediol is by hydrogenation of 2-butylene 1,4 diol. The BD market is driven by demand for poly (butylene terephtahlate) resin. There are several other routes for the manufacture of 1,4 butanediol all of which entaila catalytic hydrogenation step.

Hydrogen Peroxide. Hydrogen peroxide is produced by the indirect synthesis of hydrogen and oxygen, utilizing the autooxidation of an anthraquinone. The quinone is hydrogenated to the hydroquinone using a catalyst. Subsequent oxidation with air produces hydrogen peroxide and regenerates the quinone.

Sorbitol. Sorbitol is a polyol, like glycerin which has a sweet, cool taste. It is produced by high-pressure catalytic hydrogenation of glucose sugar derived from corn starch. Sorbitol's largest use is for the manufacture of toothpaste, toiletries and cosmetics.

Alcohols. A number of long chain (C4 to C12) monohydric alcohols are produced by the hydrogenation of the corresponding aldehyde. Two of the most important oxo and detergent alcohols are *n*-butanol and 2 ethyl hexanol.

Fats and Oils. Hydrogenation of fats and oils is carried out to reduce the degree of unsaturation in the fat/oil. This leads to a product that is more stable to thermal degradation and resistant to oxidation. Also, the fat/oil becomes more solid due to an increase in its melting point. In 1996, the actual consumption of hydrogen in the hydrogenation of edible fats and oils was approximately $238 \times 10^6 m^3$ ($8{,}500 \times 10^6$ cubic feet).

13.2. Other Uses. The metals industry, which historically used small quantities of hydrogen for annealing or reducing atmospheres, is now moving forward with implementing several new direct reduction of iron ore (DRI) processes, which require large quantities of hydrogen or HyCO syngas.

Hydrogen is used in small volumes in the electronics industry in semiconductor manufacture, quartz melting, polysilicone manufacture and fiber optic manufacture. Very high purity is required and is generally provided by gas supplied via vaporization of liquid hydrogen.

Hydrogen is also used in the reducing atmosphere in float glass production plants. It is used to cool generators in electric power plants and to prevent corrosion in nuclear power plants. The only current commercial use of hydrogen as a fuel today is for rocket propulsion.

14. Hydrogen Economy

Driven by concerns about oil dependence, deteriorating urban air quality, and recognizing the benefits of a hydrogen-based energy system, active R&D programs in hydrogen energy applications are underway in over 30 countries. In the 1970s, the concept of a hydrogen economy was introduced wherein hydrogen along with electricity would be a dominant energy carrier (197). The primary energy would be supplied by renewable sources such as solar, wind, hydro power, or biomass. Hydrogen would be the preferred carrier because it is storable and transportable, and because it can be used with essentially no pollution in combustion systems, and fuel cells. An example of a large-scale hydrogen-based energy systems development program is the ambitious 28-year (1993–2020), 300 $\times 10^9$ Yen, R&D program called World Energy Network (WE-NET) in Japan. This project is aimed at establishing a worldwide energy system based on harnessing renewable energy sources such as solar, wind, and hydro, producing hydrogen via water electrolysis, and liquefying the hydrogen for trans-oceanic distribution, via tanker ships, to the points of use. As part of the current efforts, efficient water electrolyzers, large-scale hydrogen liquefaction plants, liquid hydrogen carrier ships, and hydrogen gas turbines are being designed (198).

Catalytic combustion of hydrogen exhibits many advantages in comparison to flame combustion. It occurs at low temperatures (ambient to 800 K), is safe, and the formation of nitrogen oxides (NO_x) is almost completely suppressed. It is adequate for cooking, water heating, and space heating. Drawbacks are the possible nonuniform temperature distribution at the catalyst surface, rapid changes in the operational state, and relatively small flux densities (199).

Use of hydrogen as a fuel for road and air transportation is being actively developed, driven by stringent new clean air standards around the world that enconrage and in some cases require the use of clean alternatives to the current petroleum-based fuels. A transition from gasoline and diesel first to natural gas, followed by the gradual introduction of hydrogen, is envisioned (200).

From the earliest days of combustion science, experiments have established that hydrogen has a strong influence on the combustion of natural gas and other hydrocarbons. More recently, active development has been undertaken to promote the use of blends of hydrogen with natural gas (10–30 vol% hydrogen) in internal combustion (IC) engines (201–203). These fuels are referred to by various names such as Hythane R, and Hydrothane. These fuels lead to substantial reductions of emissions carbon monoxide (CO) and oxides of nitrogen (NO_x) compared to that achieved with natural gas alone. By achieving large emissions reductions with small additions of hydrogen, such an approach faces a smaller economic hurdle in achieving the benefits of clean air and is more likely to be favorably received by the consumer. A cost analysis for a 500-vehicle fleet operating on Hythane (15 vol % hydrogen) indicated that the fuel price would be quite competitive with regular unleaded gasoline at about $1.13 gallon gasoline equivalent (188).

The use of pure hydrogen in IC engines makes it possible to operate at very fuel-lean conditions and reduce emissions of NO_x, and CO to extremely low values (204). In Germany Daimany Daimler-benz and BMW have conducted detailed investigations of this technology over two decades. Daimler-Benz developed hydrogen IC engines for cars and vans, that used hydrogen stored in metal hydride containers. BMW's efforts have been centered on liquid hydrogen. In conjunction with German hydrogen suppliers, they have significantly improved the insulating efficiency, and compactness of onboard liquid hydrogen storage tanks. In Japan, active hydrogen vehicle projects are underway at Mazda, Toyota, Honda, and Musashi Institute of Technology. Mazda's work has been on hydrogen-fueled IC rotary engines using metal hydrides to store hydrogen onnboard the vehicle. In the U.S. a demonstration program led by Clean Air

Now and Xerox Corporation operated a fleet of four service vehicles on hydgrogen generated from solar energy at a fuel station in Los Angeles and stored onboard the vehicle as compressed gas (205).

An improvement on this concept is the hydrogen hybrid electric vehicle, which takes advantage of high-efficiency electric drive trains and the low emissions of hydrogen IC ingines. The concept involves the use of relatively small IC engines operating on hydrogen to power electric generators that charge batteries. The IC engine is sized to match the average power requirement of the vehicle and hence operates continuously at or near its optimum efficiency. The battery is sized to accommodate the peak power requirements. This reduces the weight of batteries neede for a given range and gives the vehicle rapid fueling capability. A hydrogen hybrid electric bus has been tested in Atlanta by the Westinghouse Savannah River Company.

The use of liquid hydrogen as a rocket fuel for use in space flights is well established. It is now being seriously considered for use as an aircraft fuel. A joint German Russian team including Daimler-Benz Aerospace and Tupolev are in early stages of development of a liquid hydrogen airplane called Cryoplane (206).

The most attractive energy conversion technology that uses hydrogen is fuel cells (see FUEL CELLS). A fuel cells is an energy conversion device that combines hydrogen and oxygen in an electrochemical process to produce electric power, some low-temperature heat, and water vapor as the only emissions. The electricity produced can be used for any useful purpose such as powering an electric traction motor.

Although fuel cells were first invented some 150 years ago, only recently has their pace of development accelerated dramatically. Applications for fuel cells that are being actively developed include portable power systems (25 W to 1 KW), distributed stationary power generation (1 KW up to MW scale), and as a propulsion system for road vehicles, ships, and submarines. Substantial fuel cell development efforts are underway by automobile manufacturers in the U.S., Europe, and Japan to bring fuel cell vehicle technology to the market early in this century. Daimler-Benz has committed itself to the rapid development of hydrogen fuel cell passenger vehicles, and is supporting this goal with sizable financial investments and technical resources. In 1994, they developed their first prototype fuel cell vehicle “NECAR 1” (new electric car), a research van with its entire cargo space taken up by the fuel cell systems and instrumentation. This was quiclky followed up by the unveiling of their second generation minivan called “NECAR 2” in May 1997, in which the fuel cell system was almost indiscernibly tucked away underneath the rear cargo space. In May 1997, Daimler-Benz unveiled its first 58 passenger fuel cell bus “NEBUS” (new electric bus). All of these vehicles stored hydrogen gas at high pressure onboard the vehicle. However, in September 1997 they unveiled “NECAR 3” a small sedan which made the hydrogen onboard from methanol in a reformer. Also in 1997 Daimler-Benz and Ford Motor Company formed a three-way partnership with the Canadian fuel cell company Ballard Power Systems to build fuel cell engines for the entire automobile industry.

Although fuel cell cars are still under development, hydrogen fuel cell buses are becoming a reality and small fleets (3–4 buses at eact location) have begun operation in Chicago, and Vancouver, Canada in 1998. Ballard Power Systems has developed the propulsion systems for these buses using their Proton Exchange Membrane (PEM) fuel cell technology. Hydrogen refueling stations at the bus depots have been built to load and store hydrogen onboard the buses at 24.8 mPa (3,600 psi) (207). The hydrogen is delivered to these sites as liquid and pumped to high pressures using cryogenic liquid pumps. The stations are designed for fueling a bus in about 15 minutes.

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