11. THE TRANSMISSION, STORAGE, AND DISTRIBUTION OF HYDROGEN – A. J. Konopka, J. B. Pangborn, and W.J.D. Escher

Hydrogen Transmission

It appears that small nuclear-power generators for individual customer use or even for substation use will not be commercially feasible. If the smallest economical generator size is a few hundred megawatts, waste-heat removal becomes a local problem, limiting the location of a power plant to specific areas. Because the preferred sites for such nuclear plants are near large bodies of water and most of the cooling water near load centers is already claimed, future energy-production sites will likely be large and remote.

Energy-production centers not near load centers must transmit the product energy from the concentrated production site to the centralized utilization site. Therefore, if hydrogen is to be used in large quantities, it will have to be transported in bulk, as are electricity and natural gas. One of the cheapest ways of moving energy, whether liquid or gas, is by pipeline. Because most long-distance pipelines are below ground, they do not have the disadvantage of being unsightly, as do high-voltage lines.

Transmission of hydrogen by underground pipelines can be compared with natural gas and electricity transmission over long distances. Generally, on an energy-delivered basis, natural gas will be the cheapest of the three to transmit; hydrogen will be intermediate in cost; and electricity will be the most expensive. It is evident that, because of the lower heating value of hydrogen (325 Btu/SCF) compared with that of natural gas (1050 Btu/SCF), approximately three times more hydrogen than natural gas must be transported to achieve an equivalent pipeline-energy-delivery rate.

Hydrogen is transmitted by pipeline in various parts of the world. However, compared with natural gas transmission, the distances are relatively short; and the energy flows are small. Because of economic and technical factors, the long-distance transmission of hydrogen could require the use of new, high-capacity compressors and drivers, as well as new pipeline materials. Compressors must be able to handle hydrogen's high diffusivity property (i.e., its tendency to leak), which may cause compressor-casing and valve-sealing problems.

The effect of hydrogen on pipeline components must be evaluated from a material-design viewpoint. Little is known about the effects of hydrogen on pipeline steels at high operating pressures. High operating pressures may cause "hydrogen embrittlement" of pipeline steel. Also, large compressors for pipelines may be constructed of materials that are susceptible to hydrogen attack. Undoubtedly pipelines can be constructed for hydrogen transmission; however, in order to keep transmission costs at a minimum, pipeline components that are both technically sound and economical must be developed. Because experience with hydrogen pipelining is not as extensive as that with natural gas systems, optimum-performance and minimum-cost pipeline components are not currently available.

Several research groups have studied the technological and economic aspects of large-volume, gaseous-hydrogen transmission. These studies are summarized below.

IGT Pipeline Optimization Study

The Institute of Gas Technology has conducted a pipeline optimization study of gaseous-hydrogen transmission.[18] The specific objectives were to determine a) which pipeline components are available and which would have to be developed for hydrogen transmission, and b) the best pipeline operating conditions for transporting certain quantities of energy in the form of gaseous hydrogen.

Pipeline Components

The results show that the availability of suitable compressors and drive engines for use in hydrogen transmission is questionable.

Turbocompressors and Drivers

Turbocompressors have been designed and are currently operational for high throughputs of hydrogen gas, but such high-throughput devices have never been designed to function at high operating pressures. In most instances, only a thicker casing is necessary.

The factor limiting the use of a radial turbocompressor with hydrogen is the pressure ratio achievable in one stage. This type of machine converts kinetic energy into a pressure head, and the pressure ratio is directly proportional to the rotor tip speed and is dependent on a) the physical properties of the gas and b) the rotor and diffuser geometry. For low-molecular-weight hydrogen, achievable pressure ratios are far lower than those obtainable with natural gas at the same tip speed. The maximum tip speed is limited by the mechanical properties of the rotor.

In the IGT study, it was assumed that hydrogen-fueled gas turbine drivers power the turbocompressors. Current technology makes possible the use, with pipelines, of a directly connected, aircraft-type gas turbine with a turbocompressor.

In the 1950's, researchers at Pratt & Whitney (Div. United Aircraft Corp.) did considerable work on hydrogen-fueled, aircraft-type gas turbines. They successfully modified a J-57 engine for operation on hydrogen fuel and designed, constructed, and tested a special engine specifically designed for use with hydrogen fuel. Excellent results were obtained, but the program was abandoned before 1960. Hydrogen-operated gas turbines have higher efficiencies than corresponding units operating on conventional fuels.

Reciprocating Compressors and Drivers

Reciprocating compressors could be used with hydrogen pipelines. Many reciprocating-compressor installations are now handling hydrogen under various conditions of pressure, temperature, water-vapor content, and corrosivity. Compression cylinders would have to be quite large to be able to transport pipeline quantities of gaseous hydrogen. Worthington CEI has made gas compression cylinders with a 19-inch stroke and a bore as large as 42 inches. A need for reciprocating-compressor development is not anticipated, because large cylinder compressors are available that don't sacrifice the possibility of maintaining a high pressure ratio for each compression stage. Worthington stated that compressors designed for use with hydrogen need only special steel piston rods and Teflon rings to surmount hydrogen-embrittlement problems.

The problem involved in using such a compressor with hydrogen pipelines would be obtaining a driver of sufficient speed and power. Although considerable success has been achieved in converting small, automobile-type piston engines to hydrogen use, a separate research program would be necessary to achieve an optimum scale-up to large engine size.

Other Compressors

Screw compressors have not been used in very-high-pressure applications (above about 600 psia). However, they combine the valuable features of both positive-displacement and dynamic machines and are "oil free." If developed for higher pressure applications, they could be valuable for use with hydrogen pipelines.

Axial turbocompressors under development are expected to be highly efficient machines comparable to reciprocating machines. The resulting price per unit of horsepower should approximate the radial-turbocompressor price currently quoted by Elliott Co.

In the IGT study, radial-turbocompressor and turbine-driver technical and economic data were assumed because the gas industry tends to use turbocompressors for high-throughput gas flows.

Reciprocating devices have higher capital and installation costs, in $/hp, than turbomachinery. However, reciprocating compressors provide a higher fuel efficiency for long-term operation. Currently, the break-even point for operating turbomachinery and reciprocating devices is 10 years. Turbomachinery is relatively new, and improvements may be forthcoming.

Initial Compressor

A hydrogen-transmission pipeline is expected to operate at some average pressure between 750 and 2000 psia. If hydrogen is not manufactured at this pressure, an initial compression step (employing an initial compressor) will be necessary to bring the gas up to pipeline pressure. (Pipeline compressors, which compress the gas flowing through the pipelines to compensate for pressure losses, have a much lower ratio of inlet to outlet pressure than initial compressors.) Because many electrolyzers and many thermochemical hydrogen-production processes now under investigation operate at modest pressures, it is important to consider the cost factors and technological capabilities involved in this initial compression step.

According to representatives of the Elliott Co., a manufacturer of turbocompressors, the use of an initial compressor could present a major developmental problem for turbomachinery — especially if hydrogen cannot be produced at an elevated pressure. Only a 1.4:1 pressure ratio is attainable per casing with turbocompressors. Therefore, if hydrogen is produced at atmospheric pressure, a great number of compressor casings would have to be placed in series to attain the pressures used in pipeline transport. However, if the hydrogen could be produced at 750 psia, for example, it could be put directly into the pipeline or be boosted by turbocompressors to higher pressures. (Hydrogen produced at 750 psia would need only two compressor casings, in series, to reach 1500-psia pipeline operating conditions.) Also, intercoolers must be added to multistage compressors to remove the heat of compression.

Reciprocating compressors (positive-displacement machines) achieve a much greater pressure ratio, so initial compression is less of a problem. For example, 17,000 SCF of hydrogen per minute can be compressed from atmospheric pressure to 750 psia in four stages. However, at pipeline conditions this represents only 340 CF/min. For long-distance hydrogen transmission to be economical, the capacity of these machines will have to be greatly increased, at least by a factor of 20.

Combinations of turbocompressors to handle flow and reciprocating machines to provide compression should be considered as possible economical solutions to the problem presented by the need for a large-volume initial compressor for use with hydrogen.

Optimum Operating Conditions

A computer program was employed in this study to determine the economic characteristics of a hydrogen-transmission system. Given the design throughput (flow of gas), overall transmission distance, and thermodynamic and geographical conditions, the program calculated the minimum transmission cost by —

a. Optimizing the compression section
b. Finding the optimal combination of all the optimized sections.

Figure 11-1 is a schematic view of the system of variables used for IGT's study of pipeline-section optimization.

The cost trends of hydrogen transmission were calculated including the effect of hydrogen-volume throughput in a single pipeline of varying diameters (24, 30, 36, 42, and 48 inches). Various hydrogen-fuel-production costs (from \$2 to \$4/million Btu), were assumed; and average operating pressures of 750, 1000, 1500, and 2000 psia were considered.

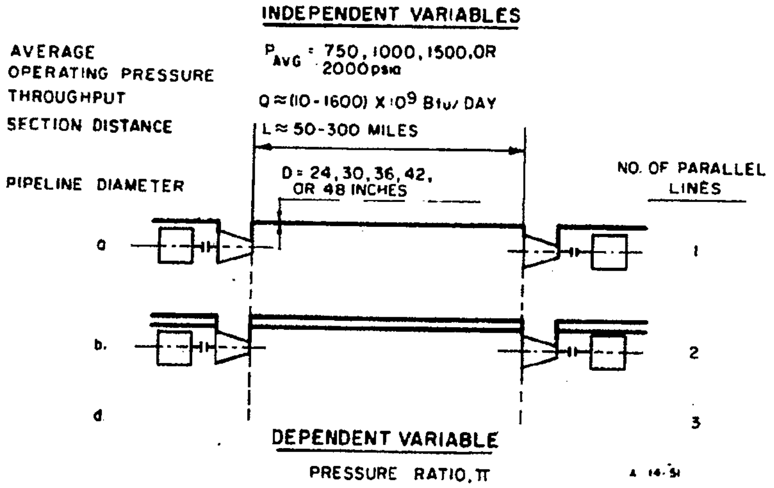


Figure 11-1. IGT SYSTEM OF VARIABLES USED TO OPTIMIZE A COMPRESSION SECTION OF GAS-TRANSMISSION LINE

The following conclusions were reached in the IGT study:

- For 24 and 30-inch pipe, operating at higher average pressures (1500 and 2000 psia) results in a major decrease in hydrogen-transmission cost.

- For 24 to 30-inch single-line pipes operating at full capacity, hydrogen-transmission cost increases markedly with compressor-section spacing length at low average pressures (750 psia).

- For pipes of larger diameter, an insignificant decrease in transmission cost is obtained by operating at a higher average pressure.

- For 48-inch-diameter and some 42-inch-diameter pipelines, hydrogen-transmission costs actually begin to increase with operation at 2000 psia. Therefore, cheapest pipeline operation is at a pressure somewhere between 1500 and 2000 psia.

- No great advantage is apparent for operation with very-long-distance compressor pipe sections (i.e., with long distances between compressors). A combination of shorter sections (i.e., closer compressor-station spacing) at a specific diameter may be used at no apparent increase in cost.

Figure 11-2 is a comparison of transmission costs for hydrogen and natural gas at optimized conditions. In completely optimized systems, the cost of hydrogen transmission (at an average operating pressure of 750 psia) will be between 3.5¢ and 5.5¢/million Btu-100 miles. This is 2 to 3 times more than today's natural-gas-transmission costs.

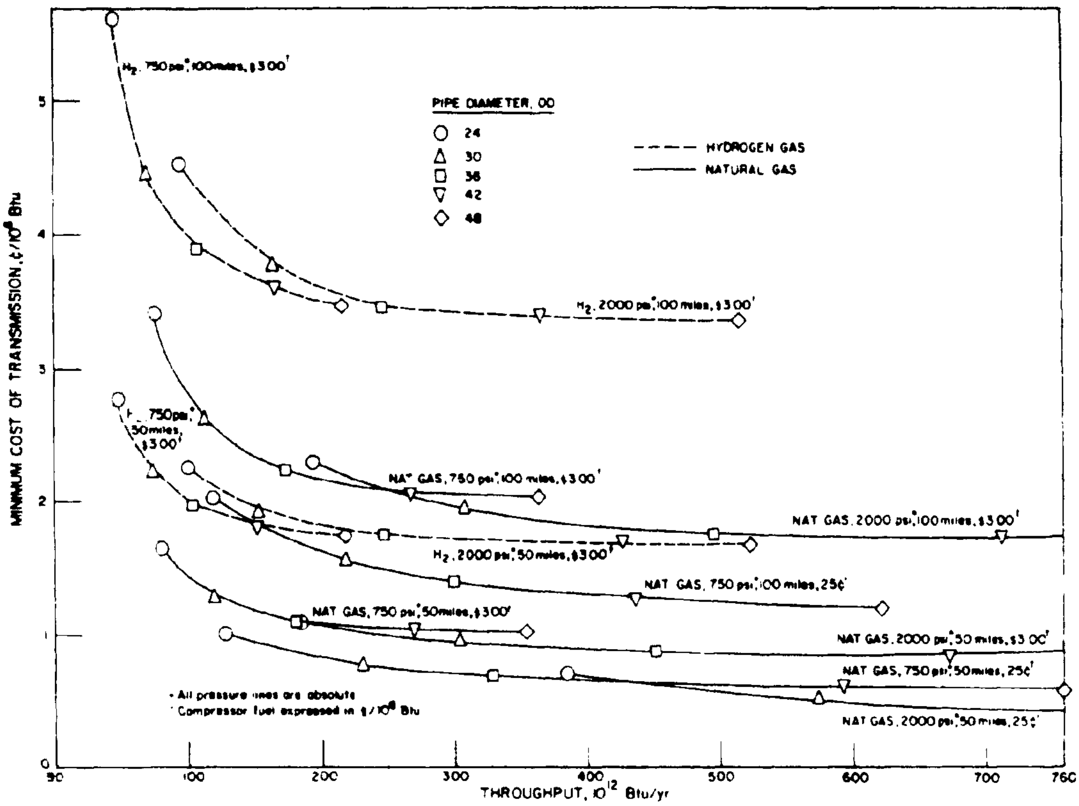


Figure 11-2. OPTIMIZED TRANSMISSION COSTS FOR HYDROGEN COMPARED WITH NATURAL GAS

Figure 11-3 is a plot of gas-transmission costs for 1000 miles (in ¢/million Btu) versus compression-section spacing that was made to determine the effect of the distance between compression stations on gas-transmission cost. Apparently there is little cost advantage in operating hydrogen lines with longer distances between intermediate compressors; however, certain cases pictured do show a slight reduction in cost with longer intermediate-compressor-station spacings.

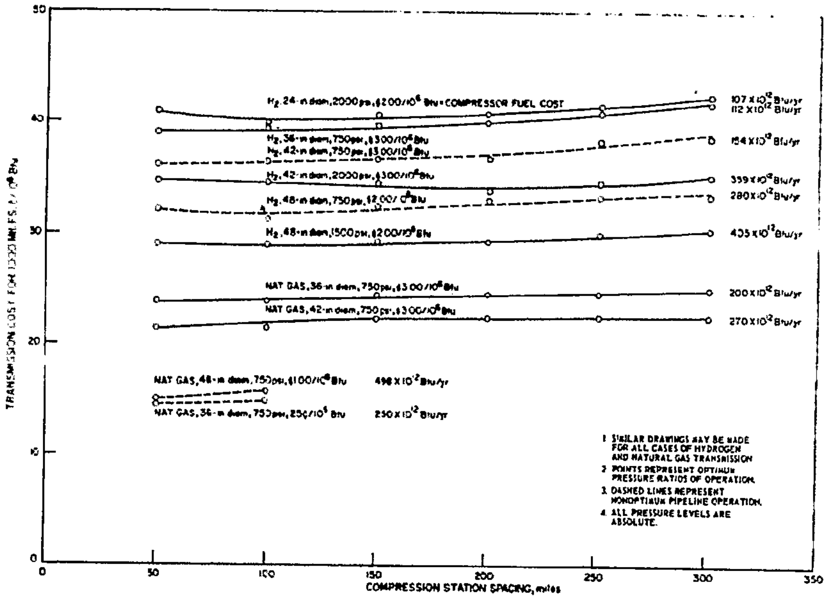


Figure 11-3. 1000-MILE TRANSMISSION COST COMPARISON FOR HYDROGEN AND NATURAL GAS WITH DIFFERENT INTERMEDIATE COMPRESSOR SPACINGS

EURATOM

EURATOM, in Italy, has conducted a study to determine the economic characteristics of transporting hydrogen, natural gas, and oxygen by an optimized pipeline network.[3] Specifically, given a design throughput, overall transmission distance, and thermodynamic and geographical conditions, the minimum transmission cost was calculated by optimizing the number of compression stations for an optimal pipeline diameter.[12] When used in an analytical form, this calculation determines the number of compression stations that result in the minimum cost of transporting a given heating value over a certain distance.[12] The minimum cost, therefore, is a function of the throughput and of the overall distance, and the resulting optimum pressure ratio, pipe diameter, and station spacing are shown as a single value. Apparently, for this study it was assumed that gas compressors would be powered by electric motors. Thus compressor-fuel costs in this study are the same for both hydrogen and natural gas.

The EURATOM report concludes that hydrogen is 30% to 50% more expensive to transport by pipeline than natural gas. Data for comparison of transmission costs for natural gas (assumed here to be methane) and hydrogen, at an operating pressure of 1280 psi, are shown in Table 11-1. The ratio of costs increases with an increase in distance and slowly decreases with an increase in throughput. It is obvious from Table 11-1 that the optimum distance between intermediate compression stations is greater for hydrogen than for methane. Similar results have also been reported at other pipeline working pressures. Pipeline investment costs (for construction of the pipeline) were also reported to be about 45% to 60% higher for hydrogen than for natural gas because of the larger diameter pipelines used with hydrogen.

EURATOM has found that an increase in pipeline operating pressures reduces the transmission cost for hydrogen, as shown in Table 11-1 for a given throughput of 250 trillion Btu/yr and a transmission distance of 621 miles. The costs shown in Table 11-1 do not take initial gas compression into account. However, EURATOM did report the effect of initial gas compression on transmission costs for both methane and hydrogen, and the findings are shown in Table 11-2. The inlet pressure is 10 kg/sq cm (142 psi), transportation pressure is 90 kg/sq cm (1280 psi), and the throughput is 125 trillion Btu/yr.

It is clear that initial compression is an important factor in the total cost, especially for short distances. Also, the impact of initial compression on total costs is greater, in absolute value and in percentage, for hydrogen than for methane.

General Electric Co. (Tempo), Calif.

R. A. Reynolds and W. L. Slager of GE have developed an analytical model for developing characteristics and costs of delivering gaseous and liquid fuels by pipeline.[23] Given the desired energy-flow rates, certain other inputs, and an initial estimate of pipe size, the model computes the first cost of the installed line and determines its required compressor stations. The procedure involves systematic variations in pipe diameter for identification of the minimum-cost configuration. Once determined, the energy-transport cost is calculated, taking into account system amortization and the fuel required to operate the line.

Table 11-1. COMPARISON OF COSTS FOR HYDROGEN AND METHANE, ACCORDING TO EURATOM[3]

Throughput, Gcal/s, 10¹² Btu/yr	Distance, (km) miles	Number of Sections		Distance Between Stations, miles		Minimum Cost, $/10⁶ Btu		Hydrogen/Methane Transmission Costs	Hydrogen/Methane Capital Costs	Compression Ratio	
		Hydrogen	Methane	Hydrogen	Methane	Hydrogen	Methane			Hydrogen	Methane
1 125	(1000) 621	2	5	311	124	0.29	0.20	1.40	1.46	1.541	1.407
2 250	(1000) 621	2	6	311	104	0.23	0.16	1.41	1.46	1.447	1.274
3 375	(1000) 621	1	5	621	124	0.19	0.14	1.38	1.61	1.500	1.298
4 500	(1000) 621	1	5	621	124	0.17	0.13	1.36	1.58	1.500	1.274
1 125	(2000) 1243	8	13	155	96	0.61	0.41	1.46	1.48	1.192	1.288
2 250	(2000) 1243	7	15	177	83	0.48	0.33	1.48	1.51	1.180	1.204
3 375	(2000) 1243	2	16	621	78	0.42	0.28	1.48	1.59	1.737	1.169
4 500	(2000) 1243	2	16	621	78	0.38	0.26	1.48	1.59	1.683	1.156
0.5 62.5	(500) 311	1	2	311	155	0.16	0.12	1.31	1.43	1.500	1.829

Pressure in the pipe is assumed to be 90 kg/sq cm.

B75092205

Table 11-2. EFFECT OF INITIAL GAS COMPRESSION ON TRANSMISSION COSTS
(EURATOM STUDY)

Gas	Distance, miles (km)	Total Transportation Cost, ¢/10^6 Btu	Initial Compression As Percentage of Total Cost, %
Methane	311 (500)	16	38
	621 (1000)	25	23
	932 (1500)	36	16
	1242 (2000)	47	13
Hydrogen	311 (500)	36	54
	621 (1000)	52	46
	932 (1500)	68	35
	1242 (2000)	84	29

In a properly designed system, the cost of transmitting hydrogen by pipeline is from 30% to 50% higher than for an equal amount (in terms of energy) of natural gas. This conclusion is based on pipelines constructed to be used under conditions representative of those in the Midwestern United States. If higher installation costs were used for both gases (methane and hydrogen), the relative transmission costs would become similar, but the absolute figures would increase.

Reynolds and Slager conclude that increased pipe diameter is the primary reason for hydrogen being more costly to transport than methane. An increase of from 25% to 50% in pipe diameter is reflected directly in the required capital costs, of which from 75% to 80% is attributed to the cost of pipe and installation and the remainder is for compressor facilities. Optimum compression ratios at compressor stations were found to be lower for hydrogen (1.1:1) than for natural gas (from 1.25:1 to 1.30:1). Compressor-station spacings of from 50 to 75 miles were related to these operating-pressure ratios.

To calculate gas-transmission costs, a compressor-engine-fuel cost of 40 ¢/million Btu has been assumed for both hydrogen and natural gas. This factor (primarily) accounts for the difference in transmission costs predicted by the GE and IGT studies. Reynolds and Slager also studied the effect of transporting cooled hydrogen gas by pipeline. They found that for temperatures from ambient to -300 °F, the optimized pipeline design requires between one and two times the compressor power of the nominal case. If an insulated pipe were assumed to be required, as would actually be the case, pipelining of hydrogen would prove to be more expensive at reduced temperatures. Therefore they have concluded that the refrigeration of hydrogen gas is not desirable.

G. G. Leeth of GE also conducted a study comparing hydrogen-transmission costs with those of other energy-transmission systems.[20] The systems studied included energy transmitted in the form of electricity (underground and overhead), hot water, chemical heat (EVA-ADAM),* hydrogen and oxygen, hydrogen (solely), oxygen (solely), and methane.

This preliminary study of energy transmission showed that for nonfossil-fueled energy centers, hydrogen is superior to the other energy-transport modes considered. An EVA-ADAM system is intermediate in cost between hydrogen and electricity. The hot-water system is slightly more expensive than overhead electricity transmission.

National Bureau of Standards

C. F. Sindt has conducted a study to determine the most economical method for delivering liquid hydrogen.[13] From economic considerations, alone, it was concluded that hydrogen should not be liquefied for transmission or transport, except when delivery is across an ocean or when the hydrogen is to be used as a liquid. However when liquid hydrogen is required, the costs of transmission, production, and liquefaction must all be considered before the most economical method of delivering the liquid hydrogen can be determined.

Sindt assumed that hydrogen could be produced by electrolysis, using power generated by a large electrical power plant. Various schemes were considered for delivering liquid hydrogen to users at distances of 50 and 100 miles.

Conclusions from this study indicate that for current electricity bus-bar costs, the most practical means for supplying liquid hydrogen to users within

---

* Heat from a nuclear reactor is used to provide the endothermic energy for a chemical reaction ($CH_4 + H_2O \rightleftarrows 3H_2 + CO$). The products are then pipelined to a number of chemical reactors (close to the customers' premises) where the chemical reaction is reversed and the heat of reaction recovered. The products of this second reaction are pipelined back to the power station where they provide feedstock for the first reaction.

about 60 miles is by truck. This method of transport is versatile because trucks can deliver liquid hydrogen to many different users. If the use is at a single installation, such as an airport, a gas pipeline with a parallel power line (to run the liquefier) is the best choice. Such a system has the added advantage of situating the liquefier so that any boil-off gases from storage, transfer, or detanking operations can be recovered and reliquefied.

For longer distances, from 600 to 1200 miles, railroad delivery of liquid hydrogen is attractive. As is the case with trucks in short hauls, railroads are versatile because two or more large users at a great distance from each other can be supplied with very little additional cost. Again, if all use is confined to a single installation or if all the users are close to a large storage dewar, a gas pipeline with a parallel electric-power line looks to be most efficient and practical. In this case, the liquefier is located so that boil-off gas from heat leaks or liquid transfer can be reliquefied. For transoceanic hydrogen transmission, liquefaction and shipping is most attractive.

Central Electricity Generating Board (CEGB), England

The total costs of gaseous hydrogen, methanol, and electricity transmission have been compared in a study by CEGB.[11] Also included in this study is a comparison of the relative costs of making electricity and electrolytic hydrogen in a base-load plant, transmitting them over 125 miles, and distributing them. (See Table 11-3.) These figures indicate that electrolytic hydrogen is much more expensive to manufacture, transport, and distribut than is electricity. CEGB concludes that development of a successful thermochemical process could reverse this situation.

CEGB, after calculating transmission costs as a function of transmission distances, has determined the break-even distances, shown in Table 11-4, above which it would be cheaper to transport nuclear energy as electrolytic hydrogen than as electricity.

According to CEGB's study, the transmission cost of hydrogen gas is approximately 7 ¢/million Btu for 200 km, and the cost of 765 kV ac of overhead electricity is 12¢/million Btu for 200 km. However over realistic distances, the total delivered cost of electrolytically produced hydrogen is not less than the cost of transmitting nuclear energy as electricity.

Table 11-3. ENERGY-TRANSMISSION STUDY BY THE CENTRAL ELECTRICITY GENERATING BOARD, ENGLAND[11]

	Manufacturing Efficiency, %	Manufacturing Cost, $\$/10^6$ Btu	Transmission Cost for 200 km, $\$/10^6$ Btu	Subtotal Cost of Energy Transmitted 200 km, $\$10^6$ Btu	Conversion and Distribution Cost, $\$/10^6$ Btu	Total Cost Distributed Energy, $\$/10^6$ Btu
Electrolytic Hydrogen (Distributed as Gas)	24-28	6.33	0.07	6.40	1.49	7.89
Electrolytic Hydrogen (Distributed as Electricity)	12-14	12.65	0.15	12.80	3.87	16.67
Electricity						
400 kVAC (Overhead)	33-40	3.79	0.20	3.99	1.98	5.97
765 kVAC (Overhead)	33-40	3.79	0.12	3.91	1.98	5.89
DC (Overhead)	33-40	3.79	0.55	4.34	1.98	6.32
DC (Underground)	33-40	3.79	0.67	4.46	1.98	6.44

Table 11-4. BREAK-EVEN ENERGY-TRANSPORT DISTANCES

Form of Electric Transmission	Generation and Transmission Only	Generation, Transmission, and Distribution as a Chemical Fuel	Generation, Transmission, and Distribution as Electricity
	miles (km)		
ac 400 kV	4780 (7700)	3,800 (6,100)	Never
ac 765 kV	4780 (7700)	38,500 (62,000)	Never
dc (Underground)	1680 (2700)	1,240 (2,000)	14,300 (23,000)

American Electric Power Service Corp.

C. A. Falcone has conducted a study[4] comparing the efficiency of a system in which electricity is converted (by electrolyzers) to hydrogen, which is transmitted and reconverted to electricity by a fuel cell, with the efficiency of an all-electric system. He shows that the energy-conversion losses in a hydrogen-transmission system would result in a much higher total-energy consumption and would necessitate greater power-plant capacity for the same level of delivered usable energy. Utilization of this mixed system would require about 2-1/2 times as much primary fuel as a purely electrical production and transmission system. Also, the hydrogen-electric system would require about 1.7 times as much plant capacity.

Falcone mentions that improvements in electrolytic hydrogen-production methods and fuel-cell technology could lower the primary-energy consumption. Also, development of a highly efficient thermochemical hydrogen-production method could significantly increase the efficiency of the conversion from primary energy to hydrogen. The study points out that if hydrogen were the preferred fuel for certain end uses in which electricity is unsuitable, the efficiency issue would be purely academic.

Stevens Institute of Technology

J. G. Hollenberg has completed a study determining the availability and desired characteristics for compressors for use in hydrogen transmission.[12] In general, before selecting a compressor for a certain application, one must determine the performance requirements. These requirements include operating-pressure ratios, efficiencies, flow rates, and special characteristics such as pulsations, possible contamination of the gas by lubricants, life time, and maintenance.

Currently two types of compressors are available for use with hydrogen: older, reciprocating machines driven by gas-fueled engines and centrifugal turbocompressors driven by gas turbines. Although centrifugal compressors may have some more desirable operating characteristics than reciprocating machines, the capability of producing high pressure ratios is not associated with turbomachinery, unless extensive multistaging is considered. Because of hydrogen's rapid diffusivity, there may be sealing problems with the reciprocating machine. The centrifugal compressor has recently replaced the reciprocating compressor in many installations because of its increased capacity, steady operating conditions, and lower initial cost and maintenance expenses.

According to Hollenberg, a third type of compressor, considered to have merit for use in hydrogen transmission, is the regenerative compressor. This compressor is capable of producing a dynamic pressure head that would require seven or eight stages for production in a centrifugal compressor. Use of the regenerative compressors has been limited because of their low specific speed and low operating efficiency (50%) in low speed regimes. Even at very low speeds, the regenerative compressor is more efficient than the centrifugal compressor. Although much work has been done on the regenerative compressor since World War I, compressors of this type over 50 hp have never been developed.

University of California, San Diego

L. Icerman has conducted a study comparing the relative costs of transmitting energy as hydrogen, natural gas, and electricity.[15] The transmission cost for each was broken down into three components: capital cost, operating cost, and annual operating cost (which includes investment, depreciation, and taxes). According to Icerman, the cost of energy transmission is dependent upon two parameters: pipeline cost and compressor-fuel cost. For example, pipeline costs for natural gas constitute from 70% to 90% of the total construction cost.

In Icerman's analysis, 30 and 36-inch diameter pipes were investigated for equivalent energy throughputs of natural gas and hydrogen at a fixed transmission distance and pressure. Although a 36-inch-diameter pipeline has a higher tonnage and consequently a higher initial cost, its horsepower requirement is considerably less. Thus, the capital and operating costs are less and result in an overall cost 13% lower for the 36-inch-diameter pipeline than for the 30-inch-diameter pipeline.

Assuming that a hydrogen pipeline delivers the same amount of energy as a natural gas pipeline, results indicate that, because of hydrogen's lower volumetric heating, 3.2 times as much hydrogen (by volume) must be moved to equal the volumetric content of natural gas. At 750 psia, the different compressibility factors for hydrogen and natural gas result in an increase in the natural gas-to-hydrogen volumetric-heating-value ratio to about 3.8:1. Compressor-fuel costs for the natural gas system account for only 2% of the total operating cost. In the hydrogen system, it accounts for 41%. The huge gas-volume-flow requirement of hydrogen (compared with natural gas) was reflected in hydrogen's high horsepower requirement (550% that of natural gas). Icerman noted that as the pipe diameter increases, resulting in lessened horsepower requirements for both natural gas and hydrogen, the ratio of hydrogen to natural gas operating costs declines.

In the comparison of hydrogen-transmission cost with that of electricity transmission, both underground cable and overhead lines were considered. The cost of hydrogen transmission is from 10% to 60% (for 700kV and 200kV ac, respectively) less than long-distance overhead electricity transmission. Comparison of underground-cable electricity transmission with overhead transmission indicates that underground transmission is from 10% to 20% more expensive than overhead transmission. In the future, the cost of electric-energy transmission may be as high as 25 times the cost of hydrogen transmission (at an equal energy-delivery rate).

Discussion of Transmission Studies

Hydrogen-transmission studies have generally included economic and technological assessments of present capabilities to transport pipeline hydrogen. The cost of transmitting hydrogen 100 miles in underground pipelines is approximately 1.4 to 1.6 times that of an equivalent energy capacity of natural gas transmitted by underground pipeline, if compressor-fuel costs of both fuels are considered to be the same (e.g., if both compressors are electrically driven).[3,23] Electrically driven compressors have been used in transmission systems, but recently intermediate pipeline compressors on natural gas transmission lines were adapted to operate on natural gas. If natural gas were assumed to drive intermediate pipeline compressors for pipeline gas transmission, the transmission cost of natural gas would be far lower, and the corresponding cost of transporting hydrogen in hydrogen-driven pipelines would be 2 to 3 times as great per 100 miles.[15,18]

Compressor and driver availability for hydrogen transmission is somewhat questionable.[12,18] Reciprocating compressors could be used with hydrogen pipelines. Many reciprocating-compressor installations are handling hydrogen under various conditions of pressure, temperature, water-vapor content, and corrosiveness. Compression cylinders would need to be quite large to transport pipeline quantities of gaseous hydrogen, but these large machines are currently available. One problem with using such a compressor for pipeline service is obtaining an engine driver that would attain sufficient power and rpm.

Currently operational turbocompressors that are designed for high throughputs of gas have never been utilized in operations involving high operating pressures. Hydrogen-fueled gas turbine drivers could be used to power centrifugal compressors; however, the technology involved is currently unproved for industrial applications. Other types of newer compressors — including axial, regenerative, and screw compressors — could be used in hydrogen transmission, as long as developmental research is undertaken.

When electricity-transmission cost is compared with the cost of pipeline transmission of natural gas or hydrogen, pipeline transmission is seen to be much cheaper (on an energy-delivered basis). Depending on the type of transmission considered, electricity may be from 5 to 20 times more costly to transmit than natural gas (for an equivalent amount of heat energy).[15,18]

Because transmission of hydrogen gas is expected (from calculations) to be cheaper than electricity transmission, the production of hydrogen from water, along with subsequent transmission, could be an economical alternative to the more costly electricity transmission associated with the nuclear era. It has been suggested that as transmission distances increase, pipeline transmission of gaseous fuel will be vastly more economical than electricity transmission.

If a customer requires electrical energy, however, transmitting the energy in the form of hydrogen and reconverting it to electricity results in large energy-conversion efficiency penalties, which result in much additional cost.[4,11] This increased cost is a direct reflection of increased capital costs for nuclear capacity. However, if the delivered hydrogen could be used directly as a fuel, the overall system efficiencies would probably be more attractive. As shown in Table 11-5,[27] production of hydrogen by electrolysis could result in an energy system less efficient than electricity. However, if space or industrial heating is desired rather than work (electricity) and/or if thermochemical methods of hydrogen production could be implemented, then an energy system that used hydrogen as its transmittable energy form would have a great deal of merit.

Table 11-5. COMPARISON OF ENERGY-SYSTEM EFFICIENCIES[27]

Future System	Nuclear Heat to fuel	Transmission, Storage, and Distribution	End Use	System Efficiency
	% Efficiency			
Hydrogen (95% Eff. Electrolyzer)	42.8	95	70 (Flame) 84 (Catalytic)	29 34
Electricity	45	90*	95	38
Hydrogen (Thermo-chemical)	55	95	70 (Flame) 84 (Catalytic)	37 44

* Estimate of transmisson and distribution efficiency.

Hydrogen Embrittlement

One of the major requirements for the handling, storage, and transmission of hydrogen is a material that will not be susceptible to severe degradation of its mechanical properties by atomic and molecular hydrogen. Because hydrogen readily diffuses into most structural materials, embrittlement is a serious factor that must be considered in designing for the containment of gaseous hydrogen. Materials for construction of compressors, pipelines, and storage vessels must be tested to determine whether or not they are suitable for use with hydrogen. For example, failures because of embrittlement in gas pressure vessels have occurred at as little as one-tenth of design pressure.[13]

Although the degradation of metals by hydrogen has been recognized in the failure of certain structures, the specific mechanism involved is not clearly understood. Currently, three explanations for the problem are proposed:

1. Hydrogen-reaction embrittlement
2. Internal hydrogen embrittlement
3. Hydrogen-environment embrittlement.

Hydrogen-reaction embrittlement is a result of the chemical reaction of hydrogen with a metal or some alloy. Some examples of hydrogen-reaction embrittlement are the formation of irreversible hydrides of titanium, niobium, zirconium, and tantalum; the decarburization of steels; and the formation of high-pressure water bubbles and methane in metal voids.

Both internal and environmental hydrogen embrittlement result from hydrogen atoms dissolving in the metal. Any hydrogen-containing chemical solution can cause internal hydrogen embrittlement. This problem is often encountered in metal- or petrochemical-processing facilities. Hydrogen-environment embrittlement is the degradation of mechanical properties resulting from the adsorption of hydrogen on the surface of a metal. This type of embrittlement manifests when a crack begins to form in a metal in the presence of hydrogen.

The degree of hydrogen embrittlement depends on the following:

a. The metal and its constituents, along with its microstructure
b. The applied stress and impurities present in the hydrogen environment.

The rate of strain is a parameter important in determining the degree of embrittlement. Low strain rates promote maximum embrittlement, allowing hydrogen transport near the crack tip. Metals conditioned for high strength are often more susceptible to embrittlement than their lower strength counterparts.

The purity of the hydrogen environment can have profound effects on the degree of embrittlement. Small amounts of oxygen and some inert gases, in some instances, have totally eliminated the embrittling capability of hydrogen. Small additions of oxygen, suflur dioxide, carbon monoxide, and carbon disulfide are also effective embrittlement inhibitors. The effects of protective coatings have also been investigated. An effective coating must have a low permeability, must be nonporous, and must adhere well to the substrate.

Protective coatings do have potential benefits for use with hydrogen, but economics will be important in the final selection.

No evidence has been presented that indicates embrittlement problems with nonmetals, although little research has been performed in this area. Permeation through polymers, although much greater than through metals, is not expected to be a problem in plastic pipes.

Because hydrogen transportation and storage systems might operate at moderate pressures (1000 to 2000 psia), there will certainly still be situations in which a combination of moderate pressure, room temperature, and high-purity hydrogen will lead to the degradation of the proposed structural materials. A considerable amount of work has been done in the area of hydrogen embrittlement of structural materials.[30] However, work done to evaluate hydrogen-embrittlement problems for materials used in pipelines, storage facilities, and other areas of the hydrogen economy is somewhat limited.

Recent work performed by the Battelle Memorial Institute for IGT and the American Gas Association was to determine whether or not hydrogen embrittlement of pipeline materials would be a significant problem in a hydrogen-energy system.[5] It was shown that certain hydrogen-induced problems (hydrogen stress cracking, loss of metal ductility, and hydrogen-environment embrittlement) could be expected with the operation of a hydrogen pipeline. Few problems are anticipated in the bulk of the pipeline, whether it is made from current standard pipe steels or from a higher strength steel with a yield strength of from about 100,000 to 112,000 psi. The abovementioned problems would be associated with regions of the pipe that exhibit abnormal properties, such as hard spots (concentrations of high-strength material or hard-weld zones) and certain defects or other factors increasing stress (such as abrupt changes in section), or that are subjected to excessively high soil stresses. Problems may also be encountered with a few of the compressor parts that are made from higher strength steels.

Conclusions from results obtained by the Sandia Laboratories indicate that the hydrogen-embrittlement problems of proposed pipeline and storage structures may be surmounted by careful and costly design.[30] Economics will be a problem because the size of the facilities and quality control dictate the use of low-cost materials. With underground pipelines, the problems are compounded by corrosive attack, which leads to the initiation of cracks.

Therefore, improved structural materials for the storage of hydrogen as metal hydrides or cryogenic hydrogen are required so that design of the unit wil be economical.

Hydrogen Storage

A capacity for storage is needed in any energy-delivery system for two fundamental reasons: 1) to be able to reconcile the seasonal variations in demand with the economic requirements for a virtually steady rate of production and transmission and 2) to accommodate temporary interruptions in production and transmission and to compensate for the inability to make accurate short-term forecasts of demand. Storage systems are incorporated in all natural-gas-energy systems, and the same capability must be provided in a hydrogen-energy system. The specific type of storage selected will be determined by various local requirements and constraints. An important parameter in the selection of a storage type is volume or storage purpose (e.g., seasonal, daily, hourly, or security). Some background on natural-gas-storage systems is provided to show the types of systems that will be required for a hydrogen-energy system.

Storage of natural gas is required to compensate for variations in demand for energy between winter and summer. The degree of the "seasonal energy swing" depends on the difference between the amount of gas required for home and commercial heating and that required for nonwinter needs. For example, Consumers Power Co., serving the mid-Michigan area, reports a typical demand of 2.2 billion SCF/day in July and 16 billion SCF/day in December. This seasonal variation factor of approximately 7 is accommodated by dependence on depleted-field underground storage, in which gas from transmission lines is injected to storage during the nonheating periods of the year.

Most gas-distribution systems experience brief periods (from 1 to 3 days) of yearly maximum demand. Instead of sizing main sources of supply to accommodate daily peaks, it is more economical to introduce supplementary supplies that are stored near the load centers. A typical form of peakshaving used in the gas industry is provision of storage facilities for either natural gas (for example, as LNG) or propane, which is mixed with air to produce substitute natural gas. In addition, a small storage capacity exists within the transmission lines. This capacity, known as "linepack," becomes available by allowing the mean operating pressure of a pipeline to fluctuate during the periods of variable demand.

Methods of Hydrogen Storage

A number of methods exist for the storage of hydrogen, whether liquid or gas. Each of these will be treated in turn.

Metal-Hydride Hydrogen Storage

Hydrogen can be stored by chemically combining it with various metals and alloys to form hydrides.[33] Heat is released during the hydriding process. During the dehydriding process, the hydride is dissociated by heating, and hydrogen gas is released for use. Hydrogen storage densities equivalent to liquid-hydrogen densities can thus be obtained. At present, the main technical drawback of metal-hydride storage is the very high overall weight and volume **involved.** Other critical factors in a hydride system are enthalpy or heat of formation, equilibrium pressure (as a function of temperature), cost, abundance, physical form, rate of formation and dissociation, physical stability, tolerance to impurities, and safety.

Many pure metals and alloys (including lanthanum, samarium, and other rare-earth-metal alloys) are considered candidates for hydride formation. Current research is focused on the development of cheap metals or alloys, rather than on development of the generally expensive rare earth metals. Development of iron-titanium alloy (FeTi), which is a relatively inexpensive material, is under way.

The basic reaction in the hydriding of FeTi alloy, a representative alloy-hydriding system, is –

$$1.08\ \mathrm{FeTi\ H_{0.1}} + \mathrm{H_2} \underset{\Delta Hf}{\overset{-\Delta Hf}{\rightleftarrows}} 1.08\ \mathrm{FeTi\ H_{1.95}}$$

The hydride decomposes readily at a pressure that is dependent upon alloy composition and temperature. Figure 11-4 illustrates this behavior in an FeTi system operating at 63 °F.[23] A characteristic curve may be drawn for any hydride at any operating temperature.

The lower curve in Figure 11-4 represents the dissociation pressure for the reverse reaction; and, as shown, higher pressures are needed for

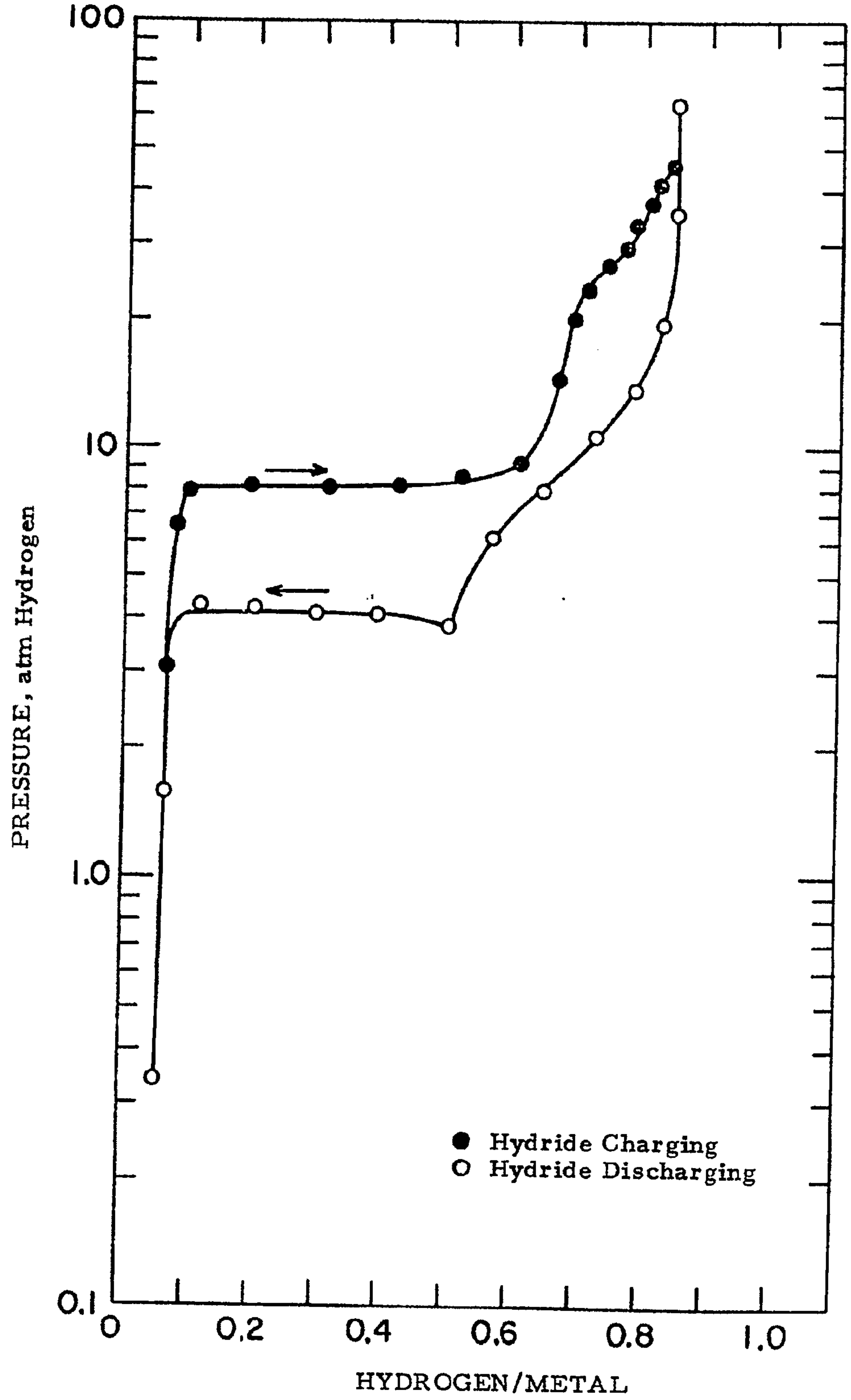


Figure 11-4. PRESSURE-COMPOSITION ISOTHERMS FOR AN $FeTiH_x$ SYSTEM[26]

the forward reaction. Impurities commonly present in commercially produced alloys can change the isotherm slope and may reduce the storage capacity of the hydride.[28]

Other candidates for metal-hydride hydrogen storage and their properties are shown in Table 11-6. These alloys are being studied at research laboratories around the world, as shown in Table 11-7.

Table 11-6. CANDIDATES FOR METAL-HYDRIDE STORAGE

Hydride Material	Heat of Formation, cal/mol	Grams of Hydrogen/Grams Metal, wt % Hydrogen	Effect of Other Gases (Water Vapor and Oxygen)	Relative Rates of Absorption
$LaNi_5$	–7,200	1.52	Small	Fast
$LaCuNi_4$	–7,500	1.35	Small	Fast
$La_{0.7}Ce_{0.3}Ni_5$	–7,000	1.6	Small	Fast
$SmCO_5$	–6,500	0.67	Small	Fast
$MmNi_5$	–6,500	1.5	Small	Fast
$Mm_{0.85}Ce_{0.15}Ni_5$	–6,500	1.5	Small	Fast
Vanadium	–9,600	5.9	Large	Fast
Niobium	–7,000	2.1	Large	
Magnesium	–17,800	7.6	Large	Slow
FeTi	– 5,500	1.8	Large	Fast
$Mg_{0.93}Ni_{0.07}$	–17,000	5.7	Large	Fast
V(0.93%Si)	–9,600	5.6	Large	Fast

---

[*] Mm = "mischmetal," a mixture of rare earth metals in their naturally occurring composition.

Two design schemes have been developed by Brookhaven National Laboratory for an FeTi-hydride, hydrogen-storage system.[26] The major difference between the two designs is the method of system heat transfer for metal hydriding and dehydriding. One scheme (circulating hydrogen gas) uses gaseous hydrogen as the heat-transfer fluid for cooling the hydride bed during hydriding and for providing heat of dissociation during dehydriding. Development of this concept has ceased because a large quantity of hydrogen (50 times as much as is being stored) is required.

Table 11-7. HYDRIDE RESEARCH IN PROGRESS

Organization	Project
Brookhaven National Laboratory	Alloy hydrides — properties Iron-titanium — engineering design Peakshaving system design
Public Service Electric and Gas Co.	Peakshaving demonstration "Gas-electric transformer" system analysis
Billings Energy Research Corp.	Iron titanium for vehicles
Ames National Laboratory (Iowa)	Basic rare-earth hydride chemistry
Allied Chemical Corp.	Basic hydride chemistry — alloys
Phillips Research	Lanthanum-nickel — basic chemistry
Denver Research Institute	Basic
University of Virginia	Basic
Sandia Laboratories	Basic
Daimler-Benz Ag	FeTi for automobiles
Battelle-Geneva	Basic
Harwell, U.K.	NiH_2 battery

The other scheme uses water, circulated in tubes throughout a fixed hydride bed, for heat transfer. Hydrogen is only circulated in the metal-alloy-containment (FeTi) section. With this system, a greater overall heat-transfer coefficient is obtained. Also, attrition (metal-alloy breakdown into small particles) resulting from the passage of hydrogen through the bed throughout its lifetime is minimized. The rate of attrition would be more rapid in a circulating-gas design because a large quantity of hydrogen is circulated. A small fixed-bed hydride system was subjected to an endurance test of 1200 cycles. (Hydriding and dehydriding equals one cycle.) Test results indicate that because of the attrition of metal particles, the hydride-bed pressure drop increased from a few inches water column to about 15 psia.

Brookhaven is currently examining the effect of the impurities contained in the hydrogen on hydride-bed performance. Oxygen (from 15 to 20 ppm), carbon monoxide, hydrocarbons, and water are expected to reduce the hydrogen-storage capacity of the hydride bed.[28]

Capital cost estimates for a fixed-bed, hydride-storage system are not reliable because they are not associated with complete plant design. Researchers at Brookhaven[25] have made a preliminary current-capital-cost estimate of $5/kWhr for a hydride-storage system operating at 32 atm, assuming high-pressure hydrogen is available for hydriding. This figure can then be multiplied by a total hydride-bed charging time (e.g., 10 hours) to arrive at a hydride-system capital cost (here, $50/kW). Brookhaven[25] personnel also pointed out that the fixed-bed, hydride-storage system would be independent of "economies of scale" because the system would be modular in design. However, the optimum modular size has not yet been determined.

Brookhaven has built a fixed-bed, hydride-storage system for Public Service Electric and Gas Co.'s experimental energy-storage system.[29] This reservoir was designed for use with an electrolyzer and fuel cell. It will take up hydrogen at a rate greater than 1.5 lb/hr and will deliver it at a rate greater than 1.0 lb/hr. (Its working capacity is significantly more than the 10 pounds of hydrogen originally specified.) A compressor is required to pressurize the hydrogen leaving the electrolyzer so that a practical sorption rate is obtained. The temperature and flow rate of the water in the heat-exchanger tubes are also important factors in sorption and desorption rates. The last two factors will be capital-intensive factors in the design of larger hydride-storage systems.

The cycle efficiency of a metal-hydride-storage system could be greater than 90%. The efficiency of the system is defined as the lower heating value of the hydrogen put into storage minus the power consumed by the hydriding-dehydriding process divided by the lower heating value of the hydrogen put into storage.

Liquid-Hydrogen Storage

The most promising application for cryogenic hydrogen lies in bulk transportation of energy by rail or truck, with certain reservations. According to Linde,[16] hydrogen should be liquefied only when long-distance transmission is required and no pipelines are available.

At the hydrogen-usage location, storage capacity for greater than 1 million gallons could be required. Liquid hydrogen has been stored in a container of about this volume at NASA Kennedy Space Center. There are several smaller liquid-hydrogen storage tanks, sized from 200,000 to 300,000 gallons, at other NASA installations. Typically, liquid-hydrogen storage for private industry ranges from 15,000 to 26,000 gallons. Smaller liquid-hydrogen tanks (from 3000 to 6000 gallons) have also been installed for industrial use. Because of the extremely low temperature of liquid hydrogen (—423° F), double-walled, vacuum-insulated dewar storage vessels are required to minimize evaporation losses and to prevent condensation of air. The spherical vessel shape is a result of design constraints posed by the vacuum-jacketed insulation system. For some containers, daily boil-off losses are as low as about 0.5%. Materials compatible with liquid-hydrogen temperatures, such as stainless steel (300 series, typically) or aluminum alloys, must be used for the inner liner. Capital costs for vacuum-insulated, liquid-hydrogen storage tanks (of larger capacities) are between $2 and $4/gal of liquid hydrogen stored.

The liquid-hydrogen transfer and handling lines that were used successfully in the space program are very expensive. Cryogenic instrumentation has not advanced significantly in the last 10 years. Instruments suitable for aerospace applications are too costly for most commercial application, so rugged and reliable instruments that can be inexpensively mass-produced are needed.[14]

It might be possible to store large volumes of liquid hydrogen below ground. Some differences[10] between above- and belowground storage systems for LNG include —

1. Gradual freezing of the soil adjacent to underground storage areas, resulting in lower temperature gradients than with aboveground systems
2. Contribution by the frozen area of some additional thermal-insulating value beyond that of any applied insulation
3. Reduction of liquid-spill problems because of the frozen-earth wall surrounding the area
4. Requirement of more soil investigation and an increased site dependence with underground systems.

The fact that the temperature of liquid hydrogen is much lower than that of LNG will amplify these four observations. In order to reduce evaporation losses to the same level as for LNG, liquid-hydrogen storage will require more insulation of underground containers. In addition, a liner that is resistant to hydrogen-gas permeation will be required to prevent gas from leaking into the insulation. There should be no appreciable difference in the effect of the liquid hydrogen on the soil, except that greater areas around the storage site will be affected because of the greater temperature gradient.

The three forms of underground liquid-hydrogen storage that could be investigated to determine their technical and economic aspects are[10] –

1. Frozen, in-ground storage (excavated pit)
2. Prestressed-concrete-tank storage (underground)
3. Underground-cavern storage.

In addition to the cost of storage, handling, and transmission equipment for liquid hydrogen, the cost of liquefying the hydrogen must also be analyzed because it can far outweigh storage costs.[17] A hydrogen liquefier typically utilizes a nitrogen precooler-expander process in which hydrogen is recycled to provide refrigeration at three temperature levels below 80 °K. Two levels of refrigeration are provided by the hydrogen turbines, and the third is achieved by Joule-Thompson throttling of a portion of the high-pressure recycle hydrogen.[19]

In addition to the work required to cool and liquefy the hydrogen, there is another energy-consuming process encountered in liquefaction that results from differences in the electron spins of the hydrogen nuclei in the molecule. Hydrogen molecules that have symmetric nuclear spins are referred to as ortho hydrogen (oH_2), and those that have asymmetric spins are referred to as para hydrogen (pH_2). Hydrogen is a mixture of oH_2 and pH_2 at an equilibrium ratio, which is a function of temperature. The equilibrium para composition is about 25% at ambient room temperature and above. However, the para content increases with decreasing temperature, reaching an equilibrium composition of 99.79% pH_2 at the atmospheric boiling point of liquid hydrogen, 20.39 °K.[19]

Consideration must be given to the two hydrogen forms because of their difference in energy. At any temperature, the para form represents the lower energy state. To liquefy hydrogen and to maintain it in a stable state, sufficient energy must be removed not only to cool and liquefy the hydrogen, but also to convert the oH_2 to pH_2. In converting oH_2 to pH_2, 609 Btu/lb-mol (which exceeds the heat of vaporization of oH_2, 385 Btu/lb-mol) must be removed. The total enthalpy change in liquefying oH_2 and converting it to 99.79% pH_2 once it is cooled to liquefaction temperature is, therefore, 840 Btu/lb-mol.

At and above 80°K, refrigeration is provided by 1) a stream of cold nitrogen gas that is used to help precool the combined feed and recycle stream and 2) a stream of nitrogen liquid that is used for additional cooling. The hydrogen feed stream is cooled, continuously, down to the temperature of the exhaust from the cold turbine, after which it is throttled, passed through a catalytic converter for trimming purposes, and then subcooled in heat exchange with hydrogen boiling at low pressure.[19]

Cold exhaust streams from the expanders are warmed in counter-current heat exchange with cooling hydrogen streams, are combined, and are finally returned to the suction of the recycle compressor. Vaporized hydrogen from the final subcooler is combined with flash vapor from throttling and is then warmed in heat exchange with a cooling stream and returned to the suction of the subcooling-fluid compressor, which in turn discharges to the suction of the recycle compressor.[19]

Linde considers the estimated capital-equipment cost for a liquid-hydrogen plant with capacity greater than 10 tons/day (and throughout the medium plant size range) to be approximately $500,000/ton of hydrogen liquefied per day.[16] Much higher relative capital-equipment costs per output would be associated with small plant sizes, and very large plants would have lower relative capital costs per output than medium-size plants. Air Products and Chemicals, Inc., considers hydrogen-liquefaction-plant design economically undesirable below a 15 ton/day plant size because the high cost of component parts are reflected in high hydrogen-product costs.[7]

The reversible work necessary to liquefy hydrogen has been determined to be 1.773 kWhr/lb in going from 308 °K (95 °F) at 1 atm to the final condition of liquid hydrogen (97% para content) at 20.57°K and 135 psia. Under these conditions, the minimum energy requirement, using current technology, is 4.9 kWhr/lb. More than half of the energy losses can be attributed to the compressor. This figure indicates that approximately one-third the lower combustion value of a pound of hydrogen is needed to liquefy it, not including energy that might be needed to purify the gaseous hydrogen feed to cryogenic standards. The practical cycle efficiency of a hydrogen-liquefaction storage cycle, defined as the net heating value of the hydrogen minus the power consumed divided by the net heating value of the hydrogen, would be from 65% to 68%.

Conversion from ortho to para hydrogen proceeds spontaneously, but at a slow rate. Autoconversion of liquid hydrogen in storage will occur, resulting in a severe boil-off (about 1%/hr, neglecting heat effects) that will decrease with increasing conversion.

As the para content of the liquefied hydrogen approaches equilibrium, the power requirement for liquefaction increases, but the storage loss decreases. Consequently, the optimum para content of the product is a function of the mean storage time. For example, calculations[19] show that for 95% para liquid hydrogen, the conversion boil-off loss is 1.24% over a 2-week period. If the plant were to produce only 75% para, product boil-off losses over a 2-week period would be 19.1%.[19] However, for each initial composition, a break-even period exists during which the energy cost for conversion equals the energy cost for the vaporized hydrogen. If the hydrogen is used within the break-even time limit, partial conversion is advantageous with respect to energy consumption.

Underground Compressed-Gas Storage

The natural gas industry currently relies on cheap underground gas storage to meet seasonal peak gas demands. There are five underground-gas-storage systems that may be applicable to hydrogen-gas storage[22]:

1. Depleted oil and gas fields
2. Aquifers (subterranean porous rock structures containing water)
3. Salt cavities

4. Natural or mined cavities in rock

5. Cavities induced by nuclear explosions.

A description of the above methods and comments on their applicability for hydrogen-gas storage are provided. A natural gas analogy is given in some instances.

Depleted Oil and Gas Reservoirs

Natural gas has been successfully stored in depleted gas and oil reservoirs. The gas is stored in the void spaces of porous rock structures such as sandstone. Sufficient porosity (providing storage volume) and permeability (to permit movement of gas into and out of the structure) are essential features. A leak-tight "cap rock" formation on top of the storage structure provides a seal. Cushion or nonrecoverable gas is required, and the pressure-injection level will determine the final quantity of gas stored.

This method may be considered for hydrogen storage because the gas-tightness of the reservoir does not depend on the nature of the gas contained. Cap rock is usually saturated with water. Capillary resistance of water within the pores will form a positive seal, regardless of gas-molecule size. Thus, hydrogen should be storable at pressures equivalent to those employed with natural gas.

For several years, the U.S. Department of the Interior, Division of Helium, has injected helium (a "leaky" gas) at a pressure of 817 psi into the Cliffside Field in Amarillo, Texas. Careful retention monitoring of the field should provide valuable information concerning possible hydrogen storage.

Aquifer Storage

Bearing much resemblance to depleted-gas-field storage, but having no native hydrocarbon deposits, aquifer storage of gas is also used. Injected gas displaces water in porous rock, forming a trapped "bubble" at or near local hydrostatic pressure. The gas-water interface is highly mobile, a function of the injection-withdrawal cycle. Gas storage is intact as long as "threshold pressure" (a gas pressure high enough to completely displace the water from the cap rock pores) is not exceeded and the aquifer maximum-volume limit is heeded.

Aquifer storage of hydrogen seems to be quite possible because the water-saturated cap rock seal can be used. An aquifer storage field in Beynes, near Paris, was operated successfully on manufactured gas (about one-half hydrogen) for about 10 years.

Salt-Cavern Storage

Salt caverns, formed in underground salt strata and salt domes by "solution mining," have been used for the storage of LPG and for limited storage of natural gas. The technique for forming salt cavities via solution mining is well developed. Basically, water is pumped in, and brine is removed so the cavity geometry is leached out. Hydrogen storage in salt cavities has already been demonstrated by the British Chemical Industry.[31] Salt strata occur in various parts of the United States, and the estimated total U.S. capacity of salt-cavity storage wells is currently about 200 million barrels. However, additional capacity can be readily added.

Natural or Mined Cavities

Where appropriate porous rock structures, salt strata, or salt domes do not exist, it is possible that natural or mined cavities could be used for the storage of gases (including hydrogen). However, experience in this area is limited. Assuming that a sealing structure functionally analogous to water-saturated cap rock exists, such cavities should be reasonably leak-tight.

Cavities Induced by Nuclear Explosions

The energy released by a subterranean nuclear explosion causes an adiabatic shock wave with temperatures and pressures on the order of 1 million ^{0}F and 1 million atm, respectively. A nearly spherical shape remains after condensation and solidification of the molten phase. However, if the reflected shock wave returns from the surface with too much force, the cavity will collapse, resulting in a "chimney formation." Much remains to be learned about threshold pressure, impermeability, fracture susceptibility, and radiation decay before gas can be stored in such cavities.

An example of such a structure is the stable spherical cavity with a radius of 87 feet at a depth of 1200 feet produced by the "Gnome Event."[32] If gas pressures of up to 1 psi/ft could be maintained, approximately 290 million SCF of natural gas could be stored there.

Linepack Compressed-Gas Storage

If pipelines of conventional sizes and numbers, comparable to those used in natural gas systems, are incorporated in the hydrogen-transmission system, linepack storage will probably play only a small role because of hydrogen's lower volumetric heating value (compared with that of natural gas). However, if pipes of larger diameters are incorporated in the systems, linepack storage could become significant.

Underwater Compressed-Gas Storage

Underwater gas storage at the equivalent hydrostatic pressure in low-cost, thin-walled containment membranes shows great promise.[32] A spherical container can be used as a storage vessel. At greater depths, the water pressure and constant low temperatures are advantageous for the storage of large quantities of gas. Another advantage would be afforded by underwater storage in oceans, in which case the salt in the water would prevent hydrate formation. Safety, leakage, collection, and contamination problems will be held to a minimum in underwater hydrogen storage.

Aboveground Compressed-Gas Storage

Current technology allows for the aboveground storage of hydrogen in medium- and high-pressure vessels. Much operating experience has been obtained in the pressure-vessel storage of hydrogen. Most pressure-vessel materials are not susceptible to hydrogen embrittlement. High-pressure storage is technically sound; however, high capital costs are involved. Pressure vessels are currently available from United States Steel Corp. for large-scale storage of hydrogen at 500, 1295, and 2400 psi, as shown in Table 11-8.

Concluding Comments

Three systems of aboveground storage may be considered for hydrogen-energy storage. Both hydrogen liquefaction with subsequent storage and compression of hydrogen with high-pressure tube storage are currently in use. Metal-hydride storage is currently under development.

Table 11-8. PROPERTIES OF U.S. STEEL CORP.'S HYDROGEN-STORAGE VESSELS

Pressure, psi	Size	No. of Vessels Required to Store 10^6 SCF	Vessel Cost, $	Vessel Mounting Cost, $	Vessel Manifolding Cost, $	Total Capital Cost for 10^6 SCF Capacity, $$10^6$
500	24-in. OD 40 ft long	265	3300	540	250	1.08
1295	24-in. OD 40 ft long	116	3500	540	275	0.50
2450	24-in. OD 20.5 ft long	136	3900	540	300	0.65

A75092207

Selection of a hydrogen-storage scheme will depend on many application features, including storage capacity, duration of storage, hydrogen-charging capacity, amount of storage-system use, and associated costs. Table 11-9 is a comparison of some of the characteristics of the three methods proposed for aboveground hydrogen storage.

Table 11-9. RELATIVE COMPARISON OF HYDROGEN-STORAGE METHODS

Point of Comparison	Metal Hydride	Liquid	Compressed Gas
Capital Equipment Cost, $/1000 SCF	400-600	1000-1300	800-1100
Energy Expenditure, kWhr/lb of hydrogen storage cycle	0.8-1	4-5	0.5-1
Intermittent-Operation Capability	Good	Fair	Good
Hydrogen Volume per Container Volume	Medium	High	Low
Storage Stability With Full Storage Volume	Good	Medium	Medium
Storage-Vessel Cost as % of Total Storage Cost	Medium	Low	High
Equipment Necessary to Admit Hydrogen Into Storage as % of Total Storage Cost	Medium	High	Low

Several alternative systems for the underground storage of gaseous hydrogen exist, and abundant experience with underground storage of natural gas has been obtained in connection with depleted gas fields and aquifer reservoirs. An advantage with these methods of hydrogen storage is the water-sealing property of cap rock, which prevents diffusion of hydrogen gas.

Much less experience has been gained with salt cavities and natural and mined cavities. Many technical and economical advantages are claimed for the underground storage of hydrogen gas. Further investigation of each underground method of gas storage is warranted.

Hydrogen in Gas-Distribution Systems

Introduction

Although there are many research and development programs (recent and current) related to hydrogen energy, none deals directly with testing the conventional gas-distribution system for use with hydrogen. Additionally, there have been no demonstrations of hydrogen delivery by conventional (modern) gas-distribution systems. Hence, very little information is available on the compatibility of this system with hydrogen. We can only describe the natural-gas-distribution system in the United States and note the compatibilities and problems expected in use with hydrogen.

The Gas-Distribution System

The U.S. gas-distribution system typically consists of one or more networks of piping that carry the gas to the consumers from the various sources of supply: city-gate station, gas-storage facilities, and gas-manufacturing plants. Figure 11-5 is a schematic of the various components of a representative distribution system that includes a manufactured gas supply.[6] The latest available statistics show the purchased and produced gas to be 18,730 trillion Btu of natural gases per year and 30 trillion Btu of manufactured and substitute natural gas per year. (Annual production of SNG is growing at a very rapid rate.[2]) Hence, the primary source of gas for most distribution systems is pipeline natural gas fed through one or more city-gate stations. The basic functions of these stations are to meter the gas and to reduce the pressure of the gas from that of the pipeline to that of the distribution system. Most stations measure the gas with orifice meters. Controlled pressure reduction is accomplished with pressure regulators that control the rate of

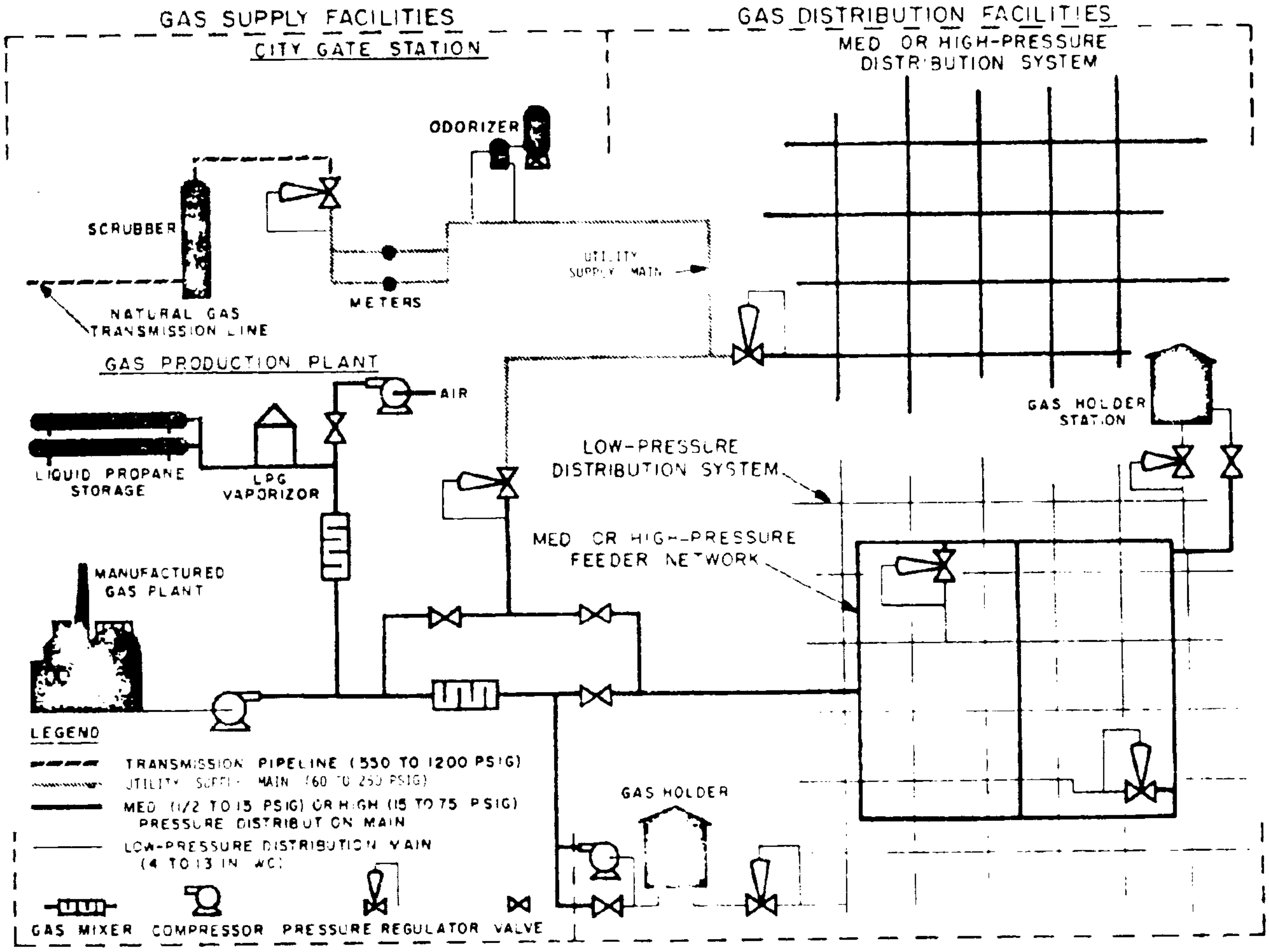


Figure 11-5. GAS-DISTRIBUTION SYSTEM WITH REPRESENTATIVE SUPPLY SOURCES

gas flow through the station, thus maintaining the desired pressure level at its outlet.

Before the gas leaves a city-gate station, a small, controlled amount of a substance with a strong, penetrating odor is injected into it with an odorizer. This odorant warns customers of the presence of unburned gas before it can accumulate to a hazardous concentration. The piping that transmits the gas from the city-gate station to the remainder of the distribution system is the supply main. Beyond the supply main, the piping in the distribution system can be categorized as[6]—

1. Trunk mains, transmitting gas from a major source (such as a supply main) to feeder mains

2. Feeder mains, transmitting gas from trunk mains to distributor mains, as well as to the services connected to them

3. Distributor mains, supplying gas primarily to services

4. Services, delivering gas from a main to customers' gas meters.

Many distribution systems consist of several superimposed networks of piping operating at different pressures. Gas from high-pressure supply mains may be fed through pressure regulators into high-, medium-, or low-pressure distribution networks. High-pressure distribution networks, operated at from 15 to 75 psig, are of two types:

1. Networks that serve customers directly

2. Networks that are used primarily to feed gas into medium- (from 1/2 to 15 psi) or low-pressure (4 to 12-inch water column) distribution networks.

Although classification of piping networks by pressure level is quite common, there is no standard terminology or pressure range covered by each classification.

The fuel lines of residential customers are usually operated at pressures of from 4 to 10-inch water column, the pressure required for proper appliance performance. Consequently, it is necessary to install a service regulator in each residence fed directly by a medium- or high-pressure distribution system. This regulator reduces the pressure from that of the main to that of the fuel line.

The basic distribution system in most older, large cities is a low-pressure, cast-iron pipe system. Most of the piping in these systems was laid during the manufactured-gas era when gas (containing up to 50% hydrogen) was produced at low pressure and compression was a relatively expensive operation. With higher pressure natural gas now available, major portions of new distribution systems are medium- or high-pressure networks of steel. Consequently, most older low-pressure systems are now ringed and overlaid with medium- and high-pressure piping grids.[6] Although these modern distribution grids were designed for use with natural gas and have never been tested with hydrogen, major problems in use with hydrogen are not anticipated. A principal concern, however, is the greater tendency of hydrogen to leak from a pressurized system.

A tremendous variety of pipes and fittings have been used, but one trend predominates in newly installed gas-distribution systems – the increased use of plastic pipes and fittings for mains of 2-inch diameter and smaller (medium- and low-pressure networks) and for services. According to a recent survey, about 87% of the gas utility companies are now installing plastic pipes for new and replacement mains, and about 92% use plastic for new and replacement services.[9] On a length or footage basis, over 55% of the distribution piping to be installed during 1975 will be plastic. At present, however, the composition of the total in-place mains and services is approximately as shown in Table 11-10.

Table 11-10. DISTRIBUTION-SYSTEM PIPE MATERIALS

Pipe Material	Mains, % of total (footage basis)	Service, % of total (number basis)
Steel	81	83
Cast and Ductile Iron	12	2
Copper	1	6
Plastic	7	9

In addition to the pipes and fittings, there are numerous flow-metering and -control devices such as valves, pressure regulators, and meters. Following is a partial list of the common materials of construction for components in distribution systems and some of their predominant uses:

- Gray cast iron (old mains)
- Ductile and wrought iron (mains)
- Copper (services and main inserts)
- Steel (mains and services)
- Brass (valves)
- Polyethylene (services and mains)
- Polyvinylchloride (services and mains)
- Fiberglass-reinforced epoxy (services and mains)

- Natural and synthetic rubber and elastomers (mechanical joint seals and meter diaphragms)
- Lead and jute (sealer for bell and spigot joints)
- Cast aluminum (meter housings and regulator parts)
- Cadmium-plated steel (internal regulator parts)
- Cork and gasket materials (meter and instrument gaskets)
- Miscellaneous plastics – ABS, CAB, PB, nylon, etc. (services and internal instrument parts).

From the diversity of equipment, operating conditions, and materials of construction, it is evident that compatibility of the distribution system with hydrogen requires verification by demonstration. Any statement that hydrogen or hydrogen-rich gases can be adequately and safely delivered to the customer through the in-place natural-gas-distribution system is a presumption.

Hydrogen Compatibility and Problem Areas

Volumetric Flow

Because of the vast differences among U.S. distribution networks (in terms of types of equipment, materials of construction, operation conditions, and age), it would be meaningless at this stage to assess overall compatibility for a single "typical" system or to attempt to quantitatively describe a "typical" system's conditions of operation with hydrogen. Generally, the conditions of operation will be determined by delivery of the quantity of hydrogen equivalent in high heating value to that of natural gas delivery. This will necessitate a proportionate increase in the volumetric flow of hydrogen relative to natural gas. This means that the volumetric flow meter used for measuring gas delivery could be undersized (by a factor of as much as 3) for hydrogen usage.

Except in some small-diameter (service) lines, the flow in natural-gas-distribution systems is (partially) turbulent. The Reynolds number, which mathematically characterizes the flow, is directly dependent upon pipe diameter and gas velocity and density and is inversely dependent upon gas viscosity. If we consider hydrogen for energy delivery equivalent to that of natural gas in a given pipe, we might have a tripled gas velocity, a 20% decrease in viscosity, and an 87% decrease in density (compared with methane). As a result, the Reynolds number for hydrogen flow could be less than half that for natural gas flow. If the Reynolds number falls to below about 2000, the resulting laminar flow with viscous drag could require significantly higher operating pressures and pressure drops for adequate flow and energy delivery.

Odorants and Illuminants

Apparently the sulfur compounds now used to odorize natural gas are compatible with hydrogen and would, therefore, be satisfactory hydrogen odorants. Because odorants have to be added on a volume basis and because the volume of hydrogen used will be 3 times that of natural gas (on an equivalent energy basis), 3 times the quantity of odorant will be required, thus maintaining the same percentages. The odorant would be burned at the appliance. Odorization should present no pollution problem, and the added cost would be insignificant.

The addition of an illuminant, which would make the hydrogen flame visible, simultaneously with an odorant should be considered. This would facilitate hydrogen use in open-flame appliances and assist in the adjustment of burners and pilots. No suitable illuminant has yet been identified, but two types of materials would be appropriate. One is a small amount of an aromatic-type organic material that would burn with a yellow flame. The other is a trace of a volatile organo-metallic sodium compound that would give the flame the characteristic sodium-yellow color. Experimentation is required to determine whether or not either of these approaches would be useful and to determine the optimum quantities to be added.

The addition of any foreign material, especially sulfur-bearing odorants, to hydrogen used in catalytic processes could cause considerable problems. Representatives of Air Products and Chemicals, Inc., told us that they had considered odorizing the hydrogen in the company's Houston transmission line, but several of the industrial users on the line could not tolerate the presence of even traces of sulfur compounds. Similar considerations may apply to the use of hydrogen in catalytic burners. It is technically possible to remove the odorant immediately before the catalytic bed, but in some applications this would be inconvenient and would add to the cost. An alternative worthy of consideration for future experimental work is to develop an odorizing material that does not contain sulfur and that does not interfere with catalysts. It may be appropriate to introduce such a "new smell" with the introduction of the "new gas" to the public, in which case a suitable odorant must be ready for application as soon as the first general use of hydrogen is introduced.

Leakage

The rate of the loss of hydrogen through leaks, whether fractures, corrosion pinholes, or leaky seals, is about 3 times greater (on a volume basis) than that of natural gas. The rate of energy loss through the leak is about the same as for natural gas; but in a confined space, the lower flammable limit of hydrogen (4.0%) will be reached in a quarter of the time required for natural gas to reach its limit.[8] Hydrogen's rapid diffusivity, 2.8 times faster than that of natural gas, will allow it to permeate rapidly through dry soil and crushed rock and therefore to escape from the point of leakage. Once it reaches the air, its low density will cause it to rise rapidly.

Cast-iron and steel pipes are, for all usual purposes, almost impermeable to both hydrogen and natural gas at ambient temperatures. In fact, even though the permeability rate of hydrogen is higher than that of natural gas, it is still so small that it is insignificant. This should also be the case for sealing materials; but to be sure, experimental confirmation should be obtained for typical seals.

Hydrogen's permeation of plastic pipes, however, warrants further consideration. Some permeability measurements of typical plastic piping compounds have been made. In these studies, the ratio of hydrogen to natural gas permeation varies widely — between about 7:1 for polyethylene and 88:1 for ABS. Table 11-11 shows some relative permeation data obtained by Battelle Memorial Institute.[1]

Table 11-11. GAS PERMEATION OF PLASTIC PIPING COMPOUNDS

Material	Methane Permeation	Hydrogen Permeation	Relative Permeation (Hydrogen/Methane)
	— 10^{-3} CF/sq ft-atm-day —		
Acrylonitrite-Butadiene Styrene, ABS-1-2	0.59	51.71	87.6
Cellulose Acetate-Butyrate, CAB/MH	11.8	157.0	13.3
Polypropylene	1.6	20.2	12.6
Polyethylene PE III-3	2.3	15.7	6.8
Polyvinyl Chloride, PVC-II-I	0.2	13.7	68.5

In the case of PVC pipe, the loss of hydrogen will be from 6 to 8 times the loss of natural gas (on a volume basis), but in absolute terms this amounts to only 83.8 SCF/yr per mile of 4-inch pipe (with a wall thickness of 0.33 inch) operated at 1 atm (or 15 psig). In comparison, Heath Survey Consultants[24] reports that a typical leakage rate for existing gas systems is between 100,000 and 4 million SCF/yr per mile of 3-inch "equivalent" pipe. Figures obtained from England indicate that a typical rate of leakage from cast-iron mains that carry manufactured gas (50% hydrogen) at a pressure of 6-inch water column is 20 SCF/hr per 1000 yards of main, or approximately 800,000 SCF/yr-mile. This apparently tolerated leakage rate makes the diffusion rate of hydrogen through PVC pipes appear insignificant.

Losses of hydrogen by diffusion through other plastic materials are higher than through PVC. Losses through CAB and ABS will be 11 and 4 times as great, respectively. In the latter case, the loss will be more than 3000 SCF/yr per mile of 4-inch pipe. Before we conclude that these leakage rates are not hazardous, experimental measurements should be made of the rate of diffusion of hydrogen through a backfilled trench and under pavement or frozen ground. It appears that PVC and polyethylene are preferable to ABS and CAB. However, long-range testing of actual pipe sections under service conditions to obtain practical proof of their suitability would be worthwhile.

Most of the serious gas leaks in distribution systems are caused by damage done to mains by construction contractors. With plastic pipe, severing of the line is common, whereas steel pipes usually only bend or crack. Fire rearely results from such an accident. With hydrogen, however, a fire will almost certainly occur if an ignition source is present. Static charges frequently build up on the inside of plastic pipes, and the fracture of a metal pipe could be accompanied by friction sparks – either of which could cause ignition. Thus, we might expect a higher incidence of fire cause by accidental damage to hydrogen pipes. This may be considered fortunate because a buildup of explosive mixtures, as can happen with unignited leaks, is prevented. However, different operational practices may have to be devised to cope with this aspect.

Leaks in industrial hydrogen systems are detected by combustible-gas detectors. A hazard unique to hydrogen leaks in aboveground hydrogen pipework is that occasionally the leaking gas ignites because of a spark from static friction caused by the leak. The resulting "invisible" flame cannot be seen in daylight. Because of this problem, flame detectors[24] have been developed for hydrogen systems.

Line Purging and Maintenance

An area of serious concern is the purging requirements for pipes, both when bringing new mains into service and when repairing existing mains. Use of an inert gas to sweep out the air or to sweep out the gas already in a used main may be necessary because the wide flammability limits of hydrogen (from 4% to 75% compared with from 5% to 15% for natural gas) would more frequently result in hazardous conditions in the main. With natural gas, welding operations can be performed when the gas-air mixture in the line is more than 15% gas. With hydrogen, however, one would have to ensure that the hydrogen air mixture was safely above 75% hydrogen. Use of some form of an oxygen-level indicator may be necessary to ensure that the line has been adequately purged. Purging procedures will have to be established through experimentation.

Peculiar Temperature Effects

Unlike methane or natural gas, hydrogen has a maximum Joule-Thompson inversion temperature of $-109^{0}F$, far below ambient temperatures. Therefore, at ambient temperatures hydrogen undergoes a temperature increase upon throttled expansion. The extent of the temperature increase depends upon the pressure drop, the initial gas temperature, and the rate of heat exchange between the hydrogen and the environment. This Joule-Thompson effect could be significant at leaks because it would increase the chances of ignition, and it could be significant with plastic components. Thermoplastic pipe for natural gas service, for instance, is not required to be pressure tested (at 50 psig or 150% of operating pressure, whichever is greater) at temperatures above 100 ^{0}F.[21]

Concluding Comments

It is possible that certain localized areas may be selected for complete transition from natural gas to hydrogen service to accelerate the use of nonfossil energy sources or to provide a market for a storable, synthetic chemical fuel. Another possibility, in a shorter time frame, is that of supplying hydrogen produced from coal, oil shale, or nuclear sources (off-peak power) to certain specialized industrial users for use as a fuel or as a chemical feedstock (for example, to ammonia producers) to relieve the shortage of natural gas. In any of these circumstances, it will be necessary to demonstrate and verify that gas-distribution equipment is compatible with hydrogen and that conventional or suitably modified techniques for handling natural gas are acceptable for use with hydrogen.

References Cited in This Section

1. American Gas Association, The Development of Improved Plastic Pipe for Gas Distribution Purposes. Arlington, Va., 1968.

2. American Gas Association, 1973 Gas Facts. Arlington, Va., 1973.

3. Beghi, G. et al., Hydrogen, Oxygen, and Natural Gas by Pipeline: Comparative Transport Costs. Ispra (Varese), Italy: EURATOM, n. d.

4. Falcone, C. A., "Hydrogen Transmission: the Significance of Efficiency." Paper No. C 75 111-0 presented at the IEEE PES Winter Meeting, New York, January 26-31, 1975.

5. Fletcher, E. E. and Elsea, A. R., "Evaluation of the Influences of Absorbed and Adsorbed Hydrogen on the Mechanical Properties and Fracture Behavior of Materials to be Used in a Hydrogen-Gas Transmission System," Summary Report to IGT by Battelle Lab., Columbus, February 1974.

6. Forwalter, J., Ed., IGT Home Study Course — Gas Distribution. Chicago: Institute of Gas Technology, 1963.

7. Foust, P., Air Products and Chemicals, Inc., letter of March 25, 1975.

8. Gregory, D. P., "A Hydrogen-Energy System." Am. Gas Assoc. Cat. No. L21173. Arlington, Va.: American Gas Association, 1972.

9. Hale, D., Ed., "P&GJ Staff Report," Pipeline Gas J. 201, No. 13, 26 (1974) November.

10. Hallet, N. C., "Study, Cost, and System Analysis of Liquid Hydrogen Production," Air Products and Chemicals, Inc., Contract No. NASZ-3894, (1968) June.

11. Hampson, P. J. *et al.*, "Will Hydrogen Transmission Replace Electricity?" Paper presented at Hydrogen Energy Fundamentals — a Symposium-Course, Miami Beach, March 3-5, 1975.

12. Hollenberg, J. G., "Hydrogen Pipeline Transmission." Paper presented at Hydrogen Energy Fundamentals — a Symposium-Course, Miami Beach, March 3-5, 1975.

13. Hord, J. *et al.*, "Selected Topics on Hydrogen Fuel," Cryogenics Division National Bureau of Standards Paper No. *NBSIR 75-803*, (1975) January.

14. Hord, J., "Research Opportunities in Cryogenic Hydrogen-Energy System." Paper presented at Hydrogen Energy Fundamentals — a Symposium-Course. Miami Beach, March 3-5, 1975.

15. Icerman, L., "Relative Costs of Energy Transmission for Hydrogen, Natural Gas, and Electricity," *Energy Sources* *1*, No. 4, 435-36.

16. Johnson, J., Union Carbide Linde Division, letter of March 24, 1975.

17. Johnson, J. E., "The Storage and Transporation of Synthetic Fuels," Oak Ridge National Laboratory Paper No. *ORNL-TM-4307*, September 1972.

18. Konopka, A. J. and Wurm, J., "Transmission of Gaseous Hydrogen." Paper presented at the Ninth IECEC, San Francisco, August 26-30, 1974.

19. Langley Research Center, "Survey Study of the Efficiency and Economics of Hydrogen Liquefaction," Contract *NAS 1-13395*. Hampton, Va., 1974.

20. Leeth, G. G., "Nuclear Heat Transmission Considerations." Paper presented at the First National Topical Meeting on Nuclear Process Heat Applications, Los Alamos, New Mexico, October 1-3, 1974.

21. "Minimum Federal Safety Standards for Gas Lines," Subpart J, Requirement 192.511 of the Code of Federal Regulations in *Pipeline Gas J.* *202*, No. 4, 49 (1975) March 15.

22. Mitchell, G. M. and Smith, J. A., "Peak Shaving by Gas Storage," in Forwalter, J., Ed., *IGT Home Study Course — Gas Distribution*, 276. Chicago: Institute of Gas Technology, 1963.

23. Reynolds, R. A. and Slager, W. L., "Pipeline Transportation of Hydrogen." Paper presented at The Hydrogen Economy Miami Energy (THEME) Conference, Miami, March 1974.

24. Rosen, B., Dagan, V. H., and Proffit, R. C., *Hydrogen Leak and Fire Protection, a Summary*, Contract *NAS 8-5604*. Washington, D.C.: NASA, Technology Utilization Division, Office of Technology Utilization, 1970.

25. Salzano, F. J., Brookhaven National Laboratory, letter of March 1975.

26. Salzano, F. J., Ed., "Hydrogen Storage and Production in Utilities." First Annu. Rep. Brookhaven Natl. Lab. Upton, N.Y., July 1974.

27. Sharer, J. C. and Pangborn, J. P., "Utilization of Hydrogen As an Appliance Fuel." Paper presented at The Hydrogen Economy Miami Energy (THEME) Conference, Miami, March 1974.

28. Strickland, G. G., Brookhaven National Laboratory, letter of March 1975.

29. Strickland, G. G. and Reilly, J. J., "Operating Manual for the PSE G Hydrogen Reservoir Containing Iron Titanium Hydride." Brookhaven National Laboratory Paper No. BNL50421, (1974) February.

30. Swisher, J. H. et al., "Survey of Hydrogen Compatibility Problems in Energy Storage and Energy Transmission Applications," Sandia Laboratories Rep. No. SAN074-8219, (1974) September.

31. Tatchell, J. A., "Hydrogen in the Chemical Industry." Lecture 4 at the Symposium on Prospects for the Hydrogen Economy, Queen Mary College, London, June 6, 1974.

32. Tek, M. R. and Wilkes, J. O., "New Concepts in Underground Storage of Natural Gas," University of Michigan Monograph prepared for the Pipeline Research Committee, Am. Gas Assoc. Cat. No. L00400, March 1966.

33. Wiswall, R. H. and Reilly, J. J., "Metal Hydrides for Energy," in Proc. Seventh Intersoc. Energy Convers. Eng. Conf., 1342 (1972) September.

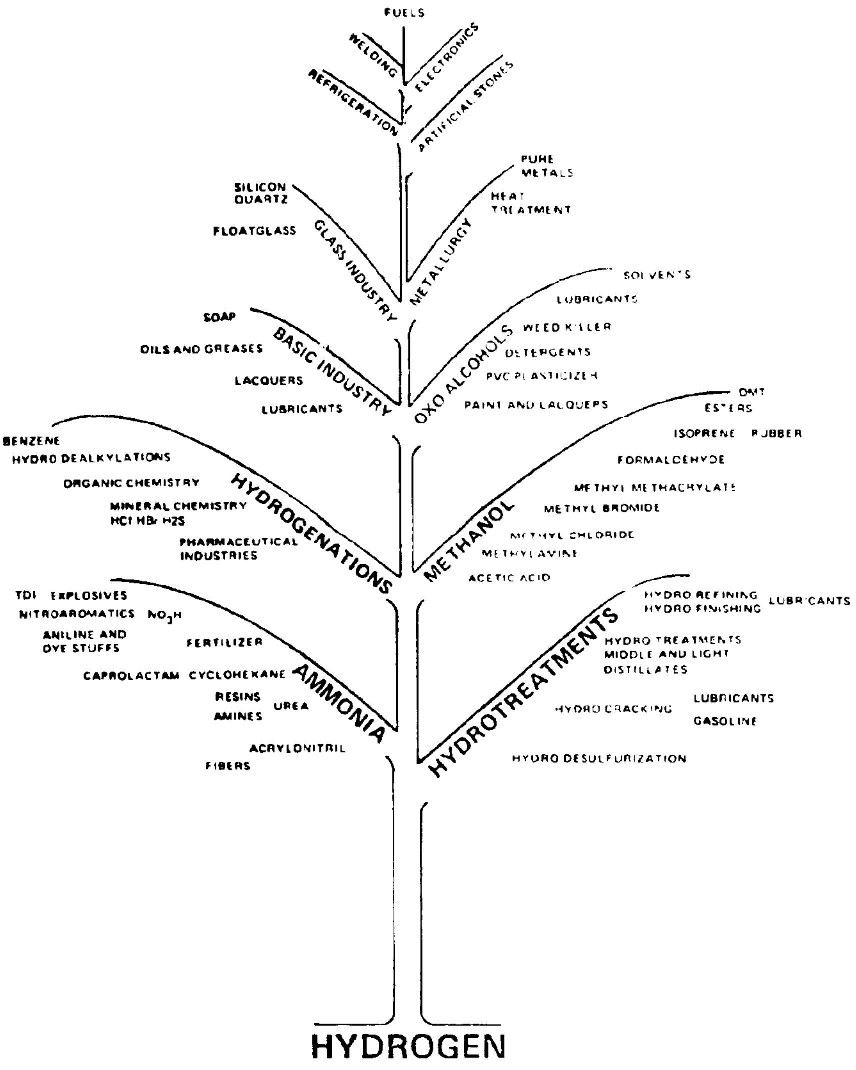
12. INDUSTRIAL HYDROGEN UTILIZATION – W.J.D. Escher and D. P. Gregory

Present Industrial Uses of Hydrogen – an Overview

Hydrogen is one of the world's leading chemical intermediates. It is produced by a wide variety of processes and has a large number of applications. A concise and somewhat generalized illustration of the current major uses of hydrogen has been put forth by Air Products and Chemicals, Inc., and is presented here as Figure 12-1. In this "hydrogen tree," the major applications of hydrogen are shown as the lower branches, while the lesser uses are nearer the top.

The larger uses of hydrogen include ammonia production (56% of the 1970 world hydrogen market[3]), hydrotreatments of petroleum feedstocks (30%), and hydrogenations of petrochemicals and methanol synthesis (totaling 14%). Usually these applications require such large quantities of hydrogen that the hydrogen is produced onsite in an adjacent plant. In many cases, plants for these processes are sited close to a petroleum refinery or a chemical-works complex in which hydrogen is interchanged between processes, almost like a utility service. This hydrogen is commonly termed "captive hydrogen" because it is rarely included in intercompany sales or transmitted over more than a few thousand feet. In some cases, hydrogen mixed with other gases can be tolerated or may be needed for the application; thus the captive hydrogen may only consist of a low-purity hydrogen stream. It is difficult to obtain figures as to the scale of the captive-hydrogen market or the typical prices paid for the commodity.

The intermediate-sized applications of hydrogen, including basic industrial processes (especially soap and fat production), oxo-alcohol production, and the glass and metallurgical industries, are usually provided with relatively pure hydrogen delivered from a remote plant. Frequently, the source of hydrogen is interconnected with a refinery or chemical works. Hydrogen is supplied to the users either in the liquid (cryogenic) state by rail or tank truck or by a small, privately owned pipeline. This hydrogen is commonly termed "merchant hydrogen" and is handled by the industrial-gases industry. Because this hydrogen is usually marketed between companies



A75081958

Figure 12-1. PRESENT MAJOR USES OF HYDROGEN
(Source: Air Products and Chemicals, Inc.)

and because it is usually handled in a relatively pure state, it is easier to find quantitative data for annual utilization rates and for typical prices for this hydrogen.

The smaller users of hydrogen typically take delivery of the hydrogen as gas in high-pressure cylinders or as the cryogenic liquid. An exception is the fuels application of hydrogen, which is a special case deserving independent discussion. There are many exceptions to the "typical" examples described here. Many of the smaller and intermediate users of hydrogen generate their own supplies from hydrocarbon feedstocks (usually natural gas), by cracking ammonia, or by the electrolysis of water.

The fuels applications of hydrogen are very small and are only justified in special cases, usually where by-product hydrogen streams are available and no more advantageous use can be made of them. Almost exclusively, fuels uses of hydrogen are tied to a captive-hydrogen type of operation, and delivery is usually by short pipelines. It is not usually economical to use hydrogen that has been purified and delivered as a liquid or as a high-pressure gas for a fuel gas.

According to the U.S. Department of Commerce, the U.S. merchant hydrogen market in 1974 was 72 billion SCF/yr. The growth rate from 1973 to 1974 was 11%. This growth rate is among the highest reported for high-volume inorganic and organic chemicals.

Projections for Hydrogen Utilization

The major markets for captive hydrogen are growing at rates that reflect the general trend of increased use of processed fuels, fertilizers, and high-volume chemicals. Major changes in this steady growth pattern cannot be predicted and are not anticipated. These markets do not represent major new uses for hydrogen, but the source of the hydrogen that they use is likely to undergo major changes in the foreseeable future. Most of the hydrogen used in these applications is produced from petroleum (in the refineries) or by steam reforming natural gas. It is important to consider the prospect for replacing these raw materials with more abundant ones, primarily coal or nonfossil sources. In general, the quality of the hydrogen or a hydrogen mixture made from coal will be similar to that of the hydrogen made from other fossil fuels; however, hydrogen from nonfossil sources is likely to be relatively pure, and in order to utilize it, the user's process may have to be modified.

The uses of merchant hydrogen are also exhibiting growth rates tied to the economies of their individual industrial sectors, and no major new applications for this hydrogen are expected. The feedstocks used by the industrial-gas suppliers, particularly natural gas, are in extremely short supply. Therefore, serious and urgent consideration is being given to the use of coal, or perhaps nonfossil sources, for central-plant hydrogen production. Major changes by the gas suppliers are not likely to have any major effects on the hydrogen-use patterns.

Two of the upper branches of the "hydrogen tree" deserve special consideration as prospective areas of growth. The fuels and the metallurgical applications for hydrogen could both expand very significantly into new uses of hydrogen, thus replacing the direct use of fossil fuels, which are in short supply. For example, replacement of large sectors of the industrial natural gas load with hydrogen produced from coal or from nonfossil sources would be easier to achieve than extensive electrification of industry. The use of nuclear-derived hydrogen as a direct reductant for iron and steel is under active consideration by the steel industry and could have a major impact on fossil-fuel use.

In considering hydrogen utilization in more detail, we shall discuss each major class of current hydrogen applications, quantitatively whenever possible; and we shall discuss the technological options for replacing the present source of hydrogen with a pipeline supply of hydrogen from an external, nonfossil-fuel source. The emphasis of this discussion will be on ammonia synthesis, methanol synthesis, hydrotreating, and hydrogenation (because they are major users) and on metallurgical and fuels applications (because they show the best prospects for revolutionary gains).

Hydrogen Utilization for Ammonia Production

Hydrogen feedstock for ammonia synthesis is currently prepared from hydrocarbon fluids, such as natural gas and naptha, and from coal or coke via reforming and/or partial oxidation processes. Hydrogen may also be made from water and electrical power via electrolysis (of particular benefit where hydropower is cheap). Table 12-1 shows the worldwide trends during the 1960's for the production of hydrogen, from these several raw materials, for ammonia synthesis.

Table 12-1. FEEDSTOCK-HYDROGEN PRODUCTION FOR THE AMMONIA INDUSTRY
(World Average)

	1962	1967*	1969†
Source	wt %		
Natural Gas and Refinery Gas	41	57	62
Naphtha	--	11	15
Fuel Oil	11	5	5
Coal or Coke	37	21	14
Electrolytic	9	4	2
Others	2	2	2
Total	100	100	100

*Nitrogen No. 51, 1 (1968) January-February.

†Chem. Mark. Rep., 15 (1970) January 26.

In Table 12-1, the shift from the less desirable raw materials (coal, coke, and fuel oil) to the cleaner, more readily converted hydrocarbons (primarily natural gas and naphtha) is clear. During this 7-year period, electrolytic hydrogen declined from 9% to 2% of the total. In the United States, virtually all present ammonia production depends on natural gas as a feedstock. The rather rapid buildup in world capacity for synthetic ammonia production from 1967 to 1973 is shown in Table 12-2.

In the United States, ammonia production is concentrated in Louisiana and Texas (based on ready natural gas availability), along the Mississippi River and its major tributaries, and near the agricultural centers of use. Production of ammonia in 1974 totaled 15.7 million tons, with an expected annual growth rate through 1980 of 4.5%. Appendix A-3 lists all the major U.S. ammonia producers and their plant output capacity. The geographic distribution of these producers is shown in Figure 12-2. About 80% of the

Table 12-2. WORLD CAPACITY FOR SYNTHETIC AMMONIA*

	1967	1969	1973
	10^6 tons		
Western Europe	12.4	14.0	18.2
U.S.A.	11.3	14.6	16.4
Japan	2.7	3.0	4.8
Asia (Non-Communist)	2.2	3.0	8.1
Others (Including Communist Asia)	4.1	6.1	8.2
U.S.S.R.	3.9	5.8	7.5
Eastern Europe	3.5	6.2	8.0
Total	40.1	52.7	71.2

*Chem. Mark. Rep., 4 (1970) January 26.

ammonia produced is consumed directly as fertilizer or as an intermediate for fertilizer production.

To synthesize ammonia, nitrogen and hydrogen are combined in a 1:3 molar ratio at a high pressure and temperature in the presence of a catalyst:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

In current U.S. practice, hydrogen is derived from the steam reforming of natural gas, during which air is added to supply the required amount of nitrogen. Oxygen is removed by combustion with natural gas in a secondary reformer.

The amount of hydrogen required to produce 1 ton of ammonia can be calculated by dividing the hydrogen content of the ammonia by the overall yield of the synthesis step. One ton of ammonia contains 353 pounds (or 66,700 SCF) of hydrogen. Older processes claim a yield of from 85% to 90%. Most of the currently installed plants use the newer processes, such as M. W. Kellogg Co.'s process, which converts 96.7% of the synthesis gas to ammonia (which corresponds to a consumption of 78,500 SCF of hydrogen per ton of product ammonia).

When an ammonia plant is based on natural gas reforming, production of 1 ton of ammonia requires about 35,000 SCF of natural gas, of which 56% is used as feedstock and 44% is fuel. Today, an economical plant size is from 750 to 1000 tons/day; but a few 1500 ton/day plants have been built.

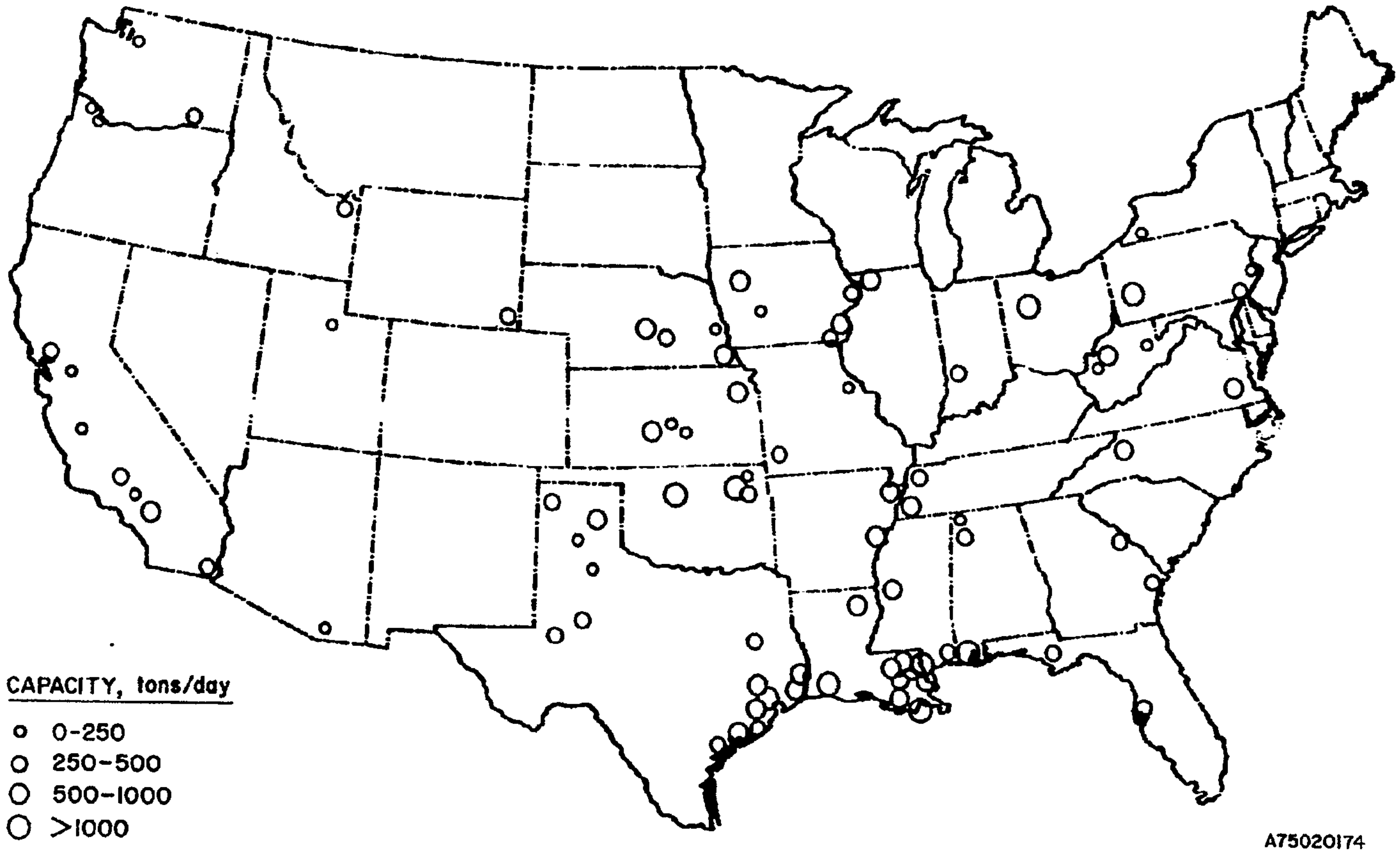
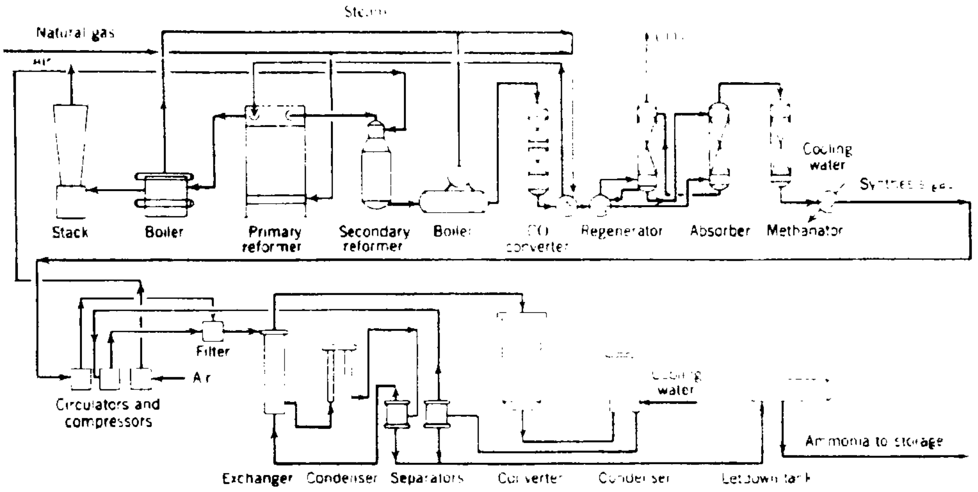


Figure 12-2. U.S. Ammonia Plants

The cost of hydrogen production is a significant percentage of the total ammonia-manufacturing cost. For this reason, the natural gas situation (i.e., its rising price and uncertain supply) is having a profound effect on U.S. ammonia production – ammonia prices having more than doubled within the last 18 months.

Ammonia Produced From Natural Gas

Figure 12-3 is a flow diagram for a typical ammonia-synthesis process, the CHEMICO Process (Chemical Construction Corp., New York). Other processes are those of the Tennessee Valley Authority, M.W. Kellogg Co., Societe Belle de l'Azote (SBA), Fauser, Casale, and Claude.[17] These processes are fundamentally equivalent in their conversion of natural gas, water, and air to ammonia; and their key by-products are carbon dioxide and waste heat. Any sulfur removed from the natural gas is either rejected as hydrogen sulfide or further converted to elemental sulfur.



A75040724

Figure 12-3. FLOW DIAGRAM OF A TYPICAL AMMONIA-SYNTHESIS PROCESS
(CHEMICO Process)

The following six steps describe the plant's operation:

1. Natural gas and steam are combined in the primary reformer to produce hydrogen and carbon monoxide in a high-temperature catalytic, endothermic process.

2. The product gases are fed into a secondary reformer, into which a measured quantity of air is provided. The mixture is combusted with oxygen, leaving atmospheric nitrogen for synthesis gas makeup and small quantities of inerts such as argon.

3. After heat is extracted from the gas stream to produce steam (in the boiler), carbon monoxide and additional steam are shifted to hydrogen and carbon dioxide in the CO converter.

4. The carbon dioxide and remaining carbon monoxide are removed by chemical scrubbing. The remaining oxides of carbon are converted to methane in the methanator. These steps protect the ammonia synthesis catalyst from oxides of carbon. The concentrations of oxygen and all oxides must be reduced to very low levels (to approximately 5 ppm).

5. The resulting synthesis gas, consisting of nominally 75% hydrogen and 25% nitrogen (molar ratio), plus inerts (methane, argon, helium, etc.) and "contaminants" (carbon monoxide, carbon dioxide, water vapor, hydrogen sulfide, and oxygen) at suitably low levels, is then compressed from reformer pressure levels of from 500 to 750 psi to synthesis pressure levels. These usually range from 3000 psi to 4500 psi and even higher, requiring considerable energy expenditure for compression. Most of the compressor drive energy is provided by waste heat from the reforming operations. (The reforming reaction itself is endothermic, but not all the heat generated to drive the reforming steps is of high enough quality to be used to drive the reactions.)

6. The synthesis converter is basically a high-pressure vessel filled with a catalyst. Compressed synthesis gas is fed into the reactor in various ways, depending on the reactor's specific design. The synthesis reaction is exothermic, and the incoming synthesis gas is usually employed to cool the catalyst beds while effecting gas preheating. Water-cooled heat exchangers condense liquid ammonia out of the circulating synthesis gas stream. The product liquid ammonia is then passed through a letdown tank to storage.

Continuous venting of the synthesis vessel is necessary to preclude the buildup of inerts, which can significantly inhibit the conversion process. Losses associated with venting, which are significant, can be reduced by minimizing the concentrations of these inerts.

Ammonia Produced From Hydrogen Feedstock

Looking ahead to the possibility of large-scale ammonia synthesis directly from hydrogen (supplied, for example, via gas pipeline), one observes that the ammonia-synthesis facility must be rather drastically changed from the baseline described above. The entire top line of Figure 12-3 — i.e., the "Stack" through the "Methanator" subsystems — is no longer required, but a new technique for deriving the nitrogen component of the synthesis gas will be necessary. The two possible approaches are 1) removal of oxygen from air by combustion of hydrogen-air mixtures and subsequent condensation of the resulting water vapor and 2) cryogenic air separation.

The first option, analogous to the use of natural gas in the secondary reformer, is not so wasteful of hydrogen as might at first be supposed. In the overall process, which approximates to —

$$1/2(O_2 + 4N_2)_{air} + 7H_2 \rightarrow 4NH_3 + H_2O$$

only one-seventh of the hydrogen is used to eliminate oxygen. This concept also eliminates the need for scrubbing out and venting the oxides of carbon. A hydrogen-air combustion system would probably be relatively simple and low cost and would also provide a source of heat for powering ancillaries such as compressors.

The second alternative, air-separation processes, are well established industrially for producing high-purity nitrogen. Of the existing large-quantity plants, the largest is Linde's (Division of Union Carbide Corp.) East Chicago facility, which produces 4200 tons of gaseous nitrogen and 5000 tons of gaseous oxygen per day. However, the air-separation process requires an energy input.

A conceptual schematic of an ammonia facility based on outside hydrogen is shown in Figure 12-4. Preliminary efficiency and product-cost comparisons for an ammonia plant fed by natural gas with one fed hydrogen are shown in Appendix A-4. Figure 12-5 shows the cost of ammonia as a function of the price of the hydrogen supplied.

More detailed analyses of the various options for producing ammonia from nonfossil fuels are required. Some work has already been done in this area. Experience with large-scale ammonia plants, for which hydrogen is supplied by hydroelectric-powered water electrolyzers, has been obtained in several countries.[8] (See Section 3.) The U.S. Army carried out extensive studies on the potential production of ammonia from nuclear electrolysis as

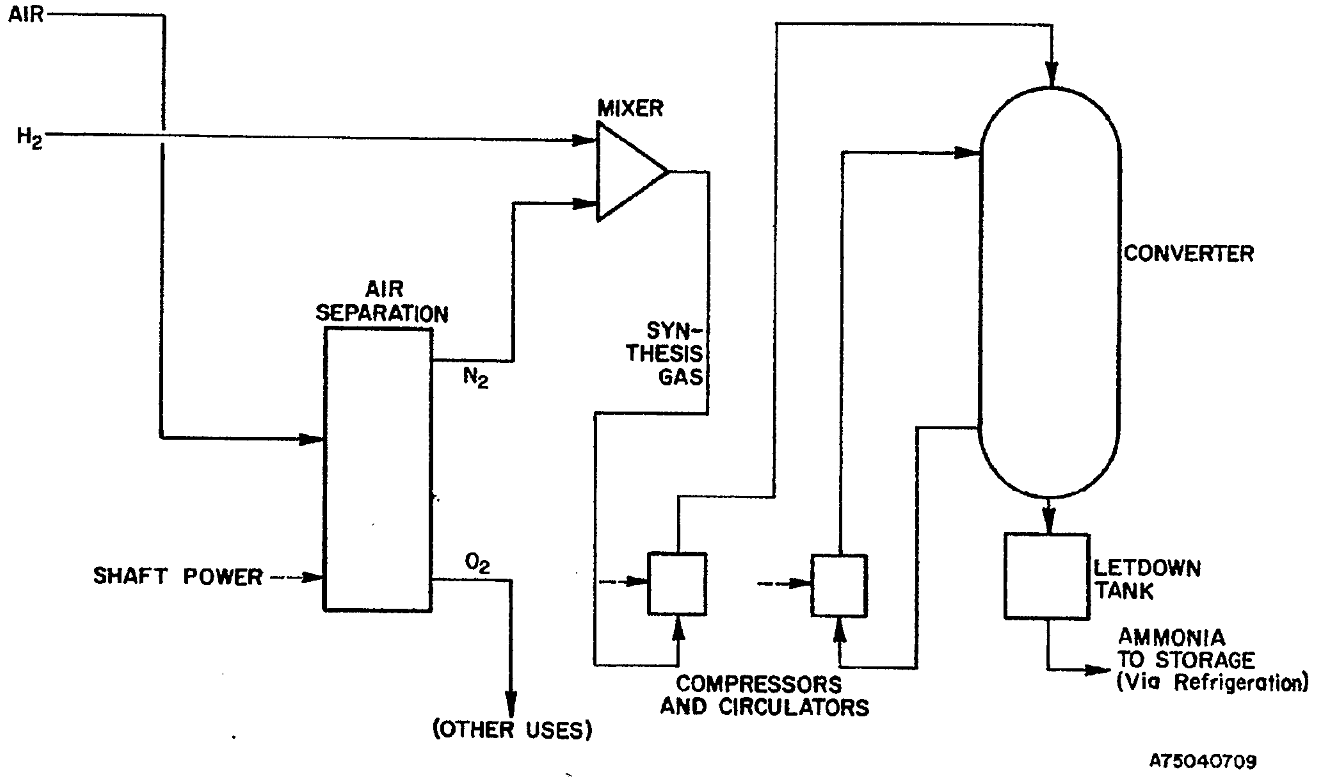


Figure 12-4. CONCEPTUAL FLOW DIAGRAM OF A HYPOTHETICAL AMMONIA-SYNTHESIS PROCESS THAT USES HYDROGEN FEEDSTOCK

part of the "Energy-Depot" concept.[9] Oak Ridge National Laboratory has studied the production of ammonia from nuclear energy in the "Argo-Industrial-Complex" concept.[4]

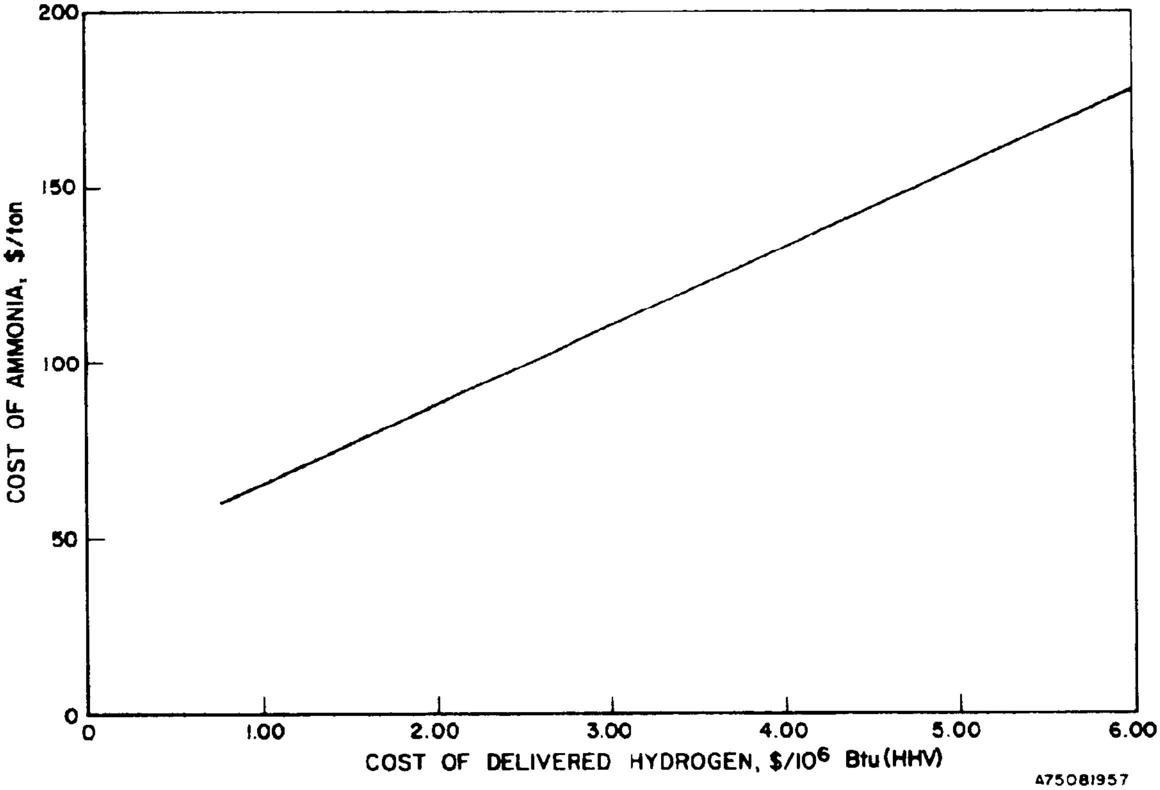


Figure 12-5. COST OF AMMONIA VERSUS COST OF DELIVERED HYDROGEN FOR A PRODUCTION FACILITY THAT USES OUTSIDE HYDROGEN

Hydrogen Utilization for Methanol Production

In industry, methanol is used as a solvent and as a raw material, mainly for the production of formaldehyde, synthetic resins, dye stuffs, and related chemical products. Table 12-3 reflects world methanol-production capacity in 1968 and 1970, exclusive of the U.S.S.R. and Eastern Europe. As seen in the table, the United States, Japan, and the Western European nations are the principal producers.

Table 12-3. WORLD METHANOL-PRODUCTION CAPACITY*
(Excluding the U.S.S.R. and Eastern Europe)

	1968	1970
	10^6 gal/yr	
U.S.A.	650	1035
Japan	380	680
West Germany	250	340
United Kingdom	120	135
Italy	85	100
France	70	70
Canada	30	40
The Netherlands	30	30
Australia	15	20
Others	90	100
Totals	1720	2550

*Conversion factors: 6.63 pounds of methanol per gallon (at 20°C), 10^6 gal/yr = 3000 tons/yr.[10]

In the United States, methanol production is sited largely in areas of ready accessibility to natural gas – mainly along the Gulf Coast. The major U.S. methanol plants are listed in Table 12-4, and their locations are shown in Figure 12-6.

In 1973, the U.S. produced 960 million gallons (or 3,180,000 tons) of methanol. Because 26 SCF of hydrogen is required per pound of methanol produced,* the total hydrogen requirement is 165 billion SCF. Since 1962 the annual growth rate has been 10%, but it is expected to be somewhat less in the future. (The growth rate was 7.8% in 1973-74.)

Methanol is synthesized from a gas (Syngas) that consists of hydrogen and carbon monoxide in a molar ratio of 2:1. The synthesis reactions is –

$$CO + 2H_2 \rightarrow CH_3OH$$

The synthesis is usually performed over a zinc-chromium or copper-zinc catalyst at a temperature of from 250° to 300°C and at 500 to 5000 psi. Low-pressure processes are also available, and these are claimed to be economically attractive.[1]

---

*Some sources claim a requirement of up to 37 SCF/lb.

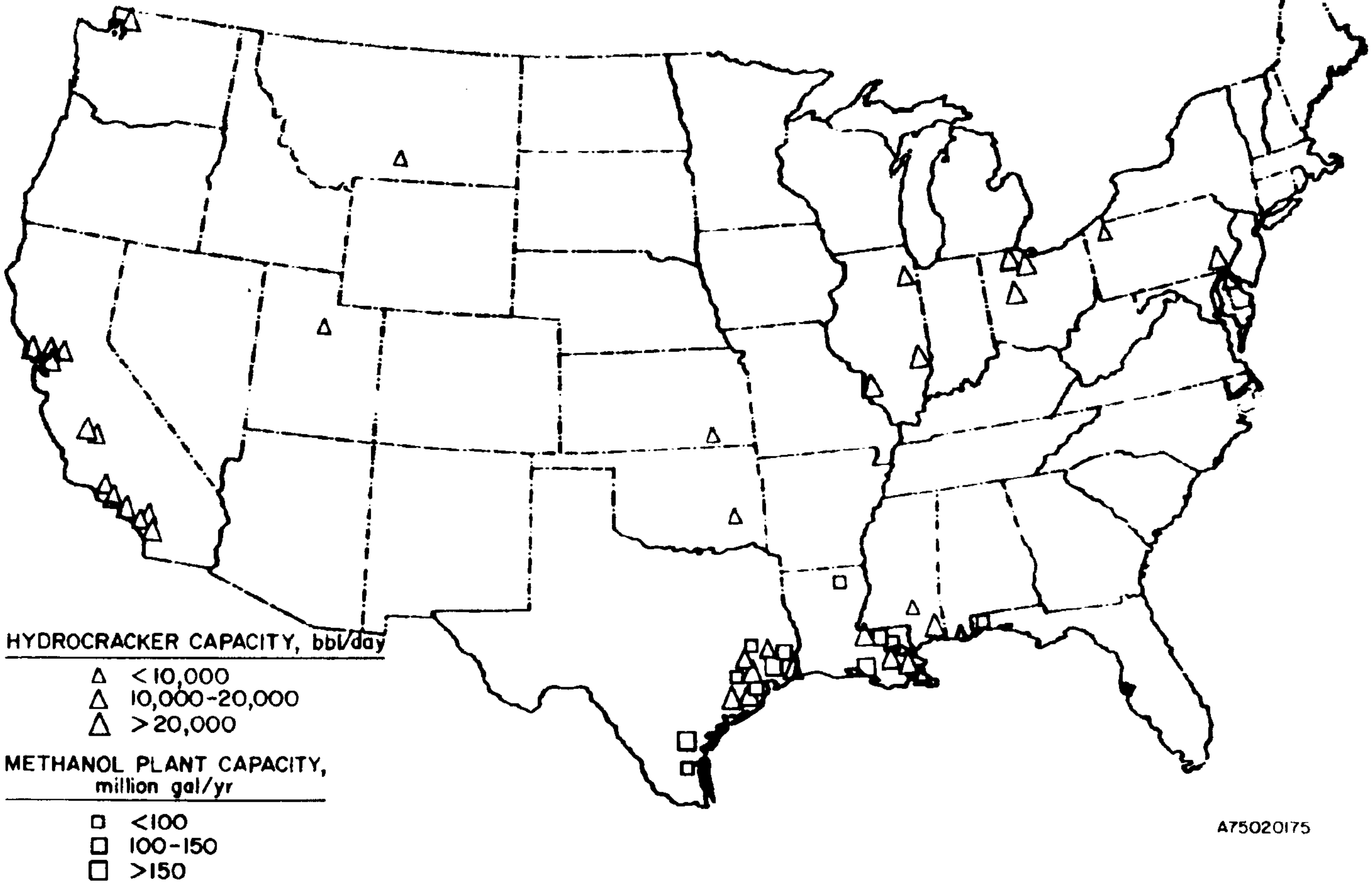


Figure 12-6. U.S. METHANOL PLANTS AND HYDROCRACKING FACILITIES

Table 12-4. U.S. METHANOL PLANTS*

Producer	Capacity, 10^6 gal/yr
Air Products and Chemicals, Inc. Pensacola, Fla.	50
Borden Chemical Div., Geismer, La.	160
Celanese Corp., Bishop, Tex.	50
Celanese Corp., Clear Lake, Tex.	230
Commercial Solvents Corp., Sterlingten, La.	50
E.I. du Pont de Nemours & Co., Inc. Orange, Tex.	100
Georgia-Pacific Corp., Plaquemine, La.	100
Hercules Inc., Plaquemine, La.	100
Monsanto Co., Texas City, Tex.	100
Rohm & Haas Co., Deer Park, Tex.	22
Tenneco Inc., Houston, Tex.	80
Total Capacity	1042

* "Chemical Profile: Methanol," Chem. Mark. Rep. 205, 9 (1974) June 17.

The synthesis train basically resembles that of ammonia production (Figure 12-3) with certain obvious differences:

a. Carbon monoxide conversion in the shift reaction is carried only to the point of establishing the 2:1 molar ratio.

b. Nitrogen is not required and, in fact, is undesirable in the hydrocarbon feedstock.

c. A special methanol-synthesis reactor is required.

Methanol Syngas can be obtained from any reforming or partial-oxidation process that uses a natural gas or oil feedstock or from coal. Also, the off gases from a basic oxygen furnace (BOF) for steel can be used as a feedstock for methanol synthesis. However, even the largest BOF installations produce only enough carbon monoxide to make 25 million gallons of methanol per year; and this rate of production is too small, by today's production standards, for such a plant to be economical.

The outlook for a methanol-synthesis plant that uses an outside supply of hydrogen is not as promising as in the case of ammonia synthesis. The requirement for a major source of carbon oxides is most easily satisfied by hydrocarbon feedstocks (which are reformed) or by coal. On the other hand, an outside pure-hydrogen source could make the use of BOF gas more competitive by eliminating the water shift reaction, which sacrifices carbon monoxide to obtain hydrogen.

Hydrogen Use in Oil Refining

The following quotation from a late-1973 U.S. Bureau of Mines commodity statement for hydrogen[18] is instructive in regard to hydrogen usage in refining.

> "In petroleum refining, hydrocracking is the most significant development with regard to hydrogen consumption. Hydrocracking is used to raise the hydrogen-carbon ratio of the heavier, high-boiling hydrocarbons. For example, lower value heavy fuel oils can be upgraded into more valuable lighter fractions, such as gasoline, light heating fuel oil, and diesel fuel oil, at the same time effecting savings in refining costs.
>
> "Raising the hydrogen/carbon ratio, as outlined above, requires copious amounts of hydrogen. For each barrel of charging stock, between 2,500 and 2,700 cubic feet of hydrogen are used. As of the end of 1972, hydrocracking capacity had expanded to about 865,000 barrels per stream day. During 1972, it is estimated that 800 billion SCF of hydrogen was used in hydrocracking, or 2.2 billion cubic feet per day. Between 1965 and 1972, hydrogen consumption for hydrocracking increased eight fold, from 100 to 800 billion SCF. Based on expansion plans, hydrocracking promises to become the largest consumer of hydrogen in the United States
>
> "Hydrotreating, the much older use for hydrogen in petroleum refining, consumed 570 billion SCF in 1972. In hydrotreating, hydrogen is reacted with refinery fractions to desulfurize feedstocks. Hydrogen is used to hydrogenate olefins and to treat lubricating oils and kerosine-type jet fuels. The growth in hydrotreating has been coincidental with the introduction of catalytic reforming, a process widely used for octane upgrading of motor-gasoline components. The net result of catalytic reforming is a hydrogen production equal to 1.5 times input. The hydrogen used in hydrotreating is that present in the off gas from a catalytic reforming unit. Since hydrotreating required a maximum of 300 cubic feet per barrel of feed, only part of the hydrogen content of the gas is consumed. The exit gas, still containing 70% to 75% hydrogen along with hydrogen sulfide generated by the hydrotreating process, is used as fuel."

It is extremely difficult to estimate the net consumption of hydrogen in refinery operations because the processes in most refineries are both consumers and producers of hydrogen. The net effect depends on the refinery process design, the composition of the crude being processed, and the product mix required. Refineries with a net deficit of hydrogen currently obtain supplies by steam reforming natural gas or naphtha. In general, only refineries with hydrocracking facilities require a net input of hydrogen. Refineries of this type are listed in Table 12-5; and their locations, primarily along the Gulf Coast and in California, are shown in Figure 12-6.

Table 12-5. U.S. REFINERIES WITH HYDROCRACKING PROCESSES[6]

Company	Location	Capacity Charged to Hydrocracker, bbl/stream day
California		
Atlantic Richfield Co.	Carson	19,700
EXXON Co., U.S.A.	Benecia	22,000
Gulf Oil Corp.	Santa Fe Springs	11,000
Mobil Oil Corp.	Torrance	18,000
Phillips Petroleum Co.	Avon	22,000
Shell Oil Co.	Martinez	19,000
Standard Oil Co. of Calif.	Bakersfield	49,000
Standard Oil Co. of Calif.	Richmond	67,500
Texaco Inc.	Wilmington	20,000
Toscopetro Corp.	Bakersfield	13,300
Union Oil Co. of Calif.	Los Angeles	21,000
Union Oil Co. of Calif.	San Francisco	30,000
Delaware		
Getty Oil Co.	Delaware City	17,000
Illinois		
Clark Oil & Refining Corp.	Blue Island	11,000
Marathon Oil Co.	Robinson	22,000
Shell Oil Co.	Wood River	33,500
Kansas		
Apco Oil Corp.	Arkansas City	2,950
Louisiana		
EXXON Co., U.S.A.	Baton Rouge	21,000
Gulf Oil Co.	Venice	11,500
Shell Oil Co.	Norco	28,000
Tenneco Oil Co.	Chalmette	18,000
Mississippi		
Amerada Hess Corp.	Purvis	3,000
Standard Oil Co., of Ky.	Pascagoula	59,000
Montana		
EXXON Co., U.S.A.	Billings	4,900
Ohio		
Standard Oil Co. of Ohio	Lima	20,000
Standard Oil Co. of Ohio	Toledo	36,000
Sun Oil Co.	Toledo	26,000
Oklahoma		
Kerr McGee Corp.	Wynnewood	4,500
Pennsylvania		
Atlantic Richfield Co.	Philadelphia	30,000
Pennzoil Co.	Rouseville	2,700
Texas		
Amoco Oil Co.	Texas City	38,000
Atlantic Richfield Co.	Houston	4,500
EXXON Co., U.S.A.	Baytown	20,000
Gulf Oil Corp.	Port Arthur	15,000
Mobil Oil Corp.	Beaumont	29,000
Shell Oil Co.	Deer Park	25,000
Texaco Inc.	Port Arthur	15,000
Union Texas Petroleum, Div.	Winnie	3,000
Utah		
Caribou Four Corners, Oil Co.	Woods Cross	1,000
Washington		
Atlantic Richfield Co.	Ferndale	35,000

A75112789

The outlook for hydrogen use in refineries is mixed. Refineries are facing increasingly strict sulfur-emissions standards and at the same time are being called upon to process products from less desirable types of crude oil. Consequently, in the last 2 years hydrotreating has grown at an annual rate of 10%, with capacity additions planned in 1975 at an even higher rate. On the other hand, hydrocracking growth has virtually come to a halt, with only nominal additions planned for 1975.[11]

The approximate ranges of hydrogen requirements per barrel of feed charged for various processes are shown in Table 12-6.

Table 12-6. HYDROGEN-REQUIREMENT RANGES

Process	Hydrogen Requirement, SCF/bbl
Hydrotreating Reformer Feed	65-150
Desulfurization	
Light gas oil	85-180
Heavy gas oil	380-500
Residual fuel oil	500-1200
Hydrocracking	1800-2500
Catalytic Reforming	+600-800 (Hydrogen produced)

These figures can be used to estimate hydrogen use in refineries, as shown in Table 12-7.

Table 12-7. REFINERY HYDROGEN USAGE

	1973 Charge,[11] bbl/stream day	% of Total Crude Charged	Ratio SCF/bbl	1973 Hydrogen Use, 10^9 SCF
Hydrotreating	5, 780, 110	39	270	542
Hydrocracking	855, 840	8. 5	2500	742
Total Hydrogen Demand				1284
Catalytic Reforming	3, 358, 038	22	700	815
Net Hydrogen Deficit				469

Metallurgy

Small quantities of merchant hydrogen are used in specialty metallurgical processing (including the production of very pure metals) and for the production of certain nonferrous metals (including tungsten, molybdenum, and tantalum). Larger quantities of captive hydrogen, usually impure and produced onsite, are used for inert or reducing atmospheres in heat-treating applications. Even larger quantities of hydrogen, in the form of blast-furnace gases, are used indirectly in the conventional reduction of iron ore (although carbon is the primary reducing material involved).

Direct Reduction of Iron Ore

There is tremendous potential for a new increased use of hydrogen, or of hydrogen-carbon monoxide mixtures, in the direct reduction of iron ore. The direct-reduction process produces "sponge iron," which is then used as a feed for steelmaking in an electric-arc furnace. Direct-reduction processes are attractive where coal is not readily available and hydrocarbon feedstocks for the hydrogen-carbon monoxide reductant stream are inexpensive and plentiful. An added incentive is that long-distance transportation of sponge iron is less expensive than moving iron ore, coal, or natural gas. Thus, direct-reduction processes have been utilized primarily in the "petroleum-rich" countries. In the United States, however, natural gas supplies are declining; costs are rising; and there is now incentive to investigate the potential for operating a direct-reduction process on an independent (non-fossil) hydrogen supply.

After 10 to 15 years of development, almost a dozen direct-reduction processes, with a variety of features, have been made commercially available. As shown in Table 12-8, one basic characteristic by which available processes can be classified is the type of reaction bed employed.

Table 12-8. CLASSIFICATION OF DIRECT-REDUCTION PROCESSES BY REACTION-BED TYPE[12]

Type of Reaction Bed	Representative Direct-Reduction Process
Vertical fixed	Hojalata y Lamina, S.A. (HYLSA)
Vertical-shaft, moving	Midrex Corp., Armco Steel Corp., Thyssen Purofer GmbH
Rotary-kiln	Steel Co. of Canada, Ltd.; Lurgi Chemie und Huttentechnik; Republic Steel Corp.; NL Industries, Inc.; Fried. Krupp GmbH; Allis-Chalmers Corp.

As of 1974, more than 11 million metric tons of metallized product were produced worldwide, the bulk of which was used in electric-arc furnaces for steelmaking.[16] Currently, the capacity of the direct-reduction plants in operation and on order totals 19 million tons of metal per year. An additional capacity of 2.8 million metal tons is in the "letter-of-intent," "advanced-planning," or "under-study" stage.[20]

Because a substantial treatment of the broad field of direct reduction of iron ore is not possible within the scope of this study on industrial hydrogen usage, the remainder of this section focuses only on iron-ore reduction with hydrogen.

Direct Reduction via Hydrogen

The "H-Iron" Process, developed by Hydrocarbon Research Inc. (HRI) in collaboration with the Bethelehem Steel Co., is a method for producing iron by direct reduction of iron ore with hydrogen. Finely divided ore is reduced in fluidized beds at temperatures below 1000°F and at pressures above 200 psig. The process resulted from efforts, in about 1950, to produce iron-based catalysts for refinery use. Developments proceeded to 50 and 183 tons/day plants in 1960 and 1961, respectively.[7]

Figures 12-7 and 12-8* are, respectively, schematic diagrams of the solids and gas circuits for the "H-Iron" Process. Hydrogen is produced in the process by steam reforming of natural gas, though other fossil and non-fossil sources are also acceptable. Conventional equipment is used to dry and grind the ore, and the ore is preheated to remove contaminants.

A sequenced batch process is used. Powdered ore, loaded into the charge hopper, is first purged of air and then pressurized (with hydrogen) to 150 psi above reduction pressure. The ore is then "pressure transferred" (fluidized) to the first of three reducing sections. Progressive reduction occurs in the hot hydrogen stream as the batch sequence proceeds. Basically, this conserves hydrogen by accomplishing a more complete reduction per pass. From the dump hopper, the metallized product, consisting of elemental iron (nominally 95% reduced) and accompanying gangue, (the worthless rock that surrounds the iron ore vein) is placed in storage. From there it can be directly utilized in the steelmaking process.

---

*Adapted from sketches in "Economics of Primary Iron and Steel Production in the West Coast From Local Iron Ores Via the 'H-Iron' Direct-Reduction Process."[7]

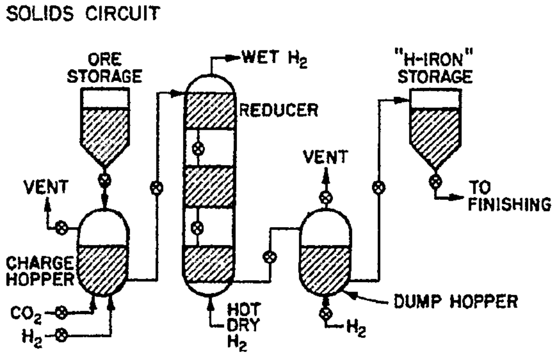


Figure 12-7. DIRECT IRON ORE REDUCTION WITH HYDROGEN VIA THE H-IRON™ PROCESS

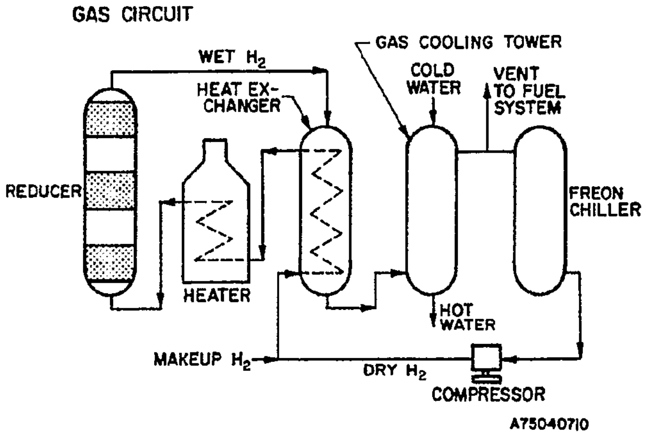


Figure 12-8. GAS CIRCUITS IN THE H-IRON™ PROCESS

The hydrogen reductant circulates in the process, as shown in Figure 12-8. It is preheated in a heat exchange with spent (i.e., "wet") reductant and is then reheated to reduction temperature (about 1000°F), following which it is routed through the reducer. Water is formed during the reduction of iron ore. This is removed from the spent stream by simple condensing processes using water and freon. The dry hydrogen is compressed, makeup hydrogen is added, and the cycle is repeated.

Although demonstrated to be technically feasible by the early 1960's, direct hydrogen reduction has had very limited application to date because of unfavorable market forces in steelmaking. Based on an IGT query to HRI, one of the few "H-Iron" facilities in operation profitably converts mill-scale (basically pure) iron oxide to a very refined metallized product that is used in welding-rod manufacturing, molding powders, and other powered metallurgy products.

Iron and steel industry representatives show an increasing interest in the potential for using nuclear energy directly in steelmaking. This growing interest in "nuclear steelmaking" has recently come to the fore in the United States, Japan, and Europe and may serve to reawaken interest in direct hydrogen reduction.

The American Iron and Steel Institue (AISI) has established the "Task Force on Nuclear Energy in Steelmaking." This is chaired by Donald J. Blickwede, Director of Research, Bethlehem Steel Corp. Mr. Blickwede and T. F. Barnhart, of U.S. Steel Corp., presented an informative paper in late 1974, "The Use of Nuclear Energy in Steelmaking — Prospects and Plans."[15] In this paper, several modes of employing nuclear process heat were surveyed; and their economics where assessed on both industrial- and utility-financing bases. Fossil fuels were generally employed as sources of hydrogen and carbon monoxide mixtures.

Direct hydrogen reduction was considered in one of the cases examined. In this instance, no fossil fuel was used; and nuclear electrolysis was the method of hydrogen production. Figure 12-9* shows one of the results — the incremental effect of liquid steel on selling price as a function of the costs of both coking coal and "fossil fuels alternatives," with a reference case being coal at $ 20/ton (the dashed lines).

The top line in Figure 12-9, "Electrolysis-Utility Financing," is the abovementioned case that uses no fossil fuel (hence the slope of zero). However, it is clear that, for the conditions studied, fossil-fuel costs must significantly escalate for this electrolytic-hydrogen case to become competitive.

---

*Adapted from "The Use of Nuclear Energy in Steelmaking — Prospects and Plans."[5]

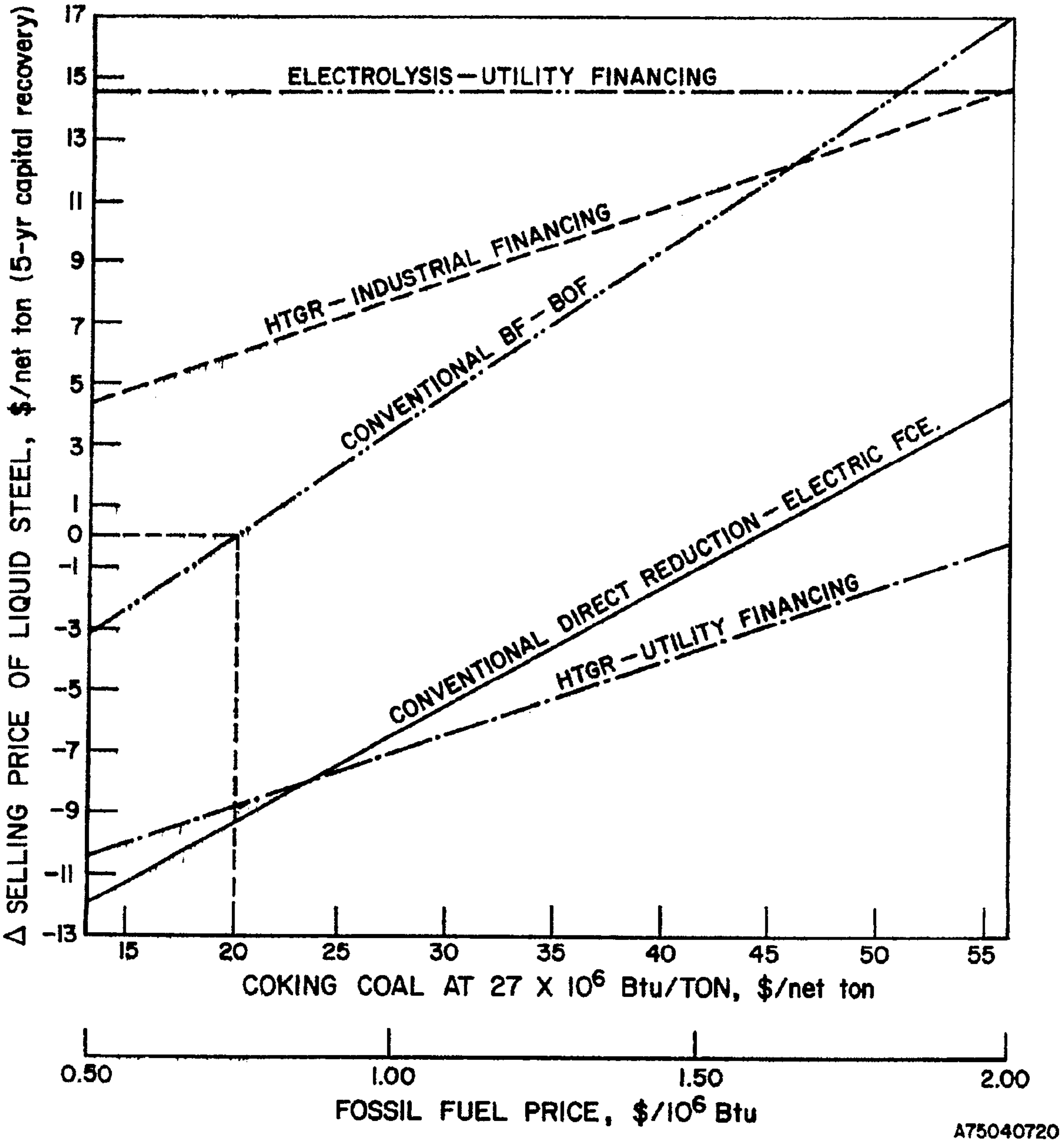


Figure 12-9. EFFECT OF FOSSIL-FUEL PRICE ON STEEL PRICE (Source: D. J. Blickwede and T. F. Barnhart, 1974)

IGT asked Mr. Barnhart for his opinion on the technical prospects for direct hydrogen reduction versus "conventional" direct reduction. (His paper pointed out a number of technical problems in the pure-hydrogen approach.) Mr. Barnhart offered the following observations and provided sources of additional information and a list of patents on hydrogen reduction.[2] (See Table 12-9.)

> "One of the principal difficulties in the hydrogen reduction of iron ore is the tendency for the reduced product to agglomerate in the reduction vessel. This has necessitated reduction at rather low temperatures, which in turn affect the productivity of the unit. Most of the work conducted by HRI was at temperatures in the neighborhood of 800° to 1000°F, which is considerably below that used in a modern direct-reduction shaft where the reducing gas may be 1400° to 1600°F. A second problem is the pyrophoric properties of the product, which in the past [have] necessitated annealing so that the material could be safely handled. Because of these difficulties and because of the success of the present direct-reduction plants, there has been little incentive for the steel industry to pursue hydrogen reduction. Therefore, there has been very little work conducted in the last decade on this subject."

He made the point, however, that such technical problems would likely be overcome if hydrogen became available at a competitive price.

Table 12-9. U.S. PATENTS RELATING TO DIRECT REDUCTION OF IRON ORE WITH HYDROGEN

Patent No.	Title	Assignee	Date
3,140,040	Iron Oxide Reduction With Hydrogen	Keith, P.C.	July 14, 1964
3,154,405	Reduction of Iron Oxide	Engle, T.M. et al.	October 27, 1964
3,224,869	Method of Reducing Iron Oxide	Keith, P.C. et al.	December 21, 1965
3,224,870	Reduction of Ilmenite and Similar Ores	Johnson, C.A. et al.	December 21, 1965
3,227,546	Direct Reduction of Metallic Ores	Johnson, C.A. et al.	January 4, 1966
3,257,198	Beneficiation of Ore	Volk, W. et al.	June 21, 1966
3,347,659	Process of Reducing Iron Oxide	Volk, W. et al.	October 17, 1967
3,383,200	Reduction of Metallic Oxides	Volk, W.	May 14, 1968
3,414,402	Beneficiation of Low-Grade Iron Ores	Volk, W. et al.	December 3, 1968

Use of Hydrogen as an Industrial Fuel

Present Use

At present, hydrogen is used as an industrial fuel only under special circumstances – for example, when an unwanted by-product stream of low-pressure or impure hydrogen is available from a nearby chemical process. Many industrial operations recover the fuel value of this by-product by using it directly as a boiler fuel. In some isolated cases, hydrogen has been considered as a space-heating fuel.

Although this use of hydrogen is extremely limited at present, its potential for growth is enormous. Until now, we have considered only chemical-feedstock uses for hydrogen. The entire use of energy resources for chemical feedstocks accounts for only about 5% of U.S. consumption. On the other hand, industrial-fuel uses account for about 27% of the total consumption. It is therefore in this area that the greatest potential for industrial hydrogen utilization lies.

Before considering the future potential of hydrogen for fuel use, we investigated some of the factors influencing the present use of hydrogen as an industrial fuel. We visited North American Manufacturing Co., Cleveland. North American, a principal U.S. industrial gas- and oil-burner supplier, designs and assembles components into fuel-air supply systems for industrial-process heat devices such as boilers, reactors, and melting furnaces. The company has processed about a dozen hydrogen-burner installations to date and anticipates an increase in this business.

In all hydrogen systems to date, North American has provided engineering services and has procured hydrogen-qualified components. However, final "piping up" was done by the customer. North American has supplied hydrogen-gas-train systems to the following concerns (presumably not an all-encompassing list):

Humko Products Div., Memphis
Hercules Powder Co., Hopewell, Va.
Bethlehem Foundry and Machine Co., Bethlehem, Pa.
J. T. Thrope and Co., Houston
Diamond Shamrock Corp., Paynesville, Ohio
Hooker Chemical Co., Buffalo
Goodyear Tire and Rubber Co., Akron (engineering only)

Hydrogen supply pressures of up to 15 psig and supply pipe sizes of up to 6 inches have been specified by the customers. Purity, in general, was "reasonably high"; but details were not given.

North American's comments on the use of hydrogen as a fuel centered mainly on the safety aspects and on the codes of practice, not on the design and operation of the burners or of the heating equipment itself.

North American uses special "precautions" in specifying the designs and component makeup of a hydrogen system. Electrical components for hydrogen service are under a different national electric code (Article 500 class) than those for use with other gaseous fuels (which are specified as "Class 1" by the code):

- Group A – atmospheres containing acetylene
- Group B – atmospheres containing hydrogen or gases or vapors of equivalent hazard, such as manufactured gas
- Group C – atmospheres containing ethyle-ether vapors, ethylene, or cyclo-propane
- Group D – atmospheres containing gasoline, hexane, naphtha, benzene, butane, propane, alcohol, acetone, benzol, laquer-solvent vapors, or natural gas.

Not many component vendors have equipment approved or listed by Underwriters' Laboratories for Class B service, which encompasses hydrogen.

According to representatives of North American, because of the liability of the company in cases of mishap involving equipment delivered to the customer, extreme precautions are considered appropriate. Specifically, the approval and/or recommendations of either (or both) Factory Insurance Agency (FIA) or Factory Mutual Engineering (FME), both of which provide regional-area cognizance, is strictly adhered to – and especially so for hydrogen service. Further, they noted that technical opinions provided by these groups vary from region to region.

Although not necessarily in agreement on their specifications/recommendations, representatives of the FIA and FME have called for an identical "minimum-system" layout for hydrogen gas trains. North American's interpretation of this specification is shown in Figure 12-10. This governs the basic layout of their hydrogen systems. A letter[13] from a representative of the local FME office to North American on the "Use of Hydrogen as a Fuel"

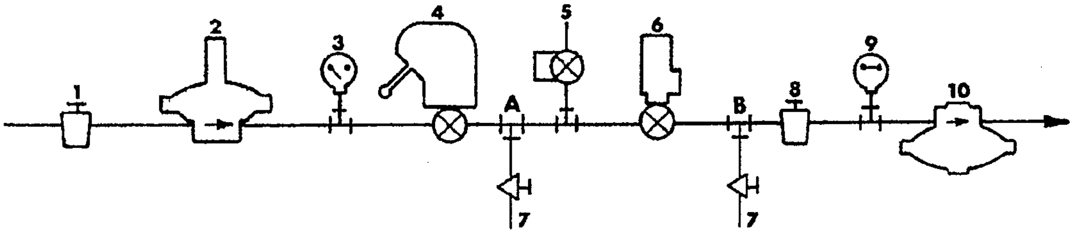


Figure 12-10. SCHEMATIC OF A GAS TRAIN FOR INDUSTRIAL BURNERS THAT USE HYDROGEN FUEL
(Source: North American Manufacturing Co.)

(High and low gas pressure limit switches must be downstream from the high gas pressure regulator. Equipment should be arranged in this order: (1) manual valve, (2) high gas pressure regulator, if used, (3) low gas pressure switch, (4) safety valve, (5) vent valve, (6) blocking valve, (7) leak test cock, (8) manual valve, (9) high gas pressure switch, and (10) ratio regulator, if used.)

is most instructive in view of the dominant influence of the FIA/FME organizations on the design and engineering of any future industrial equipment that uses hydrogen as a fuel:

> "Combustion safety equipment should, in general, be installed as per Factory Mutual standards for the particular piece of equipment if natural gas were being fired. One exception to this is that due to the low molecular weight and resulting high leakage potential of hydrogen, we recommend that a double safety shutoff valve and normally open vent assembly be used in the fuel supply line. Main burner trial for ignition periods should be limited to a maximum of 10 seconds. Requirements for pre-ignition purge should comply with existing Factory Mutual standards, but it is felt especially important that the purge involve the upper passes of the unit due to the light weight of hydrogen.
>
> "If the hydrogen is produced at the plant, it should, or course, be of high quality in regards to being free from air or oxygen. Piping at the burner should be arranged with as short a length of pipe as possible between the safety shutoff valve and the burner in order to minimize the possibility of a combustible hydrogen-air mixture forming in the piping during shutdowns. Premixing of the hydrogen with air should be avoided due to the fact that no flame arrester is completely effective under all conditions with hydrogen.
>
> "The selection of safety equipment, valves, pressure switches, etc., presents another problem. I feel that the combustion safeguard itself should be a Factory Mutual approved model. Flame detection may be a

> problem, but we understand that ultra-violet scanners have been used successfully. Perhaps a reputable manufacturer of combustion safeguards could be of assistance.
>
> "As for the remainder of the combustion safety equipment, I have been informed that no valves, pressure switches, etc., are approved by Factory Mutual for use with hydrogen. This is not to say that they could not be used with success, just that they have not been tested by Factory Mutual for this service. Accordingly, we can make no recommendation for the use of Factory Mutual approved equipment. We would, of course, recommend that good quality equipment be used and that manufacturers of the equipment be consulted regarding its use. It is likely that North American has data concerning appropriate valves for use with hydrogen, and perhaps a reputable manufacturer of pressure switches could give you advice in that area."

Potential Use

Industrial and electrical-utility usage of energy resources in the United States accounts for over one-half of the total energy usage. Figure 12-11 presents the basic breakdown, by percent, of the total U.S. energy usage. "Process energy" is approximately 32% of this total, heating fuels represent 28%, and electrical power from utilities comprises 9%.[15] An additional 4% of the total is used for feedstock purposes.

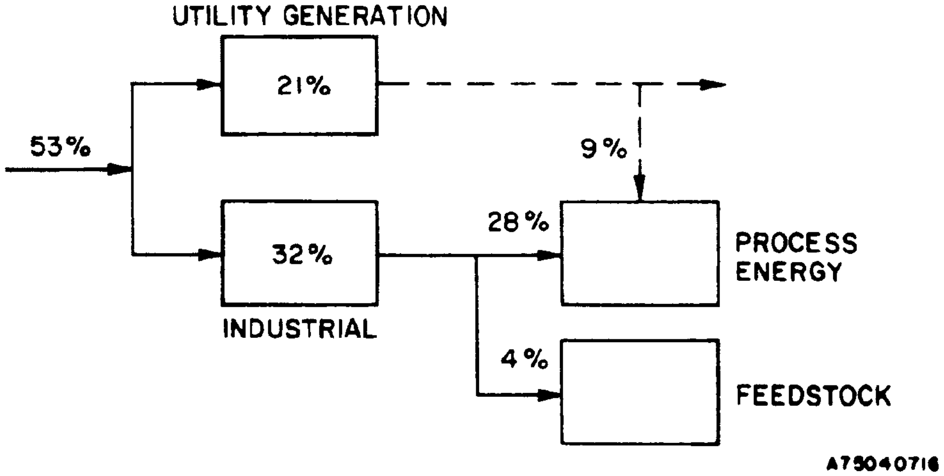


Figure 12-11. INDUSTRIAL AND UTILITY ENERGY USAGE

Figure 12-12 is a breakdown of the "process-energy" usage into steam (17.4%) and direct heat (10.9%). Note that industry generates only a relatively small amount of its consumed electricity, 0.7% as compared with the 9.3% purchased from utility companies.

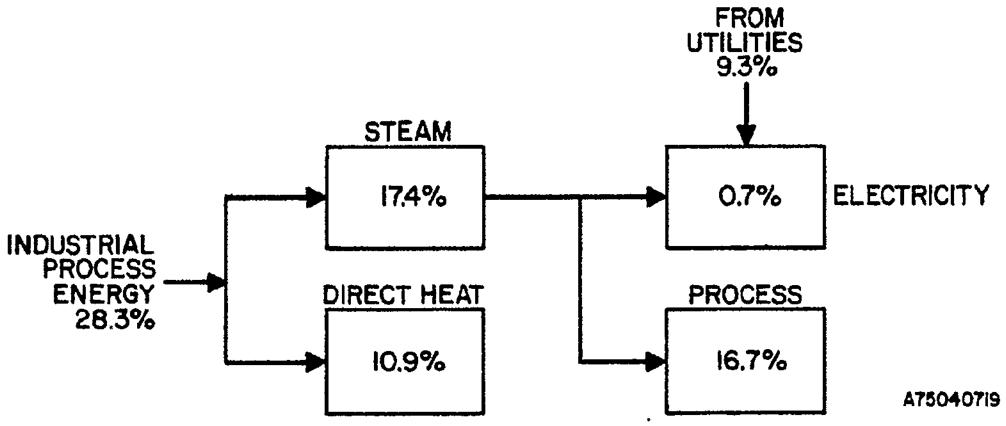


Figure 12-12. INDUSTRIAL-PROCESS-ENERGY COMPONENTS

Industrial energy needs are currently filled by natural gas (51%), oil (27%), and coal (22%). Preference is placed on natural gas because it is a clean, flexible, gaseous fuel. Significantly, hydrogen has the potential of providing these same advantages over liquid and solid fuels. The largest single industrial use of energy is for the generation of process steam. The energy consumed for this function, alone, is roughly equivalent to the total energy consumed by all automotive transportation (i.e., cars, trucks, and buses) in the United States.

The process-steam application deserves primary consideration for conversion to hydrogen utilization. Currently, about half of the energy used to provide process steam is delivered as natural gas. The conversion of conventional natural-gas-fired steam boilers to hydrogen could probably be accomplished with little modification of the conventional equipment. With development and oxygen availability, hydrogen-oxygen direct steam-generation systems may be an environmentally clean, low-cost, flexible, and compact source of process steam at a wide range of temperatures.

This unique approach to steam generation, direct hydrogen-oxygen combustion at stoichiometric conditions, yields steam at extremely high temperatures. The calculated adiabatic flame temperature (and thus the steam temperature) is approximately 6000°F. Water would be added immediately to cool the steam to the desired temperature. The mass flow of steam is commensurately increased. The technology for this process is derived from rocket-engine development in the aerospace field.

Industrial firms, such as the Rocketdyne Division of Rockwell International Corp., and the General Electric Co., have carried out research on this type of steam generation for the past several years. Usually the objective has been associated with electricity generation using high-temperature-steam turbines. For example, General Electric refers to the scheme as "Hydrogen-Oxygen Turbine, Super-High Operating Temperature (HOTSHOT)."[14] Interestingly, the original patent for an "Oxyhydrogen Steam Generator" was issued to E. E. Tucker in 1924 (Patent 1,483,917). Actually, the hydrogen-oxygen steam process can be employed for any steam requirement, given an economic source of hydrogen and oxygen. Prospective advantages of this process over conventional boilers are –

a. Higher conversion efficiency (no stack losses, minimal heat losses)
b. No environmental pollution (zero emissions)
c. Lower cost equipment that is simple and long-lived
d. Instant start-up and shutdown
e. Temperatures much higher than can be produced conventionally.

Figure 12-13 shows the estimated competitive position of hydrogen steam generation in the overall U.S. nuclear and fossil-fuel system. The flatness of the hydrogen curve suggests the feasibility (via the hydrogen-oxygen approach) of very small, efficient, hydrogen-fueled steam generators. The arrow indicates anticipated improvements in efficiency and feasible cost reductions for hydrogen systems. As a point of perspective, contemporary industrial steam may cost upward of $3.00/1000 pounds.[21]

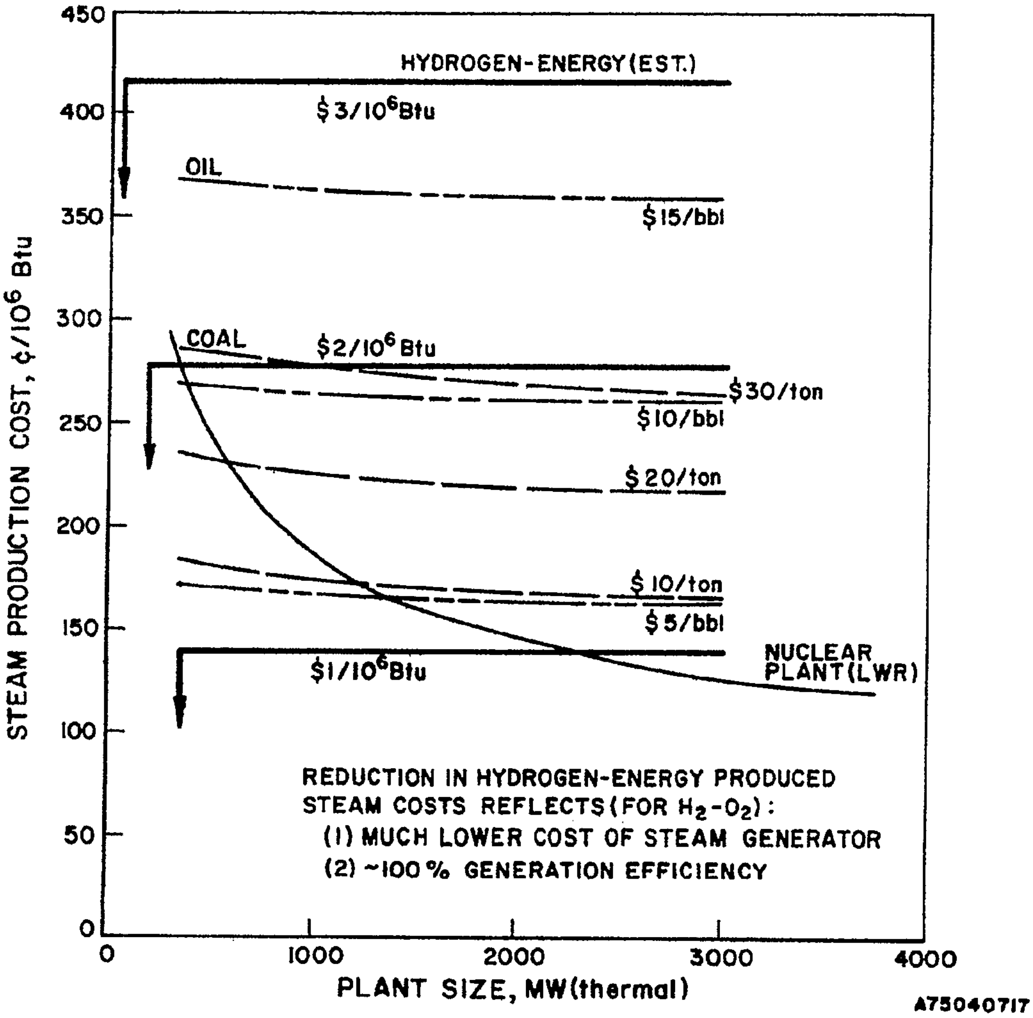


Figure 12-13. COMPARATIVE COSTS OF STEAM PRODUCTION (Source: Womack & Laughon, AEC, 1974 – Hydrogen Estimates Added)

Hydrogenations and Oxo-Alcohol Production

Chemical syntheses of products other than ammonia and methanol consume only relatively small amounts of hydrogen. For example, oxo-alcohols are synthesized by reacting olefins with synthesis gas (carbon monoxide and hydrogen in a 1:1 molar ratio). A typical process reacts synthesis gas with propylene to form butylaldehyde, which is hydrogenated to alcohol:

$$C_3H_6 + CO + H_2 \rightarrow C_4H_8O$$
$$C_4H_8O + H_2 \rightarrow C_4H_9OH$$

Oxo-alcohols are used as plasticizers, especially in the production of vinyl resins. World capacity, which is growing at 15% annually, is currently 2.5 million tons/yr. Using the above reactions as a model, the world requirement for hydrogen to produce this quantity of oxo-alcohols would be about 25 billion SCF/yr.

Other processes that use hydrogen are the hydrogenation of benzene to cyclohexane (an intermediate in the production of nylon) and the hydrodealkylation of branched aromatics to obtain benzene, an important basic petrochemical.

Other Industrial Uses of Hydrogen

General

Hydrogen is also used in a large number of small-use sectors in industry, including —

- Float-glass production and glass cutting
- Semiconductor production
- Electrical-generator cooling
- Hydrogenation of edible organic oils and inedible tallow and grease.

These applications for "distributable hydrogen" are included in the special list of hydrogen applications by Standard Industrial Classifications (SIC), Appendix A-2.

Hydrogenation of Fats and Oils

In the nonchemical hydrogen category, the largest use of hydrogen is for the hydrogenation of fats and oils. Both edible and inedible oils are hydrogenated and are used in various products, such as baking and frying fats, margarine, soap, paint, and varnish (drying oil). An order-of-magnitude estimate, derived from very limited survey data, is that this use consumes less than 10 billion SCF of hydrogen annually, based on a consumption of 15 billion pounds of fats and oils in 1973[19] at a usage rate of 0.6 SCF of hydrogen per pound of product.

If economically tenable, fats and oils processes could readily use an outside stream of hydrogen. First, the small consumption per plant (from 0.5 to 2.0 million SCF/day) makes onsite steam reforming expensive. Second, pure hydrogen is required. Third, unlike other uses, these do not require other industrial gases, such as nitrogen or carbon monoxide. Fourth, hydrogenation is carried out at ambient temperature and at low pressures, so the gas could be used directly without heating or being greatly compressed.

References Cited in This Section

1. Aacund, L. R., "Refining Capacity Registers Largest Nickel and Dime Jump in History," Oil Gas J. 72, 76-79 (1974) April 1.
2. Barnham, T. F., U.S. Steel Corp., letter of February 24, 1974.
3. Biederman, N. P. and Darrow, K. G., Jr., "Utilization of Off-Peak Power to Produce Industrial Hydrogen," IGT Prelim. Rep. EPRI Project RP 320-1. Chicago, February 15, 1975.
4. Blanco, E. R. et al., "Ammonia Costs and Electricity," Chem. Eng. Prog. 63, No. 4, 46-50 (1967) April.
5. Blickwede, D. J. and Barnhart, T. F., "The Use of Nuclear Energy in Steelmaking — Prospects and Plans." Paper presented at the First Topical Meeting on Nuclear Process Heat, Los Alamos, N.M., October 1974.
6. Cantrell, A., Ed., "Annual Refining Survey," Oil Gas J. 72, 76-79 (1974) April.
7. Dyck, W. J., MacMullan, R. J. and Stotler, H. H., "Economics of Primary Iron and Steel Production in the West Coast From Local Iron Ores Via the 'H-Iron' Direct-Reduction Process," Can. Min. Metall. Bull. 56, 888-94 (1963) December.
8. Gregory, D. P., Anderson, P. J., Dufour, R. J., Elkins, R. H., Escher, W.J.D., Foster, R. B., Long, G. M., Wurm, J. and Yie, G. G., A Hydrogen-Energy System, Am. Gas Assoc. Cat. No. L21173. Arlington, Va.: American Gas Association, 1972.
9. Grimes, P. G., "Energy Depot Fuel Production and Utilization," Soc. Automot. Eng. Pub. SP-263, 1964.

10. Hedley, B., Powers, W. and Stobaugh, R. B., "Methanol: How, Where, Who – Future, Manufacture," Hydrocarbon Process. 49, 97-101 (1970) June.

11. Hedley, B., Powers, W. and Stobaugh, R. B., "Methanol: How, Where, Who – Future, Economics," Hydrocarbon Process. 49, 275-80 (1970) September.

12. Iammartino, N. R., "Direct Reduction Roundup," Chem. Eng. 81, 56-57 (1974) August 19.

13. Leppert, J. P., Factory Mutual Engineering, letter of July 14, 1973.

14. Linke, S., Ed., Proc. First Int. Symp. Workshop Hydrogen Econ. New York, 1975.

15. Los Alamos Scientific Laboratory, Proc. First Natl. Topical Conf. Nuclear Process Heat. Los Alamos, N.M., 1974.

16. Rollinger, B., "Steel Via Direct Reduction," Iron Steel Manuf., 10-16 (1975) January.

17. Stelzoff, S. and Pan, L. C., Synthetic Ammonia. New York: Chemical Construction Corp., n. d.

18. U.S. Bureau of Mines, "Hydrogen Commodity Statement – 1972," unpublished. Washington, D.C., 1973.

19. U.S. Department of Commerce, "Fats and Oils 1973," Curr. Ind. Rep. Ser. M20K(73)-13. Washington, D.C.: Bureau of the Census, 1974.

20. "Worldwide Direct Reduction Roundup," Iron Steel Manuf., 17 (1975) January.

21. Yarway Corp., Yarway Steam Conservation. Blue Bell, Pa., n.d.

13. RESIDENTIAL USE OF HYDROGEN – M. I. Scott, J. C. Gillis, and P. A. Ketels

The use of hydrogen as a residential fuel can be justified if hydrogen gas can be produced, delivered to, and utilized by residential customers more economically than can other energy forms. Hydrogen is thus a potential alternative to natural gas, oil, or electricity. The substitution of hydrogen for natural gas or oil would come about only if the prices or availability of these fuels dictated the change.

It should be noted that total conversion to hydrogen-energy utilization is not being advocated here. It is anticipated that a combination of energy forms will continue to be consumed – i. e., fuel gas and electricity. Some applications, such as lighting requirements and electric motors, are best served by electricity. However, eventually it may be beneficial to convert applications that currently consume fossil fuel (primarily natural gas) to hydrogen consumption because a distribution network already exists that has utilization equipment potentially capable of using hydrogen as a fuel after some modification.

Residential Energy-Use Patterns

Assessed in this report section is the feasibility of using hydrogen to suppl a substantial portion of the energy requirements for a single-family dwelling unit. This assessment of residential hydrogen utilization is based on the schematic diagram presented in Figure 13-1. It is made from the point at which energy enters the residential unit and will not be concerned with the factors effecting energy production, transmission, and distribution because these are accounted for in other parts of the report. As seen in Figure 13-1, we are concerned with both the present consumer of energy and the new customer. The present energy user already owns appliances and is faced with the probability of converting these appliances from present energy forms to new ones as the conventional fossil-fuel forms of energy are depleted. The decision to convert will be based on such factors as the age of a particular appliance, the cost of conversion, and the cost of alternative energy supplies.

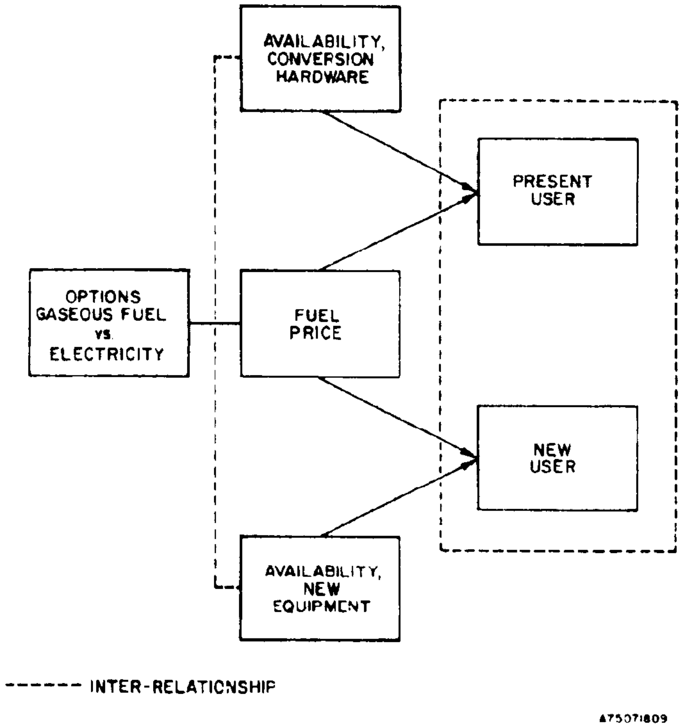


Figure 13-1. GASEOUS FUEL VERSUS ELECTRICITY

The new energy user does not currently own any appliances, but instead has to decide which to buy. The purchase decision is likely to be based on the cost and type of energy available to him and on the initial cost of the equipment. One exception to this is the availability of solar heating. It is assumed that such systems will be available within the near-term time frame; however, the cost of such a system is expected to be high, while the related energy or fuel cost will be zero (except for possible standby equipment). Should the new consumer choose some form of ready-built housing, the decision as to a specific configuration of appliances will already have been made for him.

Residential-Unit Characteristics

A prerequisite to a discussion of energy utilization in the residential market is knowledge of the quantities of various energy forms consumed for such purposes as space heating, cooling, cooking, water heating, clothes washing and drying, and lighting. For purposes of discussion and later comparison, a specific dwelling-unit type was chosen for use in quantifying residential energy consumption.[9] The consumption is not to be considered as representative of patterns across the United States, but merely serves as an example. This configuration, for a typical, single-family dwelling unit in the Northeastern United States, was developed by the Bureau of Census from data collected on housing construction techniques within that region. Table 13-1 is the resulting list of housing parameters. It can be seen that the unit outlined is dependent upon both natural gas and electricity as energy sources. Annual energy consumption within the above residence is shown, by application, in Table 13-2. The energy consumed is predicated on installation of the most modern appliances found in a newly constructed home.

Data on residential-appliance gas consumption are available from a number of sources. In this discussion we have chosen to use some information made available by a series of tests performed by Northern Natural Gas Co. of Omaha, Nebraska.[16] These data were selected because they are presented as a function of water temperatures for the ease of water-heating consumption. This method of data presentation makes the data useful and readily convertible to other geographic regions. The test data are actual measurements made in residential customers' homes through the use of specially installed meters that were monitored over a period of time.

It can be seen in Table 13-2 that space and water heating are the major energy-consuming applications within the given residential situation. It should also be noted that the quantity of electricity consumed within a residence can vary by a factor of 2 or more for a specified floor area. This variance in consumption can be primarily attributed to assorted living patterns, human factors, and the number and type of appliances within a particular situation.

Table 13-1. HOUSING PARAMETERS*

House Floor Area	1500 sq ft (finished)
House Style	Two story
House Construction	Wood frame
Exterior-Wall Construction	
Surface	Wood Shiplap
Sheathing	1/2-inch insulation board
Insulation	R-7 batting
Inside	1/2-inch dry wall
Ceiling Insulation	5 inches blown-in
Basement Type	Full (unfinished)
Attic	Ventilated, unheated
Window Area	12% of floor area
Window Type	Al casement
Storm Windows	None
Door Area (3 Doors)	60 sq ft
Door Type	Wood panel with 0.5 sq ft of glass pane
Storm-Door Area	40 sq ft
Patio Door	40 sq ft (single pane)
Window Covering	70% draped
	20% shaded
	10% open
	No awnings
External Landscaping	No shading effect
Direction House Faces	North
External Colors	White roof and walls
Roof Construction	Asphalt shingle
Heating System	Forced hot air, natural gas
Cooling System	Central, electric
Garage (Enclosed)	Attached, slab, unheated
Residents	Two adults, two children
Location	Northeastern region of U.S.

---

*In addition to the above housing characteristics, external weather conditions must be defined.

Table 13-2. ANNUAL ENERGY CONSUMPTION IN RESIDENTIAL UNIT, NORTHEAST REGION

Natural Gas Load	Energy Consumed, 10^6 Btu	% of Total Consumption
Space Heating	132.0	64.8
Water Heating	27.0	13.3
Cooking	6.4	3.1
Clothes Drying .	3.4	1.7
Subtotal	168.8	82.9
Electric Load		
Central Air Conditioning	12.5	6.1
Lighting	6.8	3.3
Refrigerator-Freezer	6.2	3.1
Clothes Washer	0.3	0.2
Color TV	1.7	0.8
Furnace Fan	1.3	0.6
Dishwasher	1.2	0.6
Iron	0.5	0.2
Coffee Maker	0.4	0.2
Miscellaneous	4.1	2.0
Subtotal	35.0	17.1
Total	203.8	100.0

Space Heating

Space heating is the single largest energy-consuming application within the example dwelling unit. As shown in Table 13-2, it accounts for 64.8% of the total energy consumed.

The estimated annual gas consumption for space heating in single-family dwellings, by size, is presented in Figure 13-2. Data are presented for house sizes ranging from 800 to 2000 sq ft of floor area and for annual degree days* ranging from 5000 to 10,000. The estimated annual gas composition can be seen to vary from 100,000 to 280,000 SCF. The estimated peak-day requirements by house size at an average daily outdoor temperature of 0°F are presented in Table 13-3. These data are useful in illustrating the changes in consumption levels for dwelling units of various sizes.

---

*Degree-day heating: A measure of the coldness of the weather experienced based on the extent to which the daily mean temperature falls below a reference temperature, usually 65°F. For example, on a day when the mean outdoor dry-bulb temperature is 35°F, there would be 30 degree days experienced. A daily mean temperature usually represents the sum of the high and low readings for the day divided by two.

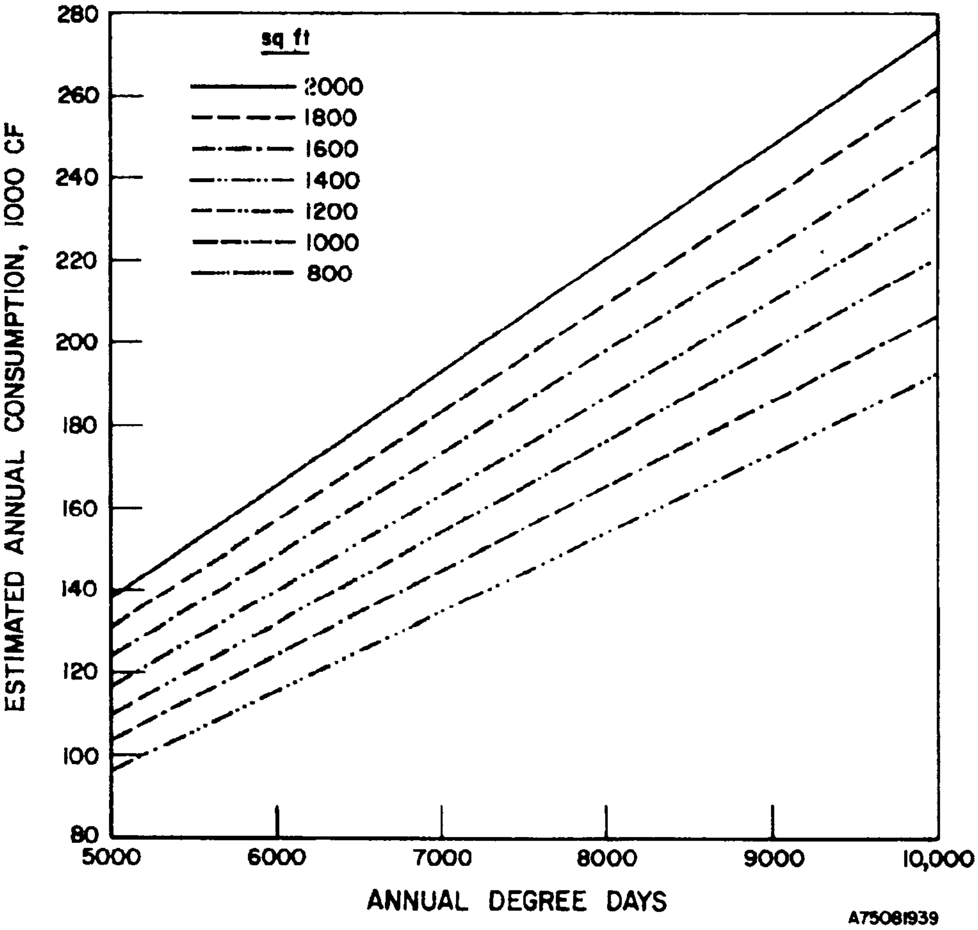


Figure 13-2. ESTIMATED ANNUAL CONSUMPTION BY DWELLING-UNIT SIZE

Table 13-3. ESTIMATED PEAK-DAY NATURAL GAS REQUIREMENTS BY HOUSE SIZE AT AN AVERAGE DAILY TEMPERATUE OF 0° F

House Size, sq ft	Peak Day, SCF
800	1302
1000	1398
1200	1494
1400	1590
1600	1685
1800	1781
2000	1877

The standing pilot flames associated with present residential space-heating equipment consume about 20 to 35 SCF of natural gas/day. At the average rate of 27 SCF/day, the heating unit will have an annual pilot-light load of approximately 10,000 SCF if the pilot burns throughout the entire year. The pilot-light load is included in the quantity of annual energy consumed listed above.

Water Heating

The annual quantity of energy required for water heating is more dependent upon the number of occupants in a home than on the number of degree days. The estimated water-heating load is presented in Table 13-2 and is equivalent to about 13.3% of the total energy consumption. It can be seen in Table 13-4 that annual energy consumption varies directly with the number of family members. For the family of four presented in the example dwelling unit, the energy consumed on an annual basis is about 41,000 SCF.

Table 13-4. ANNUAL WATER-HEATING LOAD, BY FAMILY SIZE

Occupants, No.	Estimated Load, SCF
1	32,820
2	35,660
3	38,500
4	41,336
5	44,176
6	47,016
7	49,855
8	59,691

There is a seasonal variation in the amount of energy required that is related to the temperature of the incoming water. Because the city water supply is warmer in the summer than in the winter, less heat is required to bring it to the desired thermostatically controlled temperature. This variation is shown in Figure 13-3. It can be seen that water-heating loads peak in the winter season at a value approximately 30% above the summer level.

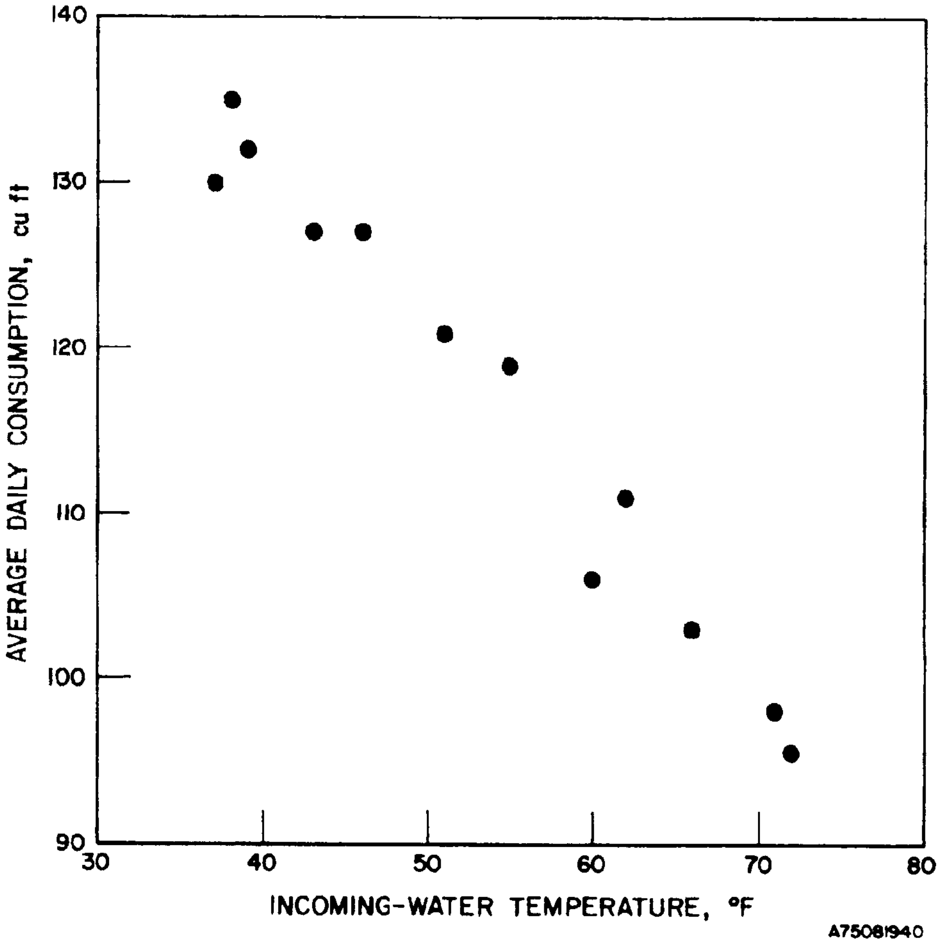


Figure 13-3. COMPARISON OF AVERAGE MONTHLY WATER TEMPERATURE AND AVERAGE DAILY WATER-HEATER CONSUMPTION, BY MONTH

The pilot-light load for water heating with natural gas is estimated at about 17 SCF/day, or 6200 SCF/yr. (These loads are included in the estimates presented in Table 13-2.) The range is 24 SCF/day, with the majority of the units consuming between 15 and 20 SCF/day.

Cooking

The natural gas requirement for cooking in our example dwelling unit is about 6.4 million Btu/yr. This is equivalent to 3.1% of the total energy consumed, as shown in Table 13-2. The pilot-light consumption is a major factor in cooking ranges and accounts for about 60% of the total amount, or 2.4 million Btu. The magnitude of the annual gas load for use in cooking is difficult to relate to family size because of existing variations in individual cooking habits.

The peak-day cooking load occurs, as might be expected, on either Christmas or Thanksgiving Day. Some heavy cooking loads also occur during July and August and can be attributed to the canning season.

Clothes Drying

The estimated annual natural gas requirement for clothes drying, as in the case of water heating, is dependent upon the number of occupants in the dwelling. As shown in Table 13-2, the amount of energy consumed in clothes drying is about 3.4 million Btu, or 1.7% of the total energy consumption. A tabulation of estimated annual gas loads for clothes drying, based on the number of occupants, is shown in Table 13-5.

Table 13-5. ESTIMATED ANNUAL DRYER LOAD, BY FAMILY SIZE

Number of Occupants	Estimated Load, SCF
2	2321
3	3391
4	4464
5	5533
6	6606
7	7680
8	8740

The estimated loads shown in Table 13-5 do not include pilot-light consumption because gas pilot flames are used only a small number of gas dryers currently in use. Generally, electric ignition systems are installed on the more expensive gas dryers. For dryers without electric ignition of the dryer flame, an annual load of approximately 3000 SCF should be added to the estimates listed in Table 13-5. It should be noted that in the case of two occupants per dwelling unit, the pilot light consumes more natural gas over the period of a year than does the operating load.

Electricity Consumption

The electric load in the example dwelling unit accounts for 17.1% of the total annual energy consumption. As shown in Table 13-2, this is equivalent to 35 million Btu, or 10,255 kWhr. As in the case of cooking, the consumption of electricity is dependent upon many variables that cannot be measured as accurately as degree days, nor can it be based simply on the number of occupants.

At present, the amount of electricity consumed within a residence can vary by a factor of 2 for any given floor area. The increase in the use of electricity within a residential unit can be illustrated by the history of New York State usage over 10 years (from 1960 to 1970). (See Figure 13-4.) The annual electrical use per customer has almost doubled. This trend has been created by the addition of appliances that are principally conveniences. The quantity of electricity consumed by various appliances on an annual basis is shown in Table 13-6.

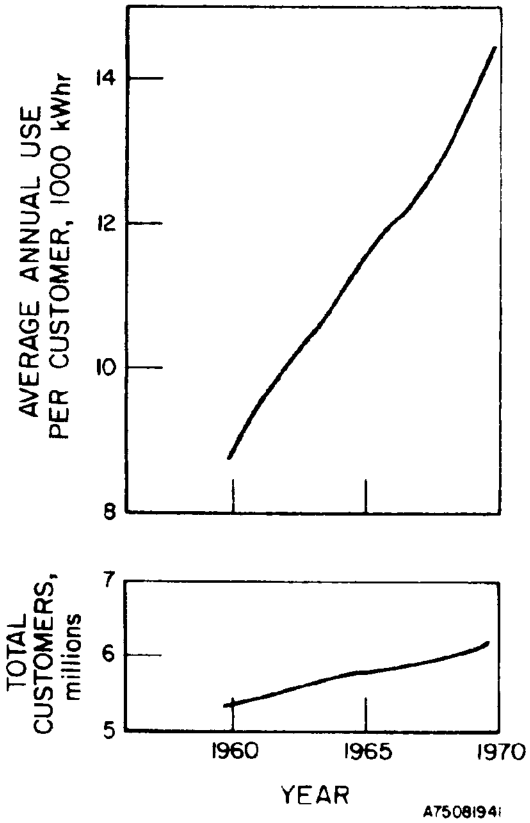


Figure 13-4. HISTORICAL ELECTRICITY GROWTH, NEW YORK STATE

The Use of Hydrogen in Domestic Appliances

If hydrogen is to replace natural gas in residential appliances, the behavior of hydrogen in burners designed to combust natural gas must be explored.

Table 13-6. ENERGY CONSUMPTION BY ELECTRIC APPLIANCES (Source: Edison Electric Institute, Marketing Division, 1969)

Appliance	Average Wattage Rating	Estimated Annual Consumption, kWhr
Air Conditioner* (Window)	1,566	1,389
Bed Covering*	177	147
Broiler	1,436	100
Carving Knife	92	8
Clock	2	17
Clothes Dryer	4,856	993
Coffee Maker	894	106
Cooker (Egg)	510	14
Deep-Fat Fryer	1,448	83
Dehumidifier*	257	377
Dishwasher	1,201	363
Fan (Attic)	370	291
Fan (Circulating)	88	43
Fan (Furnace)*	292	394
Fan (Rollabout)	171	138
Fan (Window)*	190	165
Floor Polisher	305	15
Food Blender	386	15
Food Freezer (15 cu ft)	341	1,195
Food Freezer (Frostless, 15 cu ft)	440	1,761
Food Mixer	127	13
Food Waste Disposer	445	30
Frying Pan	1,196	186
Germicidal Lamp	20	145
Grill (Sandwich)	1,161	33
Hair Dryer	381	14
Heat Lamp (Infrared)	250	13
Heater (Radiant)	1,322	176
Heating Pad	65	10
Hot Plate	1,257	90
Humidifier	117	163
Iron (Hand)	1,008	144
Iron (Mangle)	1,465	165
Oil Burner or Stoker	266	410
Radio	71	86
Radio-Phonograph	109	109
Range	12,207	1,175
Refrigerator (12 cu ft)	241	725
Refrigerator (Frostless, 12 cu ft)	321	1,217
Refrigerator-Freezer (14 cu ft)	326	1,137
Refrigerator-Freezer (Frostless, 14 cu ft)	615	1,829
Roaster	1,333	205
Sewing Machine	75	11
Shaver	14	18
Sun Lamp	279	16
Television (B&W)	237	362
Television (Color)	332	502
Toaster	1,146	39
Tooth Brush	7	5
Vacuum Cleaner	630	46
Vibrator	40	2
Waffle Iron	1,116	22
Washing Machine (Automatic)	512	103
Washing Machine (Nonautomatic)	286	76
Water Heater†	2,475	4,219
Water Pump	460	231

* Estimated for season (6 months) of peak use.

† Based on special water heating rate.

The following discussion is intended to show why hydrogen cannot be directly substituted into residential appliances and what burner modifications would be necessary before hydrogen could be used as a fuel. It should be kept in mind that similar equipment modifications were necessary when natural gas was substituted for manufactured gas.

Hydrogen has a number of combustion properties that can be beneficially exploited with burners that operate through the action of a catalyst (i.e., catalytic burners) rather than through the action of a flame (i.e., atmospheric burners). The experimental work performed to date on such burners will also be described.

Conversion of Existing Appliances

Atmospheric Burners

The burners built into domestic gas appliances are designed to burn fuel from a low-pressure (from 3 to 16 inches water column) gas source, and so they are known as "atmospheric burners." These burners operate on the same principles as a Bunsen burner.

A Bunsen burner consists of a straight, smooth metal tube with a gas-metering orifice at the lower end. Ambient air enters the tube through adjustable openings around the gas orifice and is transported (entrained) by the high-velocity gas stream (jet). The air-gas mixture is ignited as it emerges from the upper end of the tube (the burner port). The air supplied through the burner openings near the metering orifice, before combustion, is *primary air*. Ambient air mixed after ignition is *secondary air*. Figure 13-5 shows the basic construction and nomenclature of an atmospheric gas burner.

During operation, gas issues at a high velocity from the gas orifice (which also meters the gas flow into the burner), creating a vacuum or lowered pressure, which allows the primary air to enter and mix with the gas. While continuing to mix, the air-gas mixture moves down the tube and into the burner head. The mixture passes through the ports and is ignited. The amount of primary air is described as a percent of the theoretical air required for complete combustion. For example, 9.56 CF of air is required to burn 1 CF of methane (CH_4):

$$CH_4 + 2O_2 + 7.56N_2 \rightarrow CO_2 + 7.56N_2 + \text{heat} \tag{13-1}$$

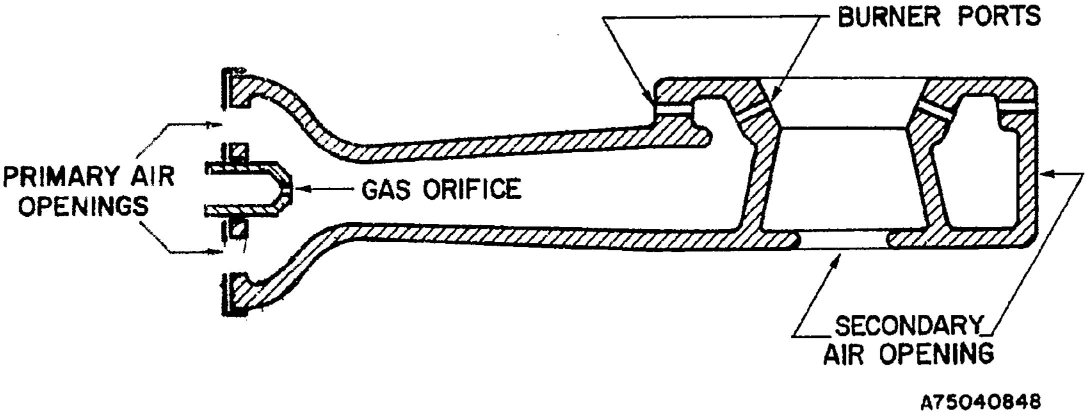


Figure 13-5. PRINCIPAL PARTS OF A TYPICAL ATMOSPHERIC BURNER

Therefore, a 65% primary air mixture would have 6.214 CF of air mixed with 1 CF of methane. The balance of the air required to complete combustion – i.e., 3.346 CF – would then be secondary air. Figure 13-6 shows flame geometry as a function of percent of primary air and natural gas.

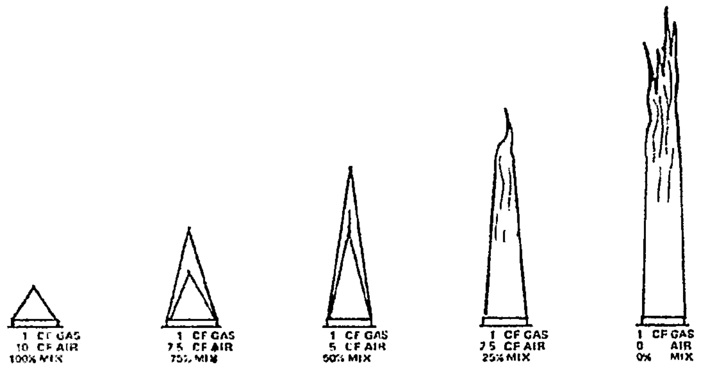


Figure 13-6. FLAME GEOMETRY VERSUS PERCENT AERATION[15]

For efficient operation, atmospheric burners must be able to perform under a wide variety of field conditions and must meet the following basic requirements[5] :

- Controllability over a wide range of turn down without danger of flashback or flame-out
- Uniform distribution of heat, including uniform flame height and good flame distribution over the area being heated
- Complete combustion – i.e., no formation of carbon (soot) or carbon monoxide (CO)*
- No lifting of the flame away from the ports
- Ready ignition – i.e., the flame traveling rapidly and without difficulty from port to port over the entire burner
- Quiet operation upon ignition, during burning, and upon extinction.

Contemporary atmospheric burners are capable of efficient operation over a wide range of input pressures. Range burners, for example, will operate at input pressures ± 50% of the normal pressure of 7 inches water column (0.253 lb/sq in.).[2] Atmospheric burners can also be designed to burn any of a variety of fuel gases, some properties of which are shown in Table 13-7.

Table 13-7. GAS MIXTURES USED WITH CONTEMPORARY ATMOSPHERIC-TYPE RESIDENTIAL BURNERS

Type of Fuel Gas	High (Gross) Heating Value, Btu/cu ft	Specific Gravity (Air = 1.0)
Natural	1075	0.65
Manufactured	535	0.38
Mixed	800	0.50
Butane	3175	2.00
Propane	2500	1.53
Butane-Air	525	1.16
Butane-Air	1400	1.42

---

* It should be noted that during start-up carbon monoxide may be formed if the flame is quenched by a cold target (e.g., water in a water heater).

Tables 13-8 and 13-9 give the physical and operating descriptions of the representative atmospheric gas burners used on residential appliances and a calibration-type Bunsen burner shown in Figures 13-7 and 13-8, respectively.

The following discussion compares the performance of unmodified burners on natural gas and on hydrogen and shows what modifications should be made during conversion of appliances from natural gas to hydrogen.

Fuel Flow Rate

The gross (high) heating value of a typical natural gas is approximately 1060 Btu/SCF, but the gross heating value of hydrogen is only 325 Btu/SCF. Thus for a burner operating on hydrogen to deliver the same amount of heat as one operating on natural gas, per unit time, it will have to pass 3.26 times as much fuel (by volume). Superficially this would seem to preclude the use of hydrogen in existing appliances without extensive modification. However, the flow of compressible fluids through nozzles (or metering orifices) is governed by the Bernoulli theorem, which can be expressed as –

$$q = YCA(h_L/\rho)^{0.5} \qquad (13\text{-}2)$$

where –

q = flow rate through the nozzle or orifice, CF/hr

Y = expansion factor (function of specific heat ratio, ratio of orifice or throat diameter to inlet diameter, and ratio of downstream to upstream absolute pressures)

C = coefficient of discharge

A = area of orifice, sq in.

h_L = the measured differential static head or pressure across the burner port, in. wc

ρ = specific gravity of gas (air = 1).

If the value of the term YCA is assumed constant for the two gases, natural gas and hydrogen, and the pressure (h_L) is held constant for the same orifice, the relative flow rates would be –

$$\begin{aligned} q(H_2) &= q(\text{nat. gas})\left[(0.599/0.0696)\right]^{0.5} \\ q(H_2) &= q(\text{nat. gas})(2.93) \end{aligned} \qquad (13\text{-}3)$$

Table 13-8. IDENTIFICATION AND DESCRIPTION OF THE BURNERS IN FIGURE 13-7

Item No.	Input Rating, Btu/hr	Total No. Ports	Total Port Area, sq in.	Burner Construction Material	Appliance
1	6,600	48	0.33	Cast iron	Range
2	12,800	64	0.64	Cast iron	Laundry boiler
3	45,000	34	0.63	Cast iron	Water heater
4	9,000	52	0.28	Aluminum	Range
5	9,000	70	0.23	Aluminum	Range
6	12,000	72	0.39	Aluminum	Range
7	5,000	1	0.15	Aluminum	--

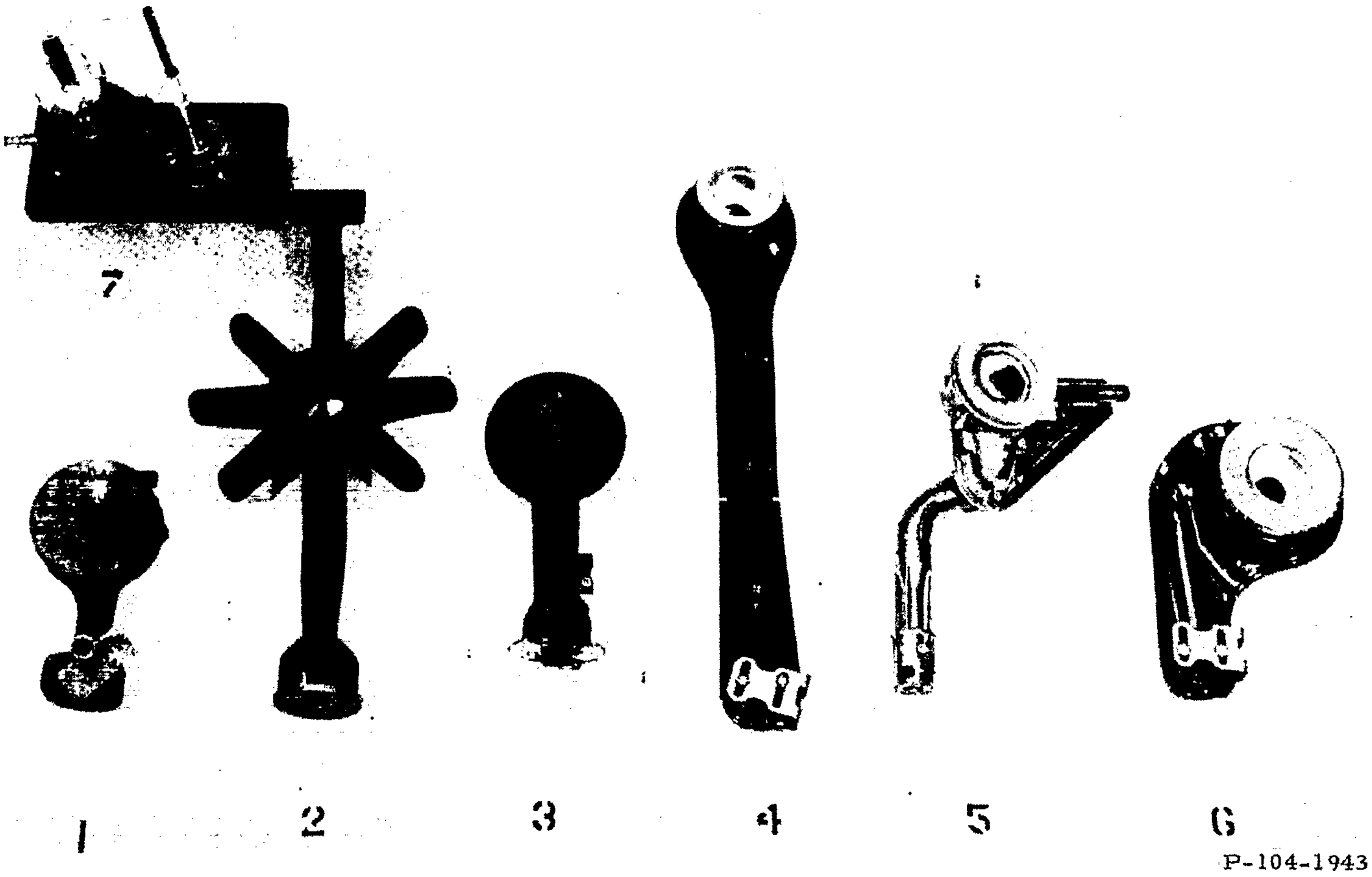


Figure 13-7. REPRESENTATIVE ATMOSPHERIC GAS APPLIANCE BURNERS (DOMESTIC) AND A CALIBRATION BUNSEN BURNER

Table 13-9. IDENTIFICATION AND DESCRIPTION OF THE BURNERS IN FIGURE 13-8

Item No.	Input Rating, Btu/hr	Total No. Ports	Total Port Area, sq in.	Burner Construction Material	Appliance
1	5,000	1	0.15	Aluminum	--
2	9,000	48	0.23	Aluminum	Range
3	30,000	55	1.79	Cold rolled steel	Furnace
4	9,000	69	0.26	Aluminum	Range
5	12,000	72	3.02	Cold rolled steel	Furnace
6	27,500	1	0.91	Cold rolled steel	Water heater
7*	40,000	20	0.02	Cold rolled steel	Water heater
8	75,500	42	1.13	Cold rolled steel	Water heater
9	48,000	34	0.63	Cast iron	Water heater
10	6,600	48	0.33	Cast iron	Water heater
11	12,800	64	0.64	Cast Iron	Laundry boiler
12	15,000	105	0.76	Cast iron	Broiler

* Uses secondary air only.

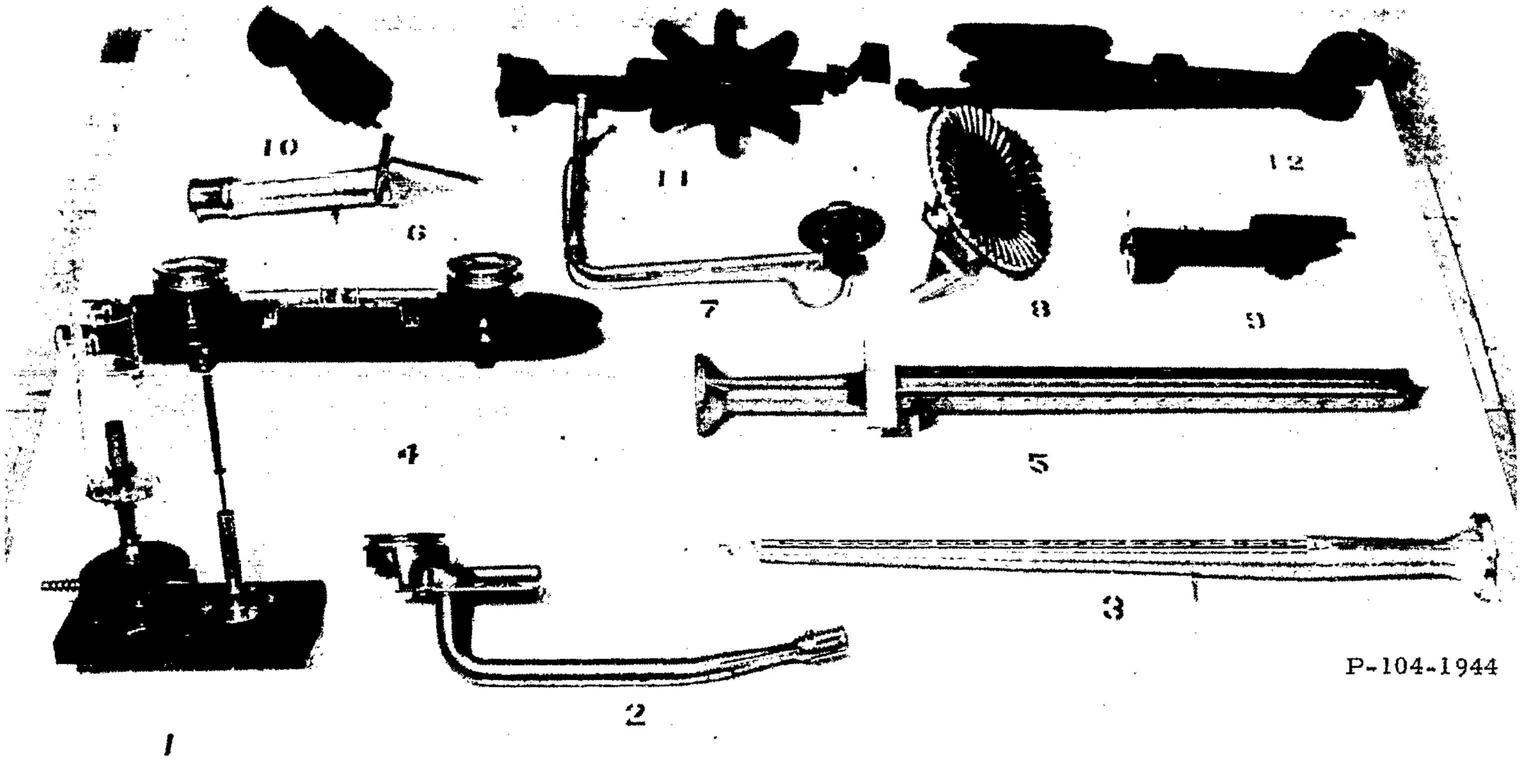


Figure 13-8. CONTEMPORARY GAS APPLIANCE BURNERS (DOMESTIC) WITH A VARIETY OF PORT CONSTRUCTIONS AND A CALIBRATION BUNSEN BURNER

Thus the burner, without any changes, will pass 2.93 times as much hydrogen as natural gas. The difference in heat-delivery rate between natural gas and hydrogen is then –

$$\frac{(325/1060)}{(1/2.93)} = 0.898 \qquad (13\text{-}4)$$

and the hydrogen burner will deliver only about 10% less heat per unit time.

Air/Fuel Ratio

The air/fuel ratio for the complete combustion of natural gas is approximately 10:1. (See Table 13-10.) The air/fuel ratio for hydrogen is calculated, based on stoichiometric combustion, to be 2.38:1. As shown in Figure 13-6, the amount of primary air entrained prior to combustion greatly effects the characteristics of the flame.

Primary-Air Entrainment

Tests on numerous burners show that, for a given burner, the percentage of primary air that is entrained closely follows the empirical equation[5] –

$$IP = K[(Pd)^{0.25}/(H)^{0.5}]/R^{0.5} \qquad (13\text{-}5)$$

where –

IP = entrained primary air theoretically required for complete combustion, percent

P = pressure of the fuel gas upstream of the entering orifice

d = specific gravity of the fuel gas

H = heating value of the fuel gas

R = energy input rate

K = experimentally determined constant.

Table 13-11 gives the values calculated for comparison of the ability of an assumed 10,000 Btu/hr-input rated atmospheric burner to entrain primary air using gases (natural gas and hydrogen) that have densities that differ by approximately 860%. The values of IP/K for hydrogen and for natural gas indicate that a higher percentage of primary air will be entrained by hydrogen than by natural gas.

Table 13-10. CHEMICAL ANALYSIS OF A HIGH-METHANE ADJUSTMENT GAS

Component	Chemical Formula	Cu Ft/ Cu Ft of Gas	Sp Gr X % Gas	High (Gross) Heating Value,[15] Btu	Air Required for Complete Combustion, cu ft
Methane	CH_4	0.9363	0.518	947.84	8.950
Ethane	C_2H_6	0.0358	0.037	63.49	0.597
Propane	C_3H_8	0.0102	0.016	25.74	0.248
Butane	C_4H_{10}	0.0040	0.008	13.06	0.124
Pentane	C_5H_{12}	0.0012	0.003	4.82	0.046
Hexane	C_6H_{14}	0.0008	0.002	3.81	0.040
Carbon Dioxide	CO_2	0.0070	0.011	--	--
Nitrogen	N_2	0.0047	0.004	--	--
Total		1.000	0.599	1058.76	10.005

Table 13-11. VALUES OF A 12,000 Btu/hr ATMOSPHERIC BURNER'S AIR INJECTING ABILITY FOR A HIGH-METHANE NATURAL GAS AND HYDROGEN

	Fuel Gas	
	Natural Gas	Hydrogen
P, in. wc	7.0	7.0
d (Air = 1)	0.6	0.07
H, Btu/SCF	1059	32.5
R, Btu/hr	10,000	10,000
$Pd^{0.15}$	1.43	0.837
$H^{0.5}$	32.54	18.03
$R^{0.5}$	100.0	100.0
$IP/K \times 10^5$	43.9	46.4

Table 13-12 gives the typical primary-air requirements for appliance burners operating on natural gas. If we assume the range-top burner is adjusted for natural gas (60% primary air) and we replace the natural gas with hydrogen, the primary aeration for the substitution would equal, by Equation 13-7, 85%.

Table 13-12. MINIMUM PRIMARY-AIR REQUIREMENTS FOR VARIOUS TYPES OF APPLIANCE BURNERS[3]

Type of Burner	Primary-Air Portion of the Total Theoretically Required Air, %
Range Top	55-60
Range Oven	35-40
Water Heater	35-40
Radiant-type Space Heater	65
Other Heating Appliances	As low as 35

Burning Velocity

The burning velocity of natural gas, using 100% of the theoretically required air, is about 1 ft/s.[3] The burning velocity of hydrogen, however, has been measured at 9.2 ft/s using only 57% of the theoretically required air. Because the hydrogen flame is so much faster than the methane flame, there may be the difficulty of flashback with hydrogen burners.

Flashback is the propagation of the flame front back through the burner ports and upstream to the metering orifice. The flame cannot travel through the orifice because the gas upstream is pure fuel and cannot sustain combustion. However, if combustion takes place at the metering orifice instead of at the burner ports, the burner head may be severely damaged.

The tendency of a burner to flashback is indicated by the boundary velocity gradient of the burner port. The boundary velocity gradient can be derived from Poiseuille's Law (the basic equation for laminar flow in ducts), which is expressed as[14] —

$$\nu_g = k(R^2 - r^2) \qquad (13\text{-}6)$$

where —

ν_g = gas velocity

k = a constant

R = gas stream radius

r = distance from stream center

The value of the constant (k) can be determined by using volume flow per unit time — i.e., gas flow rate — and the tube radius (R):

$$k = 2V/\pi R^4 \qquad (13\text{-}7)$$

where V is the volumetric flow rate. Substituting the value of k into Equation 13-6, the gas velocity (ν) is calculated to be —

$$\nu_g = (2V/\pi R^4)(R^2 - r^2) \qquad (13\text{-}8)$$

The average value of the gas velocity ($\bar{\nu}_g$) is —

$$\bar{\nu}_g = 4V/3\pi R^2 \qquad (13\text{-}9)$$

Figure 13-9 shows the velocity profile of a gas stream from a burner port. Figure 13-10 shows the interplay between the gas velocity (ν_g) and the flame speed (ν_f).

Assuming that the inner cone* of a flame from a Bunsen burner is a right cone — that is, a true cone of revolution — and that the air-gas flow is laminar, by definition,[3] the flame velocity (ν_f) is the component of the average air-gas velocity (ν_g) in a direction perpendicular to the flame front, as shown in

---

* It is also assumed that within the inner cone there exists only an unburned gas mixture.

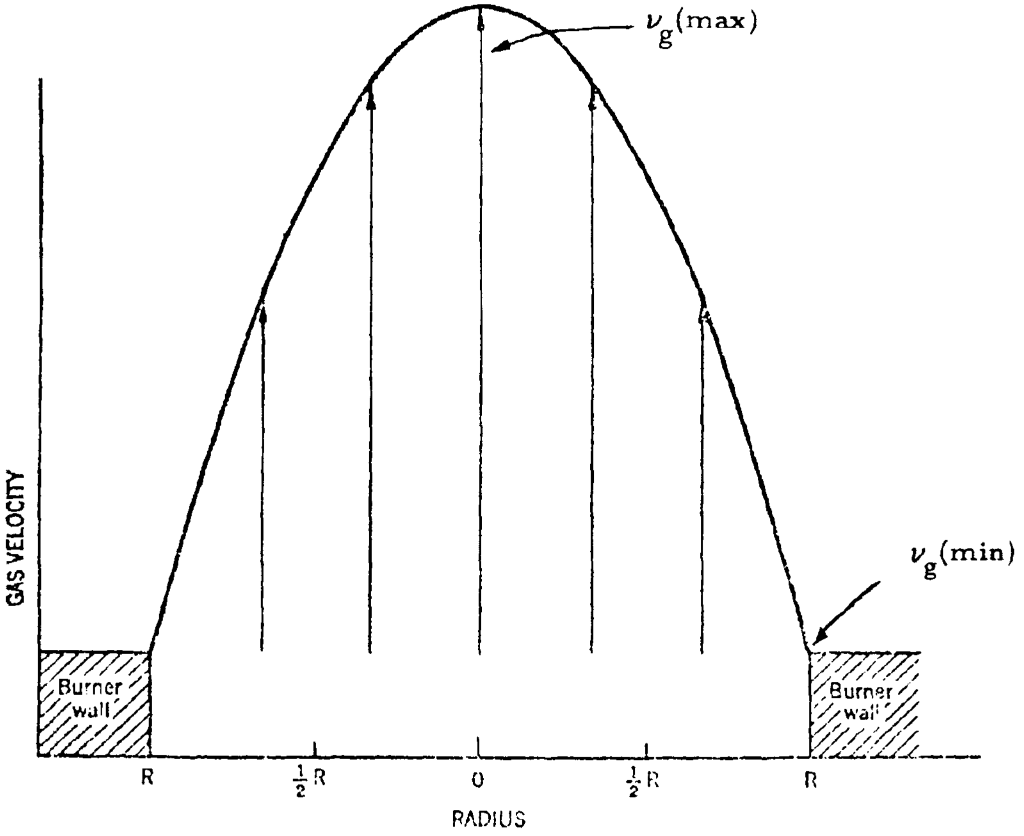


Figure 13-9. PARABOLIC VELOCITY PROFILE OF A STREAM AT A BURNER PORT[4]

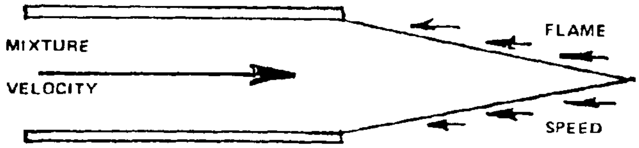
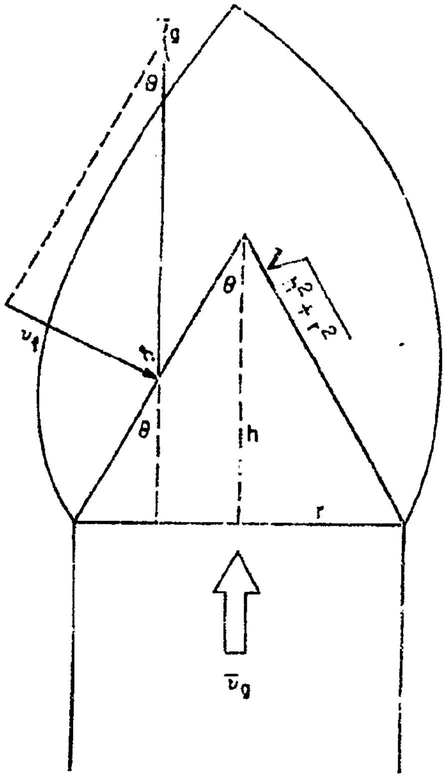


Figure 13-10. MIXTURE VELOCITY VERSUS FLAME SPEED[10]

Figure 13-11. Therefore, from Figure 13-11 –

$$\nu_f = \bar{\nu}_g \sin\,\theta \qquad (13\text{-}10)$$

under stable conditions.



A75081943

Figure 13-11. FLAME FROM A BUNSEN BURNER WITH A TRUE CONE-OF-REVOLUTION INNER CONE

If Equation 13-6 (Poiseuille's Law) is differentiated with respect to r, setting r equal to R, the boundary velocity gradient can be obtained:

$$\text{grad}\ \nu_b = 4V/\pi R^3 \qquad (13\text{-}11)$$

However, when the burner port diameter is so large that the air-gas velocity (ν_g) profile at the wave fringe may be considered linear, the air-gas velocity equation may be approximated by the equation –

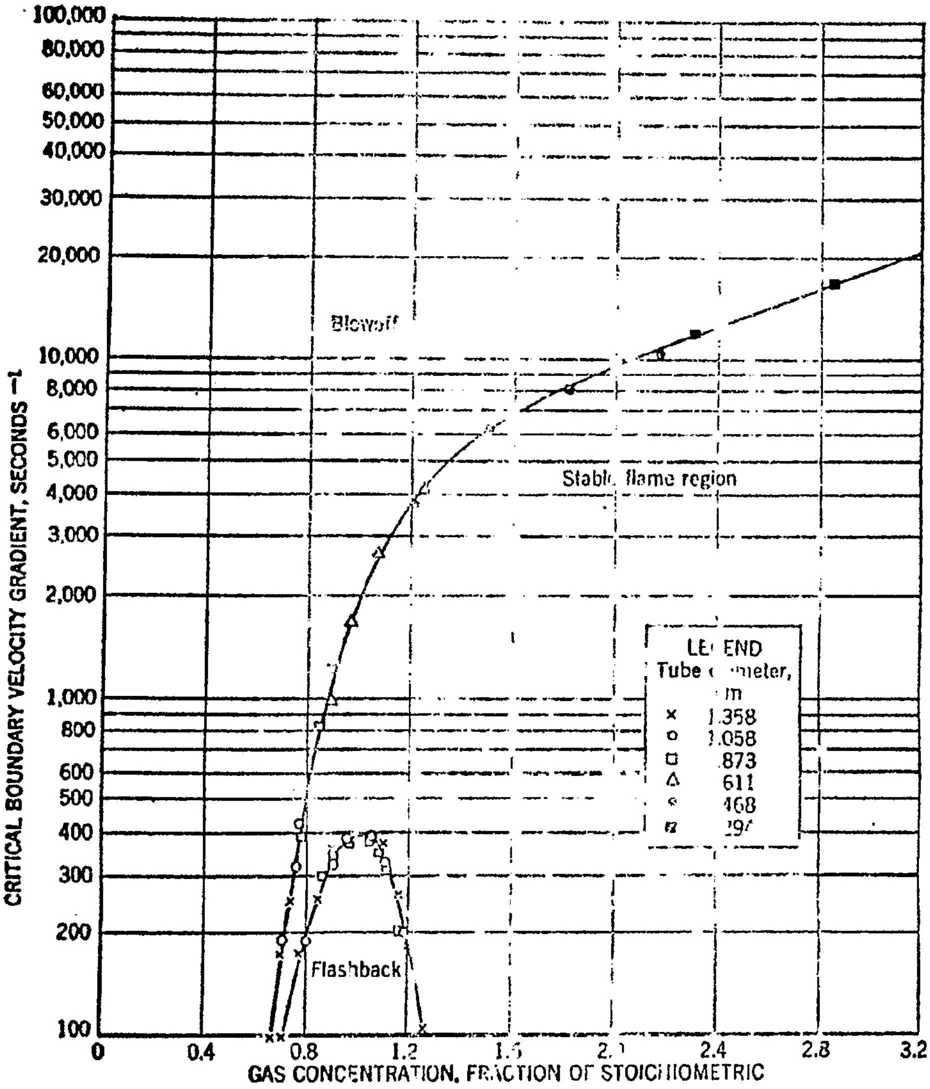
$$\nu_g = \text{grad } \nu_b \cdot d \qquad (13\text{-}12)$$

where d is the distance from the stream boundary.

Thus the gas velocity at any d is proportional to the velocity gradient; and if a state is reached in which the gas velocity (ν_g) at some point becomes smaller than the burning velocity (ν_f), the combustion wave propagates back against the gas stream into the tube – that is, it flashes back. At limiting conditions for lifting flames (blowoff), grad ν_g becomes the critical boundary velocity gradient. At this value, the air-gas velocity (ν_g) exceeds the burning velocity (flame speed, ν_f), and blowoff occurs.

The results of the investigations by Grumer, Harris, and Rowe (of the U.S. Bureau of Mines),[8] concerning flashback, lift-off, and stability of methane-air and hydrogen-air mixtures, are shown in Figures 13-12 through 13-14. In general, a hydrogen flame can be leaner than a methane flame before blowoff will occur; however, the velocity gradient (ν_b) must be maintained at a higher level to prevent flashback. To prevent flashback, the values from Figures 13-12 through 13-14 indicate that at the critical boundary values for stoichiometric mixtures of hydrogen and air, the average gas velocity ($\bar{\nu}_g$) of hydrogen should be approximately 9 times greater than the average velocity of methane.

The experimental results shown in Figures 13-12 through 13-14 were obtained from measurements taken on single-port Bunsen burners and are not strictly applicable to multiport burners found in contemporary appliances. However, if Equation 13-11 is applied to a typical Bunsen burner (for example, burner No. 1 in Table 13-9), the boundary velocity gradient is found to be approximately 2000 (assuming 60% primary air stoichiometric). Figure 13-12 shows that the burner will then be operating in stable-flame range. If the same burner were operated on hydrogen (with no adjustments), the boundary velocity gradient, calculated by using the analysis of the air/fuel ratio, primary-air entrainment, and fuel flow rate shown above, would be about 2600 at a gas concentration of 1.18 times stoichiometric. Figure 13-14 shows that flashback would then occur. Again, it should be remembered that the flashback characteristics of real appliance burners cannot be accurately determined by analysis of single-port burners and that their tendency to flash back when operated on hydrogen must be determined experimentally.



A75092306

Figure 13-12. FLAME-STABILITY DIAGRAM FOR A FUEL CONTAINING 100% METHANE[8]

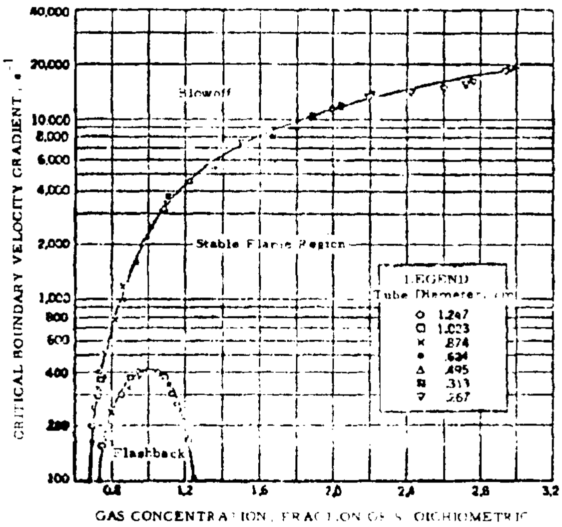


Figure 13-13. FLAME-STABILITY DIAGRAM FOR NATURAL GAS[5]
(91.5% CH_4, 5.2% C_2H_6, 1.3% C_2H_8, 0.9% CO_2, 0.6% N_2,
0.2% C_3H_6, 0.2% C_4H_{10}, 0.1% C_4H_8)

One of the consequences of hydrogen's high flame speed is a change in the shape of the flame. A standard natural gas flame is a cone about 1/8 inch high; but with hydrogen, the flame will be much shorter. To show this, we assume a natural gas flame height of 3.17 mm and a port radius of 0.377 mm. From Equations 13-3 and 13-10 –

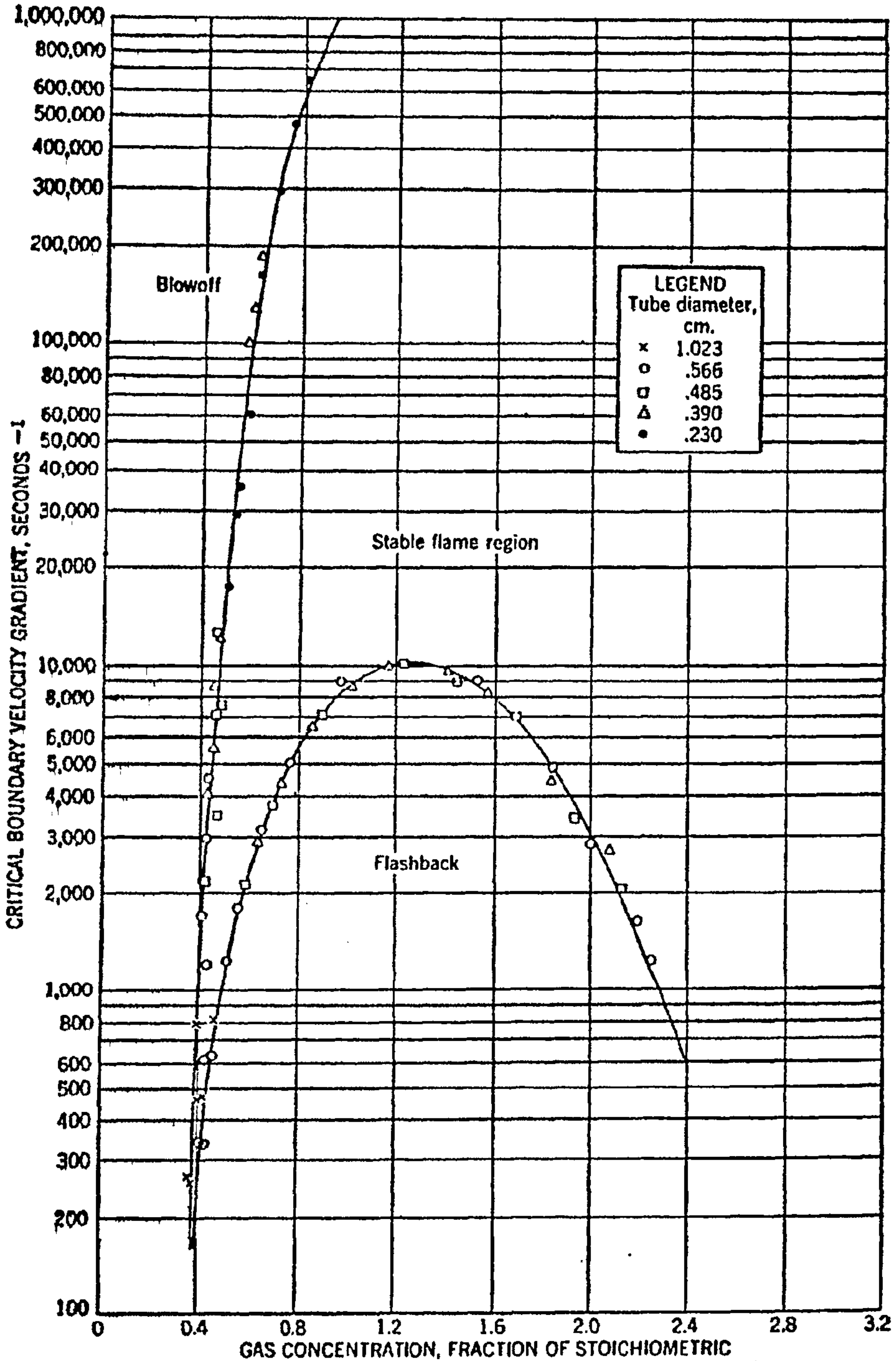
$$\nu_g(\text{nat. gas}) = 8.5 \text{ ft/s}$$

$$\nu_g(\text{hydrogen}) = (2.93)(8.5) \quad 24.9 \text{ ft/s} \qquad (13\text{-}13)$$

From Figure 13-11 –

$$h\,(\text{inner cone flame height}) = r \cot \theta \qquad (13\text{-}14)$$

and, from our assumptions, r equals 0.377 mm. Therefore, for hydrogen h equals 0.948 mm. This indicates a decrease in height of approximately 70%. If, however, the velocity of the hydrogen is increased by a factor of 9 to stop flashback, h equals 3.11 mm; and the change in inner-cone flame height would be only 2%. If the flame height is to be maintained, the velocity



A75062307

Figure 13-14. FLAME-STABILITY DIAGRAM FOR A FUEL CONTAINING 99.7% HYDROGEN AND 0.3% OXYGEN[8] of the hydrogen through the burner ports must be 9 times greater than that of the methane. (The port gas velocity could be increased either by increasing the upstream pressure or by decreasing the port diameters.)

The problem of flashback in the conversion of natural gas appliances to hydrogen can be treated in two ways. One way is to simultaneously increase the upstream pressure and decrease the port size. This can increase the flow velocity through the burner ports enough so that it is greater than the flame speed. The other method is to decrease the amount of primary air so that the mixture upstream of the burner ports is not flammable. This second technique has been evaluated experimentally at IGT with mixed, but generally favorable, results (as discussed below).

Contemporary Atmospheric Burners Without Primary Air

A feasibility investigation was conducted using hydrogen as the fuel for a 12,000 Btu/hr (natural gas) atmospheric range-top burner. The burner head was constructed of stamped aluminum. The outlet pressure of the gas appliance regulator was factory adjusted to be 6 inches water column (approximately 0.217 lb/sq in.). The only mechanical adjustment to the burner was the sealing of the air shutter so that the burner was unable to inject primary air by entrainment. The results of the feasibility study were that —

- The aluminum range-top burner rated at 12,000 Btu/hr (0% primary air, 100% secondary air) did operate in a cooking situation— i.e., it heated approximately 4 pounds of water in a glass container (coffee pot) from approximately 68° to 212°F. Heat-transfer and energy measurements were not taken.

- The burner-head temperature was warmer to the touch of the investigator when hydrogen was used as the fuel than when natural gas was used. However, no quantitative measurements were taken.

The flames appeared to burn within the burner ports. Because flame speed is a function of gas temperature and pressure, an increase in gas temperature can change the flammability limits of a gas; and, with hydrogen, the change can cause the fuel (hydrogen) to burn within the ports.[3]

The calculated theoretical (adiabatic) flame temperature, for a stoichiometric hydrogen-air mixture and at an inlet gas temperature of 60°F, considering dissociation, is approximately 3525°F.[18] The flame temperature of a hydrogen-air mixture is, therefore, approximately only 10% higher than the flame temperature of a natural gas-air mixture, and this difference is probably not sufficient to produce a sensible difference. However, if the specific flame intensities* of hydrogen and natural gas at stoichiometric mixtures are compared, where

$$I_{H_2} = 4.14 \text{ Btu/s-sq in.}^{12}$$

and

$$I_{Nat.} = 0.646 \text{ Btu/s-sq in.}^{13}$$

the specific flame intensity of the hydrogen-air mixture (I_{H_2}) is seen to be approximately 600% greater than that of natural gas ($I_{Nat.}$). For a gas-air mixture burned without primary air, the mathematical expression for flame intensity could be a qualitative indication of the flame-to-burner head heat transfer and of the heat available from the flame — thus possibly explaining why the burner head felt hotter to the investigator when the fuel was hydrogen.

Noise was generated upon burner start-up (ignition) and shutdown (extinction). The ignition noise was a sharp, cracking sound, whereas the extinction noise was a muffled sound of higher intensity than the ignition noise. On extinction of the burner, the noise was due to flashback occurring at a zero gas-flow rate. At ignition, the conditions favorable for the generation of noise were the ignition velocity (flame speed) of the hydrogen-air mixture and the composition of the mixture itself. There was no noise generated by the combustion waves during burner operation.

---

*Specific flame intensity of a fuel gas can be defined as the rate of heat release by the flame of this gas when burned in a prescribed burner of definite design and at a definite inner-flame-cone height. This can be expressed mathematically as[3] —

$$I = H\nu/A \qquad (13\text{-}15)$$

where —

I = the specific flame intensity (capacity) in Btu/s-sq in. port area

H = the net heating value in Btu/cu ft of gas-air mixture issuing from the burner in 1 second

ν = the rate of flame propagation of the gas-air mixture in ft/s

A = the ratio of the burner area to the inner-flame-cone area.

Emissions From Hydrogen-Fueled Burners

Currently, the American National Standards Institute (ANSI) has only one criterion for combustion pollutants from domestic gas appliances, and that is in regard to carbon monoxide. The maximum quantities of carbon monoxide allowed by ANSI are shown in Table 13-13.

Table 13-13. ANSI CARBON-MONOXIDE LEVEL RESTRICTIONS

Appliance	Amount of Air-Free Carbon Monoxide, ppm
Ranges	800
Refrigerators	300
Others	400

Because hydrogen contains no carbon, its products of combustion contain no carbon monoxide or unburned hydrocarbons. However, laboratory investigators have shown[1] that an open-flame hydrogen burner produces significantly larger quantities of nitrogen oxides than an equivalent unit burning natural gas. Table 13-14 shows the nitrogen-oxides emissions from hydrogen used in an atmospheric, open-flame range burner. It should be noted that natural gas used in the open-flame burner had nitrogen-oxides emission levels of from approximately 80 to 100 ppm. From Table 13-14 it should also be noted that there was an increase of approximately 30% in nitrogen oxides emissions using secondary air only compared with using hydrogen with primary air to fuel the open-flame range burner.

Table 13-14. NITROGEN-OXIDES EMISSIONS FROM AN OPEN-FLAME RANGE BURNER USING HYDROGEN AS FUEL

	Air Shutter	
	Fully Open	Closed
Nitrogen Oxides, ppm	257	335
Increase (Maximum) Compared With Natural Gas, %	221	319
Increase (Minimum) Compared With Natural Gas, %	157	235

Discussion

The most serious shortcomings of unmodified burners operated on hydrogen rather than natural gas, with respect to the criteria previously listed, will be flashback and noise. Another problem, not related to current burner requirements, will be the generation of nitrogen oxides.

There does not appear to be a simple way to change existing burner heads so that flashback will not be a problem. Burner ports can be enlarged by drilling (as they were when manufactured gas was replaced by natural gas), but reduction of the port size is not possible. The second way of overcoming flashback tendencies, which is by eliminating the primary-air supply, seems to lead to noise generation in burners (designed for use with natural gas), which have a large cavity upstream of the burner ports for gas-air mixing.

It would appear, then, that the easiest way to convert an existing natural gas appliance for operation with hydrogen would be to design a new burner head that could be installed in the field. Such a burner head could be designed to operate without primary air (the burner ports acting as the metering orifices), and the amount of gas available for "explosions" upon flame extinction could be minimized.

Replacement Burners

Burner-Head Port Sizing

A standard-sized burner head, 9000 Btu/hr, will pass about 9 cu ft of natural gas and 47.3 cu ft of air per hour. A replacement hydrogen burner head, operated without primary air, must pass 27.7 cu ft of hydrogen to deliver heat at the same rate. Because the burner ports will be the metering orifices, the pressure upstream of the ports will be the distribution line pressure (about 7 in. wc). If we assume that eight ports are used per burner head (as in Figure 13-15), their size can be calculated from Bernoulli's theorem (Equation 13-2):

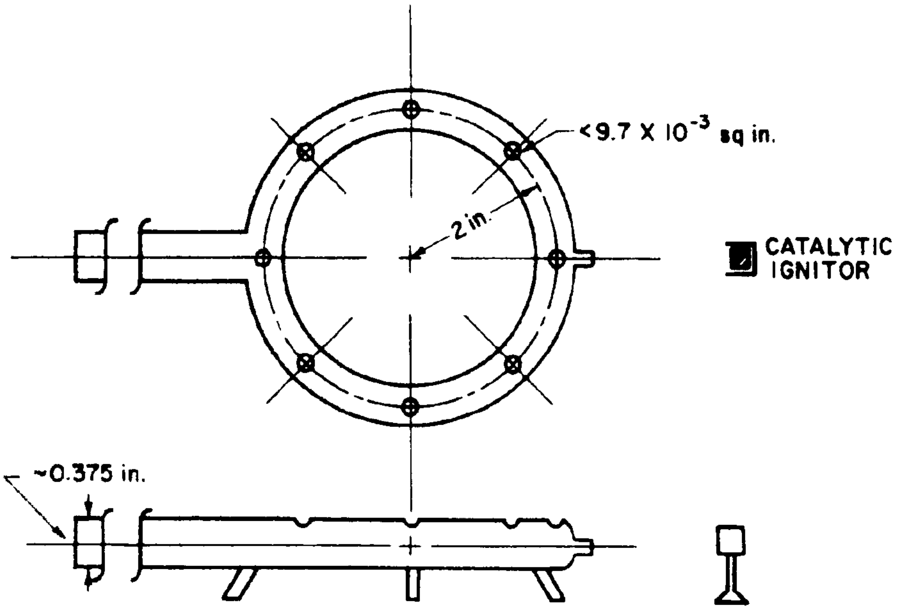
$$A = \frac{YC\,(h_L/\rho)^{0.5}}{q} \qquad (13\text{-}16)$$

$$A = 0.000296 \text{ sq in.}$$

corresponding to a diameter of 0.0097 inch.

Burner Configuration

Figure 13-15 is a suggested configuration for a hydrogen replacement burner for a range top or an automatic hot-water storage heater. An oven burner could be of long cylindrical design. However, because the anticipated small port areas may be prone to clogging by dust particles, a target or spider-type cover may be necessary to prevent blockage of the ports by foreign particles.



A75071811

Figure 13-15. SUGGESTED HYDROGEN-BURNER DESIGN

Burner Construction Material

Burner construction material would be determined by flame heating tests. Figure 13-16 shows one such method for determining temperature rise and heat transfer. The selection of an appropriate construction material would be based on a) energy input, b) pressure, c) heat conduction, d) heat radiation, e) load distance from the burner, f) heat reflection, g) size, and h) temperature rise.

Burner Ignition

The conventional gas pilot can be used to ignite the proposed hydrogen burner; however, it is more practical, in terms of fuel expenditure and air-pollutant control, to use catalytic ignition.

In catalytic-ignition systems, the initial flow of gas (hydrogen) to the appliance passes over a catalyst. The catalyst causes the hydrogen to react with the oxygen in the air at room temperature and thereby produces heat.

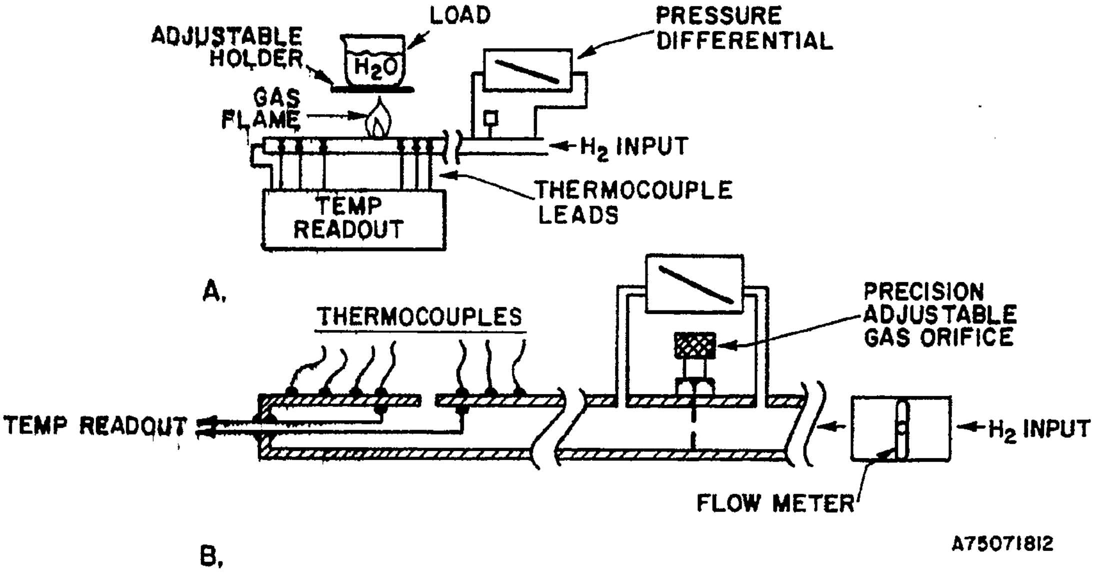


Figure 13-16. METHOD FOR CONDUCTING HYDROGEN-FLAME HEATING TESTS

The catalyst is supported on a material that heats quickly during the catalytic combustion. When the surface temperature reaches the autoignition temperature of the hydrogen-air mixture (about 1085°F), a flame is initiated.

Noise

The ignition noise will not be completely eliminated because of the anticipated concentration of hydrogen in the vicinity of the burner ports and the ignition. There should be a minimum amount of burner operation noise. The extinction noise generated by the hydrogen burner should be less than that generated by the contemporary range burner used in our feasibility investigation.[*] The reduction could be accomplished by a reduction in the available volume of hydrogen in the burner head at shutoff — i.e., the hydrogen burner would have less interval volume than the contemporary atmospheric gas-appliance burner.

---

[*] The extinction noise generated by the contemporary natural gas burner operating on hydrogen was found to be objectionable.

Appliance Regulators

Appliance regulators maintain a constant input pressure to the appliance, regardless of fluctuations in the supply pressure, and thus help to ensure optimum burner performance. In general, pressure regulators on domestic gas appliances use a vent for air movement from the atmospheric side of the regulator diaphragm. The working parts of such a domestic appliance regulator are shown in Figure 13-17.

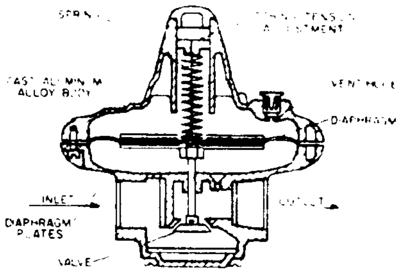


Figure 13-17. APPLIANCE REGULATOR
(Source: Rockwell Manufacturing Co.)

ANSI Standard No. Z21.18-1969 (Standard for Gas-Appliance Pressure Regulators) regarding external leakage would apply to a regulator handling hydrogen fuel. The leakage performance test uses clean air as the gas. However, the area of the vent hole appropriate for natural, manufactured, mixed, and LP gas-air mixtures (sp gr of approximately 0.64, air = 1) would be too large for use with hydrogen. The maximum allowable venting rate, as specified in ANSI Z21.18-1969 for fuel gases of specific gravities approximately equal to 0.64, is 2.5 cu ft/hr.

The lower flammability limit for natural gas (at 1 atm) is approximately 4.9%, by volume, in air.[5] For hydrogen, the lower flammability limit (at 1 atm, 72°F) is approximately 4.0%, by volume, in air.[11] If we assume that the flow rate (2.5 cu ft/hr) is such that in a well-ventilated room the lower explosion limit (LEL) for natural gas – i.e., 4.9%, by volume – is not reached, the amount of hydrogen (sp gr of 0.07, air = 1) that could be vented under these conditions would be approximately 2.0 cu ft/hr. However, approximately 7.0 cu ft of hydrogen per hour would pass through the vent sized (restricted) for natural gas. A smaller sized vent, appropriate for hydrogen, could easily be blocked by foreign particles (dirt). There are, however, vents available with check valves that allow free movement of air into the upper diaphragm chambers, but that restrict the outward flow rate of hydrogen to some designated value. Informed opinion[7] is that residential gas appliance regulators designed to regulate natural, manufactured, and mixed gases would accommodate hydrogen without deterioration of the diaphragm or other working components.

Development of Catalytic Appliances

It is possible to design appliances that combust hydrogen through the action of a catalyst, despite the fact that efforts to develop similar burners for methane have been unsuccessful.

Catalytic combustion takes place on an active surface. Because the surface is a participant in the chemical-reaction sequence of combustion, the "energy barrier" between the reactants and products of combustion can sometimes be reduced. This allows the reactions to take place at temperatures below those characteristic of flames.

Research and development on catalytic appliances is under way at Billings Energy Research Corp., Provo, Utah, under the sponsorship of the Mountain Fuel Supply Co.,[6] and at the Institute of Gas Technology, under the sponsorship of Southern California Gas Co.[17] Billings Energy Research Corp. recently converted the cooking appliances in a Winnebago motor home to catalytic hydrogen combustion. The research at IGT is concerned with the development of catalytic ranges, water heaters, and space heaters. Catalytic-igniter research, sponsored by several gas utility companies, is also under way at IGT.

There are two differing approaches to the design of hydrogen-fueled catalytic appliances. One is to design for pure catalytic combustion, wherein all combustion takes place through the action of a very active catalyst. The other is to use a flame to heat and assist a less active catalyst.

Low-Temperature Catalytic Appliances

When catalyzed by noble metals, hydrogen combustion in air can begin at room temperature. Heat is released as the hydrogen burns, thus raising the temperature of the catalyst and substrate; but combustion can be maintained at comparatively low (surface) temperatures. Most other common fuels must be heated to moderately high temperatures before they will begin to combust catalytically.

A low-temperature catalytic burner must maintain a steady rate of heat release to the load or to the environment so that it does not provide an ignition source for a flame. As was presented in the last section, it is quite possible to make catalytic igniters in which the combustion on the catalytic surface heats the catalyst to a temperature above the autoignition temperature of the mixture, thus initiating flame-type combustion. Stable catalytic combustion can be maintained if any of the three following criteria are met:

1. The laminar flow velocity of the hydrogen-air mixture over the catalyst is greater than the flame velocity of hydrogen. If this is true a flame cannot propagate away from the catalyst. This approach has been tested experimentally and was found to be impractical.[17]
2. The composition of the hydrogen-air mixture passed over the catalyst places the mixture beyond the limits of flammability. This approach is impractical if the mixture is fuel rich because it implies that unburned hydrogen will be vented by the appliance. Results of experiments with mixtures that are less than 4% hydrogen (fuel lean) have not been promising.[6]
3. No points on the surface of the catalyst ever reach the autoignition temperature of hydrogen-air mixtures (1085°F). This implies that a balance between the heat transferred away from the surface and the heat released by the combustion of incoming hydrogen is struck at a lower temperature.

Experiments at IGT have shown the third method to be the most practical.[17] Stable and complete catalytic combustion has been maintained in burner configurations at temperatures as low as 400°F (the surface temperature as determined by thermocouple measurements).

High-Temperature Catalytic Burners

At elevated temperatures, some materials that are not active catalysts for hydrogen combustion at low temperatures become active. Examples of such materials are iron and steel. Exploitation of this property by Billings Energy Research Corp. has resulted in a hybrid, flame-assisted catalytic burner. The configuration of this burner is shown in Figure 13-18.

During operation, the flame-assisted catalytic burner must be activated by an outside ignition source, such as a glow coil or a pilot light. At first,

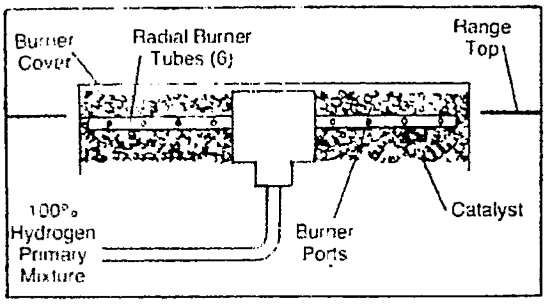


Figure 13-18. CONFIGURATION OF BILLINGS ENERGY RESEARCH CORP. FLAME-ASSISTED CATALYTIC BURNER[6]

all combustion takes place in the flame; but as the flame heats the catalytic surface, proportionately more and more combustion takes place through the action of the catalyst.

Advantages of Catalytic Combustion

It should be noted that the designing of catalytic burners is not an exact science, and a great deal of development work must be done before such devices can be marketed. The incentives for undertaking such programs are clear from the results of the first experiments performed on early burner models. Catalytic appliances can be significantly more efficient than flame burners and can virtually reduce emissions to zero.

When catalytic combustion takes place at temperatures below 1500°F, the formation of nitrogen oxides is, for all practical purposes, eliminated. Because no carbon monoxide is formed during hydrogen-air combustion, the only product of combustion is water vapor. Laboratory results of nitrogen oxides emissions from two low-temperature catalytic appliances and from four high-temperature catalytic burners are shown in Table 13-15.

The data for low-temperature catalytic appliances are reported on an air-free basis, as were the measurements by the American Gas Association Laboratories reported in the previous section. This means that the measured concentrations are adjusted to exclude the dilution effect of excess air. With excess air, the nitrogen oxides concentrations would be even lower. The experimental apparatus for making such measurements is shown in Figure 13-19. Because Reference 6 does not specify whether or not the quoted

Table 13-15. NITROGEN-OXIDES EMISSIONS FROM SEVERAL CATALYTIC APPLIANCES

	Burner Type	Nitrogen Oxides, ppm
Low-Temperature Catalytic[17]*	Chimney	0.08
	Vertical fin	0.03
High-Temperature Catalytic[6]	Standard Al range	5.2
	Stainless steel, experimental	1.8
	Al oven/broiler	4.5
	Cast iron	4.0

---

* Reported on an air-free basis.

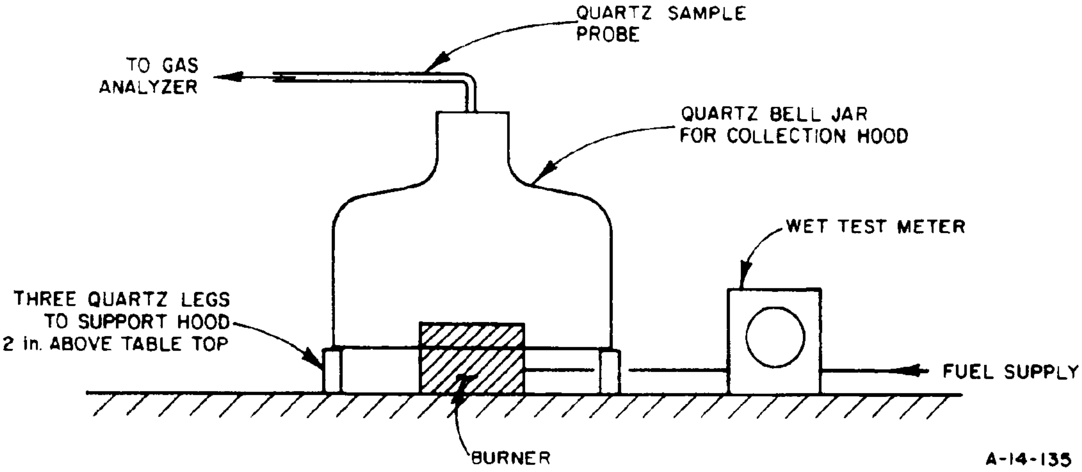


Figure 13-19. BURNER-EMISSION-TESTING SETUP

results are on an air-free basis, it is assumed that they are measured concentrations that are diluted by an undetermined amount of excess air.

The nitrogen-oxides production levels reported for the low-temperature catalytic space heaters are on about the same order of magnitude as the nitrogen-oxides levels found in ambient air. Thus it should be possible to build space heaters and other appliances that are ventless. In present-day furnaces, about 30% of the chemical energy in the fuel is lost when the combustion products are vented through chimneys. Therefore, ventless appliances could potentially operate much more efficiently than present-day appliances. At IGT, under certain intermittent operating conditions, second-generation, experimental catalytic water heaters have had measured efficiencies of greater than 80%, based on that portion of the high heating value of hydrogen that is transferred to the water.

Preliminary calculations indicate that the water formed as a combustion product in ventless space heating may or may not be a problem, depending on the tolerable humidity level and the frequency of air changes in specific houses.[17] There is also the possibility with some appliances (water heaters, for example) of installing condensing units to trap combustion-produced water vapor. These traps would then permit full utilization, by the appliance, of the higher heating value of the hydrogen burned, and they would provide a supply of relatively pure water.

Cost of Catalytic Appliances

The cost of high-temperature catalytic appliances should not be significantly higher than that of standard appliances because the only addition is a stainless-steel pad. Although low-temperature catalytic appliances make use of expensive metals (such as platinum), the catalyst-loading levels are so low that the appliance price should not increase significantly. (Preliminary estimates are that only about 10¢/1000 Btu-hr would be attributable to the catalyst material.) From Table 13-3, the estimated peak-day natural gas requirements for a 1200-sq-ft house is about 1.5 million Btu. The release of this much energy by the catalytic combustion of hydrogen would then require an investment of only $12 attributable to platinum catalyst material. This figure is conservative (high) because ventless catalytic burners will be more energy efficient than standard burners and because low-temperature appliances will not need pilot lights.

References Cited in This Section

1. American Gas Association's Cleveland Laboratory, private communication of January 1975.

2. American Gas Association, "American National Standard for Household Cooling Gas Appliances," Am. Natl. Stand. Inst. Z21.1-1974. Arlington, Va., 1974.

3. American Gas Association, Gas Engineers Handbook. New York: Industrial Press Inc., 1969.

4. American Gas Association Laboratories, "Influence of Port Design and Gas Composition on Flame Characteristics of Atmospheric Burners," Res. Bull. No. 77, (1958) February.

5. American Gas Association, Gaseous Fuel — Properties, Behavior, and Utilization, 2nd Ed. New York, 1954.

6. Baker, N. R., "Oxide of Nitrogen Control Techniques for Appliance Conversion to Hydrogen Fuel." Paper presented at the Ninth Intersociety Energy Conversion and Engineering Conference, San Francisco, August 1974.

7. Dufour, R. J., Consultant to IGT.

8. Grumer, J., Harris, M. E. and Rowe, V. E., "Fundamental Flashback, Blowoff, and Yellow-Tip Limits of Fuel Gas-Air Mixtures," U.S. Bur. Mines Rep. Invest. 5225. Washington, D.C.: U.S. Department of the Interior, 1956.

9. Hittman Associates, Inc., Residential Energy Consumption. Columbia, Md., n.d.

10. Industrial Heating Equipment Association, Combustion Technology Manual, 2nd Ed. Washington, D.C., 1974.

11. Jones, G. W., U.S. Bur. Mines Tech. Pap. No. 450. Washington, D.C.: U.S. Department of the Interior, 1929.

12. Ladenburg, R. W. et. al., Eds., Physical Measurements in Gas Dynamics and Combustion, 409-38. Princeton, N.J.: Princeton University Press, 1954.

13. Lewis, B. and von Elbe, G., "Stability and Structure of Burner Flames," J. Chem. Phys. 11, 75-79 (1943).

14. Lewis, B. and von Elbe, G., Combustion Flames and Explosions of Gases. New York: Academic Press, Inc., 1951.

15. Mason, D. M. and Eakin, B. E., "Calculation of Heating Value and Specific Gravity of Fuel Gases," Inst. Gas Technol. Chicago Res. Bull. No. 32, (1961) December.

16. Northern Natural Gas Co., Residential-Appliance Gas Consumption, Omaha, September 1970.

17. Sharer, J. C. and Pangborn, J. B., "Utilization of Hydrogen as an Appliance Fuel." Paper presented at The Hydrogen Economy Miami Energy (THEME) Conference, Miami Beach, March 18-20, 1974.

18. The North American Manufacturing Co., North American Combustion Handbook. Cleveland, 1952.