14. HYDROGEN AS A FEEDSTOCK FOR SYNTHETIC FUEL PROCESSES – T. D. Donakowski and J. C. Gillis

From the conclusions presented in the previous sections, it should be clear that hydrogen will be an expensive commodity and as such will not find much use as a fuel in the immediate future, but will be a valuable chemical feedstock. We have reviewed some of the ways present-day industries could use feedstock hydrogen, but have not yet commented on an industry, developing in the mid to long term, that has the potential to become a large market for feedstock hydrogen — the synthesis of clean fuels from coal and oil shale.

The fundamental objective of all coal-based synthetic fuels processes is to turn a low hydrogen-content fuel (coal) into high hydrogen-content fuels (oils, methanol, and methane). Hydrogen is currently produced from coal during these processes; in some processes, a great deal of the input coal (in the methanol process, about half) is used for hydrogen production.

At present, onsite hydrogen production from coal is the cheapest process available. However, coal is an exhaustible resource, the price of which will surely rise in the long term. There are possible sources of hydrogen that are tied to renewable or extremely large energy sources (solar or nuclear), which are not likely to rise as much in cost as fossil fuels in the long term. Thus, it seems likely that at some point in the future it will be economically advantageous to reserve as much coal as possible for synthetic-fuels production and to utilize some "outside" source of hydrogen.

We have investigated this possibility during the course of this study. We have focused our attention on "retrofitting" developed synthetic-fuels processes to accept outside hydrogen because the synthetic-fuels industry is likely to be well established, with great investments in process-plant equipment, before outside hydrogen becomes economically attractive.

Coal Conversion to Substitute Natural Gas

Coal has a molecular hydrogen-to-carbon ratio of about 0.8, but in methane the hydrogen-to-carbon ratio is 4. Thus, coal-to-substitute natural gas (SNG) processes are really "hydrogen-addition" processes.

Many processes have been proposed for the conversion of coal to SNG. They employ a gasifier-reactor to produce a combination of carbon monoxide, hydrogen, and methane in one or more stages. The principal chemical reactions taking place in the gasifier are –

$$C + H_2O \rightarrow CO + H_2$$
$$C + 2H_2 \rightarrow CH_4$$

A portion of the carbon monoxide in the gasifier product stream is often used to produce hydrogen in a "shift" reactor by the reaction –

$$CO + H_2O \rightarrow CO_2 + H_2$$

The carbon dioxide is then removed; and after final purification, the remaining hydrogen, carbon monoxide, and methane is sent to a "methanation" reactor. There the carbon monoxide and hydrogen are reacted to form more methane:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

and the product gas has a higher heating value, about 950 Btu/SCF.[15] The "generalized" SNG process is shown in Figure 14-1.

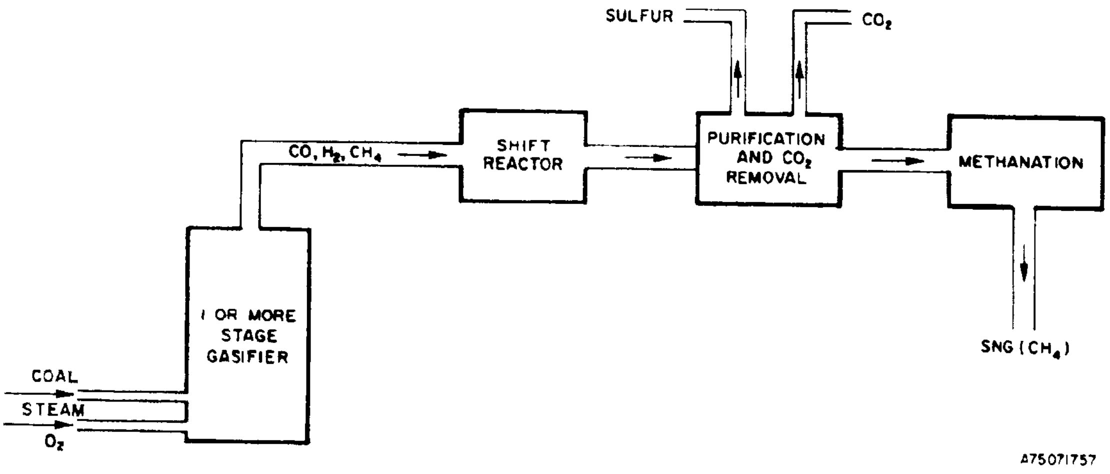


Figure 14-1. GENERALIZED SNG PROCESS

Almost all of the proposed SNG processes are of the general form presented in Figure 14-1. The differences in the processes are to be found in the approach to the first step — the gasifier. For convenience, we will divide SNG processes into groups according to the type of gasifiers they utilize: single-stage gasifiers, multistage hydrogasifiers, and other gasifiers.

The Lurgi and Koppers-Totzek SNG Processes are examples those that utilize single-stage gasification. However, the two gasifiers involved are of quite different designs and operate at different conditions. The Lurgi gasifier typically requires noncaking coal and operates at from 350 to 450 psi and at 1150° to 1400°F, producing a significant amount of methane as well as light hydrocarbon byproducts.[3] The Koppers-Totzek gasifier works with both caking and noncaking coals, but operates at near-atmospheric pressure and reaches much higher temperatures (up to 3300°F). The high temperature precludes formation of any light hydrocarbons and ensures complete gasification of almost all of the carbon matter.[7]

In both processes the synthesis gas is formed via the steam-coal reaction:

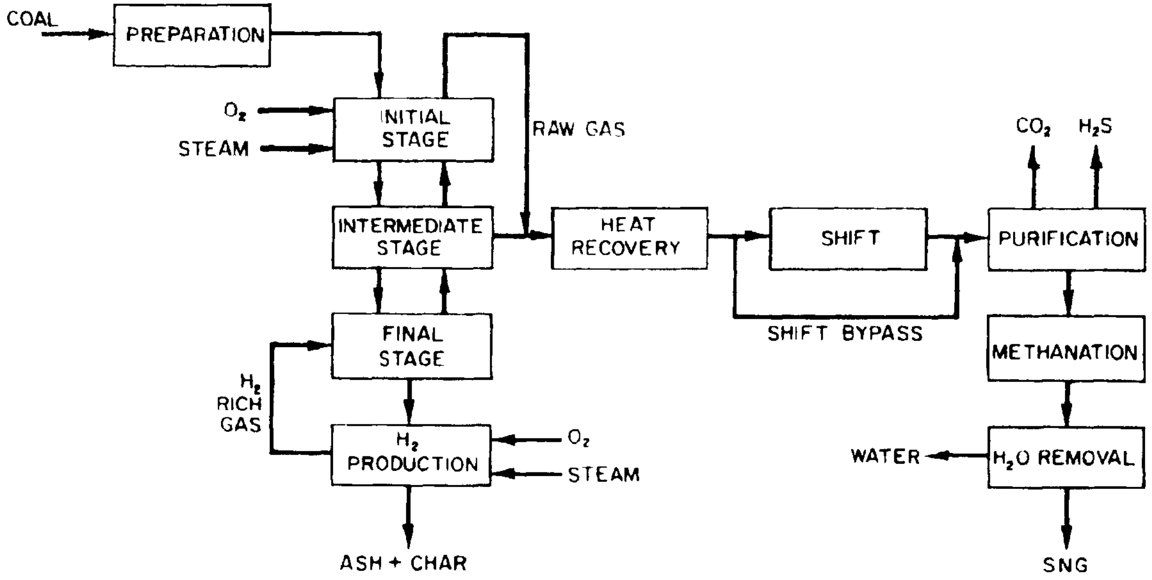
$$C + H_2O + \text{heat} \rightarrow CO + H_2$$

Water is added, in excess, to both gasifiers to partially oxidize the carbon in the coal, to serve as a source of hydrogen itself, and to act as a temperature moderator for the reactor. Some of the water is eventually used to generate more hydrogen in the shift reactor.

Heat for the steam-coal reaction is provided by combusting part of the coal with oxygen. High-purity oxygen is used to prevent dilution of the product stream with the nitrogen present in air.

As the name implies, multistage hydrogasifiers are those that involve two or more stages, in one or more vessels, in gasifying coal. (See Figure 14-2.) In general, the initial stage devolatilizes the coal and forms methane or synthesis gas. Greater heating efficiency can be obtained by the direct formation of methane in the gasifier. Heat from the methane-forming reactions can then be more effectively absorbed in situ to expedite the steam-coal reaction and to devolatilize the coal.[27] The methane reactions are —

$$C + 2H_2 \rightarrow CH_4 + \text{heat}$$
$$CO + 3H_2 \rightarrow CH_4 + H_2O + \text{heat}$$



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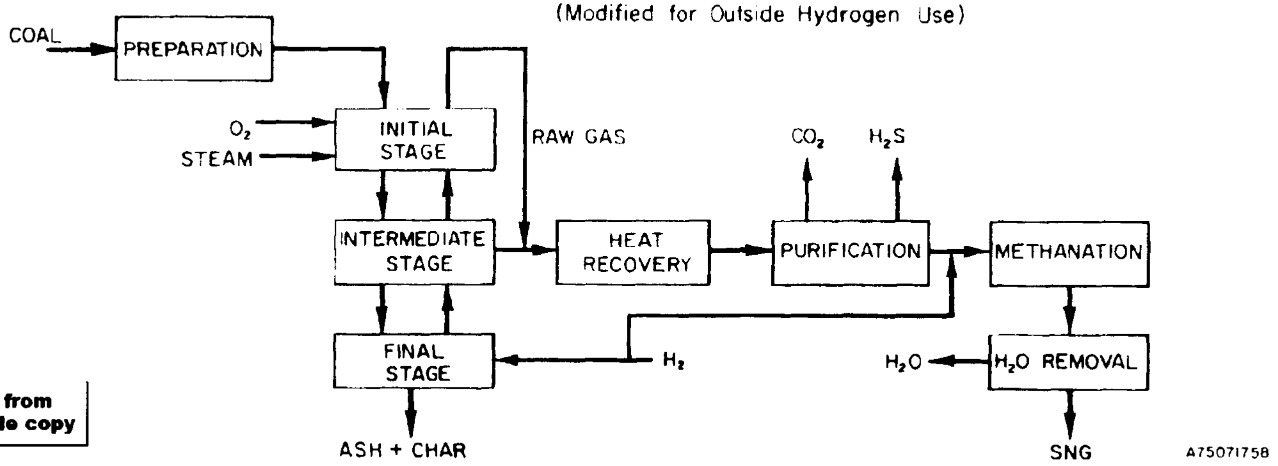


Figure 14-2. SNG PRODUCTION
(Multistage Hydrogasification Process)

The steam-coal reation is —

$$C + H_2O + heat \rightarrow CO + H_2$$

The hydrogen required for the hydrogasification step is produced in the final stage of the gasifier by the partial oxidation of char to form a hydrogen-rich synthesis gas.

Having thus produced a raw gas, the stream is cooled; shifted, if necessary, to increase the hydrogen/carbon monoxide ratio to that required for methanation; purified of carbon dioxide and hydrogen sulfide; and, finally, methanated to reduce the carbon monoxide content and to yield the SNG product.

The other gasification process schemes utilize novel features in their coal-gasification steps. The ATGAS Process uses molten iron to gasify the coal and to produce a carbon monoxide-rich synthesis gas that contains no methane. Because no methane is produced in the gasifier, a considerable amount of carbon monoxide must be shifted to obtain hydrogen for eventual synthesis to methane. The Kellogg Process uses a molten salt (sodium carbonate) as the medium for coal gasification. The salt catalyzes the steam-coal reaction and also acts as a good heat-transfer agent. The synthesis gas is shifted to produce the proper composition for methanation. Another special gasification method is the CO_2 Acceptor Process. Coal is gasified in a two stage reactor, with the required process heat supplied by the exothermic reaction of carbon dioxide with calcium oxide, forming calcium carbonate. Enough hydrogen is produced in the gasifier from the steam-coal reaction so that a shift reaction prior to methanation is not required.[3] Gasifier operating conditions and R& D statuses for SNG production are summarized in Table 14-1.

The water-gas shift reaction is an important step in almost all gasification processes. The reaction is required to increase the hydrogen/carbon monoxide ratio to that necessary for methanation, about 3.6:1. The shift reaction is —

$$CO + H_2O \rightarrow CO_2 + H_2 + heat$$

It consumes water, reducing it to hydrogen and oxygen and oxidizing the carbon monoxide produced from coal to carbon dioxide. The carbon dioxide is more difficult to convert to methane and is scrubbed from the system, along with hydrogen sulfides prior to methanation.[22] The carbon in the carbon dioxide was originally present in the coal, so that by removing

Table 14-1. COAL-TO-SUBSTITUTE NATURAL GAS PROCESSES

Process	Gasifier Conditions	R&D Status
Single-stage gasifiers		
Koppers-Totzek[4]	Any type coal, 2700°F, atmospheric pressure	16 plants in operation, methanation step not demonstrated
Lurgi[3,15,22]	Noncaking coal, 1300°F 400 psi	58 plants have been constructed since 1936; methanation step not demonstrated; commercial design, including methanation, completed by Fluor Engineering
Multistage hydrogasifiers		
BI-GAS[3,30]	First stage, 2700°F; second stage, 1700°F; 1000 psi	120 tons of coal/day pilot plant scheduled for completion fall 1975
Hydrane[15,30]	Direct reaction with hydrogen, 1650°F, 1000 psi	10 pounds of coal/hr pilot plant has been operated, design of 24 tons/day pilot plant under way
HYGAS®[5]	Direct reaction with hydrogen; first stage, 1250°F; second stage, 1750°F; 1000 psi	75 tons of coal/day pilot plant in operation since 1971
Synthane[15,30]	1800°F, 1000 psi	75 tons of coal/day pilot plant essentially completed and operations starting
Special gasifiers		
ATGAS[15]	Reaction in bath of molten iron, 2500°F, near atmospheric pressure	Bench-scale studies completed
CO_2 Acceptor[15,30]	No oxygen required, 1500°F, 150 psi	30 tons of coal/day pilot plant in operation, methanation step in start-up
Kellogg Molten Salt[15]	Bath of molten sodium carbonate, 1700°F, 1200 psi	Bench-scale testing

and venting the carbon dioxide from the system, a great deal of raw-material carbon is lost.

The final step in producing the methane for use as pipeline gas is the catalytic combination of carbon monoxide and hydrogen to form methane and water by the methanation reaction –

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

This reaction has only recently been tested on a commercial scale with the carbon monoxide concentrations as high as is typically expected.[18]

Methanation is used in some chemical processes today (e.g., in ammonia synthesis), but only in applications in which the methane-forming reactants (carbon monoxide, carbon dioxide and hydrogen) are diluted with large concentrations of nonparticipating gases.[33] Methanation of gas streams in which essentially all incoming gases participate in the reactions is still under development. The main difficulty is the removal of the large quantities of heat released in the catalytic reactor by methane formation.[20] An alumina-supported nickel catalyst is usually designed to operate in a temperature range of from 500°to 650°F, so adequate temperature control within the reactor is essential. The catalyst is also sensitive to sulfur poisoning. Sulfur depositions of 0.15% (by weight) are detrimental, so adequate hydrogen sulfide removal upstream is mandatory. Although the methanation step is the least-proved commercial technology in SNG production from coal, excellent progress has been made in small-scale methanation catalysts for refineries;[6] and a total, commercial coal-to-SNG plant should be fully realized in just a few years.

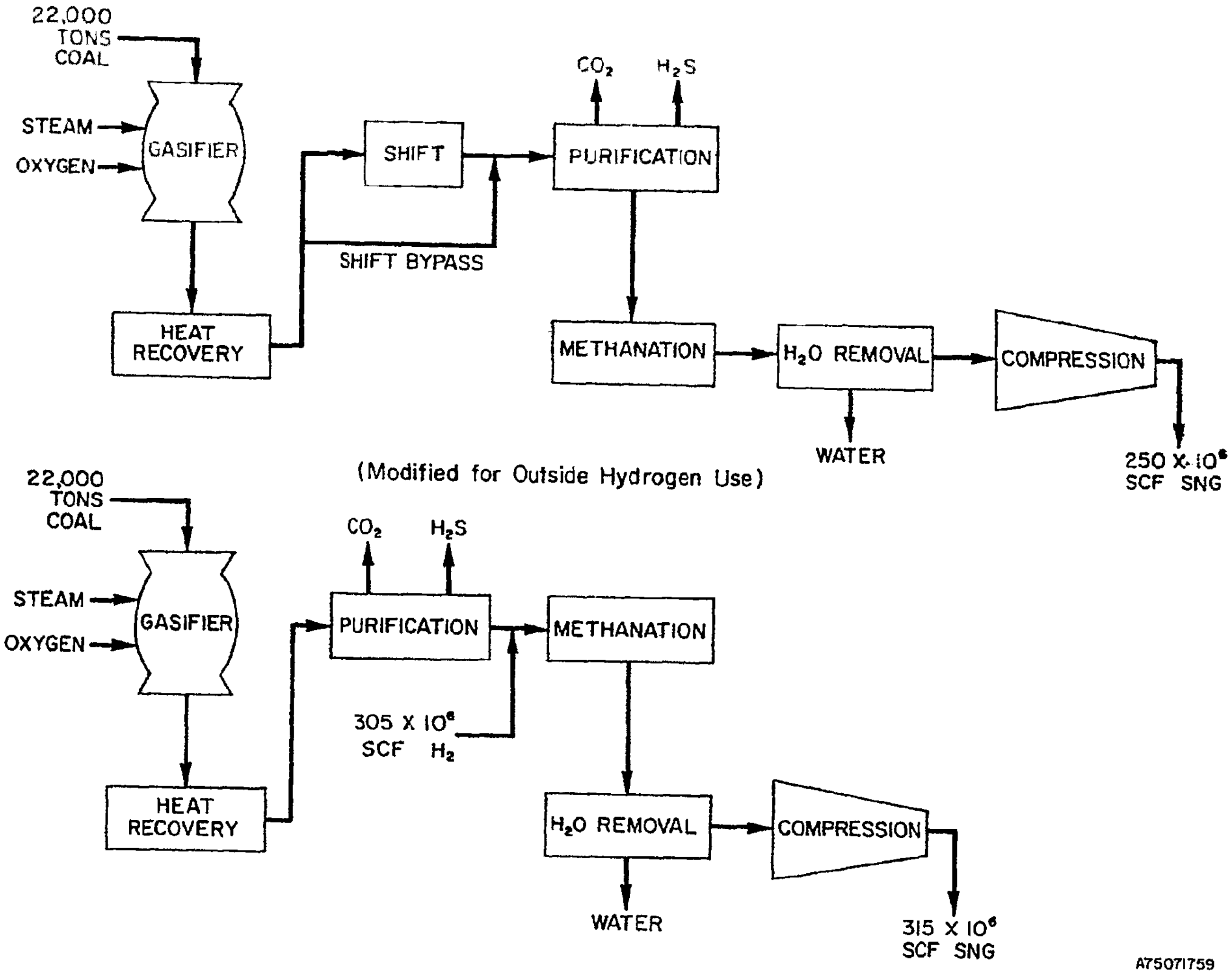
The generalized coal-to-SNG process (Figure 14-1) could be modified in two places to utilize outside hydrogen in the gasifier and in the shift reactor.

In processes using single-stage gasifiers, hydrogen is produced in the gasifier from steam.[3] In order to use hydrogen in the gasifier directly, an entirely new reactor design would most likely be necessary – a project outside the scope of this study. With hydrogasifiers, however, a reducing gas composed of hydrogen and carbon monoxide is used as input to the gasifier. This could be replaced with hydrogen. The use of rather pure hydrogen in the process allows for smaller volume flows compared with hydrogen-rich streams containing significant amounts of carbon monoxide and carbon dioxide.

The realization of smaller gas volumes allows for the use of smaller scale reactors and accompanying equipment. A flow diagram for conventional and modified hydrogasifiers is shown in Figure 14-2. The material balances around the gasifiers for a HYGAS® and a Hydrane Process, shown in Tables 14-2 and 14-3, indicate that the modified hydrogasifiers would use 1.1 to 1.5 SCF of outside hydrogen per SCF of SNG produced. Sufficient information for calculation on BI-GAS and Synthane Processes was not available; but, due to process similarity, hydrogen usage should fall within the same range as that calculated for the other hydrogasifiers.

In most coal-to-SNG processes a shift step is necessary before methanation. Here a stream of outside hydrogen could be directly added to accomplish the required increase in the hydrogen/carbon monoxide ratio; and, by so doing, the entire shift reactor and its catalyst could be eliminated. No carbon monoxide is shifted to produce hydrogen, so more is available for eventual conversion to methane, thereby increasing the product yield per amount of coal fed. With less carbon dioxide now in the process stream, the separation requirements are less severe. Process water requirements can also be reduced because water is not consumed by a shift reaction. (This could be accomplished by small reductions in the amount of steam injected to the gasifier.) In general, the addition of outside hydrogen to perform the hydrogen enrichment now accomplished by a shift reaction results in a much simpler operation with more effective coal utilization in forming product SNG.

The abovementioned modification was made to a Lurgi Process, which was then compared with the conventional scheme. (Figure 14-3 is the flow diagram). A material balance around the shift reactor is presented in Table 14-4 and shows that about 1 SCF of hydrogen can be used per SCF of SNG output from the modified process. A Koppers-Totzek Process was similarly modified to eliminate the shift step by using outside hydrogen. A material balance around the conventional shift step is presented in Table 14-5. Using a Koppers-Totzek gasification process the idealized hydrogen usage is about 2.4 times the volume of the SNG produced. This requirement is higher than that for a Lurgi process because virtually no methane is formed inside the Koppers-Totzek gasifier, but is produced indirectly by reacting the comparatively larger amount of carbon monoxide,



(Modified for Outside Hydrogen Use)

Figure 14-3. SNG PRODUCTION
(Lurgi Single-Stage Gasification Process)

Table 14-2. TYPICAL INPUT AND OUTPUT OF GASEOUS STREAMS IN FINAL STAGE OF THE HYDROGASIFIER-REACTOR, HYGAS® COAL-TO-SNG PROCESS[36]
(Hydrogen by Steam-Iron Process, 250 Million SCF/Day)

Component	Hydrogen-Rich Gas Feed	Gasifier Effluent
	Vol % (Dry)	
Carbon Monoxide	0	12.6
Hydrogen	100	51.6
Carbon Dioxide	0	9.2
Methane	0	23.7
Hydrogen Sulfide	0	1.7
Ethane	0	0.8
Other	0	0.4
Total	100	100.0
10^6 SCF/DAY	279	355

Amount of Externally Generated Hydrogen Used in Process —

$$1.0 \times 279 \times 10^6 \text{ SCF} = 279 \times 10^6 \text{ SCF}$$

Volumetric Ratio of Outside Hydrogen to SNG —

$$\frac{279 \times 10^6}{250 \times 10^6} = 1.1, \text{ or } 110\%$$

Table 14-3, TYPICAL INPUT AND OUTPUT OF GASEOUS STREAMS IN GASIFIER-REACTOR, HYDRANE COAL-TO-SNG PROCESS[38]
(250 Million SCF/Day)

Component	Hydrogen-Rich Gas Feed	Gasifier Effluent
	Vol % (Dry)	
Carbon Monoxide	0	3.9
Hydrogen	100	22.9
Carbon Dioxide	0	0
Methane	0	73.2
Total	100	100.0
10^6 SCF/Day	365	283

Amount of Externally Generated Hydrogen Used in Process —

$$1.0 \times 365 \times 10^6 \text{ SCF/Day} = 365 \times 10^6 \text{ SCF/Day}$$

Volumetric Ratio of Outside Hydrogen to SNG —

$$\frac{365 \times 10^6}{250 \times 10^6} = 1.5, \text{ or } 150\%$$

Table 14-4. TYPICAL INPUT AND OUTPUT OF A CARBON MONOXIDE SHIFT REACTOR, LURGI COAL-TO-SNG PROCESS[22]
(250 Million SCF/Day)

Component	Reactor Feed	Reactor Effluent
	Vol % (Dry)	
Carbon Monoxide	19.6	3.9
Hydrogen	38.8	46.8
Carbon Dioxide	28.9	38.2
Methane	11.1	9.6
Hydrogen Sulfide	0.3	0.3
Ethylene	0.4	0.4
Ethane	0.6	0.5
Nitrogen and Argon	0.3	0.3
Total	100.0	100.0
10^6 SCF/Day	430	490

Amount of Carbon Monoxide Shifted to Produce Hydrogen –

$$0.196 \text{ X } 430 \text{ (In)} - 0.039 \text{ X } 490 \text{ X } 10^6 \text{ (Out)} = 65 \text{ X } 10^6 \text{ SCF/Day}$$

If No Shift Is Performed –

Amount of Hydrogen Required to Replace Shifted Carbon Monoxide = 65 X 10^6 SCF/Day

Additional Hydrogen Required to React With Additional Carbon Monoxide to Form Methane = 3.7 X 65 X 10^6 = 240 X 10^6 SCF/Day

Total Hydrogen Required 305 X 10^6 SCF/Day

Additional Methane Produced (Equals Carbon Monoxide Not Shifted) = 65 X 10^6 SCF/Day

Volumetric Ratio of Outside Hydrogen to SNG

$$= \frac{305 \text{ X } 10^6}{(250 + 65) \text{ X } 10^6} = 0.97$$

Table 14-5. TYPICAL INPUT AND OUTPUT OF A CARBON MONOXIDE SHIFT REACTOR, KOPPERS-TOTZEK COAL-TO-SNG PROCESS[7]
(250 Million SCF/Day)

Component	Reactor Feed	Reactor Effluent
	Vol % (Dry)	
Carbon Monoxide	55.9	17.5
Hydrogen	37.4	52.8
Carbon Dioxide	6.0	29.1
Methane	0.0	0.0
Nitrogen	0.7	0.6
Total	100.0	100.0
10^6 SCF/Day	1030	1370

Amount of Carbon Monoxide Shifted to Produce Hydrogen —

$$0.559 \times 1030 \times 10^6 \text{ SCF/Day (In)} - 0.175 \times 1370 \times 10^6 \text{ SCF/Day (Out)} = 336 \times 10^6 \text{ SCF/Day}$$

If No Shift Is Performed —

Amount of Hydrogen Required to Replace Shifted Carbon Monoxide = 336×10^6 SCF/Day

Additional Hydrogen Required to React With Additional Carbon Monoxide to Form Methane = $3.1 \times 336 \times 10^6$ = $\underline{1040 \times 10^6}$ SCF/Day

Total Hydrogen Required 1376×10^6 SCF/Day

Additional Methane Produced (Equals Carbon Monoxide Not Shifted) = 336×10^6 SCF/Day

Volumetric Ratio of Outside Hydrogen to SNG

$$= \frac{1376 \times 10^6}{(250 + 336) \times 10^6} = 2.4$$

which must be present in the synthesis gas, with the much larger amounts of hydrogen in the methanation reactor.

The special gasification processes can similarly be modified to use an outside source of hydrogen, thus eliminating the carbon monoxide shift step. The ATGAS Molten-Iron Process produces a carbon monoxide-rich synthesis gas that contains no methane. A considerable amount of carbon monoxide must be shifted to obtain the hydrogen required for methanation. When the shift reactor is removed, the process hydrogen requirement is high, about 2.7 times the volume of the SNG produced. (See Table 14-6.) The CO_2 Acceptor Process produces sufficient hydrogen internally, due in part to the *in situ* removal of carbon dioxide by chemical reaction, so that a shifting step is not required.[3] Because of the basic design, then, this process cannot be practically modified to the use of an outside source of hydrogen.

Coal Conversion to Low-Btu Gas

Coal may also be converted to a clean-burning, low-heat-content gas (150 to 300 Btu/SCF). By gasifying the coal, sulfur is more easily removed (as hydrogen sulfide); and the fuel burns cleaner. Low-Btu gas is produced by using air instead of oxygen in any primary coal gasifier. This eliminates the costly production of oxygen by air separation. The product stream then contains nitrogen, which lowers its heating value and makes long-distance transportation of the gas uneconomical. Hydrogen is produced within the process stream, along with carbon monoxide and some methane. With a lower heating value per volume than SNG, compression and transportation, by pipeline, of the low-Btu gas is not economical; so onsite use is preferred. The electric power industry is envisioned as the principal consumer of such gas.[15] Many of the low-Btu processes, such as Westinghouse's Clean Power Gas and IGT's U-GAS,™ are designed to be part of a combined gas-steam turbine cycle for an efficient and low-polluting electric generating plant.[12,21] A brief description and the status of various processes are presented in Table 14-7.

The low-Btu gas is produced by using air to oxidize the coal, providing heat and forming the synthesis gas, with the accompanying inert nitrogen acting as a diluent and reducing the heat content. The sulfur (as hydrogen sulfide) and particulates are removed to obtain the low-Btu product. A shift reaction is not performed.

Table 14-6. TYPICAL INPUT AND OUTPUT OF A CARBON MONOXIDE SHIFT REACTOR, ATGAS COAL-TO-SNG PROCESS[19]
(250 Million SCF/Day)

Component	Reactor Feed	Reactor Effluent
	Vol % (Dry)	
Carbon Monoxide	65	16
Hydrogen	35	54
Carbon Dioxide	0	30
Methane	0	0
Hydrogen Sulfide	0	0
Total	100	100
10^6 SCF/Day	1030	1460

Amount of Carbon Monoxide Shifted to Produce Hydrogen —

$$0.65 \times 1030 \times 10^6 \text{ SCF/Day (In)} - 0.16 \times 1460 \times 10^6 \text{ SCF/Day (Out)}$$
$$= 436 \times 10^6 \text{ SCF/Day}$$

If No Shift Is Performed —

Amount of Hydrogen Required to Replace Shifted Carbon Monoxide = 436×10^6 SCF/Day

Additional Hydrogen Required to React With Additional Carbon Monoxide To Form Methane = $3.3 \times 436 \times 10^6$ = 1439×10^6 SCF/Day

Total Hydrogen Required 1875×10^6 SCF/Day

Additional Methane Produced (Equals Carbon Monoxide Not Shifted)
$= 436 \times 10^6$ SCF/Day

Volumetric Ratio of Outside Hydrogen to SNG

$$= \frac{1875 \times 10^6}{(250 + 436) \times 10^6} = 2.7$$

Table 14-7. PROCESSES FOR CONVERSION OF COAL TO LOW-BTU GAS

Process	Gasifier Conditions	R&D Status
Koppers-Totzek[4]	Any type coal, 2700°F, atmospheric pressure	16 plants in operation
Lurgi[3, 15]	Noncaking coal, 1300°F, 400 psi	58 plants constructed since 1936
ATGAS[15]	Reaction in molten iron, 2500°F, near atmospheric pressure	Bench-scale studies completed
Synthane[10, 30]	1800°F, 300 psi	75 tons of coal/day pilot plant to produce SNG essentially completed and operations starting
U-GAS™[5]	1900°F, 300 psi	High temperature (800°F) sulfur removal (i.e., hydrogen sulfide and carbonyl sulfide) not demonstrated
Westinghouse Clean Power Gas[12]	2100°F, 150-225 psi	1/2 ton of coal/day process development unit constructed and should have started operation early this year
Winkler[15]	1500°-1800°F, atmospheric pressure	16 plants constructed since 1926

Low-Btu-gasification schemes, as currently conceived then, are not amenable to an outside source of hydrogen and would not be able to use any directly in the process.

Coal Conversion to Methanol

Coal can be converted to methanol by first forming a synthesis gas (carbon monoxide and hydrogen) via the coal-water reaction —

$$C + H_2O \rightarrow CO + H_2$$

The gas is then shifted to increase the ratio of hydrogen to carbon monoxide. The gas stream is purified, compressed, and converted to alcohol in a catalytic methanol-synthesis reactor. The methanol conversion is —

$$CO + 2H_2 \rightarrow CH_3OH$$
$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

All steps in the process involve current commercial technology, but nearly all synthesis gas for methanol conversion is now made by reforming natural gas because feedstock has been inexpensive. The reforming reaction is —

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

In coal-based methanol synthesis, a convenient gasification is the Koppers-Totzek Process because minimal methane and tar byproducts are formed. The resulting synthesis gas is shifted to provide a molecular hydrogen/(carbon monoxide and 1.5 carbon dioxide) ratio of 2.05:1.[24] Table 14-8 summarizes the development status of methanol-synthesis processes.

Outside hydrogen could be used to enrich the stream, thereby eliminating the shifting step and increasing the amount of carbon monoxide available for conversion to methanol. Figure 14-4 shows such a process. The increase in product is substantial and would more than double the amount of alcohol produced from a ton of coal. This modified process is capable of using 42,000 SCF of outside hydrogen per ton of methanol produced. (See Table 14-9.) The hydrogen-rich synthesis gas stream is then sent to a pressurized catalytic reactor for conversion to methanol. About 92% of the additional carbon monoxide can be converted to product methanol. (Losses occur because of purging of unreacted carbon monoxide and some methanol.)

Table 14-8. COAL-TO-METHANOL PROCESSES

Process	Conditions	R&D Status
Gasification step		
Koppers-Totzek[4]	Any type coal, 2700°F, atmospheric pressure	16 plants in operation*
Lurgi[3,15]	Noncaking coal, 1300°F, 400 psi	58 plants constructed since 1936*
Methanol conversion step[24]		
Imperial Chemical Industries Ltd. (Low Pressure)	480°-570°F, 1500 psi	Current commercial process
Nissui-Topsoe (Medium Pressure)	460°-450°F, 2300 psi	Current commercial process
Japan Gas Chemical Co. (High Pressure)	4300 psi	Current commercial process

* None of these plants currently manufacture methanol.

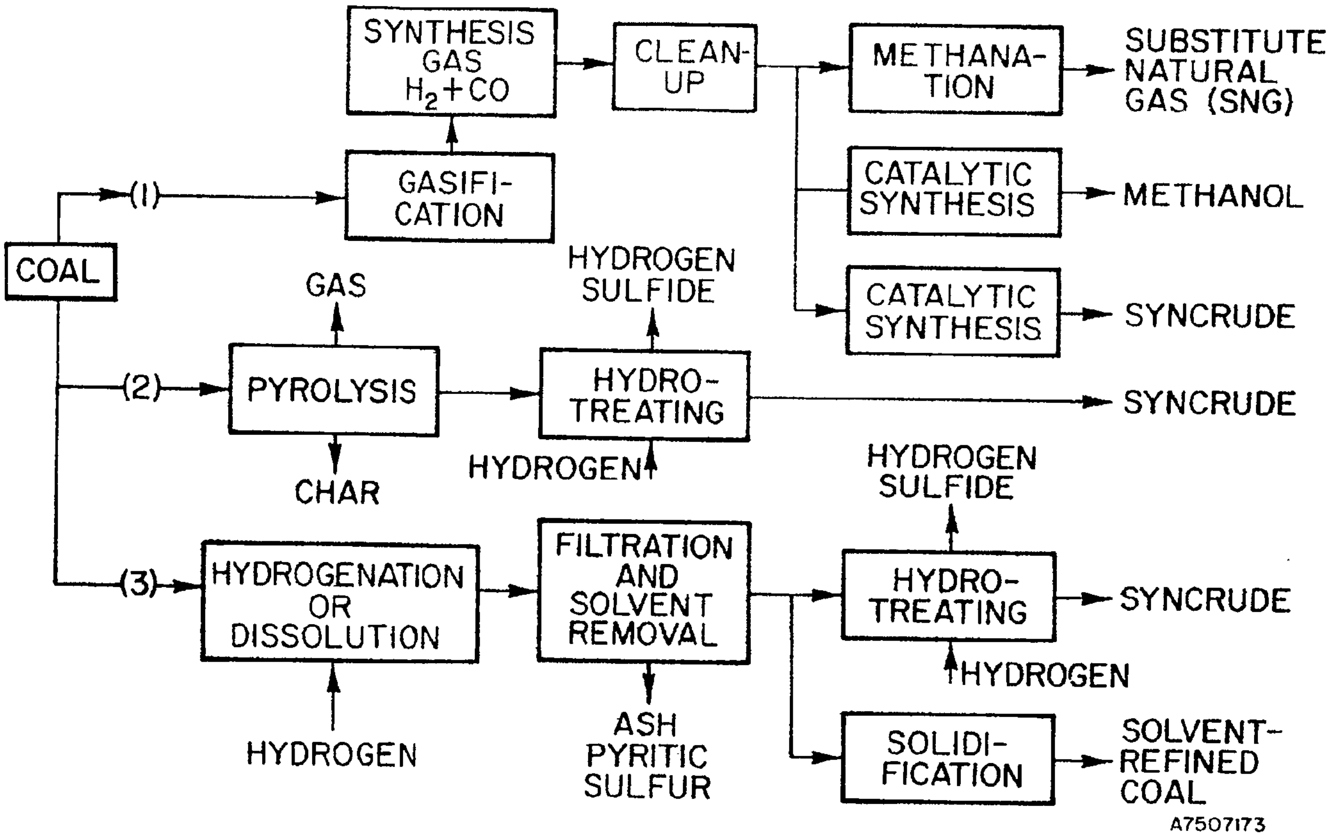


Figure 14-4. METHANOL PRODUCTION
(Koppers-Totzek Gasification and Imperial Chemical Industries Ltd. Conversion Processes)

Table 14-9. TYPICAL INPUT AND OUTPUT OF A CARBON MONOXIDE SHIFT REACTOR, KOPPERS-TOTZEK AND IMPERIAL CHEMICAL INDUSTRIES COAL-TO-METHANOL PROCESSES[24]
(5000 Tons/Day)

	Reactor Feed	Reactor Effluent
Component	Vol % (Dry)	
Carbon Monoxide	56.1	17.1
Hydrogen	33.2	50.0
Carbon Dioxide	8.3	31.3
Methane	0.1	0.1
Hydrogen Sulfide	1.2	0.9
Other	1.1	0.6
Total	100.0	100.0
10^6 SCF/Day	446	598

Amount of Carbon Monoxide Shifted to Produce Hydrogen –

0.561 X 446 X 10^6 SCF/Day (In) – 0.171 X 698 X 10^6 SCF/Day (Out)
= 148 X 10^6 SCF/Day

If No Shift Is Performed –

Amount of Hydrogen Required to Replace Shifted Carbon Monoxide = 148 X 10^6 SCF/Day

Additional Hydrogen Required to React With Additional Carbon Monoxide to Form Methanol = 2.05 X 148 X 10^6 SCF/Day = 303 X 10^6 SCF/Day

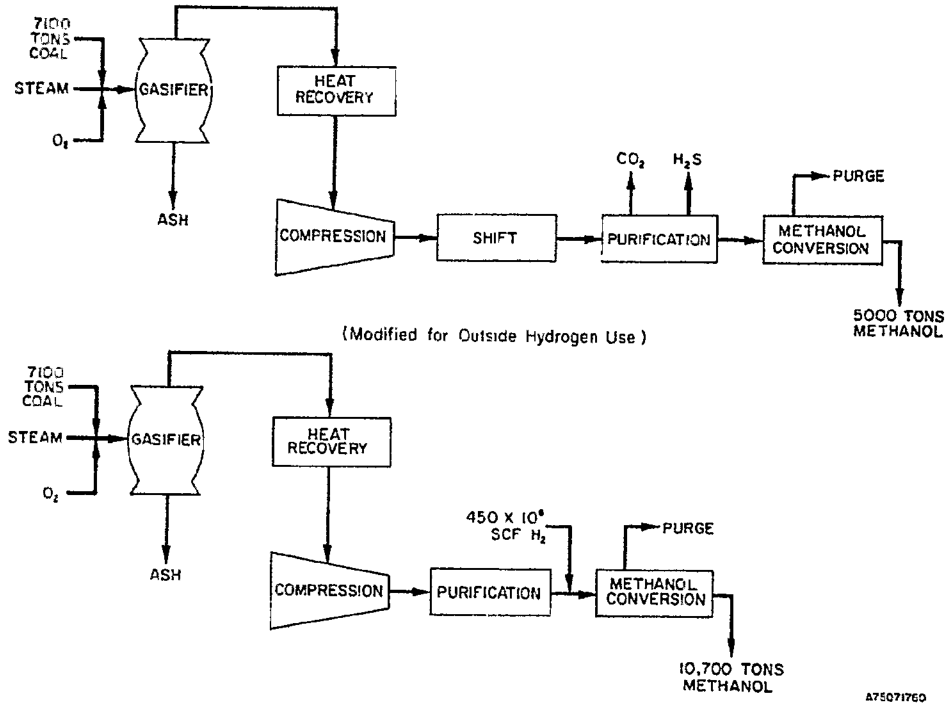
Total Hydrogen Required 451 X 10^6 SCF/Day

Additional Methanol Produced = 148 X 10^6 SCF of Carbon Monoxide/Day ÷ 380 SCF/lb-mol X 32 lb of Methanol/lb-mol ÷ 2000 lb/Ton X 0.92 Conversion Factor = 5700 Tons/Day

Volumetric Ratio of Outside Hydrogen to Methanol
= 451 X 10^6 SCF/Day ÷ (5000 + 5700) Tons/Day
= 42,000 SCF/Ton

Coal Conversion to Liquid Hydrocarbons

Coal can be transformed to conventional liquid products, such as gasoline, distillate fuels, and fuel oil, by many processes. Substantial restructuring of coal takes place, and most of the pyritic sulfur and mineral matter is removed.[15] The three routes by which coal may be liquified as shown in Figure 14-5.



(Modified for Outside Hydrogen Use)

Figure 14-5. PRODUCTION ROUTES: CLEAN FUELS FROM COAL

Coal liquids can be made indirectly by gasifying the coal, converting the gas to a rich synthesis gas (carbon monoxide and hydrogen), and catalytically recombining the carbon oxides and hydrogen to form light oils. Reactors are operated at pressures from 200 to 400 psi and at temperatures from 430°to 625°F. Various amounts of gas and light liquids can be generated by operating under different conditions of conversion severity (e.g., varying catalyst activity or tailgas recycle rate).[13] This was the first technology (Fischer-Tropsch) developed for making liquid hydrocarbons from coal, and it was used in Germany during World War II.[15]

In pyrolysis processes, coal is heated to break up polymeric carbon rings in the coal and to drive out all volatile components, which are collected, condensed, and separated into gas and oil. The raw oil is further hydrotreated to produce a synthetic crude oil product. Various amounts of fuel gas and char substance are usually produced.[34]

Coal can also be converted to liquid hydrocarbons by using a hydrogenation, or dissolution, process. Coal is slurried with a process-derived oil, heated to temperatures from 700° to 900°F, and allowed to react. A hydrogen makeup atmosphere may be present at pressures from 400 to 4000 psi. The coal dissolves and breaks up into lighter hydrocarbon fragments and gases. Hydrogen can then react with the free radicals in the coal, preventing formation of large amounts of gases or repolymerization to heavy liquids (asphaltenes). The processes also specify various liquid-solid separation schemes to remove the product oil.[15] Table 14-10 gives a brief description and status of liquefaction processes and R&D work.

As might be concluded, hydrogen is very important in the formation of liquid hydrocarbons from coal. It can be reacted directly with a coal slurry, as in a hydrogenation process, or it can be utilized to hydrotreat and upgrade a liquid or a gas produced from the pyrolysis or gasification of coal. Most processes can produce a high-quality crude with low sulfur and nitrogen contents; however, the syncrudes are more aromatic than conventional petroleum ones and will require more severe refining (i.e., hydrocracking).[14] The syncrudes typically have a specific gravity of between 15° and 30° API, a sulfur content of 0.1 to 0.2 weight percent, and a nitrogen content of 0.5 to 0.7 weight percent.

In calculating the hydrogen requirements for the processes it became apparent that, in general, production of liquids from Western U.S. coal requires more hydrogen than production from Eastern coal. It is assumed that the higher oxygen content of the Western coal is responsible for this difference, with hydrogen consumed in removing the oxygen as water.[37] Throughout this section, then, calculations are based on processing Western coals (high volatile C bituminous through lignitic).[9] In the manufacturing of hydrocarbon liquids there is concomitant fuel gas production, the proportion of which varies with each process. In performing calculations of hydrogen requirements, the number of liquid volumes produced was used as a basis

Table 14-10. COAL-TO-LIQUID HYDROCARBONS PROCESSES

Process	Reactor Conditions	Hydrogen Production Method	R&D Status
Pyrolysis			
COED[29]	4 pyrolysis zones of varying temperatures (600°-1500°F) 6-10 psi	Reform fuel gas from process, work underway to gasify char	36 tons of coal/day pilot plant in operation since 1970
Garrett[15]	1600°F, 50 psi	None specified	1/2 ton of coal/day pilot plant in operation since 1973
TOSCOAL[15]	800°-970°F, atmospheric pressure	None specified	25 tons of coal/day pilot plant in operation
Hydrogenation			
Consol Synthetic Fuel[24,25]	Noncatalytic extraction with hydrogen-donating solvent at 750°F, 150 psi; catalytic hydrogenation of solvent at 800°F, 3500 psi, ebullating staged-bed reactor	Gasify extract residue plus raw coal	20 tons of coal/day pilot plant in limited operation since 1967
Gulf Catalytic Coal Liquids[15]	800°F, 3000 psi, fixed bed catalytic reactor	Steam reform the light hydrocarbons produced	120 pounds of coal/day pilot unit in operation
H-COAL[15]	850°F, 3000 psi, ebullating catalytic reactor	Gasify raw coal and filter cake	3 tons of coal/day pilot plant in operation
SRC[2,26]	800°-900°F, 1000-2000 psi	Separate onsite coal gasification	6 tons of coal/day pilot plant in operation at Wilsonville, Alabama; 50 tons/day pilot plant recently completed in Tacoma, Washington
Synthoil[39]	800°F, 2000-4000 psi, fixed-bed catalytic reactor	Separate onsite coal gasification	1/2 ton of coal/day pilot plant in operation, 10 tons/day pilot plant in design stage
Gasification			
Fischer-Tropsch[13]	430°-625°F, 330-360 psi, fixed and fluidized catalytic-bed reactors	Reform internally produced methane	Commercial plant completed in 1955 at Sasolburg, South Africa

(i.e., SCF of hydrogen per barrel of liquids). Additional process hydrogen that could be used to synthesize SNG is not included. This factor, in addition to the different product slate of each method, makes direct comparisons of the processes difficult and possibly misleading when relying solely on hydrogen-consumption information.

Pyrolysis processes can use outside hydrogen in hydrotreating the recovered oil and can eliminate internal production of hydrogen from steam reforming of the coproduct synthesis gas. A plant conceptualized as producing 27,300 barrels of syncrude requires 136×10^6 SCF of hydrogen; thus hydrogen usage is 5000 SCF/bbl of syncrude produced.[32] More gas from the modified process is now available for use as fuel or feed for an SNG production system.

Selective hydrogenation involves formation of liquid hydrocarbons under more severe conditions of pressure, usually in the presence of a catalyst. Outside hydrogen can be directly added to the hydrogenation reactor or solvent regenerator to fulfill the hydrogen requirement. Using the H-COAL Process, 8500 SCF of hydrogen/bbl of syncrude are required to produce a high-quality crude of 32°API gravity that contains 0.1% nitrogen and 0.1% sulfur.[14] The Synthoil Process uses 6000 SCF of hydrogen/bbl of fuel oil (containing 0.2% sulfur) produced.[37] Use of outside hydrogen in these processes eliminates the need for production of hydrogen by gasification of various combinations of solid extract, char, or raw coal. Use of high-purity, pressurized hydrogen, as would be available from a pipeline, is very amenable to catalytic hydrogenation processes, which require a minimum hydrogen partial pressure of 1000 psi.

Hydrocarbon liquids can also be made by first gasifying the coal to a synthesis gas and then catalytically recombining the carbon oxides with hydrogen to make hydrocarbon liquids. This is commercially embodied in the Fischer-Tropsch Process. Production of 4000 bbls of light oils/day results in a hydrogen deficit of 6 million SCF. Currently this is mostly compensated for by reforming the product methane. Outside hydrogen usage could be about 1500 SCF/bbl. (See Table 4-11.) If outside hydrogen is used, methane need not be reformed, so more SNG is available from the process. Tar, tar oil, and naphtha produced in the gasifier could be partially oxidized to provide the carbon monoxide required for liquid synthesis.

Table 14-11. TYPICAL MATERIAL BALANCE OF GASEOUS STREAMS IN A FISCHER-TROPSCH FLUIDIZED-BED REACTOR[13]
(4000 bbl/Day)

Component	Reactor Feed	Reactor Effluent
	Vol % (Dry)	
Carbon Monoxide	25	2
Hydrogen	60	45
Carbon Dioxide	5	12
Methane	9	35
Other	1	6
Total	100	100
10^6 SCF/Day	146	55

Hydrogen Consumed in Reactor –

$0.60 \times 146 \times 10^6$ SCF/Day (In) $- 0.45 \times 55 \times 10^6$ SCF/Day (Out)
$= 63 \times 10^6$ SCF/Day

Amount of Hydrogen Available From Lurgi Gasifier –

$0.59 \times 96 \times 10^6$ SCF/Day of Synthesis Gas $= 57 \times 10^6$ SCF/Day

Hydrogen Deficiency Requirements –

$63 \times 10^6 - 57 \times 10^6 = 6 \times 10^6$ SCF/Day (Currently Supplied by Steam Reforming Internally Produced Methane)

Theoretical Volumetric Ratio of Hydrogen to Product –

$$6 \times 10^6 \text{ SCF} \div 4 \times 10^3 \text{ bbl} = 1500 \text{ SCF/bbl}$$

Oil Shale Conversion to Liquid and Gaseous Hydrocarbons

It is anticipated that oil shale will make a significant contribution to the U.S. fossil fuel supply in the foreseeable future. Kerogen and bitumen containing rock can be processed to release most of the carbonaceous matter that can be further treated to synthesize conventional refinery products.[31] Perhaps the key step in shale oil production is the retorting of the previously mined and sized shale. Heat is used to decompose the organic materials to water, carbon dioxide, liquid and gaseous hydrocarbons, and carbonaceous residue, which adheres to the spent shale. Conventional retorting is done at approximately 900°F.[1] Currently conceived retorting processes, which generally differ in their methods of heat generation and transfer, are summarized in Table 14-12.

A hydroretorting scheme is now under development at the Institute of Gas Technology (IGT) in which oil and gas are produced from shale by heating the shale in a hydrogen atmosphere. Testing indicates that a higher percentage of organic carbon is recovered with the use of hydrogen than with an inert atmosphere (98% versus 77% recovery). The additional hydrogen required for the process can be supplied by gasifying the heavy-oil fraction produced.[28]

The gas produced concurrently with the oil in the retorting step could also be used as a valuable coproduct. It is composed of carbon dioxide, hydrogen, carbon monoxide, LP gases, and hydrogen sulfide and is about 15 weight percent of the product yield.[24] After hydrogen sulfide removal, it could be used as an onsite fuel gas for process heat or electric power generation or could be further treated to make substitute natural gas.

The principal liquid product obtained from the retorting process is of a rather high specific gravity and nitrogen content. Consequently, it must be treated in some way before it can be refined to more valuable products. Catalytic hydrotreating is the preferred means of upgrading the raw oil to a synthetic crude.[16]

Currently conceived retorting schemes for the production of gases and liquids have no external hydrogen requirements. Conceptually, some hydrogen could be used in the production of SNG from fuel gas. Most retorts are designed to produce a preponderance of liquids that would be transported elsewhere for refining to marketable products. An outside source of hydrogen

Table 14-12. PROCESSES FOR OIL SHALE RETORTING TO GASEOUS AND LIQUID HYDROCARBONS[31]

Process	Retort Description	R&D Status
Development Engineering	Internal combustion of carbonaceous residue with air, countercurrent gas-shale flow	500 tons of shale/day testing completed
Gas Combustion	Internal combustion of gas and carbon residue, four functional zones	360 tons of shale/day testing completed
IGT	1200°-1400°F, 125-500 psi, three zones with externally heated hydrogen reaction atmosphere	1 ton of shale/hr pilot development unit nearly complete, laboratory thermobalance work continuing[8]
Lurgi-Ruhrgas	Externally heated sand, coke, or spent shale used in sealed, screw-type retort	12 tons of shale/day pilot plant operated (now dismantled)
Occidental	<u>In-situ</u> retorting of unmined shale by combusting with air	Field testing as of 1972
Petrosix	Externally heated gas retorts shale	2200 tons of shale/day semiworks plant in operation
TOSCO II	Externally heated spheres raise shale temperatures to 900°F at a pressured slightly above atmospheric	1100 tons of shale/day semiworks plant in operation
Union Oil	Internal gas combustion of shale fed into bottom of retort with a "rock pump"	Prototype work since 1950's on 1200 tons of shale/day unit

could not be easily integrated with proposed retorting schemes without more developmental work. A hydroretorting scheme under development at IGT would use an outside source of hydrogen in the retorting of liquids and gases from oil shale. The hydrogen consumption is 1900 SCF/bbl of oil produced and 1200 SCF/thousand SCF of SNG produced.[35]

The raw, retorted shale oil is usually too viscous for easy handling (i.e., by pipeline or tank car), so further treatment is required to facilitate transportation for refining. The raw oil also contains more sulfur and nitrogen than conventional refining catalysts can withstand. A hydroprocessing step is most convenient for upgrading the shale oil to a more typical crude.[14] About 1300 SCF of hydrogen would be consumed in producing one barrel of high-quality syncrude (36°API, 0.02% sulfur, 0.6% nitrogen, and no fraction boiling over 950°F).[11] The oil can also be made less viscous by using a coking or "vis-breaking" operation at the retort site, but this would result in more severe refining conditions and would not significantly reduce the overall hydrogen requirements.[23]

The hydrogen requirements for the synthetic fuel processes are summarized in Table 14-13.

Table 14-13. TYPICAL HYDROGEN REQUIREMENTS FOR PRODUCTION OF SYNTHETIC FUELS

Process	Amount of Hydrogen/Unit of Product
Coal to SNG	
Lurgi single-stage gasification	970 SCF/1000 SCF
Multistage hydrogasifiers	1100-1500 SCF/1000 SCF
Coal to Methanol	42,000 SCF/ton
Coal to Syncrude	
Pyrolysis	5000 SCF/bbl of syncrude
Hydrogenation	6000-8500 SCF/bbl of syncrude
Gasification (Fischer-Tropsch)	1500 SCF/bbl of light oil
Oil Shale to Syncrude	
Conventional retort	1300 SCF/bbl of syncrude
Hydrogasifying retort	1900 SCF/bbl of syncrude

The Economics of Outside-Hydrogen Utilization

The use of outside hydrogen requires process and equipment modifications that generally simplify the production of synthetic fuels. Most of the reduction in complexity is due to the elimination of the onsite hydrogen-production facility itself. The deletion of a shift reactor or special gasifier obviously reduces capital requirements, maintenance costs, and process utility requirements. An external hydrogen supply relieves the synfuel processes from having to operate at conditions to optimally make both product and feed for hydrogen production.

Because synthetic fuels processes can be greatly simplified by the use of outside hydrogen, the economics of outside-hydrogen utilization are not straightforward. A preliminary economic analysis was performed that compared the synthetic product costs for internal and external sources of hydrogen. The analysis was based on data from Volume III of "Alternative Fuels for Automotive Transportation — a Feasibility Study."[24] An item-by-item comparison of process components was made for three all-coal synfuel process plants and three coal-plus-hydrogen plants to determine the capital investment and operating cost for SNG, methanol, and liquid-hydrocarbon production. Outside hydrogen was treated as a purchased utility for each of the process families. Costs are based on constant 1973 dollars, allowing product-price determinations for comparison of synthetic-fuel processes involving internal and external hydrogen production. A discounted cash flow (DCF) method was used to determine costs, and economic values were set as follows:

- A 25-year plant life expectancy
- Depreciation calculated on a 16-year, sum-of-the-digits formula
- 100% equity capital
- A 48% Federal income tax rate
- A 12% DCF rate
- Plant startup costs as expenses in year 0.

Break-even costs for synthetic fuels were estimated by comparing an all-coal process with a coal-plus-hydrogen process (at given coal costs) to determine the hydrogen cost that would result in the same product price for both systems. We assumed that hydrogen would arrive by pipeline at 1500 psi, because transmission studies have shown that hydrogen can be moved more economically at such pressures.[17] The results are presented in Figure 14-6. Combinations of coal and hydrogen costs above and to the left of the lines indicate that it is economically desirable to utilize outside hydrogen for the processes while values below and to the right indicate that it is economically undesirable.

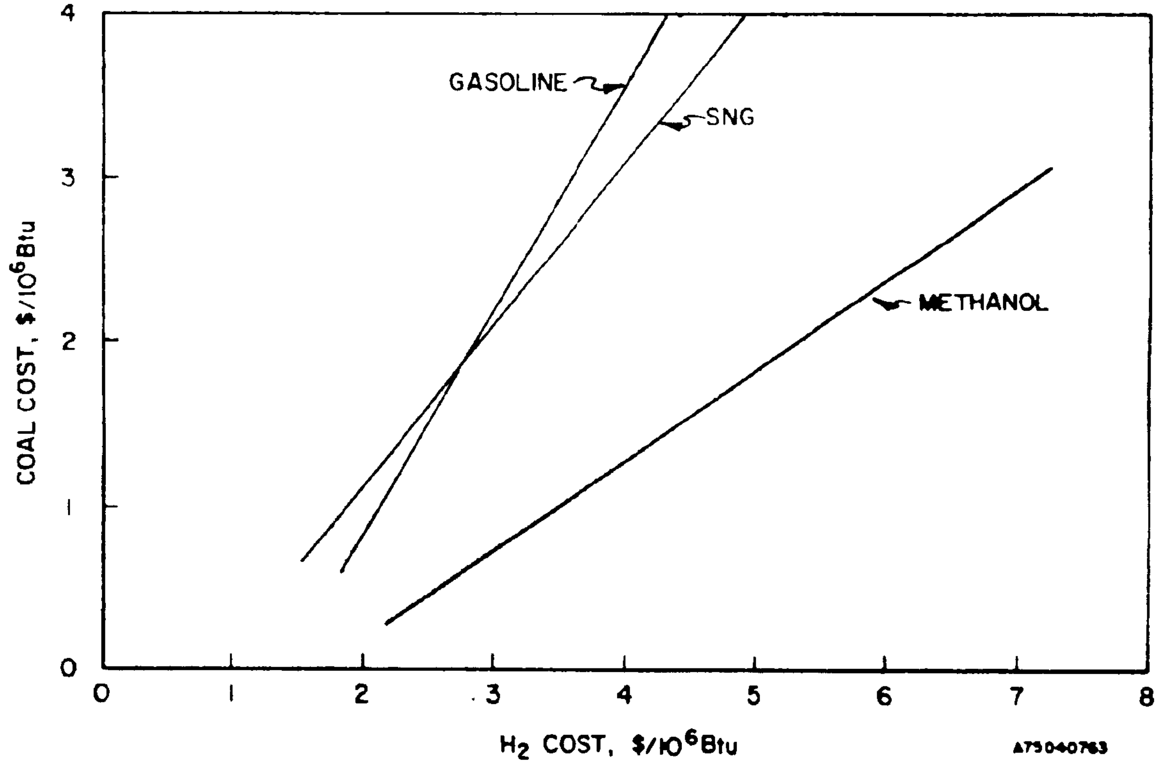


Figure 14-6. BREAK-EVEN COSTS FOR SYNTHETIC-FUELS PRODUCTION FROM COAL AND COAL-PLUS-HYDROGEN PROCESSES

By parametrically varying the cost of coal and hydrogen, it was determined that methanol production favors the use of outside hydrogen at $4.10/million Btu when coal costs exceed $1.15/million Btu. The corresponding methanol price is $115/ton.

For SNG production, a set of raw-materials costs can be determined at which the cost of manufacturing the product is the same, \$6.52/1000 SCF, for both conventional and modified processes. The resulting break-even coal cost is \$3.20/million Btu, and the hydrogen cost is \$4.10/million Btu.

Gasoline can be made from the hydrocarbon product that is made from coal by using the Consol Synthetic Fuel (CSF) Process. Detailed economic information was available for this process using Eastern U.S. coal only. The amount of hydrogen used is on the same order as that used in other processes that consume Western U.S. coal, so an economic comparison of conventional and modified CSF Processes that use Eastern coal should indicate the same trends as a comparison of other coal-to-gasoline processes that use Western coal. In this analysis, the amount of process hydrogen required for the refinery was also included.

No credit was given for by-product coal residue now available from the modified processes. The residue has a sulfur content slightly higher than that of the coal originally fed, so only if low-sulfur coal is used can the residue be marketed (e.g., as a fuel for power generation). The break-even raw-materials costs for synthetic gasoline processes are \$3.74/million Btu of coal and \$4.10/million Btu of hydrogen. The resulting gasoline product price for both types of processes is \$54.52/barrel.

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15. RESEARCH AND DEVELOPMENT RECOMMENDATIONS

From the results of this study, it is clear that there are no major technical reasons for hydrogen not becoming a key component of the future U.S. energy system. However, during the course of this study we found numerous instances in which the ultimate potential of the hydrogen-energy system was unclear because some elements had not been sufficiently developed. Many technologies that are still only conceptualizations or laboratory-scale projects could significantly lower the delivered cost of hydrogen or increase its utility. In this section of the report, we will develop a list of research and development projects that are intended to develop branches of hydrogen-related technology, with the aim of eventually introducing hydrogen on a large scale. If these programs are to be of maximum benefit, they should be completed within the next 5 years.

Production of Hydrogen

This study did not uncover any revolutionary hydrogen-production process that would completely eclipse present-day or contemplated processes. On the other hand, we did find that developmental projects could reduce costs and raise efficiency in established hydrogen-production processes (e.g., electrolysis and coal gasification), could bring advanced processes (e.g., thermochemical production) out of the laboratory, and could establish the feasibility of processes that are currently only concepts (e.g., photosynthesis and those processes based on thermonuclear fusion).

Electrolysis

Research is needed on all aspects of electrolysis. Catalysis, electrode structure, and electrode materials should be investigated. New separators and electrolytes should be developed, and the possibility of better cell design and better power-conditioning equipment should be looked into. Due to experience gained in the development of fuel cells, which are very similar to electrolyzers, some desirable directions for research on electrolyzers are obvious. Because the electrolyzer industry alone cannot afford to carry out the necessary research, this research, conducted on both alkaline and ion-exchange cells, should be supported by either the Federal Government or the potential users of hydrogen.

This support should be divided into that for basic research on electrode structure and gas evolution and that for cell R&D on other topics. Funding for basic research programs should be from $50,000 to $100,000/year. Cell R&D will be more expensive to carry out and should be funded at between $500,000 and $1,000,000 annually. An electrolyzer that operates at about 1.5 volts (a thermal efficiency of almost 100%) and at a current density of about 500 A/sq ft in a piece of equipment with a total capital cost of between $50 and $100/kW input is a reasonable research objective.

For reasons that were pointed out earlier in this report, we recommend that no research on the electrolysis of impure water be funded.

Often, possibly misleading comparisons are made between optimized nuclear thermochemical systems and nonoptimal nuclear electrolytic systems. A short, perhaps 2-year, study to determine the cost effectiveness and efficiency of a nuclear-powered electrolysis plant, specifically designed for hydrogen production, is needed. Such a study would cost between $50,000 and $100,000/year. A program of this type has been funded as a continuance of this program.

The production of hydrogen by thermal-electric or photovoltaic conversion of solar energy should also be investigated. A 3 year, conceptual-design study could be conducted, at the same level as the optimized nuclear-electrolytic study, to provide the technical and economic data needed for comparisons with other processes.

Coal Gasification

The practicality of hydrogen production by the gasification of coal should be further assessed to determine not only how this production method compares with nonfossil-based processes, but also how it compares with traditional methane reforming and partial oxidation of fuel oil. Such information would be of great interest to industries that, because of natural gas curtailments, may soon be faced with the problem of finding an alternative hydrogen source. Several studies should be performed in order to examine the numerous possible gasification schemes. Approximately $100,000 to $200,000/year would be required per study.

Thermochemical Methods

The development of a successful thermochemical water-splitting process could be the key to the introduction of hydrogen as a fuel. It seems likely that thermochemical hydrogen production could significantly lower the price of nuclear-based hydrogen. Three or four laboratory projects should be funded at from $750,000 to $1,000,000/year until a good cycle emerges. Efforts should be directed toward identifying suitable energy sources besides HTGR's and developing more efficient cycles that operate with noncorrosive reactants. These programs eventually should develop kinetic data and heat and material requirements for the most promising cycles.

Application of Controlled Thermonuclear Fusion

A short feasibility study, about 2 years in duration, at a cost of from $50,000 to $75,000 is needed to assess the possibility of water splitting by ultraviolet light beams. Further R&D should be recommended if the concept shows merit.

Photosynthesis

Photosynthetic hydrogen production is very promising for the long term, and appropriate research strategy would seem to be basic and long-range, as well as exploratory shorter range, research in the areas in which breakthroughs are expected or required. The probability of success will be proportional to the number of individual creative scientists (or scientific groups) involved, rather than to the total manpower or money invested. Several independently sponsored groups, funded in relatively small increments (e.g., from $50,000 to $200,000/yr), should maintain close communication to advance conceptual developments. Suggestions for specific projects would best be made by the investigators themselves and evaluated by peer review (with creative feedback). The interdisciplinary nature of the task should be recognized; and cooperation, as well as communication, among representatives from the various disciplines should be encouraged. In particular, colloid catalysis, electrochemistry, and ligand field theory, together with engineering theory, may be helpful. The long-range nature of the problem should be recognized, and funding should be continuous throughout the next 5 years.

Table 15-1 is a summary of the recommended hydrogen-production R&D projects.

Table 15-1. HYDROGEN PRODUCTION – GOVERNMENT RESEARCH AND DEVELOPMENT RECOMMENDATIONS, 1975-1980

Program Title	Years Pursued	Average Annual Funding Level per Program, $1000	Number of Programs	Total 5-Year Period Funding, $1000	Project Description	Project Goals
Electrolysis of Water (Basic Research)	Cont.*	50-100	1-3	250-1,500	Basic work on electrode structure and the mechanism of gas evolution	Achieve 1.5 volts at 500 amp/sq ft; $50-$100/kW capital cost (cell and ancillaries) with 750-1000 psi delivery. Derive less expensive catalytically active electrodes
Electrolysis of Water (Cell R&D)	Cont.*	500-1000	1-3	2,500-15,000	Parallel programs on alkaline and ion-exchange type cells	Increase operating temperatures and pressures; less dependence on noble-metal catalysts
Integrated Nuclear-Electrolytic Production Facility (Concept Study)	2	50-100	2	200-400	Conceptual engineering design and preliminary economic assessment of dedicated nuclear facility	Provide technical and cost information for advanced production facility planning; provide equitable "referee" concept for nuclear thermochemical facility evaluation; evaluate land- and offshore-based options
Solar Hydrogen-Production Facility (Concept Studies)	3	50-100	3	450-900	Conceptual engineering design and preliminary economic assessment of solar hydrogen plant	Provide technical and cost information for advanced production facility planning; determine relative role of thermal-electric and photovoltaic energy-conversion modes; evaluate land- and ocean-based options
Hydrogen from Coal (Application Studies)	2	100-200	[illegible]	400-800	Small programs to explore new technology (related to making hydrogen from coal) that is not being developed by other coal-gasification research	Identify ways of making hydrogen from coal that are better than those being developed as part of coal-to-methane projects. If this goal should be reached, large sums ($20-$30 million) would be needed for process development.
Thermochemical Water Splitting (Laboratory Research and Studies)	Cont.*	750-1000	3-4	11,250-20,000	Chemical-cycle derivation and thermodynamic evaluation; laboratory testing of reaction steps; heat-source/cycle interface study; detailed efficiency and flow-sheet analysis and economics assessment	Find more efficient cycles with less corrosive materials; determine operating conditions and measure kinetics; define heat requirements and materials; assess overall practicability and economics; determine suitable energy sources other than HTGR's
Controlled Thermonuclear Fusion Production (Feasibility Assessment)	2	50-75	1	100-150	Theoretical feasibility study of the applicability of fusion to hydrogen production	Assess practicability and recommend R&D as appropriate. (Large sums will be needed if these concepts show promise.)
Photosynthetic Production (Basic Research)	Cont.*	50-200	5-7	1,250-7,000	Parallel research on identification of photosynthetic water-splitting mechanisms and electron transport in both "natural" and "synthetic" systems	Determine general chemistry of photosynthetic steps; demonstrate "synthetic" photosynthetic approaches; modify steps for hydrogen production and determine stabilization techniques

* Continuous support over a 5-year period recommended.

Delivery and Storage of Hydrogen

At present, there is no widespread system for the transmission and distribution of hydrogen. The small-scale distribution systems that have been built (like those of NASA) are probably unsuitable as models for a large-scale system, which must be relatively inexpensive. Despite the success of these small systems, there are numerous technical questions about hydrogen distribution that remair unanswered and possibly some technical problems that remain unsolved.

Pipeline-Materials Compatibility Evaluation

Whether hydrogen can be transmitted through existing natural gas pipelines or whether new pipelines will be needed because of materials problems has yet to be resolved. The materials studies conducted thus far have identified potential problem areas, but have not provided any definite answers. This question should be answered soon because it has significant bearing on how and when hydrogen could be used as a "universal fuel." More than one study of the problem should be funded at approximately $300,000/yr, and results would probably be available in 2 years. These studies should investigate hydrogen-related problems such as loss of metal ductility, hydrogen stress cracking, and hydrogen-environment embrittlement in pipeline steels. If problems exist, possible solutions should be evaluated.

Hydrogen-Transmission-System Experimental Feasibility Studies

If hydrogen-environment embrittlement in pipeline steels proves to be a manageable problem, an investigation into the behavior of other gas-transmission-system equipment with hydrogen should be undertaken. The equipment should be tested under anticipated operating conditions, thereby identifying any furhter complications. Concurrently, engineering studies should be undertaken to determine the economic feasibility of hydrogen transmission. We estimate that the cost of the experimental equipment-compatability study would be $300,000/yr and that the design and costing study might require as much as $100,000/yr for about 3 years. A large-scale system test costing $5,000,000 would follow these preliminary studies.

Pipeline Compressor Evaluation

Early studies of hydrogen pipelining show great divergence on the subject of hydrogen compressors and the units that drive them. A small-scale study (approximately $100,000/yr for 2 years) could determine the best compressor-prime mover combination and could provide data for the transmission-system cost study described above.

Underground and Hydride Storage of Hydrogen

Underground cavities will allow for inexpensive hydrogen storage,if such a method of storage is possible. Preliminary feasibility studies (both theoretical and experimental) on the effects of the presence of hydrogen on the mechanisms of gas sealing should be undertaken. Two 2-year studies, costing $75,000/yr, should be adequate. Later, far larger sums will be needed for full-scale field testing.

Storing hydrogen in the form of metal hydrides may be important not only for mobile applications, but also for electric-utility peak shaving and as an alternative to underground or line-peak storage. New alloys are still being identified, and support for several laboratory efforts should continue at a minimum of $200,000/yr for the next 5 years. New alloys should be lower in weight and in volume per weight of hydrogen stored and should dissociate at practical temperatures. The specific applications will determine the optimum characteristics, but low cost will be important in almost all.

Behavior of Hydrogen in Gas-Distribution Equipment

There is a dearth of information on the behavior of hydrogen in existing natural gas distribution lines and related hardware. Experimental studies should be conducted to determine the problems encountered with the meters, regulators, and various nonferrous pipe materials in distribution systems. A study of this sort could take several years at an average cost of $300,000/yr.

Improved Cryogenic Systems

Although the amount of energy lost in hydrogen liquefaction is large because of current liquefaction technology, there may be cases in which hydrogen liquefaction is the only practical storage alternative.

Large-scale, liquid-hydrogen facilities (for both processing and storage) are not cheap, but perhaps need not be as expensive as they are now. Engineering studies directed toward the design of economical, very large-scale liquid-hydrogen tankage should be undertaken by prospective equipment manufacturers. Integrated storage schemes that allow utilization of boil-off gases would be worthwhile.

The possibility of liquid-hydrogen transmission should also be studied, especially in the context of integrating it with superconducting or "cryoresistive" cables for electric-power transmission. The advantage of being able to combine it with electric-power transmission may make the transmission of liquid hydrogen more attractive than has been the case with liquid natural gas. There seems to be little urgency for this work because cryoresistive-transmission technology has been developed to only an early stage thus far. Studies on cryogenic systems should be funded continuously at \$75,000/yr.

Hydrogen Odorants and Illuminants

Because hydrogen gas is odorless and its combustion is nonluminous, odorants and illuminants will have to be selected and added to the gas. These substances should be as pollution free in combustion as possible and should not impair the operation of catalytic devices. (Methylmercaptans, the odorants added to natural gas streams, are sulfur-containing compounds that might poison the platinum catalysts used in some experimental burners.) The identification of odorants and illuminants is not a pressing task, but it should be undertaken within the next 5 years. The effort need not be large: \$50,000 to \$75,000/yr for two programs (one on odorants and one on illuminants, with intercommunication) over a 2-year period should produce the desired results.

Table 15-2 is a summary of the recommended hydrogen-delivery R&D programs.

Utilization of Hydrogen

Studies of Hydrogen Utilization in Industry

Our study has identified at least five large industrial processes that are potential users of hydrogen. These are 1) direct reduction of iron ores, 2) ammonia synthesis, 3) methanol synthesis, 4) process-steam generation, and 5) production of synthetic fuels from coal. Although these markets for feedstock hydrogen are not as large as the market for gaseous fuel, they deserve special consideration because their economics may allow them to use

Table 15-2. HYDROGEN-DELIVERY RESEARCH AND DEVELOPMENT RECOMMENDATIONS, 1975-1980

Project Title	Years Pursued	Average Annual Funding Level per Program $1000	Number of Programs	Total 5-Year Period Funding, $1000	Project Description	Project Goals
Pipeline-Materials Compatibility Evaluation (Materials Investigation)	2	300	2	1200	Experimentally assess any hydrogen embrittlement problems encountered when transmitting hydrogen through present-day natural gas pipelines	If embrittlement problems are found to be serious, large additional programs will be needed to test solutions.
Hydrogen (Gas) Pipeline Design and Costing (Engineering Study)	5	100	1	500	Gaseous-hydrogen transmission system evaluation; to be begun after preliminary studies are completed	Establish optimized hydrogen-pipeline-system characteristics and component requirements; determine transmission economics (related to those of natural gas)
Hydrogen (Gas) Transmission System Experimental Operating Loop (Experimental Feasibility Project)	1	5000	1	5000	Testing of gaseous transmission equipment (compressors, metering devices, etc.) under actual pressures and flow conditions with hydrogen. Program to commence after preliminary studies are done	Evaluate present natural gas transmission equipment under anticipated hydrogen conditions and over extended periods; develop modified and new components and subsystems as required; derive engineering design and operating experience
Pipeline-Compressor Evaluation (Design Study)	2	100	1	200	Selection and design of large hydrogen-pipeline compressors and drives	Determine best compressor type and matched prime mover for large diameter hydrogen pipelines; document technical specifications and costs
Underground Hydrogen Storage (Feasibility Study)	2	75	2	300	Feasibility assessment of storing gaseous hydrogen underground; one study each on aquifers and mined caverns	Evaluation of suitability of present natural gas techniques for underground storage of hydrogen; estimate quantities of storage in present reservoirs and those potentially developable in the United States; develop economics of underground storage
Metal-Hydride Storage (Basic Research)	Cont.*	200	[illegible]	1000	Search for promising metal hydrides for stationary (and mobile) storage applications	Identify practical materials and evaluate on the basis of developed criteria (heat of formation, dissociation temperature, weight and volume, cost, etc.)
Hydrogen (Gas) Distribution System (Experimental Feasibility Study)	Cont.*	300	1	1500	Testing of gaseous distribution equipment (mains, meters, regulators, etc.) under actual pressures and flow conditions with hydrogen	Evaluate present natural gas distribution equipment under realistic hydrogen conditions and over extended periods of time; provide basis for modifying equipment and introducing new equipment; derive engineering design and operating experience
Improved Cryogenic Systems	Cont.*	75	2	750	Assessment of required advancements and initial hardware efforts in cryogenic hydrogen technology	Technological improvements to achieve high efficiencies and low costs; focused studies and preliminary hardware work to advance the technology in a) liquefaction, b) transmission (pipeline and vehicular) and c) storage-container (from small portable to large stationary) application sectors
Hydrogen Odorants and Illuminants	2	50-75	2	200-300	Devising of practical additives to hydrogen to provide for olfactory and visual (flame) warnings to personnel with unwanted side effects	Provide for several candidate hydrogen odorant and illuminant materials that do not adversely affect catalysts and other exposed materials; demonstrate economic feasibility and practicability in the field

*Continuous support over 5-year period recommended.

hydrogen that is too expensive to be used as a fuel. Thus, these processes, especially ammonia synthesis, may be the first applications for hydrogen technology — even while new, low-cost methods of hydrogen production are under development.

Feasibility studies, in greater depth than those done in this study, should be conducted to determine the conditions under which it will be economical to use "outside" hydrogen in these processes. Three of the processes (steam production, ammonia synthesis, and methanol synthesis) involve only a moderate amount of new technology, and feasibility studies could be conducted at a cost of from $75,000 to $100,000 per process.

The use of pure hydrogen in the direct reduction of iron ore will, as was discussed in Section 12, require the development of a few new materials-handling techniques. The problems are not serious, but they will require some experimental work. For this reason, feasibility studies on this process should be funded at a higher level, about $150,000/yr for from 1 to 2 years. Multiple efforts would be more likely to produce satisfactory results.

Outside-hydrogen utilization by the future synthetic-fuels industry will also require a more complicated feasibility study. The fundings and time scale should be about the same as that for the direct-reduction process.

Development of Hydrogen-Fueled Appliances

The assessment of the adaptability of present-day appliances to hydrogen fuel, as shown in Section 13, has not really progressed beyond the discussion stage. Nevertheless, any widespread use of hydrogen as a replacement for natural gas will probably require the conversion of many natural gas appliances. Experimental studies to determine what conversion parts and procedures will be necessary should be initiated soon. Two or three such studies at about $250,000/yr should provide answers in from 2 to 4 years.

Very little work has been done on the development of catalytic appliances. These devices exploit the full potential of hydrogen and should be developed if for no other reason than to provide a basis for comparison of hydrogen with other, more developed energy options. Better catalysts (both high and low temperature) and improved burner configurations are needed, and practical prototype appliance models should be developed. Because the work is still in a highly creative stage, multiple efforts (perhaps as many as four) should be undertaken. The cost of these programs would be from $100,000 to $250,000/yr (depending on the scale of the proposed development), and the projects should continue for the next 5 years.

Besides the across-the-board conversion of all gaseous-fuel equipment in given areas to hydrogen, hydrogen might be used as a gaseous fuel by blending it with natural gas supplies. A study of this possibility should begin immediately and should be continued at $100,000/yr for the next 5 years as the natural gas situation changes.

By-Product Credits

A potential-market study should be initiated immediately on the use and value of the oxygen produced as a by-product in the manufacture of hydrogen.* An economic analysis of long-distance oxygen transmission by pipeline should be included in this study. Studies should be made on an industry-wide basis (perhaps by the government), but the detailed equipment development probably should be performed by existing large-scale oxygen suppliers. We estimate that these studies will cost a total of $100,000/yr for a 2-year period.

The recommended R&D programs on the utilization of hydrogen are summarized in Table 15-3.

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* There is the possibility of by-product oxygen use in very rapidly growing markets, such as synthetic-fuels manufacture and sewage treatment, within the next few years.

Table 15-3. HYDROGEN-UTILIZATION RESEARCH AND DEVELOPMENT RECOMMENDATIONS, 1975-1980

Program Title	Years Pursued	Average Annual Funding Level · per Program, $1000	Number of Programs	Total 5-Year Period Funding, $1000	Project Description	Project Goals
Hydrogen for Industrial Process-Steam Generation (Applications Assessment)	2	100	2	400	Evaluation of hydrogen as an energy source for generation of process steam through 1) conventional boilers and 2) hydrogen-oxygen combustion	Determine technical steps for industrial-boiler modification to hydrogen; evolve an optimized (but otherwise conventional) hydrogen-fueled boiler design; provide commercially usable hydrogen-oxygen steam generator system designs; document supporting technology requirements
Optimized Ammonia Production Facility Based on Hydrogen Feedstock (Preliminary Design Study)	1	75	1	75	Preliminary design of an advanced technology, ammonia-synthesis plant based on hydrogen feedstock	Determine design elements of ammonia facility with sufficient costing to evaluate the economic crossover point for a range of natural gas and hydrogen feedstock prices
Optimized Methanol Production Facility Based on Hydrogen Feedstock (Preliminary Design Study)	1	75	1	75	Preliminary design of an advanced-technology, methanol-synthesis plant based on hydrogen feedstock	Determine design elements of methanol facility with sufficient costing to evaluate the economic crossover point for a range of natural gas and hydrogen feedstock prices
Direct Hydrogen Reduction of Metal Ores (Feasibility Study)	1-2	100-150	1-3	100-900	Determination of valued metals whose ore can be directly reduced with hydrogen where feasibility is not in-hand. Process development activity will be pursued in the case of iron/iron ore	Evaluation and improvements of known processes of direct iron-ore reduction with hydrogen (e.g., "H-Iron"); feasibility demonstrations in the case of nonferrous materials; supporting economic studies of commercialization potential
Hydrogen's Role in Synthetic-Fuels Production (Applications Study)	2	100-150	1	100-300	Hydrogen's role as a key constituent in synthetic-fuels production from coal; oil shale characterization and quantification	All significant synfuel-production requirements for hydrogen will be documented; its new and innovative uses will be defined; the potential role of coproduct oxygen will be assessed for synfuels production; economic crossovers will be determined based on coal and shale oil costs and on the process equipment required for onsite hydrogen manufacture versus the cost of externally delivered hydrogen
Conversion of Natural-Gas-Fueled Appliances to Hydrogen (Exploratory Development)	2-3	250	2-4	1000-3000	Investigation of procedures and hardware modifications required for retrofitting of existing fuels	Identify hardware approaches and installation procedures for across-the-board retrofitting; estimate costs for "mods" and for installation
Catalytic Combustion Devices Using Hydrogen (Applied Research)	Cont.*	100-250	2-4	1000-5000	Identification of the best catalysts for low- and high-temperature catalytic combustion; develop suitable configurations for residential, commercial, and industrial burners (including ventless units)	Demonstrate practical catalytic burners for all application sectors that provide acceptable operations, efficiency, and emissions
Hydrogen as a Natural Gas Additive (Study and Planning)	Cont.*	100	1	500	Determination of overall system implications of adding substantial quantities of hydrogen to the natural gas supply as "natural gas stretches"	Determine the ramifications to all facets of the natural gas production, delivery, and utilization areas as progressive amounts of hydrogen are added; identify the cost-optimum maximum hydrogen addition point; develop a long-range plan for this mode of conversion
Oxygen Utilization (Market Study)	2	100	1	200	Investigate new markets for coproduct oxygen	Define and quantify (as a function of price) new and innovative uses for oxygen; assess delivery requirements

*Continuous support over 5-year period recommended.

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