

this technology would be applicable to the very large-scale production envisioned in this report.

The work on high-temperature-solid-electrolyte work has virtually stopped. This approach was developed by General Electric⁶ to the point of laboratory demonstration models, but work was discontinued in 1969.* The work at Westinghouse on high-temperature fuel cells could be adapted to water (steam) electrolysis, but no programs of this nature are currently being pursued.

One of the more potentially rewarding areas for research and development appears to be in increasing the cell operating temperature, from the current $\sim 180^{\circ}\text{F}$ to $\sim 350^{\circ}\text{F}$. Specific tasks would be to find a satisfactory material to replace the asbestos separator and the gasketing and insulating materials. Another approach would be to further investigate a flow-through electrode concept which would eliminate the need for some of these special materials.

Engineering development work is required so that much larger cells than those now being made could be mass produced and that would have the required performance, lifetime, and cost. The development effort should result in the demonstration of a 10-MW(e) electrolysis modular unit that would form the basic building block of a 100-MW(e) demonstration plant. The 55-ton/day [100 MW(e)] demonstration plant using off-peak power should be a development goal for 1978-1980.

Another recommended area for future research and development is in improving the power conditioning system, particularly as it might couple with large nuclear reactors.

3.1.2 Thermochemical and radiolytic means for production of hydrogen as a fuel

Physical principles and theory. Electrolysis of water suffers from inherent thermodynamic limitations on the efficiency of initial conversion of thermal to electrical energy (currently $\sim 30\text{-}40\%$) in addition to an expected maximum realizable electrolytic efficiency of about 80 to 90%. The large-scale needs for fuel therefore justify

* In the G.E. Aircraft Equipment Division a solid polymer electrolyte system is being developed.

attempts to find processes that may exceed the 35 to 40% overall efficiency* of electrolysis for hydrogen production expected by the end of this century. With the development of high-temperature nuclear fission reactors (and the potential development of fusion reactors), two conceivable processes for the production of hydrogen from water are thermochemical and radiolytic. Solar and geothermal energy also are potential alternative heat sources for the thermochemical route.

Thermochemical production of hydrogen involves the decomposition of water via absorption of thermal energy (heat). The decomposition of water may be accomplished in a single, direct chemical reaction requiring extremely high temperatures (greater than 1500°C), or it may be caused to occur via a sequence of chemical reactions whose net result is the decomposition of water to hydrogen and oxygen. The appropriate selection of reaction steps in the sequence and the optimum operating temperatures (if chemical compounds having the necessary thermodynamic characteristics can be found or produced) is, in principle, capable of providing increased efficiency of conversion of thermal energy (and water) to hydrogen. Although thermochemical cycles also are thermodynamically (Carnot) limited in efficiency, it may be possible to employ higher temperatures than can be employed in a steam-electric generating plant, thereby providing more effective utilization of the available thermal energy from a nuclear reactor or other primary heat source.

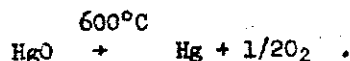
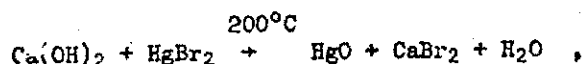
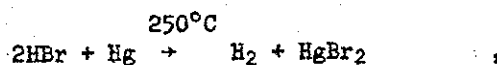
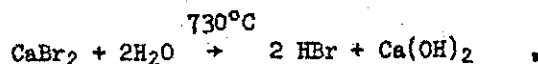
Radiolytic production of hydrogen involves the direct absorption of fission energy, from fission fragments, gamma, or other nuclear radiation, by water to form hydrogen and oxygen, which must then be separated. Efficiencies are described in terms of "G" values, numbers of molecules of product formed per 100 eV of energy absorbed, or as percentages of thermal yield of desired product.

Current status of technology. Thermochemical or radiolytic processes to produce hydrogen for an energy source are not in use today. However, a reasonably comprehensive overview of current research and development is provided by some of the papers presented at a Symposium on Nonfossil Fuels held at the Boston meeting of the American Chemical Society, April 6, 1972.

*As indicated above, this efficiency is closely coupled to the efficiency of electricity generation and may eventually achieve a level of 50% or more.

A paper, "A Chemical Process to Decompose Water Using Nuclear Heat," by G. DeBeni and C. Marchetti, describes work by the only group that is really active at present.* It is a 25-man effort funded by the Euratom Atomic Energy Establishment. The paper describes a multistep reaction scheme involving HgBr_2 and CaBr_2 with a claimed efficiency estimated at 40 to 60%.

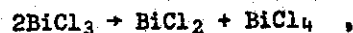
The proposed reaction sequence is as follows:



A paper on "Thermodynamics of Multistep Water Decomposition Processes," by J. E. Funk, stemmed from a 5000 man-hour effort sponsored by the U.S. Army in connection with interest in a portable energy depot. The work was done by the Allison Division of General Motors from November 1964 to November 1965, and the project has not been active since then. Part of the work involved a thorough thermodynamic survey that covered virtually the entire periodic table and led to the definite conclusion that no simple two-step process would suffice. More optimistic results were produced by evaluations of several three- and four-step reaction sequences such as:



*Other efforts are believed to be starting at the Institute of Gas Technology, Gulf General Atomic, General Electric Co., and in Germany.



A detailed analysis of one four-step process involving chlorides of vanadium showed that when all heats of reaction and reaction inefficiencies are allowed for, the thermal energy requirement is greater than that which would be used to generate the electricity required for a water electrolysis process.

A paper on "A Review of Nuclear Sources of Nonfossil Chemical Fuels" by Meyer Steinberg, Brookhaven National Laboratory, arose from a background of numerous radiolytic schemes that were exhaustively studied in the 50's and early 60's. Radiolytic methods seemed generally impractical because of the low yields.

That nuclear heat is not an essential was shown in a paper on "A Macro System for the Production of Storable, Transportable Energy from the Sun and the Sea," by W. J. D. Escher. The proposed concept used solar energy to convert seawater (purified) via electrolysis into cryogenic hydrogen and oxygen in a 1000-MW system.

Another possibility, using a solar furnace operating at 4000°F, has been suggested by J. M. Holmes of ORNL. His process calls for the thermal decomposition of CO_2 to give CO, followed by the reduction of water by CO to give hydrogen. The thermal energy consumption would be about 40 kWhr/lb of H_2 , compared with 60 kWhr/lb of H_2 for electrolysis in combination with nuclear electricity at current process efficiencies.

The novel method of producing hydrogen from water was proposed by B. J. Eastlund and W. C. Gough.⁷ It is known that ultraviolet light of wavelength below 1849 Å will produce hydrogen from water with a quantum yield of about 0.4. Photons of such energy can be produced with high efficiency when high-atomic-weight elements, such as aluminum, are injected into the ultrahigh temperature, low density hydrogen plasmas which are characteristic of controlled fusion experiments. The photons

would be allowed to escape from the plasma through ultraviolet windows into chambers containing water vapor at appropriate pressures. On the basis of several assumptions regarding efficiencies of the processes involved, the authors calculate an overall efficiency for hydrogen production higher than obtainable by electrolysis using fission-reactor-produced power.

Direct thermal dissociation of water has also been proposed using either solar energy⁸ or nuclear heat from a power type reactor operating at 2200°K.⁹

Economics. The total thrust of the work on thermochemical and radiolytic schemes is to make energy more economically (as well as more cleanly, which may also be an economic advantage). None of the proposed processes have been developed to the point where meaningful cost estimates are available. In principle, however, the direct use of thermal energy and the total recycle of the chemicals would point toward attractive process economics. However, with the four-step processes, the process flow sheet is likely to be complicated by chemical separation equipment and heat recovery systems.

Ultimate potential. The role of thermochemical or radiolytic processes in a future hydrogen economy is problematical but requires further consideration because it is potentially so valuable. At present the main goal is to compete with electrolysis of water.

Although thermochemical methods of producing hydrogen from reactor heat do not now appear likely to result in large savings compared with the electrolysis route, even a 1% advantage would result in an annual savings approaching \$1 billion, because of the large scale of production if natural gas and gasoline are replaced by hydrogen or hydrogen-based synthetic fuels. This potential saving would seem to justify a considerable amount of research. If economical cycles can ultimately be developed to replace electrolysis (which presumably would have to replace steam reforming of fossil fuels, as their supply diminishes and the environmental costs increase), hydrogen plants may be incorporated into nuclear power plants, but may require new plants capable of

achieving higher temperatures than obtainable from those currently used or planned.

It has not yet been demonstrated that thermochemical processes may become competitive with electrolysis for conversion of nuclear heat to hydrogen. They may find application as topping cycles, producing hydrogen thermochemically by absorbing nuclear heat at temperatures higher than usable in a steam cycle, and delivering heat, at a lower temperature, to the steam cycle. Any such cycle must be demonstrated competitive with other topping cycles such as thermomechanical cycles using potassium vapor as the working fluid.¹⁰

Environmental and resource effects. As with any thermal process, a certain fraction of the degraded heat must be discarded to the environment, but development of more efficient processes would reduce this waste heat. Pollution control must be designed into the specific process employed; for example, the DeBeni-Marchetti process under investigation at Ispra employs large quantities of mercury, whose escape to the environment must be prevented. However, the main effects are quite beneficial, for example, more efficient use of energy, less pollution, and elimination of land despoilment by strip mining, etc. Chemical cycles are at present insufficiently well defined for assessment of environmental effects of production facilities. Direct thermal decomposition of water, if proved feasible, will have the least environmental effect since it utilizes no inputs other than heat and water and no intermediates as would be required in stepwise chemical processes.

The coupling of thermochemical or radiolytic processes with nuclear breeder reactors would virtually remove the demand on nonrenewable resources.

Safety and reliability aspects. Thermochemical or radiolytic processes are not likely to present any new safety problems or hazards that are not already associated with industrial or utility practice.

Because of materials problems due to corrosion at high temperatures, a considerable amount of research and development will be required for most thermochemical schemes to achieve assured reliability.

The combination of corrosive chemicals and high temperatures (and pressures) that characterize most of the proposed processes leads to difficult compatibility problems.

Research and development requirements. Assessment of the ultimate potential of thermochemical or radiolytic hydrogen production is hampered by the lack of feasibility demonstrations, experimental or theoretical, for commercial processes on a large enough scale to supply even a fraction of projected energy requirements as a replacement for natural gas. Estimates to date have failed to demonstrate a possible efficiency advantage over electrolysis, but the possibility of such an advantage has not been ruled out. In view of the potential benefits of a scheme which could surpass electrolysis in reduced thermal energy requirements, a definitive evaluation of the potential of thermochemical methods is required. This should involve the following steps:

1. A review of existing theoretical thermodynamic methods for screening proposed chemical cycles. The aim of this review should be to establish criteria and their reliability for estimating process efficiencies, particularly for multistep processes.
2. Examination of thermodynamic data available for screening proposed processes. It may prove necessary to generate new thermodynamic and kinetic data for some classes of compounds to permit reliable evaluation of process feasibility.
3. Detailed evaluation of the potential efficiency of currently proposed processes such as the Mark I (DeBeni and Marchetti) and halogen-water reactions.
4. Examination of the thermodynamics of combined processes, such as thermochemical plus electrolytic and radiolytic plus thermochemical, to evaluate prospects of increased efficiency. These include proposals for additives in electrolytic processes to utilize mechanisms involving hydrated electrons, which would, however, necessitate an additional chemical recycling step.
5. A definitive comparison of the relative efficiencies achievable for hydrogen production by topping cycles consisting of chemical cycles, direct or indirect, and thermochemical topping cycles, for example, with

potassium as the working fluid.

6. Economic analysis of relatively small-scale hydrogen production facilities employing fission waste heat or radiolysis, urban wastes, etc. Can the hydrogen produced, considering capital costs involved, in fact, pay for part of the costs of safeguarding the fission products, disposing of wastes, etc., or will they simply add to the cost?

There should be a search for new thermochemical and radiolytic methods not previously proposed. The proposed processes are still in the stage of requiring further laboratory research to establish feasibility. Even after establishing theoretical feasibility, there remain the questions of materials compatibility, etc. In fact, the reaction systems currently proposed have serious unresolved materials problems. Since these proposed processes are in a feasibility proving stage, it is difficult to define a complete research and development schedule required to bring them into commercial practice. It is already fairly well known that chemonuclear plants are not now feasible economically. Also efficient two-step thermochemical processes for producing hydrogen apparently do not exist.

Interest recurs in the possible direct cracking of water and separation of the hydrogen at elevated temperatures. The extremely high temperatures required, greater than 2000°C, pose severe materials and corrosion problems, but employment of the technology of the high-temperature "Rover" nuclear rocket engine at Los Alamos has been suggested. An investigation of means of separation would be required since the suggested scheme of expansion of the gases may not be sufficiently rapid to prevent recombination of hydrogen and oxygen.

Because of the high temperature required, thermochemical processes would be feasible only with relatively high-temperature energy sources, solar, nuclear, etc. Such energy systems may also play an important interim role in providing heat for coal gasification and a long-term role in supplying industrial heat requirements. Thus the development of thermochemical production is coupled with the development of a sizable high-temperature primary energy industry.

3.1.3 Biological production of hydrogen and other synthetic fuels

Biological processes for the production of synthetic fuels in a limited manner have been in use for many years. Primary examples are the generation of methane from sewage and the fermentation of grains and sugars to produce alcohol. Many of these processes will be discussed in the reports of other panels, Solar Energy, Use of Urban Waste, etc., so that no technology or economic details will be repeated here. In most cases, such systems are dependent on the diffuse solar energy input or the relatively slow processes of bacterial action and therefore may be difficult to scale up economically to the very large sizes required to meet a significant share of the future demand for fuels.

It is possible to use photosynthetic organisms in a photochemical fuel cell. Plants and blue-green algae can utilize water as a reductant in light-dependent generation of compounds (such as reduced ferredoxin and viologens) which are equivalent to molecular hydrogen as reductants. In addition, in the living organism, the reduced ferredoxin and adenosine triphosphate are then used to reduce carbon dioxide to cell material. However, the production of cell material is not a necessary step in the harnessing of light energy. Energy storage as hydrogen would be more efficient and more direct. Such a conversion could be accomplished if the photochemically reduced reductants (ferredoxin, etc.) were coupled to a hydrogenase. Essentially this process would represent a photolysis rather than an electrolysis of water. The requirements for such an aqueous system would be (1) light, (2) a stabilized photochemical apparatus capable of generating reductants from water, (3) ferredoxin or a similar electron carrier, and (4) a ferredoxin-coupled hydrogenase. The critical requirement of this system is the stabilization of the photochemical apparatus.

The efficiency of the proposed photosynthetic fuel cell appears to be sufficiently high to be economically useful. Energy conversion yields up to 10% are encountered in the isolated photosynthetic apparatus under laboratory conditions. If such yields can be obtained with a stabilized photochemical system, it can be readily calculated

that of the $0.8 \text{ cal cm}^{-2} \text{ min}^{-1}$ of solar energy which strikes the earth's surface every day, the total yield of the proposed photosynthetic fuel cell would be around $500 \text{ kcal m}^{-2} \text{ day}^{-1}$. A 500-ton/day hydrogen production plant would require an area of 14,000 acres, or about 22 sq miles.

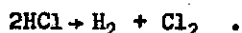
There has not been sufficient research to permit an evaluation of the economic merit of this approach. Research into the photolytic production of hydrogen should be increased at least to the point where economic evaluations are possible.

3.1.4 Combination production systems

Several hydrogen production systems have been studied which combine two of the above production processes. One which was evaluated as part of the hypersonic transport system (HST)¹¹ makes use of a thermal process followed by an electrolytic one, as follows:



elect.

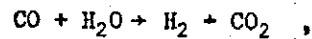
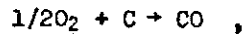
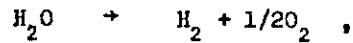


The first reaction is assumed to take place at 1500°F and 770 psia and requires a reaction energy of 2.48×10^4 Btu/lb-mole Cl_2 . The second electrochemical reaction was assumed to require 12.06 kWhr/lb H_2 (at 300 psia), which in itself is about 30% less electrical energy than required for direct water electrolysis.

The first reaction was studied as part of the work related to the Energy Depot Program¹² and was found to have quite serious material problems and relatively low yields. Therefore this system does not appear to offer serious competition to the water electrolysis system. However, if a large HCl waste stream were already available, it should be an attractive system for producing hydrogen and a valuable by-product, Cl_2 .

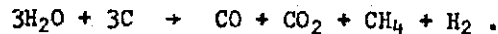
Another combination system which should be considered combines water electrolysis with a synergistic steam-coal chemical reaction as follows:

elect.



and

heat

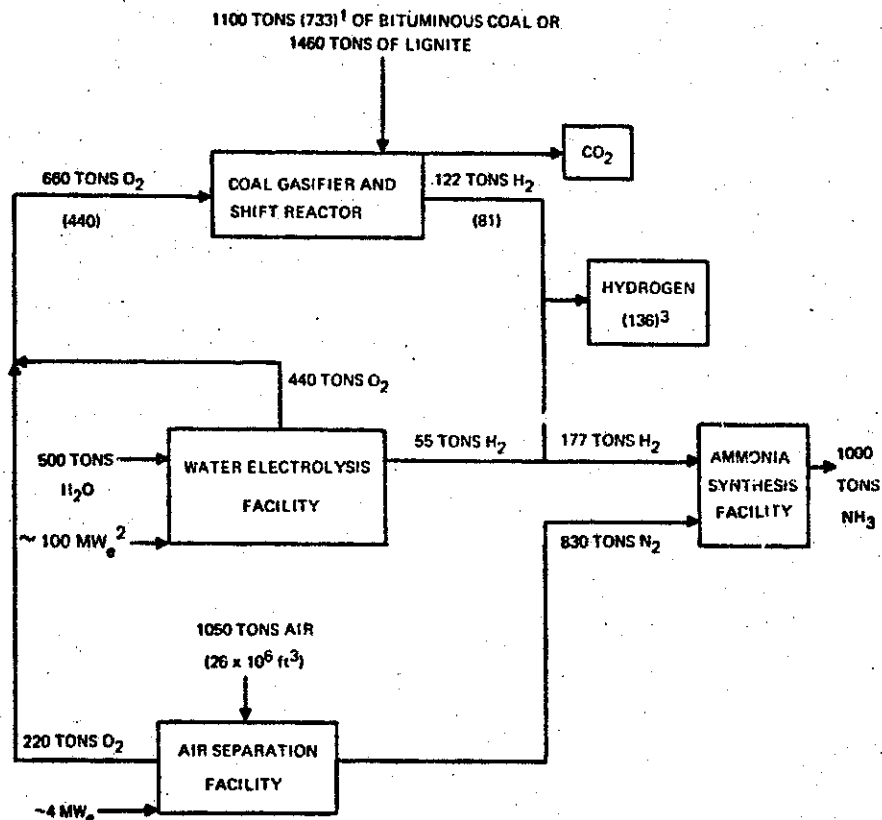


The oxygen-steam process was also evaluated as part of the HST study and shown to be an attractive process, particularly if low-cost coal or lignite were available (see Sect. 3.3). With the above combined process, it is estimated that 40% of the hydrogen produced would be via the electrolytic route, while 60% would be attributable to the coal processes. A 500-ton/day hydrogen plant would require an electrical input of 370 MW(e) plus a coal input of 2700 tons/day. A simplified flow sheet is shown in Fig. 6. Such a fossil-electrolytic production process would likely be more economical than an entirely electrolytic plant in the near term.

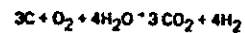
3.2 Other Synthetic Fuels

Hydrogen can be converted into other fuel forms which may be able to overcome some of the disadvantages of the low-density or cryogenic handling problems associated with hydrogen. The production of such fuels is described below and includes ammonia, methanol, and hydrazine. Other synthetic fuel forms which could be considered as a nondepleting resource and also of nonfossil origin are the metals. For example, aluminum or magnesium produced by electrolytic processes could be stored

ORNL-DWG 73-3887



OVERALL COAL GASIFICATION REACTION (THEORETICAL):

¹Quantities in parentheses are for H₂ - only plant²Electrical capacity for 55 ton/day of H₂ production³Production of 500 tons H₂/day would require 37(1) MW_e and 2700 tons coal/day

or shipped and then burned in air to release energy. The oxides could then be collected and reconverted to the metal form for further use. Since this system did not appear to be as attractive from an overall efficiency standpoint as the hydrogen-based system, it was not considered further by this survey.

3.2.1 Ammonia

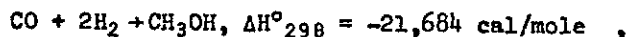
Ammonia is produced by direct catalyzed synthesis from hydrogen and nitrogen (2000-5000 psi and 200-500°C). The basic process has been in commercial use for many years and is considered to be a highly developed technology. As new plant capacities have increased from 300 tons/day in the 1950's to 1700 tons/day at present, the price of ammonia has decreased steadily from \$45/ton to the present \$20 to \$25/ton. Part of the cost decrease is also attributable to improved technology, including improved and larger compressors, improved catalysts, use of higher pressures, and vastly improved heat recovery systems. In addition, present excess capacity results in very great competition. It is doubtful whether further cost reductions greater than 5 to 10% can be achieved. The present process is so cheap and efficient that it is also very unlikely that it will be supplanted by alternative methods now being evaluated, including biological production, use of transition metal complexes, thermochemical methods, or magnetohydrodynamic generation; in fact, the last two methods appear to produce only nitrogen oxides and not ammonia. The U.S. production capacity is approaching 20×10^6 tons/year.

The only significant future change is in the use of new sources of hydrogen. The present low cost of ammonia is dependent to a great extent on the use of low-cost natural gas. As natural gas is depleted and costs increase, hydrogen production from steam-naphtha reforming and partial oxidation of various petroleum fractions will become more competitive. Likewise, as petroleum reserves dwindle, the higher-cost hydrogen from coal and shale oil will be required. At some point in time it appears that water electrolysis, particularly in high-efficiency

cells, will produce hydrogen competitively in the U.S. with hydrogen from coal and oil shale. It should be noted that water electrolysis and certain of the future fossil fuel hydrogen production methods will require an air liquefaction facility to provide the required nitrogen. A schematic flow sheet for a combined water-electrolysis/coal gasification arrangement to produce 1000 tons of ammonia per day is provided in Fig. 6. Such a facility utilizes the oxygen co-product from water electrolysis for coal gasification, and the only waste streams are carbon dioxide and coal ash.

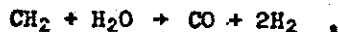
3.2.2 Methanol

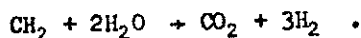
Physical principles and theory. Methanol is produced by reacting synthesis gas (composed of carbon monoxide, carbon dioxide, and hydrogen in the proper proportions) at various temperatures and pressures in the presence of a catalyst. The high-pressure processes (300°C, 4300 psig) use a zinc-chromium oxide catalyst, medium-pressure processes (400 to 560°C, 1500 to 2000 psig) use a copper-zinc catalyst, and low-pressure processes (250°C, 750 psig) use a copper-based catalyst.¹³ The synthesis gas reactions are as follows:



Synthesis gas is usually produced by reacting steam with methane which forms hydrogen, carbon monoxide, and carbon dioxide. It can also be produced from other carbonaceous materials including, of course, coal as discussed in Sect. 3.3.

In order for the ideal stoichiometric synthesis gas to be produced, the hydrocarbon feed to the reformer should have the empirical formula CH_2 .





Essentially all methanol manufactured in the U.S. is based on natural gas. Carbon dioxide is usually added to the feed to balance the excess hydrogen in natural gas.

Current state of technology and economics. The present rate of methanol production is approximately 1.34×10^9 gal annually¹⁴ (4.4×10^6 tons), representing 8.05×10^{13} Btu, which, for example, would amount to approximately 0.5% of the energy consumed in the transportation sector in 1968.

The average sales value of synthetic methanol was 17.5¢/gal¹⁵ (\$3.05/10⁶ Btu) in 1968 in large quantities and seems to have changed little since then. Since high-purity methanol is required in the chemical industry, it is reasonable to expect that a fuel-grade methanol can be produced with some reduction in retail prices. This is reflected in cost estimates made by Vulcan Cincinnati, Inc.,¹⁶ for methanol manufactured for consumption as methyl fuel (methanol + higher alcohols). A methyl fuel plant requiring an investment of \$150 million with a capacity of 20,000 short tons/day (~110,000 bbl/day) using a foreign natural gas feedstock of 10¢/10⁶ Btu equivalent will produce methyl fuel for approximately 3¢/gal (~52¢/10⁶ Btu), excluding the return on the investment.

A methyl fuel plant producing 20,000 tons/day of methyl fuel has a by-product of 200 million gallons of isopropanol per year and 100 million gallons of isobutanol per year. The value of these by-products to the chemical industry would probably limit the quantity incorporated in methyl fuel.¹⁷

Ultimate potential. Since the production of methanol is accomplished by reacting the most basic components (CO, CO₂, and H₂), it is not reasonable to assume that future developments would greatly improve the present process except for savings which might be realized by going to huge plant sizes. Since there are a number of possible sources for synthesis gas, it is reasonable to expect that methanol raw materials will be available for relatively long-term future needs.

Some of the sources for synthesis gas are as follows:

1. catalytic reforming of hydrocarbons;
2. partial oxidation of any carbonaceous materials such as coals, lignites, shale oils, agricultural wastes, etc.;
3. with supplementary hydrogen; basic oxygen furnace off-gas (CO) or ammonia synthesis by-product gas (CO_2);
4. producers gases or water gases;
5. hydrogen from electrolysis of water and CO_2 from limestone or the atmosphere.

There appear to be many sources of CO and CO_2 available as either a by-product or a primary product for many years to come. For the very long-term future, however, obtaining a source for carbon as required for the production of methanol would represent a relatively costly process. Large quantities of CO_2 are, however, available from the atmosphere (~0.03%), from seawater (as bicarbonate), and from limestone.¹⁸

Section 3.3.2 of this report contains an estimate of the economics of methanol from coal in which the costs of synthesis gas manufacture and of conversion to methanol are separately identified.

Environmental and resource effects. In the basic part of the process no pollutants are released to the atmosphere (catalytic reaction of the synthesis gas), although waste heat is rejected at 140°F. When coal becomes the basic raw material, ash will be generated during the synthesis gas production. Since the catalyst can be regenerated and recycled, this will not represent a significant depletion of irreplaceable resources.

Safety and reliability aspects. Methanol can be handled and used safely if the safety precautions are observed which normally apply to toxic and flammable liquids. The maximum allowable methanol vapor concentration for an 8-hr day is 200 ppm in air (500 ppm for gasoline). The ignition temperature for methanol in air is 693°F (gasoline 495°F). Inhalation of methanol vapors at 1000 ppm may cause slight symptoms of poisoning, but 50,000 ppm will cause profound and perhaps fatal narcosis in 1 to 2 hr. Oral intake will produce blindness or death; 1 or 2 oz