

Meeting U.S. Transportation Needs in the Hydrogen Economy

Hydrogen-fueled fuel cells promise clean, efficient, and sustainable energy that will help the United States meet its energy needs in the coming century and beyond, provided that there are economical and environmentally sound methods for hydrogen production. By far the greatest need will be in the transportation sector.

The following summary discusses the scale of hydrogen production required to meet U.S. transportation needs, current hydrogen manufacturing processes and use, and near- and long-term research on new methods of hydrogen production. Storage and distribution are not addressed.

Required Hydrogen Production

The U.S. consumed 7.9 million barrels of gasoline per day in January 2003. On that basis, 210 million kilograms per day of hydrogen would be required to operate the Nation's automotive fleet by fuel cell power. To produce the required amount of hydrogen using electricity, we will need 500 gigawatts of new electrical generating capacity.

Current Manufacturing Processes

Worldwide production of hydrogen is about 100 million kilograms per day, most of which is produced from natural gas by **steam methane reforming**. The energy efficiency for the conversion of natural gas to hydrogen is 58% if the carbon dioxide is sequestered. The hydrogen has small quantities of carbon monoxide, carbon dioxide, and hydrogen sulfide as impurities and, depending on use, may require further purification. Reactions similar to those that occur in steam methane reforming are used to produce hydrogen from water and other fossil fuels.

A small amount (~5%) of higher-purity hydrogen is made by **electrolysis** of water. This process is about 60–70% efficient in converting electrical energy to hydrogen energy. However, since the efficiency of making electricity from the primary fuel is between 30 and 40%, the overall efficiency of making hydrogen by electrolysis is between 20 and 30%.

Hydrogen made by steam methane reforming is used primarily as feedstock for the manufacture of ammonia or for upgrading heavy crude. Hydrogen made by electrolysis (higher purity) is used mostly in metallurgy and the manufacture of electronics and fine chemicals.

The hydrogen that will be needed for long-term efficient operation of polymer electrolyte membrane (PEM) fuel cells (the type used for transportation) must be high-purity, because carbon monoxide and hydrogen sulfide are common catalyst poisons.

Research for Hydrogen Production

Steam Methane Reforming: Research continues into steam methane reforming (see Appendix A), with concentration on better catalysts and heat sources other than natural gas to provide the process heat to drive the reaction.

Today, the catalysts used in steam methane reforming are made of fine particles of nickel dispersed on an alumina support. These catalysts have a lifetime of two to three

years, after which they lose their effectiveness. Three mechanisms lead to this loss of activity: *sintering*, in which the nickel particles agglomerate to form large inactive nickel particles; *poisoning*, in which trace quantities of sulfur in the natural gas feedstock react with the active catalytic site; and *fouling*, in which the feedstock decomposes to form coke that covers the active catalyst sites. The solutions to the three problems are similar—trace quantities of other elements added to the alumina support or to the nickel particles. The additives modify the behavior of the catalyst and change the deactivation rate. There has been a great deal of success in modifying the process or catalyst to solve any one of the problems noted above; however, for the process to be useful, improved resistance to sintering, poisoning, and fouling must occur concurrently. Research is focused on the understanding of the interactions among support, catalyst, and additives.

Because the steam methane reforming process is highly endothermic there is an opportunity to supply this heat from an external source. Of particular note is the use of nuclear heat at the HTTR facility in Japan. At this facility, the heat generated in a gas-cooled reactor is transported 80 meters to provide process heat for the reforming pilot plant.

On-board production of hydrogen from gasoline or diesel fuel continues to be a near-term option. Advantages include the ability to use the existing gasoline distribution network. The chemistry of **autothermal reforming** is similar to that of steam methane reforming, but differs in that there is a concurrent partial oxidation step, using a catalyst, to provide the energy for the reforming (hydrogen production). The hydrogen that is produced must be purified to remove hydrogen sulfide and carbon monoxide, both of which poison the fuel cell catalyst. Research in this area includes development of improved and poison-tolerant catalysts. Much of this work is done at Argonne National Laboratory.

Splitting water is a promising option for hydrogen production. Unfortunately, water is a very stable compound and does not break into significant quantities of hydrogen and oxygen until a high temperature is reached—between 2,500 and 3,000°C. Three major research thrusts aimed at producing hydrogen from water at much lower temperatures. The first is the use of **thermochemical cycles**, in which the energy for splitting the water is supplied in a series of steps. The second is **thermolysis** using catalysts and element-specific membranes. The third is high-temperature or **advanced electrolysis**.

Thermochemical cycles: A thermochemical cycle for water splitting is a series of reactions that, in total, are equivalent to the dissociation of water into hydrogen and oxygen (see Appendix B). All other chemicals are recycled, with no net consumption. Notable examples are the sulfur-iodine, calcium-bromine, magnesium-bromine, copper-chlorine, and iron-chlorine cycles. Each cycle depends on multiple oxidation states to split the water in a series of cyclic reactions.

The challenges for thermochemical cycles are the high temperature (~900°C) needed for at least one of the steps, the corrosive nature of many of the reactants, and phase changes in many of the gas/solid reactions. The advantages are that these reactions are amenable to normal chemical engineering processes and that their efficiency (the ratio of the heat content of the hydrogen produced to the heat required for the process) is in the 40–60% range. The sulfur-iodine process has been studied extensively by General Atomics and by Japan Atomic Energy Research Institute and flow sheets have been developed. The Japanese have also invested heavily in the calcium-bromine cycle. This cycle has been demonstrated at pilot-plant scale and is the one closest to commercial development. Overall efficiencies of 45–49% have been predicted for a plant that generates both electricity and hydrogen. While the calcium-bromine cycle has been disclosed in broad terms, comparatively little detail is known. Argonne is also studying a modified calcium-bromine cycle and a copper-chlorine cycle that promises to work at operating temperatures of less than 500°C. The latter cycle's heat requirements are within the range of current nuclear and fossil-fueled plants. For each of these processes, we are examining economics, unit operations, and environmental issues as a part of the project.

Thermolysis: A longer-term research program addresses the rapid thermolysis of water combined with efficient separation of the hydrogen and oxygen before they have an opportunity to recombine (Appendix C). The technology uses ceramic membranes through which oxygen ions can quickly pass, removing the dissociated oxygen from the water. Without the oxygen available to recombine with the hydrogen, the water continues to dissociate. This work, conducted at Argonne National Laboratory and sponsored by the National Energy Technology Laboratory, is in its early stages.

Advanced (high-temperature) electrolysis: The energy efficiency of electrolysis of water can be improved by increasing the temperature of the water even to above critical temperature. High temperatures make the electrolysis more efficient by reducing the energy required for dissociation, increasing the mobility of the ions, and reducing the overpotential. The major challenge for electrolysis will continue to be the efficiency with which heat can be converted into electricity.

Comparison of Hydrogen Production Methods

The table below provides estimates of the relative efficiencies of various hydrogen production methods. The efficiency is the ratio of the energy value of the hydrogen produced to that of the heat used in the process, except in the case of steam methane reforming, where it is the ratio of the energy of the hydrogen produced to that of the methane consumed.

Method	Maximum Process Temperature (°C)	Overall Efficiency (%)	Status
Sulfur-Iodine Thermo-chemical Cycle	850	45-49	Calculation ^a
Calcium-Bromine Thermochemical Cycle	760	36-40	Pilot Plant ^b
Copper-Chlorine Thermochemical Cycle	500	41	Bench ^c
Electrolysis	90	20-30	Commercial ^d
High-Temperature Electrolysis	800	40	Experiment ^e
Steam Methane Reforming (SMR)	900	77	Commercial ^d
SMR with CO ₂ Sequestration	900	58	Calculation ^f

^a Calculated from laboratory experiments and thermodynamic data. A full-scale pilot plant has not yet been built.

^b A pilot plant has been constructed.

^c The efficiency calculation is based on thermodynamics.

^d Commercial data.

^e Calculated from commercial electrolysis data and thermodynamic data. No pilot plant data are yet available.

^f Calculated from SMR commercial plant data and estimates of the energy required to sequester the CO₂.

Summary

- Steam methane reforming is a very efficient and cost-effective way to manufacture hydrogen. The issues are natural gas supply and carbon sequestration.
- Electrolysis is well understood, but its overall efficiency depends largely on efficient electrical generation.
- Thermochemical cycles have the potential to produce hydrogen from any high-temperature heat source with high efficiency in very high volumes. New research into lower-temperature cycles will increase the applicability.

- Other processes are being studied, but the technologies are not yet well enough developed for their potential to be evaluated.

Appendix A. Steam Reforming of Methane

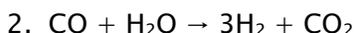
The most common method of producing hydrogen commercially is steam methane reforming (SMR).

SMR is a two-step process. In the first step, methane mixed with steam is passed over a nickel oxide catalyst at 900°C and about 30–40 atmospheres.



This reaction requires a large energy input, currently provided by burning natural gas or another fossil fuel.

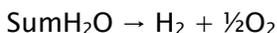
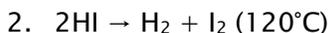
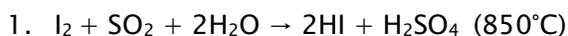
The second step is a water-gas shift reaction, sometimes known as a shift reaction, in which the carbon monoxide produced in the first reaction reacts with steam over a copper-on-zinc-oxide catalyst at about 200°C and 30–40 atmospheres, to form hydrogen and carbon dioxide.



The composition of natural gas is primarily methane, but like most fossil fuels, natural gas contains small amounts of sulfur-bearing compounds. In the methane steam reforming process, the sulfur species in the natural gas are converted to hydrogen sulfide. The hydrogen produced by SMR contains small quantities of hydrogen sulfide and carbon monoxide. Further purification steps yield hydrogen that is suitable for use in fuel cells.

Appendix B. Thermochemical Cycles

A thermochemical cycle for water splitting consists of a series of chemical reactions that, when summed, are equivalent to the dissociation of water into hydrogen and oxygen. All other chemicals produced in the cycle are reused, with no net consumption. The sulfur-iodine (S-I) process is used as an example:



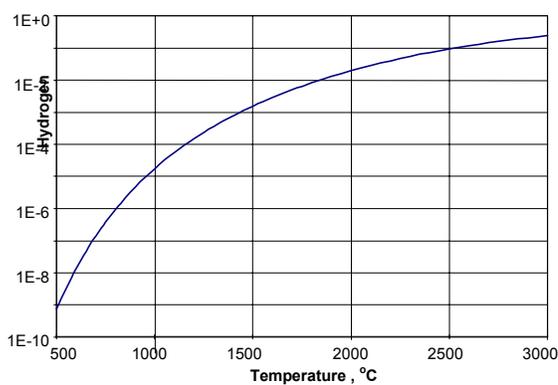
The water that is to be converted to hydrogen and oxygen is introduced in reaction 1. The hydrogen and oxygen products are produced in reactions 2 and 3, respectively. The other products from reactions 2 and 3 are the feedstock for reaction 1. If we sum the three equations, the overall result is H₂O decomposing to H₂ and ½O₂ (twice as much hydrogen as oxygen).

Water is a very stable compound and enough energy to create temperatures higher than 2,500°C normally is required to produce significant quantities of hydrogen and oxygen. Thermochemical cycles allow us to provide the energy in a stepwise fashion, at significantly lower temperatures.

Appendix C. Thermolysis

Water is a very stable compound that decomposes to hydrogen and oxygen in significant quantities only at temperatures above 2,500°C. The decomposition is highly temperature-dependant: at 1,000°C only 0.001% of the water is decomposed, at 2,000°C 1% and at 3,000°C 20%. This dependence is shown in the graph. (Note that the scale on the graph is logarithmic.)

There are ways to operate at temperatures below 2,500°C. One system uses a membrane that is permeable only to oxygen and not to either hydrogen or water. The membrane is made of an oxygen ion conductor. Water at 1,000°C flows on one side of the membrane and the small quantity of oxygen (0.001%) in the partially decomposed water is transported through the membrane. The water decomposes further and more oxygen is passed through the membrane. The water stream becomes a mix of hydrogen and water.



The system works because at 1,000°C water rapidly decomposes to hydrogen and oxygen (reaction 1 below) and the hydrogen and oxygen products rapidly recombine (reaction 2) to reform the water. There is a small equilibrium pressure of hydrogen and oxygen. If we remove the oxygen as it is formed, then the reverse reaction (2) does not occur and water continues to decompose to hydrogen and oxygen.

1. $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$
2. $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$

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