FUELS DECARBONIZATION AND CARBON SEQUESTRATION: REPORT OF A WORKSHOP

BY THE MEMBERS OF THE REPORT COMMITTEE

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EXECUTIVE SUMMARY

A plausible technological approach is beginning to emerge for the successful human management of carbon on a global scale indefinitely—without requiring, *a priori*, the sacrifice of the energy value of oil, gas, and coal. Using the vast quantities of carbon in fossil fuels in new ways could significantly reduce the rate of increase in the concentration of carbon dioxide in the atmosphere.

Implementing this "safer fossil" concept will require the traditional industries of oil, gas, and coal to assume a lead role. Effective partnerships will require the involvement of industry, government, academia, national laboratories, and non-governmental organizations.

The core idea is to separate the energy function from the carbon content of fossil fuels. Fuels would be "decarbonized" and used efficiently. The removed carbon would be deliberately "sequestered," that is, disposed of at a high concentration in such a way that the carbon does not reach the atmosphere for centuries or longer. Climate concerns would be directly addressed.

For example, natural gas could be "steam reformed" into hydrogen and carbon dioxide. The hydrogen could provide the fuel for fuel cells and combustion systems where hydrogen has a comparative advantage as a fuel. The carbon dioxide could be pumped into saline aquifers a kilometer or more below ground or into the deep ocean.

The sequestration capacity in the deep ocean and in deep aquifers appears to be adequate for at least several centuries of carbon disposal, although in both cases there are important unresolved questions related to integrity of storage, the interaction of deep and surface waters, accident hazard, and direct environmental impact.

Earlier studies have explored the sequestration of carbon dioxide produced at point sources, especially power plants. This report expands the objective to include the sequestration of carbon dioxide that would ordinarily be produced at dispersed sites, as a result of combustion in vehicle engines and at industrial and commercial facilities. Such a broad use of fossil fuels in ways compatible with the sequestration of their carbon could permit a significant fraction of the carbon in the fossil fuels used over the next several centuries not to be emitted directly to the atmosphere.

Many of the component technologies required for the "safer fossil" option have already been developed and are in various stages of commercial readiness:

> About 1% of U.S. primary energy production is converted to hydrogen for industrial chemical use, especially in refineries and ammonia plants. Significant amounts of hydrogen are piped and trucked hundreds of miles.

> Prototype buses and automobiles using hydrogen as a fuel are being tested. The development of hydrogen as a fuel is being spurred by the hydrogen fuel cell, an attractive emerging technology that has the potential to eliminate nearly all local air pollutant emissions and to improve vehicle fuel efficiency dramatically.
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> Limited quantities of carbon dioxide are currently routinely transported hundreds of miles through long-distance pipelines and pumped deep underground, principally to enhance the recovery of oil.
>
> Since 1996, Statoil, the largest Norwegian oil and gas company, has been separating carbon dioxide from offshore natural gas and sequestering it in a deep nearby aquifer for the explicit purpose of preventing atmospheric emissions. Confronted with an extension of Norway's tax on atmospheric releases of carbon dioxide to offshore oil and gas processing, Statoil is developing new technology and learning how to reduce costs.

Research on fuels decarbonization and carbon sequestration is already internationally coordinated. The total global effort is small, and the U.S. role is relatively small within it. Many new ideas deserve attention. Not only conventional natural gas but also coal, heavy oils, unconventional hydrocarbon fuels, biomass, and municipal wastes are potential feedstocks for hydrogen production. Methanol, ethanol, and methane are candidates for alternative "hydrogen-rich" secondary fuels when the decarbonized primary fuel is coal. The costs of fuels decarbonization may become less sensitive to scale. Slurries of carbon dioxide clathrates (ice crystals with carbon dioxide locked within them under pressure) may lead to less costly separation of carbon dioxide from other gases and less costly pipeline transport. Forms of sequestered carbon other than carbon dioxide may include carbonate rocks and elemental carbon.

The least costly first steps toward fuels decarbonization and carbon sequestration will probably involve industrial-scale production of hydrogen from natural gas and sequestration of the byproduct carbon dioxide. From this perspective, it may be productive to conduct a few pilot projects soon, involving the nearby sequestration of carbon dioxide point sources associated with industrial-scale hydrogen production at ammonia plants and oil refineries. In parallel, research can be conducted pertaining to what will probably be later stages of fuels decarbonization, where the fuel being decarbonized is other than natural gas, the hydrogen is supplied at a small scale to many dispersed users, or both.

Note that, in addition to industrial carbon sequestration (the subject of this report) there is a second kind of carbon sequestration, accomplished by green plants. Those human actions that enhance carbon sequestration by green plants are quite different from the actions required to sequester carbon directly in an industrial setting. Industrial carbon sequestration generally starts with carbon that is hundreds of times more concentrated than in the atmosphere. Deliberately pursuing carbon sequestration by green plants is important in its own right as a climate change mitigation strategy, but quite distinct.

It would be a great mistake to allow the preliminary attractiveness of the concept of safer fossil energy to crowd out the essential work now underway dedicated to developing complementary routes to the world's future energy system. No single technological approach, on its own, can do the full job of safely providing the energy needed for the next century—not renewable energy, not energy efficiency, not nuclear fission, not nuclear fusion, and not decarbonized fuels with carbon sequestration. The energy-environment challenge demands parallel work along many tracks at once. Only a broadly based effort can be defended.

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THE WORKSHOP AND THIS REPORT

A workshop, "Technological Opportunities for Fuels Decarbonization and Carbon Sequestration," was held in Washington, D.C., on July 28-29, 1997. Its goal was "to expand the set of greenhouse-gas technology options through a coordinated university/industry/laboratory program in fuels decarbonization and carbon sequestration." Its three purposes were:

- To assess the assumptions and results of existing integrative studies of greenhouse-gas mitigation achieved through the use of decarbonized fuels and carbon sequestration.

- To review the relevant studies on (a) conversion of carbonaceous feedstocks to hydrogen and alternative fuels, (b) carbon sequestration and utilization, and (c) fuels management and use.

- To identify opportunities for research and development.

The decision to hold a workshop was made in the course of several meetings of the Laboratory Research and Development Working Group of the U.S. Department of Energy, where the concepts of fuels decarbonization and carbon sequestration were reviewed. The U.S. Department of Energy (DOE) funded the workshop.

The 99 workshop participants had their institutional homes in industry, universities, the federal government, non-governmental organizations, and the DOE national laboratories. Among the attendees were DOE research managers based in several of its divisions. A full list of participants is found at the back of this report.

The workshop consisted of both plenary sessions and parallel sessions of three subgroups. The areas of concern of the subgroups reflected the second purpose listed above, which conceptualizes the topic under consideration as having separable but interlocking parts dealing with the processing of fuels, the sequestering of carbon, and the managing of hydrogen and other decarbonized fuels. The program of the workshop is also found at the back of this report.

This report seeks to capture several of the points of view developed during the workshop about how to frame a new technological concept so that the research community can become productively engaged. In Part One, the Overview, we present our broad findings. In Part Two we present our more detailed observations within the three areas of the workshop, under three headings: Technology Status, Barriers and Uncertainties, and Research Opportunities. The three sections of Part Two are not independent reports from the breakout groups: rather, material has been rearranged and substantial new material has been added, with the goal of minimizing duplication and providing a coherent narrative.

Although each section of Part Two of this report concludes with a list of research opportunities, these lists should be regarded only as illustrative. At the workshop, the participants did not seek to develop a comprehensive list of research areas, nor to prioritize within research areas.

The report contains a Technical Appendix that provides numbers not usually available in one place. It was developed, in part, to lower those barriers to working on these issues that come in the form of parallel metric and non-metric worlds.

A list of suggested readings is found near the end of this report. Much of the technical argument in the report is buttressed by these materials.

The Report Committee (its membership is listed on the title page) includes the members of the workshop's Organizing Committee, the workshop's three rapporteurs, and those other workshop participants who chose to become active in the preparation of this report.

The workshop and this report benefited immeasurably from the dedication of many individuals at DOE. Phil Stone and Ehsan Khan at the Office of Energy Research, Robert Kane and David Beecy at the Office of Fossil Energy, and Allan Hoffman and Sigmund Gronich at the Office of Energy Efficiency and Renewable Energy were particularly committed to the success of the enterprise. Assisted by James Caverly and Juanita Hayes, Robert Marlay functioned as DOE coordinator and provided wise council throughout the project.

At Princeton, Michelle Marean, Elaine Kozinsky, and Sean O'Brien worked tirelessly and cheerfully to gather the participants' suggestions and to produce this report.

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PART ONE: OVERVIEW

A NEW ENERGY STRATEGY

It has been widely assumed that the atmosphere is the only possible direct recipient of the carbon dioxide produced as energy is obtained from fossil fuels. A workshop held in Washington, D.C. on July 28-29, 1997, challenged this assumption. The workshop explored the possibility that safe and reliable technological systems could capture much of this carbon dioxide and send it to other destinations, such as deep underground or deep in the ocean.

In today's world, where increasing effort is being devoted to the task of developing a greenhouse-responsive global energy system, the implications are profound. The conventional view today is that any greenhouse-responsive energy strategy requires curtailing the use of fossil fuels. Because fossil fuels currently provide about three quarters of global primary energy (and almost 90% of U.S. primary energy), curtailing their use entails great dislocations. We suggest that the conventional view is incomplete. The full set of greenhouse-responsive options includes strategies that use fossil fuels in new, but entirely recognizable ways.

The name of the workshop, "Fuels Decarbonization and Carbon Sequestration," captures the new systems idea, but requires unpacking. "Fuels decarbonization" means separating the energy function from the carbon content of fuels. Carbonaceous (carbon-containing) primary fuels are transformed into secondary fuels with less carbon per unit of useful energy. For example, natural gas can be treated with steam to produce hydrogen, a fuel with no carbon at all.

"Carbon sequestration," in this context, means deliberately modifying today's dominant energy technologies so that carbon that would normally end up in the atmosphere is instead isolated from the atmosphere for a period of time measured in centuries or longer. Several sequestration strategies appear feasible. For example, the carbon removed from a fossil fuel could be sequestered as carbon dioxide deep in the ocean or deep underground in saline aquifers. Vexing part-scientific, part-philosophical issues related to sequestration include the "permissible" level of impact on the present-day environment and public health, as well as on future generations—if, for example, the sequestered carbon gradually finds its way to the atmosphere.

Juxtaposing "fuels decarbonization" and "carbon sequestration," emphasizes that the two concepts have the potential to be joined symbiotically in a new energy strategy, a strategy where they are opposite sides of the same coin. If the carbon intensity of a fuel is diminished by decarbonization, the byproduct will be a carbon-rich waste stream. The carbon in the waste stream can be sequestered instead of going directly to the atmosphere. For example, natural gas can be processed to yield separate streams of hydrogen and carbon dioxide; subsequently, the hydrogen can provide the fuel for fuel cells or combustion systems where hydrogen has a comparative advantage as a fuel, while the carbon dioxide is sequestered.

A novel world energy system emerges. In response to a heightened concern for greenhouse issues, the fossil fuel industries are transformed, at least partially, into hydrogen production and distribution industries. The carbon dioxide waste stream resulting from the processing of fossil fuel into hydrogen is injected into deep underground aquifers or into the ocean in massive quantities.

Hydrogen, to be sure, is a secondary energy carrier, not a primary energy source like coal, crude oil, wellhead natural gas, uranium, or the sun, nor is hydrogen a processed fuel like pipeline natural gas or gasoline. Like electricity, hydrogen has to be made from something else. Secondary energy carriers enter the economy because they are more easily distributed, offer greater convenience and control, and may reduce environmental impacts.

In the United States and globally, roughly two thirds of primary energy is utilized as processed or unprocessed fuels, and one third is transformed into electricity. Thus, a global greenhouse strategy must address both fuels and electricity. To date, research on sequestration has mostly considered sequestering the carbon dioxide produced at power plants. The idea of fuels decarbonization and carbon sequestration specifically addresses the complementary issue of sequestering the carbon in fuels.

It would be preferable for the carbon in a fuel not to become a waste stream at all after the fuel is used, but rather to find a second use with economic value. New uses of carbon dioxide in the fossil fuel industries may augment its current role in enhanced oil recovery, while also providing for its sequestration. Discoveries in chemistry and bioprocessing could lead to productive uses of carbon dioxide or carbon to produce chemicals, materials, or even food constituents, and some of these uses may also be compatible with sequestration. The quantity of carbon in the carbon dioxide produced by fossil fuel combustion, however, is currently many times larger than the quantity of carbon used in all industrial processes and products (a list that includes asphalt, plastics, solvents, and thousands of other intermediate and final goods). Thus, at least in the near future, only a small fraction of the fossil-fuel carbon used to provide energy can be used again. For the rest, direct sequestration seems to be the most climate-responsive option.

The concept of fuels decarbonization and carbon sequestration has taken on new plausibility for two reasons: (1) hydrogen fuel cells are developing rapidly and could become one of the principal energy conversion devices of the 21st century; and (2) estimates of the storage capacity available underground for the sequestration of carbon dioxide have been revised upward, based on new geological insights. Both the ocean and deep saline aquifers appear to have the capacity to contain centuries, if not millennia, of carbon dioxide released to the environment by fossil fuels used at current rates, although leakage rates, accident hazards, and environmental impacts are among the many unresolved issues at this time.

Fuels decarbonization with carbon sequestration is just one of several complementary approaches to reducing the rate of increase of carbon dioxide in the atmosphere. Other approaches include efficiency improvements, fuel switching, carbon-free renewable and nuclear energy sources, biomass energy, and biological sequestration of carbon dioxide. There is an evident need for a coordinated global research and development effort within which all will receive increased attention.

FINDINGS

Seven principal findings emerged from the workshop:

A. Several of the key enabling technologies for fuels decarbonization and carbon sequestration are already commercialized or close to commercialization.

B. At the scale of deployment in industry today, fuel decarbonization and carbon sequestration are well matched; they might be combined effectively in pilot programs.

C. Matching the distributed character of transportation energy use with the more centralized character of sequestration poses significant challenges.

D. There is a rich array of prospective technological routes both to fuels decarbonization and to carbon sequestration.

E. Environment, health, and safety are compelling concerns and appropriate subjects for research.

F. The necessary work cannot be done without new partnerships.

G. What is proposed here is not a panacea.

A. Several of the key enabling technologies for fuels decarbonization and carbon sequestration are already commercialized or are close to commercialization.

Hydrogen production technology

Hydrogen is produced from fossil fuels on a large scale today within petroleum refineries and within factories that make ammonia and ammonia-based fertilizers. A significant, although smaller amount of "merchant" hydrogen is produced by specialty companies that transport hydrogen to customers by pipeline at high pressure or by truck as a cryogenic liquid. With the exception of hydrogen used as rocket fuel, these applications utilize hydrogen as a chemical source, not an energy source.

The hydrogen fuel cell

Fuel cells are becoming competitive in energy conversion markets because the fuel cell extracts the energy content of a fuel not by combustion but by an electrochemical process that is intrinsically less polluting and more energy efficient. The fuel cell is particularly well matched to hydrogen fuel, so much so that, in many applications, when the fuel source is another fuel, such as methanol, a fuel processor is placed between the fuel and the fuel cell that converts the fuel into a hydrogen-rich gaseous mixture. Fuel cells are beginning to penetrate niche markets in both transportation and decentralized electricity generation.

Carbon dioxide management

Carbon dioxide is managed on a large scale in the oil and gas industries. In the largest application, enhanced oil recovery, the carbon dioxide typically originates in a natural reservoir where it is present at a very high concentration, and it is often piped hundreds of miles before being pumped into a partially depleted underground oil reservoir. Although sequestration of carbon dioxide is not the objective, much can be learned from studying how effectively sequestration is accomplished.

Carbon dioxide is also routinely removed along with natural gas liquids when wellhead natural gas is processed prior to transport to markets.

Within the past year a carbon dioxide sequestration project was begun whose sole purpose is to prevent carbon dioxide from reaching the atmosphere. Statoil, the largest Norwegian oil company, is separating carbon dioxide originally present in the natural gas produced at Sleipner West, a gas reservoir in Norwegian waters in the North Sea, and is reinjecting the carbon dioxide into a nearby reservoir, about 1,000 meters (3,000 feet) below the sea floor. In this first-of-a-kind demonstration, Statoil is adapting existing technology and learning how to lower costs. Statoil is conducting this project in response to a decision by the government of Norway to extend its carbon dioxide emissions tax to emissions associated with oil and gas production. The tax is $55 per metric ton of carbon dioxide, the equivalent of $200 per metric ton of carbon. Also imposed as a portion of the tax on gasoline, Norway's tax is equivalent to about 50 cents per U.S. gallon. (Throughout this report, we report numerical results in multiple units; see the Technical Appendix for unit conversions and definitions.)

B. At today's scale of deployment in industry, fuel decarbonization and carbon sequestration are well matched; they might be combined effectively in pilot programs.

The steam reformers being built for oil refineries and chemical plants today are, at the same time, both large providers of hydrogen and large point sources of carbon dioxide. Quantitatively, the magnitudes of the point sources of carbon dioxide associated with today's large hydrogen production units are well matched to the magnitudes of carbon dioxide managed by today's sequestration technology.

Consider the following calculation. The typical hydrogen production capacity of the large steam methane reformers currently being built is 1 billion Nm^3 per year (100 million standard cubic feet per day). Assuming that, measured by volume, three times as much hydrogen as carbon dioxide is produced (an approximately energy-based balanced reaction—see technical appendix , the same plant is a source of 600,000 metric tons of carbon dioxide per year (30 million cubic feet of carbon dioxide per day). By comparison the carbon dioxide point source arising from natural gas production at Norway's Sleipner West field, and now being sequestered, is 1 million metric tons of carbon dioxide per year. Thus, the two carbon dioxide point sources are of comparable size.

Of course, one cannot conclude from this calculation alone that carbon dioxide capture from centralized hydrogen production is a viable idea, even when the distance between a current fuel decarbonization site and a potential carbon sequestration site is small. But one can conclude that at least one relevant sequestration technology is already at hand. It would seem worth exploring whether some of the carbon dioxide point sources associated with industrial-scale hydrogen production at ammonia plants and oil refineries could be the targets of pilot experiments designed to co-optimize hydrogen production and carbon sequestration.

C. Matching the distributed character of transportation energy use with the more centralized character of sequestration poses significant challenges.

The transportation system will not easily convert to hydrogen fuel. The Chrysler Corporation argues that getting hydrogen fuel-cell cars into production will require "reforming" gasoline into hydrogen onboard the vehicle. Chrysler has announced a development program with that goal. Because all of the carbon in the gasoline will be vented to the atmosphere as carbon dioxide during the reforming, reducing the climate impacts of transportation through this approach will be achieved only to the extent that the vehicle uses gasoline more efficiently.

In addition to gasoline, other fuels, such as methanol, ethanol, and methane, have the potential to be reformed into hydrogen onboard a vehicle. Several auto companies are now exploring the methanol option. Even though the carbon will become carbon dioxide onboard and is unlikely to be recovered, both methanol and ethanol fuels represent potential routes to climate-friendlier transportation, if they are derived from biomass grown renewably.

Over a longer period of time, however, vehicles carrying hydrogen fuel may prevail. They have an attractive simplicity and favorable local environmental impacts, whether the hydrogen is converted to shaftpower by a combustion engine or by a fuel cell. The Ford Motor Company is basing its own fuel-cell program on a car that stores compressed hydrogen gas onboard.

The relationship between hydrogen-powered automobiles and carbon sequestration appears to be new territory. If hydrogen is manufactured from natural gas, the carbon byproduct could be sequestered somewhere. But suppose the natural gas comes out of the ground in Oklahoma, and hydrogen is needed for a million cars in Washington, D.C. Where should one make the hydrogen?

One answer is to make the hydrogen in Oklahoma, near where the natural gas is coming out of the ground. The hydrogen output of perhaps a dozen "large" methane steam reformers would be sent through a single long large-diameter pipe and delivered to a network of service stations in Washington, D.C., where it would be stored and dispensed. One large methane steam reformer should be able to supply hydrogen for about a million fuel-efficient hydrogen-powered cars. (For numerical details, see the Technical Appendix to this report.) The carbon dioxide byproduct of each Oklahoma reformer might be able to be used for enhanced oil or gas recovery nearby. As we have already noted, the carbon dioxide byproduct would be produced in a quantity similar to that being captured and sequestered in the North Sea today.

Another answer is to pipe natural gas from the Oklahoma gas field all the way to each Washington, D.C., service station, where hydrogen would be produced at a "small" methane steam reformer for comparable unit costs. At the service station, hydrogen would be stored and dispensed as before. The small reformer would be matched to the fuel needs of about ten thousand cars, so there would be a hundred service stations to take care of a million cars. Therefore, in this case, the byproduct carbon dioxide would be generated in Washington, and at a hundred different locations. It seems unlikely that such local methane reforming could be conducive to carbon dioxide collection and sequestration. The more the carbon atoms are dispersed, the harder it is to retrieve them for managed treatment.

Making the hydrogen in Oklahoma may be the better of the two strategies from the point of view of carbon dioxide sequestration. But, piping hydrogen rather than natural gas from Oklahoma to Washington is likely to be more expensive. Even if someday a hydrogen gas transmission and distribution system were as developed as today's natural gas system, so that capital and operating costs were spread across a fully utilized system, the cost of sending hydrogen from Oklahoma to Washington would still be about twice the cost of sending natural gas. Hydrogen demands higher quality pipe and more compressors along the pipeline.

There is a third alternative, a hybrid of the first two, where natural gas is piped from Oklahoma to Washington's "city gate" (near where, today, there is a transition between the long-distance, high-pressure transmission lines and short-distance, low-pressure distribution lines), hydrogen is made from natural gas in large-scale reformers at the city gate, and hydrogen is distributed locally. If a large regional sequestration site is available, requiring the transport of carbon dioxide only a moderate distance (say, a few hundred kilometers) from the city boundary, perhaps this hybrid system will have the lowest system-wide costs of the three for sequestering carbon dioxide when the users of hydrogen are small and dispersed.

To be sure, such a three-way systems comparison will be useful not only when the dispersed users of hydrogen are vehicles. Hydrogen fuel may find dispersed applications throughout the energy system, such as at small industrial and manufacturing facilities and in residential and commercial buildings.

In the shorter term, if hydrogen-powered vehicles and other small-scale users of hydrogen are to be linked with sequestered carbon dioxide, the scale mismatch and locational problems described above will have to be solved with simpler and more targeted strategies. One way to launch hydrogen-fueled transportation and hydrogen-fueled cogeneration in conjunction with carbon dioxide sequestration is to conduct the first pilot projects where it is straightforward to tap into an already developed industrial hydrogen production system, such as in cities close to oil refineries or ammonia plants.

D. There is a rich array of prospective technological routes both to fuels decarbonization and to carbon sequestration.

The core idea of fuels decarbonization and carbon sequestration has many branches requiring exploration. For much of the discussion in this report and at the workshop, the reference system (the main stem) has natural gas as the primary fuel, hydrogen as the secondary fuel, carbon dioxide as the form in which the carbon is to be sequestered, and deep aquifers or the deep ocean as the destination. All four elements of the reference system (and, of course, many others) can be varied, as sketched here and discussed in somewhat greater detail in Part Two of this report.

Decarbonization of solid fuels, instead of natural gas

Hydrogen can be made from every primary energy source. Because coal is abundant and widely used, developing advanced processes for the efficient conversion of coal to hydrogen will eventually be critical for the strategy explored here. Coal can be decarbonized by combining gasification and steam shifting, producing hydrogen-rich gas and carbon dioxide at pressure, available for sequestration.

Another potential source of hydrogen is biomass grown renewably on a large scale. Renewable biomass fuels can include wood, grasses, agricultural wastes, and the vegetable matter and paper products in municipal solid wastes. The various chemical steps to hydrogen production are almost the same as those used for coal, beginning with a stage of gasification of the solid fuel.

A particularly interesting biomass energy source is municipal solid waste (MSW) at the scale available in a large city. MSW often is a negative-cost fuel, because the alternative is costly disposal (and, from an environmental perspective, in the most frequent disposal option, greenhouse gas emissions in the form of methane emissions from landfills). The paper, plastic, and other energy sources in MSW could be processed into hydrogen for the fuel-cell buses that are driven in the municipality where the MSW originated.

Secondary fuels other than hydrogen

A primary fuel is decarbonized when it is converted into a secondary fuel that has a higher hydrogen-to-carbon ratio. Of particular importance is the decarbonization of coal (roughly $CH_{0.8}$) to "hydrogen-rich" methanol (CH_3OH), ethanol (C_2H_5OH), or methane (CH_4). Although during any decarbonization process, there can be a carbon dioxide co-product and it can be sequestered, the fraction of the carbon in the fuel that becomes available for sequestration when the secondary fuel is methanol, ethanol, or methane will be much smaller than when the secondary fuel is hydrogen. Nonetheless, liquid fuels such as methanol and ethanol have advantages, especially in transportation, and methane has the advantage of a preexisting natural gas infrastructure, so these secondary fuels have a place in a strategy of fuels decarbonization and carbon sequestration. The relative competitiveness of hydrogen versus hydrogen-rich fuels in various applications will become fully clear only after much further research and development.

Destinations for carbon dioxide other than the ocean or deep aquifers

Depleted oil and gas reservoirs may well lead the list of sequestration sites for carbon dioxide in terms of near-term readiness for sequestration, because they are frequently close to sites of current fuels processing, and the retention of fluids in these formations has persisted over geological times. At some of these sites, the costs of sequestration may be partially offset by enhanced oil or gas recovery.

Deep coalbeds are another destination for carbon dioxide where sequestration may be able to be accompanied by fuels production. Today about 5% of U.S. natural gas is produced from coal deposits so deep that the coal itself cannot be mined. The methane that is extracted had been adsorbed on coal surfaces under pressure. It may be possible to modify current methane production technology so that carbon dioxide plays two roles: it helps free methane adsorbed on the coal, and it is itself adsorbed on the coal in methane's place. If the methane were processed to hydrogen and carbon dioxide near the site of methane extraction, perhaps only hydrogen would leave the site, the carbon being returned below ground for long-term sequestration.

Carbon dioxide may also be recycled, by adding energy from a non-carbon source. This is what green plants do, but carbon dioxide recycling can also be done industrially. The result can be chemicals that otherwise would have been produced from fossil fuels.

Sequestering carbon in chemical forms other than carbon dioxide

Interesting work has been done on alternatives to the sequestration of carbon as carbon dioxide. Carbon can be sequestered in highly stable mineral carbonates, as a result of a chemical reaction of carbon dioxide with alkaline minerals that are less stable; in effect, the geological process of "weathering" is accelerated. Several candidate minerals are abundant.

In another proposal, carbon dioxide is not produced in the first place. The starting point is the thermal decomposition of natural gas to hydrogen and elemental carbon. The elemental carbon is either stored in that form, or it becomes a precursor for chemicals. In this system, part of the economic value of the fuel is realized over the short term, when the hydrogen fuel is utilized, and part only much later: about half of the fuel energy of the methane is still stored in the elemental carbon. If the elemental carbon can be sequestered retrievably, the remaining energy might be released by oxidation to carbon dioxide at a later date. By contrast, in the reference system above, all of the fuel energy of methane is consumed once the hydrogen fuel is utilized, because the end products, carbon dioxide and water, are both fully oxidized.

The special case of biomass sequestration

In discussions of energy and environmental issues, the most common use of the word "sequestration" applies to natural uptake of carbon dioxide by plants. Indeed, carbon is sequestered from the atmosphere when there is an increase in the amount of wood above ground or the amount of humus below ground. And such a buildup of carbon can be made to occur by deliberate human action, such as by intensively managing a plantation of short-rotation woody crops or perennial grasses where previously the land had sparse vegetation. One might even be able to assure that such sequestration could persist for centuries or longer. However, those human actions that could bring about such sequestration are quite different from the actions required to sequester carbon directly in an industrial setting. In the latter case one is generally starting with carbon that is hundreds of times more concentrated than in the atmosphere. In organizing our workshop, we decided that we could draw a relatively clear boundary and discuss "concentrated" carbon sequestration, while setting aside the topic of "diffuse" carbon sequestration by biomass accumulation.

The boundary is less distinct in one important instance, however—when biomass is grown renewably and then chemically processed to hydrogen and carbon dioxide. Such a biomass-to-hydrogen system removes dilute carbon dioxide from the atmosphere and creates a concentrated stream of carbon dioxide for sequestration. It provides a mechanism for removing carbon dioxide from the atmosphere indefinitely.

E. Environment, health, and safety are compelling concerns and appropriate subjects of research.

A shorthand for the concept of fuels decarbonization and carbon sequestration is "safer fossil." For "safer" to be appropriate, the concept must be implemented in such a way that human health is protected, catastrophic accidents are ruled out, significant damage to below-ground and ocean environments is avoided, and significant releases of carbon dioxide to the atmosphere through leakage are minimized.

Defining the objectives of sequestration programs

Defining the objectives of sequestration programs will require the integration of physical understanding of the global environment with ethical reasoning. For example, broad agreement will need to be reached about the total amount of carbon that should be sequestered and about the minimum acceptable retention time, averaged over sequestration sites. A retention time of ten years (a leakage rate of one part in ten each year) would postpone climate-related impacts only a decade, and would almost surely not be worth the effort. But if much longer retention times can be achieved, there may be benefits both to present and future generations.

Thus, independent of efforts to establish the likely leakage times associated with various sequestration options, there will need to be work that illuminates, at any level of fossil fuel use, the minimum capture fractions and retention times that are, in a broad sense, permissible.

The ocean environment

As a result of the increased concentration of carbon dioxide in the atmosphere, relative to pre-industrial times, there is currently a net flow of carbon dioxide from the atmosphere to the ocean. The direct result is a surface ocean that is more acidic and has a lowered carbonate concentration, relative to the pre-industrial ocean. Gradually, in a process that will continue for hundreds of years, these effects will be transferred to the deeper ocean by ocean circulation. The consequences for the ocean's individual organisms and for its ecosystems are largely unknown. The advocates of ocean sequestration have proposed the goal of assuring that the adverse environmental impacts of deliberate ocean sequestration are substantially less than the avoided adverse environmental impacts of equivalent emissions to the atmosphere.

Global environmental impacts of hydrogen fuels

The resurgence of interest in hydrogen as an energy carrier is largely the result of its perceived environmental benefits, especially for regional air quality. Like electricity, hydrogen is a premium energy carrier that can be used with high energy efficiency and near-zero local emissions.

Again like electricity, important environmental impacts are not avoided entirely, just displaced. In addition to local impacts where the hydrogen or electricity is generated, global impacts need to be considered. In particular, when either hydrogen or electricity provides onboard vehicle power, the details of the overall system determine whether there is a net increase in global carbon dioxide emissions. For electric vehicles, the power plant that makes the electricity matters, and for hydrogen-powered vehicles the chemical processor that makes the hydrogen matters. For both, the fuel efficiency of the vehicle matters. Key to the argument that cars powered by hydrogen offer net benefits, even before one considers carbon dioxide sequestration, is the high efficiency of production of hydrogen from natural gas and the expected high fuel efficiency of the hydrogen-powered car.

Global environmental impacts of reformulated gasoline

Regulations designed to improve local air quality are leading to the production of "reformulated" gasoline. Relative to the gasoline it is replacing, reformulated gasoline leads to an increase in carbon dioxide emissions at the refinery per gallon of gasoline produced. A significant fraction of the extra carbon dioxide emissions at the refinery is associated with dedicated hydrogen production. The oil and gas industry repeatedly reoptimizes its facilities as it accommodates new environmental regulations. It might be useful to investigate how another round of optimization might occur in response to requirements for "climate-friendly reformulated gasoline," translated into requirements for carbon dioxide capture and sequestration where hydrogen is produced.

Hydrogen safety

A culture of safety appears to be in existence in those industries where hydrogen is produced and used, likened to the culture of safety in the air transportation industry. It is not clear how hard it would be to transfer this culture to a workforce that would provide hydrogen fuel for vehicles. Comparisons to the management of gasoline and compressed natural gas lead to a point of view that each fuel, including hydrogen, has its unique hazards, and that safely managing hydrogen for transportation should be an achievable objective. Those most involved emphasize that performance early in the effort will be especially important.

Hydrogen safety is discussed in somewhat greater detail in Part Two, Section Three, I.E.

Carbon dioxide safety

The integrity of carbon dioxide sequestration is important not only to prevent the adverse climate impacts of carbon dioxide leaking too rapidly into the atmosphere, but also to prevent catastrophic releases, both from reservoirs and pipelines. Air with only 25% carbon dioxide is lethal. Because carbon dioxide gas is heavier than air, a large release at ground level could displace air locally in valleys and home basements and cause asphyxiation. Much experience resides in the oil and gas industry to prevent catastrophic releases. As with hydrogen safety, those most involved are risk averse. They recommend choosing pilot projects with no foreseeable adverse consequences of containment failure, such as projects where sequestration is in aquifers near the coast but below the sea floor.

F. The necessary work cannot be done without new partnerships

To explore the concept of fuels decarbonization and carbon sequestration, the fossil fuel industries will have to be engaged. International collaborations will need to be strengthened. A broad consensus on the objectives of sequestration and on risks and benefits will have to be achieved.

The involvement of the oil, gas, and coal industries

The research and development programs of the fossil fuel industries over the past decades have resulted in an institutional capability uniquely suited for grappling with the issues posed by this workshop. Their expertise encompasses exploration and production, chemical processing, and the marketing of fuel.

The oil and gas industry has a wealth of experience related to subsurface geology and reservoir management. Its worldwide knowledge of the particularities of individual oil and gas resources could be invaluable in selecting the sites for pilot sequestration projects.

There is a public interest in monitoring those sequestration projects that are already underway, or that soon will be. Understanding reservoir integrity, for example, goes beyond the interests of those involved in any particular project. Finding mutually agreeable arrangements for public sector research to be conducted in concert with industrial sequestration activity will be critical to learning quickly at minimum cost.

International coordination

Under the auspices of The International Energy Agency (IEA), a Greenhouse Gas Research and Development Programme coordinates international research in carbon sequestration. Many of the researchers share a history of involvement with the needs of the coal industry, whose interest in carbon dioxide sequestration is heightened by the fact that, per unit of energy produced, more carbon dioxide is generated from coal than from oil or natural gas. Because coal at this time is used principally to produce electricity, the IEA program has focused more on electricity than on fuels.

In the future, internationally coordinated research on fuels decarbonization and carbon sequestration could conceivably take unfamiliar forms, because the interests of many countries will be engaged in new ways. Countries that are fuels producers, for example, could become the sites where new technologies are demonstrated and where field experience is monitored. Countries that expect to be heavily dependent on coal may see opportunities to counter the greenhouse impacts of that fuel.

To become an important climate-responsive energy-supply option, fuels decarbonization with carbon sequestration eventually will have to be judged cost-effective relative to alternative supply-oriented approaches, such as biomass-based, renewable, and nuclear energy-supply systems. An internationally coordinated research and development effort will be needed to clarify where and under which circumstances decarbonization with sequestration will be competitive for each country. Those countries for which this option is particularly favorable might be expected to become most deeply engaged in supporting the necessary research to bring this option to fruition.

The development of a public consensus

Many ideas proposed for components of the future energy system share an unfortunate history: Advocates oversell. Public funds are committed. Broadly based examination reveals areas of unacknowledged weakness or uncertainty. Programs crash or gently disappear with the termination of subsidies.

The workshop participants desire a different future for the idea of fuels decarbonization with carbon sequestration. To minimize ineffectiveness, the articulation of dissenting views should be encouraged and the process of arriving at public investment decisions should be broadly democratic.

G. What is proposed here is not a panacea.

The technology research community must avoid overpromising, with respect to every option being developed for the world's future energy system. No single technological approach can provide all the needed energy on its own—not renewable energy, not energy efficiency, not nuclear fission, not nuclear fusion, and not decarbonized fuels with carbon sequestration. The energy-environment-economy challenge demands parallel work along many tracks at once.

Over the next decades major investments will be made worldwide in energy infrastructure. How large an investment should be made in two separate and novel infrastructures for hydrogen and carbon dioxide cannot yet be estimated. The concentrations of demand that justify long-distance transmission will at best develop slowly. There are parallels with the history of the U.S. natural gas infrastructure, which took decades to mature.

The idea of safer fossil energy has synergisms with efforts underway elsewhere in the U.S. government's energy research and development program. The hydrogen fuel-cell car plausibly will have a fuel economy equivalent to 100 miles per gallon of gasoline equivalent, or more, but only if energy-efficient materials and designs are developed. Solar-assisted methane steam reformers, where focused solar energy at a high-temperature drives the endothermic steam reforming reaction, permit a higher fraction of the carbon in the methane to be captured and a greater amount of hydrogen to be produced. In decentralized, grid-independent situations, wind or photovoltaics may provide the power for hydrogen production from water.

The ideas here are new and exciting. It would be a great mistake, however, if their attractiveness were to result in reduced commitments to support the development of other components of the world's future energy system. The global challenge is daunting and has long been underestimated. Only a broadly based effort can be defended.

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PART TWO: COMPONENT TECHNOLOGIES

SECTION ONE: FUELS DECARBONIZATION

This section describes industrial-scale processes for producing hydrogen and hydrogen-rich decarbonized fuels from various feedstocks. See Section Three, "Hydrogen Management and Use," for a discussion of small-scale hydrogen production and hydrogen distribution.

I. TECHNOLOGY STATUS

A. The hydrogen industry

Large quantities of hydrogen are currently used as a reducing agent in the chemical process industries, principally in petroleum refining and ammonia production. In 1990, U.S. industry used about 9 million metric tons of hydrogen (a rate of use of 10 billion standard cubic feet per day), of which 60% was in petroleum refineries, 30% in ammonia plants, and 10% elsewhere. (Worldwide, in 1993, 47% of global hydrogen production occurred at ammonia plants and 37% at refineries; the U.S. share of global nitrogen fertilizer production is smaller than its share of oil refining.) In most uses, the hydrogen is desired primarily as a chemical and secondarily as a fuel; a small exception is hydrogen rocket fuel.

Industry distinguishes "on-purpose" hydrogen production and "byproduct" hydrogen production. On-purpose hydrogen is produced in dedicated facilities; almost all U.S. on-purpose production is from natural gas, although in a few refineries the feedstock is petroleum. Byproduct hydrogen becomes available especially in petroleum refineries; for example, hydrogen is released in processes like ethylene production and catalytic processing of the lightest hydrocarbons into heavier ones. Somewhat more than half of U.S. industrial hydrogen production is on purpose, since about 40% of the hydrogen in petroleum refineries (2.2 million metric tons per year, or 2.5 billion standard cubic feet per day) is produced in dedicated facilities, as well as probably nearly all of the hydrogen at ammonia plants. Taking into account inefficiencies in production, we estimate that in the U.S. about 1 exajoule of primary energy (more than 1% of U.S. primary energy and about 5% of U.S. natural gas) is dedicated to the production of hydrogen.

Installed hydrogen production capacity is documented at the level of the individual refinery, worldwide. As of January 1, 1992, total hydrogen production capacity at the world's refineries was about 7 million metric tons per year (7 billion standard cubic feet per day). Production capacity at each of seven individual U.S. refineries exceeded 90 thousand metric tons per year (100 million standard cubic feet per day); these seven refineries are located in five states and are owned by five different oil companies.

The oil industry is steadily expanding its investment in hydrogen production facilities. In the U.S. a major factor driving this expansion is the imposition of stricter specifications for the content of gasoline and diesel fuel in recent air quality regulations. These regulations both reduce total byproduct hydrogen (e.g., the aromatics content is being reduced, and aromatics production is a source of byproduct hydrogen) and increase total hydrogen requirements at the refinery (e.g., the sulfur content is being reduced, and hydrogen is used to desulfurize fuels). The trend to heavier crudes also increases in-refinery demand for hydrogen.

Hydrogen is produced from gasified coal throughout the world. In the U.S., where, prior to the 1940s, 90% of U.S. hydrogen production capacity was based on coal, hydrogen production from both lignite and bituminous coals has continued to be economical in limited niche markets. In China roughly 30 million metric tons of coal are gasified to make hydrogen for ammonia production.

The existing hydrogen infrastructure could provide the impetus toward the initial use of hydrogen in energy markets. Assume that a typical fuel-cell car will use hydrogen fuel at a rate of 100 kg/yr (or 100 standard cubic feet per day), which is the rate of energy use for a car that gets the energy equivalent of 100 miles per gallon and is driven 10,000 miles a year. Under these conditions a large methane steam reformer, producing about 100,000 metric tons of hydrogen per year (100 million standard cubic feet per day) can supply the fuel needs of one million cars.

Merchant hydrogen

The vast majority of industrial hydrogen is used on-site (e.g., at the refinery or chemical plant where it is produced). A much smaller "merchant hydrogen" market involves hydrogen produced by one firm for distribution and sale to another. About 2% of total 1990 U.S. hydrogen production was merchant hydrogen: about 200,000 metric tons per year (200 million standard cubic feet per day).

The large steam methane reforming plants in the United States producing hydrogen for the merchant market are comparable in size to the units producing hydrogen on-site at refineries. The existing merchant hydrogen distribution system consists of several hundred miles of dedicated local hydrogen pipelines (mostly located near refineries and chemical plants) and a fleet of liquid-hydrogen trucks that provide hydrogen to customers up to a thousand miles away.

B. Production costs and incremental costs for sequestration

The two principal technologies for hydrogen production from fossil fuels are steam reforming and partial oxidation. These technologies are "mature," that is, they are commercially available from multiple vendors with cost and performance guarantees. The energy efficiency for this conversion in new plants, starting with natural gas, is about 75%. The cost of hydrogen produced from natural gas via large-scale steam reforming is roughly \$5/GJ, or \$60/thousand Nm^3, or \$1.70 per thousand standard cubic feet. About half the cost is feedstock and half is the cost of capital, operations, and maintenance. (For merchant hydrogen, transport by truck or small pipeline can add another \$10/GJ to the price paid by the customer.)

The incremental cost of carbon dioxide sequestration has been estimated for the case of hydrogen production from natural gas in a "large" steam reformer. The incremental costs of separating the carbon dioxide coproduced with hydrogen and compressing it to pipeline pressure are estimated to be about \$0.50/GJ (\$6/thousand Nm^3, or \$0.17 per thousand standard cubic feet.), adding about 10% to the cost of the hydrogen. The incremental costs of transport and injection into an aquifer have not been estimated for a pipeline serving a single reformer. There are strong economies of scale in pipeline transmission, with the result that the overall incremental cost of sequestration may be in the range of \$0.10/GJ to \$0.50 per GJ, if, for example, several hydrogen-production plants use a single 150 kilometer (100 mile) pipeline.

Although, currently, carbon dioxide is not recovered when electricity is produced, the incremental cost of adding sequestration to existing electricity generation systems has been estimated for several technologies. In the system most extensively studied, the fuel is coal, electricity rather than hydrogen is the desired product, and the power is produced via an Integrated Coal-Gasification Combined Cycle (IGCC). To capture carbon dioxide using this system, the synthesis gas resulting from coal gasification and already suitable for electricity production requires additional processing prior to combustion in a turbine. The synthesis gas passes through a shift reactor, transforming carbon monoxide into carbon dioxide, and then carbon dioxide is separated from the other components of the shifted synthesis gas, principally hydrogen and water vapor. (A shift reactor is already required for hydrogen production, so the cost of this hardware enters the incremental cost calculation only for electricity production.) Based on technology available today, capturing carbon dioxide and compressing it to a pressure suitable for pipeline transmission as a supercritical fluid (a pressure of 100 atmospheres or more) adds an estimated 20% to the cost of electricity when carbon dioxide is simply vented to the atmosphere.

Including the costs of a pipeline servicing only this plant and running about 150 kilometers (100 miles) and the costs of aquifer sequestration will lead to an approximate 50% overall cost increment (from about 6 cents to about 9 cents per kilowatt hour). As above for carbon dioxide co-produced with hydrogen, the cost of transport by pipeline of carbon dioxide coproduced with electricity could be considerably smaller if the costs were shared among several users.

In the absence of sequestration, the cost of electricity when pulverized coal is burned directly is somewhat lower than the cost of electricity produced from coal gasified and then combusted using the IGCC system. But when the costs *with* sequestration are compared, direct combustion is more expensive, because direct combustion requires the carbon dioxide to be removed from the post-combustion flue gases, where the partial pressure of the carbon dioxide is lower than in the shifted synthesis gas produced in the IGCC process.

Gas separation and cleanup

For hydrogen production, the crucial step of gas separation, following steam reforming or partial oxidation, can be accomplished commercially with technologies based on adsorption, absorption, or membrane separation. The most common commercial process is pressure swing adsorption (PSA), where carbon dioxide is selectively adsorbed, usually on activated carbon; during PSA the hydrogen is generally "polished" for final delivery, to yield a purity near 99.999%. The absorption process of amine scrubbing is commonly used for removal of carbon dioxide from natural gas, and this technique also can be applied to hydrogen separation. Advanced membrane technologies are being developed that may prove to be superior to both of these processes. Further in the future lie clathrate-based and other advanced separation technologies (see Section III below).

Electrolysis

Hydrogen is made at large-scale via electrolysis of water at some dams, using low-cost off-peak power. Electrolysis is a competitive route to hydrogen only when electricity is inexpensive (roughly one to two cents per kilowatt hour), a situation that may occur with off-peak pricing. An expanded role for electrolysis will require lower-cost electrolyzers; one approach is to use the fuel cell in reverse to produce hydrogen at off-peak times, and then to produce electricity from that hydrogen at on-peak times.

II. MAJOR BARRIERS AND UNCERTAINTIES

A. Field tests are required to fully understand the opportunities for co-optimizing the sequestration of carbon dioxide and the production of hydrogen from natural gas and solid fuels. A project involving coal gasification in North Dakota and enhanced oil recovery in Saskatchewan, Canada, could provide useful insights.

While industry has considerable experience both (1) producing hydrogen from natural gas and solid fuels, and (2) separating carbon dioxide from other constituents of wellhead natural gas, there are not many examples where both fuel decarbonization and carbon dioxide extraction are happening in the same project. One example will soon be in operation: the Dakota Gasification Company recently announced a project that will combine coal gasification with the sale of carbon dioxide offsite. Specifically, it has signed a 15-year contract with PanCanadian Petroleum Limited to deliver up to 1.8 million metric tons per year (95 million standard cubic feet per day) of carbon dioxide from its Great Plains Synfuels Plant in North Dakota to oil fields 320 kilometers (200 miles) away in Saskatchewan, Canada, for enhanced oil recovery. This project currently lacks a field research program that explores advanced technologies.

B. The addition of two new infrastructures, one for hydrogen and one for carbon dioxide, is daunting.

Infrastructures are usually built independently, yet in view here is the co-development of two of them. A hydrogen infrastructure that reaches beyond the industrial sector poses significant technical challenges. A carbon dioxide infrastructure is vulnerable to changes in judgment about greenhouse impacts.

III. RESEARCH OPPORTUNITIES

A. Co-optimization of carbon capture and industrial hydrogen production

Because the technologies for large-scale production of hydrogen from fossil fuels (steam reforming, partial oxidation, etc.) are judged to be mature, there has been little recent public-sector research. A program of collaborative research, with the participation of the fossil fuel industries, should clarify the technical feasibility and incremental cost of producing hydrogen and sequestering carbon dioxide at industrial scale in a single co-optimized system.

B. Decarbonization of coal, biomass, and municipal solid waste

In the production of hydrogen from coal or biomass energy sources, two priority research areas are solids handling and the cleanup of the gases exiting the gasifier. Research on reaction kinetics, reactor design, and feeding of fuel to pressure vessels can lead to reduced capital and operating costs.

Because biomass has a high content of volatiles, gasification of biomass can occur at a lower temperature than gasification of coal, permitting a high energy content to be achieved for the biomass synthesis gas by indirect heating; the costs of the oxygen plant used in coal gasification are avoided. Better methods of drying are needed, as well as improved gasifiers.

An important biomass energy source is municipal solid waste (MSW). In the United States MSW consists, on average, of about two thirds potentially renewable biomass products (such as paper and food wastes). MSW is a negative-cost fuel, because not using it creates costs for disposal in landfills. Where the resource is large and concentrated, such as in a large U.S. city, one can combine MSW gasification with the production of either electricity or hydrogen. The cost of power generation via MSW gasification should be competitive with conventional waste-to-energy schemes based on mass burning and steam-turbine power generation, when projected commercially mature gasification costs are realized. The cost of hydrogen via MSW gasification should be competitive with the cost of hydrogen from natural gas, with natural gas prices at 1995 levels, in places where tipping fees are high, as in New York City. Improved gasifiers and better management of potentially toxic byproducts are needed.

C. Advanced separation technology

New approaches to the physical separation of gases are being commercialized. In the following three examples, U.S. national laboratories have a lead role. One approach uses capillary condensation, which separates substances by selective wicking; it might be used for efficient cryogenic separation of carbon dioxide from a gas mixture. A second approach uses an aluminum oxide membrane with very small (50 nanometer diameter) pores that passes only hydrogen and thereby efficiently separates hydrogen from other gases. A third uses an electrically conductive matrix monolith of activated carbon fibers that selectively adsorbs carbon dioxide from a gas mixture and then desorbs the carbon dioxide when a voltage is put across the matrix. In most adsorption-desorption systems, desorption is accomplished either by heating or by depressurization, with energy penalties; in one application using voltage-driven desorption, the pressure of a wellhead mixture of carbon dioxide and natural gas can be maintained while the separation is accomplished.

D. Clathrates for separation

The separation of hydrogen from carbon dioxide can be achieved using water near 0°C and at pressures of 10 to 100 atmospheres (150 to 1500 psi) to produce carbon dioxide "clathrates," which are ice crystals that contain gas molecules within them. (Carbon dioxide clathrates are formed, but hydrogen clathrates are not.) The formation of clathrates may also remove sulfur. It has been proposed that the clathrates could be transported as a slurry in chilled pipelines at much lower pressures than supercritical carbon dioxide, reducing the considerable costs of compression prior to entry into the pipeline system. The slurry might be sequestered directly in the ocean or in a deep aquifer. The combined costs of carbon dioxide separation and pressurization, sulfur removal, and carbon dioxide sequestration might be considerably reduced, relative to current approaches

SECTION TWO: CARBON SEQUESTRATION

The broad subject of carbon sequestration was extensively reviewed at the Third International Conference on Carbon Dioxide Removal, held in Cambridge, Massachusetts, September 9-11, 1996. The papers presented at that meeting were edited by Howard Herzog, one of our workshop participants, and have been published in a supplementary issue of *Energy Conversion and Management* (Vol. 38, Suppl., 689 pp., 1997). These papers provide a full view of the field. The following short summary cannot do justice to the richness of ideas now under discussion.

I. TECHNOLOGY STATUS

A. Carbon dioxide in the oil and gas industry

Enhanced oil recovery by carbon dioxide injection involves mature technology. The required carbon dioxide management system features carbon dioxide extraction from natural underground reservoirs of carbon dioxide (and, to a much lesser extent, from industrial sources), carbon dioxide pipelines, and carbon dioxide injection at high pressure into active, partially depleted oil reservoirs.

The sources of most of the carbon dioxide for enhanced oil recovery are usually natural underground deposits where carbon dioxide is present at high concentration. One of the largest deposits, McElmo Dome in southwestern Colorado, has carbon dioxide reserves of 500 million metric tons of carbon dioxide (10 trillion cubic feet of carbon dioxide, or 140 million metric tons of carbon), at 97% carbon dioxide concentration. A 760 millimeter (30 inch) diameter pipeline running about 800 kilometers (500 miles) connects McElmo Dome to oil fields in western Texas. The total amount supplied from all developed deposits in the U.S. in 1984 was about 40 million metric tons of carbon dioxide (a rate of about 2 billion cubic feet per day, or about 10 million metric tons of carbon per year). This is roughly 1% of the carbon dioxide released annually in recent years from the burning of fossil fuels in the United States.

Carbon dioxide is transported in pipelines at pressures exceeding its critical pressure (73 atmospheres, or 1072 psi), to reduce pumping costs. When the objective is enhanced oil recovery, a high carbon dioxide pressure is also useful to meet the need below ground for a high-pressure differential to drive the carbon dioxide into the reservoir. The price paid for carbon dioxide for enhanced oil recovery in the U.S. is currently $10-$17 per ton.

The units costs for transporting carbon dioxide 250 kilometers (150 miles) are estimated to be about seven dollars per metric ton, assuming a 400 millimeter (16 inch) diameter pipeline; such a pipeline is matched to the onshore transport of about three million metric tons of carbon dioxide per year. The unit costs for the same distance might fall to about one dollar per metric ton for a 1600 millimeter (64 inch) diameter pipeline, much larger than any now built, and matched to a flow of about 100 million metric tons per year (O. Skovholt, *Energy Conversion and Management*, 34, 1095-1103, 1993).

Roughly 80% of the commercial use of carbon dioxide is for enhanced oil recovery. Most of the carbon dioxide sent into underground oil reservoirs for enhanced oil recovery stays below ground, although average retention times are not well understood. Two other large uses of carbon dioxide, food refrigeration (via dry ice) and beverage carbonation, do not result in the sequestration of carbon dioxide.

B. Injection into depleted oil and gas reservoirs

Building on the experience with enhanced oil recovery, carbon dioxide can be injected into depleted oil and gas reservoirs for sequestration. The global sequestration capacity in abandoned reservoirs is estimated to be 130 to 500 gigatons of carbon. This capacity is equivalent to 20-80 years of current global carbon consumption via fossil fuels, since about six gigatons of carbon are emitted into the atmosphere globally each year from fossil fuels. Considerable research and field testing are necessary to validate these capacity estimates. Although these formations contained pressurized fluids for geological periods, the release of gas may have altered the formations and affected reservoir integrity.

C. Injection into deep aquifers

Deep aquifers may be the largest long-term underground sequestration option. ("Deep" is defined to be deeper than 800 meters, or 2500 feet, the depth at which carbon dioxide in hydrostatic equilibrium reaches its critical pressure; at its critical point the density of carbon dioxide is about half the density of water.) Such aquifers are saline, and usually they are hydraulically separated from the shallower "sweet water" aquifers and surface water supplies used by people. Deep aquifers are widely distributed below both the continents and the ocean floor. Their potential sequestration capacity may be thousands of gigatons of carbon, corresponding to as much as a thousand years of carbon production from fossil fuels at current rates of use.

The sequestration capacity available in deep aquifers is many times larger if carbon dioxide can be sequestered in large horizontal reservoirs instead of being limited to reservoirs that are analogous to the structural or stratigraphic traps in which oil and gas are found. The judgment that many of the world's abundant large horizontal reservoirs will confine carbon dioxide is based on the expectation that the carbon dioxide will dissolve into the surrounding formation water before migrating more than a few kilometers toward the basin margins. The idea that large horizontal reservoirs will provide secure sequestration is relatively new; it has led to an increase in confidence that long-term sequestration of a significant fraction of the next several centuries of carbon dioxide production from human activity may be feasible.

Deep aquifer sequestration solely for reasons related to climate change is currently being demonstrated: carbon dioxide from Norway's Sleipner West gas field is being injected into an undersea aquifer in the North Sea. A substantially larger project soon will be undertaken by Exxon, Mobil, and Pertamina at Indonesia's offshore natural gas field at Natuna, north of Borneo in the South China Sea. When the Natuna field is in full production, carbon dioxide will be brought to the surface in association with natural gas at a rate of 100 million metric tons of carbon dioxide per year (30 million tons of carbon per year, or 5 billion standard cubic feet of carbon dioxide per day), about 100 times the rate that it is brought to the surface at Sleipner West. The rate of carbon dioxide co-production at the Natuna field will be 0.5 percent of the rate at which carbon dioxide is produced globally from all fossil fuel uses. The plan for Natuna natural gas production includes stripping 90% or more of the carbon dioxide from the gas brought to the surface and the injection of this carbon dioxide into a nearby deep aquifer for sequestration.

Industrial experience in managing fluids in underground reservoirs is not restricted to sites of active energy production. For many years the chemicals industry has disposed of liquid wastes and acid gases in deep aquifers, a practice permitted in some but not all of the states of the U.S. The natural gas industry routinely stores natural gas from summer to winter in underground reservoirs close to load centers, to level winter peaks in gas transmission.

D. Ocean sequestration

The world's oceans represent the largest potential sink for anthropogenic carbon dioxide. They already contain about 40,000 gigatons (billions of metric tons) of carbon, largely as bicarbonate and carbonate ions. Estimates of ultimate sequestration capacity in the world's oceans can be derived by choosing a nominal allowable change in the average acidity of all ocean water: such estimates are in the range of 1,000-10,000 gigatons of carbon, the equivalent of 200 to 2,000 years of current carbon emissions from fossil fuels. If the injected carbon dioxide can be incorporated in the general oceanic deep water circulation, a residence time of up to 1,000 years can be anticipated.

The surface layer of the ocean (roughly, the first 100 meters) contains some water that has come up from a great depth after being below the surface for centuries. In pre-industrial times, the upwelling carbon dioxide brought the same amount of carbon dioxide into the surface ocean as the downwelling carbon dioxide removed, with no net flow between the atmosphere and the ocean. As a result of the buildup of carbon dioxide in the atmosphere over, roughly, the past century, this balance no longer obtains. Instead, there is a net flow of carbon dioxide from the atmosphere to the upper layer of the ocean, currently at a rate of about 2 gigatons of carbon per year. The ocean will eventually absorb roughly 90% of present-day atmospheric emissions. Thus, discharging carbon dioxide directly into the ocean would accelerate a slow natural process by which anthropogenic carbon dioxide already enters the ocean indirectly.

The best injection option in the near-term appears to be dissolution at depths between 1,000 and 1,500 meters (3,000 to 5,000 feet) by pipeline or towed pipe. For the longer-term, however, very deep injection may be desirable. Laboratory measurements reveal that the density of carbon dioxide exceeds the density of seawater beginning at a depth of 3,500 meters (2.2 miles). Carbon dioxide placed on the ocean bottom at that depth or greater may form a relatively immobile "lake."

E. Injection into coalbeds

There are synergies between carbon dioxide sequestration and coalbed methane production: the injection of carbon dioxide into deep coal seams can lead, simultaneously, to the displacement of methane adsorbed on coal surfaces and its replacement by adsorbed carbon dioxide. Measurements have shown that carbon dioxide is sequestered at adsorption densities greater than those of the methane it replaces. Assuming, conservatively, that the replacement will be one-for-one, and using the estimate that there are 7.4 trillion normal cubic meters (275 trillion standard cubic feet) of recoverable coalbed methane resources in the United States, the sequestration capacity for carbon dioxide in these coalbeds is 15 billion metric tons of carbon dioxide (4 Gt of carbon), the equivalent of about three years of current carbon dioxide production in the United States from all fossil fuel use.

Injection of carbon dioxide into coalbed methane reservoirs to enhance methane production is an embryonic technology. To date, the San Juan basin in New Mexico is the only site where this process has been used, although a second field test is scheduled for 1998 in Alberta, Canada.

II. MAJOR BARRIERS AND UNCERTAINTIES

A. The path to public acceptance is unclear, particularly with respect to ocean sequestration

The viability of every sequestration option as a greenhouse gas mitigation strategy hinges on finding social and political consensus. In view of public precaution toward the ocean, ocean sequestration is particularly likely to be debated. Assuring broad public participation in early discussions is critical.

B. Retention in aquifers will be many times larger if large horizontal aquifers are available for sequestration; the capacities of such aquifers and their leakage rates need to be better understood.

The capacity of aquifers to sequester carbon is many times larger if large horizontal aquifers are available for sequestration, relative to the situation where only aquifers analogous to those in which oil and gas are found can be used. Accordingly, the basic physical and chemical processes determining how long carbon dioxide sequestered in large horizontal aquifers will stay isolated from the atmosphere needs to be better understood. One goal is to predict retention times accurately.

There is also a need to understand leakage of carbon dioxide from deep saline aquifers from the point of view of avoiding the contamination of overlying sweet-water aquifers. And there is a need to be assured that leaks do not result in a buildup of lethal pockets of carbon dioxide in valleys or in individual basements.

C. Biological impacts in the ocean are uncertain

Effects on marine organisms and marine ecosystems of injection of carbon dioxide into the deep ocean have been little studied. The most significant impacts will come indirectly, from the lowered pH that results when additional carbon dioxide is added to seawater. Depending on the method of release, pH can be expected to vary from as low as 4 very near the injection point, to its ambient value of about 8. Zooplankton, bacteria, and bottom-dwelling plants and animals living at the depth of injection would be the principal organisms affected.

III. RESEARCH OPPORTUNITIES

A. Learning from Sleipner West and its successors

There is a public interest in learning from Statoil's first-of-a-kind, climate-driven sequestration project at the Sleipner West field in the North Sea, 240 kilometers (150 miles) off the coast of Norway. By means of two separation units installed offshore on platforms (the first of which weighs about 8,000 tons), about 1 million metric tons of carbon dioxide per year (three fourths of the 9% carbon dioxide contaminant of natural gas produced) will be stripped from the natural gas on its way to shore and sequestered in an aquifer near the production site, a thousand meters (3,500 feet) below the sea floor.

Statoil is already taking core samples from the Utsira formation, and it is planning to use seismic methods to follow the carbon dioxide "bubble" as it develops there. Statoil and its oil company partners are discussing public release of these data for research purposes.

The ability of oil fields to sequester the carbon dioxide injected for enhanced oil recovery (to date, injected without a goal of long-term sequestration) is another promising area of collaborative effort.

Quite generally, public-sector research conducted in conjunction with commercial activity needs to be carefully designed to provide joint benefits. Proprietary concerns must be addressed, while creating an opportunity to do experiments with great leverage at much reduced cost relative to stand-alone experiments.

B. Clarifying the goals of sequestration

The exploration of sequestration options cannot be conducted productively in the absence of research that clarifies the design specifications that ultimately will be imposed.

Permissible sequestration leakage and its relationship to total carbon emissions sequestered, permissible environmental harm, and permissible accident risk will all require careful framing and debate.

C. Understanding carbon dioxide transport and fate in aquifers and in the ocean

Research on underlying physical and chemical processes is needed on multiple scales to understand capacity, long-term integrity, and costs. For aquifers, an understanding of interactions is needed on the pore level, the well level, the reservoir level, the basin level, and the global level. Critical issues relate to caprock integrity and solution rate. For oceans, general ocean circulation, the frequency of extreme disturbances, and interactions with a changing global atmosphere are all important. An improved understanding of carbon dioxide "lakes" below 3500 meters will require research into the formation of clathrates and interactions with ocean sediments.

D. Ocean engineering

Optimization of the injection of carbon dioxide into the ocean entails exploring sites and modes of discharge, near-field plume behavior, and hydrate formation. Global ocean circulation models can assist in selecting best sequestration sites and evaluating their effectiveness.

Alternative designs of injection devices can be tested, including devices that disperse carbon dioxide as it dissolves; such devices should minimize biological impacts that result from changes in acidity. The coinjection of alkaline minerals in solution or slurries may be useful as a buffer to maintain the local pH value.

E. Present and future biological consequences of anthropogenic carbon entering the ocean

An experimental program to study biological impacts of carbon dioxide additions to the ocean resulting from human activity could develop along two parallel paths: (1) baseline studies of the marine biological impacts of ocean acidification, carbonate concentration reduction, and other changes to the ocean environment that are the result of about two gigatons per year of anthropogenic carbon dioxide moving from the atmosphere into the near-surface ocean at present; and (2) studies of impacts of deliberate ocean sequestration of carbon dioxide via deep-water injection. Results could then be compared from various perspectives.

An improved understanding of the physiological response of aquatic organisms can be developed with the help of laboratory experiments under pressurized conditions, as well as in situ field experiments.

F. Field testing and modeling of coalbed sequestration

The injection of carbon dioxide into deep coal seams can lead, simultaneously, to methane production and carbon dioxide sequestration, because, as explained above, the carbon dioxide displaces the methane adsorbed on coal surfaces. The sequestration capacity can be better estimated with improved understanding of adsorption and diffusion processes and coalbed permeability.

G. Generation and assessment of novel science-based concepts

The U.S. Department of Energy has initiated a search for broadly applicable, science-based chemical and biological conversion technologies to recycle or sequester carbon dioxide. The goal is to find innovative and cost-effective advanced technologies capable of processing significant quantities of carbon dioxide and, relative to current practice, significantly improving overall cradle-to-grave system efficiency, measured by energy consumption, greenhouse gas impact, and local environmental impact. Two examples of technologies under investigation — direct solar reduction of carbon dioxide for subsequent synthesis into chemicals or fuel and chemical sequestration as mineral carbonates — are briefly developed in items H and I, respectively, immediately below.

H. Direct solar reduction of carbon dioxide to carbon monoxide for subsequent synthesis of chemicals or fuels

Direct solar reduction of carbon dioxide is aimed at the recycling of atmospheric carbon dioxide into useful chemicals and fuels, instead of making the same products from fossil fuels. Thus, it is an industrial equivalent of the renewable production of biomass for chemicals and fuel, but it does not compete with agriculture for land or water. The key step uses high-temperature solar energy to reduce carbon dioxide to carbon monoxide; carbon monoxide is a precursor in organic synthesis of many compounds, or a precursor to the synthesis of fuels such as methanol.

A process has been developed that uses rapid bulk heating and photolysis. The chemistry is frozen against the back reaction (carbon monoxide returning to carbon dioxide) by the injection of a five-fold excess of unheated carbon dioxide. The whole system is robust and amenable to high throughput processing.

I. Sequestration as mineral carbonate

Carbon dioxide can be sequestered in many kinds of rocks by chemical reactions that transform existing minerals into carbonates. For example, carbon dioxide reacts with several abundant magnesium and calcium minerals to form highly stable carbonates; in nature this reaction occurs on geological time scales, but for some minerals it can be performed in industrial settings in minutes. Carbonate minerals produced in this way are stable solids that are already common in nature, and they are environmentally benign and non-hazardous. An accidental release of carbon dioxide from the carbonate mineral is unlikely. A process where peridotites and serpentinite rocks react with carbon dioxide to form magnesium carbonate is being developed.

J. Sequestration as elemental carbon

Rather than steam-reforming methane, thereby producing carbon dioxide and hydrogen, methane can be thermally decomposed in one step into elemental carbon and hydrogen. Sequestration of elemental carbon results in about 44% of the energy originally stored in the methane being stored in the elemental carbon, available for release when elemental carbon is oxidized to carbon dioxide at a later time. Elemental carbon is more retrievable than carbon dioxide, and it is conceivable that carbon dioxide would be desired someday at a high concentration and in large quantities.

If sequestration is not required, elemental carbon can be used as a commodity, for example, as a construction material or as an additive for strengthening tires.

SECTION THREE: HYDROGEN MANAGEMENT AND USE

Issues discussed in this section include the local production of hydrogen at small scale; the distribution of hydrogen; distributed uses of hydrogen, including personal transportation; and hydrogen safety. Our observations related to industrial-scale hydrogen production are presented in Part Two, Section One, "Fuels Decarbonization." "Large-scale" or "industrial-scale" production is production by single units with production capacity of approximately one billion normal cubic meters of hydrogen per year (100 million standard cubic feet per day, or 400 thermal megawatts); "small-scale" production is production at units roughly 100 to 1,000 times smaller.

I. TECHNOLOGY STATUS

A. Production of hydrogen at small scale

The principal technologies available to produce hydrogen at small scale are steam reforming, partial oxidation, and electrolysis. For some details about the chemical reactions involved in these processes, see the Technical Appendix.

Steam reforming of natural gas

The appropriate size for a "small-scale" reformer depends on the application. The most important economic factor is the cost of associated labor. Thus, the optimum size of a small reformer producing hydrogen for a fuel-cell cogeneration system at a commercial building might be ten times smaller than a small reformer producing hydrogen at an automobile service station, because the commercial building system would not be continually attended, whereas the service station probably would be attended.

Accordingly, the "small" reformed analyzed for the application of providing hydrogen at a service station has a unit capacity of approximately 10 million normal cubic meters of hydrogen per year (1 million standard cubic feet per day, or 4 thermal megawatts), matched to the fuel needs of approximately 10,000 highly efficient (100 mile-per-gallon-equivalent) hydrogen-fuel-cell cars.

Reformers with a capacity of 1 million normal cubic meters of hydrogen per year (100,000 standard cubic feet per day, or 400 thermal kilowatts) are more representative of the fuel-cell cogeneration systems now providing electricity and heat to buildings. The efficiency of conversion of hydrogen to electricity is about 50%, resulting in electric power production at an average rate of about 200 kilowatts.

Two types of small methane steam reformers are available at this range of capacities: (1) "conventional" reformers, which are small versions of reformers designed for refineries, and (2) "fuel-cell-type" reformers, originally developed to provide the hydrogen fuel for fuel-cell cogeneration systems. Fuel-cell-type reformers have entered the market within the past year. Because they operate at a lower temperature and a lower pressure than conventional reformers, they are more compact and use less expensive materials, thus lowering the construction costs per unit of capacity.

Typically, the hydrogen emerges with about 75% of the energy originally available in the methane. Most of the heat required for the endothermic steam-reforming reaction is provided by burning waste gases recovered in the hydrogen purification stage. The economic optimum might reach 85% for higher-cost natural gas, and could be achieved by even greater investment in thermal integration.

Partial oxidation

Partial oxidation reactors are simpler devices than steam reformers and are suitable for making hydrogen from a wider range of fuels. Partial oxidation is used at large scale to produce hydrogen at some refineries, operating with relatively pure oxygen as the oxidizer, rather than air. Small scale partial oxidation systems are now available. They use air as the oxidizer (because at small scale oxygen production is too expensive), thereby accepting inefficiencies and additional downstream cleanup costs related to handling inert nitrogen.

Water electrolysis

Water electrolysis is a third commercially available method for producing hydrogen at small scale. The technology is modular, and the electric capacity of electrolysis systems ranges from a few kilowatts to more than 100 megawatts. The efficiency of electrolyzers of all sizes can be as high as 80-85%.

Although alkaline electrolyzers dominate the current market, proton exchange membrane (PEM) electrolyzers, now being developed, may cost less once they are mass-produced.

The cost of electrolytic hydrogen is sensitive to both the cost of electricity and the capital cost of the electrolyzer. Electrolysis is a competitive hydrogen production technology where power is priced in the range of 1-2 cents/kWh; off-peak power, hydropower, and "surplus" power stranded because of capacity limitations of transmission lines is sometimes available at these prices. Electrolytic hydrogen may also be marketable where there is a high-priced demand for hydrogen, and fossil fuels are unavailable. For transportation applications, electrolytic hydrogen is likely to be competitive only at a scale at least 100 times smaller than what has been defined above to be a "small" reformer for transportation applications, that is, for refueling stations servicing one hundred or fewer fuel-efficient cars.

B. Distribution of hydrogen

Industrial hydrogen is distributed today via small-scale pipelines and trucks. Several dedicated hydrogen transmission pipelines carrying hydrogen 100 to 300 kilometers (50 to

200 miles) are in use in the United States and in Europe. These pipelines operate at pressures of up to 100 atmospheres (1,500 psi). The hydrogen usually originates at dedicated facilities for hydrogen production, but hydrogen also can be captured by a pipeline routed to pass near chemical plants where hydrogen is in excess (such as an ethylene or methanol plant). When distribution is by truck, the hydrogen is usually carried in cryogenic tanks as a liquid.

C. Hydrogen use for vehicles and electric power

The expected advantages of the hydrogen fuel cell motivate much of the development of hydrogen as a fuel. Fuel cells are attractive energy conversion devices because they promise high efficiency and low emissions. The hydrogen fuel is particularly well matched to fuel cells, in that the hydrogen fuel cell can have a high power-to-weight ratio. The superiority of hydrogen as a fuel for fuel cells derives from its significantly higher activity relative to other fuels at the catalysts on the anode (negative) electrode, where the fuel for a fuel cell is ionized by catalytic activation.

The fuel-cell vehicle combines positive features of both the electric-battery car and the gasoline-powered car. Like the electric-battery car, it offers the prospect of near-zero local air emissions. Like the gasoline-powered car, it achieves long range by using a portable, high energy density fuel, stored in a tank and consumed during driving. The fuel can either be hydrogen or another fuel, such as gasoline or methanol, that is converted into hydrogen onboard.

Transportation applications of fuel cells are focused on the Proton Exchange Membrane (PEM) fuel cell. It operates near ambient temperature (about 80°C or 175°F), enabling a fast start-up time, and it has a high power density that permits the fuel cell system to fit comfortably in the vehicle. Over the past 15 years, dramatic reductions have been made in the amount of platinum catalyst required, so that the cost of the platinum no longer inhibits commercialization. The energy conversion efficiency during a driving cycle ranges from about 50% to about 60%; taking into account the energy required to pump the gases and otherwise operate the fuel cell, net efficiencies are about 10 percentage points less. When combined with an efficient electric drive train, advanced aerodynamic design, and the incorporation of lightweight, high-strength materials, a vehicle comparable in size and performance to today's passenger car, powered by a hydrogen fuel cell, should achieve a fuel economy equivalent to about 100 miles per gallon of gasoline. Several vehicle manufacturers are working on concept or prototype vehicles that use PEM fuel cells, including Chrysler, Ford, General Motors, Daimler Benz, Honda, and Toyota.

The most widely deployed non-transportation application of fuel cells to date is the provision of decentralized electricity in conjunction with usable heat ("combined heat and power," or "cogeneration"). This application is less demanding than the vehicle-power application, because there are more permissive weight and cost constraints. Cogeneration has been demonstrated by several electric utilities and is in place at facilities, such as hospitals, where a premium is placed on non-interruptable power. About 100 fuel cell cogeneration systems are in operation today; phosphoric acid fuel cells dominate this market, although PEM fuel cells may soon be available at a lower cost. In the next few years some of the first experience with hydrogen infrastructure may be gained from distributing hydrogen to users of fuel cells for cogeneration.

Hydrogen also has advantages in combustion devices, relative to other fuels such as gasoline or natural gas, especially with respect to air emissions. With hydrogen combustion in air, the only pollutant emissions are nitrogen oxides, not hydrocarbons or carbon monoxide. Even the nitrogen oxide emissions should be lower in an engine designed for hydrogen fuel, because it is possible to run an engine much leaner (and, therefore, cooler) with hydrogen than with hydrocarbon fuels. Hydrogen may have cost advantages as a combustion fuel in electric power production by chemically recuperated gas turbines. Very high efficiency electric power production may be possible with a hybrid system where the fuel residue exiting a high-temperature fuel cell is burned in a gas turbine. Thus, a cost-effective hydrogen infrastructure may ultimately contain fuel cells, combustion systems, and hybrid devices.

D. Hydrogen storage

Hydrogen has been stored on experimental vehicles as a compressed gas, a cryogenic liquid, and a metal hydride. For vehicle fuel management, compressed hydrogen gas has the benefit of simplicity, as well as similarity to compressed natural gas, which is already widely used. For fuel-cell-powered buses that are nearly ready for commercial service, the hydrogen is stored at 250 atmospheres (3600 psi) in cylinders mounted on the roof of the vehicle.

Higher storage pressures (up to 350 atmospheres, or 5,000 psi) are not difficult to achieve, and innovative designs for pressure tanks made of composite materials should raise the percent by weight of hydrogen in a full tank from its current value of 7% to 13%. The electrical energy required to compress hydrogen from a typical production pressure of 14 atmospheres (200 psi) to 350 atmospheres (5,000 psi) is equivalent to about 5% of the total energy stored in the hydrogen. Although storage at still higher pressures is technically possible, compression energy requirements and costs tend to make compression beyond 350 atmospheres (5,000 psi) uneconomic.

Hydrogen today is also routinely stored as a very cold liquid, at or near -253°C, the temperature at which hydrogen boils at atmospheric pressure. Because liquid hydrogen in a cryogenic container has a higher energy density than compressed hydrogen gas in a tank, it is favored for bulk truck delivery to small users located far from the hydrogen production site. The energy penalty for liquefying hydrogen, however, is about 30%, making storage as a liquid less attractive than storage as a compressed gas both from the point of view of net energy and (if the energy of liquefaction comes from fossil fuels) from the point of view of full-fuel-cycle greenhouse gas emissions.

Hydrogen also can be stored in solids, including metal hydrides. Typically, these metals take up hydrogen at ambient temperature and a pressure of a few tens of atmospheres (a few hundred psi), then release the hydrogen when heated to a few hundred degrees Celsius. Hydrides are costly and are used at present only for specialized, very small-scale applications. Novel solids for hydrogen storage based on carbon nanostructures are currently being explored.

E. Hydrogen safety

Industry routinely handles large quantities of hydrogen safely. A culture of safety in dealing with hydrogen in the gas-products industry has been likened to a similar culture of safety in the airline industry.

How safe is hydrogen compared with commonly used fuels such as natural gas (effectively, methane) and gasoline? The overall conclusion is that no one fuel is safest in all situations. Hydrogen's physical properties influence its relative safety as a fuel:

> Hydrogen is lighter than air. As a result, it disperses quickly from a leak. It is difficult to build up flammable or explosive concentrations of hydrogen when it is used outdoors (as in a car tank) or in an adequately vented space. This property is shared to a lesser extent by methane, but not by gasoline, whose vapors are heavier than air and can linger around a leak, causing flammable mixtures even outdoors.
>
> Hydrogen is flammable over a wide range of ratios of hydrogen to air. Mixtures with from 4% to 75% hydrogen by volume in air will support a flame. Flammability limits for natural gas are 5-15%, and for gasoline they are about 1-8%. The lower ("lean") flammability limit is relevant for ignition in situations where the fuel concentration builds up gradually; in this situation, hydrogen and natural gas are similar and are intrinsically less flammable than gasoline. The upper ("rich") flammability limit is relevant to the management of hydrogen in pipelines: it might be necessary to purge hydrogen pipelines with an inert gas, such as nitrogen, prior to commissioning or after a maintenance shutdown, so that rich flammable mixtures do not form.
>
> Hydrogen has a very low minimum ignition energy in air. At stoichiometric conditions (about 30% hydrogen by volume in air), the ignition energy of hydrogen is one tenth the ignition energy of methane or gasoline, while the ignition energies are much closer to one another under lean conditions. The ignition energies for all three fuels, however, are low enough that weak sources such as sparks or hot surfaces can cause ignition.
>
> Hydrogen has a leak rate (for example from a cracked weld or a damaged seal) about three times faster than the leak rate of methane. Molecular hydrogen readily leaks through the type of pipeline delivery system that is considered "tight" for natural gas, where 1% overall system leakage occurs. The addition of odorants to

aid detection is standard practice for natural gas, but is difficult to achieve when the fuel is hydrogen.

All three characteristics—the very wide flammability limits of hydrogen in air, hydrogen's very low ignition energy, and the propensity of hydrogen to leak—raise the risk of fires at leaks, and lead the hydrogen industry to stress inherently leak-proof designs.

There is considerable experience with public use of manufactured fuel gases containing up to 50% hydrogen. Until the 1940s or 1950s, when long-distance pipelines were built linking natural gas fields in the Gulf States and the Southwest with the Midwest and the Northeast, most U.S. gas utilities manufactured a fuel gas ("town gas") from coal or wastes. The fuel gas typically contained about half hydrogen and half carbon monoxide, with small fractions of methane, and was piped to homes for heating, cooking, and lighting. Town gas is still widely used today in China, South Africa, and elsewhere in the world where natural gas is expensive or unavailable. The hazard of carbon monoxide, rather than the hazard of hydrogen, is generally the focus of attention. Pure hydrogen and hydrogen in town gas, however, have sufficiently different properties that it is difficult to derive definitive information about the risk of accidents with pure hydrogen from experience with town gas.

The U.S. Department of Energy (DOE) supports work on hydrogen safety through the Hydrogen R&D Program and through the Office of Transportation Technologies. The National Hydrogen Association, with support from the U.S. DOE, is conducting a series of hydrogen safety workshops and developing hydrogen codes and standards. The International Energy Agency has a Hydrogen Annex that coordinates work on hydrogen safety in its member countries.

II. MAJOR BARRIERS AND UNCERTAINTIES

A. Hydrogen safety is a major concern

Codes and standards for hydrogen utilization are at an early stage of development, particularly with respect to safety. Systems for managing hydrogen safely outside the traditional hydrogen industry will need to be developed and proven.

Public perceptions with respect to hydrogen safety are a potential barrier to the routine use of hydrogen beyond the industrial plant. People associate hydrogen with danger. Public anxiety is unlikely to be allayed without systems in place that operate safely under conditions that correspond to those of ordinary use.

B. The cost and performance of fuel cells is still unclear

The ultimate cost and performance of hydrogen fuel cells for vehicle applications is still unclear. In current PEM fuel cells the catalyst can be poisoned by carbon monoxide (CO) in the fuel at levels above 10 parts per million; additional costs are incurred to provide high-purity hydrogen or, alternatively, catalysts with better tolerance for carbon monoxide. Present efforts to reduce manufacturing costs are concentrated on the fuel-cell membrane (largely a matter of increasing production volumes) and other fuel-cell system components such as bipolar plates and auxiliaries. With current technology, even at high-volume production, PEM fuel cells would cost perhaps $300 per kilowatt (kW) and would not be competitive with internal combustion engines, which cost perhaps $25-50/kW. However, recent studies by General Motors, Ford and others indicate that, with further improvements, PEM fuel cells could be mass-produced for $50-100/kW.

A significant fraction of current automotive research on fuel cells is directed toward making hydrogen onboard the vehicle by "reforming" a hydrogen-rich carbonaceous fuel such as gasoline, methanol, ethanol, or methane. Still in the laboratory is research on fuel cells where fuels other than hydrogen, such as methanol or methane, are used directly, without making hydrogen as an intermediate step. In both approaches, carbon is onboard the vehicle. To the extent that either of these approaches to fuel-cell energy conversion captures market share relative to hydrogen fuel cells, in transportation and in other distributed applications, this will have the indirect effect of complicating the task of carbon sequestration, since costs are likely to prohibit collecting and sequestering the carbon.

C. Transmission and distribution is more expensive for hydrogen than for natural gas

If a hydrogen delivery infrastructure were in place, one as convenient as the one already in place for natural gas, a wide variety of competing hydrogen uses would emerge, especially in fuel-cell applications. But there is a significant cost barrier: pipeline transmission and distribution systems for gaseous hydrogen will cost considerably more than comparable natural gas systems. The combined capital cost for a pipeline and compressors might be 50% higher for hydrogen than for natural gas, and the levelized cost of transmission might be roughly twice as high, in part because the hydrogen requires greater energy expenditures for compression. Nonetheless, the energy used in a hydrogen pipeline for hydrogen compression is at most a few percent of the energy contained in the hydrogen.

D. Plastic pipe in natural gas distribution systems is incompatible with hydrogen

The natural gas infrastructure of transmission and distribution is at present not as compatible with hydrogen as it once was and as it could be again. Currently, the problem is less with the long-distance transmission system, characterized by large-diameter steel pipes that carry gas for long distances at pressures of up to 55 atmospheres (800 psi). It may be possible to condition some of the pipes in place, so that they could transport hydrogen. The problem is with the local distribution systems. Here, the pressures are generally below 4 atmospheres (60 psi), widening the range of choices for pipeline materials. Over the past few decades, through replacement and new construction, distribution networks are gradually being converted from steel and cast iron to plastic. The first-generation plastic (used in the U.S. in the 1960s and 1970s), polyvinyl chloride (PVC), is far too porous to hydrogen to be used for hydrogen distribution. The second-generation plastic (used in the U.S. since the 1980s), high-density polyethylene (HDPE), although less porous to hydrogen than PVC, is still not suitable.

E. The chicken-and-egg problem inhibits the development of a hydrogen infrastructure

As with similar attempts to introduce compressed natural gas, methanol, and ethanol as vehicle fuels, the use of hydrogen is deterred by a "chicken and egg" problem. Until there is widespread utilization of hydrogen as a fuel, there is no economic incentive for constructing a hydrogen gas transmission and distribution system for distributed applications, and until there is a transmission and distribution system, there is little incentive to commercialize vehicles and other distributed end-use devices that use hydrogen.

III. RESEARCH OPPORTUNITIES

A. Hydrogen fuel cells

Successful development of hydrogen fuel cells (especially low-temperature fuel cells, such as PEMs) for stationary power and transportation applications will make hydrogen much more competitive as an energy carrier. Among the research goals are better membranes and better integrated systems. For the reforming of carbonaceous fuels for fuel-cell use, research is focused on catalysts with a higher tolerance for carbon monoxide.

B. Combustion devices

Hydrogen engines offer higher efficiency and reduced emissions, relative to natural gas or gasoline engines. The development of hydrogen engines and hydrogen fuel cells can proceed in parallel.

C. Compatibility of natural gas pipelines

Although the technology for hydrogen pipelines is well known, there is merit in reexamining the use of pure hydrogen or hydrogen blends in the existing natural gas transmission system, thereby avoiding the high capital cost of new hydrogen transmission pipelines. The concern for hydrogen embrittlement of pipeline steels might be addressed by recoating pipes in situ or by adding gases which inhibit embrittlement.

A new low-cost metal pipe might replace high-density polyethylene (HDPE) pipe for distribution systems to deal with the incompatibility of HDPE pipe with long-duration hydrogen distribution.

D. Storage

Although existing and near-term compressed-gas hydrogen storage systems appear to be adequate for stationary and transportation applications, a breakthrough in hydrogen storage technology could greatly facilitate the use of hydrogen. Solid-state storage of hydrogen, including storage in carbon nanostructures, appears promising.

E. Codes and standards for safety

The growing national and international efforts to develop hydrogen codes and standards need to be well buttressed by research and development. Hydrogen vehicle systems need to become "transparent" to the driver and "mistake proof" for the person attending to refueling.

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TECHNICAL APPENDIX

A. Prefixes

Metric, universal

E ("exa") = 10^{18}; G ("giga") = 10^9; M ("mega") = 10^6; k ("kilo") = 10^3

e.g.: 1 MJ = 1 million Joules

U.S. units, volumes of gas

M ("thousand") = 10^3; MM ("million")= 10^6; B ("billion")= 10^9; T ("trillion")= 10^{12}

e.g.: 1 MMscf = 1 million standard cubic feet

B. Metric Equivalents

Volume: 1 cubic meter = 1000 liters = 35.31 cubic feet
= 264.2 gallons
= 6.290 barrels (1 barrel = 42 gallons)

1 Nm^3 = 37.24 scf; 1 scf = 0.02685 Nm^3

Here: "scf," used in the U.S., is "standard cubic feet," and refers to gases at 14.73 pounds per square inch (1.0023 atmospheres) and 60°F (15.6°C) temperature. Nm^3, used widely elsewhere is "normal cubic meters," and refers to gases at exactly 1 atmosphere pressure and 0° C (32°F) temperature.

Mass: 1 metric ton (t) = 1000 kilograms (kg) = 2205 pounds (lb) = 1.102 English tons (ton)

Pressure: 1 atmosphere = 14.696 pounds per square inch (psi)

Energy: 1 million Joules = 947.8 Btu 1 Btu = 1055 Joules

1 EJ = 0.948 Quads A "Quad" is 10^{15} Btu

1 calorie = 4.186 J

Power: 1 kilowatt (kW) = 1.341 horsepower

C. Chemical and Physical Properties of Hydrogen

Chemical formula: H_2

Molecular weight: 2.016; *Gas constant*: R = 4.124 kJ/kg-K

Density at 1 atmosphere (assuming an ideal gas):

1 kg = 11.12 Nm^3 = 414.0 scf

1 lb = 5.04 Nm^3 = 187.8 scf

Energy content (all values of energy content refer to the *higher* heating value, HHV, unless indicated)

1 kg = 141.9 MJ 1 gram-mole = 286.0 kJ
1 lb = 64.4 MJ = 61,010 Btu

1 Nm^3 = 12.76 MJ
1 scf = 343 kJ = 325 Btu

1 GJ = 7.05 kg = 15.54 lb = 78.3 Nm^3 = 2918 scf

Note: The *lower* heating value (LHV) is 120.0 MJ/kg or 10.800 MJ/Nm^3

The higher heating value is the energy available when the product water is condensed to a liquid. For the lower heating value the product water is assumed to be a vapor.

Flow rate (all energy flows refer to the *higher* heating value)

1 million scf/day = 9.80 million Nm^3/yr
= 2.663 U.S. tons/day
= 971.8 U.S. tons/year
= 881.6 metric tons/yr
= 125,100 GJ/year
= 3.97 MW

Boiling point at atmospheric pressure: 20 K = minus 253°C

D. Commercial Production and Use of Hydrogen

Thermodynamics of Methane Steam Reforming

Ideal overall reaction:

$CH_4 + 2\ H_2O \longrightarrow CO_2 + 4\ H_2$ (endothermic)
input energy for thermodynamic ideal reaction (HHV)
254 kJ/(gram-mole CH_4) = 15.8 MJ/kg (CH_4)

$CH_4 + 1.12\ H_2O + 0.44\ O_2 \longrightarrow CO_2 + 3.12\ H_2$
energetically balanced, H_2O liquid
"ideal" reforming in absence of external energy sources, could be achieved either, per mole of total carbon, (a) by recycling and oxidizing 0.88 moles H_2 or (b) by separating out and oxidizing 0.22 moles of CH_4.

At 1:3.12 mole ratio for $CO_2 : H_2$, approximating "ideal" energetically neutral reaction, the volume ratio of product is 1:3.12 and the mass ratio of product is 44:6.24 = 7.05:1

Thus: 1 scf carbon dioxide is produced with 3.12 scf hydrogen

7.05 kg carbon dioxide is produced with 1 kg hydrogen

Some Commercial Routes to Hydrogen

A. Steam Reformer Route from Methane to Hydrogen

1. Steam reformer:

$CH_4 + H_2O \longrightarrow CO + 3\ H_2$ (endothermic)

Large reformers: 850°C, 15-25 atmospheres

Small reformers: 700°C, 3-5 atmospheres

2. Shift reactor, where most of the carbon monoxide (CO) is converted to hydrogen:

$CO + H_2O \longrightarrow CO_2 + H_2$

The gas exiting the shift reactor is typically 70% hydrogen and 25% CO_2, with a few percent methane and less than 1% CO (on a dry basis).

3. Gas cleanup, in one or more stages depending on the purity of hydrogen desired.

Production rate at a "large" methane steam reformer:
100 million scf/day = 1.0×10^9 Nm^3/year = 400 MW

Associated rate of CO_2 generation (at $3{:}1 = H_2{:}CO_2$)
33 million scf (CO_2)/day = 640 kt (CO_2)/yr = 175 kt (C)/yr

Sufficient hydrogen for 1 million "fuel-cell cars" (see below)

Production rate at a "small" methane steam reformer:
1.0 million scf/day = 10×10^6 Nm^3/year = 4 MW

Associated rate of CO_2 generation (at $3{:}1 = H_2{:}CO_2$)
330 thousand scf (CO_2)/day = 6.4 kt (CO_2)/yr = 1.75 kt (C)/yr

Sufficient hydrogen for 1 thousand "fuel-cell cars" (see below)

B. Partial Oxidation (POX) Route from Methane to Hydrogen

1. Partial oxidation reactor:

$CH_4 + 1/2\ O_2 \longrightarrow CO + 2\ H_2$ (exothermic)

For large systems, oxygen rather than air is used. For small systems, nitrogen is a diluent and the percent of hydrogen in the gas at each step is greatly reduced.

2. Shift reactor: Similar to the steam methane reformer.

3. Gas cleanup: Similar to the steam methane reformer.

C. Water Electrolysis Route to Hydrogen

One step: H_2O + electricity -> $H_2 + 1/2\ O_2$

D. Thermal Decomposition of Methane to Elemental Carbon

$CH_4 \longrightarrow C + 2\ H_2$ (endothermic)

If the elemental carbon is stored and energy is obtained only from the oxidation of the hydrogen, then, under thermodynamically ideal conditions, only 56% of the energy content of the methane is extracted, while 44% stays in the carbon.

Rate of Hydrogen Use for a Reference Hydrogen-powered Fuel-cell Car:

Approximately 100 kg/year = approximately 100 scf/day = 400 W

Assumptions: 100 miles per gallon of gasoline energy equivalent (130 MJ/gallon), 10,000 miles per year.

E. Carbon Dioxide

Chemical formula: CO_2

Molecular weight: 44.01; *Gas constant* = 0.189 kJ/kg-K

Density at 1 atmosphere (assuming an ideal gas)

1 kg = 0.509 Nm^3 = 19.0 scf

1 lb = 0.231 Nm^3 = 8.60 scf

Fuel energy content: Zero

Flow rate

1 million metric tons per year = 509 million normal cubic meters per year

= 52.0 million standard cubic feet per day

Critical point

Temperature	= 31°C = 88°F	
Pressure	= 7.39 MPa = 73 atm = 1072 psi.	(Equivalent water depth is about 800 m.)
Density	= 466.7 kg/m^3	(The density of sea water at 800 m is about 1040 kg/m^{-3})

All fluids have a "critical pressure," where the distinction between gas and liquid ceases. A supercritical fluid is a fluid under a higher pressure than the critical pressure.

Gas fields

Location	Percent CO_2	Extraction Rate (million t CO_2/yr)	
Sleipner West, Offshore Norway	9	1	(byproduct, present)
Natuna, Offshore Indonesia	71	100	(byproduct, future)
McElmo, Colorado	97	7	(product, present)

F. Chemical and Physical Properties of Methane

Note: Commercial natural gas is defined by its energy content, not its chemical content. While natural gas is usually almost entirely methane, it can contain as little as 55% methane. Other constituents include carbon molecules with 2-5 carbon atoms, nitrogen, carbon dioxide, and hydrogen. Propane and air are added locally in the winter to extend the supply.

Chemical formula: CH_4

Molecular weight: 16.04 *Gas constant:* $R = 0.5183$ kJ/kg-K

Density at 1 atmosphere

1 kg = 1.395 Nm^3 = 51.95 scf

1 lb = 0.633 Nm^3 = 23.57 scf

Energy content (all values of energy content refer to the *higher* heating value, HHV, unless indicated)

1 kg = 55.50 MJ 1 gram-mole = 890 kJ

1 lb = 25.17 MJ = 23,860 Btu

1 Nm^3 = 39.78 MJ

1 scf = 1.068 MJ = 1,013 Btu

1 GJ = 18.01 kg = 39.72 lb = 25.14 Nm^3 = 936 scf

Note: The *lower* heating value (LHV) is 50.01 MJ/kg or 802 kJ/gram-mole, or xx MJ/Nm^3

Boiling point at atmospheric pressure: -161.5°C

G. Select Properties of Liquid and Solid Fossil Fuels

Crude oil

Energy unit: 1 metric ton of oil equivalent (toe) = 10.0×10^9 calories = 41.9 GJ

Gasoline

Energy Content (values vary with source, by a few percent)

1 gallon = 125,000 Btu = 131.9 MJ (HHV) ($1.00/gallon = $7.58/GJ)

Coal

Energy unit: 1 metric ton of coal equivalent (tce) = 7.0 x 10^9 calories = 29.3 GJ

Elemental carbon

Energy Content ($C + O_2 \longrightarrow CO_2$)

1 kg carbon release 33 MJ (HHV or LHV)

Typical C:H:O composition (ratios of atoms) Note: ratios can vary widely.

Natural gas	1:3.9:0.0
Petroleum fractions	1:1.7:0.0
Anthracite coal	1:0.5:0.07
Bituminous coal	1:0.8:0.1
Lignite	1:0.9:0.3
Dry biomass	1:1.5:0.7

H. Energy and Carbon Content of Fuels

(all energy values are higher heating values)

	kg(C)/kg	MJ/Nm^3	kg/Nm^3	kg(C)/Nm^3	kg/GJ	kg(C)/GJ
Hydrogen	0.0	12.77	0.0899	0.0	7.04	0.0
Methane	0.750	39.8	0.717	0.538	18.0	13.5
Reference natural gas, dry[a]	*0.723*[b]	*40.2*[c]	0.759	0.549	*18.9*[b]	13.7
Reference crude oil	*0.850*[d]	36,100	*860*[e]	730	**23.9**[f]	20.3
Reference gasoline	0.850[g]	34,800[h]	740		21.1[I]	18.0
				630		
Reference coal	*0.707*[j]	-----[k]	-----[k]	-----[k]	*34.1*[l]	24.1

Source for natural gas, crude and coal: G. Marland, *et al.*, "Estimates of CO_2 emissions from fossil fuel burning and cement manufacturing, based on the United Nations energy statistics and the U.S. Bureau of Mines cement manufacturing data." Oak Ridge National Laboratory, Environmental Sciences Division, Publication No. 3176, 1989.

Source for gasoline: J.B. Heywood, *Internal Combustion Engine Fundamentals*, McGraw-Hill, New York, 1988.

Italicized entries: Found in or derived directly from sources; specific page numbers are given in below. Bold entry: Extra assumption. All others can be calculated from those that are footnoted.

Footnotes to Table:

a. "Dry natural gas is natural gas with "natural gas liquids" removed. Constituents of dry natural gas vary widely. This Table uses 1976 U.S. "adjusted dry gas" (Marland, *et al.* 1989, p. 616). Its constituents are, by volume percent: 92.88% methane, 3.91% ethane, 0.62% propane, 0.0% carbon dioxide, 2.59% "other" (non-carbon, assumed here to be nitrogen).

b. Calculated from the gas composition, using integer atomic weights and the following higher heating values (MJ/kg-mole): 890.4 (methane), 1559.9 (ethane), 2220.0 (propane). The H:C ratio is 3.90.

c. Stated as 1023 Btu/scf (Marland, *et al.* 1989, p. 616).

d. Stated as 85.0% +/- 1% (Marland, *et al.* 1989, p. 622).

e. "World average crude appears to have an API gravity of 32.5° +/- 2°" (p. 620). Specific gravity = 141.5/(API gravity + 131.5).

f. Extra input, not found in Marland, *et al.* (1989). A frequent choice for the reference higher heating value of a metric ton of crude oil, 10x10^9 calories, is chosen here.

g. Gasoline is assumed to have the same carbon fraction, by weight, as crude oil.

h. This is the conventional value: 125,000 Btu/gallon.

i. The higher heating value of gasoline is 47.3 MJ/kg (Heywood 1988, p. 915).

j. "70.7 percent carbon describes coal equivalent within +/- 2%" (Marland, *et al.* 1989, p. 623). This percentage is consistent with the bituminous coal atomic ratios of $CH_{0.8}O_{0.1}$, if the coal is 85% ($CH_{0.8}O_{0.1}$) and 15% (other), by weight. "Other" might be ash.

k. No reference density for coal has been chosen here.

l. "A higher heating value of 7000 cal/g is a reasonable standard for coal equivalents" (Marland, *et al.* 1989, p. 622). This widely used standard is a typical value for hard coals. A typical value for lignite is 11,300 MJ/kg (2700 cal/g); values for soft coals range between those for lignite and hard coals.

I. The Carbon Cycle

Note: When carbon is in the form of carbon dioxide, the mass of carbon dioxide is 44/12 = 3.67 times greater than the mass of carbon.

STOCKS (quantities of carbon)

Carbon in atmosphere	750 Gt
Carbon in oceans	40,000 Gt
Global sequestration capacity	
Oceans, "practical limit"	1000 to 10,000 Gt
Deep aquifers	100 to 1000 Gt
Abandoned oil and gas reservoirs	100 to 500 Gt
Depleted coalbed methane	100 Gt

FLOWS

Global fossil fuel carbon emissions to the atmosphere (1995)

solids (coal)	2.5 Gt/year
liquids (oil + nat. gas liquids)	2.6
gases	1.1
gas flaring	0.1
TOTAL	6.3 Gt/year

Global rate of buildup of carbon as carbon dioxide in the atmosphere	3 Gt/year
Global fossil fuel carbon entering the ocean from the atmosphere	2 Gt/year

FURTHER READING

Part One: Overview

H.J. Herzog, ed., "Carbon Dioxide Removal," Proceedings of the Third International Conference on Carbon Dioxide Removal, Cambridge, MA, 9-11 September 1996, *Energy Conversion Management,* Vol. 38, Suppl., 689 pp., 1997.

B. Hileman, "Fossil fuels in a greenhouse world," *Chemical and Engineering News,* pp. 34-37, August 18, 1997.

A.K.N. Reddy, R.H. Williams, and T.B. Johansson, *Energy After Rio,* UNDP, New York, 1997.

R.H. Williams, "Fuel decarbonization for fuel cell applications and sequestration of the separated CO_2," *Princeton University, Center for Energy and Environmental Studies Report No, 295,* January 1996; and, in *Eco-Restructuring,* Robert U. Ayres, et al. Eds., United Nations University Press, Tokyo, in press.

Part Two-Section I: Fuels Decarbonization

G.R. Dickens, C.K. Paul, P. Wallace, & the ODP Leg 164 Scientific Party, "Direct measurement of *in situ* methane quantities in a large gas-hydrate reservoir," *Nature,* Vol. 385, pp. 426-428.

H. Ishitani, and T.B. Johansson. eds. "Energy Supply Mitigation Options," chap. 19 in *Climate Change 1995, Impacts, Adaptations and Mitigation of Climate Change: Scientific Analyses.* Cambridge University Press, 1996.

G.D. Holder, V.A. Kamath and S.P. Godbole, "The potential of natural gas hydrates as an energy resource," *Annual Review of Energy,* Vol. 9, pp. 427-445, 1984.

T.B. Johansson, R.H. Williams, H. Ishitani, and J.A. Edmonds, "Options for reducing CO_2 emissions from the energy supply sector," *Energy Policy,* Vol. 24, Nos. 10/11, pp. 985-1003, 1996.

O. Kaarstad and H. Audus, "Hydrogen and electricity from decarbonised fossil fuels," *Energy Conversion Management,* Vol. 38, Suppl., pp. S431-S436, 1997.

G.J. MacDonald, "The future of methane as an energy resource," *Annual Review of Energy,* Vol. 15, pp. 53-83, 1990.

I.R. MacDonald, "Bottom line for hydrocarbons," *Nature,* Vol. 385, pp. 389-390.

D.F. Spencer and W.J. North, "Ocean systems for managing the global carbon cycle," *Energy Conversion Management,* Vol. 38, Suppl., pp. S265-S271, 1997.

M. Steinberg and H. C. Cheng, "Modern and prospective technologies for hydrogen production from fossil fuels," *International Journal of Hydrogen Energy,* Vol. 14, No. 11, pp. 797-820, 1989.

R.H. Williams, E. Larson, R. Katofsky, and J. Chen, "Methanol and hydrogen from biomass for transportation with comparisons to methanol and hydrogen from natural gas and coal," *Princeton University, Center for Energy and Environmental Studies Report No. 292*, July 1995.

R.H. Williams and B. Wells, "Solar-assisted hydrogen production from natural gas with low CO_2 emissions," Presented at the International Conference on *Technologies for Activities Implemented Jointly*, IEA Greenhouse Gas R&D Programme (proceedings to be published), Vancouver, BC, Canada, May 26-29, 1997.

Part Two-Section II: Carbon Sequestration

E.E. Adams and H.J. Herzog, "Environmental impacts of ocean disposal of CO2," Volume 1 - Executive Summary, *MIT Energy Laboratory Report*, MIT-EL 96-003, 1996.

M. Aresta and G. Forti, Eds., *Carbon Dioxide as a Source of Carbon*, D. Reidel Publishing Co., 1987.

P.D. Bergman, E.M. Winter and Z.Y. Chen, "Disposal of power plant CO_2 in depleted oil and gas reservoirs in Texas," *Energy Conversion Management*, 38, Suppl., pp. S211-S216, 1997.

K. Blok, R.H. Williams, R.E. Katofsky and C.A. Hendriks, "Hydrogen production from natural gas, sequestration of recovered CO_2 in depleted gas wells and enhanced natural gas recovery," *Energy*, Vol. 22, No. 2/3, pp. 161-168, 1997.

S.J. Barer and K.M. Stern, "Sources and economics of carbon dioxide," in *Catalytic Activation of Carbon Dioxide*, W.M. Ayres, Ed., American Chemical Society, Washington, D.C., pp. 1-7, 1988.

J.A. Caulfield, D.I. Auerbach, E.E. Adams, and H.J. Herzog, "Near field impacts of reduced pH from ocean CO_2 disposal," *Energy Conversion Management*, 38, Suppl., pp. S343-S348, 1997.

R.D. Doctor, J.C. Molburg and P.R. Thimmapuram, "Oxygen-blown gasification combined cycle: carbon dioxide recovery, transport, and disposal," *Energy Conversion Management*, Vol. 38, Suppl., pp. S575-S580, 1997.

B. Eliasson, "CO_2 Chemistry: an option for CO_2 emission control?" in *Carbon Dioxide Chemistry: Environmental Issues*, J. Paul and C.M. Pradier, Eds., The Royal Society of Chemistry, Stockholm, pp. 5-15, 1994.

W.D. Gunter, T. Gentzis, B.A. Rottenfusser, and R.J.H. Richardson, "Deep coalbed methane in Alberta, Canada: a fuel resource with the potential of zero greenhouse gas emissions," *Energy Conversion Management*, 38, Suppl., pp. S217-S222, 1997.

N. Gupta, F. Herlihy, and B. Sass, "Feasibility of Underground Carbon Dioxide Injection in the Midwest: A Literature Review." *Battelle Corporate Report*, prepared for U.S. Department of Energy, Pittsburgh Energy Technology Center, Contract No. DE-AF22-96PC1006, 1997.

H.J. Herzog and E.E. Adams, Eds., "Environmental impacts of ocean disposal of CO_2, Volume 2-Topical Reports," *MIT Energy Laboratory Report* MIT-EL 96-003, 1996.

H.J. Herzog, E. Drake and E. Adams, "CO_2 capture, reuse and storage technologies for mitigating global climate change," Energy Laboratory, Massachusetts Institute of Technology, Cambridge MA, *DOE Order No. DE-AF22-96PC01257,* January 1997.

S. Holloway, "An Overview of the Joule II Project : The underground disposal of CO_2," *Energy Conversion Management,* Vol. 37, Nos. 6-8, pp. 1149-1154, 1996.

G. Marland, and T. Boden, "Global Annual Carbon Dioxide Emissions from Fossil-Fuel Burning and Cement Production: 1950-1995". Carbon Dioxide Information Analysis Center, Environmental Sciences Division, Oak Ridge National Lab, September 1997.

C.S. Mathews, "Carbon dioxide flooding," in *Enhanced Oil Recovery, II: Processes and Operations,* E.C. Donaldson, G.V. Chilingarian and T.F. Yen, Eds., Elsvier, Amsterdam, pp. 129-156, 1989

O. Skovholt, "CO2 Transportation System," *Energy Conversion Management,* Vol. 34, No. 9-11., pp. 1095-1103, 1993.

M. Steinberg, "CO_2 mitigation and fuel production," *Brookhaven National Laboratory, Report,* USDOE Contract No. DE-AC02-76CH00016, 1997.

W. Turkenburg, "Sustainable development, climate change, and carbon dioxide removal," *Energy Conversion Management,* Vol. 38, Suppl., pp. S3-S12, 1997.

Part Two-Section III: Hydrogen Management and Use

J.G. Hansel, G.W. Mattern and R.N. Miller, "Safety considerations in the design of hydrogen powered vehicles," *International Journal of Hydrogen Energy,* Vol. 18, No. 9, pp. 783-790, 1993.

J. Hord, "Is hydrogen a safe fuel?" *International Journal of Hydrogen Energy,* Vol. 3, pp. 157-176, 1978.

H. Isalski, "Hydrogen recovery from fuel gas can help meet refinery demand," *Oil and Gas Journal,* pp. 60-65, Mar. 22 1993.

G.G. Leeth, "Transmission of gaseous hydrogen," in *Hydrogen: Its Technology and Implications, Vol. II: Transmission and Storage,* K.E. Cox and K.D. Williamson, Eds., CRC Press, Cleveland, OH, pp. 3-9, 1977.

J.M. Ogden, "Infrastructure for hydrogen fuel cell vehicles: a southern California case study," *Proceedings of the '97 World Car Conference,* pp. 315-330, 1997.

J.M. Ogden and J. Nitsch, "Solar hydrogen," in *Renewable Energy,* T.B. Johansson, H. Kelly, A.K.N. Reddy, and R.H. Williams, Eds., Island Press, Washington, D.C., pp. 925-1010, 1993

J.M. Ogden, M. Steinbugler and T. Kreutz, "Hydrogen as a fuel for fuel cell vehicles: a technical and economic comparison," *Proceedings of the 8th National Hydrogen Association Meeting*, Arlington, VA, March 11-13, 1997, pp. 469-506, 1997.

J. Pottier, E. Blondin, A. Garat, and G. de France, "Large scale storage and transmission of gaseous hydrogen," in *Hydrogen Energy Progress VII*, Proceedings of the 7th World Hydrogen Energy Conference, Moscow, USSR, 25-29 September 1988, T.N. Veziroglu and A.N. Protosenko, Eds., pp. 1095-1107, 1988.

J.T. Ringland, "Safety issues for hydrogen powered vehicles," *Sandia National Laboratories Report*, SAND94-8226, UC-407, March 1994.

K.A. Simonsen, L.F. O'Keefe and W.F. Fong, "Changing fuel formulations will boost hydrogen demand," *Oil and Gas Journal*, pp. 45-58, Mar. 22 1993.

L.A. Thrash, "Worldwide refining," *Oil and Gas Journal*, pp. 39-81, Dec. 23 1991.

P. Van Blarigan, "Development of a Hydrogen Fueled Internal Combustion Engine Designed for Single Speed /Power Operation", *SAE Future Transportation Technology Conference*, SAE Paper 961690, Vancouver, Canada, 5-8 August, 1996.

P. Van Blarigan, and J. O. Keller, "A Hydrogen Fueled Internal Combustion Engine Designed for Single Speed /Power Operation", *Hydrogen Energy Progress XI, Proceedings of the 11th World Hydrogen Energy Conference*, Stuttgart, Germany, 23-28 June 1996.

Workshop on Technological Opportunities for Fuels Decarbonization and Carbon Sequestration

Sponsored by the U.S. Department of Energy

WORKSHOP PROGRAM

Monday, July 28

Session I: Setting the Context for Technology (plenary). Chair: Robert Socolow

9:00 Welcome and Charge to the Group, Marc Chupka, USDOE.

9:10 Goals of the Gathering. Robert Socolow, Princeton University, and Anthony Chargin, Lawrence Livermore National Laboratory

9:20 "Technology on Behalf of Global Environmental Objectives." Henry Kelly, White House Office of Science and Technology Policy

10:00 "The Diplomatic Context of Greenhouse-related Research and Development." Dirk Forrister, Chairman, White House Climate Task Force.

11:00 "A Systems Overview of Fuel Decarbonization." Robert Williams, Princeton University.

11:40 Discussion

12:00 "An Environmentalist's Perspective". David Hawkins, Natural Resources Defense Council.

Session II. Introduction to the Three Component Areas of Technology R&D (plenary). Chair, Anthony Chargin

1:00 "An Industrial Perspective on Hydrogen Production", Clifford Detz, Chevron.

1:30 "Carbon Dioxide Sequestration." Howard Herzog, MIT

2:00 "Hydrogen Systems Issues." Joan Ogden, Princeton University

Session III. Breakout Groups

3:00 Presentations, followed by structured discussion of a) technology status and performance goals; b) major technology barriers and areas of greatest uncertainty; c)inter-group synergies; d) synergies beyond the workshop; and e) research opportunities.

Group A: Fuel Processing
Group B: Carbon Sequestration
Group C: Hydrogen Management

Tuesday, July 29

Session IV: Field Experiences with Carbon Dioxide Sequestration (plenary). Chair, Anthony Chargin

8:00 "Sequestration of Associated CO_2 in the Sleipner Field, offshore Norway." Olav Kaarstad, Statoil.

8:25 "Sequestration of CO_2 from Electric Power Plants in Norway." Olav Falk-Pedersen, Kvaerner Engineering.

8:50 "Sequestration of CO_2 from the Great Plains Coal-Gasification Electric Power Production Complex." Kent Janssen, VP, COO., Dakota Gasification Co.

9:15 Discussion

Session V. Breakout Groups Reconvene

10:00 Structured discussion. Content of presentation to final plenary.

Session VI: Summary Session: Reports of Breakout Groups to the Full Group and to Department of Energy R&D Program Managers (plenary). Chair, Robert Socolow

1:30 Oral presentations of Breakout Groups

3:00 Dialog with Marc Chupka, Acting Assistant Secretary for Policy and International Affairs; Patricia Godley, Assistant Secretary, Fossil Energy; Martha Krebs, Director, Energy Research; Joseph Romm, Acting Assistant Secretary for Energy Efficiency and Renewable Energy.

4:00 ADJOURN

Wednesday, July 30

Meeting only of Steering Group, Breakout Group Leaders, and Writing Team

8:00 Agree on the conclusions to be presented in the workshop report and clarify writing assignments.

2:00 ADJOURN

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