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LLNL Input to FY94 Hydrogen Annual Report
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Lawrence Livermore National Laboratory

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Task Title: Technical and Economic Assessments of the Transport and Storage of Hydrogen

Contractor: Lawrence Livermore National Laboratory*

Principal Investigator: Robert N. Schock

Researchers: Gene D. Berry, Pamela Campos

Task Funding (K$) FY94: 100

Hydrogen Program Area: Infrastructure

Objective:

This project seeks to estimate delivered hydrogen costs at each step in energy transmission, storage, and distribution and to identify promising low-cost hydrogen energy pathways, particularly early in a transition to hydrogen vehicles. This work is part of LLNL's systems approach to developing the critical technologies necessary to support the introduction of hydrogen or hydrogen-natural gas mixtures as transportation fuels, which would provide a sustainable, environmentally benign alternative to the use of imported petroleum.

Approach/Background:

We are performing integrated technical and economic assessments of present and future hydrogen technologies so as to estimate the delivered costs at each step in energy transmission, storage, and distribution. We are attempting to identify promising low-cost hydrogen energy pathways, particularly early in a transition to hydrogen vehicles. In addition to microeconomic parameters, the issues of market size and structure, infrastructure vulnerability, market flexibility, energy efficiency, and time scales are being addressed, all in the context of the existing energy infrastructure. Alternative options for hydrogen delivery, such as local hydrogen production using small-scale electrochemical or thermochemical methods, are also being examined as a viable first stage of a smooth transition to hydrogen.

The lack of an infrastructure to supply hydrogen at a competitive price and in a form compatible with the utilization technology is the chief barrier to the introduction of hydrogen as an alternative fuel. Such an infrastructure helps determine not only price but also the absolute availability of fuel. Investments in today's energy infrastructure are already-sunk costs, and a future energy infrastructure will require market risks not faced by energy suppliers within the current infrastructure. A smooth hydrogen transition will require a good match among technologies, markets, consumers, and producers. The pathway from production to end-use must be well-integrated in temporal, economic, and technological terms. To accomplish this, hydrogen infrastructure systems need to be analyzed and evaluated using a consistent and clear methodology. The results of an infrastructure analysis will allow planning for transitional strategies that can achieve rapid energy market penetration. Analysis and minimization of infrastructure losses and costs is especially important for early, successful hydrogen development because hydrogen production costs are expected to be initially high and because hydrogen infrastructure generally has higher costs and lower energy efficiency than conventional energy infrastructure (natural gas, gasoline, electricity).

Various yardsticks apply to each infrastructure issue. For example, a good measure of the scale of a technology is the number of hydrogen vehicles or homes required to make it viable. Flexibility and vulnerability are both economic and physical issues and infrastructure options vary widely in their flexibility and vulnerability. Safety encompasses the dimensions of probability and magnitude of accidents. Energy efficiency is the fraction of final delivered energy used by the infrastructure to transform, transport, store, and deliver a unit of hydrogen energy. The separation of costs into capital, energy, and operating are important distinctions that make the assumptions of economic projections clear and subject to critical review.

Accomplishments/Status:

FY94 Accomplishments

We have completed an outline of the options for small-scale production and distribution to enable the beginnings of a transition to hydrogen vehicles. Emphasis has been on assembling technologies and costs for steps from production, through transportation and storage, to transfer to the vehicle. The data were assembled and analyzed on a uniform basis with regard to costs and the utilization system and technology and were differentiated as near-term, mid-term, and long-term technologies. The final product is consumer costs for various methods. We have examined electrolysis at the home with storage as compressed gas or metal hydride, and liquid hydrogen distribution to small fleets. Assuming that a home-size electrolysis unit can be purchased for $3500, an individual hybrid-electric car can be operated for about 9¢/mile. This compares with 5¢/mile for a 25-mpg conventional car operating on $1.25/gallon gasoline. For fleets operating on liquid hydrogen at today's prices, the operating costs drop to 4.5¢ to 6¢/mile, depending on the exact cost of the hydrogen. Comparable costs operating on hydrogen reformed from natural gas at a small service station are estimated to be 4¢/mile. We have supplied Energetics Inc. with the input data for pathways analysis of the scenarios studies.

Publications/Awards:

Gene D. Berry, Alan D. Pasternak, Glenn D. Rambach, J. Ray Smith, and Robert N. Schock, *Hydrogen as a Future Transportation Fuel.* LLNL Report UCRL-JC-117945 (1994).

Students associated with the Program (undergraduate, graduate, post doctoral)

Gene D. Berry (University of Illinois, Urbana-Champagne)
Pamela Campus (Massachusetts Institute of Technology)

Future Directions/Industry Interactions:

FY95 Efforts

We will provide updated assessments of small-scale production options, emphasizing those that look most feasible and economic from the previous general assessment. We expect to expand the assessment to include local station or fleet refueling using gas or liquid made by on-site steam reforming, electrolysis, or truck transport from a central production facility and to include various fleet and station technologies, such as natural gas direct conversion, mediated electrochemical oxidation, and high-temperature steam electrolysis, as well as steam-iron production and storage as ammonia. For steam reforming at a local station, we will rely on the analyses of Joan Ogden at Princeton, also part of this DOE program. Regional effects, such as off-peak electricity or natural gas processes, will also be examined. Distribution variations—such as truck, rail, and ship—will be studied to examine the expansion of the hydrogen infrastructure and the practical economic paths likely to be followed.

FY96 Efforts

We will prepare a final report on infrastructure options for a transition to a hydrogen economy. This report will include up-to-date assessments for all phases of the infrastructure, with emphasis on the cost of the individual technical components and the delivered cost to the consumer. Data from other infrastructure studies will be incorporated. Analyses will be integrated with work at Princeton and Energetics Inc., to provide balanced input into the Hydrogen Program Plan.

*Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Task Title: Research and Development of an Optimized Hydrogen-Fueled Internal Combustion Engine

Contractor: Lawrence Livermore National Laboratory*

Principal Investigator: J. Ray Smith

Researchers: Salvador Aceves

Task Funding FY94: $50K

Hydrogen Program Area: Utilization

Objective:

The objective of this project is to develop the design guidelines for a hydrogen-fueled or hydrogen/natural gas-fueled, high-efficiency, low-emissions internal combustion engine for use in hybrid automobiles. These design guidelines will be validated by laboratory demonstration of a prototype hydrogen-fueled engine that exceeds 45% brake thermal efficiency with NOx emissions of less than 100 ppm without an exhaust catalyst.

This work is part of LLNL's systems approach to developing the critical technologies necessary to support the introduction of hydrogen or hydrogen-natural gas mixtures as transportation fuels, which would provide a sustainable, environmentally benign alternative to the use of imported petroleum.

Approach/Background:

This is a team effort of LLNL, Los Alamos National Laboratory, Sandia National Laboratories, California, and a not-yet named industrial partner. LLNL will lead the development by doing vehicle simulation studies to size the hybrid engine and to establish the energy-equivalent mileage and the required hydrogen storage for a given range. The storage requirement, which is the quantity of hydrogen per refueling, will be used in infrastructure studies to size stations and distributed storage requirements and to estimate vehicle fuel operational costs. LLNL will design engine experiments to be performed by Sandia on existing research engines and will also design and fabricate research engine modifications to acquire necessary data. An early task is to confirm literature data on indicated thermal efficiency and NOx emissions as a function of compression ratio and equivalence ratio. Emissions, indicated thermal efficiency and heat transfer losses in the engine experiments will be modeled by LANL using upgraded versions of KIVA 3 that employ improved kinetic packages from LLNL. The results of these experiments and simulations will be used to specify the combustion chamber geometry, engine speed, ignition system, and fuel delivery system to the engine manufacturer/industrial partner. The engine manufacturer will build the pre-prototype and prototype versions of the optimized engine using currently accepted industry standards and practices and assume the lead in friction-reduction efforts.

It is also an LLNL task to coordinate this work with the Office of Transportation Technology for potential use of this engine technology in the Partnership for the Next Generation Vehicle "mechanical thrust."

Accomplishments/Status:

FY94 Accomplishments

During FY94 we completed vehicle simulation studies that indicate that 80–90 miles-per-gallon energy-equivalent mileage is achievable using a series hybrid-electric vehicle. Assuming a five-passenger sedan of 2,500 lb empty weight and industry recommendations for drag coefficient and cross-sectional area product, this automobile requires 3.5 to 4 kg of hydrogen for a 300-mile range. A paper describing the vehicle simulation code and its application to the hydrogen hybrid sedan design has been accepted for presentation at the 1995 Society of Automotive Engineers Congress and Exposition.

Based on a detailed review of the hydrogen engine experiments in the literature, it is concluded that an optimized engine must be a homogeneous charge to keep NOx low, that heat-transfer losses are minimized at reduced combustion chamber surface-to-volume ratio (this implies a long-stroke engine), that acceptable friction is likely only at moderate engine speed (<3600 rpm), and that specific power output will be low. This analysis will be presented in a paper at the SAE'94 Convergence Congress.

An engine experiment was designed using an existing Sandia research engine (Council for Lubrication Research engine) that demonstrated on neat hydrogen less than 5 ppm NOx emissions at equivalence ratio of 0.35 for 8.25–13.7 compression ratios and 1200–2400 rpm. Exhaust gas temperatures were measured at over 300°C and therefore likely to be adequate for releasing hydrogen from advanced hydride storage systems. NOx emissions exceeded the target 100 ppm level at equivalence ratios of 0.5 but were below this level at equivalence ratio of less than 0.45. Both NO and NO_2 varied dramatically with ignition timing delays and equivalence ratio changes, respectively. This data may serve as a stringent test of the NOx kinetic model. The highest indicated thermal efficiency achieved was 42.5%, which is well below literature values for the compression ratios used. This is thought to be due to high heat-transfer losses caused by the large "squish area" in this engine.

The design of an open chamber (no squish) cylinder head for the available Sandia Onan diesel engine is complete. This conversion of the diesel engine to a spark ignition engine uses dual ignition for the quiescent chamber design. Initial studies will be at 15:1 compression ratio. This configuration should allow direct comparison to similar experiments in the literature.

Efforts FY95

We will have the Onan head design fabricated and will design the experiment parameter range. Both neat hydrogen and hydrogen/natural gas blends will be used. The initial effort will be to achieve optimum burn duration (about 30 crank angle degrees, based on Japanese studies) using the dual ignition system. After indicated thermal efficiencies and emission data are measured, brake thermal efficiency (indicated efficiency minus engine friction) will be determined. A series of experiments will then be designed to reduce engine friction by modifying the standard piston ring package while still achieving low blow-by and low oil transport into the combustion chamber. The use of alternative lubricating oils will be considered.

By midyear an industrial partner will be chosen to help refine the design specifications of the pre-prototype of the optimized engine. A conceptual design review will be held to get comments by hydrogen engine researchers and representatives of major automobile manufacturers. The drawings for the pre-prototype engine will be made by the industrial partner and because compromises are always necessary in a detail design, another design review will be held before fabrication is started. The delivery of the pre-prototype engine to Sandia for testing will be targeted for the fourth quarter of FY95.

Publications/Awards:

1. Cowart, J. S.; Keck, J. C.; Heywood, J. B.; Westbrook, C. K.; and Pitz, W. J., "Engine Knock Predictions Using a Fully-Detailed and a Reduced Chemical Kinetic Mechanism," Twenty-Third Symposium (International) on Combustion, p. 1055, The Combustion Institute, Pittsburgh (1991).

2. Westbrook, C. K., and Pitz, W. J., "Numerical Modeling of Combustion of Complex Hydrocarbon Fuels," in *Numerical Approaches to Combustion Modeling,* J. P. Boris and E. Oran, eds., *Prog. Astr. Aero.* **135**, American Institute of Aeronautics and Astronautics, Washington (1991).

3. Beeson, H. D.; McClenagan, R. D.; Benz, F. J., Pitz; W. J.; Westbrook, C. K.; and Lee, J. H. S., "Detonability of Hydrocarbon Fuels in Air," *Prog. Astro. Aero.* **133**, 19 (1991).

4. Chevalier, C.; Pitz, W. J.; Warnatz, J.; and Westbrook, C. K., "Hydrocarbon Ignition: Automatic Generation of Reaction Mechanisms and Applications to Modeling of Engine Knock," submitted for publication (1992).

5. Westbrook, C. K.; Pitz, W. J.; and Leppard, W. R., "The Autoignition Chemistry of Paraffinic Fuels and Pro-Knock and Anti-Knock Additives: A Detailed Chemical Kinetic Study," Society of Automotive Engineers Report SAE-912314 (1991).

6. Pitz, W. J.; Westbrook, C. K.; and Leppard, W. R., "Autoignition Chemistry of C_4 Olefins Under Motored Engine Conditions: A Comparisons of Experimental and Modeling Results," Society of Automotive Engineers Report A-SAE-912315 (1991).

7. Hair, L. M.; Pitz, W. J.; Droege, M. W.; and Westbrook, C. K., "Modeling of the Catalytic Oxidative Coupling of Methane," American Chemistry Society National Meeting, April 1992.

8. Ronney, P. D.; Shoda, M.; Waida, S. T.; Westbrook, C. K.; and Pitz, W. J., "Knock Characteristics of Liquid and Gaseous Fuels in Lean Mixtures," Society of Automotive Engineers Paper SAE-912311 (1991).

9. Smith, J. R., "A Comparison of Ignition Locations in a High Swirl Engine," presented at the Western States Section of the Combustion Institute, Oct. 1979; also Sandia National Laboratories Report No. 79-8715.

10. Smith, J. R., "Temperature and Density Measurements in an Engine by Pulsed Raman Spectroscopy," *Transactions of the SAE* **89**, pp. 808–816, Feb. 1980 (SAE Paper 800137).

11. Smith, J. Ray, "The Influence of Turbulence on Flame Structure in an Engine," in *Flows in Internal Combustion Engines*, edited by T. Uskan, pp. 67–72; presented at the American Society of Mechanical Engineers Winter Meeting, Phoenix, AZ, Nov. 14–19, 1982.

12. Smith, J. R., "Turbulent Flame Structure in a Homogeneous-Charge Engine," Society of Automotive Engineers Paper 820043, presented at the SAE International Congress and Exposition, Feb. 1982; selected for the SAE Transactions.

13. Green, R. M.; Smith, J. R.; and Medina, S. C., "Optical Measurements of Hydrocarbons Emitted from a Simulated Crevice Volume in an Engine," Society of Automotive Engineers Congress and Exposition, Detroit, MI, Feb. 1984.

14. Smith, J. R.; Green, R. M.; Westbrook, C. K.; and Pitz, W. J. "An Experimental and Modeling Study of Engine Knock," 21st Combustion Symposium (International), Ann Arbor, MI, Aug. 1984.

Students associated with the Program (undergraduate, graduate, post doctoral):
Salvador Aceves, Postdoctoral Research Staff

Future Directions/Industry Interactions:
Efforts in FY96

In FY96, we plan to complete experiments on the pre-prototype engine and analyze the data for further optimization. The experimental results combined with the KIVA will be used to specify the prototype optimized engine. The industrial partner will do detail design and fabricate the prototype optimized engine and deliver it to Sandia for testing by fourth quarter of FY96.

We will request that the California Air Resources Board review the testing of the prototype engine on the dynamometer at Sandia and declare it Zero Emission Vehicle equivalent technology. Concurrently we will request that CARB accept similar tests on hydrogen/natural gas blends as Ultra Low Emission Vehicle equivalent technology.

Efforts in FY97

Four additional prototype optimized engines will be ordered from the industrial partner. One will be used at Sandia for long-term life testing and to obtain wear and late-life emission data. The other three engines will be made available for the OTT hybrid program or to any major US automobile manufacturer that would like to do their own evaluation. Detailed documentation of the design guidelines that were developed for optimizing the hybrid engine will be made available to U.S. automotive manufacturers.

*Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Task Title: Hydrogen Storage in Engineered Microspheres

Contractor: Lawrence Livermore National Laboratory*

Principal Investigator: Glenn Rambach

Task Funding (K$)FY94: 50

Hydrogen Program Area: Storage

Objective:

The objective is to develop a novel storage method that will permit the safe, effective and economical bulk storage and transport of hydrogen. New, high-strength glass microspheres filled with pressurized hydrogen exhibit densities that make them attractive for such bulk hydrogen storage and transport.

This work is part of LLNL's systems approach to developing the critical technologies necessary to support the introduction of hydrogen or hydrogen-natural gas mixtures as transportation fuels, which would provide a sustainable, environmentally benign alternative to the use of imported petroleum.

Approach/Background:

Commercially produced glass microspheres were studied in the late 1970s for their application to storage of hydrogen. These spheres have diameters of 25 to 500 µm and wall thicknesses of approximately 1 µm. At elevated temperatures of 200–400°C, the reduced permeability of the glass permits them to be pressurized with hydrogen. Fill rates are a function of glass properties, permeating gas, and temperature and pressure differentials. The commercial spheres were usually made by spraying glass frits or gels into a furnace. Because of defects in the sphere membrane, the hoop stress at failure of the commercial microspheres was limited to about 50,000 psi. Because LLNL's Laser Fusion Program needed glass microspheres made under much more controlled conditions, a method of microsphere production was developed that resulted in defect-free microspheres with ultimate hoop stress of about 150,000 psi, permitting a three-fold increase in pressure limits for microsphere of the same dimensions and materials as the commercial ones.

A bed of 50-µm-diameter engineered microspheres with 1.1-µm-thick membranes and 150,000 psi hoop stress at burst, containing hydrogen at 9000 psi at a 1.5 safety factor, could exhibit a hydrogen mass fraction of 10% and a hydrogen bed density of 20 kg_{H_2}/m^3. Analysis of several infrastructures, production, end-use, and market scenarios indicate that hydrogen rail transportation in glass microspheres can be competitive with liquid hydrogen.

Accomplishments/Status:

In 1995 we will complete a CRADA with Praxair and W. J. Schafer Associates (WJSA) focused on the production of sufficient quantities of glass microspheres to evaluate the critical intrinsic bed properties that are relevant to near-term commercialization. They will be manufactured by the process developed at LLNL, which results in defect-free microspheres. A glass microspheres production facility will be assembled at WJSA to produce cm^3-quantities of microspheres for evaluation. Small beds of current-technology glass microspheres will be produced at WJSA. A microsphere hydrogen storage evaluation test facility will be assembled at LLNL within the high-pressure facility. This will be capable of loading and unloading small beds of spheres at temperatures up to 400°C and pressures up to 10,000 psi.

Several small microsphere beds, spanning a range of concentration of network modifiers, will be evaluated for their actual hydrogen storage mass fraction and volumetric density. The loading and unloading kinetics will also be measured, and the measurements will be used to validate and enhance the density and kinetic model developed for microsphere hydrogen storage beds.

To identify development pathways for improving on the storage density and charge/discharge kinetics, we will perform a literature study to identify all material candidates that may satisfy the properties necessary in microspheres for high mass fraction storage of hydrogen and that potentially offer increased permeability control compared to current glass microspheres.

We will design the microsphere PVT test cell which will be used to supply the controlled pressure, volume and temperature environment necessary to accurately measure the loading characteristics and behavior cm^3-quantities of the microspheres as they are developed. Heating will be accomplished with resistive heating elements. The system will also have the capability of containing the microsphere samples in a container of low heat capacity and conductivity. This apparatus will perform the equivalent function of a Sieverts apparatus used in the evaluation of metal hydrides for hydrogen storage. A piezoelectric pickup will be included to measure the pressure burst and crush statistic of the microspheres. Fabrication will begin in FY95.

Publications/Awards:

Students associated with the Program (undergraduate, graduate, post doctoral)

Future Directions/Industry Interactions:

*Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Task Title: Synthesis, Characterization, and Modeling of Carbon Aerogels for Hydrogen Storage

Contractor: Lawrence Livermore National Laboratory

Principal Investigator: R. W. Pekala

Researchers: C. T. Alviso

Task Funding (K$) FY94: 100

Hydrogen Program Area: Storage

Objective:

The objective of this work is to synthesize, characterize, and model carbon aerogels as a medium for hydrogen storage. This work is part of LLNL's systems approach to developing the critical technologies necessary to support the introduction of hydrogen or hydrogen-natural gas mixtures as transportation fuels, which would provide a sustainable, environmentally benign alternative to the use of imported petroleum.

Approach/Background:

Hydrogen can be adsorbed at high densities on the surface of activated, cryogenic carbons. The overall density of the hydrogen in the carbon/hydrogen system increases as the adsorbing surface area per unit volume increases. Conventional superactivated carbons have high surface-to-mass ratios but their typically low density results in a low surface area per unit volume. Carbon aerogels, however, permit the independent control of density and surface-to-mass ratio. Hence, the surface-to-volume ratio may be optimized for hydrogen storage. At LLNL low-density carbon aerogels have already exhibited hydrogen densities that correspond to values greater than 30 kgH_2/m^3 at 80 K and 3600 psi. There are early indications that the organic precursor to the carbonized aerogel may be able to adsorb more hydrogen per unit area than the final carbon aerogel. This is probably a result of the extremely high surface areas achievable in organic aerogels.

Using the current carbon aerogel as a point of departure, we will optimize the density for organic and carbon aerogels exhibiting the highest surface-to-mass ratio. The adsorption loading and kinetics will be measured as a function of temperature. The mass and heat transfer rates will be measured as a function of aerogel density, so that a system with reasonable charging and cooling/heating rates can be designed. These measurements will be used to update the current aerogel hydrogen storage model. To optimize container fill, aerogel samples will be fabricated in micropellet form. An engineering prototype carbon aerogel storage system will be built to study the real charge, discharge, handling and capacity characteristics. It will be pressurized to 3600 psi to utilize the void space within the aerogel as an enhancement to the adsorbed hydrogen storage. We will also generate a computer model employing molecular dynamics to help predict the hydrogen storage performance of aerogels.

Accomplishments/Status:

FY94 Efforts

• Continued development of inverse emulsion process for the production of organic aerogel micropellets and their carbonized derivatives. Demonstrated that >50 g batches of material can be synthesized using this process.

• Produced 150 cc of carbon aerogel micropellets for evaluation in a prototype pressure vessel at A.D. Little.

• Examined particle size distribution and studied hydrogen adsorption properties of carbon aerogel micropellets.

• Compared the hydrogen adsorption properties of carbon aerogels that have been supertcritically dried vs. air dried.

• Developed method for the chemical activation of aerogel micropellets, leading to increased surface area and improved hydrogen storage.

• Initiated a computer modeling effort using a molecular dynamics simulation to generate amorphous carbon networks.

Publications/Awards:

F.M. Kong, J.D. LeMay, S.S. Hulsey, C.T. Alviso, and R.W. Pekala, "Gas Permeability of Carbon Aerogels," J. Mat. Res., **8**(12), 3100 (1993).

R.W. Pekala and C.T. Alviso, "Carbon Aerogels and Xerogels," in *Novel Forms of Carbon*, C.L. Renschler, J.J. Pouch, and D.M Cox, eds., MRS Symp. Proc. **270** , 3 (1992).

Pekala, R.W.; Alviso, C.T.; Kong, F.M.; and Husley, S.S. "Aerogels Derived from Multifunctional Organic Monomers," *J. Non-Cryst. Solids* , **145,** 90–98 (1992).

Pekala, R.W. "Organic Aerogel from the Polycondensation of Resorcinol with Formaldehyde," *J. Mat. Sci.*, **24,** 3221–27 (1989).

Students associated with the Program (undergraduate, graduate, post doctoral)

None

Future Directions/Industry Interactions:

FY95 Efforts

• Begin computer modeling of hydrogen adsorption at carbon surfaces as a function of micropore diameter and surface group distribution.

• Examine the chemical derivation of resorcinol-formaldehyde (RF) and melamine-formaldehyde (MF) aerogels as a method for improving hydrogen storage.

• Evaluate the effects of chemical doping (e.g., P) on carbon structure and subsequent hydrogen storage.

• Demonstrate that carbon aerogels can be doped with metals that have a high affinity for hydrogen adsorption.

• Select optimum carbon aerogel formulation and measure hydrogen adsorption properties over complete temperature range (77–273 K) and pressure (0–3600 psi). In effect this will yield the phase diagram for hydrogen on this aerogel.

• Select optimum RF and MF aerogel formulation and measure hydrogen adsorption properties over complete temperature range (77–273 K) and pressure (0–3600 psi). In effect this will yield the phase diagram for hydrogen on this aerogel.

FY96 Efforts

• Demonstrate the production of a 200-g batch of carbon aerogel micropellets using an inverse emulsion process.

• Design and build a 2-liter hydrogen tank with optimized carbon aerogel micropellets.

*Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Task Title: Chemical Kinetic Modeling of H_2 Applications

Contractor: Lawrence Livermore National Laboratory*

Principal Investigator: Charles K. Westbrook

Researchers:

Task Funding (K$) FY94: 200

Hydrogen Program Area: Utilization

Objective:

The objective of this work is to develop more detailed kinetic models to be used for hydrogen applications.

This work is part of LLNL's systems approach to developing the critical technologies necessary to support the introduction of hydrogen or hydrogen-natural gas mixtures as transportation fuels, which would provide a sustainable, environmentally benign alternative to the use of imported petroleum.

Approach/Background:

This project includes two principal elements. In the first approach, the physical geometry of the combustion system is simplified to deal with a zero or one-dimensional formulation. This makes it possible then to deal in great detail with selected subprocesses, including the detailed chemical kinetics of fuel oxidation, NO_x production, and pollutant emission. On the other hand, it is also possible to simplify the detailed chemical and physical process submodels and deal in detail with the multidimensional fluid mechanics. Both approaches have been used extensively in the past to study combustion in practical systems, including particularly internal combustion engines. In the present program, both approaches are being pursued, using current models for complex chemical kinetics and multidimensional fluid mechanics. As our program develops in time, it will eventually become feasible to combine both features together and carry out model analyses on a scale that was not possible previously, eventually moving the modeling work onto massively parallel computers.

With both of these approaches in mind, the work at LLNL has carried out kinetic and fluid mechanical models that both advance our current capabilities and also address specific applications problems. In the area of simplified fluid mechanics modeling, we have examined a number of problems associated with hydrogen oxidation. We have also developed and applied simplified kinetic submodels for use within complex fluid mechanics models.

This general approach will be continued in the coming years within this program. This work will be coordinated with other research activities at LLNL, at Sandia National Laboratories, and other projects within the DOE/OUT program.

Accomplishments/Status:

This project includes two principal elements. In the first approach, the physical geometry of the combustion system is simplified to deal with a zero or one-dimensional formulation. This makes it possible then to deal in great detail with selected subprocesses, including the detailed chemical kinetics of fuel oxidation, NO_x production, and pollutant emission. On the other hand, it is also possible to simplify the detailed chemical and physical process submodels and deal in detail with the multidimensional fluid mechanics. Both approaches have been used extensively in the past to study combustion in practical systems, including particularly internal combustion engines. In the present program, both approaches are being pursued, using current models for complex chemical kinetics and multidimensional fluid mechanics. As our program develops in time, it will eventually become feasible to combine both features together and carry out model analyses on a scale that was not possible previously, eventually moving the modeling work onto massively parallel computers.

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Publications/Awards:

1. J. A. Gray and C. K. Westbrook, "High Temperature Ignition of Propane with MTBE as an Additive: Shock Tube Experiments and Modeling," *International Journal of Chemical Kinetics*, in press (1994).

2. J. W. Bozzelli and W. J. Pitz, "The Reaction of Hydroperoxy-Propyl Radicals with Molecular Oxygen," Submitted to the 25th International Symposium on Combustion, Aug. 1994.

3. J. D. Naber, D. L. Siebers, S. S. Di Julio, and C. K. Westbrook, "Effects of Natural Gas Composition on Ignition Delay Under Diesel Conditions," Submitted to the 25th International Symposium on Combustion, August 1994.

4. E. Ranzi, A. Sogaro, P. Gaffuri, G. Pennati, C. K. Westbrook, and W. J. Pitz, "A New Comprehensive Reaction Mechanism for Combustion of Hydrocarbon Fuels," Submitted to the 25th International Symposium on Combustion, Aug. 1994.

5. C. K. Westbrook and W. J. Pitz, "A Chemical Kinetic Mechanism for the Oxidation of Paraffinic Hydrocarbons Needed for Primary Reference Fuels," Western States Section of The Combustion Institute, Salt Lake City, Utah, March 1993. LLNL Report UCRL-JC-112696.

6. J. D. Naber, D. L. Siebers, S. S. Di Julio, and C. K. Westbrook, "Natural Gas Fuel Variability Effects on Ignition Delay Under Diesel Conditions," Western States Section of the Combustion Institute, Menlo Park, California, Oct. 1993.

7. L. D. Cloutman and L. Brookshaw, "Numerical Simulation of Radiative Heat Loss in an Experimental Burner," Western States Section of The Combustion Institute, Menlo Park, California, Oct. 1993. LLNL Report UCRL-JC-115048.

8. W. J. Pitz, C. K. Westbrook, A. E. Lutz, R. J. Kee, S. Senkan, and J. G. Seebold, "Numerical Modeling Capabilities for the Simulation of Toxic By-Products Formation in Combustion Processes," Third International Congress on Toxic Combustion By-Products, Cambridge, MA, June 1993. *Combustion Science and Technology*, in press (1994).

9. W. J. Pitz, C. K. Westbrook, A. E. Lutz, and R. J. Kee, "Chemical Kinetics Pathways for the Emission of Trace By-Products in Combustion Processes," Western States Section of The Combustion Institute, Salt Lake City, Utah, March 1993. LLNL Report UCRL-JC-113086.

10. A. Burcat, W. J. Pitz, and C. K. Westbrook, "Comparative Ignition of Hexane and Octane Isomers in a Shock Tube," 18th International Conference on Shock Waves and Shock Tubes, Sendai, Japan, July 1992.

11. C. K. Westbrook and W. J. Pitz, "Numerical Combustion with Complex Chemistry," 5th International Conference on Numerical Combustion, Garmisch-Partenkirchen, Germany, Sept. 1993.

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Students associated with the Program (undergraduate, graduate, post doctoral)

Future Directions/Industry Interactions:

Efforts in FY95

Some of the above activities will be continued into FY95 and other new activities will be initiated. These include the following:

Detailed Kinetic Modeling—We are using our detailed models to examine conditions related to the recent engine experiments carried out at Sandia with hydrogen fuel. The experiments examined very lean conditions and focused on production of NO_X in the engine. We are combining our detailed kinetic model with the current best kinetics for NO_X chemistry to see what reactions are most important in determining the NO_X production under these conditions. We are also calculating the results of adding small amounts of other fuels, especially methane and natural gas, but also other species as well. This work will be completed by December 1994.

Model Development—We will complete our tests of the composite model of KIVA with detailed kinetics for hydrogen by January 1995. We will then begin to use that model in several interrelated studies. These will include using hydrogen as a fuel in internal combustion engines. We will attempt to use the same engine model as used in previous LANL studies, which used global reaction models. We will also examine in detail hydrogen oxidation in burners similar to those currently being simulated with a global kinetics mechanism. These studies will begin once the model itself has been tested, as noted above, and should be completed by October 1995 at the end of FY95.

Colorado State University—A group at CSU is building large-scale internal combustion engines and using mixtures of natural gas and hydrogen as fuel. They have asked LLNL to do some preliminary two-dimensional calculations to suggest optimal operational conditions for these engines, and we have provided them with some information and a few computed sets of results. We expect this effort to continue at a relatively low level in FY95 and feel that this is an appropriate minor task to carry out within the DOE/OUT program.

LLNL Hybrid Engine Effort—We expect to provide computational support for this concurrent research project during FY95. This work will explore optimal operating conditions for this engine to minimize NO_x production and maximize efficiency. As other issues arise we will work closely with this project to resolve issues that relate to combustion questions.

Efforts in FY96 and FY97

As the massively parallel version of KIVA and its related other codes becomes available with detailed submodels for chemical kinetics, we will continue to use that model to examine hydrogen combustion in practical systems. The emphasis of our work, as always, will be to identify physical and chemical mechanisms that lead to improved performance and reduced pollutant emissions. Hydrogen reaction mechanisms will be combined with NO_x reaction mechanisms, along with hydrocarbon systems in applications where that is appropriate. We would be available to collaborate with other projects supported by DOE/OUT where it is appropriate and mutually productive.

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Task Title: Municipal Solid Waste to Hydrogen

Contractor: Lawrence Livermore National Laboratory*

Principal Investigator: Jeffery H. Richardson

Researchers: Charles B. Thorsness, Henrik Wallman

Task Funding (K$) FY94: 400

Hydrogen Program Area: Production

Objective:

The ultimate goal of this project is to develop a commercial process for gasifying municipal solid waste (MSW) to produce hydrogen for use as a premium fuel. A potential use of the hydrogen is in fuel cells. Another important use would be as a feedstock for methanol production, which is a key component for the new gasoline/oxygenate formulations (legislation is pending that requires a fraction of all oxygenates to come from a renewable source, such as MSW). This work is part of LLNL's systems approach to developing the critical technologies necessary to support the introduction of hydrogen or hydrogen-natural gas mixtures as transportation fuels, which would provide a sustainable, environmentally benign alternative to the use of imported petroleum.

Approach/Background:

Our approach is to couple innovative MSW preprocessing technology with established gasification technology. Texaco has developed a high-temperature gasification process that has been applied commercially throughout the world. However, all applications are fossil fuel-based, and the extension to MSW fueling is difficult. The advantages of high-temperature gasification include a slagged glass-like ash byproduct that is expected to be nonhazardous, even under conditions where the corresponding combustion-derived ash would be classified as hazardous under RCRA. Interestingly, the high-temperature condition required by the slagging process results implicitly in a high yield of hydrogen. Hence hydrogen production and environmentally sound MSW treatment are intimately coupled. An advantage of gasification over MSW combustion is that gasification produces a small-volume fuel gas that is easily cleaned relative to the cleaning of a large-volume flue gas that contains pollutants as low concentrations.

Successfully accomplishing the project goal would lead to reduced landfill disposal, a mandated goal throughout the United States, and to reduced air pollution because hydrogen-fueled power production would displace "dirtier" fossil fuel-based power. Since MSW-fueled power production has the potential of being an "ultra-clean" technology, urban plant locations will be feasible, thus reducing today's transportation-generated air pollution associated with hauling MSW long distances. A commercial MSW-to-hydrogen process also has strong export potential, particularly to Europe where the pressure to reduce landfill volume is even greater than in the United States.

LLNL and Texaco will cooperatively develop a physical and/or chemical treatment method for preparing and converting MSW to hydrogen by gasification and purification. Initially proposed pretreatments include processing by hydrothermal or dry pyrolysis techniques. Metrics for continual project evaluation range from slurry viscosity and calculated heating values to overall process economics and performance in test runs at the Texaco pilot plant gasifier. This work will analytically evaluate the process to optimize the production of hydrogen, perform bench-scale experiments to measure process variables, and ultimately scale the project for demonstration in the Texaco pilot facility. MSW will initially be modeled using biomass (e.g., cellulose) and subsequently considering other components and related wastes (e.g., sludge, plastics).

The project will consist of six research areas or tasks:

1. A survey of process research on waste and biomass upgrading, slurrying, and liquefaction and of the availability of various potential waste and biomass feedstocks.
2. Determination of the effects of pretreatment on heating value and viscosity properties of slurries. This work will focus on conversion of cellulose and/or general wood polymeric material, recognizing that some plastics will be present.
3. A system analysis of the feed preparation/gasification process to allow process tradeoffs to be evaluated on an economic basis.
4. Production of a quantity of feed material for gasification testing and evaluation.
5. Demonstration of MSW and biomass slurrying, characterization of slurrying parameters, and gasification of the MSW and biomass slurries.
6. Development of a measurement/control system to ensure a slagging ash for variable feeds.

Accomplishments/Status:

FY94 Accomplishments

In our work to establish a sound approach to MSW processing, we had invaluable help from the survey conducted by SRI International under DOE/NREL sponsorship and published in 1982. Our survey of existing technology (task 1) was thus easily completed.

Task 3 was also completed in terms of its objective of establishing a process approach. This analysis was presented at the DOE contractors' review meeting at Sandia, Livermore in April 1994. A detailed system analysis will continue throughout the project.

Based on the work in tasks 1 and 3, we concluded that the Texaco gasification process with its requirement for a pumpable feed stream can be adapted to MSW fueling by augmenting the process with a preprocessing step for slurry preparation. As expected, MSW proved in the laboratory tests to be difficult to turn into a pumpable suspension by purely mechanical means with the exception of very dilute conditions. However, our preliminary economic analysis showed that gasification economics is sensitive to the Btu-content of the slurry feed; a dilute feed stream results in poor economics and a very dilute feed cannot be gasified at all. In collaboration with Texaco, we determined that high-pressure hydrothermal preprocessing similar to pulp digestion used in papermaking was an appropriate approach to solve the feed preparation problem. Hydrothermal treatment as applied to waste streams such as sewage sludge has been shown by Texaco and others to produce a high Btu-content slurry.

We also started laboratory test work in support of the MSW preprocess development. This work has shown that hydrothermal treatment of newspaper produces a concentrated slurry with an acceptable viscosity at a solids content of 40 wt% ($\approx$ 4500 Btu/lb). Further optimization of the conditions should make a 50 wt% slurry possible. We have also started the laboratory work on two real MSW samples, one obtained from pilot plant tests conducted by BioMass Inc. of San Leandro.

Publications/Awards:

A. D. Pasternak, J. H. Richardson, R. S. Rogers, C. B. Thorsness, H. Wallman, G. N. Richter, and J. K. Wolfenbarger, *MSW to Hydrogen*, LLNL Report UCRL-JC-116421 (April 1994).
R. Rogers, *Hydrogen Production by Gasification of Muncipal Solid Waste*, LLNL Report UCRL-ID-117603 (May 1994).
C. B. Thorsness, *Processing Modeling of Hydrogen Production from Municipal Solid Waste*, LLNL Report UCRL-IC-119231 (Nov. 1994).

Students associated with the Program (undergraduate, graduate, post doctoral)
Robert Rogers III, SERS student from Rutgers University.

Future Directions/Industry Interactions:

FY 95 Efforts

The laboratory work on MSW samples will be carried out to establish favorable hydrothermal processing conditions for real MSW. A study of individual plastic components will be performed because different plastics respond differently. Some shearing of the samples during the treatment will be attempted in the laboratory because of the expected benefit of such shearing to the final slurry properties. Further work on slurry rheology is also planned at both LLNL and Texaco.

The main FY95 activity will be modification and operation of a Texaco-built hydrothermal preprocessing pilot plant and experimental testing at LLNL. This modification is necessary because the batch laboratory work cannot be scaled up without pilot plant testing. The initial experimental testing will be conducted with newspaper as feedstock because an MSW feedstock requires further additions to the pilot plant. The nominal capacity of the hydrothermal pilot plant will be 1 ton/day (dray weight), but experimental runs will typically be limited to about 8 h. The objective is to demonstrate that the high-Btu-content slurry preparation process based on hydrothermal treatment works with an idealized MSW feedstock. Information for our system study will also be gathered.

Gasification pilot plant tests will be started at Montebello with feed slurry prepared from newspaper. Texaco will complete a Phase I economic study of the overall process, including analysis of the market as well as hydrogen cost. Texaco will also complete a laboratory-scale gasifier that will be able to accept feed slurry from LLNL in the latter part of FY95 and FY96.

FY96 Efforts

In FY96, extension to real MSW feedstock will occur for the preprocessing unit, and the MSW-derived slurries will be used in gasification tests at Montebello.

The 1 ton/day hydrothermal pilot plant will be modified additionally to include continuous operation capability. For example, a new dewatering step is needed for preparing the final high-Btu-content slurry (and for recycling the separated water back to the front end of the plant). Additional augmentation includes adding a size-reduction and initial separation step so that real MSW can be fed to the unit. Negotiations are underway with BioMass Inc. to use their pilot plant as a starting point for this work. This pilot plant reduces the material in particle size and separates the material based on density, all in a water suspension. The main product consists of a water suspension of the organic, combustible fraction of the MSW which will subsequently be fed to the hydrothermal treatment unit. Recycling of water to avoid production of excess waste water is an important issue.

Samples of the slurries produced at LLNL will be shipped to Texaco's pilot plant in Montebello for gasification tests. The objective is to determine product yields and properties, particularly the properties of the ash byproduct. Laboratory leaching studies will be performed to assess this product relative to RCRA and California waste disposal regulations.

FY 97 Efforts

The FY97 plan calls for integrated MSW-to-hydrogen tests at Montebello. The hydrothermal pretreatment unit, which is built on trailers, will be transported back to Montebello for continuous test runs. One objective is to determine product qualities (including ash byproduct) in the face of varying feed quality (MSW is inherently more variable than other fuel feedstocks). Another objective is to gather data for scaling up the process towards commercial size.

*Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.